



Rubber:

Rubber molecules are capable of considerable deformation even under of weak force and of rapidly returning to their original dimension and shape, when the external force is removed. Material with rubber like property at room temperature is generally elastomer. Elastomers are macromolecules having double bonds or some other active sites located at intervals along the molecular chains. Rubber is also an elastomer. Rubber is a macromolecular substance, with T_g lower than 0°C , composed of long flexible molecules, which are randomly agglomerated and entanglements are present. Rubber is generally collected in the form of latex (milky aqueous dispersion of rubber material). Natural rubber is a white liquid similar to milk. It is the colloidal system i.e. suspension of rubber particles in an aqueous medium. These are called serum (Rubber hydrocarbon, Protein). The process technology of making waterproof objects based on rubber-coated fabric passed into an advanced phase with the discovery of coal tar naphtha as a good solvent of rubber by Charles Macintosh in 1823. This led to the development of the sandwich process for the so called double texture fabric, imparting much improvement in the performance of the waterproof garments, but the inherent drawback in the susceptibility of rubber to changes of temperature, still remained unsolved thus limiting expansion and diversification of its use. The difficulty was finally overcome through the discovery of vulcanization of rubber using sulphur by Charles Goodyear after many years of trial and error method in 1839 in USA. The process was also development by Thomas Hancock in London at about the same time.

At present, in the market a lot of rubber types are available that can be divided into more groups in accordance with different criterion (e.g. natural and synthetic, saturated and unsaturated, crystallizing and non-crystallizing, and polar and non-polar). From the basic properties and the application point of view these can be divided into two groups:

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



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

M – Rubbers with saturated hydrocarbon chain of methylene type

N – Rubbers containing nitrogen in polymer chain

O – Rubbers containing oxygen in polymer chain

Q – Rubbers containing oxygen and silicium in polymer chain

R – Rubbers with unsaturated hydrocarbon polymer chain (diene)

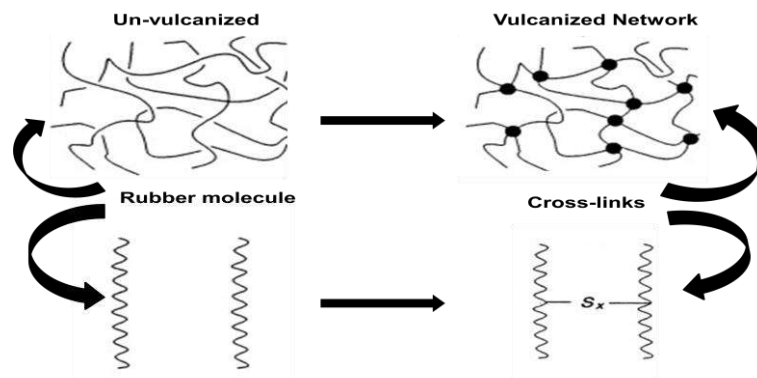
T – Rubbers containing sulfur in polymer chain

U – Rubbers containing carbon, oxygen and nitrogen in polymer chain

Z – Rubbers containing phosphor and nitrogen in polymer chain

Vulcanization:

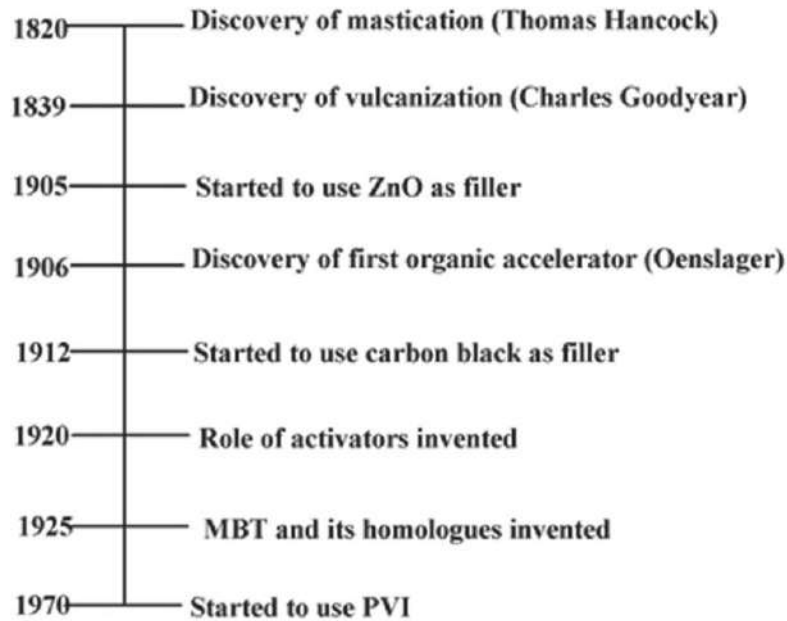
Vulcanization is a chemical cross linking process by which the physical properties of natural or synthetic rubber are improved, finished rubber has higher tensile strength and resistance to swelling and abrasion, and is elastic over a greater range of temperatures. In its simplest form, vulcanization is brought about by heating rubber with sulphur.



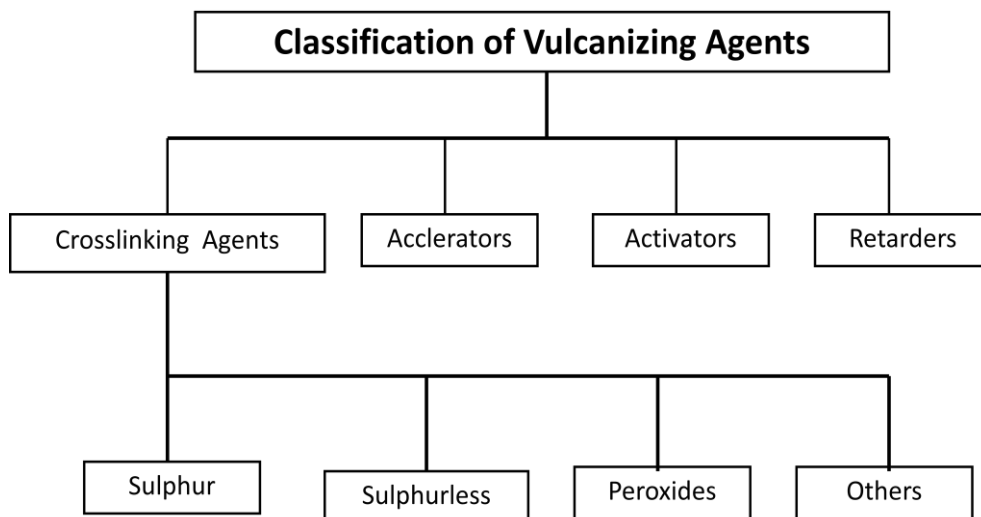
Vulcanization of rubbers by sulphur alone is an extremely slow and inefficient process. The process takes around 6 hours at 140°C for completion, which is uneconomical by any production standards. The vulcanizates thus produced are extremely prone to oxidative degradation and do not possess adequate mechanical properties for practical rubber applications. These limitations were overcome through inventions of accelerators which subsequently became a part of rubber compounding formulations as well as subjects of further R&D. Sulphur vulcanization is usually carried out industrially by heating the mechanically plasticized rubber with sulphur and auxiliary vulcanizing agents such as organic accelerators, ZnO, long chain fatty acids or the zinc soaps of these acids (activators).



Additional ingredients may include antioxidants, antiozonants, fillers and reinforcing agents such as carbon black. Major effects of vulcanization (Bateman et al.,1963; Coran,1978; 2003) on use related properties include increased tear strength, tensile strength, elastic recovery, fatigue life, toughness, low hysteresis and compression set, etc. The timeline of various developmental stages in the history of sulphur vulcanization is given below.



Vulcanization Chemicals:





Accelerators:

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

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

- ✓ Guanidines
- ✓ Thiazoles
- ✓ Sulfenamide
- ✓ Thiurams
- ✓ Dithiocarbamates
- ✓ Xanthates
- ✓ Aldehydamines
- ✓ Other accelerators.

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

- ✓ Slow (guanidines, some aldehydamines)
- ✓ Fast (thiazoles)
- ✓ Very fast (thiourams)
- ✓ Ultra fast accelerators (dithiocarbamates, xanthates)



Chemical structure of the most commonly used accelerators and sulphur donors:

Name	Common abbreviation	Chemical Structure	Remarks
Guanidines			
Diphenylguanidine	DPG		Slow accelerator, used predominantly as secondary accelerator
Di-O-tolyguanidine	DOTG		Slow accelerator, used predominantly as secondary accelerator
Thiazoles			
2-Mercaptobenzothiazole	MBT		fast, frequently used accelerator; it is used preferably in combination with other accelerators
Dibenzothiazyl disulfide	MBTS		fast accelerator with slightly delayed start
Sulfenamide			
N-cyclohexyl-2-benzthiazol sulfenamide	CBS		fast accelerator with scorch delay, used also in semi EV and EV systems
N-tert-Butyl-2-benzthiazol sulfenamide	TBBS		accelerator with shorter scorch delay and lower cure ratio than CBS
N-oxydiethylenedithiocarbonyl-N'-tert-butyl sulfenamide	OTTBS		accelerator with scorch delay and high cure rate, used also in combinations with other accelerators



Dicyclohexyl-2-benzthiazol sulfenamide	DCBS		accelerator with longer scorch delay and lower cure ratio than CBS
Thiurams			
Tetramethylthiuram monosulfide	TMTM		very fast accelerators, used also in semi EV and EV systems
Tetramethylthiuram disulfide	TMTD		very fast accelerators, used also in semi EV and EV systems; sulfur donors
Tetraethylthiuram disulfide	TETD	R = Methyl, Ethyl, Benzyl	
Tetrabenzylthiuram disulfide	TBzTD		
Dithiocarbamates			
Zinc dimethyldithiocarbamate	ZDMC		ultra accelerators, used also at low (room) temperatures and for vulcanization of latex compounds
Zinc diethyldithiocarbamate	ZDEC		ultra accelerators, used at low (room) temperatures and for vulcanization of latex compounds
Zinc dibutyldithiocarbamate	ZDBC		ultra accelerators, used at low (room) temperatures and for vulcanization of latex compounds



Zinc dibenzyl dithio-carbamate	ZBED		ultra accelerators, used also at low (room) temperatures and for vulcanization of latex compounds
Xanthates			
Zinc isopropylxanthate	ZIX		the fastest ultra accelerators, used predominantly for vulcanization of latex compounds
Aldehydamines			
Trirotonylidene tetramine	TCT		Very slow accelerator for hard rubber, used as secondary accelerator
Butyraldehydeaniline	BBA		Very fast accelerator, leads to high crosslink density
Hexamethylene tetramine	HEXA		Very slow accelerator, used only as secondary accelerator
Other accelerators			
Bis-disopropylthio-phosphoryl disulfide	DIPDIS		Have optimum accelerating effect in combination with thiazoles



Selection of Accelerators for Rubber Compounds:

Selecting an accelerator system is one of the most difficult problems in compounding. A number of factors must be considered while selecting an accelerator. Selection of the proper accelerator and the amount to be used for any application depends on:

- ✓ Free flowing for automatic weighing and bulk handling systems
- ✓ No caking in transit and storage
- ✓ Supply forms need to resist abrasion and break-up
- ✓ Accelerators solubility in rubber (high solubility to avoid bloom and improve dispersibility)
- ✓ Particle uniformity to prevent separation of blends in bulk storage
- ✓ Improved processing and dispersion to shorten mixing cycles for 'scorch free' processing operations
- ✓ Faster curing rate for economical production of rubber product
- ✓ Vulcanisation method to be used (mode of heat transfer)
- ✓ Maximum vulcanisation temperature available
- ✓ High purity to target specific reaction sites
- ✓ High activity to prevent undesirable side effects
- ✓ Shelf-life stability of the compound
- ✓ Dust free to meet industrial hygiene standards

Activity and uses of different type of accelerator:

Guanidine Class Accelerators:

Guanidines are condensation products of aromatic amines (aniline) and carbon-disulfide with subsequent substitution of the thione functionality ($>C=S$) for a primary ketimine group ($>C=NH$). In practice the most often used is diphenyl-guanidine (DPG) and N, N'-diorthotolyl guanidine (DOTG) eventually o-tolyl-biguanidine. Guanidines are slow accelerators with short induction period and broad vulcanization plateau and require the use of zinc oxide for activation. They have alkaline character. They are suitable also into compounds containing additives of strongly acidic character and into compounds filled with SiO_2 . Guanidines are good choice for thick walled rubber products. The vulcanization in the presence of guanindes has relatively high crosslink density and good physical-mechanical properties; they are less resistant to thermo-oxidative ageing, because polysulfide cross-links



dominate in their network. However, guanidines are not recommended for light colored goods because they cause a brown discoloration.

Thiazole Class Accelerators:

Thiazoles are some of the most widely used primary vulcanization accelerators. They are suitable for vulcanization of high (NR, BR, SBR) and low (IIR, EPDM) unsaturated rubbers. The most common commercial thiazoles are 2-mercaptobenzothiazole (MBT) and bis-(2-benzothiazol) disulphide (MBTS) and eventually zinc salt of 2-mercaptobenzothiazole (ZMBT). . They have improved scorch safety and allow for cure at quite high temperatures with short curing time and broad vulcanization plateau but relatively low crosslink density. From this reason the vulcanizates that are vulcanized under presence of solitary thiazoles does not have optimal strength and elastic properties. Also from this reason they are very often combined with other accelerators. All thiazole accelerators can be further boosted to increase their cure speed, they are often combined with small amounts of basic accelerators such as diphenyl guanidine (DPG), diorthotolyl guanidine (DOTG), Tetramethylthiuram monosulfide (TMTM), Tetramethylthiuram disulfide (TMTD), ZDC, etc.

Activity of Thiazole accelerators with respect to cure characteristics can be summarised as follows:

1. Scorch Safety \longrightarrow Longer.... (ZMBT>MBTS>MBT)
2. Cure Rate \longrightarrow Faster..... (MBT>MBTS>ZMBT)
3. Crosslink Density \longrightarrow Higher at equal dosage..... (MBTS>MBT>ZMBT)

Sulfenamide Class Accelerators:

Sulfenamides are made in two ways: by the reaction of 2-mercaptobenzothiazole (MBT) with an N-chloramine and by oxidation of the appropriate amine salt of 2-mercaptobenzothiazole. Their activity in vulcanization process depends mainly on type of amine used during production of appropriate sulfenamide. The various amine functional groups of sulfenamides reflect their scorch time and cure rate differences. The scorch time is lower and increase curing rate if the used amine salt during sulfenamide preparation is highly basic in character. Recently the most frequently used sulfenamides are N-cyclohexyl-2-benzthiazol sulfenamide (CBS), N-tert-butyl-2-benzothiazol sulfenamide (TBBS) and dicyclohexyl-2-benzothiazol sulfenamide (DCBS).



Activity of sulphonamide type's accelerator with respect to cure characteristics can be summarised as follows:

1. Scorch time \longrightarrow CBS < TBBS < DCBS

2. Cure rate \longrightarrow DCBS < TBBS < CBS

Sulfenamide accelerators are suitable also for EV and semi-EV systems. Sulfenamide accelerators are created very effective accelerating systems giving good scorch time, fast curing and reduced reversion with secondary accelerators like TMTD.

Thiurams Class Accelerators:

Thiurams are very speedy and also fast i.e ultra-accelerators. They are made from secondary amines and carbon disulfide. They are suitable for vulcanization of low unsaturated and into semi EV and EV vulcanization systems. Mutually they differ by character of the number of sulfur atoms in sulfur bridges (1, 2, 4, 6) and the substituents in amine groups (e.g. methyl-, ethyl-, pentamethylene-). Their stability decreases with increasing number of sulfur atoms and they are easily decomposed with sulfur creation. In practice the most commonly used of this class are tetramethylthiuram disulfide (TMTD), tetraethylthiuram disulfide (TETD) and tetramethylthiuram monosulfide (TMTM). According to their activity the above three thiuram class accelerator can be arranged as $TMTD > TETD > TMTM$. If TETD is substituted for TMTD, about 10% more TETD should be used. They are used in combination with other accelerators, mostly with sulfenamides and thiazoles in various times. It is also used as sulfur donors. However, the monosulfide is not strong enough to cure satisfactorily without added sulfur. Their disadvantage is generation of secondary amines in the process vulcanization. These unwanted effects are not obtained by thiurams with hindered substituents in amine groups (e.g. benzyl-, piperidyl-).

Dithiocarbamates Class Accelerators:

Dithiocarbamates are metallic (the most often salts of Zn and Na, but also Se, Te, Pb, Cd, Bi) or ammonium salts of dithiocarbamoic acids. They can be differentiating with respect to the cation as well as alkyl substituents in the dithiocarbamate group. They are low soluble in non-polar rubber due to their polar character, so they bloom at higher concentration. With the increase of carbon number in alkyl substituents, the solubility of dithiocarbamates in rubber molecules is also increases. They belong to ultra fast accelerators. Usually they are paired



with thiazole or sulfenamide accelerators to adjust the cure rate of a stock. Some of them are soluble in water. They are used not only during vulcanization of rubber and latex compounds, but also rubber solutions. The most popular and common members of this class are the zinc dimethyl dithiocarbamates (ZDMC), zinc diethyl dithiocarbamates (ZDEC) and zinc dibutyl dithiocarbamates (ZDBC). Dithiocarbamates are infrequently used alone except in such specialty applications as spread goods (fabric covered with a rubber coating: e.g. hospital sheeting) due its powerful activities.

Xanthates Class Accelerators:

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

Aldehydamines Class Accelerators

The condensation products of aldehydes and amines are aldehydeamines. The main aldehydeamine accelerators are triotonylide tetramine (TCT), butylaldehyde aniline (BBA) and hexamethyllene tetramine (HEXA). Among this three the butylaldehyde aniline is the most common commercial vulcanization accelerator. Their accelerating effect is mainly determined by:

- The aldehyde type and
- Mole ratio of aldehyde and amine in the reaction mixture used for their preparation.

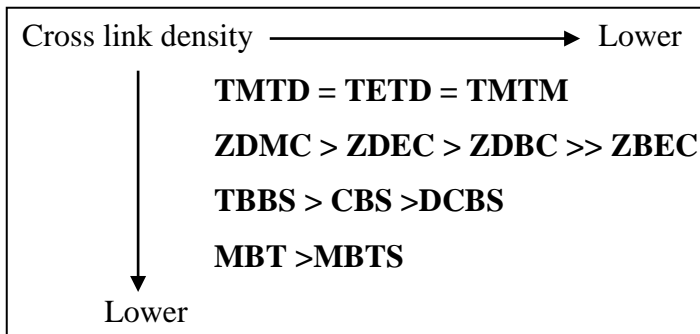
Butylaldehydeaniline (BBA) is very fast accelerator which is a red-brown liquid and colours the vulcanisate and high network density of vulcanizates is achieved by its presence in rubber



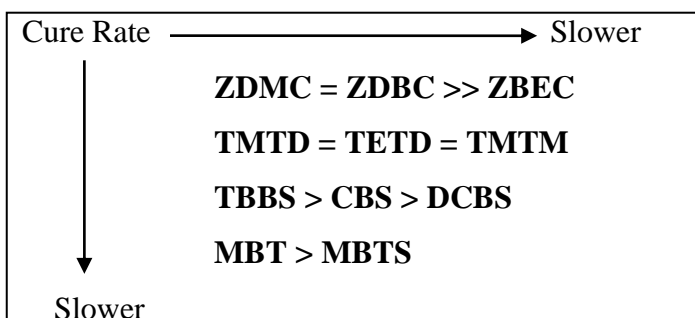
compound whither the tricrotonylidenetetramine and hexamethylenetetramine acts as very slow accelerator. Aldehydeamines belong to less used accelerators and they are used as secondary accelerators with the combination of thiazoles and sulfenamides type accelerator.

Summary: Cure Activities of the Accelerators:

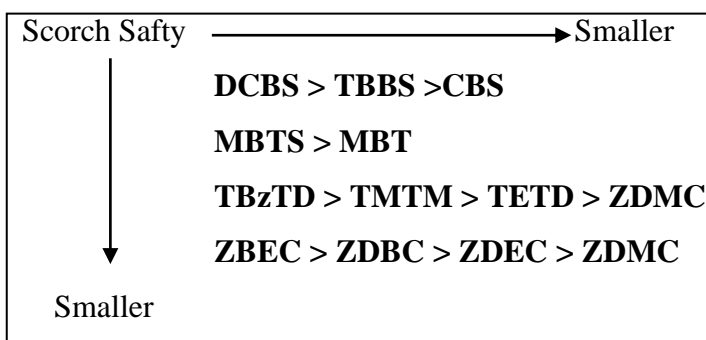
With respect to crosslink density



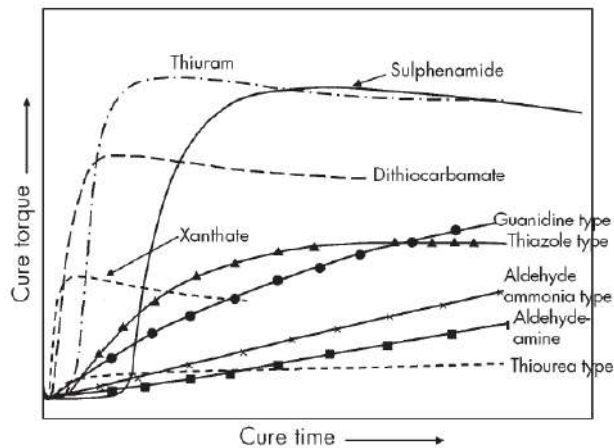
With respect to cure rate



With respect to scorch safty



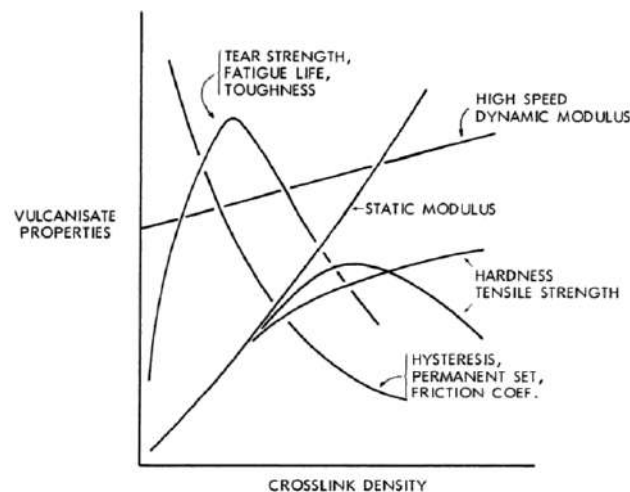
Rheographs:



Model vulcanisation curves for different types of accelerator in natural rubber

Vulcanization System:

• Cross link density & Vulcanizate properties:



The dependence of various vulcanizate properties on cross-link density (From Rodger, 1979.)

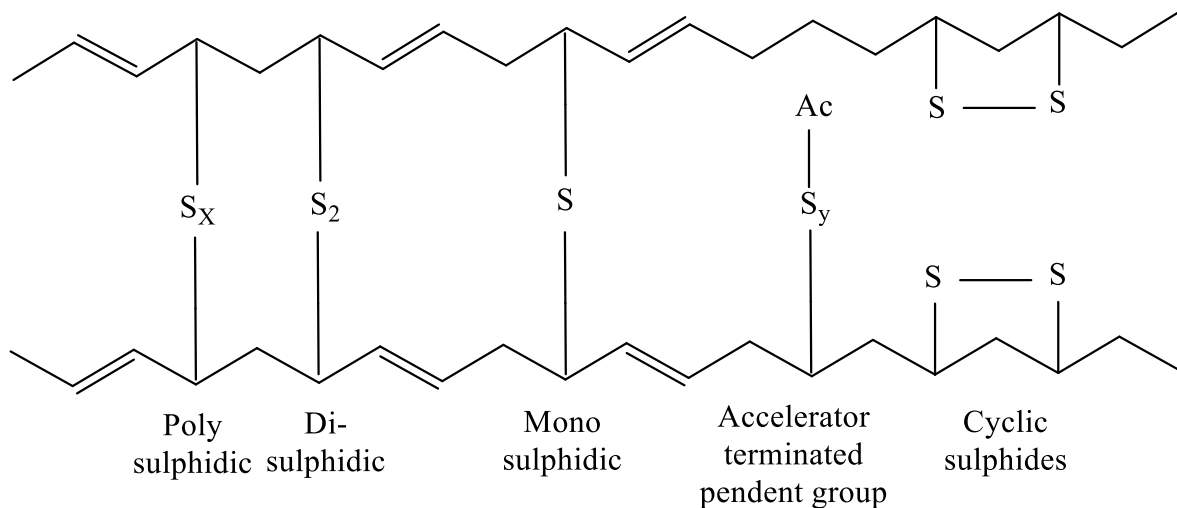
Once the basic polymer has been selected, performance characteristics of the vulcanisate are determined principally by the amount and the type of crosslinks produced by the vulcanisation system. A detailed knowledge of the principal features of the crosslink structure and the factors which influence their generation is of practical importance in designing vulcanisation systems to meet performance and production criteria.

Cross link density = Number of molecules of cross linked units per unit weight of the cross linked polymer.



Degree of cross linking = Number of molecules of cross linked basic units per total number of polymer basic units.

In the vulcanisation network sulphur is combined in a number of ways. In the form of crosslinks it remains as monosulphide, disulphide or polysulphide. It may also be present as pendent sulphides or cyclic monosulphides or disulphides as shown:



The structure of the cross-links formed mainly depends on the type and amount of the accelerator in the rubber mixture although it can be influenced by various technological parameters of the vulcanisation process. The presence of slow accelerators mainly leads to the formation of polysulphidic cross-links while, by the application of fast accelerators, the number of sulphur atoms in the sulphidic bridges is lower. The structure of the cross-links formed in vulcanisates has a significant influence on their properties (González et al., 2005). The longer the sulphidic cross-links are the more readily they decompose and the lower the resistance to elevated temperature they have. Accordingly, vulcanisates with high levels of polysulphidic cross-links are not very heat-proof and exhibit a high compression set (mostly at higher temperatures). This is largely due to the low bonding energy of sulphidic cross-links with a higher number of sulphur atoms. On the other hand, they generally show good physical-mechanical and dynamic properties and good resistance to dynamic fatigue. This is largely due to the capacity of polysulphidic cross-links to be rearranged under the influence of external stress and to dissipate it without reducing the number of crosslinks. In vulcanisates with a dominance of polysulphidic cross-links, elastomer chains are connected with longer sulphur bridges which render the micro-Brown motion of rubber chain segments between the crosslinks easier, which subsequently results in an improvement in the elastic and dynamic properties of vulcanisates (Kyselá et al., 2010).



The crucial factor determining the number of sulphur atoms in sulphidic cross-links is the amount of sulphur and the ratio between the accelerator and sulphur. Depending on the sulphur accelerator ratio the sulphur vulcanising systems can be categorised as: conventional (CV), semi-efficient (semi-EV) and efficient (EV).

Type	Sulphur (S)/phr*	Accelerator (A)/phr*	A/S ratio/phr*
Conventional	2.0-3.5	1.2-0.4	0.1-0.6
Semi- efficient	1.0-1.7	2.4-1.2	0.7-2.5
Efficient	0.4-0.8	5.0-2.0	2.5-12.0

Table: CV, SEV and EV vulcanisation systems

* phr- Parts per hundred rubber

Conventional Vulcanization System (CV):

Conventional vulcanization systems continue to find widespread general purpose use for the products that do not require sustained heat resistance during manufacture or service. The course of vulcanization, to a large extent, depends on the nature of the accelerators used. In the conventional curing (CV) systems, the sulfur dosage is high (above 1.5 phr) and correspondingly the accelerator is low (0.5 to 1.0 phr). The CV systems provide better flex dynamic properties but worse thermal and reversion resistance. The CV systems provide higher amounts of poly- and disulfidic crosslinks and higher proportions of sulfidic and non-sulfidic modifications. These systems are comparatively less expensive. The general formulation of natural rubber compounds in parts per hundred is given below.

Ingredients	CV system
Natural Rubber	100
ZnO	5
Stearic acid	2
CBS	0.7
Sulphur	3
Antioxidant	1.5

Efficient Vulcanization System (EV):



In EV systems, the network will contain an abundance of mono sulphidic crosslinks, usually accounting for at least eighty percent of the total. As a measure of the improved crosslinking efficiency, the number of sulphur atoms combined for every chemical crosslink is unlikely to exceed five and can be as low as two. EV systems are those where a low level of sulfur (below 0.4-0.5 phr) and a correspondingly high level of accelerator (2.5 to 5.0 phr) or sulfurless curing are employed in vulcanisates for which an extremely high heat and reversion resistance is required. These systems are usually suitable for products that need improved reversion resistance during vulcanization. But these systems are comparatively expensive. Typical formulation of natural rubber compounds in parts per hundred is given below.

Ingredients	EV system
Natural Rubber	100
ZnO	5
Stearic acid	2
CBS	2.9
Sulphur	0.8
Antioxidant	1.5

Semi Efficient Vulcanization System (SEV):

For optimum levels of mechanical and dynamic properties of vulcanisates with intermediate heat, reversion, flex and dynamic properties, the so-called SEV systems with an intermediate level of accelerator and sulfur are employed. Many studies have documented both the advantages (increased age resistance), and the disadvantages (impaired fatigue resistance) of EV and SEV systems. The worse fatigue resistance correlates to lower amounts of polysulfidic crosslinks in the network. This combination provides high flex fatigue resistance but at the expense of heat and reversion resistance. Typical formulation of natural rubber compounds in parts per hundred is given below.

Ingredients	SEV system
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Natural Rubber	100
ZnO	5
Stearic acid	2
CBS	1.40
Sulphur	1.45
Antioxidant	1.5

The vulcanizate structures and properties for CV, SEV and EV systems are shown in table below.

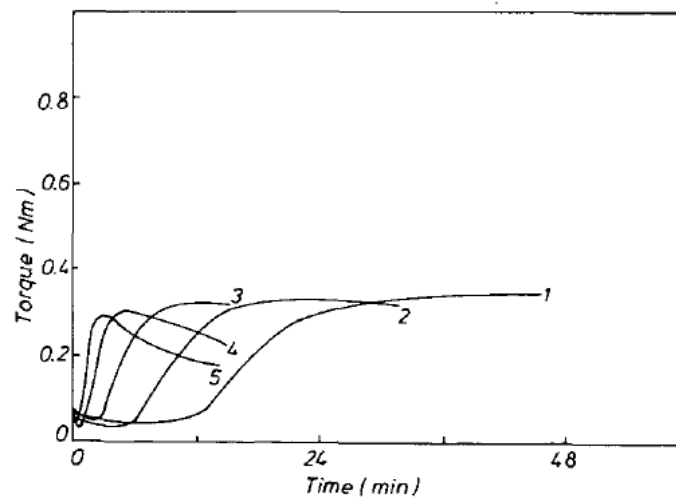
Vulcanizate structures and properties			
Features	Systems		
	CV	SEV	EV
Poly- and disulfidic crosslinks (%)	95	50	20
Monosulfidic crosslinks (%)	5	50	80
Cyclic sulfide (conc.)	High	Medium	Low
Non-sulfidic (conc.)	High	Medium	Low
Reversion resistance	Low	Medium	High
Heat ageing resistance	Low	Medium	High
Fatigue resistance	High	Medium	Low
Heat build up	High	Medium	Low
Tear resistance	High	Medium	Low
Compression set (%)	High	Medium	Low

Effect of vulcanization temperature:

The cure curves of the compound at 140°C, 150°C, 160°C, 170°C, and 180°C are shown in figure below. The curing becomes faster with an increase in vulcanization temperature as reflected in the decrease in the cure time. The scorch safety also decreases with an increase in vulcanization temperature as expected. The maximum torque, a measure of the crosslink density, decreases with an increase in vulcanization temperature. This indicates that the crosslink density decreases with an increase in the vulcanization temperature. Molecular



changes resulting in a reduction in the overall viscosity of the system might be another reason for the decrease in the maximum torque.



Cure curves of NR compound at 140°C (1), 150°C (2), 160°C (3), 170°C (4), and 180°C (5).

Retarders:

In order for good quality vulcanization to take place, the rubber, sulfur, accelerants, activators and other compounds must be fully mixed to give a homogeneous liquid. In practise this can involve melting the sulfur (melting point 115 °C) and at these temperatures vulcanization can begin prematurely i.e. scorch. Modern curing systems provide a scorch delay time, during which heating produces no crosslink followed by a period of rapidly crosslink formation. Then the compounder adjusts process conditions to provide enough heat to eliminate most of the scorch delay so that the cure time will be minimized. Since the compounder is balancing processing against cure suitable and sometimes uncontrollable changes in factory equipment or operating parameters can produce unprocessable rubber stocks. Such changes can be compensated for by making adjustments in the curing system or in the processing conditions. However relationships between curing system and properties are complex and considerable effort is generally required to develop a new formulation. Thus the need exists for an additive which increases only the scorch delay time with minimal effects on the other cure parameters and vulcanizate properties. Such compounds are called retarders or antiscorch agents. It has been assumed that the retarder and the vulcanization accelerator form a complex which is stable at processing temperatures but which dissociates at the higher vulcanization temperature (at about 140°C), releasing the accelerator. A retarder slows down both the onset and rate of vulcanization, whereas inhibitors only delay the start

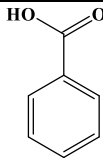
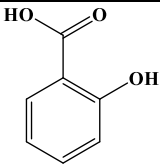
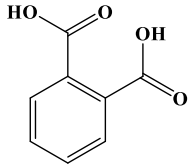
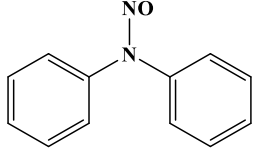


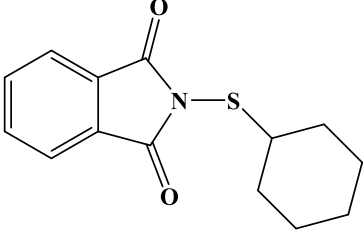
of vulcanization and do not affect the rate to any great extent (Sadhan K. De; Jim R. White, Rubber Technologist's Handbook. iSmithers Rapra Publishing, ISBN 978-1-85957-262-7, pp. 184–, 2001). For many years a number of formulations included a retarder, such as benzoic acid, salicylic acid, phthalic acid, N-nitroso diphenylamine (NDPA), N-(cyclohexylthio) phthalimide (CTP), etc. at a level of 0.5-2.0 phr.

The choice of a Retarder depends upon:

- ✓ The accelerator system
- ✓ Cost and
- ✓ Side effect

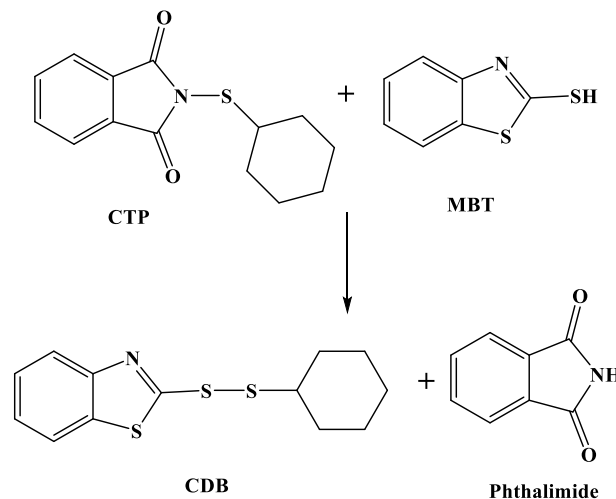
Chemical structure of the most commonly used retarders:

Chemical Type	Chemical Structure	Uses and Comments
Benzoic acid		Weak acid; improves shelf aging; activates cure; reduces compound viscosity.
Salicylic acid		Moderate acid; moderate retarding of thiazoles; promotes reversion resistance; activates cure.
Phthalic acid		Best retarding acid with thiazoles; minimal effect on state-of-cure.
N-nitroso diphenylamine (NDPA)		Major use is believed to be as an anti-scorching agent; as a staining retarder for natural and synthetic rubbers; works effectively at dosages (0.5-1.0 phr) in a variety of rubbers at processing temperatures; does not interfere with the action of the organic accelerators at vulcanizing temperatures.

<p>N-(cyclohexylthio)phthalimide (CTP)</p>		<p>Outstanding retarder with most systems; very effective with sulfenamides; Low dosages (0.10-0.30 phr) are typical.</p>
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Pre Vulcanization Inhibitor:

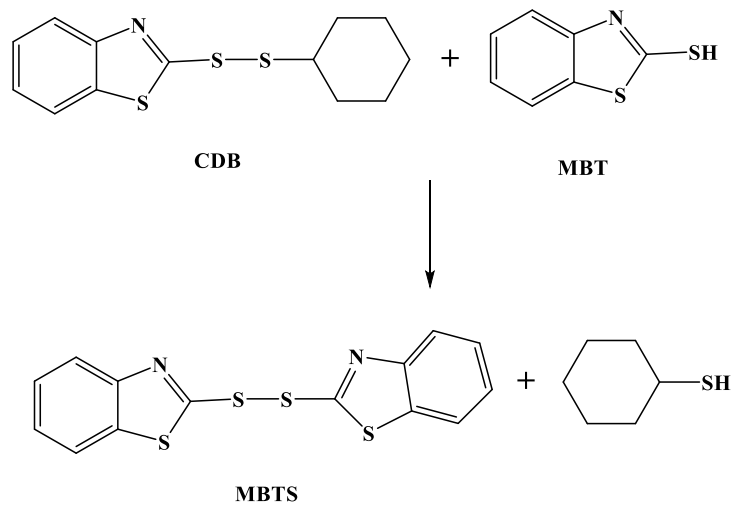
Used in natural rubber and synthetic rubber. It can effectively protect the compound rubber scorching during the process, enabling extrusion to operate at high temperature and high speed. Provides improvement in production, storage stability of the rubber compound and protects the natural vulcanization. It has function recovery for rubber compounds with high heating or dangers of scorching. In general pre-vulcanization inhibitor (PVI) are preferred, with N-cyclohexylthiophthalimide (CTP) being the most common example. CTP has little or no or little adverse effect on thiazole / sulfenamide cure and does not cause any staining but increases scorch safety and permits processing at higher temperatures which increases productivity. It has been shown that CTP reacts rapidly with thiazoles to form 2-cyclohexyldithiobenzothiazole (CDB) and phthalamide as shown below (R. I. Leib, A. B. Sullivan, C. D. Trivette Jr, Rubber Chem. Technol., Vol. 43, No. 5, 1970).



The CTP reacts faster with 2-mercaptobenzothiazole (MBT), the active accelerator fragment, than MBT reacts with the primary accelerator to form 2-2'-dithiobis(benzothiazole) (MBTS) (MHS. Gradwell, and N.R. Stephenson, Rubber Chem. and Technol., Vol. 74, no. 1, pp. 44 – 56, 2001). The CDB slowly converts back into the vulcanization system, for example by



reacting with more MBT to yield MBTS (see below) which then undergoes reactions which result in the formation of crosslinks.



Generally 0.1 – 0.2 phr dosage of CTP is sufficient. CTP is most effective with the fastest curing polymers and the approx. order of response is NR > NBR > SBR > EPDM > IIR > CR.

Activators:

The spectacular effects of modern organic accelerators in sulphur vulcanization of rubber are observed only in the presence of some other specific additives commonly known as accelerator activators. The activator, not only activate cure but also improve the efficiency of sulphur based cure systems and to achieve the end-use properties. For this purpose inorganic as well as organic compounds are used. From the inorganic compounds these are mostly metal oxides such as ZnO, PbO, MgO etc. and from organic compounds higher fatty acids include stearic, lauric, palmitic, oleic and naphthenic acid and their salts, some amines or their derivatives. Zinc oxide is the most important of these additives. Originally ZnO was used as an extender for cost reduction, and then it was found to have a reinforcing effect and was later found to reduce vulcanisation time (D. L. Hertz Jr., *Elastomerics*, p.17, November 1984). Usually in practically activators are two-component systems a combination of a metal oxide and long chain fatty acid. A combination of zinc oxide and stearic acid is known to produce quite satisfactory results and is almost used universally. 5 phr of zinc oxide with 1-3 phr of stearic acid is the commonly accepted combination (B. G. Crowther, P. M. Lewis and C. Metherell, "Natural Rubber Science and Technology", A. B. Roberts, Ed., Oxford University Press, Ch.6, p.1888, 1988). Activation effect of ZnO is ascribed mostly to its



ability to create complexes generating curing sulphuric fragments with sulphur and accelerators. Participating acids increase solubility of these complexes in rubbers; they improve dispersive capacity of powder additives in compounds and sometimes they also prolong induction period of the vulcanization. The importance of the activator can be appreciated from the data given in the table (Jr. B.S. Garvey and G. Thompson, Ind. Eng. Chem., 25, 1295, 1933) below.

Table: Effect of activator on vulcanization

Time of cure (min.)	Tensile strength, psi	
	ZnO in parts	
	0.0	5.0
15	100	2300
30	400	2900
60	1050	2900
90	1300	2900

Sulfur Vulcanization Chemistry:

Raw rubbers have little commercial significance as they cannot be used in load bearing applications. Owing to unique properties of rubber has gained importance as an essential industrial raw material. But to be practically useful, all rubbers will have to undergo the process of vulcanisation. Because unvulcanized rubber has poor mechanical properties and is not very durable. Vulcanisation is the process of conversion of rubber by any treatment, from a plastic substance of very low strength and breaking elongation to a resilient highly elastic material of considerable strength. From the chemical point of view vulcanisation is the process whereby the flexible, discrete rubber chains are joined together by crosslinking reactions giving a three dimensional network. The cross-linking process is rather complicated and involves a sequence of reactions. Studies on the chemistry of vulcanisation play a central role in the efforts to achieve better product performance from natural and synthetic rubbers. Understanding the network structure of the cured elastomers is important. There are two tendencies towards the interpretation of the general nature of chemical reaction of sulphur with rubber. Farmer and co-workers (E. H. Farmer and F.W. Shipley, Journal of Polymer Science, 1, 293, 11946) proposed a free radical chain mechanism whereas Bateman (L. Bateman, CG. Moore and M. Porter, J. Chem. Soc., 2866, 1958) and co-workers favoured a polar mechanism for the structural changes in rubber during vulcanization. The most common vulcanization agent is sulfur. Vulcanization of rubber by sulfur alone is extremely slow and can take several hours at elevated temperatures (140°C or more). This is

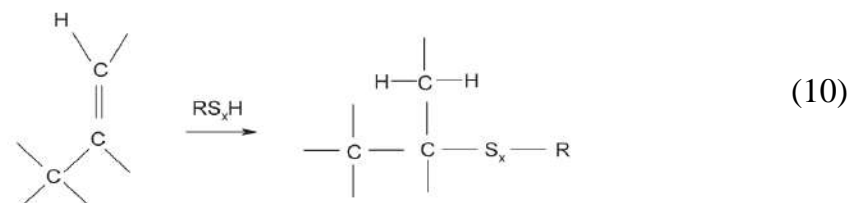
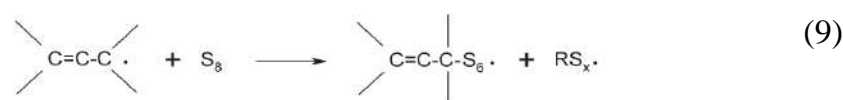
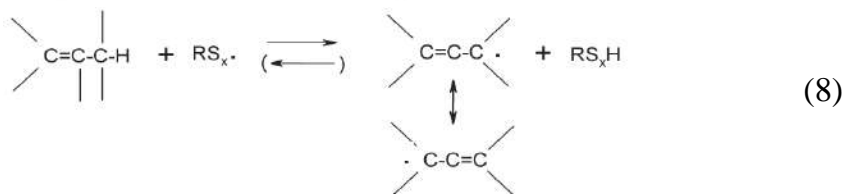
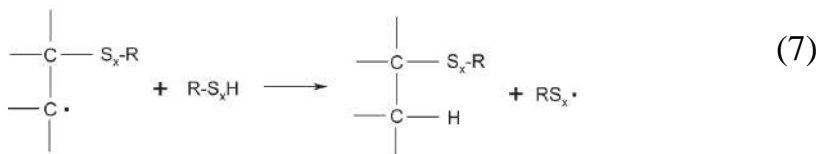
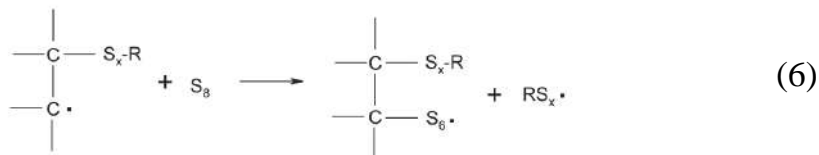
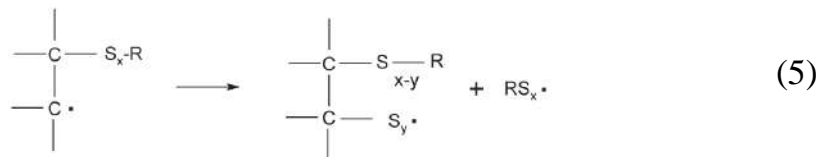
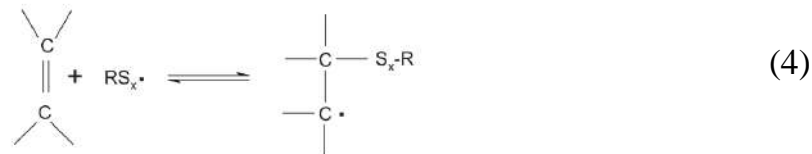


problematic because long exposure to temperature and oxygen leads to oxidative degradation which, in turn, results in poor mechanical properties. It is also not very economical. To minimize rubber degradation and to speed-up the vulcanization process, accelerators are usually employed. An accelerator is defined as a compound that increases the speed of vulcanization and that enables vulcanization to proceed at lower temperature and with greater efficiency. Accelerator also decreases the amount of sulfur needed to cross-link the polydiene thus improving the aging properties of the vulcanized rubber.



Sulphur Vulcanization Mechanism:

A: Radical Mechanism:



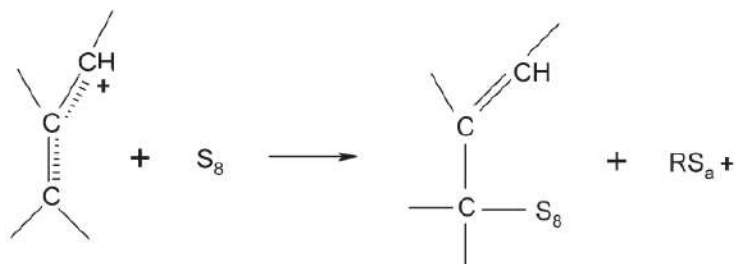
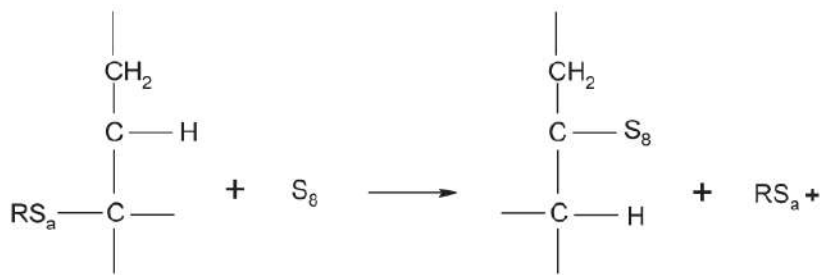
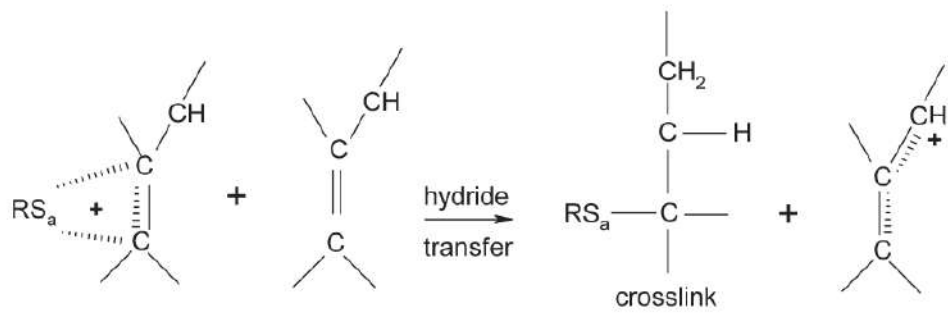
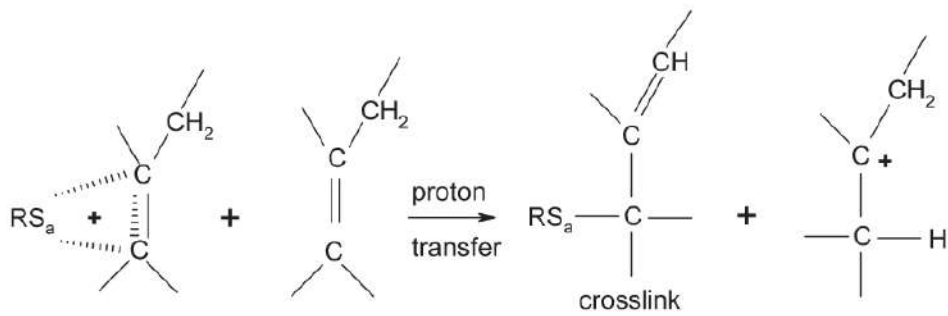
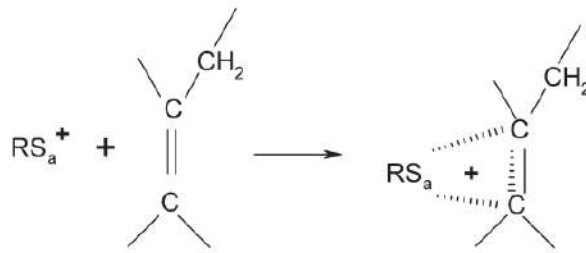
Free-radical mechanism for sulphur vulcanisation (Akiba, M., & Hashim, A. S., Progress in Polymer Science, 22, 475–521, 1997)

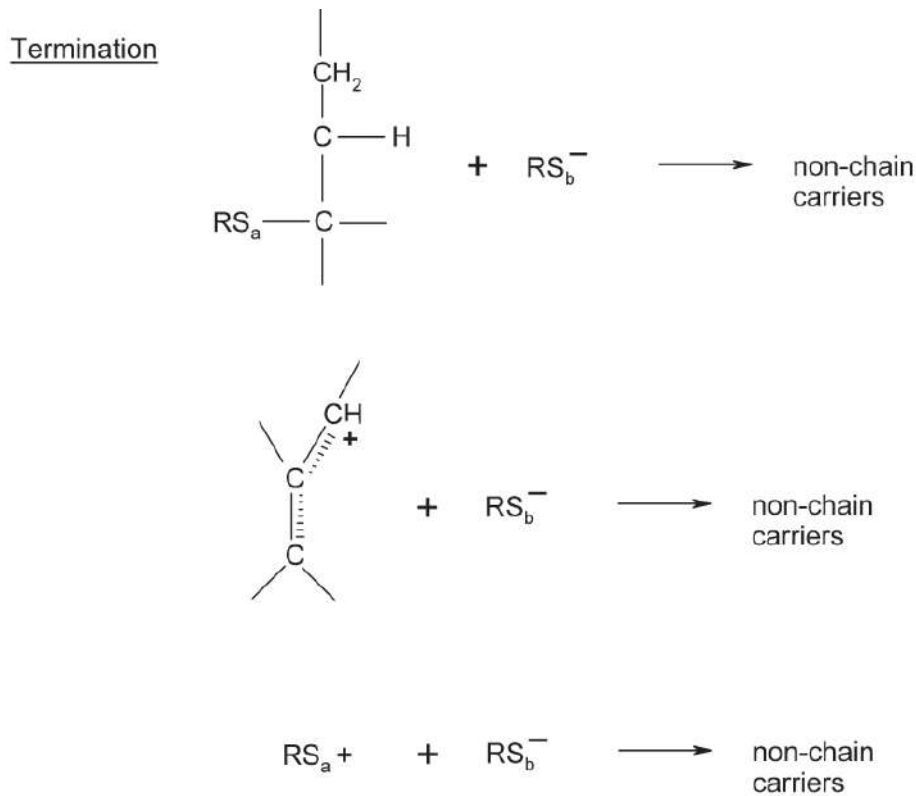
B. Ionic Mechanism:

Initiation



Propagation





Ionic mechanism for sulphur vulcanisation (Quirk, R. P., Progress in Rubber & Plastics Technology, 4, 31–45, 1988).

Accelerated Sulfur Vulcanization:

Accelerators are essential ingredients in all sulphur vulcanisation systems. They increase the reaction speed and cross-linking density, they improve the yield of the sulphur forming cross-links and can be used to adjust the ratio between the induction period, reaction speed and types of cross-links. From the technological point of view, the presence of accelerators in the vulcanisation process leads to a reduction in vulcanisation time, they reduce the vulcanization temperature and the amount of sulphur in the rubber mixture. Proposed mechanisms of accelerated sulphur vulcanization have ranged from radical to ionic and the resultant effect depends largely on the compounding formulation. Several researchers have concluded that both radical and ionic mechanisms are operative at different stages of the overall vulcanization reaction depending on the vulcanizing system.

There are at least three competing reactions that occur during the cure and network maturing period.

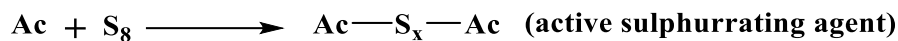
- ✓ Cross linking
- ✓ Degradation
- ✓ Desulfuration



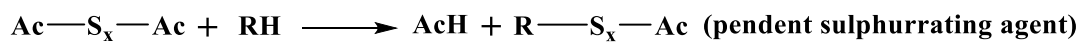
Almost all accelerators need metal oxides for the development of their full activity. Zinc oxide is the most common activator for sulphur vulcanization, which is almost always used in combination with appropriate fatty acids, mainly stearic, lauric acid or their zinc salts (J. Kruželák et al., Chemical Papers 70, 1533–1555, 2016).

A generally accepted scheme of the reactions is as follows:

- ❖ Accelerator (Ac) and activator interacting with sulphur to form the active sulphurating agent.



- ❖ The rubber chains interact with the sulphurating agent to form polysulphidic pendant groups terminated by accelerator groups.

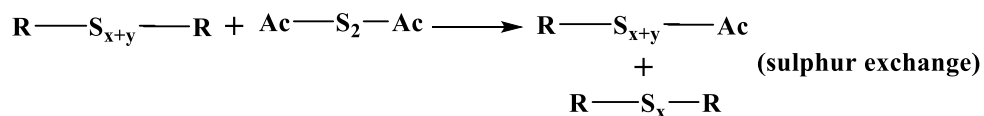
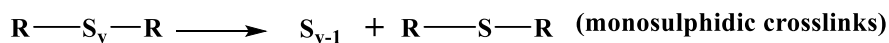


Where RH is the rubber chain.

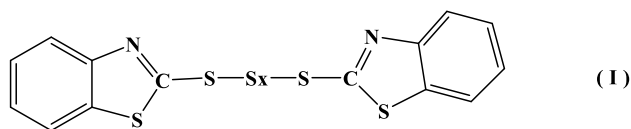
- ❖ Polysulphidic crosslinks are formed.



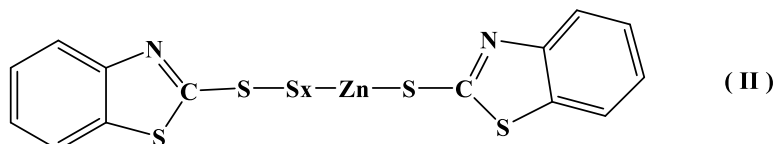
- ❖ Network maturing and competing side reactions and thermal decomposition leads to the following reactions.



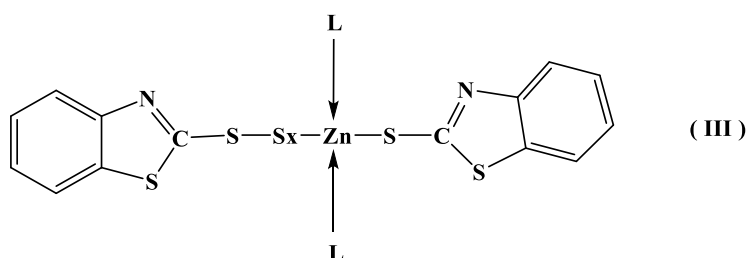
The first step in sulfur vulcanization is the formation of an active sulfurating species, which is a prerequisite for the formation of a crosslink precursor. A sulfurating species is a molecule that is able to insert sulfur in the form of crosslinks into the elastomer, where it has been long recognized that accelerator polysulfide complexes are better sulfurating species than molecular sulfur. In the absence of an activator such as ZnO, the polysulfides are formed of Type I. The organic pendent group in this Type 1 molecule is benzothiazole (when other than thiazole accelerator is used; the organic pendent group will be different but the polysulfidic nature is the same).



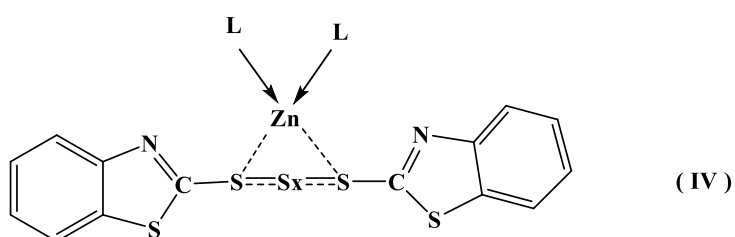
When ZnO is present, the zinc complexes with the accelerator polysulfides, resulting in structures of Type II:



If ligands L such as amines and carboxylate ions are also present in the system, structures of Type III can result:



These structures suggest that Zn is covalently bonded as a part of polysulfidic chain in the accelerator species. However, it is more probable that the Zn complexes with the sulfur in the accelerator polysulfide as shown in IV, where the dotted lines indicate the formation of a complex of zinc with sulfur.



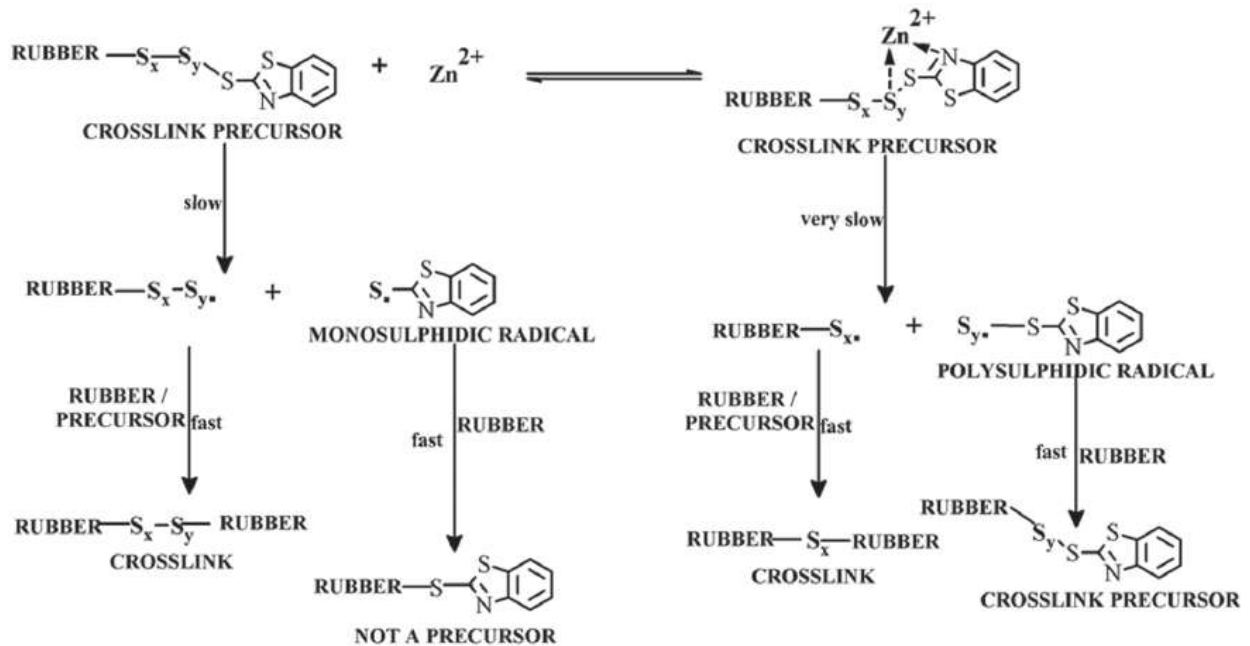
Structures of Type I, II and III or alternately IV are all capable of sulfurating the rubber chains and therefore are considered active sulfurating species.

Effect of zinc ions in sulphur vulcanization:

As shown in following scheme, radical mechanism controls the formation of crosslinks from precursors in the absence of ZnO where as the presence of ZnO stabilizes sulphur bonds through zinc chelation thereby changing the most likely breakable bond (Ghosh et al., 2003).



Such bond scission leads to crosslink byproducts (accelerator polysulphides) that can further crosslink and thus enhance the rate and efficiency of vulcanization. On the other hand in the absence of zinc species the bond cleavage during the conversion of a crosslink precursor to a crosslink may result in accelerator monosulphides which cannot contribute to further crosslinking. The effect of zinc ions on the efficiency of crosslink formation is being depicted in the scheme below.



Scheme: Effect of zinc ions in sulphur vulcanization

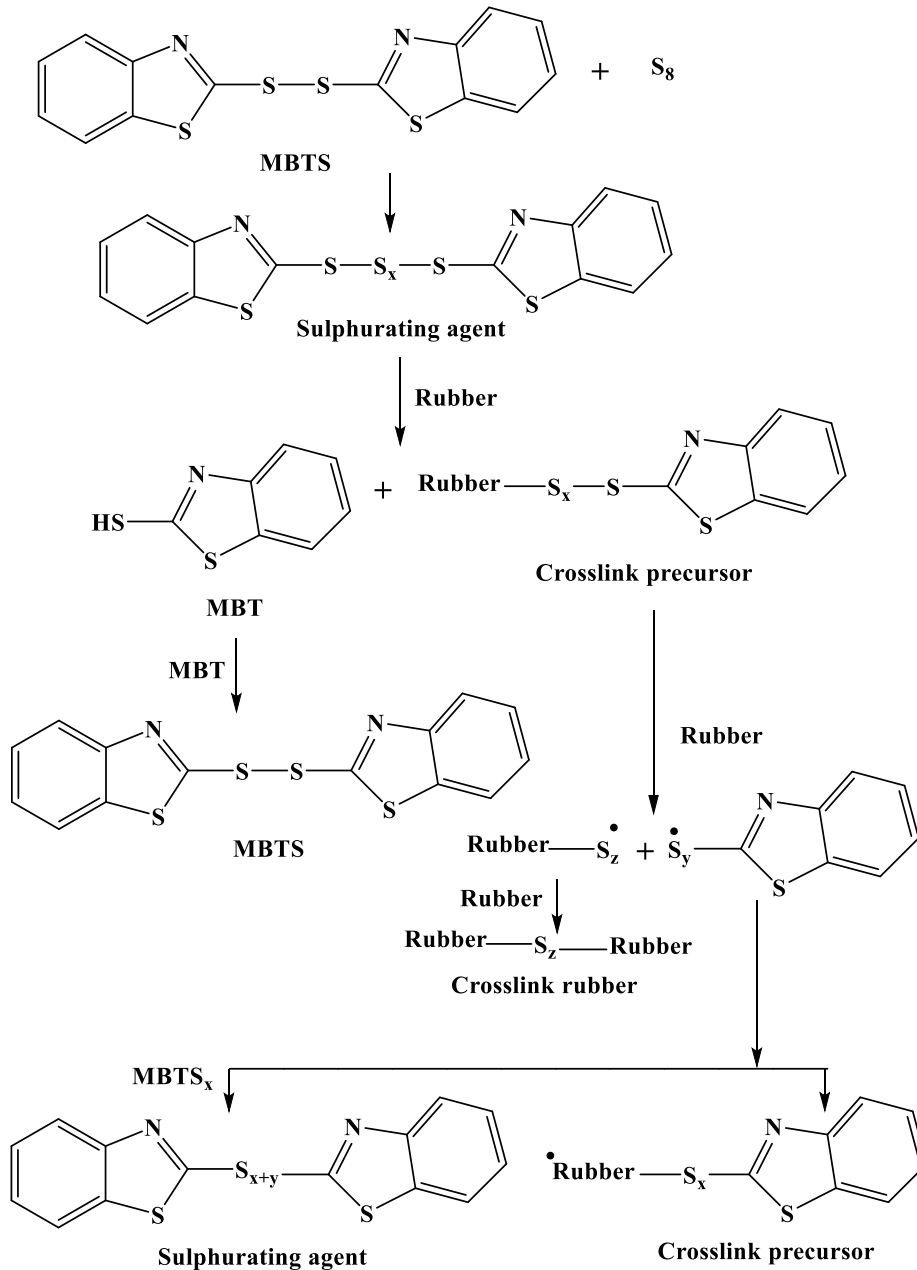
Thiazole accelerated sulfur vulcanization:

The most commonly used vulcanization accelerators are thiazoles. They form sulfur bridges between individual polymer molecules when heated with rubber. A possible reaction mechanism for 2-2'-Dithio-bis-(benzothiazole) (MBTS) accelerated sulfur vulcanization of rubber is shown below.

- ✓ In the absence of an initiator, MBTS reacts with a sulfur molecule (cyclic S_8) to form a polysulfide sulfurating agent.
- ✓ The polysulfide sulfurating agent then reacts with a rubber unit to form a crosslink precursor and a 2-mercapto-benzothiazole molecule (MBT).
- ✓ Two of these MBT molecules react to form MBTS again whereas the sulfurated rubber decomposes into a rubber-polysulfide and MBT radical.



- ✓ MBT polysulfide radicals combine to form new sulfurating agents and/or they react with rubber to form more rubber crosslink precursors whereas the polymeric persulfenyl radicals either combine or react with other rubber molecule to form sulfur bridges, i.e. cross-linked rubber.



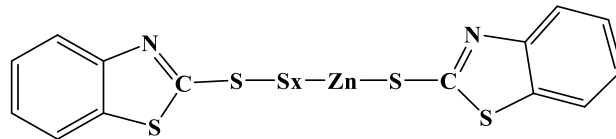
MBTS accelerated sulphur vulcanization

Sulfenamide Accelerated Sulfur Vulcanization:

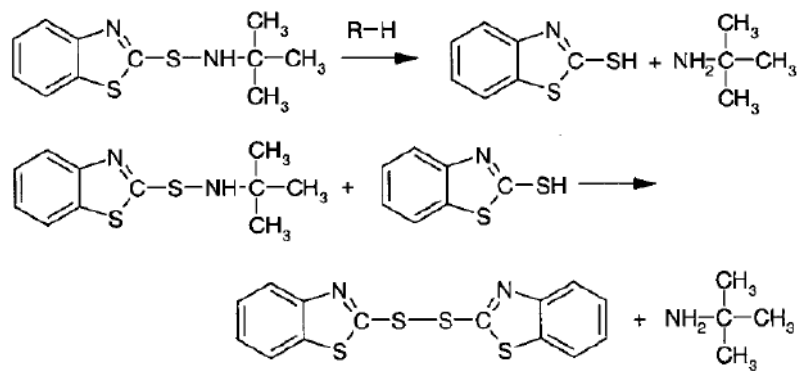
Gradwell and McGill (M. H. S. Gradwell, W .J. McGill, J. Appl. Pol. Sci. 51, 177, 1994) investigated the interaction of sulfenamide accelerators with sulfur, ZnO and stearic acid in



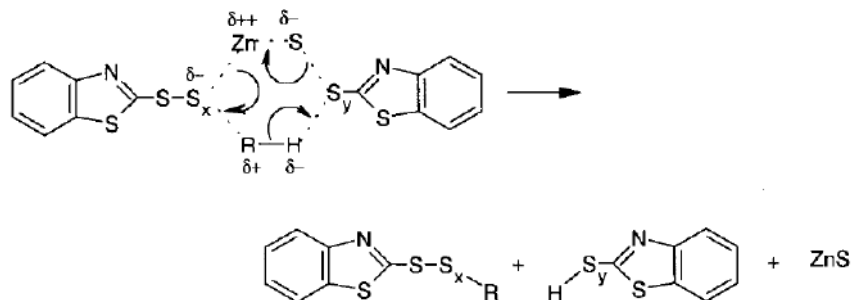
the absence of rubber. They found that ZnO does not react with sulfonamide accelerators like CBS and TBBS. The only way zinc accelerator complexes can be formed is via the reaction of MBT with ZnO to produce ZMBT, which eventually is converted into the active sulfurating complex. MBT is initially formed by the thermal decomposition of the accelerator (TBBS), as shown in figure below. With the MBT quickly converted into MBTS, it is likely that only small amounts of the zinc accelerator complex are formed in that stage. The majority of the active sulfurating species are zinc-free structures. In the crosslinking stage, more MBT is formed and this leads probably to the formation of additional zinc-accelerator complexes. The formation of rubber bound intermediates, the so-called crosslink precursors, is a key stage in accelerated sulfur vulcanization. The mechanism of crosslink-precursor formation can be described as a concerted mechanism involving a six-membered ring in the transition state, with ZnS formed as a byproduct of this reaction.



Complex with the zinc ion

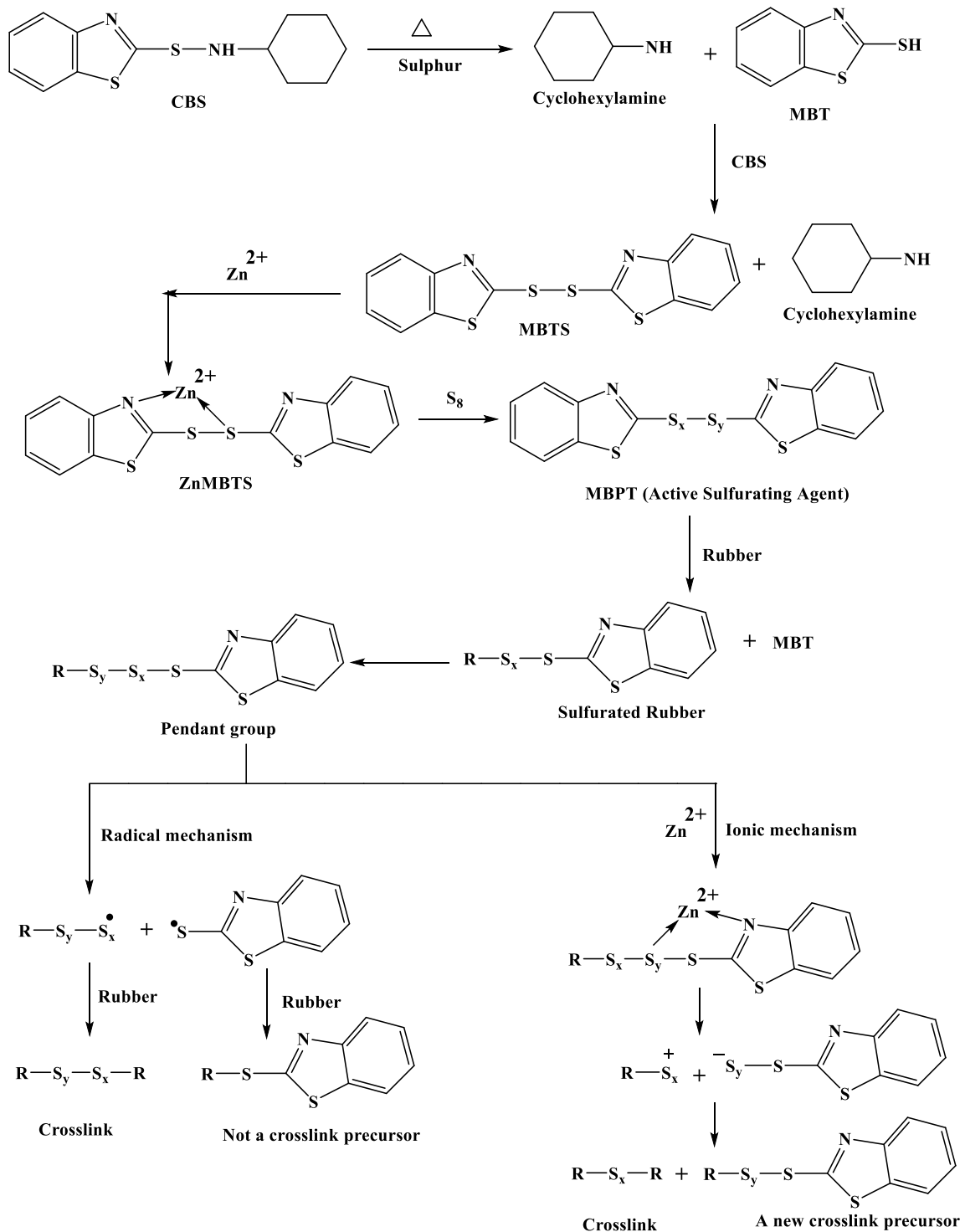


Thermal decomposition of TBBS and formation of MBTS (R-H = Rubber hydrocarbon)



Crosslink precursor formation via a mechanism involving a six-membered ring.

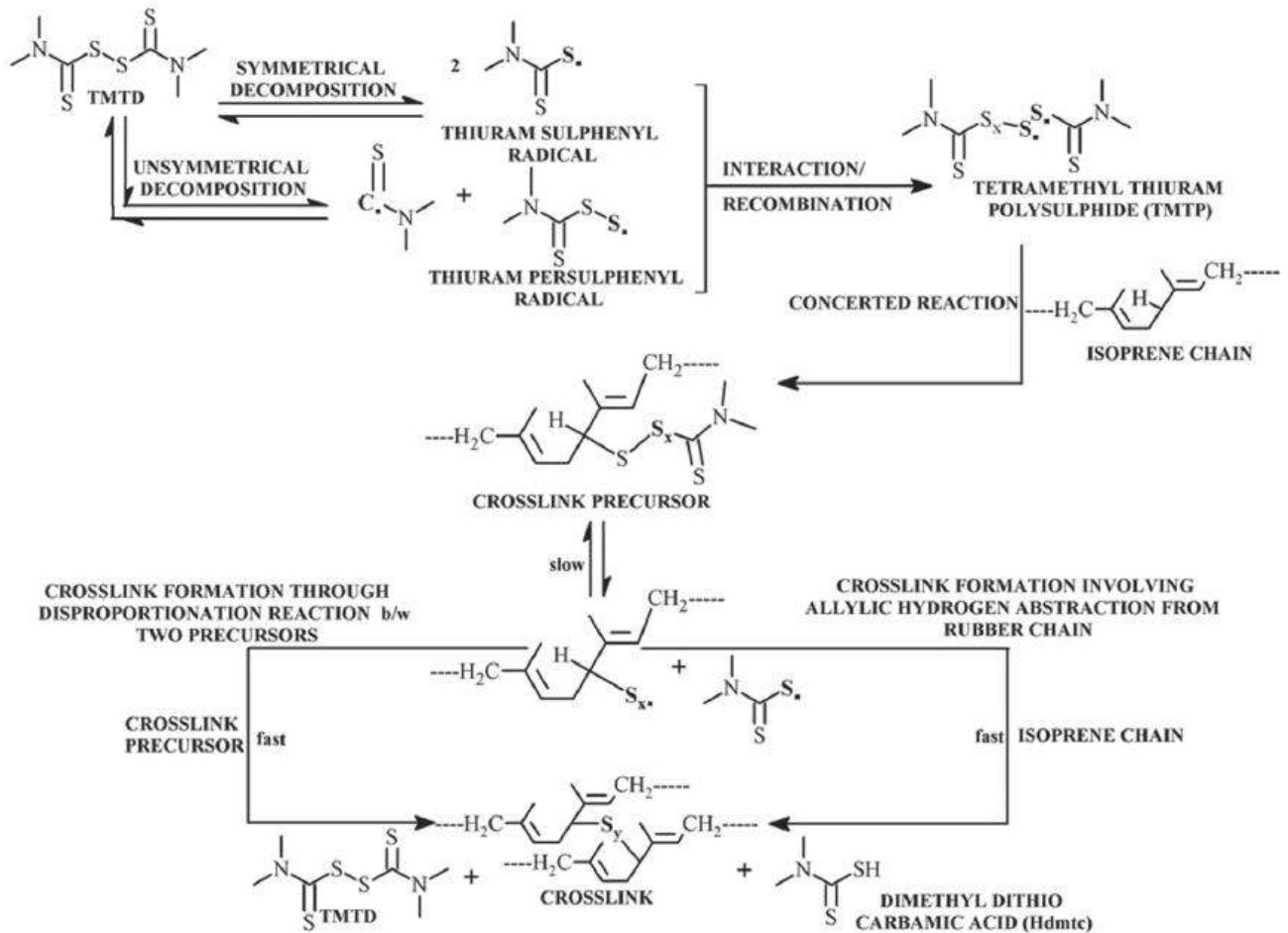
CBS Accelerated Sulfur Vulcanization:



Thiuram accelerated vulcanization:

According to radical mechanism given below, the first step in TMTD-NR vulcanization should be the symmetrical and unsymmetrical decomposition of TMTD into free radicals (Dogadkin, B. A. and Shershnev. V. A., Rubber Chemistry and Technology, 33, 401-411,

1960) at vulcanization temperatures whose interactive recombination will lead to the formation of accelerator polysulphides (TMTPs) (Coleman, M. M., Shelton, J. R. and Koenig, J. L., Rubber Chemistry and Technology, 46, 957-980, 1973). These sulphurating agents will form crosslink precursors on reaction with rubber. Crosslink precursors can form crosslinks either interacting with a precursor molecule or with a rubber molecule.



Vulcanization by TMTD – radical pathway

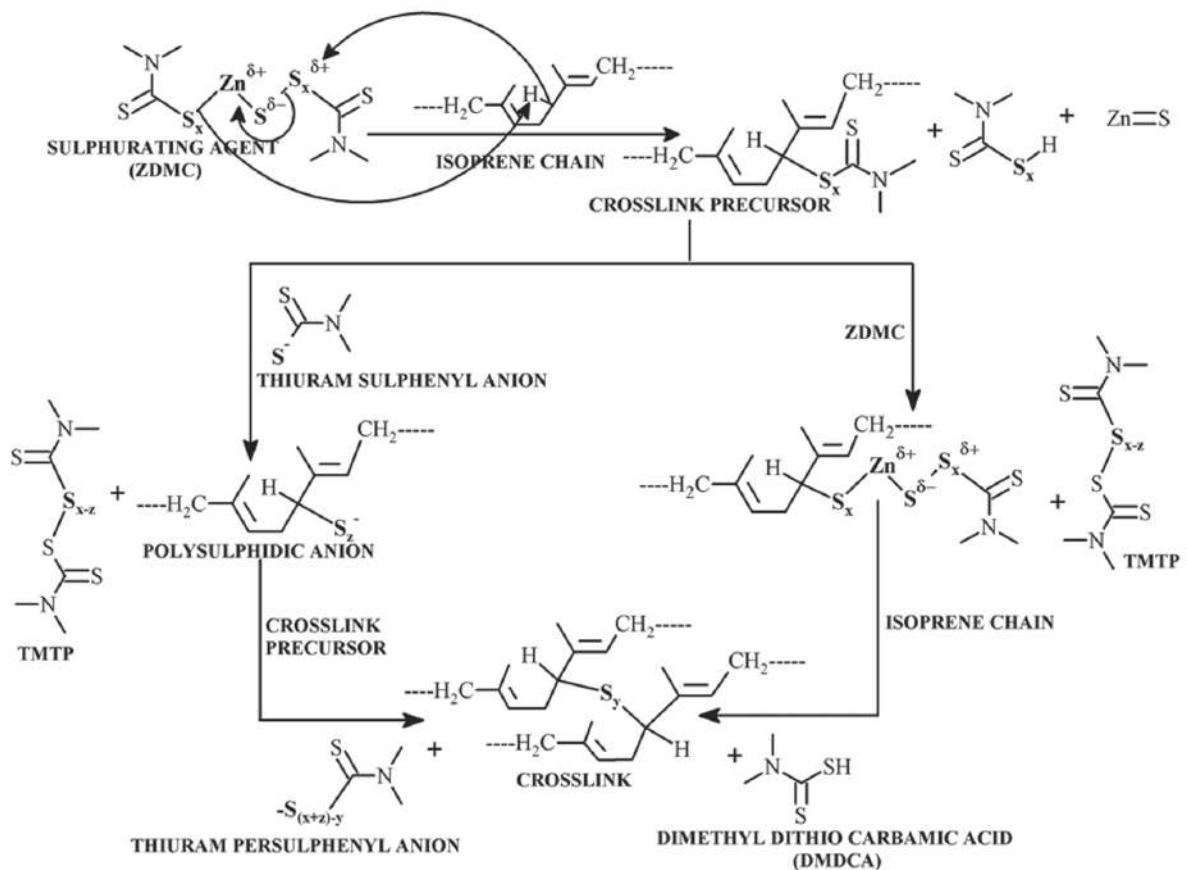
In the presence of zinc oxide, TMTD vulcanization of NR may follow a polar route also, as shown in figure below.

- ✓ Here the active sulphurating agents are both zinc perthiomercaptides (ZDMC) and thiuram polysulphides (TMTPs).
- ✓ The formation of zinc perthiomercaptides (sulphurating agent) is followed by the formation of network bound accelerator residues (pendent groups/ crosslink precursors) on reaction with rubber hydrocarbon, which will form crosslinks



(Gradwell, M. H. S. and McGill, W. J., Journal of Applied Polymer Science, 61: 1515-1523, 1996) via nucleophilic reactions.

- ✓ The precursor may react with a thiuram persulphenyl anion derived from ZDMC to form a rubber polysulphidic anion or with ZDMC itself to form a zinc containing precursor.
- ✓ These two species on reaction with another precursor or isoprene chain respectively will give rise to crosslinks.
- ✓ As per the mechanism, the formation of pendent groups proceeds via a concerted reaction between the sulphurating agent and the rubber chain in which the S-S bonds are broken and new C-S bonds are formed through a concerted reaction without the formation of true intermediates.
- ✓ Formation of mono or disulphidic crosslinks (efficient vulcanization) resulting in a reversion resistant vulcanizate network is being manifested as the highlight of using sulphur donating accelerators such as TMTD.

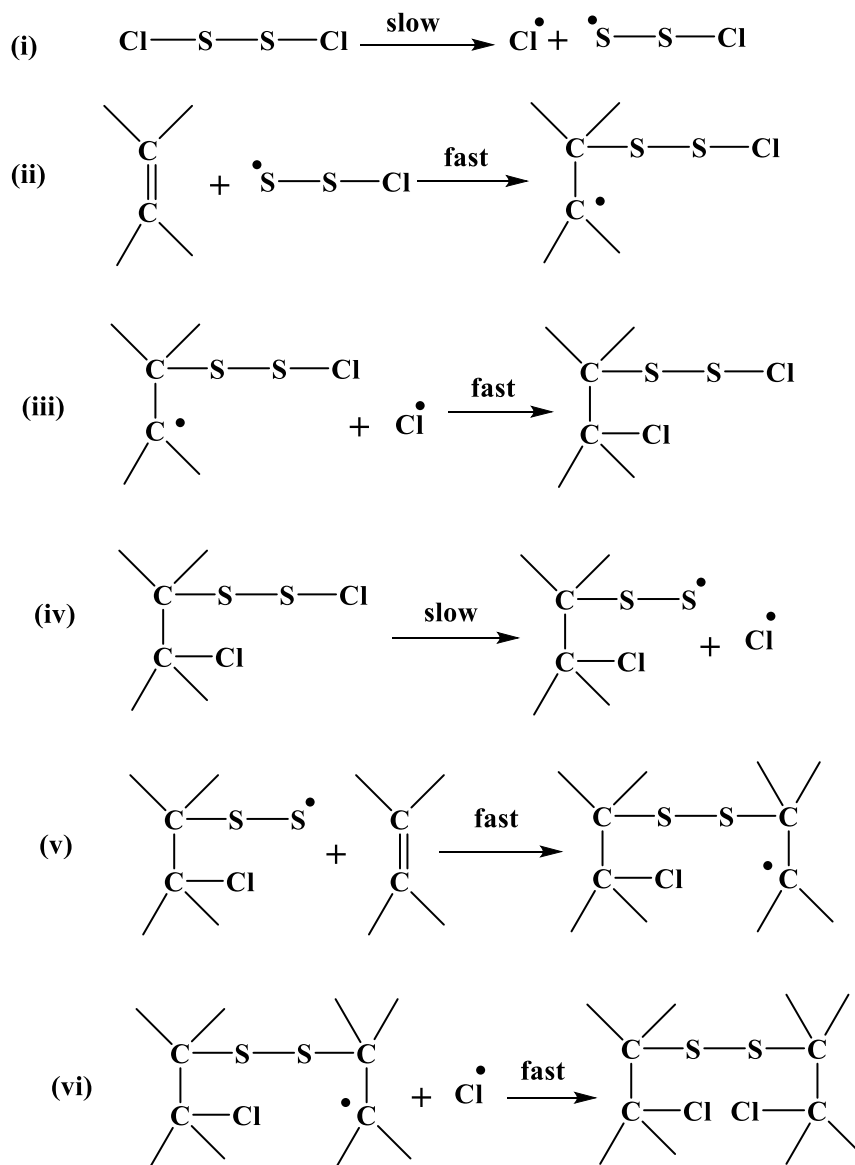


Vulcanization by TMTD – polar pathway



Sulphur Monochloride (S₂Cl₂) Cure:

Sulphur Monochloride also known as sulphur chloride or as disulphur dichloride. This material has relative density of 1.68 to 1.71 and a boiling point of 130°C. It is a clear, yellowish red, pungent, fuming liquid. It irritates the eyes, nose and throat and is toxic. Mainly used in solution is carbon disulphide or in petroleum solvents as a cold vulcanizing agent to cold cure, thin-walled material made from natural rubber at room temperature. In such cases traces of iron may accelerate the deterioration of cold vulcanizates (if the iron is in a state which does not react with hydrochloric acid then this problem will not normally arise). Sulphur Monochloride, not very popular due to high toxicity of S₂Cl₂ solution and poor aging properties of the vulcanizate. The reaction sequence of that cure system is given below.





Non-sulfur Vulcanization Systems:

The saturated elastomers materials that backbones (haven't double carbon bond), cannot be crosslinked with sulfur and so require alternate curing agents such as peroxides are used in general cases, also the phenolic resins, quinones, metal oxides etc. are used in special cases. However, sulfur interlinking is still the first curing agent that choice for rubber vulcanization. Therefore, when vulcanization (interlinking) of rubber with other than sulfur can be carried out by free-radical reactions, that do not require the presence of C=C bonds in the rubber chain. Free radicals are formed by irradiation with ultraviolet light, by electron beam, by nuclear radiation, or by thermal decomposition of unstable additives. In each case, hydrogen atom is broken away from the elastomer molecule chain, and remove to generate a highly reactive carbon atom (the free radical), that will react with another carbon atom to form a stable C–C bond (crosslinking), between elastomer molecular chains.

Organic peroxides cure:

The peroxides are one type of curing agent that most widely used as alternative to sulfur for elastomers vulcanization. Unlike sulfur vulcanization, carbon-carbon double bonds are not required for peroxide curing. The cross-linking of rubbers with organic peroxides was first examined by Ostromislensky in 1915. Not just unsaturated, but also saturated elastomers can be efficiently cured with peroxides. Industrial interest in the application of peroxides as cross-linking agents increased with the introduction of a number of saturated rubbers, for examples (ethylene-propylene rubber, chlorinated polyethylene rubber, chlorosulfonated polyethylene rubber, and silicone rubber). Also, the peroxides are used with unsaturated elastomers. The application of organic peroxides in crosslinking elastomers leads to the formation of covalent carbon–carbon cross-links between the elastomer chain segments. C—C bonds have higher dissociation energy than sulphidic cross-links, so peroxide-vulcanised elastomers also exhibit higher thermal stability and good resistance to thermo-oxidative ageing. Good electrical properties, low compression set and no discoloration of the final products are the next distinctive features of peroxide-cured vulcanisates but they provide generally poor tensile and tear strength. Also peroxides are readily crosslinks elastomers and incompatible with many of the antioxidants that used in rubber. Finally, the peroxides cannot be used with butyl rubber because they cause chain scission and depolymerization. There are several other advantages and disadvantages associated with peroxide cross-linking, as discussed by Aprem et al. (A. S. Aprem, K. Joseph and S. Thomas, *Rubber Chemistry and Technology*, 78, 458-488, 2005) and these are summarised in table below.



Table: Advantages and disadvantages of peroxide cure

Advantages	Disadvantages
Simple compounding	Expensive cross-linking agents
Good heat ageing resistance	Low mechanical strength
Low tension set and strain	Higher curing time
No contamination	Difficult hot-air cure
Low compression set	Poor resistance to flex fatigue
Transparent rubbers possible	Needs secondary cure of high temperature

The main reactions involved in peroxide cross-linking are those of free radicals. Cross-linking using peroxides can be simplified to three steps:

- ✓ Decomposition of peroxide to form a radical.
- ✓ Hydrogen abstraction from the polymer, transferring the radical to the polymer chain. The facility of hydrogen abstraction depends on the structure of rubber. The following sequence shows the facility by which elastomer radicals can be formed via the abstraction of hydrogen from different chemical groups: benzylic = allylic > tertiary carbon > secondary carbon > primary carbon > vinyl > phenyl.
- ✓ Cross-link formation or coupling *via* the radical on the polymer chain. This occurs when two polymer chains containing radicals come into contact. A covalent bond is formed through the coupling of unpaired electrons.

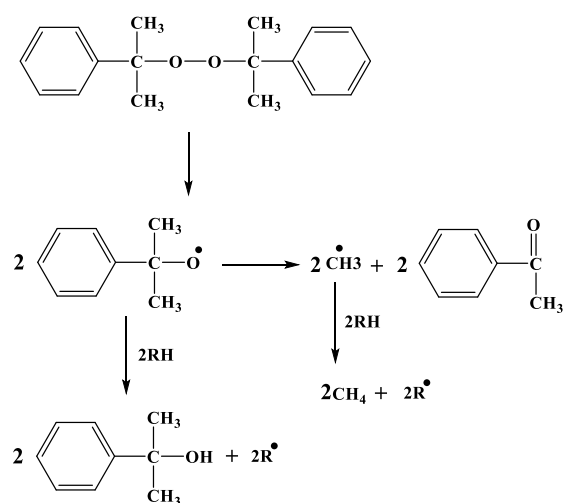
Examples of the peroxides used for vulcanization:

Peroxide	Chemical formula
Dibenzoylperoxide	
Bis (2,4-dichloro)benzoylperoxide	

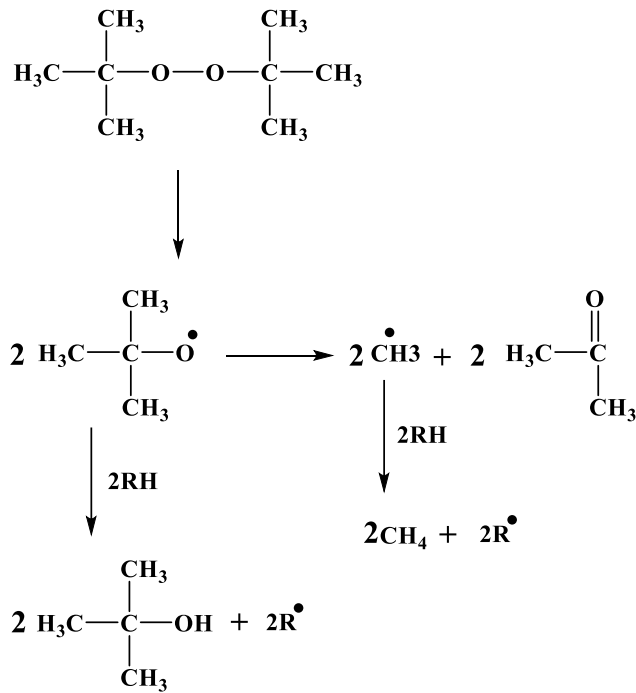


Di-tert-butylperoxide (DTBP)	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{H}_3\text{C}-\text{C}-\text{O}-\text{O}-\text{C}-\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$
Dicumylperoxide (DCP)	
Terc-butylcumylperoxide	
1,4-bis(tert-butylperoxyiso propyl) benzene (DTBPIB)	
2,5-bis-(tert.butylperoxy)-2,5-dimethylhexane (DDTBPH)	
4,4 di-tert.butylperoxy-n-butylvalerate	

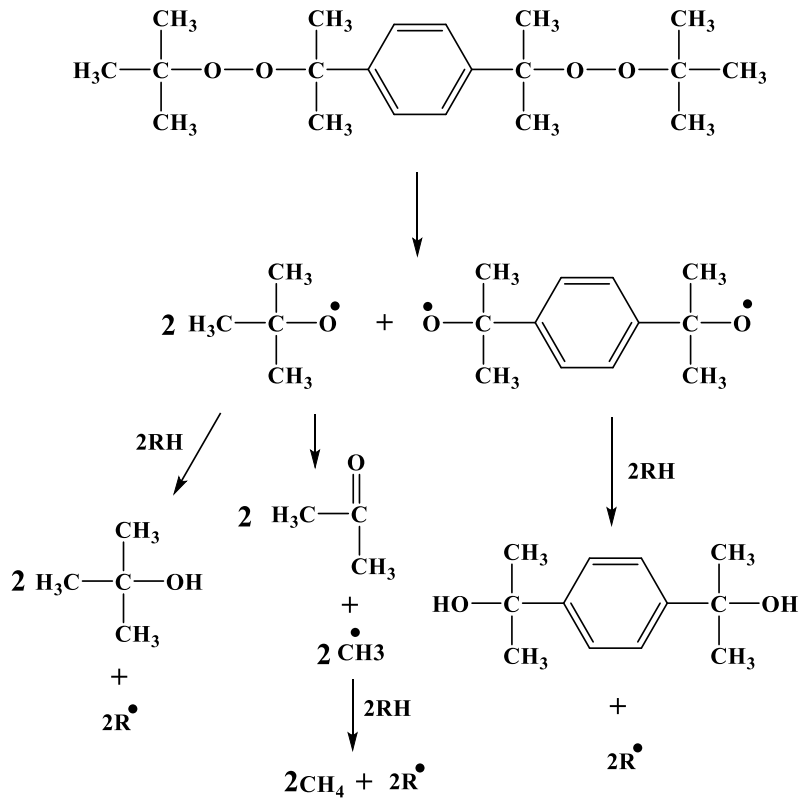
The main mechanisms of most frequently used peroxide to generate radicals are shown in the following schemes.



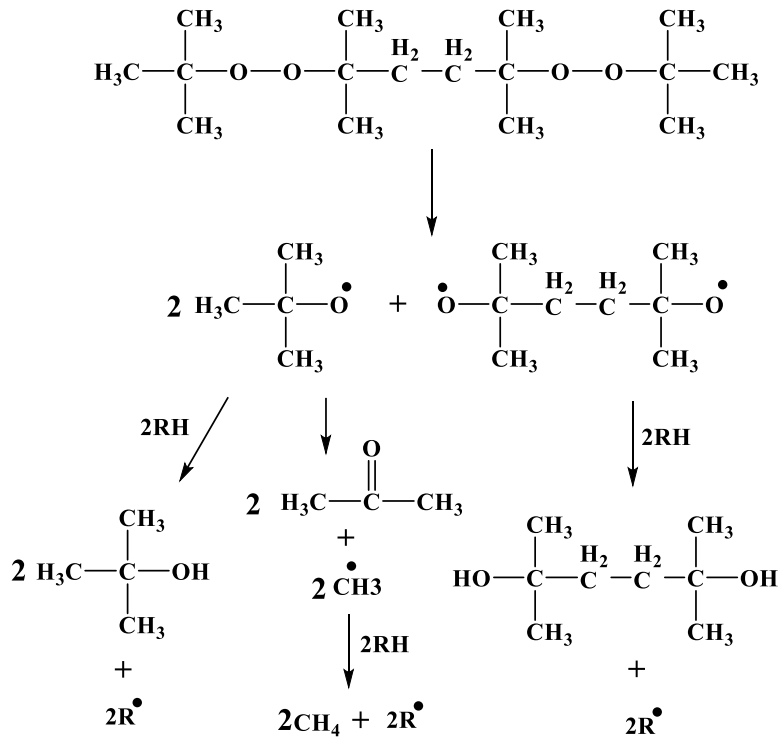
Decomposition mechanism of dicumylperoxide



Decomposition mechanism of di-tert-butyl peroxide

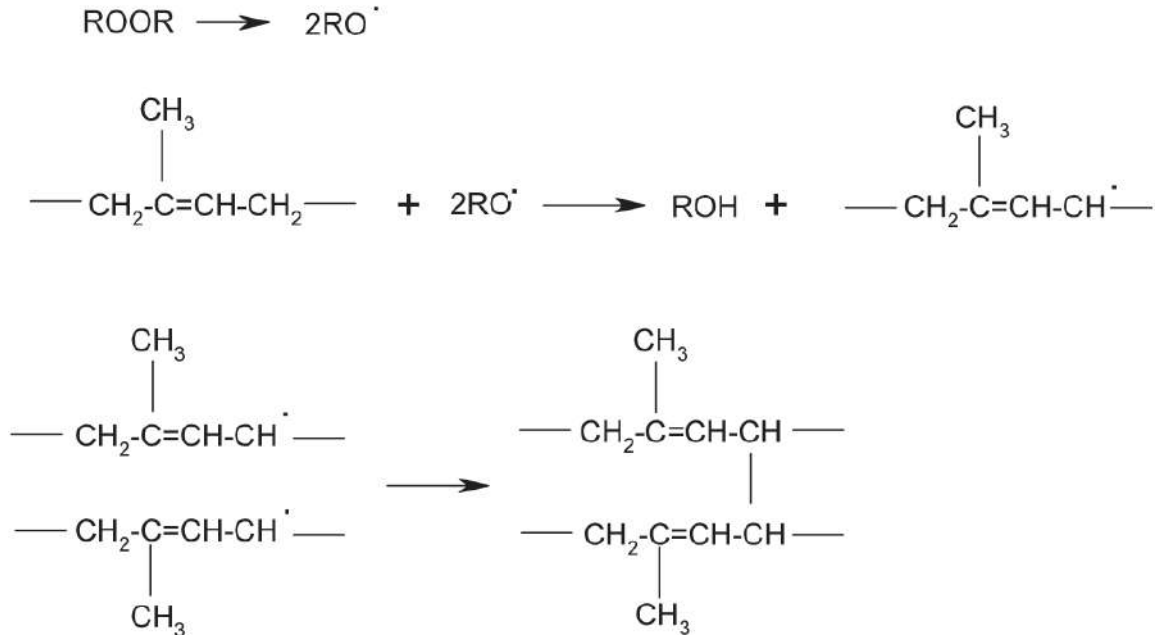


Decomposition mechanism of di(tert-butylperoxyisopropyl)benzene

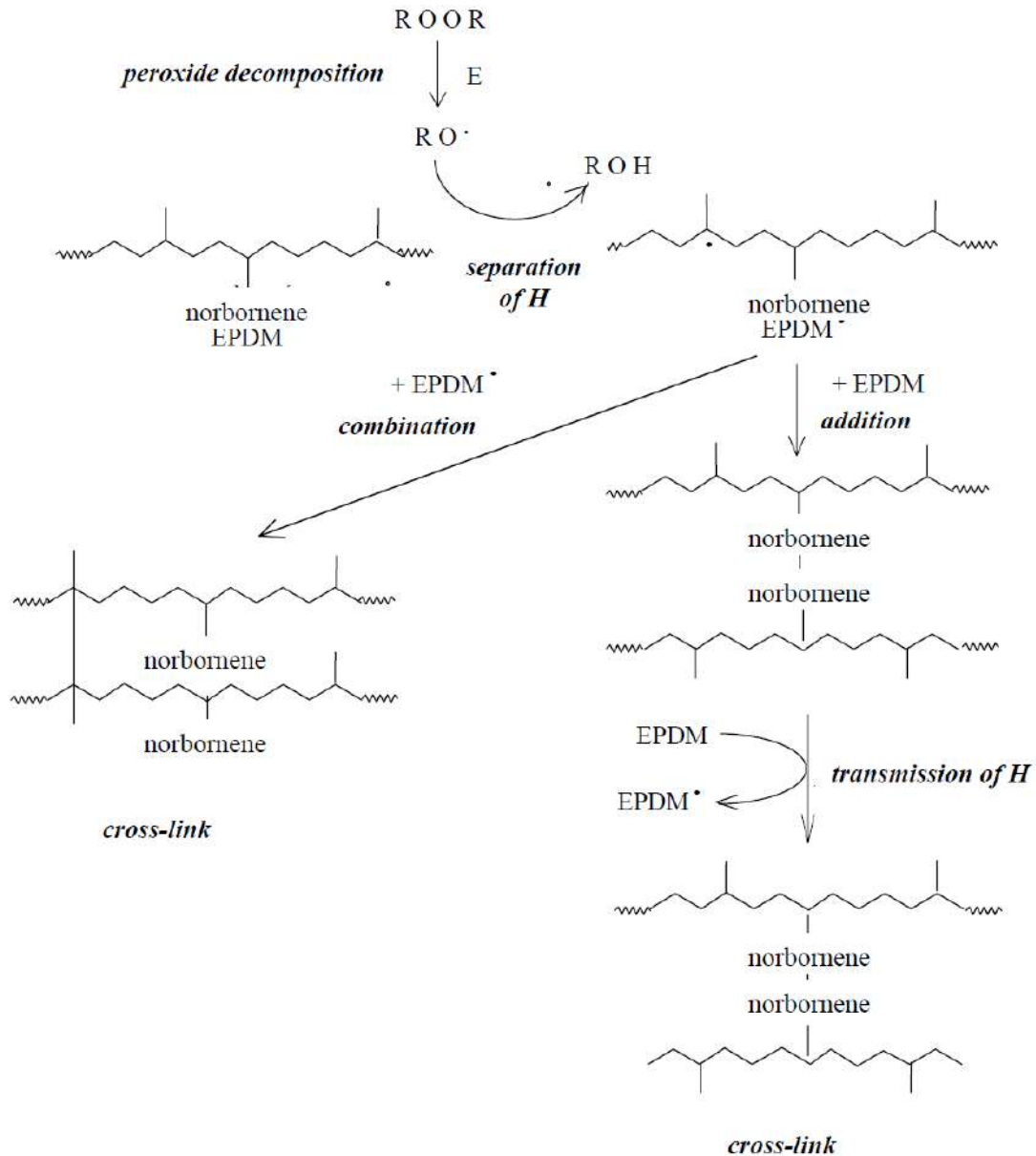


Decomposition mechanism of 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane

The general scheme for the peroxide cross-linking mechanism of NR is illustrated in the following scheme.



In the case of ethylene-propylene diene terpolymer (EPDM), the forming of chemical intermolecular bonds by the addition of EPDM macroradicals to the double bonds in its unsaturated structural units is practically equivalent to the recombination of macroradicals.



Simplified reaction scheme of peroxide cross-linking of EPDM

Co-activators:

The cross-linking of rubbers with organic peroxides can be effectively enhanced by the application of co-agents. Co-agents are multi-functional organic compounds which exhibit high reactivity towards free radicals (Dluzneski, P. R., *Rubber Chemistry & Technology*, 74, 451–492, 2001). The performance of peroxide-curing in the absence of co-agents is sometimes fairly low due to the occurrence of side-reactions which can deplete free radicals. Co-agents are able to boost peroxide effectivity by suppressing unfavourable side-reactions to a large extent. They are introduced to increase the cross-linking performance of the vulcanisation process but also to increase the cross-link density of final vulcanisates (Likozar, B., & Krajnc, M., *Journal of Applied Polymer Science*, 110, 183–195, 2008). Accordingly,



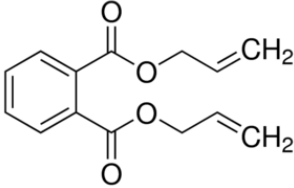
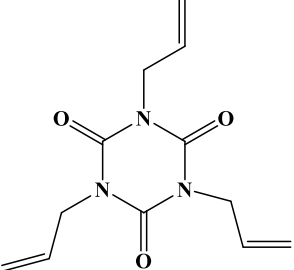
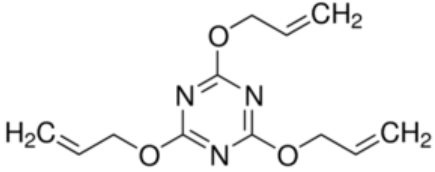
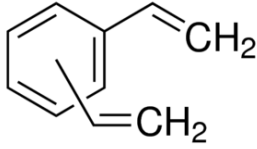
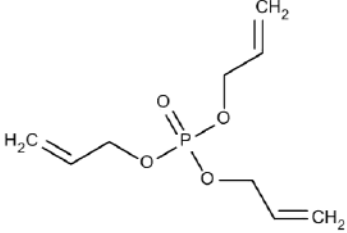
physical-mechanical properties, such as tensile strength, modulus, abrasion resistance, dynamic properties, adhesion to polar substrates and the process ability of peroxide-vulcanised elastomers are also improved. According to their contribution to the vulcanisation process, co-agents are divided into two basic groups: Type I and Type II (Alvarez Grima, M. M., Talma, A. G., Datta, R. N., & Noordermeer, J. W. M., Rubber Chemistry & Technology, 79, 694–711, 2006).

Type I co-activators applied to peroxide vulcanisation of elastomers:

Chemical Name of type I co-activators	Chemical Formula
Ethylene glycol dimethacrylate (EGDMA)	
Zinc acrylate (ZDA)	
Zinc methacrylate (ZDMA)	
N,N'-m-phenylenedimaleimide (PDM)	
Trimethylolpropanetriacrylate (TMPTMA)	
Pentaerythritol triacrylate (PETRA)	

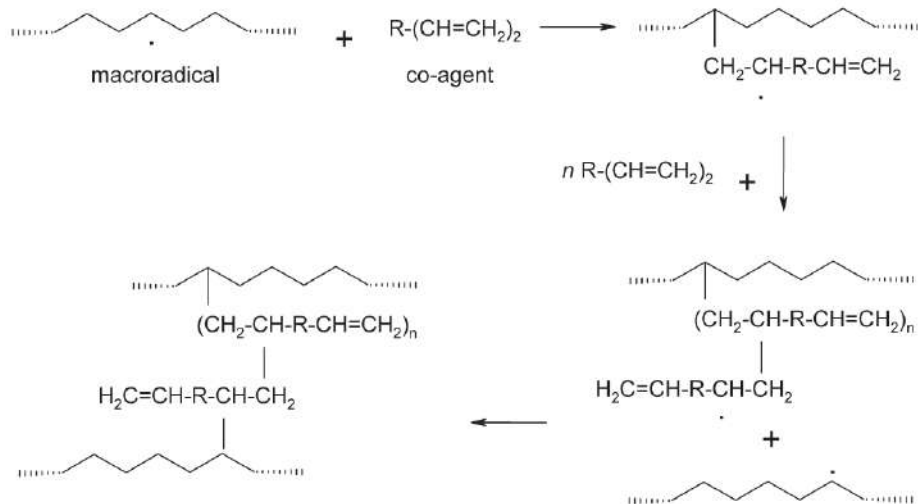


Type II co-activators applied to peroxide vulcanisation of elastomers:

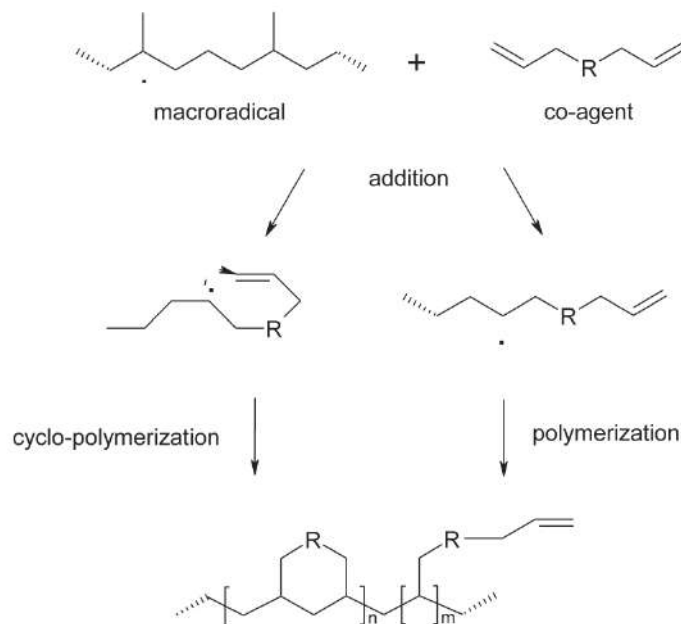
Chemical Name of type II co-activators	Chemical Formula
Diallyl phthalate (DAP)	
Triallyl isocyanurate (TAIC)	
Triallyl cyanurate (TAC)	
Divinylbenzene (DVB)	
Triallylphosphate (TAP)	

Co-activator assisted peroxide cross-linking:

Both type co-activators vary in their reactivity and reaction mechanism in the vulcanisation process. Type I co-activators can be homopolymerised and/or grafted onto macroradicals forming effective cross-links through radical addition reactions whereas Type II co-activators with readily extractable allylic hydrogens have been shown to take part in intermolecular propagation reactions as well as in intramolecular cyclisation reactions.



Reaction mechanism of certain Type I co-agents with elastomers (Kyselá, G., Hudec, I., & Alexy, P., Manufacturing & processing of rubber (1st Ed), Bratislava, Slovakia: Slovak University of Technology Press, 2010).



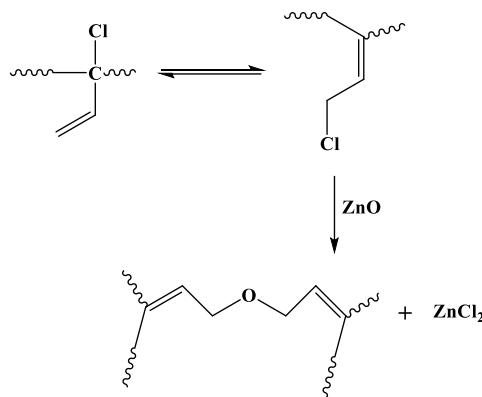
Reaction mechanism of certain Type II co-agents with elastomers (Van Duin, M., Chemistry of EPDM cross-linking, Kautschuk Gummi Kunststoffe, 55, 150–156, 2002).

Metal Oxide Cure:

Some elastomers materials can be crosslinked by using metal oxides as curing agents, which includes (ZnO, MgO and Pb_2O_3). Generally, mixtures of (ZnO and MgO) are used because ZnO alone is too scorchy and MgO alone is inefficient. Also metal oxides that usually contain (zinc oxide and lead oxide) for improved water resistance. Generally, the metal oxides are used as cross-linking agents for halogenated elastomers such as polychloroprene rubber, butyl

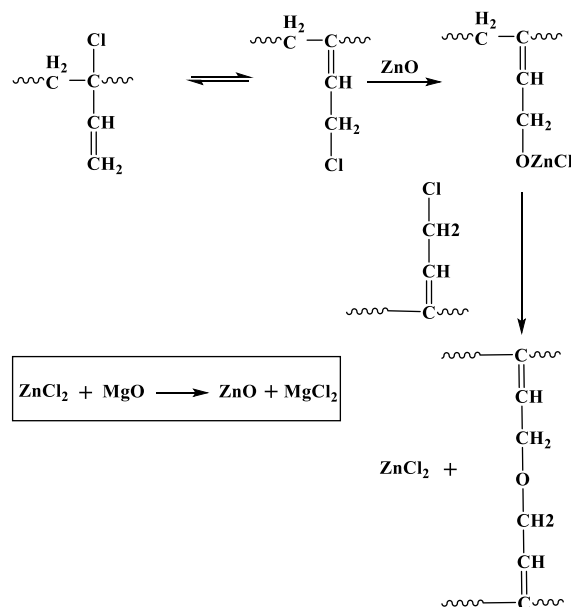


rubber, and chlorosulfonated polyethylene rubber. The metal oxide abstracts the halogen from adjacent elastomer chains to form an oxygen crosslink plus the metal chloride salt. In case of Polychloroprene rubber (CR), it is a high-performance material with a wide diversity of applications. Unlike other diene elastomers, polychloroprene rubber cannot be cross-linked with sulfur due to the presence of substantially inactive $>C=C<$ bonds. Therefore, Polychloroprene rubber is conventionally cured with 5 phr of zinc oxide in the presence of 4 phr of magnesium oxide. One of the earliest theories for cross-linking polychloroprene was through the formation of an ether linkage with the oxygen derived from ZnO as shown below.



Scheme: 'Ether linkage-forming' cross-linking mechanism for zinc oxide in CR.

The cross linking mechanism in the presence of ZnO + MgO combination may be represented as follows:



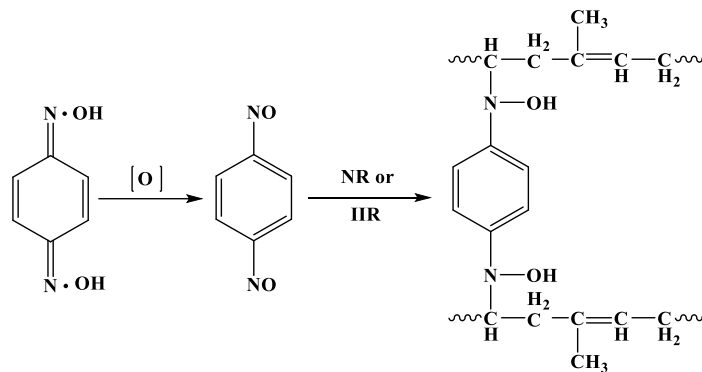
Scheme: Vulcanization mechanism of chloroprene rubber

Here, ZnO is the main cross linking agent and MgO is a chlorine acceptor. However, ZnO also serves as a chlorine acceptor (like MgO) and small amounts of MgO do take part in cross linking reaction.



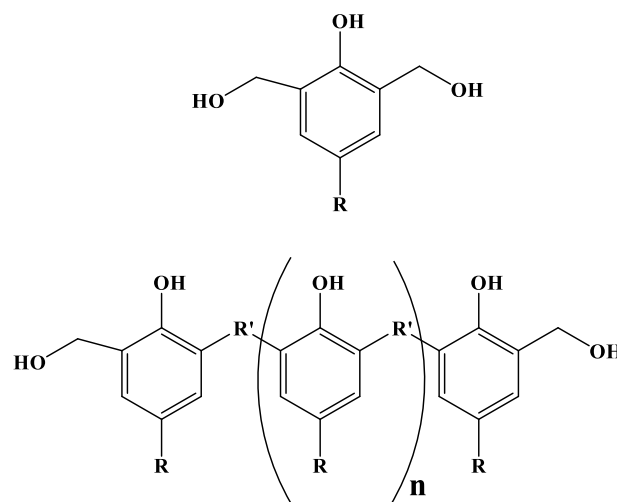
Quinone Dioxime Cure:

The use of quinone dioxime as a commercial vulcanizing agent is limited to butyl rubber (IIR) where sulfur cures are undesirable (too slow or sulfur presence is objectionable) and curing may be effected at fast rates when used in combination with red lead or MBTS. Any other diene rubber including natural rubber (NR) may be vulcanized with the dioxime. The curing is believed to take place through oxidation of the dioxime to p-dinitrosobenzene which then acts as the actual cross-linking agent. The vulcanizates exhibit good tensile and compression set resistance properties and heat aging resistance.



Phenol Resin Cure:

The use of phenolic resins as curing agents for diene rubbers was first investigated over 83 years ago (Honel, 1936). In the 1940s it was discovered that phenolic resins were able to cross-link unsaturated polymers. A major technical advancement for increasing the service life of curing bladders was the development of phenol/ formaldehyde resins for vulcanizing IIR. The basic curing resins used are generally 2, 6-dihydroxymethyl-4-alkyl phenol or their condensation polymers.



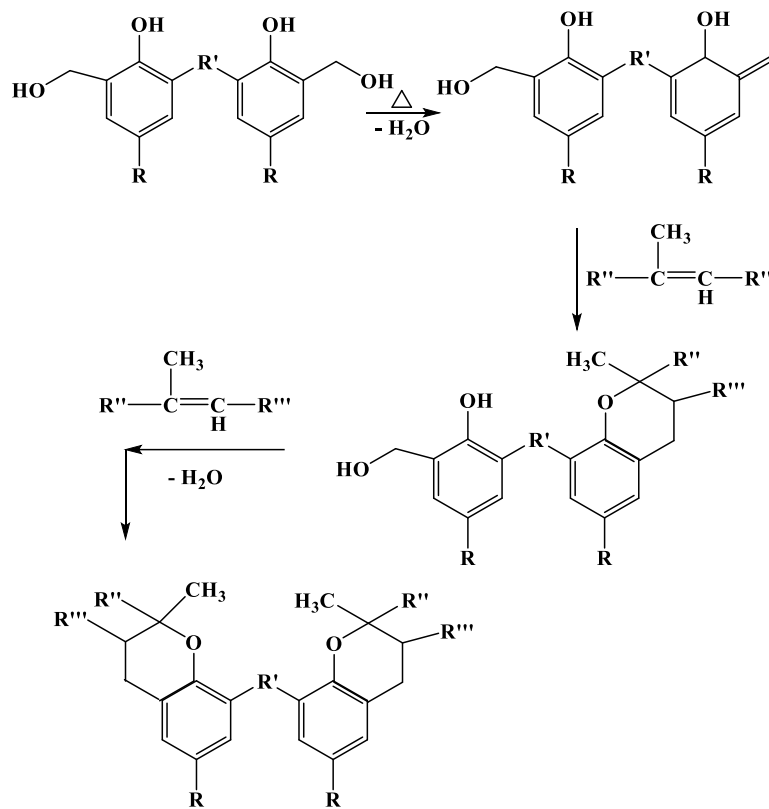
R = methyl, t-butyl or t-octyl in commercial resins

Basic curing resins



There are two types of reaction occurred during vulcanization

- ✓ Self-condensation of the resin and
- ✓ Reaction between the resin and the rubber molecules.



Chroman mechanism of resin cure

Vulcanization with resin alone is a very slow process even at high temperatures so some catalysts such as SnCl₂, FeCl₃, or highly chlorinated organic compound are needed additionally to increase the rate of vulcanization. The most common application for resin cross-linking is with of butyl rubber, with the final product being used for high temperature applications.[26] Although natural rubber, styrene-butadiene rubber, ethylene-propylene-diene-monomer rubber and other rubbers can also be cross-linked using this mechanism.

Practical Test Methods for Monitoring Vulcanization:

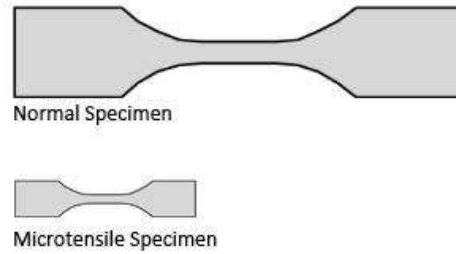
Stress-Strain Properties:

The tensile mechanical properties were measured by universal testing machine at room temperature (25 ± 2°C) at a uniform speed of separation 500 mm/min. The test samples were cured at a particular vulcanization temperature for the respective optimum cure times (t = t₉₀) using a compression press at a particular vulcanization temperature with 2 mm thick sheets. The dumb-bell shaped test specimens were punched out from the cured rubber sheets after 24 h of vulcanization by a tensile specimen cutter. Dumbbell-shaped samples were cut from the vulcanized sheets according to ASTM D 412–93. The values of the modulus at 100, 200, 300



% elongation, tensile strength and percentage elongation at break were determined from the stress strain curves.

Tensile test specimen are displayed in the following figure



Tensile test piece

Elongation was monitored by an extensometer attached to the central point of the specimen. The assessment of the cross-link density of the rubber vulcanizates was based on the Mooney-Rivlin equation derived from the stress-strain measurement as in

$$F = 2A_0 (\lambda - \lambda^{-2}) (C_1 + \lambda^{-1}C_2)$$

where F is the force required for stretching the specimen, A is the crosssectional area of the unstretched specimen, λ is the extension ratio, and C_1 and C_2 are constants characterizing the vulcanizate. The degree of cross-linking at $(25 \pm 2 \text{ }^\circ\text{C})$ was obtained by modifying the above equation:

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

We have plot $\sigma / (\lambda - \lambda^{-2})$ and $1 / \lambda$, then the intercept of curve on the $\sigma / (\lambda - \lambda^{-2})$ corresponds to the value of $2C_1$ whereas its slope corresponds to the value of $2C_2$.

For swollen rubber the Mooney-Rivlin equation becomes:

$$F = 2A_0 v_r^{-1/2} (\lambda - \lambda^{-2}) (C_1 + \lambda^{-1}C_2)$$

Science the value C_1 and C_2 decreases to zero at high degrees of swelling ($v_r \leq 0.25$) then the above equation reduces to the form predicted by the simple statistical theory:

$$2C_1 (\text{swollen}) = \rho RT M_C^{-1}$$

Where R is universal gas constant, T is the absolute test temperature and M_C is the number average relative mol. mass between the cross links. The finding that the dependence of stress upon strain in the simple extension of highly swollen vulcanizates agrees with the simple statistical theory is the basis of the assumption that under these conditions the statistical theory is obeyed.

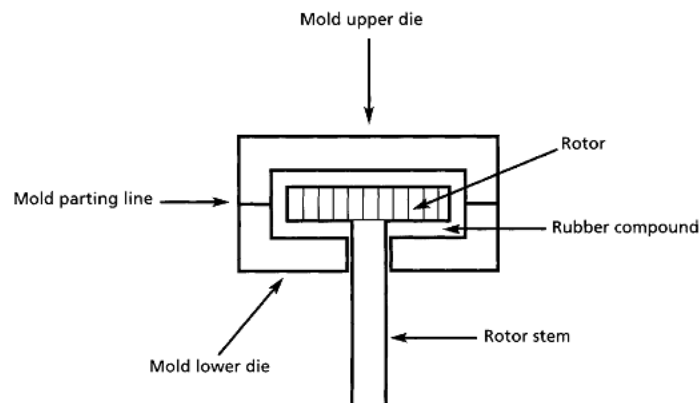


Measurement of The tensile modulus at 100 % elongation (E) was measured by using the following equation:

$$E = 3\rho_rRT / 2M_C$$

Mooney Viscometer:

- ✓ Most widely used rotational plastimeter is mooney viscometer. A disc shaped rotor rotates inside a cylindrical cavity filled with rubber, thus producing shear between the surfaces of rotor and cavity. The resulting torque on the shaft of the rotor gives a measure of the effective viscosity of rubber.
- ✓ The rotor is driven at 2 r.p.m. through a gear box by electric motor. The viscosity of the sample causes a breaking action on the rotor, which is transmitted to the arm to give a resultant thrust. This thrust is registered by a u-beam to give a small displacement depending on the torque needed to keep the disc rotating.
- ✓ The displacement actuate a gauge graduated in thou (1 thou = 1/1000 inch.) corresponding to one mooney unit.
- ✓ As the viscosity varies during the test, a series of readings are taken at specified times to allow to plot a viscosity vs. time curve.



Mooney viscometer

Test Procedure:

Motor is turned on after 1 minute preheating time. For plotting of curve manually, readings are taken every 30secs. or 1 min. and the viscosity vs. time graph is drawn.

Report:

(A) Viscosity report:

A typical test would be reported as follow:

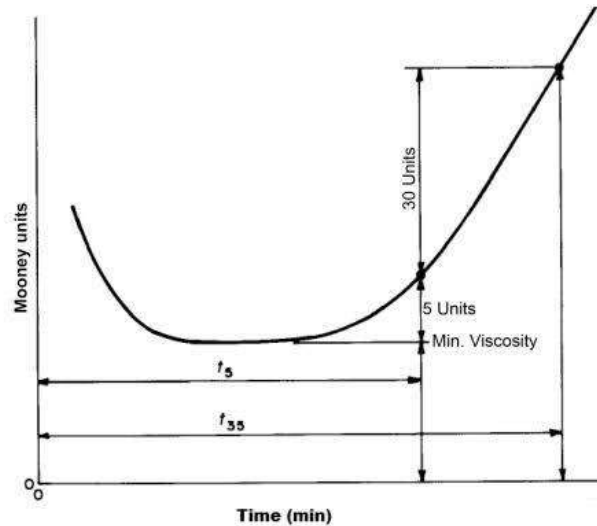
50 ML (1 + 4)100°c, where

50 M = mooney viscosity units,



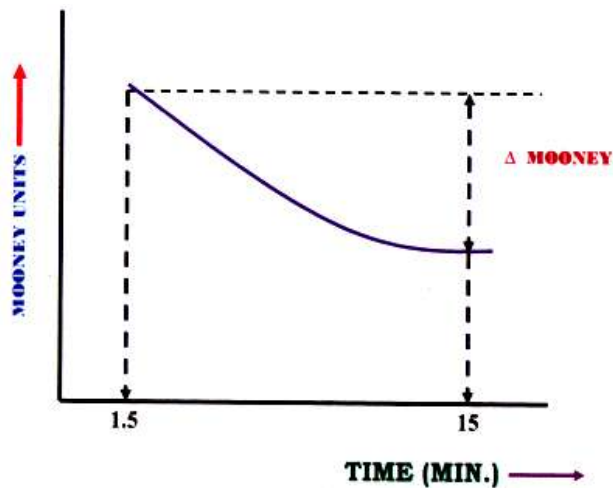
L = use of large rotor,
 1 = 1 minute preheating time,
 4 = running/reading time in minutes after start of motor,
 100°C = test temperature.

(B) Curing characteristics:



t_5 = mooney scorch time (for large rotor); t_3 = mooney scorchtime (for small rotor)
 t_{35} = time to cure at mv + 35; Δt_L = cure index = $t_{35} - t_5$; $t_5 + 10(t_{35} - t_5)$ = optimum cure time

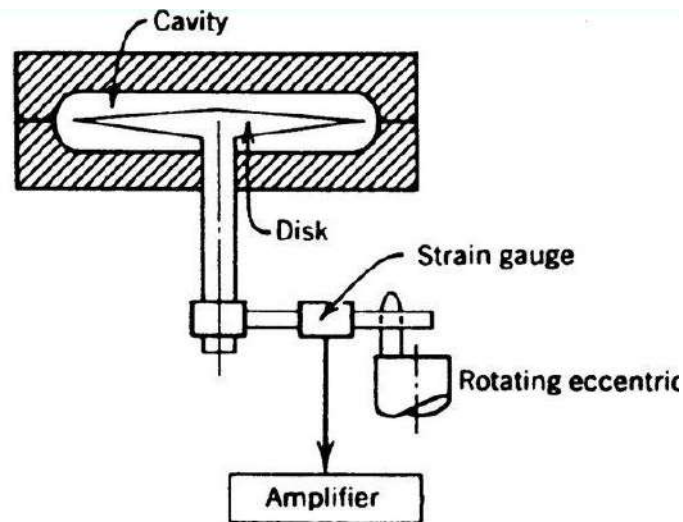
Delta mooney:



- ✓ Δ mooney is the difference between the mooney viscosity at 1.5 min. and 15 mins. It is a measure of processability of the rubber.
- ✓ A higher value of Δ mooney is an indication of good processing behavior.

Oscillating Disc Rheometer (ODR):

- ✓ ODR gives a continuous cure curve to determine curing characteristics of a compound or to check batch to batch uniformity
- ✓ An uncured rubber sample is placed in a die cavity located in electrically heated platens. die temperature can be selected within the range of 100 – 200°c
- ✓ Cavity is formed by fixed lower die and a moveable upper die. The rotor consists of biconical disc with a shaft. The disc is oscillated at 100 CPM through an ARC of 1, 3 or 5 degrees by a motor driven eccentric to the shaft through a connecting link and a torque arm
- ✓ The force required to oscillate the disc is measured electronically by the torque arm transducer.



Oscillating Disc Rheometer

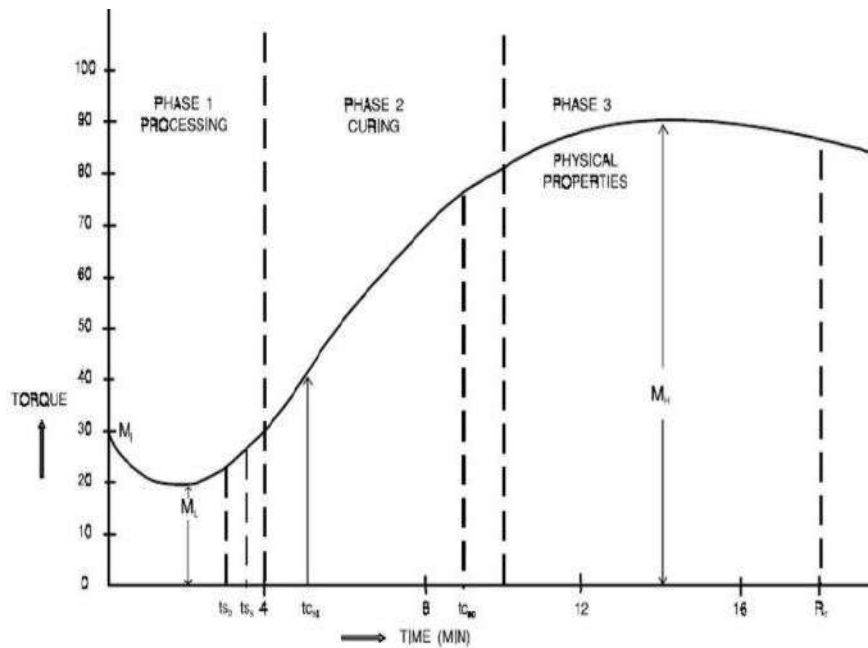
Analysis of rheograph:

The rheograph can be divided into three phases.

Phase 1: Similar to a mooney curve and is indicative of the viscosity prior to vulcanisation.

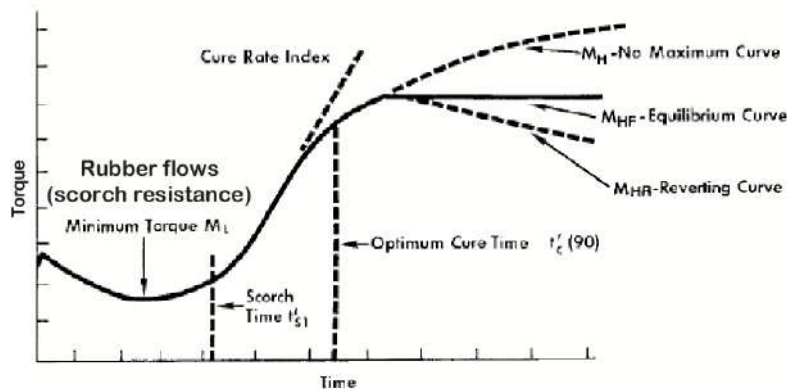
Phase 2: Indicative of rate of cure.

Phase 3: Shows maximum level of cure obtained an indication of state of physical properties.



TYPICAL RHEOMETRIC CURVE

Measure of critical points from rheograph:



Rheological Graphs

The important points on the cure curve are as follows:

- M_L —————> minimum torque (N.m OR lbf.in)
- M_{HF} —————> plateau cure or equilibrium curve (N.m OR lbf.in)
- M_{HR} —————> maximum torque (reverting curve) [N.m OR lbf.in]
- M_H —————> marching curve where no plateau or maximum torque has reached (N.m OR lbf.in)
- t_{s2} —————> time for torque to increase 2 units (lbf.in) above m_l in minutes (referred to as scorch time)
- t'_{90} —————> time for torque to reach $M_L + 0.9 (M_H - M_L)$ in minutes (referred to as optimum cure time).



Cure rate \longrightarrow slope of the rheograph curve in steep region, i.e., $100/t'90 - t_s2$.

Moving Die Rheometer:

- ✓ Much accepted instrument. in many cases replacing ODR
- ✓ Two directly heated low mass biconical dies with the lower die oscillating, thus eliminating the use of rotor
- ✓ Reaction torque is measured by a transducer attached to the upper die
- ✓ MDR has shorter temperature recovery times than ODR, because MDR has no rotor, specimen is thinner (about half the mass of MDR specimen). Therefore has better testing productivity
- ✓ Due to unique and sophisticated electronic system, MDR gives separation of complex torque into elastic torque (s') and viscous torque (s'') and the ratio of s''/s' gives a dynamic property called tan delta ($\tan \delta$)

Chemical Method: (Swelling in solvent):

The crosslinking efficiency of the cured vulcanizate was evaluated in terms of crosslink density using an equilibrium solvent swelling test method, ASTM D 471. The specimens $10 \text{ mm} \times 5 \text{ mm} \times 2 \text{ mm}$ were accurately weighted (m) and immersed in toluene and allowed to swell in closed bottles for 22 h at room temperature. Then, the specimen was removed and the surface of the swollen samples was quickly wiped and weighed (m_s). The degree of swelling and the crosslink density was calculated by using appropriate relations reported afterwards. The degree of swelling was calculated by using the relation (S.J. Park and K.S. Cho, J. Colloid Interface Sci., 267, 86, 2003).

$$Q(\%) = \frac{m - m_s}{m} \times 100$$

where m and m_s are the masses of the sample before and after swelling.

The crosslink density, V_e per unit volume is defined (S.E. Gwaily, M.M. Badawy, H.H. Hassan and M. Madani, Polym. Test., 22, 3, 2003) as the number of elastically effective chains totally included in a perfect network, and is given by the equation:

$$V_e = \frac{\rho_r N_A}{M_C}$$

where ρ_r is the rubber density, N_A is the Avogadro's number, and M_C is the average molecular weight between cross-links.



According to Flory–Rehner theory (P.J. Flory, J. Chem. Phys., 18, 108, 1950), for a perfect network:

$$M_c = -V_1 \rho_r \frac{(\phi_r^{1/3} - \frac{\phi_r}{2})}{[\ln(1 - \phi_r) + \phi_r + \chi \phi_r^2]}$$

where V_1 is the molar volume of the solvent, ρ_r the rubber density, ϕ_r the volume fraction of rubber in the swollen gel and χ is the Flory-Huggins interaction parameter between solvent and rubber.

Determination of Cross link type:

Sulphur crosslinking system is expected to generate polysulphidic, mono- and disulphidic crosslinks in the vulcanised rubber, depending on the several factors. Carbon carbon crosslinks generated by radical reactions such as those initiated by peroxide and radiation have the same characteristics as those of mono- and disulphidic crosslinks. The decreasing order of the proportion of mono-sulphidic or carbon-carbon crosslinks in the curing systems are Dicumyl peroxide (DCP) > Tetrabenzylthiuram disulphide (TBzTD) > Tetramethylthiuram disulphide (TMTD) > Sulphur > 2-ethylhexyl zinc dithio-phosphate (ZDT) + sulphur > 1,6-bis(N,N'-dibenzylthiocarbamoyl-dithio)-hexane + sulphur > 2,2'-dibenzothiazyl disulphide (MBTS) + sulphur > N-cyclohexyl-1-benzothiazyl sulphenamide (CBS) + sulphur > 1,3-diphenylguanidine (DPG) + sulphur. It is essential to quantify the proportion of different sulphidic crosslinks because it influences the mechanical and chemical resistance properties of the vulcanised rubber. The chemical determination of the percent polysulfidic and monosulfidic crosslinks was performed using a vulcanizate analysis. The types of crosslinks were identified through the use of chemical probes in conjunction with the determination of the total crosslink density. The analysis for the types of crosslinks was based upon the chemical reactivity of the particular chemical probe. The total crosslink density was determined by swelling tests. Samples of the compounds were immersed in a low molecular solvent, heptane, and allowed to swell. The solvent was changed twice before the final mass of the swollen sample was measured. By changing the solvent any uncured polymer present in the sample was allowed to dissolve into the solvent. This led to an accurate value of the total crosslink density as well as the determination of the levels of soluble polymer within the material due to aging. The analysis was based upon the fact that S-S bonds undergo an exchange reaction with thiolate ions. The sulphur-sulphur bond in polysulfidic crosslinks are more susceptible to nucleophilic attack by thiolate ions than the sulphur-sulphur bond of the



disulphidic crosslinks. Provided a thiolate ion of limited reactivity was chosen, only the tri and higher sulfides would be attacked leaving the di and mono sulfides intact. This selective attack was achieved by use of a secondary thiolate ion in dilute solution. The determination for the quantity of mono and disulfidic crosslinks was treatment of the vulcanizate with a solution of propane-2-thiol (0.4 M) and 0.4 M piperidine in heptane at 20°C for 2 hours. This treatment broke polysulfidic crosslinks leaving di and monosulfidic crosslinks intact. The treatment for the cleavage of di and polysulfidic crosslinks was exposure of the vulcanizate to 1 M hexane 1-thiol in piperidine for 48 hours at 25°C. The determination of the total crosslink density from swelling tests performed before and after treatment with the thiolate ion allowed for the summation of the individual contributions of the mono, di and polysulfidic crosslinks.

$$\nu = -\frac{2}{\Phi V_s} \frac{\ln(1 - v_r) + v_r + \chi v_r^2}{v_r^{1/3} - v_r/2}$$

Where,

ν = Crosslink density mol per unit volume (mol / cm³)

V_r = Volume fraction of rubber in equilibrium swollen vulcanized rubber sample

V_s = Mole volume of used solvent at room temperature in cm³ / mol (from molecular weight and density)

χ = Flory-Huggins polymer-solvent interaction parameter

ϕ = Functionality of the crosslink point, normally assumed to be tetra-functional where $\phi = 4$.