Effect of different sulfur content in Natural Rubber mixtures on their thermo-mechanical and surface properties

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Abstract— *In this study, a field experiment was conducted to find out the effect of different levels of sulfur on natural rubbers mixtures. Vulcanization is a chemical process for converting natural rubber or related polymers into more durable materials by heating them with sulfur other equivalent curatives with accelerators. These additives modify the polymer by forming cross-links (bridges) between individual polymer chains. Vulcanized materials are less sticky and have superior mechanical properties. The results indicated that the application of sulfur -as a vulcanasing agent-had significant effect on mechanical (Shore A hardness test), thermal (DSC calorimetry) and surface-optical properties (SEM microscopy) of mixtures.*

Keywords— ***vulcanization, sulfur, natural rubber, additives, cross-links.***

I. INTRODUCTION

By far the most common vulcanizing methods depend on sulfur. Sulfur, by itself, is a slow vulcanizing agent and does not vulcanize synthetic polyolefins. Even with natural rubber, large amounts of sulfur, as well as high temperatures and long heating periods are necessary and one obtains to an unsatisfactory crosslinking efficiency with unsatisfactory strength and aging properties. Only with vulcanization accelerators can the quality corresponding to today's level of technology be achieved. The multiplicity of vulcanization effects demanded cannot be achieved with one universal substance; a large number of diverse additives, comprising the "cure package," are necessary. The combined cure package in a typical rubber compound consists of sulfur together with an assortment of compounds that modify the kinetics of crosslinking and stabilize the final product. In this study the following sulfur quantities were used per samples: S_1=3,80 g; S_2=7,6 g; S_3=11,40 g; S_4=15,20 g; S_5=19 g at pressure 220 bar and temperature 145°C and t=10 minutes.

II. THEORETICAL APPROACH OF VULCANISATION WITH SULFUR

Vulcanization is a chemical process that converts natural rubber elastomers into cross-linked polymers. The most common vulcanization agent is sulfur. It forms bridges between individual polymer molecules when heated with rubber. Often a catalyst and initiator is added to accelerate the vulcanization process. The cross-linked elastomers have much improved mechanical properties. In fact, unvulcanized rubber has poor mechanical properties and is not very durable.

The cross-linking process is rather complicated and involves a sequence of reactions. A free-radical mechanisms was originally assumed which has been described in great detail by Paul J. Flory (1953) and others [1]. However, all evidence points to an ionic mechanism because neither radicals could be detected nor do free-radical inhibitors and retarders effect sulfur vulcanization whereas organic acids, bases as well as solvents of high dielectric constant accelerate sulfur cure [2]. A possible reaction mechanism for polyisoprene (natural rubber) is shown below. The process starts with the formation of a persulfonium ion (I) by reaction of an isoprene unit with a polarized sulfur molecule or with a sulfur cation. The persulfonium ion reacts than with another isoprene unit by allylic hydrogen abstraction to produce a polymeric allylic carbocation (II). In a third step a sulfur molecule (cyclic S8) combines with the allylic cation to produce another sulfonium ion (IV) which releases (monomeric) sulfur. The polymeric sulfonium ion then undergoes crosslinking by anionic addition to a polymeric double bond to create a new carbocation (V) which then either reacts with another sulfur molecule or it abstracts hydrogen from another isoprene unit to create a new polymeric cation (II).

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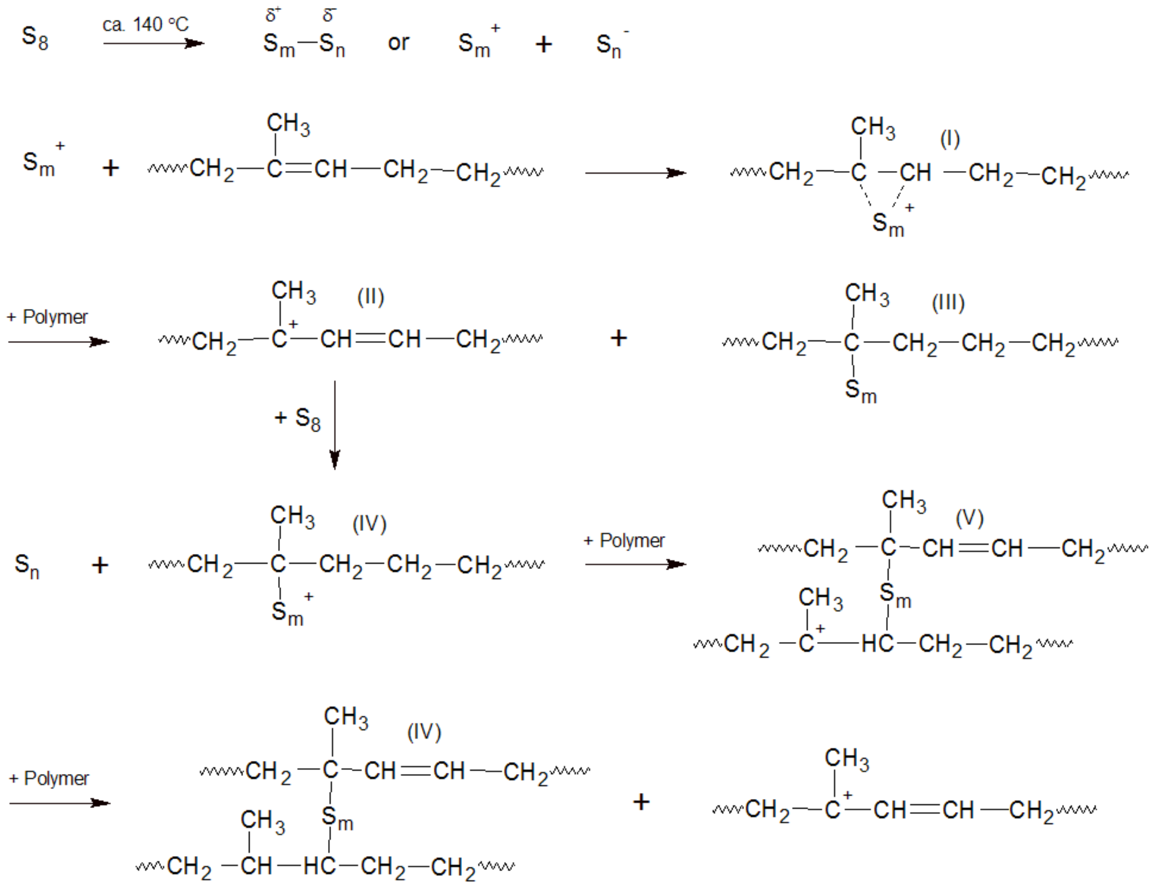

FIG.1. A POSSIBLE REACTION MECHANISM FOR POLYISOPRENE WITH SULPHUR

The polysulfide crosslinks formed by these reactions may contain four to six sulfur atoms at low temperatures whereas at higher reaction temperatures shorter sulfur bridges are formed. 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.

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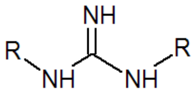
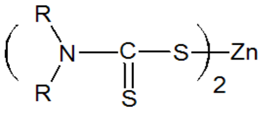
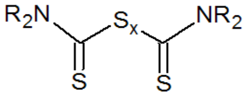
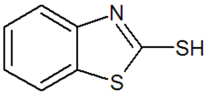
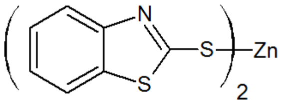
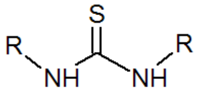
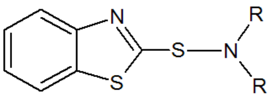
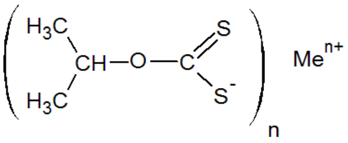
The accelerators can be further classified as primary and secondary accelerators. The *primary accelerators* are typically used at 0.5 to 1.5 phr. The vulcanization speed of these systems can range from slow to ultra fast depending on composition and type of accelerator. Common primary accelerators include thiazoles and sulfenamides whereas thioureas and dicarbamates can function as both primary and secondary accelerators. Very fast are *thioureas* and *dicarbamates* (see table below) and semi-fast are *thiazoles* whereas *aldehydeamines* and *guanidines* are rather slow. Some other curatives such as *sulfenamides* are fast curatives and cause a delay in the onset of vulcanization which is often desired in rubber processing because it increases the scorch time. Both the cross-link density and the cure speed depend on the type and dosage of accelerator, or in other words, the number of sulfur atoms in the sulfur bridges, their average number per polymer and the reaction rate depend on the type and composition of the sulfur cure system. Many of the sulfur-based vulcanization systems require activators. For example, dithiocarbamate and thiazole accelerators are activated with *zinc oxide* and *stearic acid* which also increase the speed of vulcanization.

TABLE 1
ACCELERATORS SYSTEM [4]

Compound	Chemical Structure	Side Groups (R)
Guanidine (Moderate)		R = Phenyl, Toluoyl R = Alkyl
Dithiocarbamate (Very fast)		R = Phenyl, Toluoyl R = Alkyl
Thiuram (Very fast)		R = Alkyl
2-Mercaptobenzothiazole (Moderate)		
Zinc-2-mercaptobenzothiazole (Very Fast)		
Thiourea (Very fast)		R = Alkyl, Phenyl
Benzothiazole Sulfenamide (Fast - Delayed Cure)		R = H, Alkyl R = Phenyl
Isopropylxanthate (Ultra Fast)		$Me^{n+} = Zn^{2+}, Na^{+}$

An important factor in the vulcanization process is the cure temperature which also affects the crosslink density and structure. To minimize thermal and oxidative degradation vulcanization should be done at the lowest possible temperature. However, to increase productivity, higher cure temperatures are often chosen. In our study we used the follow vulvanisation's system: sulfur with ZnO, stearic acid and bis (2-benzothiazole) disulfide (MBTS).

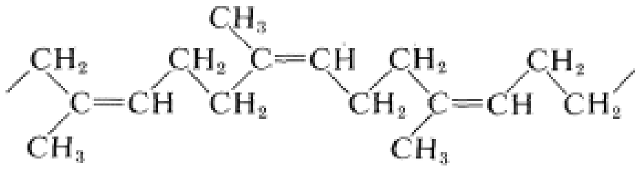
III. APPLIED MATERIALS AND METHODS

3.1 Natural Rubber (NR)

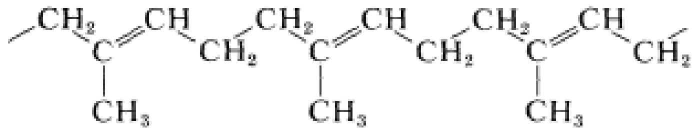
Natural Rubber is an elastic substance obtained from the latex sap of trees, especially those trees which belong to the general Hevea Brasiliensis. Technically speaking, natural rubber is an elastomer or an elastic hydrocarbon polymer. Natural rubber is one of the types of rubber that also include vulcanized rubber which is finished into a variety of rubber products. Natural rubber is also known by the names of India rubber, gum elastic, and caoutchouc [4].

The raw material from which natural rubber is made comes from the sap of rubber trees. The rubber plants are tapped for collecting the rubber latex. For this, an incision is made into the bark of the rubber tree and the latex sap is collected in cups.

After collecting the latex sap, the raw natural rubber is refined to convert it into a usable rubber. Initially an acid was added to the latex which used to make the sap set like a jelly. The latex jelly thus obtained was then flattened and rolled into rubber sheets and hung out to dry. In the year 1839, Charles Goodyear invented a more sophisticated way of making rubber stronger and more elastic. This was the process of rubber vulcanising. The unprocessed natural rubber is sticky, deforms easily when warm, and is brittle when cold. In such a state, it cannot be used to make products having a good level of elasticity. Vulcanization prevents the polymer chains from moving independently. As a result, when stress is applied the vulcanized rubber deforms, but upon release of the stress, the product reverts to its original shape.



natural rubber (*cis*-1,4-polyisoprene)



gutta-percha (*trans*-1,4-polyisoprene)

FIG.2. CHEMICAL STRUCTURE OF NATURAL RUBBER (cis-1,4-polyisprene) AND GUTTA PERCHA (trans-1,4-polyisoprene) [5]

3.2 Vulcanisation's system

3.2.1 Sulfur

The cross-linking reaction between sulfur and rubber occurs mainly at the carbon-carbon double bonds (C=C) in large excess of sulfur. Often accelerators are added to speed up the vulcanization and to reduce the amount of free sulfur which has a detrimental effect on the properties of the cured rubber.

3.2.2 Bis (2-benzothiazole) disulfide (MBTS)

The most widely used (primary) vulcanization accelerators are thiazoles. They form sulfur bridges between individual polymer molecules when heated with rubber. Often an initiator is added to accelerate the vulcanization process. This process is rather complicated and involves a sequence of reactions. A possible reaction mechanism for 2-2'-Dithiobis (benzothiazole) (MBTS) accelerated sulfur vulcanization of rubber is shown below. In the absence of an initiator, MBTS reacts with a sulfur molecule (cyclic S8) to form a polysulfide sulfurating agent which 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. Assuming a radical mechanism [6], MBT polysulfide radicals combine to form new sufurating 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 (Figure 3.).

Thiazoles are only medium fast curatives. To increase their cure speed, they are usually combined with small amounts of basic accelerators such as diphenyl guanidine (DPG) or diorthotolyl guanidine (DOTG). These accelerators not only increase the cure speed but also improve scorch delay and crosslink density and thus, improve the mechanical performance of the rubber. Furthermore activators such as ZnO / stearic acid are usually added which further increase the efficiency of sulfur based cure systems and produce flat cure with improved reversion resistance. The activity of an accelerator depends on three major factors: the basicity of the amine, the strength of the sulfur-nitrogen bonds and the concentration of MBTS. The greater the basicity of the amine, the shorter is the scorch delay and the faster is the cure rate. Sterically hindered amines (secondary amines) usually improve scorch safety and result in slower cure. The same is true for more stabilized S-N bonds.

The activity of thiazoles and sulfenamides (and other accelerators) in vulcanization systems also depends on the type of rubber and the vulcanization condition, that is, accelerators can have very different reactivities in different rubber systems and can lead to different crosslink densities [3].

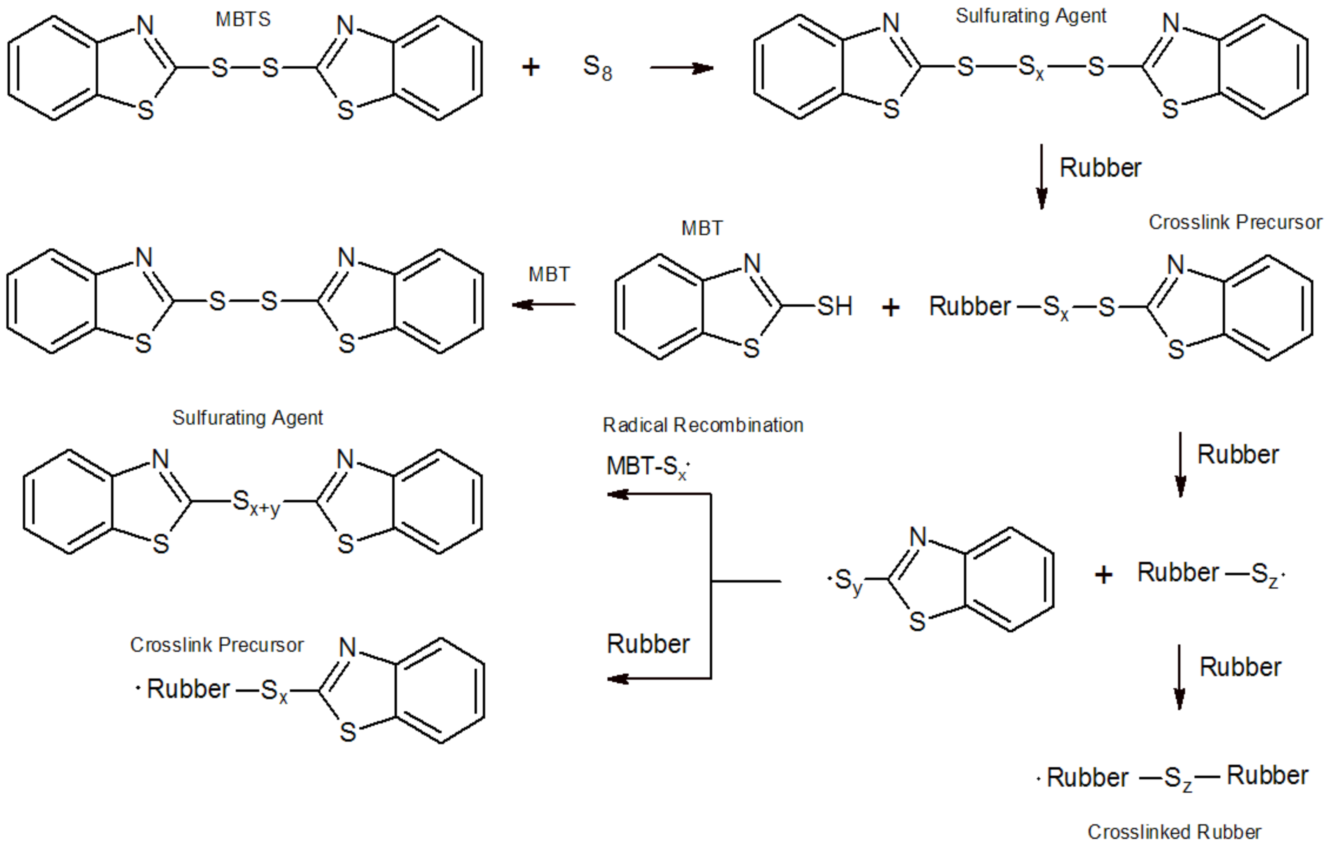


FIG.3.MECHANISM OF MBTS AND Zn CATALYSTS

3.3 Activators for sulfur vulcanization

3.3.1 Stearic acid and ZnO

Typical rubber vulcanization systems consist of rubber, sulfur accelerator, metal oxide and fatty acid, where the last two ingredients represent the activator. They are important rubber processing additives that not only activate cure but also improve the efficiency of sulfur based cure systems. In fact, almost all organic accelerators require the addition of an organic activator to achieve the desired cure and end-use properties. The most common activator is zinc fatty acid ester which is often formed in-situ by reaction of fatty acid with zinc oxide. The most common fatty acids include stearic, lauric, palmitic, oleic and naphthenic acid. The fatty acid solubilizes the zinc and forms the actual catalyst [6]. The ZnO can also act as a filler or white colorant in rubber products whereas the fatty acid improves filler incorporation and dispersion by wetting the oxide particles and reducing interfacial tension (wetting agent). The addition of activators in combination with secondary alkaline accelerators also allows for a more controlled onset of cure. The mechanism of zinc catalyzed sulfur vulcanization is very complex and is often not fully understood [7].

The main catalyst is zinc whereas the fatty acid functions as a solubilizing agent for the zinc which forms a complex with sulfur in the accelerator-polysulfide or is covalently bonded to sulfur atoms in the accelerator molecules as shown below. Both the solubility and reactivity increases if the zinc coordinates with an amine or amide, for example with sulfenamide. The chelated amines increase the nucleophilicity of the sulfur in the polysulfide complex and thereby increase the reaction rate of precursor formation. The exact position where zinc complexes in the accelerator complex is often unknown [8]. Three possible structures of a Zn – polythio-bis(benzothiazole) complex are shown below. The position of the zinc in the accelerator complex affects both the reaction path and the product distribution:

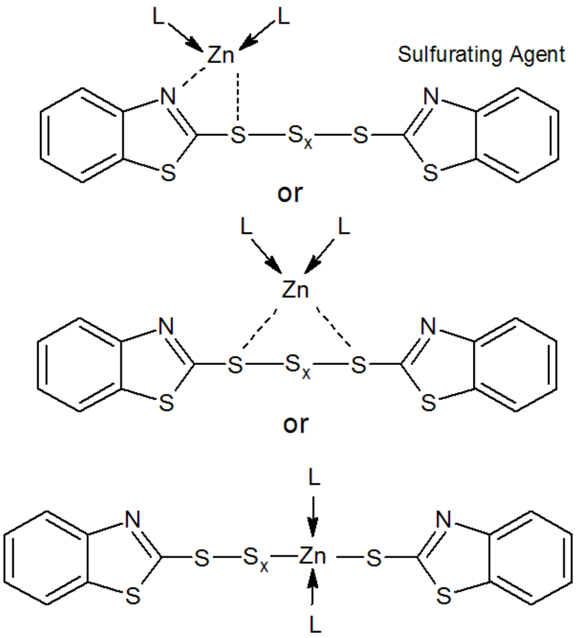


FIG.4. THE ZN-ACCELERATOR COMPLEX [8]

The accelerator complex plays an important role in both the insertion of sulfur atoms into the complex and in the formation of initial polysulfidic crosslinks.[2] As it is the case with other catalysts, remarkable small quantities of solubilized zinc are needed to initiate and speed up the vulcanization process. In the case 2-2'-dithiobis(benzothiazole) (MBTS), the zinc is assumed to complex with the nitrogen atom of a benzothiazole ring [8] as shown below.

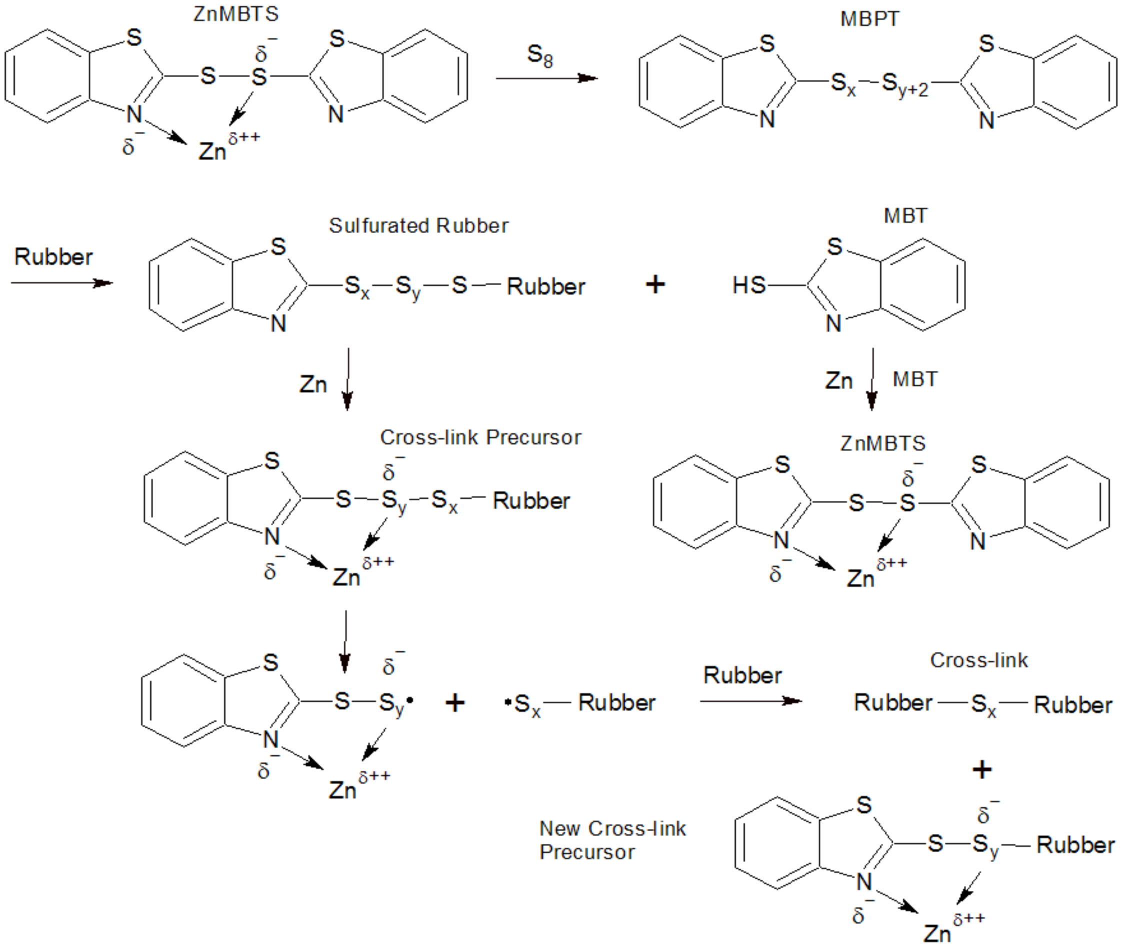


FIG.5. THE COMPLEX WITH THE NITROGEN ATOM OF A BENZOTHIAZOLE RING [8]

The zinc catalyst lowers the energy of dissociation of the sulfur bonds and allows for faster insertion of sulfur molecules (cyclic S8) into the polysulfide sulfurating agent which then reacts with rubber to form a crosslink precursor and 2-mercapto-benzothiazole (MBT). The later reacts with another MBT molecule in the presence of zinc to form another MBTS-zinc complex. Assuming a radical mechanism [8], the cross-link precursor cleaves homolytically into a rubber-polysulfide and polysulfidic benzothiazole radical. The later reacts with rubber to form a new cross-link precursor whereas the polymeric persulfenyl radicals either combine or react with other rubber molecules to form sulfur bridges.

The crosslinks that are formed initially are predominantly polysulfides. During post cure or service life, these polysulfidic crosslinks can degrade (desulfurate) to more stable mono or disulfidic crosslinks which changes the original rubber properties markedly, and/or the polysulfidic crosslinks degrade to elastically ineffective cyclic sulfides or pendant groups. The reaction rate of these post-vulcanization reactions is higher for longer sulfur bridges, since the S-S bonds are weaker when the crosslinks are longer.

3.4 Carbon black

Carbon blacks are mainly used as reinforcing fillers in tire and other rubber products. The reinforcement effect is influenced by the interaction between the elastomer molecules, between the carbon black particles themselves and between the carbon black particles and elastomer matrix also. For elastomer reinforcement, the primary particle size (specific BET surface area) a surface activity of the carbon black types are important as well as their carbon black structure. In addition, the degree of carbon black dispersion achieved and the carbon black loading used in the elastomer composite play a role. The type of carbon black can significantly influence the properties of the resulting rubber compounds. This explains the existence of many different standardized industrial carbon black grades being used in rubber compounds for the body and tread of tires.

Carbon blacks are expected to continue to dominate the rubber market for the foreseeable future, but they are coming under considerable pressure from precipitated silica in some important tire applications. This is because the silica offers lower rolling resistance properties and hence improved fuel economy and lower emissions. This trend is expected to continue to grow.

3.5 Sunflower oil

Plasticizers make it possible to achieve improved compound processing characteristics, while also providing flexibility in the end-use product. Ester plasticizers are selected based upon cost-performance evaluation. The rubber compounder must evaluate ester plasticizers for compatibility, processibility, permanence and other performance properties. They are in production include sebacates, adipates, terephthalates, dibenzoates, gluterates, phthalates, azelates, and other specialty blends. This broad product line provides an array of performance benefits required for the many elastomer applications such as tubing and hose products, flooring, wall-coverings, seals and gaskets, belts, wire and cable, and print rolls. Plasticizer-elastomer interaction is governed by many factors such as solubility parameter, molecular weight, and chemical structure. Compatibility and performance attributes are key factors in developing a rubber formulation for a particular application.

Sunflower oil is a monounsaturated (MUFA)/polyunsaturated (PUFA) mixture of mostly oleic acid (omega-9)-linoleic acid (omega-6) group of oils. The oil content of the seed ranges from 22% to 36% (average, 28%): the kernel contains 45–55% oil. The expressed oil is of light amber color with a mild and pleasant flavor; refined oil is pale yellow. Refining losses are low and the oil has good keeping qualities with light tendency for flavor reversion. The oil contains appreciable quantities of vitamin E, sterols, squalene, and other aliphatic hydrocarbons [9, 10].

TABLE 2
COMPOSITIONS OF MASTER BATCH FORMULATIONS

Material	Weight [g]				
	Sample 1.	Sample 2.	Sample 3.	Sample 4.	Sample 5.
NR	152,00	152,00	152,00	152,00	152,00
Stearic acid	4,55	4,55	4,55	4,55	4,55
Carbon black	76,00	76,00	76,00	76,00	76,00
ZnO	7,60	7,60	7,60	7,60	7,60
MBTS	0,91	1,82	2,74	3,65	4,56
Sulphur	3,80	7,60	11,40	15,20	19,00
Sunflower oil	30,00	30,00	30,00	30,00	30,00

The parameters of mixing procedure were the follow: the vulcanisation's temperature at 145°C, pressure at 220 bar during 10 minutes. The amount of sulfur and MBTS were increased proportionally (show Table 2.).

Base mixtures of NR, carbon black, antioxidant, zinc oxide and stearic acid were prepared in a Banbury internal mixer with a rotor speed of 65 rpm. Curatives were added on an open two-roll mill in a second stage mixing. The base mixes were then crossblended using a masterbatching technique to ensure uniform dispersion of the ingredients and to minimise between-mix variations. The termo-mechanical and optical properties of the mixtures were examined by a Short A hardness tests; DSC (differential scanning calorimetry) and a SEM (scanning electron microscope) instruments. The next chapter contains the results of them.

IV. RESULTS AND CONCLUSION

The Shore A hardness test of the rubber samples containing different Sulphur showed was a significant difference between Sample 1 and Sample 5. (Fig. 6.). The results demonstrate the influence of sulphur and MBTS during the different stages of the vulcanization. With sulfur present, the crosslinked product distribution is influenced as well.

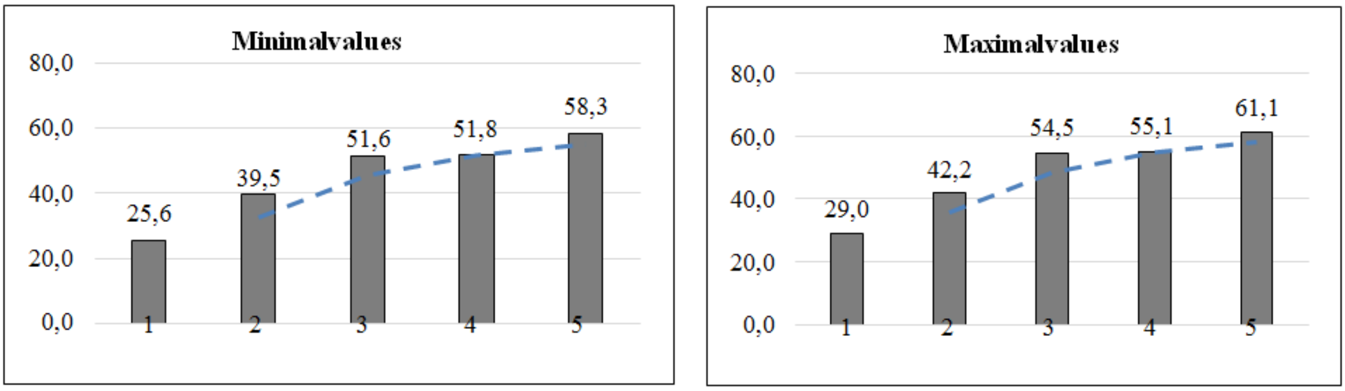


FIGURE 6. a.) THE MINIMAL AND b.) MAXIMAL VALUES OF SHORE A HARDNESS TEST

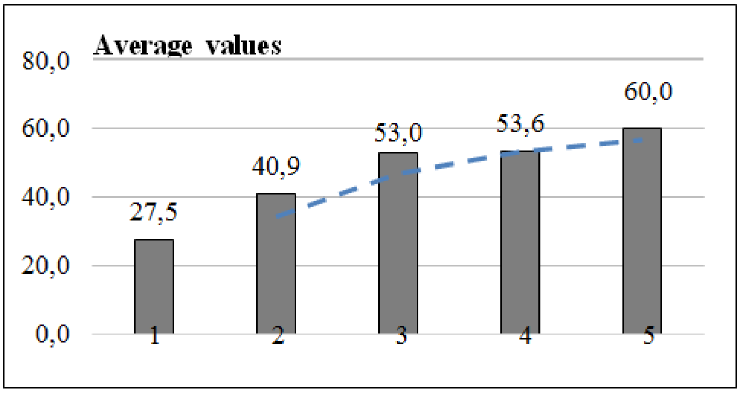


FIGURE 7. THE AVERAGE VALUES OF SHORE A HARDNESS TEST

NR-based master batches, even when similarly compounded, exhibit different cure behavior and cure properties depending on the cure system used, the duration and temperature of cure. The results of DSC tests show that the difference between the samples (Fig.8.). **DSC** (differential scanning calorimetry), is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment.

Differential scanning calorimetry can be used to measure a number of characteristic properties of a sample. Using this technique it is possible to observe fusion and crystallization events as well as glass transition temperatures Tg. DSC can also be used to study oxidation, as well as other chemical reactions. In this case we checked the process of vulcanization.

Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time (from +60°C to +180°C). The cross-linking of polymer molecules that occurs in the curing process is exothermic, resulting in a positive peak in the DSC curve that usually appears soon after the glass transition. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. We collected the results below.

TABLE 3
THE RESULTS OF DSC MEASUREMENTS

Sample ID	Color of curve	Glass-transition temperature [°C]	Heat capacity[J/g]
Sample 1.	purple	116,74	-1,89
Sample 2.	red	116,15	-1,01
Sample 3.	green	120,52	-1,41
Sample 4.	claret	119,03	-1,10
Sample 5.	orange	115,43	-1,28

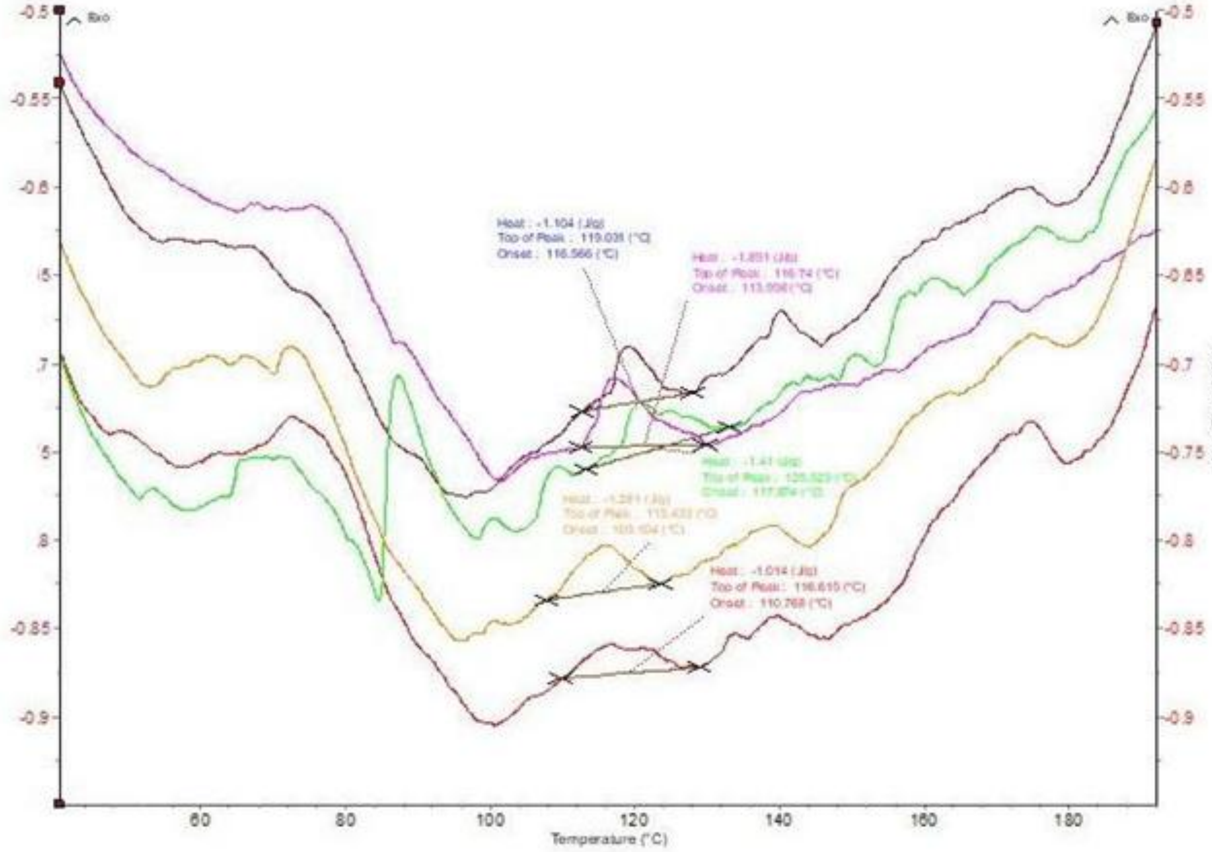


FIGURE 8. THE DSC CURVES OF THE SAMPLES

The aim of the **SEM** investigation was the examination of blending of raw caoutchouc and rubber mixtures (base polymer with additives) in 50x and 1000x magnification. It is evident, that besides the surface impurities, Sample 3. and Sample 5. generated a lot of sulfur aggregation from the vulcanising agent used based on the recipe.

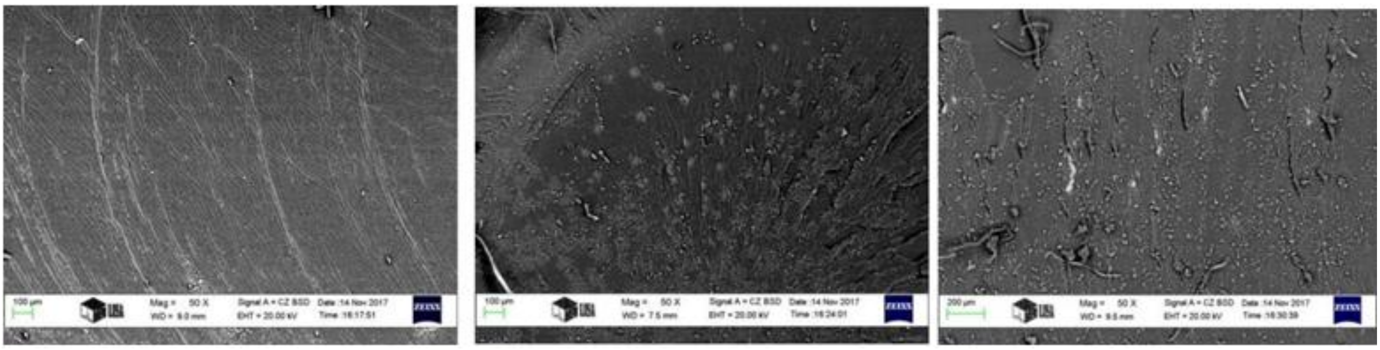


FIGURE 9. THE SEM RESULTS OF a.) SAMPLE 1., b.) SAMPLE 3. AND c.) SAMPLE 5. IN 50x MAGNIFICATION

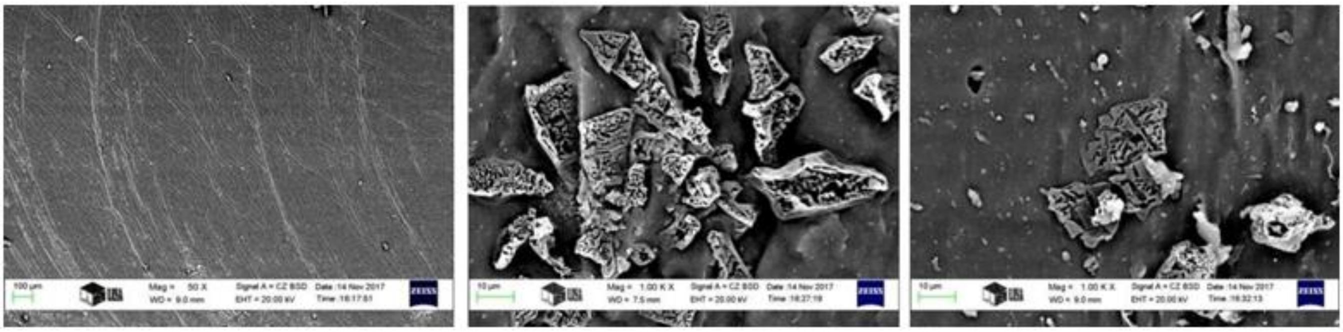


FIGURE 10. THE SEM RESULTS OF a.) SAMPLE 1., b.) SAMPLE 3. AND c.) SAMPLE 5. IN 1000X MAGNIFICATION

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