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DOCTORAL THESIS

Title NEW INSIGHTS IN VULCANIZATION CHEMISTRY USING MICROWAVES AS HEATING SOURCE

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A mis padres y a mi hermano

“La utopía es como el horizonte.
Me acerco dos pasos y ella se aleja dos pasos.
Camino diez pasos y el horizonte se aleja diez pasos más allá.
Por mucho que yo camine, nunca la alcanzaré.
¿Para qué sirve entonces la utopía?
Para eso sirve: para caminar”

Eduardo Galeano

“Utopia is like the horizon.
I move two steps closer, and it moves two steps further away.
I walk ten steps, and the horizon moves ten steps further away.
As much as I may walk, I will never reach it.
So, what is the purpose of utopia?
The purpose is this: to keep walking”

Eduardo Galeano

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Summary

Microwaves vulcanization is a mature process and there is no doubt about its efficiency on producing high quality goods. Microwaves are found not only to speed up the processing and increase the energy transfer efficiency, but also to be in some cases able to change reaction pathways. There are some evidences, based on changes in physical properties when comparing conventional and microwaves vulcanization, that suggest that some changes occur when working with different heating sources. However, there is a lack of information of the effects of MW in vulcanization chemistry. Therefore, the principal aim of this thesis consists of studying microwave-assisted vulcanization from a new perspective, focusing on the effects of this radiation in the main ingredients of a rubber compound, in the vulcanization mechanism, in the final crosslinked network and also in the devulcanization process.

The first part of the work consisted in developing and optimizing all the analytical methods necessary to explore all the steps of vulcanization process and identifying all the intermediates formed. Model Compound Vulcanization (MCV) studies, using squalene as a model molecule, have been used to understand better the influence of this radiation in the reaction mechanism, even though some tests have been also performed in natural rubber samples. Techniques as HPLC-MS, MALDI-TOF or GPC have been used to characterize the MCV samples, whereas swelling measurements, stress-strain measurements, compression set or hardness have been used to characterized natural rubber samples.

Two of the most common vulcanizing systems have been studied (using sulfenamide and/or thiuram accelerator types). In addition, a special emphasis has been given to the study of the microwaves influence on the activator system, trying to reduce ZnO contents and finding more environmental friendly substitutes through different strategies. Finally, all the knowledge acquired in all these studies has been used to optimize the devulcanizing behavior of diphenyl disulfide (DPDS) with the help of microwaves, proving that microwaves can help to advance in the search of a solution to the problem of waste rubber recycling.

Resumen

La vulcanización por microondas es un proceso maduro y no cabe duda sobre su eficiencia para producir artículos de caucho de alta calidad. Las microondas son conocidas no sólo por su capacidad de acelerar los procesos y aumentar la eficiencia de la transferencia energética, sino que también son capaces en ciertos casos de cambiar los caminos de reacción. Hay evidencias, basadas en cambios en propiedades físicas al comparar productos vulcanizados con el método convencional y con microondas, que indican que algunos cambios pueden suceder al trabajar con diferentes fuentes de calentamiento. Sin embargo, hay una falta de información sobre los efectos que las microondas tienen en la química de la vulcanización. Por lo tanto, el principal objetivo de esta tesis se basa en estudiar la vulcanización asistida por microondas desde una nueva perspectiva, centrándose en los efectos de esta radiación en los ingredientes principales de las formulaciones de caucho, en el mecanismo de vulcanización, en la reticulación de la red polimérica y también en el proceso de devulcanización.

La primera parte del trabajo consistió en desarrollar y optimizar todos los métodos analíticos necesarios para explorar todas las etapas del proceso de vulcanización y identificar todos los intermedios formados. Estudios de Model Compound Vulcanization (MCV) utilizando escualeno como molécula modelo se han realizado para entender mejor la influencia de esta radiación en el mecanismo de la reacción, aunque algunos experimentos también se han realizado con muestras de caucho natural. Técnicas como HPLC-MS, MALDI-TOF o GPC se han utilizado para caracterizar las muestras de MCV, mientras que medidas de inflamiento, de tensión-elongación, compresión y dureza se han realizado para caracterizar las muestres de caucho natural.

Dos de los sistemas de vulcanización más comunes han sido estudiados (sulfenamidas y tiuramos). Además, se ha dado un especial énfasis al estudio de la influencia de las microondas en el sistema activador, intentando reducir el contenido en ZnO y buscar, a través de diversas estrategias, substitutos más amigables con el medio ambiente. Finalmente, todo el conocimiento adquirido en estos estudios se ha utilizado para optimizar el comportamiento devulcanitzante del disulfuro de difenilo (DPDS) con ayuda de las microondas, demostrando que las microondas pueden ayudar a avanzar en la búsqueda de una solución al problema del reciclaje de los residuos de caucho.

Resum

La vulcanització per microones és un procés madur i no hi ha dubte sobre la seva eficiència per produir articles de cautxú d'alta qualitat. Les microones són conegudes no només per la seva capacitat d'accelerar els processos i augmentar la eficiència de la transferència energètica, sinó que també són capaces en certs casos de canviar els camins de reacció. Hi ha evidències, basades en canvis en propietats físiques al comparar productes vulcanitzats amb el mètode convencional i amb microones, que indiquen que alguns canvis poden succeir al treballar amb diferents fonts d'escalfament. No obstant això, hi ha una falta d'informació sobre els efectes que les microones tenen en la química de la vulcanització. Per tant, el principal objectiu d'aquesta tesi es basa en estudiar la vulcanització assistida amb microones des d'una nova perspectiva, centrant-se en els efectes d'aquesta radiació en els ingredients principals de les formulacions de cautxú, en el mecanisme de vulcanització, en la reticulació de la xarxa polimèrica i també en el procés de devulcanització.

La primera part de la feina va consistir en desenvolupar i optimitzar tots els mètodes analítics necessàris per explorar totes les etapes del procés de vulcanització i identificar tots els intermedis formats. Estudis de Model Compound Vulcanization (MCV) utilitzant esqualè com a molècula model s'han realitzat per entendre millor la influència d'aquesta radiació en el mecanisme de la reacció, encara que alguns experiments també s'han realitzat amb mostres de cautxú natural. Tècniques com HPLC-MS, MALDI-TOF o GPC s'han utilitzat per caracteritzar les mostres de MCV, mentre que mesures d'inflament, de tensió-elongació, compressió i duresa s'han realitzat per caracteritzar les mostres de cautxú natural.

Dos dels sistemes de vulcanització més comuns han estat estudiats (sulfenamides i tiurams). A més, s'ha donat un especial èmfasi a l'estudi de la influència de les microones en el sistema activador, intentant reduir el contingut de ZnO i cercar, a través de diverses estratègies, substituts més amigables amb el medi ambient. Finalment, tot el coneixement adquirit en aquests estudis s'ha utilitzat per optimitzar el comportament devulcanitzant del disulfur de difenil (DPDS) amb l'ajut de les microones, demostrant que les microones poden ajudar a avançar en la recerca d'una solució al problema del reciclatge dels residus de cautxú.

Main Symbols and Abbreviations

ε''	dielectric loss
ε'	dielectric constant
μ	dipole moment [D]
tan δ	loss tangent
λ_0	wavelength in free space
ϕ_2	volume fraction of the polymer [-]
ρ	density [g/cm^3]
λ	extension ratio, elongation at break [%]
χ	rubber-solvent interaction parameter or Huggins interaction constant [-]
ν_e	network chain density [mol/cm^3]
A	collision frequency between the molecules with proper geometry to react
A_0	original cross sectional area [mm^2]
AgTFA	Silver trifluoroacetate
APCI	Atmospheric Pressure Chemical Ionization
ATR	Attenuated Total Reflectance
BET	BET Adsorption Isotherms
C_1	elastic constant
C_2	constant of the effects of chain ends and chain entanglements.
CB	carbon black
CBS	N-cyclohexyl-2-benzothiazol sulfenamide
CH	Conventional Heating
CHT	Conventional Hydrothermal Treatment
CV	conventional system
DHB	Dihydroxibenzoic acid
DMDCA	Dimethyldithiocarbamic acid
DPDS	Diphenyl Disulfide
DTA	Differential thermical analysis
DVR	Compression set [%]
E	electric field
Ea	Activation Energy [J/mol]
EI	Electronic Impact
ESI	Electrospray Ionization
ESR	Electron Spin Resonance
EPDM	Ethilene Propylene Diene Monomer
EV	efficient system
f	crosslink functionality [-]

F	force [MPa]
FTIR	Fourier Transform Infra Red
GC	Gas Chromatography
GPC	Gel Permeation Chromatography
HPLC	High Performance Liquid Chromatography
IR	Infra Red
IRDH	International Rubber Hardness Degree
k	reaction rate constant [s^{-1}]
LC	Liquid Chromatography
m	mass [g]
M_H	maximum torque reached during vulcanization in a rheometer [dNm]
M_L	minimum torque reached during vulcanization in a rheometer [dNm]
M_P	molecular weight between crosslinks [g/mol]
m.a.	more activator
MBT	2-mercaptobenzothiazole
MBTS	Dibenzothiazole disulfide
MBTP	Dibenzothiazole polysulfide
MALDI	Matrix-Assisted Laser Desorption/Ionization
MCV	Model Compound Vulcanization
MHT	Microwave Hydrothermal Treatment
MS	Mass Spectrometry
MW	Microwaves
P	vapor pressure of diluted solvent with polymer
P^0	vapor pressure of the pure solvent
PB	Particle Beam
PG	Pendant Group
phr	part per hundred rubber
P_v	power dissipated in the system per unit volume [watts]
NMR	Nuclear Magnetic Resonance
NR	Natural Rubber
R	universal gas constant [J/mol·K]
RSM	Reaction Stage Modeling
R_v	reversion [min^{-1}]
S/A ratio	sulfur/accelerator ratio [-]
SBR	Styrene Butadiene Rubber
Semi-EV	semi efficient system
Sq	Squalene
Sq-PG	Squalene with pendant group
Sq-S-Sq	Monosulfidic crosslinks
$Sq\text{-}S_2\text{-}Sq$	Disulfidic crosslinks
$Sq\text{-}S_3\text{-}Sq$	Trisulfidic crosslinks
$Sq\text{-}S_4\text{-}Sq$	Tetrasulfidic crosslinks

T	temperature [K]
t_1	scorch time [min]
t_{90}	optimum vulcanization time [min]
TG	Thermogravimetrical analysis
TIC	Ion Chromatogram
TME	2,3-simethyl-2-butene
TMTD	Tetramethylthiuram disulfide
TMTM	Tetramethylthiuram monosulfide
TMTHe	Tetramethylthiuram polysulfide
TMTPe	Tetramethylthiuram pentasulfide
TMTTe	Tetramethylthiuram tetrasulfid
TMTTr	Tetramethylthiuram trisulfide
TMTU	Tetramethylthiurea
TPhTD	Tetraphenylthiuram disulfide
TOF	Time Of Flight
UV	Ultraviolet
V	volume [cm^3]
V_0	solvent molar volume [cm^3/mol]
Vis	Visible
w.a.	without activator
x	half power depth
XLD	crosslink density [mol/cm^3]
ZDAC	Zinc dimethylperthiocarbamate
ZDMC	Zinc dimethyldithiocarbamate

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Chapter 1

A Novel Perspective of Studying Microwave Vulcanization

This introductory chapter provides a general outline of the topic of this thesis and gives some insights in the reasons to perform this research. The story of microwaves and its use in rubber vulcanization is briefly summarized and the aims of this thesis are proposed and discussed.

1.1. HISTORICAL REVIEW

Recently, there has been an increasing interest by the chemical industry in the optimization of energetic supply to the processes in order to make them more efficient. The main objective consists of minimizing the energetic supply and obtaining an improvement in the reaction control. Some advances have been made developing alternative energy sources to improve the energy transfer to the chemical reactions. The main types of alternative energy, applied for vulcanization purposes, are ultrasounds and microwaves and they are used to optimize the reaction time and yield, as well as reduce the amount of undesired products and the economic costs[1-2].

The present thesis focuses on the use of microwaves for rubber vulcanization and devulcanization as an alternative to conventional heating. The development of microwaves technology was driven by the Second World War and discovered accidental during radar research using magnetrons. In 1946, the engineer Dr. Percy LeBaron Spencer, who worked for the Raytheon Corporation, was working on magnetrons[3]. One day at work, he had a candy bar in his pocket, and found that it had melted. He realized that the microwaves he was working with had caused it to melt.

After experimenting, he realized that microwaves would cook foods quickly, even faster than conventional ovens that cook with heat.

The Raytheon Corporation produced the first commercial microwave oven in 1954; it was called the 1161 Radarange. It was large, expensive, and had a power of 1600 watts. The first domestic microwave oven was produced in 1967 by Amana (a division of Raytheon).

The application of microwaves in industry started in the 50's with different drying processes. In 1966 James W. Jacobs patented a novel polymerization process of polyisocyanates and polyesters to form polyurethane foams using microwaves[4]. In 1969, Dietmar Anders published the first paper of a continuous vulcanization process with microwave as an alternative to the conductive heating[5] and E. J. Bunclark patented in 1973 a microwave assisted vulcanization system of different polymer mixtures[6]. However, it was not until the 80's when the effects of microwaves were studied in typical organic synthesis reactions such as dehydrogenations, condensations and nucleophilic or electrophilic substitutions. R. Gedye and R. J. Giguere are considered the first authors who in 1986 raised the use of microwave as an alternative energetic source for organic synthesis studying the differences in the reaction mechanisms[7-8].

From then on, microwaves were considered interesting not only because of the reaction rate increases, but also because of the improvements of reaction yields, production of cleaner chemistries and discovery of new reaction pathways. Because of its efficient way to transfer energy to the system, in comparison with conductive heating methods, microwaves synthesis creates completely new possibilities in performing chemical transformations. Thus, microwaves create a new realm in synthetic organic chemistry.

The concept of performing reactions in short periods of time with this advanced energy source was starting to take hold, but was not yet fully mature, due to issues with instrumentation. Although its promising expectation, microwaves development for organic chemistry has been relatively slow in comparison with the implementation of other techniques. This is due to the lack of control of the temperature and pressure, the lack of reproducibility, security aspects like the inflammability of organic solvents and also the lack of knowledge in the basis of dielectric heating by microwaves.

In the last years, a significant increase in the publications of organic synthesis assisted by microwaves has been observed (Figure 1.1). This growth is a clear indicator of the higher interest in this kind of alternative energy. This interest is based on the positive results obtained, which provide a glimpse of the promising future for microwaves as a substitute of conventional heating methods, although there is still a lot of work to do. Nowadays the research in this area is centered in two different fronts: the development in the technical advances of microwaves ovens, software, design and scale-up of processes to their application in the industry; and the study of the influence of this energy in different kind of reactions and in their mechanism.

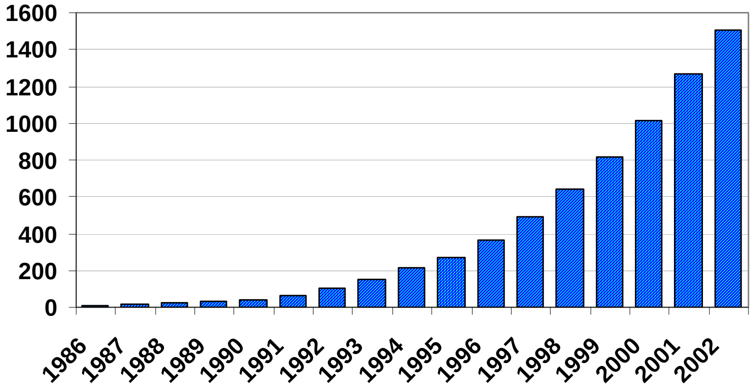

Figure 1.1. Number of publications in organic synthesis assisted by microwaves between 1986-2002[9].

1.2. MICROWAVES THEORY: HOW CAN THIS ENERGY CHANGE A REACTION PATHWAY?

A microwave is a form of electromagnetic energy defined within the frequency range between 300 and 300,000 MHz and with a wave length interval between 1mm and 30 cm. Within this region of electromagnetic energy, only molecular rotation is affected, not molecular structure. By International agreement, four frequencies were originally reserved for the use of electromagnetic fields for industrial, scientific and medical purposes other than communications: 915±25, 2450±13, 5800±75 y 22125±125 MHz, in order to avoid interferences between the equipments. These frequencies are known as **ISM (Industrial, scientific and medical) band**. From these four frequencies 2450 MHz (λ=12.2 cm) is preferred because it has the right penetration depth to interact with laboratory scale samples[3].

The core of a microwave oven is a magnetron, an oscillator that converts high voltage pulse into a pulse of microwave power[10]. The microwave is a wave, constantly moving forward and transitioning between positive and negative values. As the wave moves, it generates pockets of high energy and low energy due to constructive and destructive interference. This leads to the presence of high-energy fields, low-energy fields, and a point where the amount of energy is equal to zero, called the node. This energy is driven to a cavity, where the waves interact with the sample. Depending on its design, we can find two types of microwaves ovens: Multimode and Single Mode (Figure 1.2.)[11]

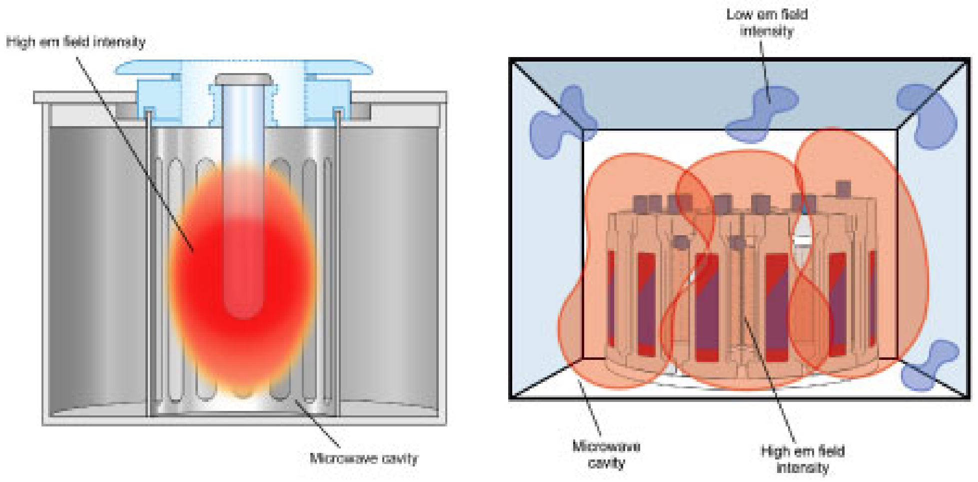

Figure 1.2. Single energy distribution in Single Mode (left) vs Multiple nodes generated in Multiple Mode Microwave (right)[12].

MULTIMODE OVENS: They are conceptually similar to the commercial ovens for cooking. Due to its design there are multiple active points in the cavity, multiple modes and nodes. The problem of this kind of ovens is the lack of reproducibility, since they cannot control the temperature and pressure during the reaction. Furthermore, the lack of stirring could give rise to high localized temperatures, known as “hot spots” (pockets of high and low energy generated), that could take the reaction to an incident or explosion caused by superheating of certain points[11].

SINGLE MODE OVENS: This type of oven is normally smaller and with a unique cavity, which is a restriction, because only one sample can be irradiated every time. Single Mode ovens were designed in order to improve the reproducibility problems of multimode ovens. In these ovens there is the generation of a single mode of energy during the irradiation cycle. Instead of allowing the presence of multiple modes and nodes of microwave energy, the single mode cavity is designed for the length of only one wave, therefore generating only one mode of microwave energy. The wave generates a center of high electromagnetic field intensity with homogeneous energy distribution in the cavity where the reaction takes place[12]. Normally, single mode systems have the possibility of temperature and pressure monitoring, for safety and chemical control reasons, and also a stirring device incorporated in the system in order to improve the reproducibility issues.

When comparing both oven types, another major difference between them is the energy density. Although most of the single mode cavities have a maximum power output of only 300 Watts, the amount of energy in a given amount of space within the cavity is actually much greater. Since in single mode ovens microwaves are focused in a small space, in comparison with larger multimode cavities, the energy per unit area is higher. As a comparison, a typical single mode cavity, with a volume of 0.5 L, can generate 900 W/L with 300 W of power applied to the reaction. A multimode cavity, on the other hand, will generate 20-25 W/L with 1200 W of energy applied[12].

1.2.1. HOW DOES MICROWAVE HEAT A SUBSTANCE? WHY IS IT MORE EFFECTIVE THAN CONDUCTIVE HEATING?

The action of the microwave radiation on chemical systems is still under debate. Many researchers think that the observed acceleration of the reaction rates could be due to the different mode of transferring heat to the reagents and solvent. Others, on the contrary, suggest that absorption of microwave radiation has some specific activating effect on the reagent molecules[10].

First of all, and concerning the behavior of molecules when interacting with microwaves, substances can be divided into three broad categories:

i) Materials which reflect microwaves (ex. metals).
ii) Materials which do not interact with microwaves, they are transparent to this kind of energy (ex. hydrocarbons).
iii) Materials which absorb the radiation and are therefore, able to start the heating or the activation of the chemical reaction (ex. water).

It is necessary to clarify that usually materials do not behave completely as a microwave absorbent, nor as a reflector, nor as a transparent material to microwaves. Most of the time, material behavior can be explained as a combination of the three. Furthermore, the chemical composition of the material, as well as its size and shape will affect its behavior in a microwave field[8].

At 2450 MHz microwaves the oscillation of the electric field of the radiation occurs $4.9 \cdot 10^9$ times per second; the timescale in which the field changes is about the same as the response time (relaxation time) of permanent dipoles present in most organic and inorganic molecules. This fact represents a fundamental characteristic for an efficient interaction between the electromagnetic field of microwaves and a chemical system[13]. Heating by microwave is the result of a complex interaction between the electromagnetic and dielectric fields. Although microwave is an electromagnetic radiation, only its electric field is responsible of the energy transfer to heat substances, since magnetic interactions do not occurred in chemical synthesis[3]. This electric field can heat the matter through three different mechanisms[3] :

i) **Dipole rotation:** is an interaction in which polar molecules try to align themselves with the rapidly changing electric field of the microwave. The rotational motion of the molecule as it tries to orient itself with the field results in a transfer of energy. The coupling ability of this mechanism is related to the polarity of the molecules and their ability to align with the electric field (see section 1.2.3.).

ii) **Ionic conduction:** this is an interaction that occurs when there are free ions or ionic species present in the substance being heated. The electric field generates ionic motion as the molecules try to orient themselves to the rapidly changing field. This causes the instantaneous superheating as in the previous case. The temperature of the substance also affects ionic conduction: as the temperature increases, the transfer of energy becomes more efficient. In case of metals, very conducive substances, the main microwaves energy does not penetrate the metal surface, it is reflected and the induced voltage generates electrical discharges that could cause an explosion. That is the reason why metals should not be introduced in a microwave oven.

iii) **Interfacial ionization:** this third mechanism is less common than the other two. This interaction occurs in systems with inclusions of conductive materials in a non-conductive matrix. The combination of these products causes that the whole material behaves as a good microwave absorbent as a combination of the other two mechanisms explained above.

Once the basics of microwaves heating are understood, it is possible to compare the way conductive heating works with microwave, in order to understand why this kind of energy is a more effective heating source.

In **Conductive heating** there is an external heating source and the heat is driven into the substance, passing first through the walls of the vessel in order to reach the solvent and the reactants (Figure 1.3.).

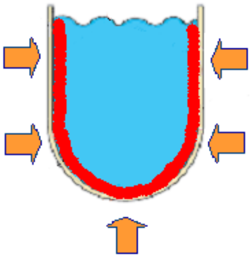

Figure 1.3. Conductive heating with an external heat source. Heat is driven through the vessel walls[3].

This is a slow and inefficient method for transferring energy into the system and this lack of efficiency causes some drawbacks[3]:

- The temperature of the vessel is always higher than the temperature of the reaction mixture inside. Thus, there is generation of thermal gradients.
- The energy transfer depends on the thermal conductivity of the vessel and the materials being heated present in the reaction medium.
- The reaction times are longer due to the difficulty to reach a thermal equilibrium.

Microwave heating, as it has been explained in this section, is a very different process. As shown in Figure 1.4., the microwaves couple directly with the polar molecules or ions that are present in the reaction medium, leading to a rapid increase in the temperature. Thus, in this case, the heat does not go from outside to inside. The heat is directly generated inside the material and it is driven to its surface. Furthermore, as stated before, there are materials transparent to this kind of radiation and these materials can be used to construct the vessel and the oven cavity, minimizing the lost of heat in the energy transfer to the system. So, the lost of heat in the energy transfer to the system is minimized. Teflon®, polyethylene or polypropylene are normally used as materials in microwave chemical reactors[10].

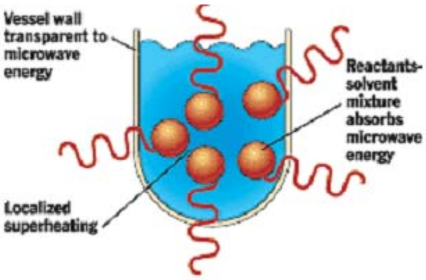

Figure 1.4. Microwave heating. Waves couple directly with the molecules that are present in the reaction medium[3].

Summarizing what has been stated until this point, microwave heating advantages in comparison with conductive heating are[2]:

- Microwave causes reduction of the reaction times due to its higher efficiency to transfer energy to the reactants[14]. Furthermore, in some cases it makes possible to overcome high energetic barriers and promote transformations that are currently not possible using conventional heating. This is creating new perspectives in synthetic chemistry.
- It is easy to reach the temperature equilibrium and also the chemical control of the reaction, due to the homogeneity of the electrical field.
- It is a selective heating source, since its ability to heat depends on the dielectric constant of every substance. It causes high localized temperatures (“hot spots”) inside de reaction medium.
- Due to the fact that the energy is transferred through molecular excitation, the heating is fast and it has a high penetration power. As a consequence, reactions are more uniform[15].
- Industrial application of microwave is cleaner and cheaper because it is possible to work continuously. Furthermore, because of the increase in reaction rates, it causes a reduction in the production lines length, which implies a reduction in space and costs[15].

This heating method has also some disadvantages[15]:

- It is necessary a high initial capital to invest in the equipment of electromagnetic energy application.
- Sometimes, this selectivity of heating of microwaves would be more a limitation than an advantage.
- There could be problems of uniform heating due to the change in the dielectric constant of the system during the reaction.
- As stated before, the rapid increase of temperatures could bring the system to a final explosion. Due to this heating power, security is more important when working with microwaves.

1.2.2. HOW DOES MICROWAVE INCREASE REACTION RATE?

In a typical reaction coordinate, the process begins with reactants (A and B), which have a certain energy level (E_R). In order to complete the transformation, these reagents must collide in the correct geometrical orientation to become activated to a higher-level transformation state (E_{TS}). The difference between these energy levels is the activation energy (E_a) required to reach this higher state ($E_{TS} - E_R = E_a$). The activation energy is the energy that the system must absorb from its environment in order to react and it is related to the speed constant (k) through Arrehnius equation (Equation 1.1.). Once enough energy is absorbed, the reactants quickly react and return to a lower energy state (E_P), the products A-B.

$$k = A \cdot e^{\frac{-Ea}{RT}}$$

Equation 1.1. Arrhenius Speed constant (k) depending on: A, which is the collision frequency between the molecules with proper geometry to react, and the exponential indicates the fraction of the molecules which have the minimum energy necessary to go beyond the activation energy barrier (E_a).

There has been some speculation that microwaves affect the orientation of the molecular collisions and the activation energy, but there is no evidence that supports either of these ideas[2,16]. The most accepted theory is that microwave irradiation does not affect the activation energy, but provides the momentum to overcome this barrier and complete the reaction more quickly than conventional heating methods. Microwaves affect temperature parameter in Arrhenius equation. An increase in temperature causes molecules to move more rapidly, which leads to a greater number of more energetic collisions. This occurs much faster with microwave energy, due to the high instantaneous heating of substances above the normal bulk temperature, and is the primary factor for the observed rate enhancements.

Microwave will transfer energy in 10^{-9} seconds with each cycle of electromagnetic energy. The kinetic molecular relaxation from this energy is approximately 10^{-5} seconds. This means that the energy transfers faster than the molecules can relax, which results in the non-equilibrium condition and high instantaneous temperatures that affect the kinetics of the system. This enhances the reaction rate, as well as the products yield. In addition, the lifetime of activated complexes is approximately 10^{-13} seconds, and thus, is much shorter than the rate at which energy is transferred with microwaves. Activated complexes do not normally exist long enough to have an opportunity to absorb microwave energy. However, there are a number of resonance-stabilized intermediates that are much longer lived. Many of these have lifetimes longer than 10^{-9} seconds, so the opportunity exists in certain chemical reactions, for intermediates generated in this approximate time frame, to couple directly with the microwave and be further enhanced. Most intermediates are highly polar species and many of them are ionic in character, making them excellent candidates for microwave energy transfer, and giving rise in some cases to new byproducts that are not able to be formed when using conductive heating (see section 1.2.3.).

1.2.3. THE ROLE OF SOLVENT IN MICROWAVE SYNTHESIS

Solvents play an important role in microwave synthesis. Most reactions take place in solution, and therefore, choice of solvent can be a crucial factor in the outcome of the reaction. One of the most important characteristics of the solvent is its polarity (See Appendix 1.). With microwave heating, this becomes a more significant factor, as microwaves directly couple with the molecules that are present in the reaction medium. The more polar the reaction mixture is, the greater its ability to couple with the microwave energy. As discussed in the previous section, this interaction leads to a rapid rise in temperature and faster reaction rates[3]. In addition, in most cases it also induces an increase in the reaction yield.

Although the solvent absorbance will provide a significant amount of information as to how the reaction mixture will absorb microwave energy and, therefore, heat; it will not tell the complete story. As each component within a given reaction (the starting materials, catalyst, solvent, other reagents, etc.) will absorb microwave energy differently. The absorbance of the reaction mixture as a whole is related to all of the components in the reaction mixture. In general, if a high temperature is required, a very polar solvent can be used to reach high temperature very rapidly. Lower absorbing solvents, however, can still be used to reach high temperatures because, in most cases, either the starting materials, catalyst or other reaction components will absorb microwave energy.

From the mechanistic point of view and although it could seem like a paradox, the most interesting is that the absorption of the microwave radiation limits to the reactants. Thus, depending on the absorption effects, which will vary with the polarity of the reaction medium, two different situations can be observed[2]:

- Working with a **polar solvent**, the main absorption occurs between the microwaves and the polar molecules of the solvent. In this case, the reactants receive the energy from the solvent molecules and then, the results are mechanistically the same than the ones obtained with conductive heating.
- Working with a **non polar solvent**, there is only a weak interaction between the solvent molecules and microwaves. In this situation, solvent is like transparent for the radiation, and the reactants receive specific absorption of the radiation, and this causes that some mechanistic changes could occur in the reaction in comparison with conductive heating results, due to the high efficiency of the energy transfer when working with microwaves that makes possible in some cases to overcome high energetic barriers.

In order to understand how microwaves can change a reaction pathway, it is necessary to review the difference between kinetically and thermodynamically controlled reactions (Figure 1.5.).

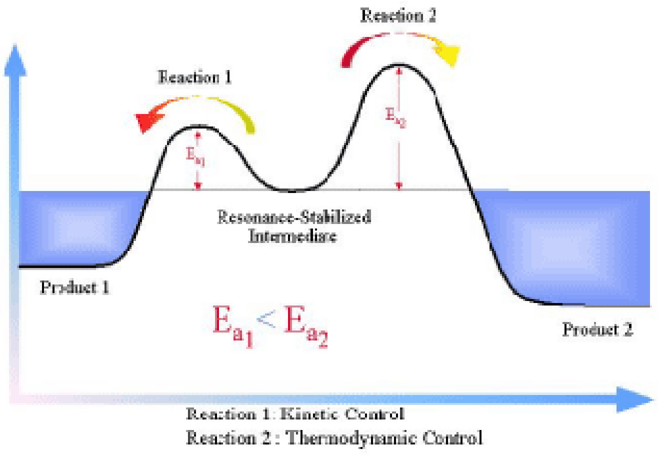

Figure 1.5. Kinetic control vs Thermodynamic control[12].

Conventional synthesis does not always provide enough energy to overcome the greater activation energy of the thermodynamic product. Although the thermodynamic product is energetically more stable than the kinetic product, the thermodynamic product has a higher energy barrier to surmount. The reaction is forced to take the lower energy path to the kinetic product, meaning the majority of the products will be from the kinetic reaction instead of the thermodynamic reaction. The addition of energy directly to the reactants, via microwave irradiation, allows the thermodynamic energy barrier to be overcome in a microwave, forming the desired lower energy product. One example of this thermodynamically control synthesis when using focused microwaves irradiation has been published in 2001 by N. Kuhnert and T. N. Danks studying highly diastereoselective synthesis of 1,3-ozazolidines under solvent-free conditions[17]. This possibility of changing reaction pathways, when working with microwaves and non-polar solvents, opens new goals in the study of the influence of microwaves in the mechanism of different chemical reactions.

Related to the ability of microwaves to change reactions pathways, a crucial concept that must be taken into account in microwaves synthesis is the difference between **macroscopic** and **microscopic temperature**. On one hand, the bulk reaction achieves a macroscopic temperature that can be measured by a thermoset device and that is comparable with the temperature at which the process takes place when working with conventional heating. But on the other hand and as stated before, microwaves are known to cause high localized temperatures (“hot spots”) that make the temperature higher at microscopic scale and will be in some way responsible for the changes in the reaction mechanisms. Moreover, it may suggests that microwaves not only affect the rates of reaction, but also permit performance of chemical processes at lower macroscopic temperatures than conventional heating, without affecting reaction yields. Thus, microwaves provide a potential way of saving time and energy at industrial scale.

1.3. MICROWAVES VULCANIZATION

Vulcanization is the key process in the worldwide commercial manufacturing industry of rubbers. This process was discovered by chance by Charles Goodyear in 1839. It has been defined by A. Y. Coran as the process, which increases the retractile force and reduces the amount of permanent deformation after removal of the force[18]. Said in other words, vulcanization is a process by which rubber is changed from essentially a plastic material to either an elastic or hard material. As a plastic material unvulcanized rubber readily undergoes permanent deformation; whereas, vulcanized rubber is highly elastic and resistant to plastic deformation[19]. Rubber elasticity is defined as entropic elasticity due to the ability of this material to store strain energy thermally. Furthermore, vulcanization decreases the plastic flow, diminishes surface tackiness and increases tensile strength. These changes in physical properties are generally accomplished by chemical changes at molecular level due to the formation of a three dimensional network. There are two types of vulcanization: peroxide vulcanization and sulfur-based vulcanization. This thesis is centered in the sulfur-based vulcanization.

Rubber is normally vulcanized by heating with a vulcanizing agent (usually sulfur in combination with an accelerator) at a temperature between 120 and 200ºC in a mold of the desired shape and size. Vulcanized rubber is thermosetting since it cannot be remolded, in contrast to a thermoplastic material which can be. The properties of rubber are improved dramatically by vulcanization. Vulcanization involves the formation of chemical crosslinks between the long polymer chains constituting the rubber molecules[18]. As a result of the crosslink network the independent motion of the polymer chains is markedly restricted. Thus the chains cannot move past each other as readily as before vulcanization, with elongation decreasing and resistance to deformation (modulus) increasing. Furthermore, the crosslinks give the chains a much greater tendency to return to their original geometric arrangement when the deforming force is removed, which explains the greater elasticity and resistance to deformation. The three dimensional crosslinked structure renders vulcanized rubber more insoluble in solvents and more resistant to attack by heat, light and chemicals. The crosslink is relatively low, only one of every 100-200 atoms of carbon along the polymer chain reacts with sulfur to form crosslinks, so only 2-3% of the rubber double bonds react during vulcanization. More details about this complex process and its evolution and optimization since 1839 will be expounded and discussed in the next chapters of this thesis.

Nowadays microwaves are mainly used in the rubber industry for the curing extruded rubber profiles. This is a process requiring a combination of both temperature and time. Conventional systems to vulcanize profiles are the steam autoclave, the salt bath, the fluid bed continuous vulcanization and the continuous vulcanization in hot air[15]. All these systems are still used in the rubber industry, although they present important drawbacks as the high consumption of energy and long production line lengths. But maybe, the main problem presented by these techniques is the low quality in the vulcanizate homogeneity considering the crosslink density. There is a bad heat distribution in the material due to the low thermal conductivity of rubber mixtures[14]. This temperature gradient causes a non homogeneous crosslink density when comparing the surface of the material and the interior of the profile. Due to the higher ability of heating and also due to its higher penetrating power, microwaves were presented as possible solutions for the homogeneity problems in the rubber profiles. The idea was to affect the temperature distribution in order to improve the quality of the final product. Microwaves heating effect causes a more homogeneous and 10-fold faster reaction[14].

As stated before, microwave vulcanization of extruded rubber profiles started in the 1960’s as a means to improve productivity and quality. At the beginning machines used waveguide type ovens or short resonant structures. There were enormous problems in terms of uniformity of heating. Many materials were marginal in terms of dielectric loss factor, and shapes were extremely complex with thin fingers, plus combinations of dense and sponge rubber often had to be co-extruded into the same part. Additionally, various extrusions contained metals cores as a means for attaching the rubber weather stripping to the automotive body. Resonant devices were very sensitive to the position of rubber and were too short in length, resulting in excessively rapid increases in temperature. The faster things are done, the greater the problems in uniformity, particularly when compounds are marginal.

The Microwave Industry looked at improving the microwave receptivity by increasing the power. This lead to the use of “L” band frequencies at 896 or 915 MHz, where there were higher magnetrons of 30kW. To accommodate this, the waveguide applicator structures were changed to meandors, or serpentines, so that the rubber would go through multiple passes for longer exposure. Under such an arrangement, the power gradient was highest where the microwave first entered the meander and the edge of the rubber facing this input was heated excessively. Furthermore, in case of polar rubbers, the hotter the rubber hot spot, the more receptive it became; thereby exacerbating problems of uniformity.

Polar rubbers such as neoprene and nitrile have good microwave receptivity. However, many of the basic elastomers such as NR, EPDM (Ethylene-Propylene-Dienemonomer) and SBR (Styrene Butadiene Rubber) are poor in microwave receptivity. This situation presented a challenge to the rubber chemist who had to find microwave-receptive components to produce a compound which would still yield good physical properties and not have a substantial increase in material cost. Fortunately, almost all automotive compounds are reinforced with carbon black to improve tensile strength and other mechanical properties. Carbon black aids the microwave heating of rubber through the principle of ohmic or resistive conduction[15]. The heating ability is almost in direct relationship to the reinforcement performance of the different blacks. The smaller the grain structure, the greater the surface area, the greater is the receptivity to microwave energy. Furthermore, chemicals, accelerators, blowing agents, etc. in the compound must be considered.

The majority of applications were in the automotive area, because the penetrating heat benefit of microwaves gave high quality results. The benefits of the microwave process explained earlier in this chapter played a very important part in helping this application of microwaves to grow rapidly. Microwave systems matured with substantial protection devices, instrumentation and data processing and logging features.

As stated before, vulcanization to be completed requires not only temperature from the microwaves oven, but also sufficient residence time at elevated temperature to complete the chemical crosslinking. Residence time is provided by downstream high technology hot air ovens. The length of these ovens depends upon the cure time of the compound and the oven heat transfer capability. Very soon the microwave manufacturers found that to control the vulcanization process, they also needed to control the downstream hot air ovens, and their product lines expanded to include them. High velocity hot air ovens, or radiant infrared pre-heaters, were added to the product line. So the evolution of the industry was from a microwave heating company to a rubber processing machinery company. With this broader vision of thinking, many problems of uniformity of heating which the manufacturer tried to correct through alterations in microwave devices, were better identified as systems problems, and not microwaves problems. So, the tendency along the years has been using the microwaves in combination with hot air ovens, to decrease the production lines and increase the vulcanization rate, but controlling the temperature and the curing homogeneity through the conventional heating sources.

Polar polymers, having high loss factors, heat up rapidly, whereas non-polar polymers such as natural rubber have low loss factors and do not respond as quickly to microwave energy[20]. Natural Rubber responds slowly to microwave energy in white-filled mixes containing clay or calcium carbonate, but silica-filled mixes heat up about as quickly as mixes containing Carbon Black. As stated before, heat generation is enhanced a little bit by many normal compounding ingredients such as zinc oxide, stearic acid, accelerators and antioxidants[21-22]. To get the best results when heating with microwave energy the formulation may be modified by using more amounts of these ingredients. Furthermore, the high temperature of the microwave equipment and the hot-air ovens used as supplementary heating aid necessitate the addition of a powerful antioxidant to protect against oxidative degradation[20].

Regarding the discussion of section 1.2.3., and taking into account all the concepts explained in this chapter, microwave vulcanization of non-polar rubbers, such as Natural Rubber, could be mechanistic dependent. As stated before, there is only a weak interaction between the rubber and microwaves. In this situation, the polymer is like transparent for the radiation, and the reactants receive specific absorption of the radiation, and this causes that some mechanistic changes could occur in the reaction in comparison with conductive heating results, due to the high efficiency of the energy transfer when working with microwaves that makes possible in some cases to overcome high energetic barriers. There are no studies about the possible mechanistic changes caused by microwave radiation in rubber vulcanization. Thus, to explore these possible changes is the main goal of this thesis.

1.4. AIM AND STRUCTURE OF THIS THESIS

There is no doubt about the efficiency of microwaves to vulcanize rubber, nowadays it is a mature process in the industry, as stated in section 1.3. There are more than a thousand production lines of microwave continuous vulcanization around the world producing thousands of tons of high quality rubber for the automotive, building and structural industries[15]. As stated before, the main benefits of microwave vulcanization processes compared with those carried out with conductive heating are the high rate and efficiency of the energy transfer, the deeply penetrating heating power, the selectivity in the heating and cleanness of the process[5,6]. This is because, when using conductive heating, part of the heat is absorbed by the vessel walls therefore reducing the amount of energy being passed to the reactants. The heating mechanism of microwave is completely different to conventional heating mechanism, because microwaves couple directly with the molecules that are present in the reaction mixture, leading to a rapid rise of temperature, becoming an independent process upon the thermal conductivity of the vessel material and making easier the reaction control[23-24]. In some cases, this increment in the energy transfer to the reagent could allow the system to overcome energetic barriers, which could not be reached by conductive heating, leading to different reaction pathways[25].

Furthermore, the increase in certain mechanical properties and in the ozone-crack resistance of the final microwave vulcanizates has been described widely in the literature[26-29]. However, other publications contradict this and state that microwave-vulcanized samples have lower hardness, tensile strength and elongation than press-vulcanized samples[30]. Therefore, it could be expected that this difference in the heating mechanism could influence a change in the vulcanization mechanism which would explain the changes observed in the mechanical properties of vulcanizates. Since there is a lack of information in the literature about the mechanistic differences between microwave assisted and conductive-heating vulcanization, the aim of this thesis is the study of microwaves-assisted vulcanization from a new perspective taking into account not only microwave power to accelerate processes, but also its potential to change reaction pathways and focusing on the discovery of these possible changes in vulcanization chemistry.

Thus, the objectives of this thesis are:

1. The development of all the analytical methods to follow the mechanism of all the reactions taking place in vulcanization and devulcanization processes of squalene and NR with CH and MW.
2. The study of the influence of microwaves on the accelerator system.
3. The study of the influence of microwaves on the activator system.
4. The study of the influence of microwaves in devulcanization.

Therefore, the thesis is divided into 6 chapters, as outlined:

Chapter 2 of this thesis gives an overview about the different methods scientist have been using to study the sulfur-based vulcanization since it was discovered. A detailed description of the Modeling Approach is given in this chapter. This is the methodology used in this thesis to study the mechanism of vulcanization. The development and optimization of the analytical methods, used in this thesis, to follow the intermediates formed during vulcanization for the model molecules has been also reported in this chapter, just as the techniques and methods used for the characterization of Natural Rubber samples.

In **Chapter 3** the influence of microwaves in the mechanism of vulcanization focusing on the accelerator role is explored. This study has been performed using Model Compound Vulcanization (MCV) and squalene as a model molecule. The accelerators studied are sulfenamides, thiurams and accelerators systems combining both accelerator types.

In **Chapter 4** the influence of microwaves on the activator system is studied. In this chapter, not only MCV studies are presented, but also the results with natural rubber and the influence of microwaves in the final properties. Both results are compared. Some substitutes of ZnO are test in order to develop more environmental friendly activators for vulcanization reaction. A family of mixed oxides of Zn and Mg has been also synthesized and tested as ZnO substitutes.

In **Chapter 5** the possibility of using microwave to devulcanize rubber has been studied. MCV studies have been performed and the influence of microwaves in diphenyl disulfide (DPDS), a well known devulcanizing agent, has been investigated.

The final conclusions are given in **Chapter 6**.

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Chapter 2

Studying Rubber Vulcanization: from Model Compound to Natural Rubber

This chapter gives an overview about the different methods scientists have been using to study the sulfur-based vulcanization since it was discovered. A detailed description of the Modeling Approach is given in this chapter. This is the methodology used in this thesis to study the mechanism of vulcanization. The development and optimization of the analytical methods, used in this thesis, to follow the intermediates formed during vulcanization for the model molecules has been also reported in this chapter, just as the techniques and methods used for the structural characterization of Natural Rubber (NR) samples.

2.1. INTRODUCTION

Vulcanization was discovered accidentally by Charles Goodyear in 1839. He heated up natural rubber (NR) and sulfur in an oven and he observed how the polymer changes irreversibly its thermoplastic character to a thermoset behavior (it does not melt on heating). The reason to this irreversible change consists in the formation of crosslinks, chemical bonds or bridges that associate the rubber macromolecules. The words curing, vulcanization and crosslinking are synonymous and are used interchangeably. This crosslink process provides the elastomer its elastomeric behavior, i. e. the ability to regain its original shape after deformation in compression or tension. It also improves some physical properties of the material, as hardness, or chemical resistance. A better toughness under static or dynamic stress is also obtained, just as a higher abrasion resistance and impermeability to air and water. Thus vulcanization opened the door for an enormous market for rubber goods.

Since those early days, there has been continued progress toward the improvement of the process and in the resulting vulcanized rubber articles. In addition to Natural Rubber (NR) over the years, many synthetic rubbers have been introduced. The concept Rubber refers to a group of different polymers with the shared characteristic of being elastomer. An elastomer is a material with the mechanical property that it can undergo much more elastic deformation under stress that most materials and still return to its previous size without permanent deformation. This group can be divided in Natural Rubber (NR) and Synthetic Rubbers. NR can be considered as the first elastomer discovered and its chemical structure corresponds to cis-1,4-polyisoprene. NR comes from the latex of a tree called Hevea Brasiliensis. The revolutionary improvement that vulcanization brought to NR caused an increased demand for rubber products, and within a few years, demand began to outstrip the availability of crude NR. Prices of rubber were growing sky high and then, scientist from German chemical companies started research aimed at finding a method for preparing synthetic rubbers on an industrial scale. In 1909, Fritz Hofmann developed for Bayer the first workable Synthetic Rubber based on butadiene. Along the next years, different synthetic rubbers were developed, with similar structure to NR but with different functional groups, from the polymerization of a variety of monomers including styrene; isoprene (2-methyl-1,3-butadiene); 1,3-butadiene; chloroprene (2-chloro-1,3-butadiene) and isobutylene (methylpropene) with a small percentage of isoprene for crosslinking. Furthermore, these and other monomers can be mixed in various desirable proportions to be copolymerized for a wide range of physical, mechanical, and chemical properties. Polymerization of pure monomers can be better controlled to give a desired proportion of *cis* and *trans* double bonds. The development of synthetic rubber increased during the Second World War. Neoprene was the first elastomer put on the US market in 1931 by Dupont. Nowadays both rubber types (synthetic and natural) coexist, and each of which has a defined position in the properties/price spectrum.

Even though almost two centuries of improvements have greatly modified the rubber formulations increasing their complexity, the recipes still use sulfur as vulcanizing agent. Many other curing systems have been discovered (e.g. organic peroxides, phenolic curatives and quinoid), but, so far, none of them has been able to establish the overall balance of desirable properties that is achieved by modern sulfur-based systems. Peroxide vulcanizates for instance, which give rise to carbon-carbon crosslinks, have the best heat resistance, but they do not offer good tensile strength and fatigue resistance[1]. Greensmith et al.[2] related the tensile strength (the stress applied to the material at the point when its elastic properties fails) with the crosslink density. They observed that the tensile strength passes through a maximum value with increasing crosslink density. They also reported that the tensile strength of NR gum decreased according to the mechanism of vulcanization in the sequence accelerated sulfur > sulfurless > peroxide > high energy radiation. Nowadays, only elastomers with no or low unsaturation are cured with peroxides. In this thesis emphasis is placed on the vulcanization of high-diene rubbers, using NR as an example of this family, by sulfur in the presence of organic accelerators. As it will be seen along the next chapters, this work studies the effect of microwaves in NR sulfur vulcanization focusing on different chemical reactions of this global process.

Perhaps the most important and fascinating aspect concerning the chemistry of sulfur vulcanization is the problem of determining the structure of rubber vulcanizates. There are two concepts related to the characterization of a network structure: ***crosslink density*** and ***crosslink structure***. There are different ways to measure this crosslink density and also different parameters to express this concept (see section 2.3.), but generally, this term tries to quantify the vulcanization yield (crosslink degree) for a determined vulcanizing system in order to compare its crosslink ability with other vulcanizing systems. As it will be seen along this chapter, the difficulty lies in the fact that the term “crosslink” in sulfur-based vulcanization does not involve only one type of network connectivity, as in peroxide vulcanization, but also a large variety of different chemical structures. Therefore, to properly express crosslink structure, it is necessary to define the various kinds of chemical crosslinks present in a network as well as their relative and total amounts.

As it has been stated before, at the beginning Goodyear studied vulcanization using only sulfur as vulcanizing agent. If only sulfur was added to rubber, the crosslinking reaction was very slow and has a very poor efficiency (crosslink density and crosslink structure). Large amounts of sulfur and relatively long curing times were required. Overvulcanization, which leads to a marked deterioration of physical properties was also a serious problem. Furthermore, sulfur alone takes a commercially prohibitive length of time to cure a rubber. Therefore, Goodyear also described the use of basic lead carbonate to accelerate the reaction of sulfur with rubber. In the years that followed, a number of inorganic compounds were found to accelerate vulcanization. However, although inorganic accelerators implied an improvement over vulcanization with sulfur alone, there was still a lot to be desired. The vulcanizates tend to show sulfur blooming (diffusion of sulfur to the surface) and exhibited poor aging resistance. Moreover, the network derived from sulfur-alone vulcanization (or in the presence of inorganic accelerators) contained not only different kind of intermolecular sulfidic crosslinks (sulfur bridges between rubber chains with different number of sulfur), but also large proportion of main chain modification as mono- and disulfidic cyclic structures (intramolecular crosslinks), conjugated diene and triene moieties and cis/trans isomerization of the double bond[3]. The change in properties resulting from vulcanization is due almost entirely to intermolecular crosslinks. Intramolecular crosslinks have no effect, except in those instances where they aid the physical entanglements of adjacent chains.

The next major breakthrough in the subject of vulcanization chemistry, after the discovery of Goodyear, came with the organic accelerators in the early 1900s[4]. These products not only increased the rate of vulcanization, but also allowed carrying out the process at lower temperatures which implied the optimal use of heat and equipment. Consequently, the rubber was not subjected to drastic conditions during vulcanization, and the possibility of thermal and oxidative degradation was minimized. Furthermore, the sulfur content could be reduced resulting in the reduction of blooming, improving the appearance, and still retaining optimum physical and aging properties of the vulcanizate. Concerning the final network structure, accelerated sulfur vulcanization formed a higher sulfidic crosslink network (higher crosslink density), spreading homogeneously sulfur in the polymer matrix (better crosslink structure), and forming less main chain modification. The final network structure contains the functionalities shown in Figure 2.1. (from left to right): Pendant group (a sulfur chain with an accelerator fragment at the end); mono-, di- and polysulfidic crosslinks, essentially between different polymer molecules, although mono- and disulfidic cyclic structures can also be formed in little amounts; as well as modified network (conjugated diene and triene moieties) products of dehydrogenation of the rubber.

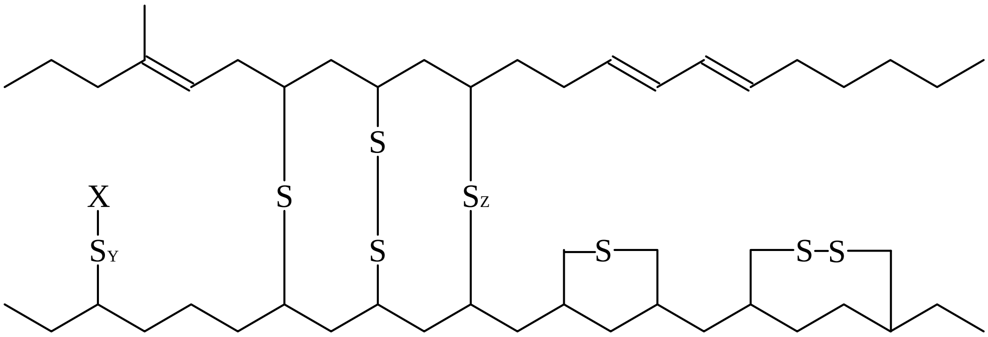


Figure 2.1. Structural features of an accelerated sulfur vulcanizate of Natural Rubber (X= accelerator fragment, $y \geq 1$, $z \geq 3$)[5].

The period 1906-1937 witnessed a succession of rapid advances in the use of organic materials to accelerate the cure of rubber (Figure 2.2.). In 1906, Oenslager found that aniline and other amines accelerated the vulcanization of rubber with sulfur, and in Germany, Hoffman and Gottlob in 1912 obtained a patent for the use of basic organic or inorganic compounds with ionization constants of 10^{-8} or greater. Subsequently, aniline was increasingly used despite its toxicity until 1907 when thiocarbanilide, a derivate of aniline, was found to circumvent the toxicological problems of aniline[5]. Other basic accelerators developed during that period were the diarylguanidines. In 1919, dithiocarbamate accelerators came into use, as extremely active accelerators, and from these thiuram sulfides were developed. This group of accelerators is still widely applied for low temperature and rapid high-temperature vulcanization. Around 1920, it was discovered that a combination of ZnO with stearic acid was effective as an activator for accelerated sulfur vulcanization (See Chapter 4). The first delayed-action vulcanization systems were introduced in 1925 with the use of 2-mercaptobenzothiazole (MBT) and 2,2'-bisbenzothiazole disulfide (MBTS). Even more delayed action and yet faster curing systems were made possible by the first commercial benzothiazolesulfenamide accelerator. The latter formed the last new accelerator class of great commercial significance to be introduced. In Chapter 3 the effect of microwaves in the mechanism of vulcanization with Sulfenamides and Thiurams accelerators is deeply discussed.

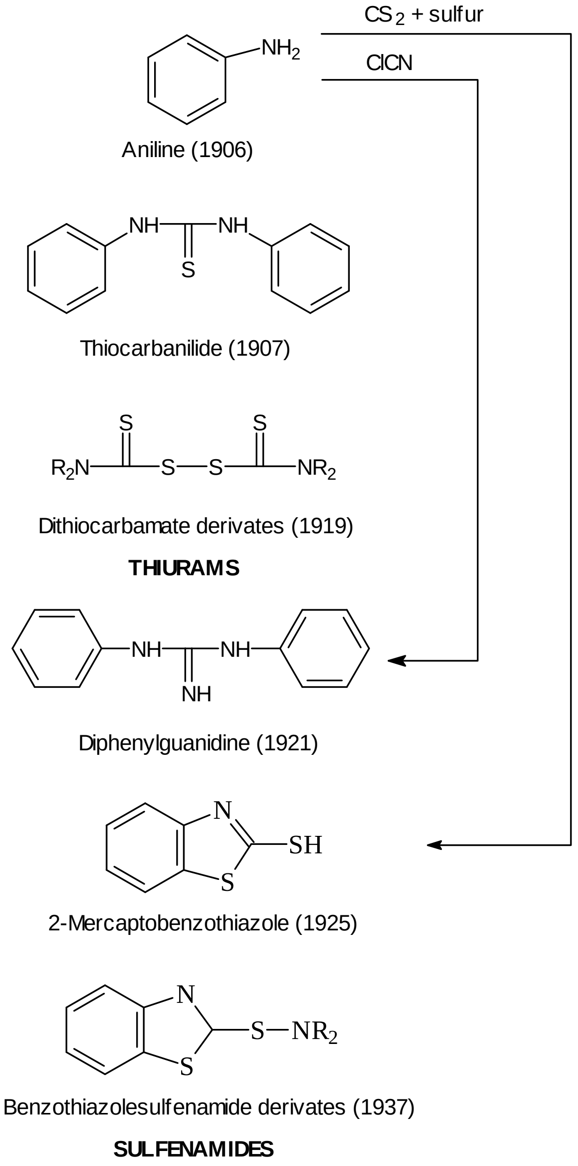


Figure 2.2. Chemical history of accelerator synthesis[3].

At present time, modern sulfur-based systems are very complex and consist not only of rubber and sulfur, but also of different types of compounds. Next, there is a list with the function of the major compounding ingredients[6]:

i) **Elastomers:** this is the most important ingredient in rubber formulation. Specific elastomers are selected for desired compound properties.

ii) **Vulcanizing or crosslinking agents:** These chemicals, upon heating, crosslink elastomer molecules to provide harder, more thermally stable elastic products. The most common ones are sulfur or sulfur-bearing compounds, or a combination of both. However, in some cases peroxides can be used as well.

iii) **Organic accelerators:** Organic compounds meant to reduce the required time for proper vulcanization or to allow the use of lower temperatures.

iv) **Activators:** These chemicals form complexes with accelerators and further activate the curing process. Zinc oxide and stearic acid are commonly used activators.

v) **Processing Aids:** These materials are used to help in mixing, calendaring, extrusion and molding by lowering the viscosity of a compound. Examples are various oils and plasticizers.

vi) **Antidegradants:** These chemicals are used to protect rubber both in uncured and cured states, from oxidation, ozonization and aging and, therefore, aid in extending product life.

As stated before, during curing process, a three-dimensional crosslinked network is formed. The extent and rate of vulcanization is measured by using a rheometer which gives a curve plotting modulus or torque as a function of cure time. Figure 2.3. shows a typical rheometer curve. Each type of accelerator has a different effect on the vulcanization process and on rheometer curve. The overall process can be divided in three different stages: Scorch time, Curing or Crosslink and Plateau.

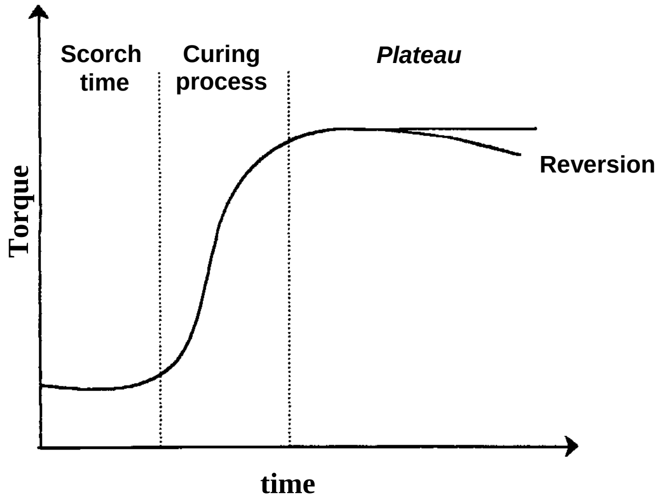


Figure 2.3. Different steps of vulcanization curve.

The optimal accelerator should produce a short scorch time but long enough to obtain an homogeneous mixture and to avoid pre-vulcanization, as well as a fast crosslinking kinetics, (related with the slope of the curve), and a high maximum torque (modulus) which is somehow related with the crosslink density. As the number of crosslinks increases the elastomer chains are more restricted in their motion and the force required to produce a given deformation (modulus) becomes greater. Depending on the crosslink structure (type of crosslinks) a reversion in the maximum torque can be observed due to aging of the network. It is important to look for vulcanizing systems with less reversion to enlarge the rubber products' life and increase fatigue resistance. Of all the accelerator types presented, sulfenamides are perhaps the closest approach to the ideal one.

The final network structure and the crosslink distribution depend on the vulcanization conditions: vulcanization system, cure time and temperature. Changes in the sulfur/accelerator ratio (S/A ratio) cause significant changes in the vulcanizate structure, which are, in turn, reflected in changes in physical properties and aging behavior[7]. The S/A ratio is particularly important in determining the type of crosslink formed (crosslink structure). Depending on this ratio, vulcanization systems can be divided in three different groups[8]:

i) **Conventional systems (CV):** These systems contain high sulfur levels, e. g. 1.5 to 3.5 phr and low levels of accelerator, e. g. 0.5 to 1 phr (S/A ratio from 1.5 to 70). At optimum cure the vulcanizate contains mostly polysulfidic crosslinks with relatively high level of chain modification. The higher the sulfur content, the more polysulfidic crosslinks. This kind of crosslink gives little resistance to reversion and oxidative ageing and poorer long-term flexlife[9]. Otherwise, these vulcanizates show good tensile and tear strengths, resistance to fatigue and good low temperature properties.

ii) **Efficient systems (EV):** These systems contain low sulfur levels, e. g. 0.25 to 0.7 phr and high levels of accelerator, e. g. 2.5 to 5 phr (S/A ratio from 0.05 to 0.3). They will form mainly mono- and disulfidic crosslinks and much less chain modification. Monosulfidic crosslinks are more stable than polysulfidic crosslinks. Short crosslinks provide poor fatigue life and compression set[9]; but improve resistance to reversion and oxidative ageing. However the drawbacks include lower tear strength, fatigue resistance and abrasion resistance. These kind of systems are appropriate for thick rubber items.

iii) **Semi-Efficient systems (Semi-EV):** These systems are designed to avoid the drawbacks of conventional and efficient systems, trying to find an equilibrium between them (S/A ratio from 0.3 to 1.5). At optimum cure this kind of vulcanizate contains around 35% mono-, 35% di- and 30% polysulfidic crosslinks. Therefore, these kinds of compounds are designed to give the best overall properties with minimum trade-off[9].

The number of sulfur atoms per crosslink is of much importance. The efficiency of sulfur as a crosslinking agent varies inversely with the average number of S atoms per crosslink. As it will be seen in section 2.3.2. several chemical techniques have been developed for analyzing vulcanizates to determine the distribution of mono-, di- and polysulfidic crosslinks in a given vulcanizate. The physical and chemical properties of a vulcanizate can be correlated with the relative amounts of the different crosslink types. The correlation between tensile strength and crosslink density studied by Greensmith et al.[2] permitted Mullins[10] to conclude that tensile strength depends not only on the crosslink density, but also on the type of crosslink present in the network and their distribution. Tensile strength decreases in the following order: polysulfidic > di- and monosulfidic > carbon-carbon, which means that tensile strength and bond strength have an inverse relationship. Mullins suggested also that the weakest bond, polysulfidic, is labile and able to break under stress at the critical point of failure. However, there is experimental evidence that does not agree with this hypothesis. Effectively, Lal[11] demonstrated that the tensile strength in NR does not depend at all on the type of sulfur crosslinks. Polysulfidic crosslinks were systematically converted in di- and monosulfidic and the tensile strength of both treated and untreated rubber apparently were similar at the same crosslink densities. With these arguments it can not be explained that the tensile strength depends on the type of crosslink or its lability. González et al.[8] tried to sort out this discussion, and studied the tensile strength and other physical properties of different conventional and efficient systems increasing the crosslink density. They concluded that physical properties are superior for the conventional cure system at similar crosslink values, according with the results of Mullins[10]. They explained these results by differences in the vulcanization mechanism of the two cure systems. The conventional cure system produces an homogeneous network while the efficient cure system produces a significant polymerization of double bonds of adjacent chains. This leads to a network of unevenly distributed crosslinks and results in impediment to NR crystallization and stress concentration that anticipates the compound failure. In other words, efficient system induces high crosslink areas, overcrosslinked domains, that inhibit the correct stress distribution, accumulating higher stress areas where micro-crack can be formed and crack propagation is increased.

Although there is a lot of controversy about how crosslink density and crosslink structure affect the final compound properties, the fact is that both factors have a strong effect in some of them. Layer[12] summarized the effect of increasing crosslink density and length in different vulcanizate properties (Table 2.1.). All these examples demonstrate that little changes in the vulcanizing system cause differences in the crosslink density and structure, and what is more important, in the final properties. The sense of this lies in the complexity of vulcanization mechanism. The reactions of sulfur-accelerated vulcanization are usually very complex, since many substances are involved. In addition to the ingredients mentioned above, there are other substances present in the process: sometimes an additional accelerator, the rubber itself, and impurities such sterols and proteins for NR and emulsifiers and stabilizers for synthetic rubber. There are already strong evidences that the vulcanization of diene rubbers proceeds by the sequence of many reactions. The complexity has given rise to many contradictory publications referring to the mechanism of the vulcanization process[13-15].

Table 2.1. Effect of increasing crosslink density and length[12].

Property	Crosslink density	Crosslink length
Tensile strength	↑, then ↓	↑
Elongation	↓	↑
Modulus	↑	↓
Flex life	↓	↑
Compression set	↓	↑
Hysteresis	↓	↑
Resilence	↑	↓
Thermal stability	↑	↓
Oxidative stability	↑	↓
Rolling resistance	↓	=
Tear strength	↑, then ↓	↑
Abrasion	↑	↑

The organic accelerators play a major role as they transform the relatively stable sulfur molecules into a more reactive state. Figure 2.4. shows the general scheme of sulfur accelerated vulcanization process, although this scheme changes in every particular case depending on the accelerator.

The accelerators do not act merely as conventional catalyst, remaining unchanged, but they decompose. These decomposition reactions occur during the scorch time, and give rise to substances known as active sulfurating agents, which have a different structure depending on the accelerators used in the vulcanizing system, but basically they are formed by two fragments of accelerator connected by a polysulfidic chain[3]. These species have a higher reactivity with the rubber chain than sulfur alone and are responsible of the crosslink process. The active sulfurating agents are produced by a multi-step reaction. The first step involves the reaction of zinc oxide, fatty acid and accelerator to produce the polysulfidic species. Campbell and Wise[16] have found that with sulfenamide sulfur accelerated vulcanization, the sulfenamide concentration decrease rapidly in the induction period and crosslinking did not occur until the sulfenamide was consumed. They concluded that the sulfenamide was not the effective accelerator, but that the products derived were active sulfurating agents. Also, Coran[17] proposed in the kinetical study of NR and sulfenamide accelerators, that the initial reaction takes place between the accelerator and sulfur to produce polysulfidic species, which could then react with the rubber chain to form pendant groups[18]. Once the sulfenamide accelerator is consumed, the crosslinkining process is rapid due to the high concentration of pendant groups. This mechanism will be discussed more deeply in Chapter 3 for sulfenamides and thiurams.

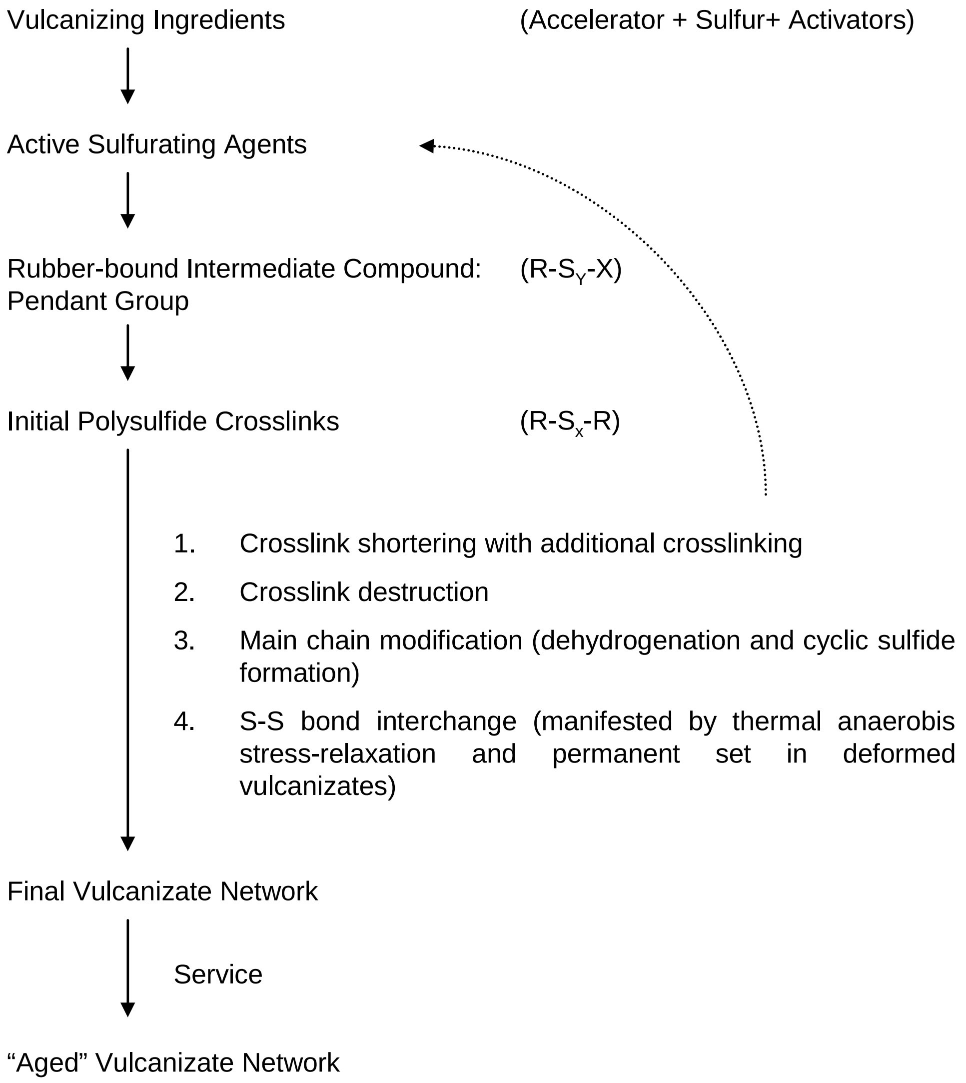


Figure 2.4. Overall course of sulfur-accelerated vulcanization.

Rubber vulcanization involves not only the improvement of the properties of the material, but also the beginning of the development of formulations for rubber, i.e. and the addition of several ingredients to the rubber to improve both processing and final product properties. However, since Goodyear discovery, the progress has been mainly achieved by empirical efforts. The traditional approach to develop formulations for rubber products combines the expert compounder’s experience with some experimental work on one or two ingredients and a few trials. The result is sent to production. Sometimes the compound meets the final properties specified and is a relative success. At other times, problems show up in production due to possible variation in materials or variations in processing, for example time, temperature and mold variations. At this time the expert compounder must reformulate under emergency conditions, using more expensive materials and more costly processing steps. The new formulation is sent to production again. Sometimes they must once again reformulate. Sometimes the business is lost to another supplier due to the client dissatisfaction with the delay and uncertainty of an acceptable product. And sometimes, the expert compounder cannot find a solution given the constrains he or she has to meet. This is the way rubber industry works. At the moment, there exist modern ways to do this using an experimental design methodology combined with recent desirability methodology for specifying important final properties to achieve an optimum product[18,19]. But the problem still remains just partially solved because statistical experimental designs are based on previous results of formulations and not on scientific reasoning.

Despite all though, these efforts have been quite successful so far. But there is still a lot of work to be done. The need of characterizing the material and the process still exists to provide technologists with an increasingly realistic picture of the vulcanizate structures, from which correlations between physical properties and chemical structure may be deduced.

The rubber chemist, in an attempt to understand the chemistry of rubber vulcanization, is interested in the application of techniques which are either aimed at understanding the mechanism of rubber vulcanization, or at elucidating the chemical structures present. Two parameters are necessary to define the network structure: the *molecular network structure* (different structures presents) and the *microphysical network structure* (number of crosslinks, loose ends, entanglements). Rubber chemistry and technology require the use of numerous methods in order to establish composition, properties and structure of vulcanizates[20-21]. Among all the aspects concerning rubber research, studies on the chemistry of vulcanization occupy a central position in current efforts to achieve better product from available rubbers. The complexity of the vulcanization reactions, the types and relative concentrations of crosslinks formed, and the nature and extend of main chain modification vary considerably depending on the curing system itself and the conditions of vulcanization[22]. It would be necessary to understand the vulcanization process, sufficiently advanced in chemical mechanistic terms, to predict the effect of changes in the system on vulcanizate structure.

There are two major problems scientists have to deal with when studying the mechanism of rubber vulcanization. First of all, the fact that during the process many simultaneous reactions take place, each component influencing the reactivity of the others. Furthermore, it is well known that the eight-membered sulfur ring has the potential of undergoing homolytic and heterolytic fission. In fact, for the sulfur vulcanization without accelerator, some investigators claim that the mechanism involve free radical[23], while others support mechanisms involving ions[24]. The accelerated sulfur vulcanization complicates the situation even more, because it is necessary to understand how the accelerators interact and how these interactions affect the vulcanization mechanism. There are still many unanswered questions and there is reason to believe that both free radical and ionic reactions take place simultaneously with one or the other predominating at the different stages of the overall vulcanization process depending on the vulcanizing system[25].

The structural analysis of sulfur vulcanizates is experimentally very thorny. The low concentration of chemical crosslinks, the insolubility of the polymer three-dimensional network after vulcanization and the difficulty of discriminating between different types of crosslinks; make difficult the applicability of standard analytical and chemical methods. Although significant improvements have been made in the field of physical analysis, such as Fourier Transform techniques and IR, Raman and NMR spectroscopy and solid state ^{13}C NMR; most of the present knowledge originates from the use of model systems; i.e. from a study of the reactivity of sulfur and other vulcanizing ingredients with olefins with a similar structure to rubber, but with lower molecular weight (see section 2.2.). Advantages of this low molecular weight model approach are the solubility of the reaction products and the applicability of standard separation (e.g. HPLC or GC) and spectroscopic techniques.

Information of high-polymer structures can be gained through the use of chemical probe reagents which are introduced into a network to carry out specific chemical reactions with one or more of the extended chemical network features. The amounts of mono-, di- and polysulfidic crosslinks present in the networks are then calculated from the crosslink concentrations per unit volume (crosslink density) before and after treatment with the chemical probes. Therefore, in addition to chemical probe treatment, characterization of networks requires the determination of the crosslink density. The experimental techniques most commonly used for this purpose, namely elongation, compression and swelling, will be discussed in section 2.3. The theoretical background of these techniques, which help to establish the structural features of sulfur links in vulcanizate networks, will be also described.

Several techniques have been used in this work in order to study the mentioned process and all the chemical reactions involved. Modeling approaches have been used to understand the mechanism of the different reactions, to study their kinetics and to elucidate the chemical structures present after the process; as well as the effect of microwaves in all the process and ingredients in the vulcanizing system (see section 2.2.). Real NR samples have been also characterized using different methods (see section 2.3.). Crosslink density and crosslink structure have been also studied in this NR samples, using Conventional heating (CH) and also Microwave (MW). The crosslink structure results observed in real rubber samples have been correlated with the changes observed in some physical properties, and also compared with the results obtained for the model compound in the modeling approach[18].

2.2. MODELING APPROACH: MODEL COMPOUND VULCANIZATION (MCV) AND REACTION STAGE MODELING (RSM)

The Modeling Approach can be defined as an alteration of the composition of a vulcanization mixture in order to simplify a certain problem. In this thesis two modeling approaches have been used: Model Compound Vulcanization (MCV) and Reaction Stage Modeling (RSM).

2.2.1. MODEL COMPOUND VULCANIZATION (MCV)

As stated before, the complexity of sulfur accelerated vulcanization has given rise to many contradictory publications for the mechanism of the vulcanization process. There are two main difficulties which scientists have to deal with: the nature of rubber samples and the simultaneity of reactions. In order to simplify the study, a modeling approach has been traditionally used. The most well known modeling approach for vulcanization is without any doubt the Model Compound Vulcanization (MCV) and is still considered today a useful tool to study polymer reactions and interactions. This method consists in substituting in the formulation the polymer by a similar low molecular-weight model for rubber, an olefin. Such an approach is allowed because the reactive position believed to play a principal role during the vulcanization is the allylic one, i. e. the carbon atom next to the double bond. Model Compound Vulcanization can cover the whole process of vulcanization; from the formation of the active sulfurating agents, the precursor formation, until crosslink shortening and formation of the final network. After the vulcanization reaction with the chosen molecule, the products present in the mixture should be analyzed. Since most of the time we are dealing with liquid samples, the handling of the samples becomes easier and a wider range of analytical techniques can be applied. Furthermore, the vulcanized model-compound mixtures usually do not contain all the ingredients present in a real rubber formulation, allowing a better focus on the products that have an active role in the process. However, the method also has some aspects that must be taken into consideration:

i) usually the structural differences between the model compound and the polymer chains are quite big.

ii) mixtures can be very simple and the influence of ingredients such as fillers, for instance, are not considered.

iii) the solid state diffusion is not considered. There is some controversy when results are extrapolated to long polymeric chains. Different processes could take place in a solid matrix than in a liquid media.

Robert T. Amstrong[26] published in 1944 the first MCV studies using simple mono-olefin analogs to study the sulfur vulcanization of rubber. He used 2-methylbut-2-ene as an analog to NR and vulcanized it with sulfur, 2-mercaptobenzothiazole, zinc oxide and zinc laureate. The identification of the compounds formed after the reaction was carried out by determining physical constants and chemical composition of the olefin-sulfur reaction products. The conclusion of this work was that the main product of the reaction consist of the olefin bridged by sulfur at the α-methylene carbon atoms. Lautenschlaeger introduced the use of CG-MS to identify intermediate products formed during MCV studies[27]. It was possible to detect different isomers of mono-, di- and trisulfidic compounds separately. He also investigated the effect of reaction time and curative concentrations of different accelerators[28]. The major disadvantage of the method is that it subjects the vulcanized products to high temperatures (>200ºC) which are necessary for GC analysis. These conditions are known to cause isomerization and/or degradation of di- and polysulfidic products. Therefore, the results must be treated with caution, especially when they relate to the yield of the different isomers. As a solution to this problem, Duynstee et al.[29] were the first to use only low-temperature techniques (TLC and HPLC) for product separation and identification of the present compounds during MCV vulcanization reaction. With HPLC it is possible to follow the accelerator decomposition, the intermediates compounds and final products, as well as the resulting compounds of the model molecule crosslinking. The only parameter that should be taken into account, when developing an HPLC method, is that solvents have a profound effect on the reactivity (degradability) of polysulfidic organic compounds. The degradability of these compounds is lower in non polar solvents, such as pentane, but higher in solvents like methanol.

Throughout literature, several models can be found for the study of vulcanization process of different type of rubbers[30-33] such as NR, butyl rubber, styrene butadiene rubber (SBR) or ethylene propylene diene monomer (EPDM) (Table 2.2. and Figure 2.5.). However, it is noteworthy to point out that to obtain reliable results using the MCV approach, the choice of the model molecule needs to be based on the polymer material under investigation. The molecule structure and the number of reactive sites are the two main variables to take into account.

Table 2.2. Molecules used as Model Compound for vulcanization studies.

Number	Name	Number	Name
1	Geraniol	7	2,3-dimethyl-2-butene
2	Geraniol	8	Cycloocten-1,5-diene
3	Squalene	9	Cyclohexadeca-1,5,9,13-tetraene
4	Cyclohexene	10	Trans-3-hexene
5	2-methyl-2-pentene	11	1-decene
6	ethylidene norbornene	12	2,3-dimethyl-1-butene

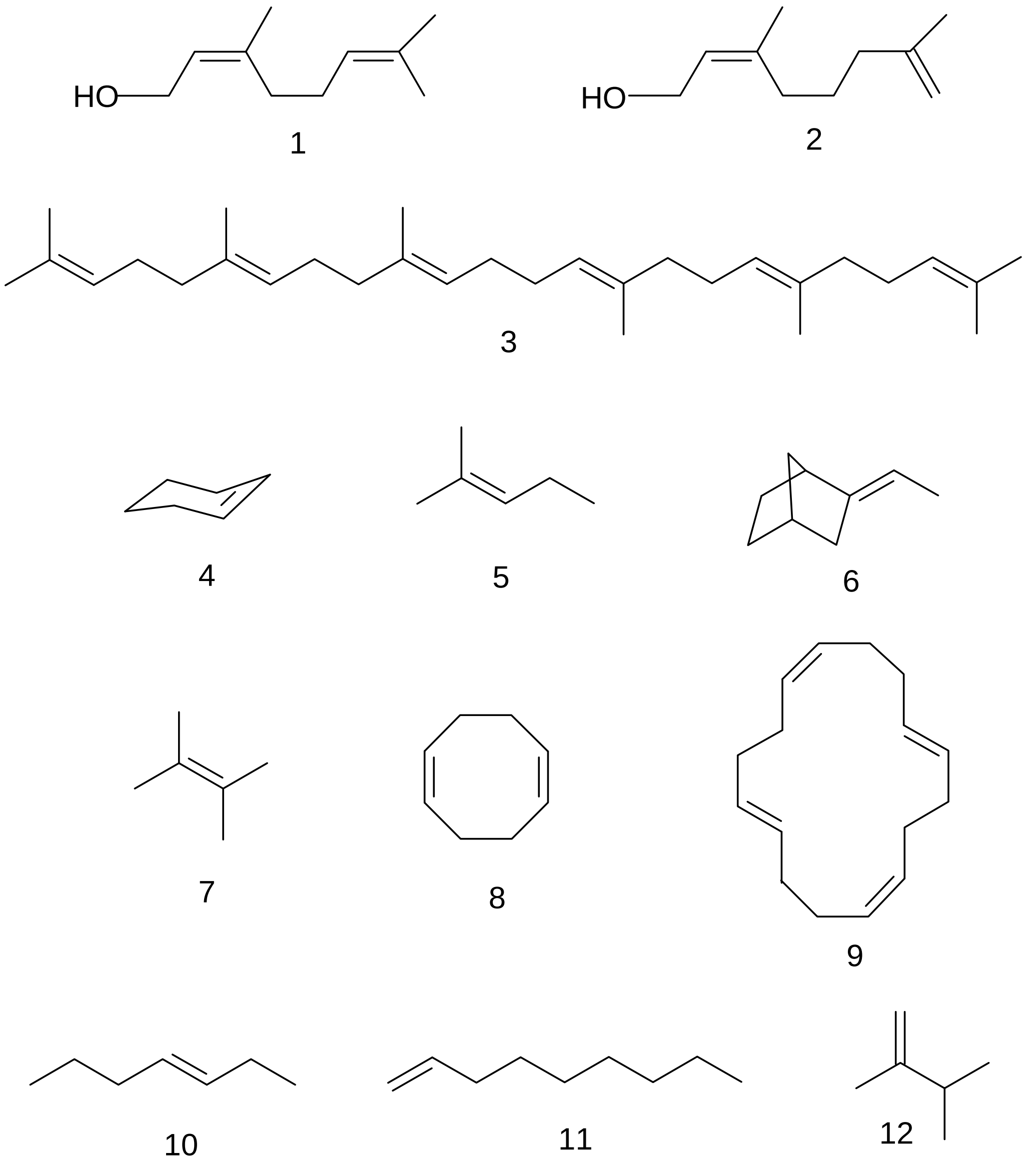


Figure 2.5. Compounds used as models of different elastomers[34].

Though squalene (6 isoprene units) and 2-methyl-2-pentene (1 isoprene unit) are the model compounds commonly used to create a system similar to NR; 2,3-dimethyl-2-butene (TME) is without a doubt the most used model. TME is not directly comparable with any specific rubber but it is a more general model compound. It is used quite often because a clear picture of the structure of the vulcanized products can be obtained. It contains only equivalent allylic positions; therefore hardly any cis-to-trans isomerization takes place. On the contrary, vulcanization of squalene or 2-methyl-2-pentene leads to a much more complex product mixture than with TME. On the other hand, it is disadvantageous that in TME the double bound occupies a stable tetra-alkyl-substituted position. This means that, if double bond isomerization plays an important role in the mechanism of vulcanization, the double bond will have to shift from the tetrato a less stabilized disubstituted position. The energy barrier involved must be overcome, and this could make this model less reactive than other compounds. Another drawback of using small model compounds is the high concentration of end groups (CH_3) that exist in a much lower concentration in a polymer chain. By using larger groups as squalene this disadvantage can be partly overcome.

The vulcanization mechanism of natural rubber using squalene as a model compound using conventional heating has been studied for years[18,35,36]. Regarding squalene structure (molecule 3 in Figure 2.5.), it can be seen, that compared with other models, its molecular weight is relatively high. It consists of six units of isoprene; hence, its structure is more similar to natural rubber polymer chains than other smaller models that consist only of one isoprene unit. Moreover, even after vulcanization, samples are still soluble in most of the common solvents, which permits better sample handling and the application of a wider range of analytical techniques. This thesis will study these mechanisms in depth, for sulfenamide and thiuram accelerator paths, using squalene as model compound, focusing also on the effect of microwaves in these reaction pathways.

2.2.2. REACTION STAGE MODELING (RSM)

Despite the use of low-molecular weight olefins (MCV) to study the vulcanization, some mechanistic aspects of the process are still complex due to the fact that MCV simplifies sample handling, but can not simplify the complexity of the reactions taking place simultaneously. In those cases where specific aspects of the reactivity of certain intermediate compounds or polysulfidic crosslinks need to be studied, Reaction Stage Modeling (RSM) may provide an outcome. In this approach, specially synthesized models for components or intermediate compounds are studied under well defined conditions. Once again, the results must be looked at with precaution because this is an extreme simplification which might give results not representative for real rubber. It must be taken into account though, that although RSM is useful to study isolated reactions, it may present two major problems:

i) the results obtained by RSM on the particular reactivity of a compound could be very valid for that specific compound, but it might lose sense in real rubber formulations, where other ingredients are present.

ii) the choice of the experimental conditions, as stated before, must be done very carefully, and in most cases the choice is based on postulations that might not be valid for rubber matrixes.

RSM could be defined as the choice of experimental conditions for a detailed study of events during one particular stage of vulcanization. In practice, a carefully chosen model compound is subjected to reaction conditions that reflect the situation of the vulcanization stage of interest[37].

Reviewing literature, it can be observed that this type of approach started being used around mid 1980's. Morrison and Porter[38] investigated the thermal stability of model crosslinks, as well as of various model precursors. Most of the subsequent studies using this approach were focused on reversion or aging studies to study the behavior of the different crosslink types under thermal or chemical attack. In this thesis, this approach has been used in devulcanization studies to explore the reversion of mono- and disulfidic crosslinks under different conditions using conventional heating and microwave (see Chapter 5).

2.3. STRUCTURAL CHARACTERIZATION OF VULCANIZATES: CROSSLINK DENSITY AND CROSSLINK STRUCTURE

As stated before, the crosslink degree and the distribution of crosslinks are important factors to determine final properties of vulcanizates. In order to close the gap between the modeling studies and real rubber, structural characterization of real rubber samples is required to a better understanding of the whole process. Next, different methods to measure crosslink density and crosslink structure in rubber vulcanizates will be exposed.

2.3.1. DETERMINATION OF CROSSLINK DENSITY

There are three widely used parameters to measure the crosslink density[39]. The first involves the number of network chains, where a network chain is defined as one which extends from one crosslink to another. This quantity is usually expressed as the chain density ν_e.

$$\nu_e = \frac{Number\ of\ Network\ chains}{Volume\ of\ the\ (unswollen)\ network}$$

Equation 2.1.

A second measure, directly proportional to it, is the density of crosslink XLD. The relationship between ν_e and XLD must obviously depend on the crosslink functionality f.

$$XLD = \frac{2}{f} \cdot \nu_e$$

Equation 2.2.

A final and inverse measure of crosslink density is the molecular weight (M_P) between crosslinks. This is simply the mass per unit volume ρ of the network divided by the chain density.

$$M_P = \frac{\rho}{\nu_e}$$

Equation 2.3.

A relationship between the molecular weight of the network chains and an elastic constant C_1 comes from the kinetic theory of rubber elasticity[40].

$$M_P = \frac{\rho \cdot R \cdot T}{2 \cdot C_1}$$

Equation 2.4.

where R is the gas constant and T is the test temperature in Kelvin. The elastic constant C_1 of vulcanizate can be calculated from the stress-strain data or equilibrium volume swelling measurements.

2.3.1.1. DETERMINATION OF NETWORK CHAIN DENSITY (ν_e) FROM STRESS-STRAIN DATA

The stress-strain behavior of dry networks up to moderate strains conforms to the empirical Mooney-Rivlin-Saunders expression[41]:

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

Equation 2.5.

where F is the force, A_0 is the original cross sectional area, λ is the extension ratio, C_1 is the elastic constant and C_2 is a constant which would account for the effects of chain ends and chain entanglements.

The values of the constants C_1 and C_2 can be obtained graphically by plotting stress-strain data (obtained for λ values up to 2) in the form $F/[2 \cdot A_0 \cdot (\lambda - \lambda^{-2})]$ as a function of λ^{-1} (see section 2.4.5.3.). These constants are directly related with the network chain density (ν_e). In the case of NR networks, it is then found that the values of C_1 so obtained agree well with C_1 values derived from stress-strain data obtained with networks highly swollen with a liquid, in which case the C_2 term of equation 2.5. disappears.

An advantage of testing swollen samples is the better fit of stress-strain behavior to elastic theory due to separation of network chains and reduction in entanglement effects. This facilitates obtaining the elastic equilibrium. The Mooney-Rivlin-Saunders expression then takes the form[42]:

$$F = 2 \cdot A_0 \cdot \left(\frac{1}{\lambda^2} - \lambda \right) \cdot C_1 \cdot \phi_2^{\frac{-1}{3}}$$

Equation 2.6.

where ϕ_2 is the volume fraction of rubber in the swollen network:

$$\phi_2 = \frac{V_2}{V_1 + V_2} = \frac{m_2}{\frac{\rho_2}{\rho_1} \cdot m_1 + m_2}$$

Equation 2.7.

where V_1 and V_2 are the volumes, m_1 and m_2 are the masses, ρ_1 and ρ_2 are the masses per unit volume of solvent and rubber respectively.

But difficulties arise from the fact that the volume fraction of rubber in the swollen network does not remain constant during the elongation test (evaporation of the solvent). Therefore, F is not only a function of the extension ratio but also of ϕ_2.

2.3.1.2. DETERMINATION OF NETWORK CHAIN DENSITY (ν_e) FROM EQUILIBRIUM SWELLING DATA

For a given elastomer in a given solvent the degree of dissolution of elastomer in the solvent and swelling of solvent into the elastomer will be determined by the degree of crosslinking. An uncrosslinked elastomer will be completely dissolved in the appropriate solvent. With crosslinking the solvent will only diffuse into the elastomer until the osmotic pressure of the solvent is equal to the elastic retractive forces of the stretched polymer chains. Any uncrosslinked portion of the elastomer will dissolve and diffuse out of the swollen rubber. The elastic retractive forces are inversely proportional to the weight of polymer chain between the points of crosslinking. Thus, the swelling will decrease in proportion to the crosslink density. An elaborate theory has been developed by Flory to permit the calculation of crosslink density from the amount of a specific solvent imbibed by a vulcanizate.

Networks swell to equilibrium extends when immersed in liquids, forming a gel in which segments of polymers between crosslinks become stretched, what results in a decrease of the conformational entropy. The fundamental equation describing the equilibrium degree of swelling in derived from the statistical entropy and the thermodynamics of mixing a liquid with the networks chain:

$$\Delta F_m = \Delta F_{el}$$

Equation 2.8.

where ΔF_m is the free enthalpy of mixing and ΔF_{el} is the free elastic energy.

Formulations for the free enthalpy of mixing by Flory and Huggins on the one hand and the free elastic energy by Flory and Rehner[43] on the other hand lead to:

$$-\left[\ln(1-\phi_2)+\phi_2+\chi\cdot\phi_2{}^2\right]=\rho\cdot V_0\cdot M_P^{-1}\cdot\phi_2^{\frac{1}{3}}$$

Equation 2.9.

later modified to:

$$-\left[\ln(1-\phi_2)+\phi_2+\chi\cdot\phi_2{}^2\right]=\rho\cdot V_0\cdot M_P^{-1}\cdot\left(\phi_2^{\frac{1}{3}}-\frac{2\cdot\phi_2}{f}\right)$$

Equation 2.10.

where V_0 is the molar volume of the solvent and χ is an interaction constant, characteristic of both, rubber and solvent, commonly termed the “rubber-solvent interaction parameter” or Huggins interaction constant. The relations are strictly applicable only to a hypothetical network free from entanglements and chain ends.

Assuming that crosslinks are tetrafunctional (f=4, almost invariably obtained upon joining two segments from different chains), equation 2.10. gives:

$$\nu_e=\frac{-\left\lfloor\ln(1-\phi_2)+\phi_2+\chi\cdot\phi_2{}^2\right\rfloor}{V_0\cdot\left(\phi_2^{\frac{1}{3}}-\frac{\phi_2}{2}\right)}$$

Equation 2.11.

An interesting approach to the estimation of χ values in rubbery networks is to be found in the experimental work of Flory and Huggins[40]. They expressed the rubber-solvent interaction parameter as a function of the volume fraction of polymer and the ratio between the vapor pressure of pure solvent P^0 at the experimental temperature and the vapor pressure of diluted solvent P with polymer:

$$\chi = \frac{\ln\left(\frac{P}{P_0}\right) - \ln(1-\phi_2) - \phi_2}{{\phi_2}^2}$$

Equation 2.12.

It is necessary to use a vapor pressure apparatus whose principle was described by Tait and Livesey[44].

2.3.2. DETERMINATION OF CROSSLINK STRUCTURE

The Chemical-Probe method is aimed at obtaining a detailed distribution of the combined sulfur among the various features present in the final vulcanizate (see Figure 2.1. in section 2.1.). It is one of the oldest techniques used in the study of vulcanizates structures dating from 1950s, and it consists of treating the networks with reagents (the so-called chemical-probes) which react quantitatively with specific sulfurated groups. This method is based on the selectivity and reactivity of the reagents used. Thus, measuring the crosslink density by swelling before and after the treatment, allows to estimate the proportion of each kind of crosslink type in the total crosslink density. These reagents must be capable of homogeneous distribution in the rubber network and the excess must be easily removed after treatment. Saville and Watson[39] provided a wide bibliography of much laboratory work on low molecular weight compounds to leave little doubt about the specificity of each chemical probe discussed. This approach opened the way for them and subsequent workers to distinguish between poly-, di- and monosulfidic bonds in NR vulcanizates.

There is a variety of chemical-probes and each one have a different application. Next, the main chemical-probes will be briefly exposed, focusing on the thiol-amine reagents, the chemical-probe that has been used in this thesis to determine the crosslink structure.

2.3.2.1. METHYL IODIDE

Selker and Kemp[45] reported work on model low molecular weight compounds to show the specificity of methyl iodide in breaking monosulfidic bonds. The level of network-bound iodide after reaction reflects indeed the concentration of monosulfidic groups since simple saturated organic monosulfides react as follows:

$$R_2S + CH_3I \rightarrow R_2S^+ CH_3I^-$$

Disulfides react very slowly with methyl iodide and no reaction is observed with polysulfidic bonds.

At the very outset, this chemical-probe seemed to be of interest in determining the proportion of monosulfidic bonds but experiments were hampered by the insolubility of the vulcanizates in methyl iodide. Furthermore, Moore[46] concluded that the reaction of methyl iodide with organic mono- and polysulfides was not sufficiently specific to determine precisely the nature of the sulfurated crosslinks.

2.3.2.2. LITHIUM ALUMINIUM HYDRIDE

Studebacker[47] pioneered the use of lithium aluminium hydride as a chemical-probe. This reagent reacts with di- and polysulfidic crosslinks, leaving monosulfidic linkages intact. When organic polysulfides are treated with $LiAlH_4$ in an ethereal solvent at moderate temperatures, and then with a weak acid, the terminal groups are converted to thiol and the interior sulfur atoms are liberated as hydrogen sulfide:

$$RSS_XSR' \xrightarrow{LiAlH_4} RSH + x\ H_2S + HSR'$$

Hence, the quantification of hydrogen sulfide gives an estimate of the average sulfur chain-length. $LiAlH_4$ under appropriate reaction conditions cleaves disulfidic bonds, giving two molecules of thiol:

$$RSSR' \longrightarrow RSH + HSR'$$

Therefore, after quantitative reaction of $LiAlH_4$ with a rubber network, two thiol groups are formed for each di- and polysulfidic group originally present. In principle, the contributions of di- and polysulfidic crosslinks to the total crosslink population are determinable from the initial chemical crosslink density and the yields of thiol functions from lithium aluminium hydride treatment of the vulcanizate. But difficulties are frequently experienced in determining the thiol content of the treated vulcanizate.

2.3.2.3. SODIUM Di-n-BUTYL PHOSPHITE

Sodium di-n-butyl phosphate is used to distinguish carbon-carbon and monosulfidic crosslinks from di-and polysulfidic crosslinks. This chemical probe has been thoroughly discussed by Moore and Trego[48]. It reacts:

i) with dialkyl disulfides at 25ºC according to the following reaction where R is alkyl,

$$RS_2R + (nBuO)_2PONa \rightarrow RSNa + RSPO(O\text{-}nBu)_2 \rightarrow RS\text{-}nBu + RSPO(O\text{-}nBu)ONa$$

ii) with dialkenyl trisulfides and disulfides at 25ºC as shown in the following equations where R' is alkenyl,

R'SSSR' + $(nBuO)_2PONa \rightarrow$ R'SSR' + $OP(O\text{-}nBu)_2SNa$

R'SSR' + $(nBuO)_2PONa \rightarrow$ R'SNa + $R'SOP(O\text{-}nBu)_2 \rightarrow$ R'S-nBu + R'SOP(O-nBu)ONa
R'SR'Na + $OP(O\text{-}nBu)_2SNa$

iii) according to the previous equations with alkenyl alkyl disulfides.

The only drawback of this method, is that the reactions viewed in section ii) involve the conversion of disulfidic crosslinks (R'SSR') into monosulfidic crosslinks (R'SR') and it can lead to an overestimate of monosulfidic crosslinks and an underestimate of di- and/or polysulfidic crosslinks.

2.3.2.4. TRIPHENYLPHOSPHINE

Moore and Trego[48,49] investigated the reaction of a wide range of organic sulfur compounds with triphenylphosphine, mainly using dry benzene as solvent and found that the utility of triphenylphosphine depends on its abilty to convert:

i) simple dialkyl and dibenzyl polysulfides to disulfides at 80ºC where R is alkyl or benzyl,

$$RSS_xSR + x\ Ph_3P \rightarrow RSSR + x\ Ph_3PS$$

ii) dialkenyl di- and polysulfides and alkenyl-t-alkyl di- and polysulfides to monosulfides where R' is alkenyl or alkyl and R'' is alkenyl,

$$R'SS_xSR'' + (x+1)\ Ph_3P \rightarrow R'SR'' + (x+1)\ Ph_3PS$$

Moore and Trego found that triphenylphosphine can be readily transported in and out of natural rubber networks in benzene, and that the reaction product, triphenylphosphine sulfide, is also completely extractable by benzene at room temperature. The amount of sulfur removed from the network by the triphenylphosphine treatment is then calculated by determination of the sulfur present in the benzene extract as triphenylphosphine sulfide.

2.3.2.5. THIOL-AMINE REAGENTS

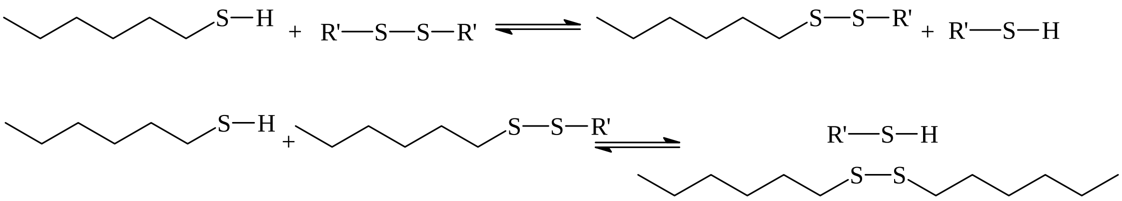
The use of two specific thiol-amine chemical probes allows to determine the proportion of monosulfidic, disulfidic and polysulfidic crosslinks in a vulcanizate[42,50].

Campbell and Saville[51] showed that treatment of NR vulcanizates with a thickness of 1mm with hexane-1-tiol (1M) in piperidine for 48h at 25ºC cleaves disulfidic and polysulfidic crosslinks while treatment with propane-2-thiol (0,4M) and piperidine (0,4M) in n-heptane for 2 hours cleaves only polysulfidic crosslinks (Figure 2.6.). The sulfur-

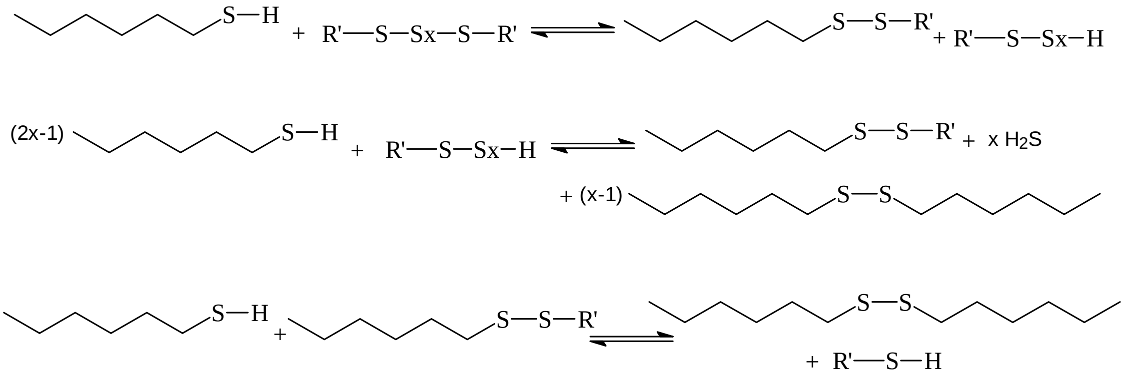
sulfur bonds of the latter are cleaved via nucleofilic displacement. The reaction with polysulfides is rapid and quantitative, but disulfides react at least 1000-fold slowly.

HEXANE-1-THIOL

Cleavage of disulfidic crosslinks:



Cleavage of polysulfidic crosslinks:



PROPANE-2-THIOL

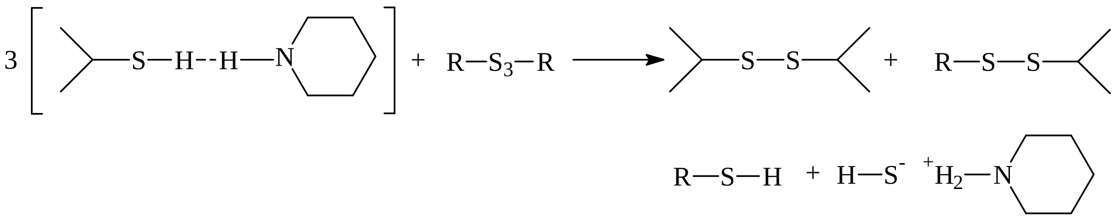


Figure 2.6. Desulfuration of poly- and disulfides by thiolates.

The reactivity and specificity of the thiol-amine chemical probes is then sensitive to factors such as: the structure of the thiol, the concentration of reagent, the reaction time, the reaction temperature and the dimensions of the sample.

2.4. EXPERIMENTAL

2.4.1. MATERIALS

Model Compound Vulcanization (MCV): Squalene (Fluka, 97%) was used for the present study without further purification. Sulfur (CEPSA), Tetramethylthiuram disulfide (TMTD) (Lanxess), Tetraphenylthiuram disulfide (TPhTD) (Perkacit® Lanxess), N-cyclohexyl-2-benzothiazol sulfenamide (CBS) (Lanxess), zinc oxide (Silox), magnesium oxide (Silox), calcium oxide (Silox) and stearic acid (Calià&Parés) were provided by IACP-JEVSA, (Castellbisbal, Barcelona, Spain) and used for the vulcanization of the model compound (MC). Diphenyl disulfide (DPDS) (Fluka, 97%) was used without further purification as devulcanizing agent.

Reaction Stage Modeling (RSM): Geranyl bromide (Aldrich, 95%), Sodium sulfide (Aldrich), Sodium hydrosulfide hydrate (Aldrich), Ethanol (Pareac), Diethyl ether (Sigma-Aldrich), Sodium sulfate (Fluka, ≥99.0%).

Analytical methods: Solvents used in the investigation were all HPLC grade: Acetonitrile (J. T. Baker); 2-propanol and n-hexane (Panreac); Tetrahydrofuran and Methanol (Aldrich). Silver trifluoroacetate (AgTFA) (Fluka, purum >98%) and dihydroxibenzoic acid (DHB) (Fluka, >97%) were used as cationazing agent and matrix respectively in MALDI-ToF method. Silver nitrate (Sigma-Aldrich, >99%) was used as cationizing agent in HPLC-ESI-MS method.

Real rubber mixtures: NR creppe (Weber & Schaer (Hamburg) Thick Pale crepe 1x), EPDM (Keltan 512), ZnO (Zincweiss RS), MgO (Maglite DE (Lehmann & Voss & Co), Stearic acid (Stearinsäure), Sulfur (Mahlschwefel), N-cyclohexylamine-2-benzothiazole (CBS) (Vulkacit CZ CHT-0183/6), Carbon Black N550.

Sweeling and Thiol-amine Chemical-Probe: Toluene (Fluka, ≥99.0%), 1-Hexanethiol (Fluka, ≥95.0%), 2-Propanethiol (Fluka, ≥97.0%), Heptane (Fluka, ≥99.0%), Piperidine (Sigma-Aldrich ReagentPlus® 99%), Petroleum ether (Aldrich).

2.4.2. MODEL COMPOUND VULCANIZATION (MCV)

The experiments were carried out using a conventional vulcanizing system (S/A ratio = 1.67-3.33) (see section 2.1.). The basic vulcanization recipe is given in Table 2.3. The work was performed using two different accelerators: N-cyclohexylamine-2-benzothiazole sulfenamide (CBS) as sulfenamide type and Tetramethylthiuram disulfide (TMTD) as thiuram type, and also mixtures of both (Chapter 3). Tetraphenylthiuram disulfide (TPhTD) was also studied as primary accelerator of thiuram type as it will be seen in section 3.2.3. The study on the role of activator was also performed working with different amount of activators: ZnO, MgO and CaO, and mixtures of them (Chapter 4). Diphenyl disulphide (DPDS) has been also tested as a vulcanizing/devulcanizing agent with both heating methods (Chapter 5). All formulations (containing CBS and DPDS) were heated for 60 minutes at 140ºC using both heating methods to study vulcanization behavior. After that, the resulting mixtures were for other 60 minutes heated at 200ºC for reversion and devulcanization studies.

Table 2.3. Model Compound Vulcanization recipe.

INGREDIENTS	CONCENTRATION, phr
Squalene	100
CBS or TMTD or TPhTD	1.2
Sulfur	2-4
ZnO (or substitutes)	0-5
Stearic acid	2
DPDS	0-2

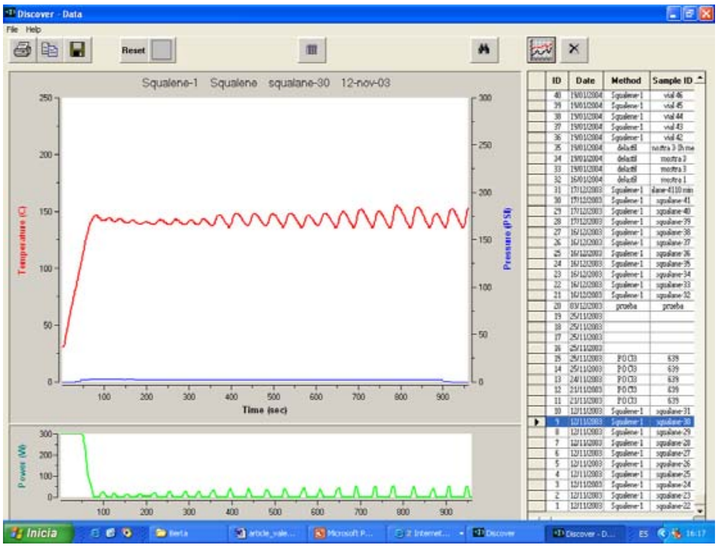
For the conventional heating experiments (CH) the vulcanization reaction is carried out in different vessels. A thermostatic oil bath was used, adjusted to a temperature of 140ºC. The model mixtures are continuously stirred to insure its homogeneity and reactions were carried out under nitrogen environment in order to avoid the oxidation of the double bonds of squalene. During the reaction, vessels are taken from the oil bath at different times and quickly cold quenched to stop the reaction.

A commercially available microwave oven (CEM Focused Microwaves Synthesis System, Model Discover) was used for the microwave heating experiments (MW) (Figure 2.7.). Chemical reactors must be transparent to microwaves and are made of Teflon or polyethylene; glass is also a suitable material, especially for high temperature reactions, but it is not completely transparent to microwaves[52].

Figure 2.7. CEM Focused Microwave Synthesis System, Model Discover[53].

As with conventional heating, vulcanization was carried out in a closed vessel, under nitrogen environment and the model mixture is continuously stirred to guarantee homogeneity. Mechanical stirrers, made of Teflon® and glass, are preferred to a magnetic bar. In most cases, however, stirring is not necessary to homogenize the distribution of heat, since microwaves can reach the bulk of even a slurry mass directly[52].

The equipment, a single mode microwave oven (see section 1.2.), can work in two different modes: Power-time and Standard mode. In the former, power and time are fixed whereas temperature changes during the reaction. In the later, temperature remains constant during the reaction time and power varies on time to maintain this temperature. In this case, a standard mode method has been developed fixing the temperature at 140ºC and maximum pressure was set at 15 bar. Maximum power was set at 300 W and it has varied during the reaction in order to maintain the temperature at 140ºC. A particular problem in this context is the measurement of the temperature, which cannot be obtained using conventional instruments, such as mercury thermometers or metal thermocouples. The temperatures can be measured by thermal indicators or indirectly by the melting of suitable probes: glass fiber thermocouples are suggested[51]. This microwave oven includes an infrared temperature sensor which permits the control of this parameter. During the reaction these parameters were monitored in order to control the reaction and its repeatability (Figure 2.8.). All the mixtures were quickly cold quenched to stop of the reaction at the predetermined time.



ID	Date	Method	Sample ID
40	19/01/2004	Squalene-1	vial 46
39	19/01/2004	Squalene-1	vial 45
38	19/01/2004	Squalene-1	vial 44
37	19/01/2004	Squalene-1	vial 43
36	19/01/2004	Squalene-1	vial 42
35	19/01/2004	delactil	mostra 3 2h me
34	19/01/2004	delactil	mostra 2
33	19/01/2004	delactil	mostra 3
32	16/01/2004	delactil	mostra 1
31	17/12/2003	Squalene-1	dane-4110 min
30	17/12/2003	Squalene-1	squalane-41
29	17/12/2003	Squalene-1	squalane-40
28	17/12/2003	Squalene-1	squalane-39
27	16/12/2003	Squalene-1	squalane-38
26	16/12/2003	Squalene-1	squalane-37
25	16/12/2003	Squalene-1	squalane-36
24	16/12/2003	Squalene-1	squalane-35
23	16/12/2003	Squalene-1	squalane-34
22	16/12/2003	Squalene-1	squalane-33
21	16/12/2003	Squalene-1	squalane-32
20	03/12/2003	prueba	prueba
19	25/11/2003		
18	25/11/2003		
17	25/11/2003		
16	25/11/2003		
15	25/11/2003	POCl3	639
14	25/11/2003	POCl3	639
13	24/11/2003	POCl3	639
12	21/11/2003	POCl3	639
11	21/11/2003	POCl3	639
10	12/11/2003	Squalene-1	squalane-31
9	12/11/2003	Squalene-1	squalane-30
8	12/11/2003	Squalene-1	squalane-29
7	12/11/2003	Squalene-1	squalane-28
6	12/11/2003	Squalene-1	squalane-27
5	12/11/2003	Squalene-1	squalane-26
4	12/11/2003	Squalene-1	squalane-25
3	12/11/2003	Squalene-1	squalane-24
2	12/11/2003	Squalene-1	squalane-23
1	12/11/2003	Squalene-1	squalane-22

Figure 2.8. Temperature (above), pressure (in the middle) and power (bellow) monitoring during the microwave reaction.

The mixture needed 2 minutes to reach this temperature and the hold time was variable in order to follow the different steps of the reaction. All the mixtures were rapidly cold quenched in an ice bath to stop the reaction at a certain time. The higher the level of microwaves energy, the higher the instantaneous localized temperatures will be with regard to the bulk temperature. One method for increasing the microwave energy that is delivered is to use simultaneous cooling during the microwave irradiation. This allows a higher level of microwave power to be directly administered, but will prevent overheating by continuously removing latent heat[54]. Experiments were carried out using the cooling option of the oven, which cools the vessel cavity with compressed air during the hold time in order to maintain a continuous microwave supply during the vulcanization reaction. Table 2.4. sums up the optimized conditions of the microwave vulcanization method.

Table 2.4. Microwaves Parameters for Vulcanization.

PARAMETERS	Value
Power	300 W
Ramp Time	2:00 min
Hold Time	Variable
Temperature	140 °C
Pressure	15 bar
Stirring	On
Simultaneous Cooling	On

2.4.3. ANALYTICAL STRATEGY USED FOR MCV

All the model compound vulcanization mixtures were characterized by two analytical methods of High Performance Liquid Chromatography (HPLC) to cover both aspects of the process, the fading of the accelerator and the formation of crosslinks between the model molecules. Furthermore, two different methods, Matrix Assisted Laser Desorption Ionization (MALDI-ToF) and Gel Permeation Chromatography (GPC), were used to identify the vulcanization intermediates in order to compare the ones formed with microwaves to the ones already described to be formed when vulcanizing with conductive heating. Figure 2.9. shows a scheme of all the analytical methods used in this thesis to study the vulcanization mechanism of squalene as a model of NR.

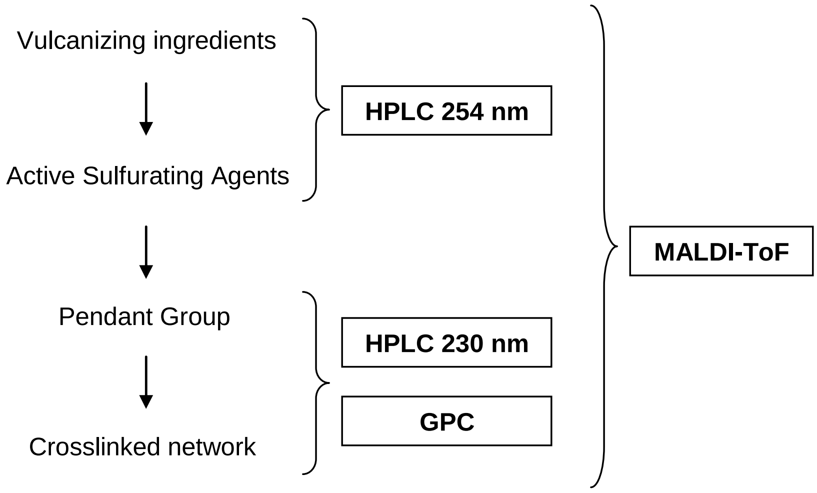


Figure 2.9. Analytical methods used to study the squalene vulcanization mechanism.

2.4.3.1. HPLC METHOD FOR THE CHARACTERIZATION OF THE ACCELERATOR EVOLUTION

This method was used to follow the accelerator degradation and the formation of the active sulfurating agents[55]. A Hewlett Packard Series 1100 High Performance Liquid Chromatograph has been used. Data acquisition and treatment has been made using HP ChemStation for LC. The ultraviolet detector was set to 254nm and the mobile phase was an isocratic mixture of acetonitile (HPLC quality) and water in proportion 90:10. The flux was set to 1 mL/min, the injected volume was 20μL and the total time of the chromatogram was 15 minutes. A Teknokroma Kromasil 100 C-18 (5μm,15x0.4cm) column has been used. Samples were prepared as follows: 0.1g of the cold quenched vulcanizate was dissolved in 5mL acetonitrile for 5 minutes in an ultrasonic bath at room temperature. Before injection, samples were filtered with a 0.45μm Nylon filter in order to remove insoluble particles that would damage the column.

This method was developed to study primary accelerator vulcanizing systems. Following the concentration of the different peaks during the vulcanization process it is possible to understand the mechanism of formation of the different intermediates. The same method was used for the samples containing CBS, TMTD or TPhTD as accelerator.

Analysis of CBS vulcanizing system

A representative chromatogram of a vulcanized sample using CBS is presented in Figure 2.10. The different intermediates were identified comparing the results with those obtained earlier in our research group as well as by analyzing samples using HPLC-MS.

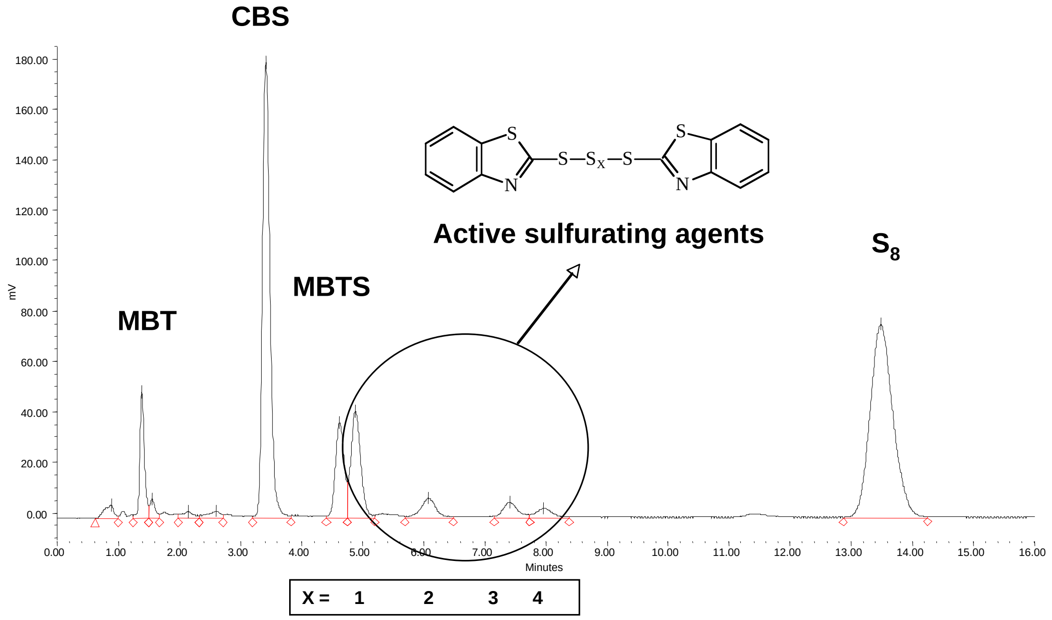


Figure 2.10. Chromatogram for CBS intermediate compounds.

The presence of 2-mercaptobenzothiazole (MBT), a decomposition product of CBS degradation; CBS; dibenzothiazole disulfide (MBTS) and sulfur can be seen (at 1.4, 3.4, 4.6 and 13.5 respectively) and it was identified by external standards. Peaks with retention times of 4.9, 6.1, 7.4 and 7.9 minutes correspond to the active sulfurating agents. The elution time increases when increasing the number of sulfur in the chain. The identification of these peaks was done by comparison with previous work published by our research group[55].

Analysis of TMTD vulcanizing system

A representative chromatogram of a vulcanized sample using TMTD as accelerator is presented in Figure 2.11. and the identification of the different species is shown in Table 2.5. The elution order of the substances is similar to their analogs for sulfenamide vulcanization, but the retention times are lower in this case. First of all, the elution of tetramethylthiourea (TMTU) is observed, followed by the peak corresponding to the accelerator TMTD. After some peaks appear corresponding to the active sulfurating agents, with structure of tetramethylthiuram polysulfides (TMTP). As for sulfenamides, the elution time increase when increasing the number of sulfur in the chain.

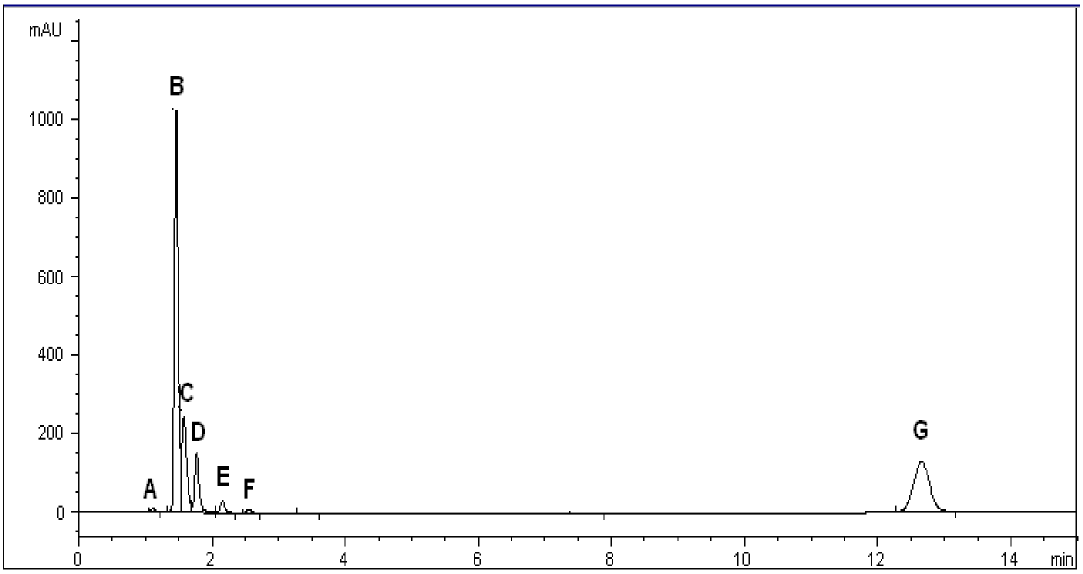
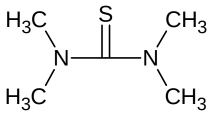
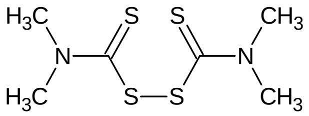
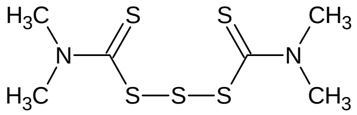
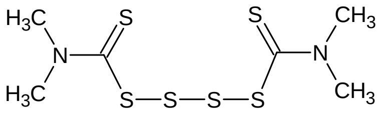
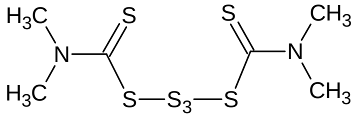
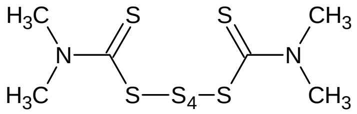


Figure 2.11. Chromatogram for TMTD intermediate compounds.

The identification of these peaks was performed by a HPLC-APCI$^+$-MS method developed in this thesis. The experiments were conducted with a Waters Separations Module 2695 chromatograph. The same chromatographic conditions, as described at the beginning of this section, have been used for this method, except for the mobile phase. To facilitate protonation water has been substituted as eluent for a 0.1% solution of formic acid. A gradient elution with acetonitrile and formic acid (0.1%) has been developed as a substitute of the isocratic elution described above. The aim of this change was to improve the peak separation from the peaks A to F.

Table 2.5. Identification of TMTD intermediate compounds

Peak	Structure	Abbreviation
A		TMTU
B		TMTD
C		TMTTr
D		TMTTe
E		TMTPe
F		TMTHe
G	S_8	Sulfur

The gradient program used is presented in Table 2.6. and Figure 2.12. shows the UV chromatogram at 254nm with the isocratic method, the UV chromatogram at the same wavelength of the gradient method and the corresponding Total Ion Chromatogram (TIC) for 20V cone voltage. The compounds were identified by coupling the chromatograph with a Micromass ZMD detector single quadrupole mass spectrometer equipped with an electrospray ionization source. The experiments were carried out in the positive ion mode. Nitrogen was used as the nebulizing gas and as the drying gas and it was generated from compressed air. The nebulizing gas pressure was 50psi and the drying gas was held at 500L/h. The drying gas temperature was 400ºC and the source temperature 100ºC. The ion spray needle voltage was kept at 4,5kV and the cone voltage at 20V. The range m/z 50-350 was scanned over 2s. Peak B and peak G could also be identified by external standards. The development of this method allows the identification of peak A' as tetramethylthiuam monosulfide (TMTM). The mass spectra of the rest of the peaks can be found in Appendix 2.

Table 2.6 Gradient Program for HPLC-UV

Time	ACN	0.1% Formic Acid
0	60	40
5	60	40
10	90	10
25	90	10
28	60	40
30	60	40

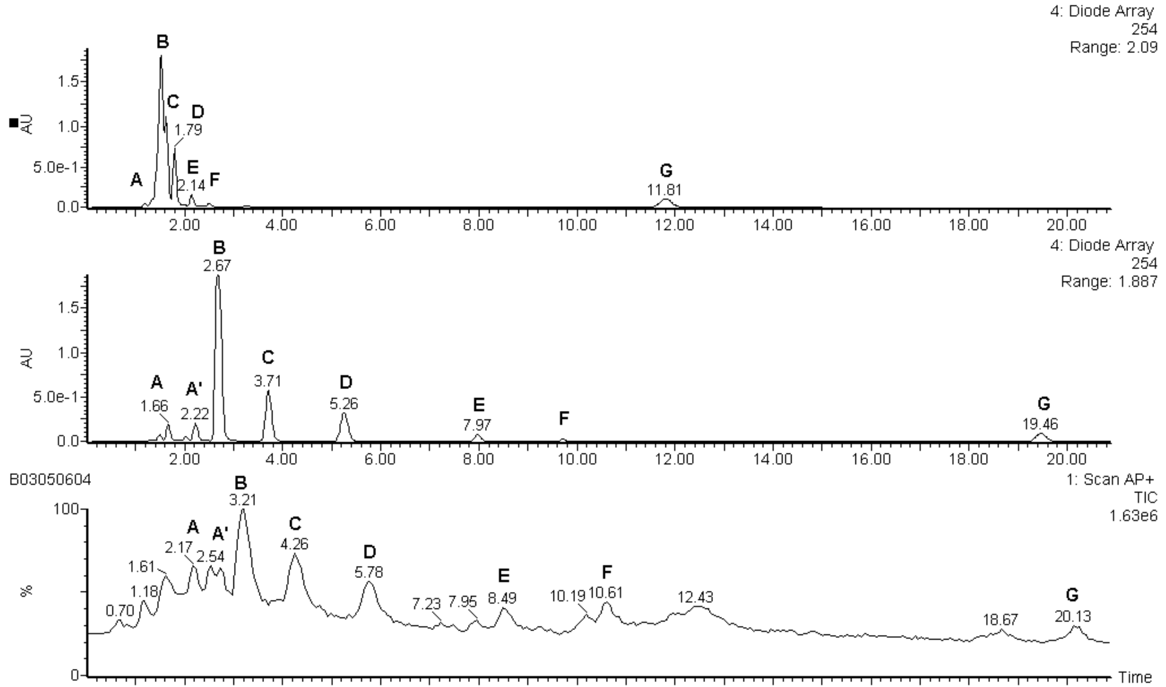


Figure 2.12. Chromatogram of a TMTD vulcanizate at 254nm with the isocratic method (above), of the gradient method (middle) and the corresponding Total Ion Chromatogram (TIC) for 20V cone voltage (below).

Analysis of TPhTD vulcanizing system

Tetraphenylthiuram disulfide (TPhTD) was also studied as a primary accelerator. The same HPLC-APCI$^+$-MS method described above for TMTD samples, has been used for analyzing TPhTD intermediates. The chromatogram obtained was similar to the one shown in Figure 2.11. for TMTD vulcanizates. The elution order was first the accelerator followed by the active sulfurating agents (increasing the elution time with the increase in sulfur atoms in the polysulfide chain) and the sulfur. In this case, this method was not able to ionize TPhTD due to steric hindrance of the phenyl group and the higher molecular weight of these molecules. However, although TPhTD active sulfurating agents could not be identified, TPhTD and sulfur were identified with external standards, and their evolution was studied using this HPLC method.

Analysis of DPDS evolution

The same method was also used to follow the devulcanizing agent (DPDS) and its intermediates. The identification of the chromatographic peaks is shown in Figure 2.13. In this case, as happened for TPhTD, the ionization of the active sulfurating agents was not possible, but DPDS and sulfur were identified with external standards, and their evolution could be followed by this HPLC method.

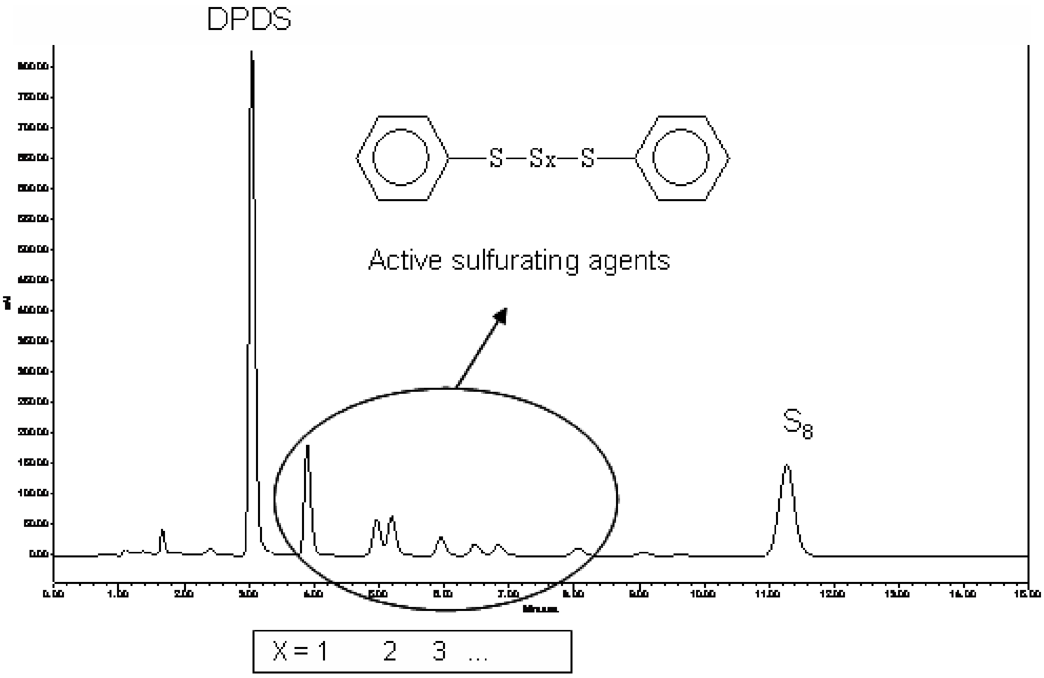


Figure 2.13. Chromatogram for DPDS intermediate compounds.

Analysis of CBS+TMTD vulcanizing system (secondary accelerator)

Besides the above mentioned method to analyze primary accelerator systems or devulcanizing agent residues and intermediate compounds, another method has been developed, applying a gradient program with a buffer solution for better peak separation, when analyzing a vulcanizing system containing both accelerators (secondary accelerator): N-cyclohexyl-2-benzothiazolsulfenamide and Tetrametyl-thiuram disulfide (CBS+TMTD).

For this analysis a Merck Hitachi Chromatograph (L-6200 Intelligent Pump, L-4000 UV Detector, T-6300 Column Thermostat) and a Teknokroma Kromasil 100 C-18 (5µm, 15x0.4cm) column have been used. The Waters Millenium Chromatography Software Version 3.2 has been used for data acquisition and treatment. All parameters beside the composition of the mobile phase have been kept unchanged. The gradient program is shown in Table 2.7 A solution of 5 mmol ammonium acetate in water was used as a buffer[55].

Table 2.7 Gradient Program for HPLC-UV

Time	ACN	H_2O	Buffer
0	40	0	60
2	40	0	60
5	60	0	40
5.1	60	40	0
19	100	0	0
30	100	0	0
32	40	60	0
32.1	40	0	60
37	40	0	60

The different peaks have been identified by comparison with earlier results obtained in our research group[18,55]. Figure 2.14. shows the separation of the different intermediate compounds that are formed during the vulcanization process when using CBS and TMTD as accelerators. The identification of the different species is shown in Table 2.8.

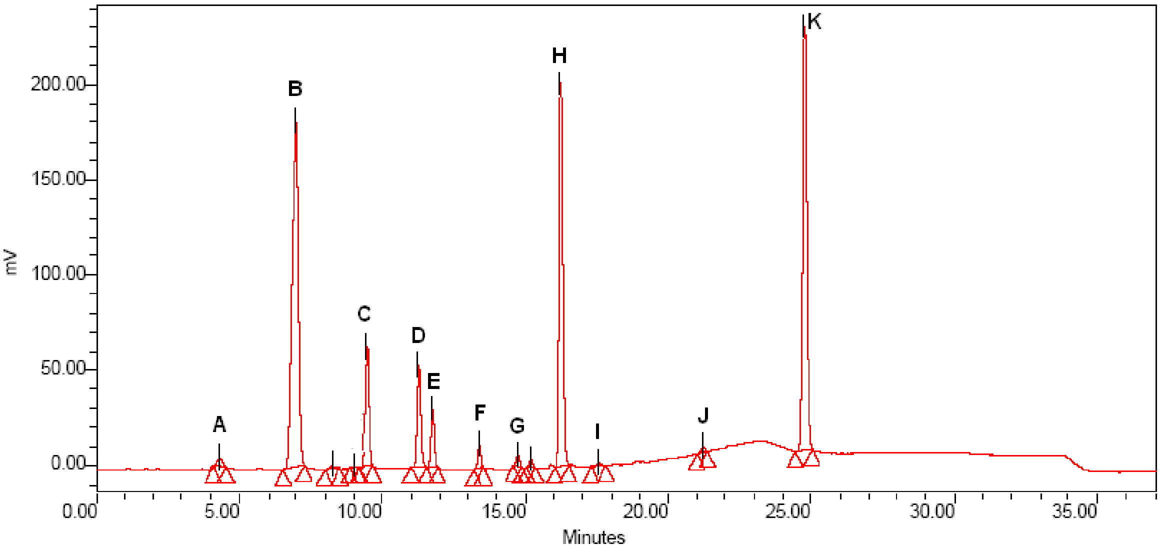
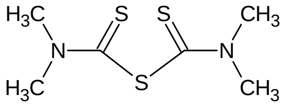
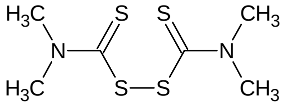
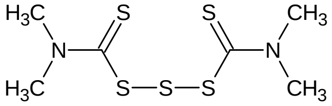
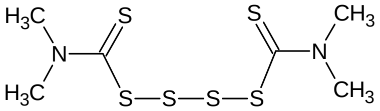
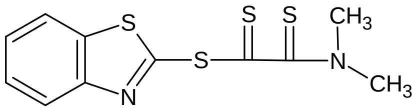
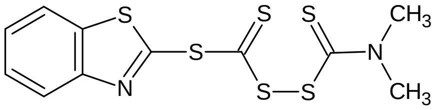
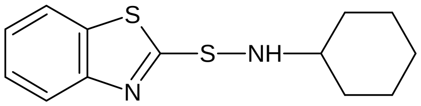
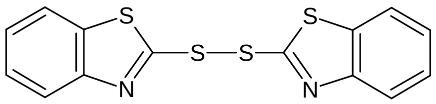
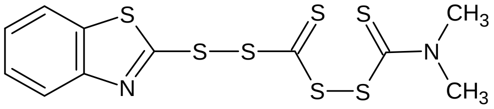


Figure 2.14. Chromatogram of TMTD and CBS intermediates.

Table 2.8. Identification of intermediate compounds formed during CBS and TMTD accelerated sulfur vulcanization

Peak	Structure	Abbreviation
A		TMTM
B		TMTD
C		TMTTr
D		TMTTe
E		
F		
G		CBS
H		MBTS
I		
K	S_8	

2.4.3.2. HPLC METHOD FOR THE CROSSLINK PROCESS MONITORING

The HPLC-UV method used was optimized to follow the polysulfidic crosslinks (Sq crosslinked) and the evolution of squalene (Sq) and squalene with pendant group (Sq-PG)[56]. The UV detector was set at 230 nm and the mobile phase was acetonitrile/ 2-propanol/ n-hexane (72:17:11). Samples were prepared as follows: 0.1g of the cold quenched vulcanizate was dissolved in 10mL eluent for 5 minutes in an ultrasonic bath at room temperature. Before injection, samples were filtered with a 0.45μm Nylon filter. The flux was set to 1 mL/min, the injected volume was 20μL and the total time of the chromatogram was 18 minutes. A Kromasil 100 C-18 (5μm,25x0.4cm) column was used. Although this method provides a good separation of the different crosslink species, there was controversy about the identification of the chromatographic peaks which has been previously assigned by MS using electronic impact (EI) ionization[56] using a particle beam (PB) interface. Electronic impact produces strong fragmentation which gives a lot of structural information but hinder the identification of the molecular ion. Although fragments give some information about the molecule structure, it would be interesting to find another MS technique with a softer ionization in order to discern between the different crosslinked squalene (with a very similar structure) and to assure the complete identification of the chromatographic peaks. Thus, a novel HPLC-ESI-MS method with post-column silver nitrate derivatization has been developed during this thesis[57].

HPLC-ESI-MS with silver nitrate post-column derivatization

In this method, after all by-products were separated by reverse-phase liquid chromatography, analytes formed complexes with silver cation by mixing with a silver nitrate solution. The positive ion ESI mass spectra of squalene, squalene by-products and intermediates of vulcanization process showed $[M+Ag]^+$ and/or $[M+Ag+AgNO_3]^+$ ions. The method developed overcomes the ESI technique limitations related to the ionization of hydrocarbons. Thanks to adduct formation, the applicability of electrospray ionization is extended to the analysis of neutral hydrocarbons with double bonds in its chain.

HPLC experiments were conducted with a Waters Separations Module 2695 chromatograph. A Teknokroma Kromasil 100 C-18 (5μm, 250 mm x 4mm) column was used with an UV detector set at 230 nm, and a mobile phase flow of 0.8 mL/min. The mobile phase should be modified, in comparison with the mobile phase of the previous method, to acetonitrile/2-propanol (70:30), because hexane is not a suitable solvent in ESI-MS system. 2mM silver nitrate solution was added post-column at a flow rate of 0.2 mL/min by using a T-connector and an isocratic pump, which results in an overall concentration of silver ions of 0.4 mM. After the liquid junction, the HPLC flow rate was 1mL/min and the injected volume was also 20μL.

The compounds were identified by coupling the chromatograph with a Micromass ZMD detector single quadrupole mass spectrometer equipped with an electrospray ionization source. Nitrogen was used as the nebulizing gas and as the drying gas and it was generated from compressed air. The nebulizing gas pressure was 50psi and the drying gas was held at 500L/h. The drying gas temperature was 400ºC and the source temperature 100ºC. The ion spray needle voltage was kept at 4,5kV and the orifice voltage at 5, 20 and 40 V. The range m/z 400-1200 was scanned over 2s. The experiments were carried out in the positive ion mode. A chromatogram of a mixture heated 15 minutes with microwaves with the peaks identified by mass spectrometry is presented in Figure 2.15. There are a large number of peaks, but there will be taken into account only those eluted after 7 minutes. The peaks eluted before correspond to the accelerator and its intermediates, and they will be identified and quantified using the HPLC methods presented in section 2.4.3.1. At 7.5 minutes appears a peak corresponding to sulfur. It should be remarked the identification of peaks with retention times between 8 and 14 minutes corresponds to the squalene reaction products. Thus peaks between 8 and 9 minutes correspond to tetrasulfidic crosslinks (Sq-S_4-Sq). Peaks around 10 minutes have been identified as different isomers of trisulfidic crosslinks (Sq-S_3-Sq). Peaks between 11 and 12 minutes can be assigned to different isomers of disulfidic crosslinks (Sq-S_2-Sq). and peak at 14 minutes corresponds to monosulfidic crosslinks (Sq-S-Sq). At 13 minutes there is a signal corresponding to the squalene with pendant group (Sq-PG) and after squalene peak, at 15 minutes, there is also a small signal corresponding to modified squalene. The identification of these peaks was done by mass spectra and they can be found in Appendix 3.

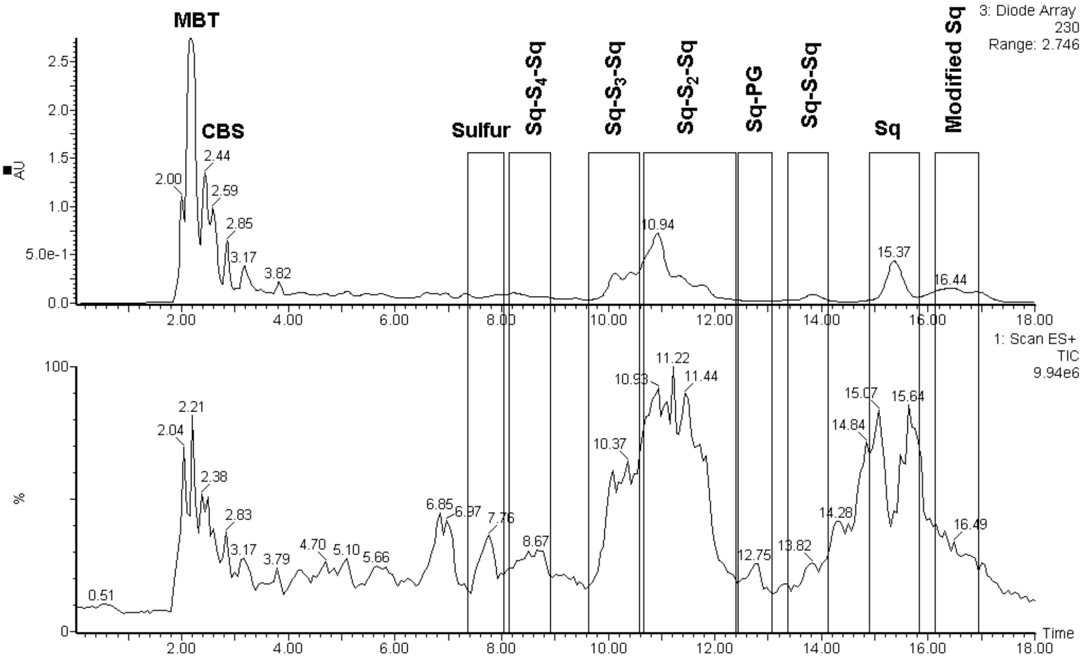


Figure 2.15. Peaks identification of a chromatogram at 230 nm and mass spectra of a simple vulcanized for 60 minutes, where cross-linked and modified squalenes can be seen.

2.4.3.3. GPC METHOD FOR THE CROSSLINK PROCESS MONITORING

Given the fact that squalene has quite a high molecular weight (MW=410 g/mol), gel permeation chromatography (GPC) was thought to be a suitable technique to follow its crosslinking. An analytical method was optimized, in our research group, to follow the vulcanization process[55]. GPC experiments were carried out in a Merck-Hitachi T-6300 Column Thermostat chromatograph coupled with a UV detector Merck-Hitachi L-4000. The Waters Millenium Chromatography Software Version 3.2 has been used for data acquisition and treatment. The mobile phase was THF and the UV detector was set at 273nm. This wavelength was selected because squalene, which is the main specie in the vulcanizate, does not absorb at 273nm. Therefore, there is no squalene signal which could cover the minority signals as crossliked or modified squalene, which are the substances susceptible of being analized. Samples were prepared as follows: 0.1g of the cold quenched vulcanizate was dissolved in 10mL THF for 5 minutes in an ultrasonic bath at room temperature. Before injection, samples were filtered with a 0.45µm Nylon filter in order to remove insoluble particles that would damage the column. The mobile phase flow was 1 mL/min and the injection volume 20 µL and the total time of the chromatogram was 15 minutes. A Waters HR 0.5 Styragel (7,8x300 mm) was used. To identify the peaks in the GPC chromatogram, the obtained results were compared with those obtained earlier in our research group. Figure 2.16. shows a typical GPC chromatogram, where peak A correspond to crosslinked squalene and peak B to modified squalene.

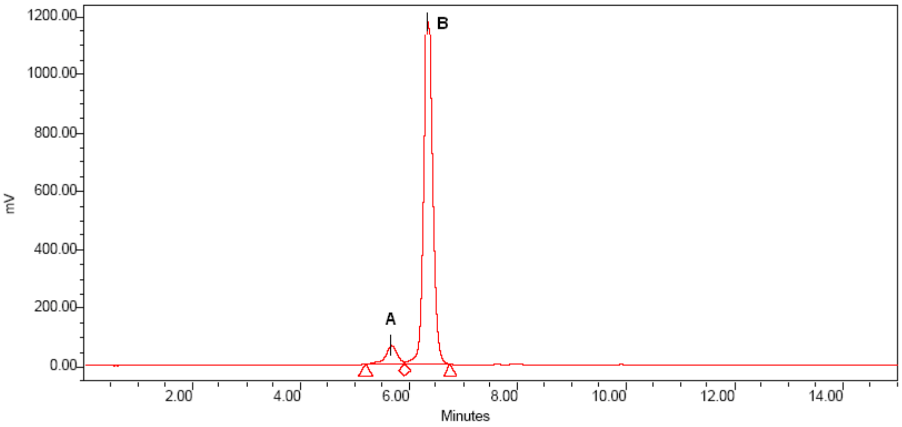


Figure 2.16. GPC chromatogram of vulcanized squalene.

2.4.3.4. MALDI-TOF METHOD FOR THE IDENTIFICATION OF VULCANIZATION BY-PRODUCTS

This MALDI-ToF method has been developed in our research group[58]. These analysis were carried out with a Kratos Analytical Compact MALDI2 K-Probe, which uses a 3ns pulse from a nitrogen laser (λ=337nm) at a target area of 100µm diameter, and pulse extracts the ions down a linear flight tube (2m) in a vacuum of 10^{-6} Torr (1 Torr = 133.3 Pa). Spectra were run in positive high-mass mode. Samples were prepared as follows: 0.1g of the cold quenched vulcanizate was dissolved in 10mL Tetrahydrofuran (THF) for 5 minutes in an ultrasonic bath at room temperature. Separately, solutions of 10 mg/mL were prepared for the matrix, in this case dihydroxibenzoic acid (DHB), and the cationizing agent, in this case silver trifluoroacetate (AgTFA). To study the crosslink process of squalene and the intermediates formed 0.5μL of a mixture of 8μL of the matrix solution and 0.5μL of the sample solution was deposited in the stainless-steel sample holder and air dried. Squalene and its reaction products can be followed adding cationizing agent in order to ionize non polar molecules. 0.5μL of a mixture of 8μL of the matrix solution, 0.5μL of the sample solution and 0.5μL of the cationizing sample solution were deposited in the stainless-steel sample holder and air dried. When working with cationizing agent a big signal appears in m/z= 518 corresponding to the silver adduct of squalene $[Sq+Ag]^+$, and only low signal of the rest of intermediates can be observed. Figure 2.17. shows at low values of m/z some signals corresponding to the matrix (DHB). Also in this figure, but with low intensity, the ions $[MBT+H]^+$ at m/z=168, $[CBS+H]^+$ at m/z=264 and $[MBTS+H]^+$ at m/z=333 can be observed. The signals between m/z 400 and 600 are the fragments from crosslinked squalene breakage (this part of the spectrum is enlarged above): $[Sq\text{-}S+H]^+$ at m/z=443, $[Sq\text{-}S_2+H]^+$ at m/z=473, $[Sq\text{-}S_3+H]^+$ at m/z=511 and $[Sq\text{-}S_4+H]^+$ at m/z=539.

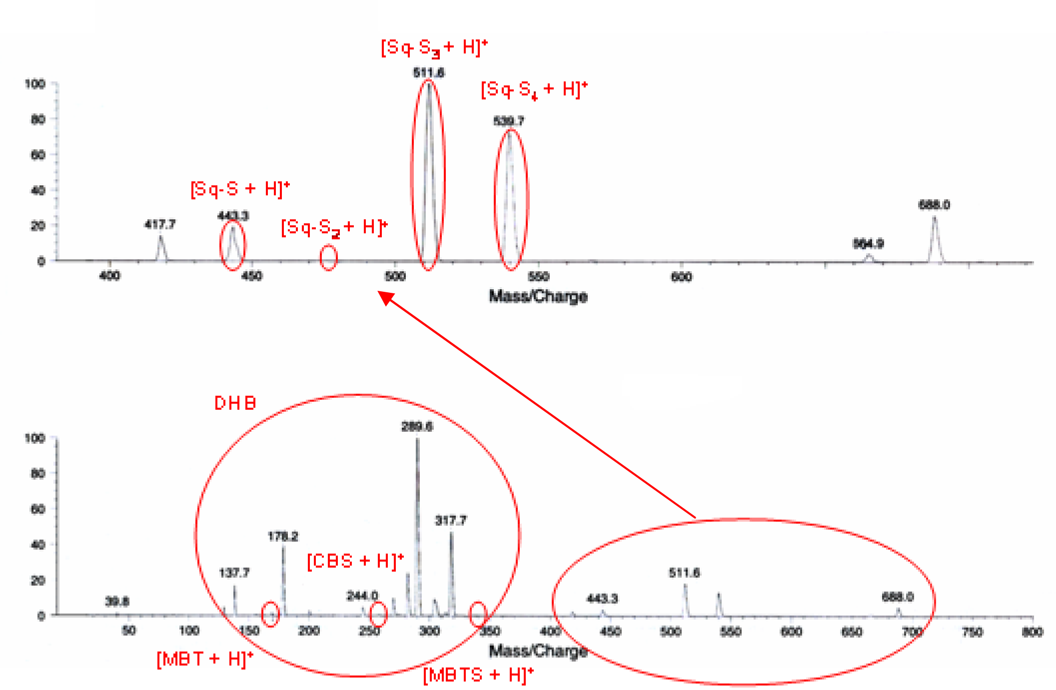


Figure 2.17. MALDI-TOF spectrum of a microwave vulcanizated sample using DHB as matrix and without cationizing agent.

2.4.4. REACTION STAGE MODELING (RSM)

Digeranyl monosulfide and disulfide have been synthesized following Mantegani and Bonardi synthetic route[59] (Figure 2.18.), and have been tested as models using

Reaction Stage Modeling (RSM). All the experiments have been performed using both heating sources: CH and MW. The results obtained with both methods have been compared.

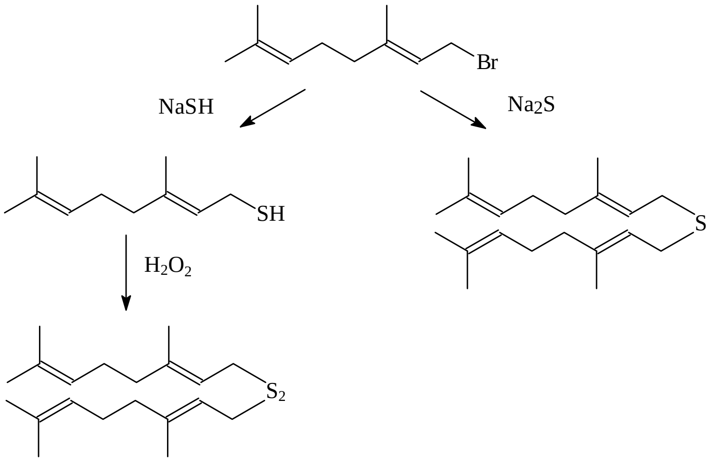


Figure 2.18. Synthesis of digeranyl monosulfide and digeranyl disulfide.

2.4.4.1. SYNTHESIS OF DIGERANYL MONOSULFIDE (Ge-S-Ge)

15g of lyophilized $Na_2S{\cdot}xH_2O$ were dissolved in 70mL ethanol, and the solution was sealed in an inert atmosphere of nitrogen. 10g of geranyl bromide were slowly added, and the solution was stirred overnight at room temperature. Then, ethanol was evaporated under reduced pressure. A liquid-liquid extraction with 50mL water and 50mL diethyl ether was performed in order to concentrate the NaBr formed during the reaction in the aqueous phase and the desired product in the organic phase. The organic phase was dried overnight with Na_2SO_4 and filtered, and the solvent evaporated under reduced pressure. A light yellow oil was obtained and identified as digeranyl monosulfide by ^{1}H-NMR, IR and HPLC-UV (Yield: 90%). Figure 2.19. shows the chromatogram profile of a sample of this product dissolved in methanol and analyzed with the HPLC-UV method described below. Retention time of digeranyl monosulfide is 12.1 minutes. In Figure 2.20. the ^{1}H-NMR spectrum of digeranyl monosulfide is presented.

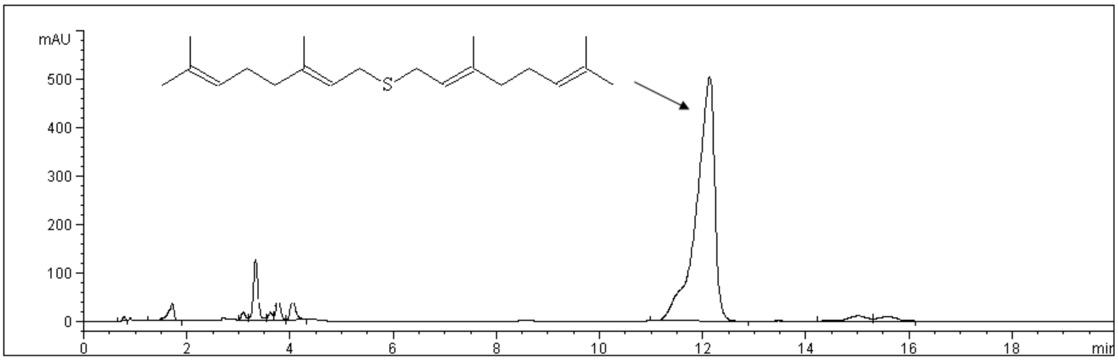


Figure 2.19. HPLC-UV Chromatogram of digeranyl monosulfide (retention time: 12,1 minutes).

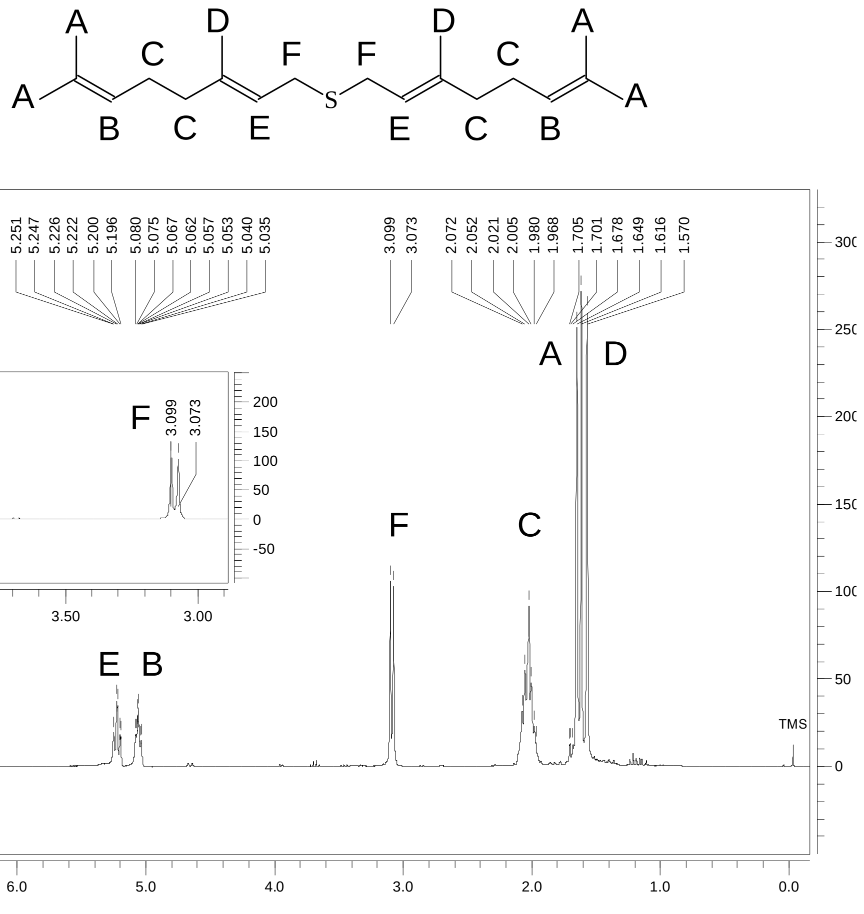


Figure 2.20. ^{1}H-NMR spectrum of Ge-S-Ge.

2.4.4.2. SYNTHESIS OF DIGERANYL DISULFIDE (Ge-S_2-Ge)

Mantegani and Bonardi[59] route to form digeranyl disulfide consist in a first step to form the mercaptogeranyol and a subsequent oxidation with H_2O_2 to form the digeranyl disulfide (Figure 2.18.). 15g of lyophilized NaHS·xH_2O were dissolved in 100mL ethanol, and the solution was sealed in an inert atmosphere of nitrogen. 10g of geranyl bromide were slowly added, and the solution was stirred overnight at room temperature. Then, ethanol was evaporated under reduced pressure. A liquid-liquid extraction with 50mL water and 50mL diethyl ether was performed in order to concentrate the NaBr formed during the reaction in the aqueous phase and the desired product in the organic phase. The organic phase was dried overnight with Na_2SO_4 and filtered, and the solvent was removed under reduced pressure. A light yellow oil was obtained. The identification of the product, formed after the first step of the reaction, by ^{1}H-NMR, IR and HPLC-UV shows that there was a mixture (25%-75%) of digeranyl monosulfide and disulfide respectively (Yield: 85%) instead of the expected mercaptogeranyol. Figure 2.21. shows the chromatogram profile of a sample of this product dissolved in methanol and analyzed with the HPLC-UV method described below. The peak corresponding to digeranyl disulfide is bimodal, this could be explained by the formation of two different isomers of this product (cis-trans isomers). The retention times of these isomers are 15.3 and 16.2 minutes. At 12.1 minutes there appears also a peak corresponding to digeranyl monosulfide. The ratio between the both signals determines the proportion of the mixture (25%-75%).

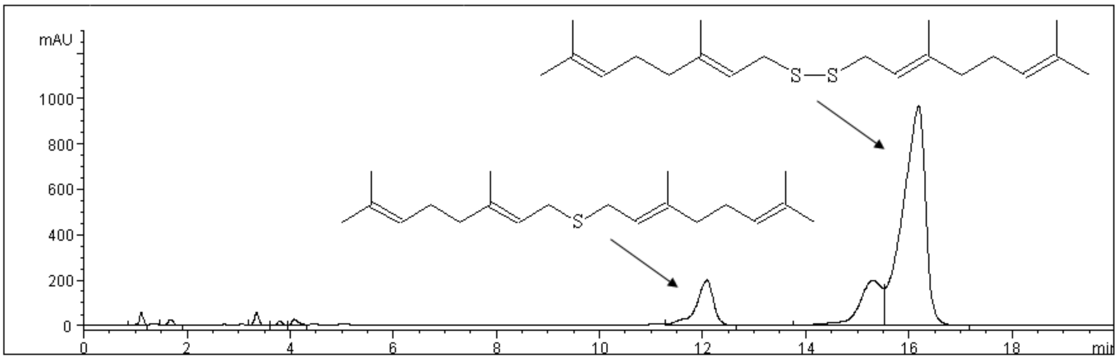


Figure 2.21. HPLC-UV Chromatogram of a mixture of 25% digeranyl monosulfide (retention time: 12,1min) and 75% of two isomers of digeranyl disulfide (retention time: 15,3 and 16,2min).

Figure 2.22. shows the ^{1}H-NMR spectra of both products: digeranyl monosulfide above and below the spectrum of the second product, which also proves the formation of a little amount of digeranyl monosulfide in the synthesis of digeranyl disulfide.

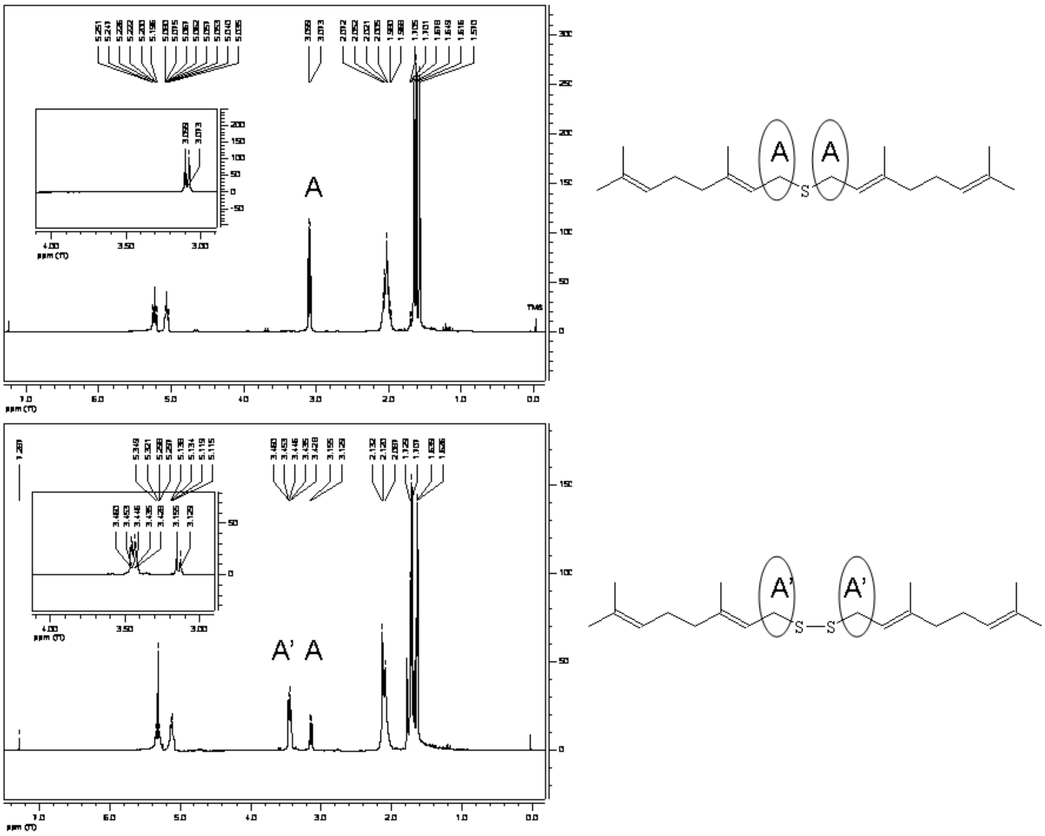


Figure 2.22. ^{1}H-NMR Spectra of the two reaction products. The one above has been identified as digeranyl monosulfide and the one below as a mixture of the monosulfide and disulfide models.

2.4.4.3. RSM PROCEDURE AND ANALYTICAL METHODOLOGY

Reaction Stage Modeling (RSM)

About 1g of the model molecule (digeranyl monosulfide or disulfide) was transferred into a vial (5mL) and sealed with a septum under an inert atmosphere of nitrogen. Thermal degradation of both models was studied separately at 140ºC and 170ºC. The effect of DPDS and ZnO on their degradations was also studied. Table 1 shows the different formulations tested.

Experiments of CH have been performed using a silicon bath. For MW a CEM Focused Microwaves Synthesis system, model Discover, has been used. For both procedures, the temperature was set at 140°C and 170°C to study the effect of temperature in the devulcanization process. To reach these temperatures the microwave oven was set at a maximum power of 300W. During the reaction the oven cavity was cooled with compressed air in order to maximize the microwave power input while maintaining the temperature constant. The reaction was stopped at 3, 5, 10, 30, 60 and 90 minutes, and samples of approximately 0.1g were taken and quickly cold quenched.

HPLC methods

Two different HPLC-UV methods were used to characterize samples: one to study DPDS degradation and the other to study the model compounds evolution. For the first method, 0.1g of the devulcanized product was dissolved in 5mL of acetonitrile. Before injection, samples were filtered with a 0.45μm Nylon filter. A HP-1100 chromatograph was used with a Kromasil 100 C-18 (5μm, 25x0.4cm) column. The UV detector was set at 254 nm and the mobile phase was acetonitrile:water (90:10), with a flow of 1mL/min and an injection volume of 20μL. For the second method, 0.1g of the devulcanized product was dissolved in 5mL of methanol with subsequent 0.45μm Nylon filtration. The chromatographic characteristics were nearly the same, except for changing the mobile phase by methanol:water (93:7).

2.4.5. NATURAL RUBBER MIXTURES AND CHARACTERIZATION

To prepare the real rubber recipes an internal mixer with Banbury® rotors has been used (Thermohaake Polylab system Reocord/Rheomix 3000 Type 557-9300). The software Polylabmonitor v 4.16 (2004) has been used for data acquisition. In Table 2.9. the basic vulcanization recipe is given.

Every formulation was scaled-up to 250g taking into account the density of every ingredient to avoid overpressure problems inside the internal mixer. Temperature was set at 50ºC for the cavity and it was controlled during the mixing process avoiding always to overcome 100ºC to prevent pre-vulcanization of the material and the speed of the rotors was maintained at 50Hz. A three steps mixing procedure is used:

- t=0’ rubber mastication
- t=3’ activating system (stearic acid and ZnO or substitutes)
- t=6’ accelerator + sulfur (for 3 minutes)

Table 2.9. Real Rubber recipe.

INGREDIENTS	CONCENTRATION, phr
NR (crepe) or EPDM	100
CBS	1.2
Sulfur	2-4
ZnO (or substitutes)	0-5
Stearic acid	2
CB (N550)	0-2

In case of using carbon black (CB), it has been mixed with the rubber after the step of rubber mastication and before adding the activating system. After the mixing process, an open two roll mill (Paul Troester Maschienenfabrik, Hannover (62(0)6/66)) have been used to prepared pressed sheets of the unvulcanized mixture ready for vulcanization.

2.4.5.1. VULCANIZATION: CONVENTIONAL HEATING (CH) AND MICROWAVES (MW)

To determine the vulcanization behavior of a mixture and to decide the conditions of vulcanization (temperature and time) the rheometer curve of the material have been analyzed (see section 2.4.5.2.). In this thesis vulcanization has been performed with two heating systems: with a Press (CH) and with a microwave oven (MW).

CH vulcanization was performed with an electric hot press (Leuze Lumiflex (2004) (Rucks Maschienenbau GmbH) Type ES234 230/400 V 50 Hz 10kW). Sheets of different thickness have been prepared (1mm, 2mm or 6mm) depending on the physical or chemical properties that would be measure with the samples:

- sheets of 1mm thickness for the thiol-amine treatment and the determination of crosslink density by swelling measurements.
- sheets of 2mm thickness for the determination of crosslink density by elongation measurements and for IRDH.
- sheets of 6mm thickness for testing compression set and Shore A.

The low thermal conductivity of rubber (0.15 $W \cdot m^{-1} \cdot {}^{o}C^{-1}$ for NR)[60] poses an additional problem in the vulcanization of articles thicker than 4-5 mm, when conventional conduction heating is used. Since the heat can only reach the interior by flow from the outside, the interior does not reach cure temperature until the surface region is well on the way to cure. On the other hand, when the mold opened and the article removed, the interior will continue to cure after the surface has creased.

The vulcanization temperature was set at 140ºC and the cure time corresponded to t_{90} for every vulcanizing system (see rheometer in section 2.4.5.2.). It is very common to use the rheometer t_{90} as a basis for calculating an optimum cure at a given temperature; for low mass articles the t_{90} itself can be used, for larger articles some multiple is applied. For 1mm thickness plates, vulcanization time was t_{90} minutes, for 2mm was t_{90}+2 minutes and for 6 mm was t_{90}+6minutes. The procedure consists on pre-heating the press and the mold at the desired temperature and after fill the mold with 20-30g of the unvulcanized mixture, apply vacuum at 280bar for 10s and after heating the sample, with the same pressure but without vacuum, for t_{90} minutes. The reaction is stopped by cooling at room temperature.

MW vulcanization was performed with a microwave oven for continuous vulcanization of rubber profiles (MUEGGE MW-GTRYJ1540-1K2-08 0497) with a magnetron (Philips 2722 163 02071, 2425-2475 GHz, 13K/2450 PDR 26 D5B1). Normally for continuous vulcanization a profile extruder is disposed just before the resonator entrance and the resonator is arranged in vertical position, to avoid the rubber profile to get in contact with the reactor walls. In this case samples are heated only for 5 to 10 seconds, the time that they pass through the resonator, and normally materials with high polarity are used to achieve high temperatures in short times. Figure 2.23. shows how the geometry of the reactor was changed to work in batch instead of continuously.

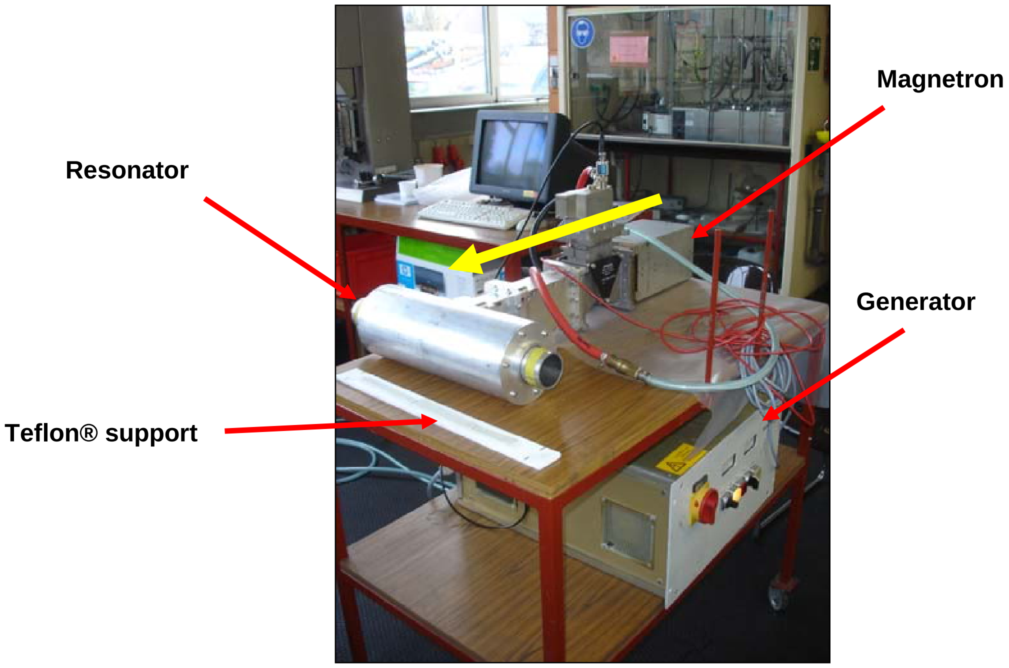


Figure 2.23. Microwaves oven for real rubber samples (Muegge).

The microwaves are created in the magnetron and they move to the resonator following the direction of the yellow arrow. The resonator is the part of the microwave oven where the samples are heated and in our case was arranged horizontally in order to see the effect of microwaves in the rubber samples for longer times. A Teflon® support was constructed to perform as a tray in order to avoid rubber samples touching the resonator's walls.

The microwave generator consists of a display of the power input that can be tune by hand and another display to see the microwave reflection (the lower the reflection, the higher the microwaves absorption by the samples). The length of the resonator can be changed manually in order to optimize the microwave absorption. The way to do that consists in increasing the power input, and changing the geometry looking for the minimum reflection. The position in the resonator is also a critical point when working in a batch process. This parameter has been studied and Figure 2.24. shows the most active place in the resonator (red circle), where all the experiments have been performed.

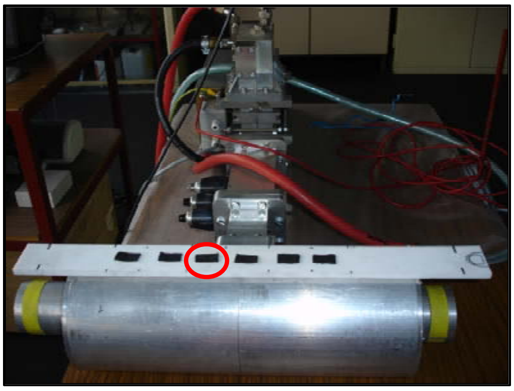


Figure 2.24. Resonator zone with higher microwaves absorption.

Contrary to the microwaves oven used for MCV studies, this oven for real rubber samples is a multimode oven (see section 1.2.). As stated before, there are two different working modes: Power-time and Standard mode. In the former, power and time are fixed whereas temperature changes during the reaction. In the later, temperature remains constant during the reaction time and power varies on time to maintain this temperature. This microwave oven is designed to work only in a Power-time mode. There is no way to maintain the temperature constant during the reaction and also there is not a device to measure rubber temperature. In this thesis, a thermo-camera (VarioTherm^{TM} Jenoptik JENA Laser Optik Systeme) has been used in order to control temperature, with the software IRbis plus v2.2. (Infratec GmbH, Dresden) for data processing. In this study, the input power has been set at a certain value in order to heat the sample approximately at 140ºC. This temperature has been controlled with the thermo-camera. The interest of our study to maintain this parameter constant during vulcanization resides in reproducing CH vulcanization conditions in order to compare final results. Figure 2.25. shows the image of a heated rubber sample monitored with this thermo-camera with the software mentioned above.

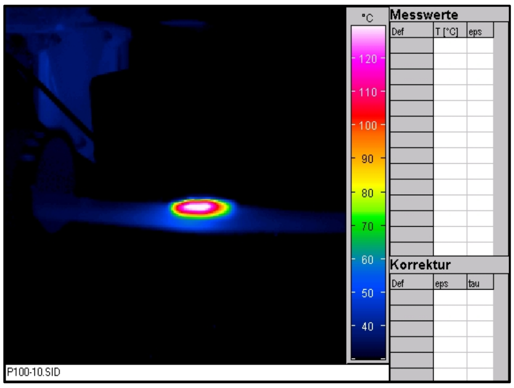


Figure 2.25. Thermo-camera image of a rubber sample heated by the microwave oven.

Because in this oven there is no press during vulcanization to mold the sample, pre-vulcanized 1mm thickness sheets were prepared, with the electric press presented before in this section, heating at 80ºC for 10 minutes at 280mbar. It was previously checked with the rheometer that these conditions were not vulcanizing any compound.

2.4.5.2. VULCANIZATES CHARACTERIZATION: RHEOMETER, HARDNESS AND COMPRESSION SET

The physical properties of elastomers are determined mainly by the chemical nature of the polymer, the reinforcement through fillers and the crosslinks formed during vulcanization. Modifications of the vulcanizing system or the cure time are known to considerably influence these properties. Thus, the physical testing of rubber is also important in order to understand the effect of crosslink density and structure in final properties.

Rheometer

One of the most used and easiest ways to characterize a rubber compound is monitoring the curing process with a rheometer or curemeter. Concerning the chemistry of the reaction, the information given by rheometer curves is limited, i. e. it does not determine the intermediate compounds formed, reaction mechanisms or final molecular network structures. The rheometer is an oscillating disk reomether and the sample to be studied is enclosed in a heated cavity. A metal disk that oscillates sinusoidally in its plane about its axis is embedded in the rubber sample. Vulcanization is measured through the increase in the torque required to maintain a given amplitude of oscillation at a given temperature. The torque is proportional to a low-strain modulus of elasticity. The increase in torque during vulcanization is proportional to the number of crosslinks formed per unit volume of rubber.

In this thesis a Moving Die Rheometer MDR 2000E (Monsanto) has been used for compound characterization and the software Alpha 2000R version 2 has been used for data acquisition. The curves were not only tested at 140ºC (vulcanization temperature used for vulcanization), but also at 130ºC, 150ºC, 160ºC and 170ºC to see the temperature effect in the different materials tested and in its reversion. Interesting parameters such as the scorch time, the crosslink degree and the reactions kinetics can be obtained from this test. A typical rheometer curve was shown in figure 2.3. Next, the main parameters, that provide information about the reaction kinetics and the crosslink density, which can be obtained from this curve are briefly presented[61]:

- **t_1**: cure time in which there is an increase of 1% of the initial torque. It is also called t_s (scorch time).
- **t_{90}**: cure time in which 90% of the final torque is reached. Is considered the optimal time for the rubber vulcanization as overheating the material could lead to reversion processes.
- **M_L**: The minimum torque achieved during the vulcanization. Is an indication of the material viscosity. Is an indicative of the rubber's resistance to flow during processing
- **M_H**: The maximum torque attained during test period.
- **M_H – M_L**: The difference between the maximum torque and the minimum torque, which is closely related to the crosslink density of the material.
- **Rv:** reversion gives an idea of the degradability and aging behavior of the material tested. It can be calculated from t_{90} and t_s.

$$Rv = \frac{1}{t_{90} - t_S}$$

Equation 2.13.

- **Vulcanization rate**: This parameter can be measured from the uphill slope of the curve. Norm DIN 53529 has been followed to calculate the speed constant (k) and the activation energy (E_a).
  The equation which defines the velocity of a reaction of first order is:

$$-\frac{\partial x}{\partial t} = k \cdot (1 - x) \ where \ x = \frac{M_t - M_L}{M_M - M_L}$$

Equation 2.14.

then the plot of ln(1-x) as a function of time gives rise to a graph as the one shown in Figure 2.26.

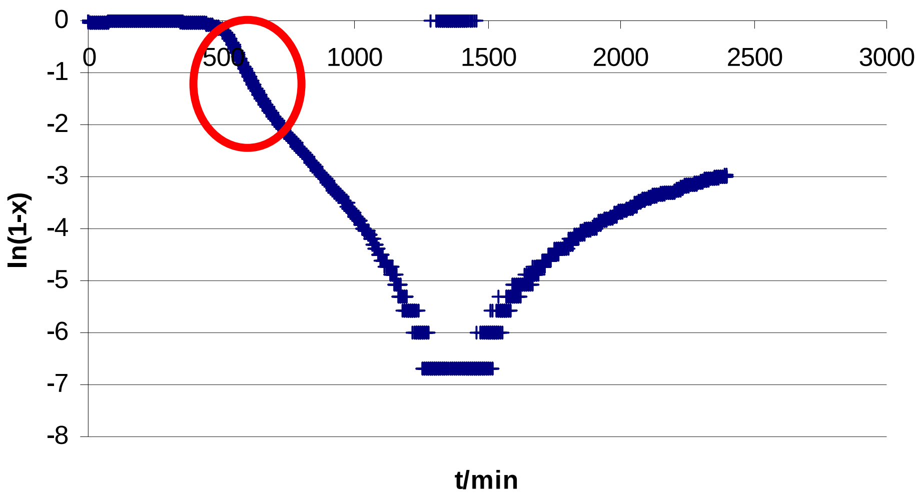


Figure 2.26. Typical graph obtained when representing ln(1-x) as a function of time.

The circle marks the linear part of the curve. Its slope corresponds to k. The following equation relates the Ea with k:

$$\ln(k) = \ln(k_0) - \frac{M \cdot Ea}{R \cdot T}$$

Equation 2.15.

where M=0.4343, R is the universal gas constant 8.31 J mol^{-1} K^{-1}, T is the temperature in Kelvin and Ea is the activation energy in J mol^{-1}. When having a table with speed constants (k) at different temperatures for a vulcanizing system, the plot of ln (k) as a function of T^{-1} gives rise to a straight line. Its slope divided by 0.0523 (M/R) corresponds to the Ea in J mol^{-1}.

Hardness

A basic test of surface hardness is attractive in its simplicity and relative ease of performance, given the availability of rugged, pocketsize devices. A small indentor which is spring loaded is used to measure hardness in rubber samples, as the resistance to penetration. When the durometer is carefully pressed against the rubber surface, a relative measure of this resistance is observed on the durometer face, using a scale of 0-100, although the accuracy and precision of the measurements become questionable towards either end of the scale[62]. Therefore, several scales exist, ranging from the Shore OO for foams to the Shore D for the very hard rubbers. The most commonly applied is the Shore A. There is also the International Rubber Hardness Durometer scale (IRHD), which is very similar to the Shore A.

An equipment Type U72/93E 38230 was used to measure hardness. This parameter was measured in two different scales: Shore A (baielss 3445 DKD-K-16501) and IRHD (baielss 6444 DKD-K-16501 (DIN 53519-2)). Samples of 6mm thickness where used for Shore A measurements and of 2mm thickness for IRHD measurements. Each hardness value was calculated as an average of 5 measurements for each vulcanizate.

Compression set

Elastomers are viscoelastic, which means they will store energy reversibly (elasticity), but also that they will dissipate energy through viscous behavior, like a shock absorber. Viscous behavior means that molecules undergo some form or another of flow or rearrangements. This amounts to stress relaxation, a time dependent phenomenon. Compression Set under constant deflection in air is calculated as the percentage of the original deflection. 6mm thickness rubber buttons are compressed 25% in a metal fixture. After the test condition has been maintained for a time and temperature appropriate to the rubber and the application, rubber samples are removed from stress and allowed to recover. The difference between the recovered dimensions of the rubber button and its original dimensions is referred to as set, and the amount of set is an indicator of how much stress relaxation the rubber underwent while subjected to a deformation. If the rubber did not recover at all but retained the dimensions imposed during the test that would be a set of 100%, which would of course correlate with complete stress relaxation[62].

Norm DIN ISO 815 has been followed to calculate compression set of vulcanizates. Samples of dimensions 13mm diameter and 6mm thickness are compressed by 25% for 24 hours at 70ºC. Compression set was calculated as an average of 5 measurements for each vulcanizate using the following equation:

$$DVR = \frac{h_0 - h_1}{h_0 - h_S} \cdot 100$$

Equation 2.16.

where h_0 is the inicial thickness, h_1 is the final thickness and h_S is the compressed thickness ($h_S = 0.75 \cdot h_0$). The thickness was measured with a Mitutoyo CXP847 device.

2.4.5.3. STRESS-STRAIN MEASUREMENTS (MOONEY-RIVLIN)

Tensile testing of rubber is preferably performed on standard specimens. The test specimen is secured in the clamps of a tensile test machine and stretched at a specified rate until it breaks. The final force required for the break is recorded, along with the amount of stretch that was achieved at the break point. The forces in effect at various degrees of elongation of the specimen are also usually recorded. These forces are used to calculate the stresses per unit area at those elongations, which are reported as tensile moduli. These are usually abbreviated, so that the stress at 100% strain is referred to as the 100% tensile modulus, or the M-100. Stresses at higher strains are then referred to as the M-200, M-300, etc.

In this study elongation measurements were performed using samples of 2mm thickness (S2 specimen). The instrument (Zwick/Roell Z010) operated using a maximum load force tranducer equal to 2000N and a traction rate of 200mm/min. Software Zwick/Roell Textexpert v9.01 was used for data adquisition. The specimen thickness was measured before the assay with a Mitutoyo CXP921 device. Strain-stress curves were calculated as an average of 3 measurements for each vulcanizate (3 different S2 specimens). The stress-strain data were acquired in % elongation (λ) and force (F) in MPa.

Mooney-Rivlin approach to measure network chain density (ν_e) from the results of elongation measurements was based in the relationship showed in equation 2.5. The kinetic theory of rubber elasticity gives a relationship between the elastic constant (C_1) and the network chain density (ν_e):

$$\nu_e = \frac{2 \cdot C_1}{R \cdot T}$$

Equation 2.17.

The resulting data are generally interpreted in terms of “reduced stress” or modulus defined by:

$$[F^*] = \frac{F}{2 \cdot A_0 \cdot \left(\lambda - \frac{1}{\lambda^2} \right)}$$

Equation 2.18.

The resulting value of [F*] are then usually plotted against the inverse of the elongation, as suggested by the semi-empirical equation of Mooney and Rivlin:

$$[F^*] = C_1 + \frac{C_2}{\lambda}$$

Equation 2.19.

As illustrated in Figure 2.27., the dependence of [F*] on the inverse of the extension ratio (λ^{-1}), is generally found to be linear in the region of moderate elongation (λ^{-1} from 0.5 to 0.8). An extrapolation is then required to obtain the desired elastic constant C_1. Then, by using equation 2.17. the network chain density (ν_e) value is obtained.

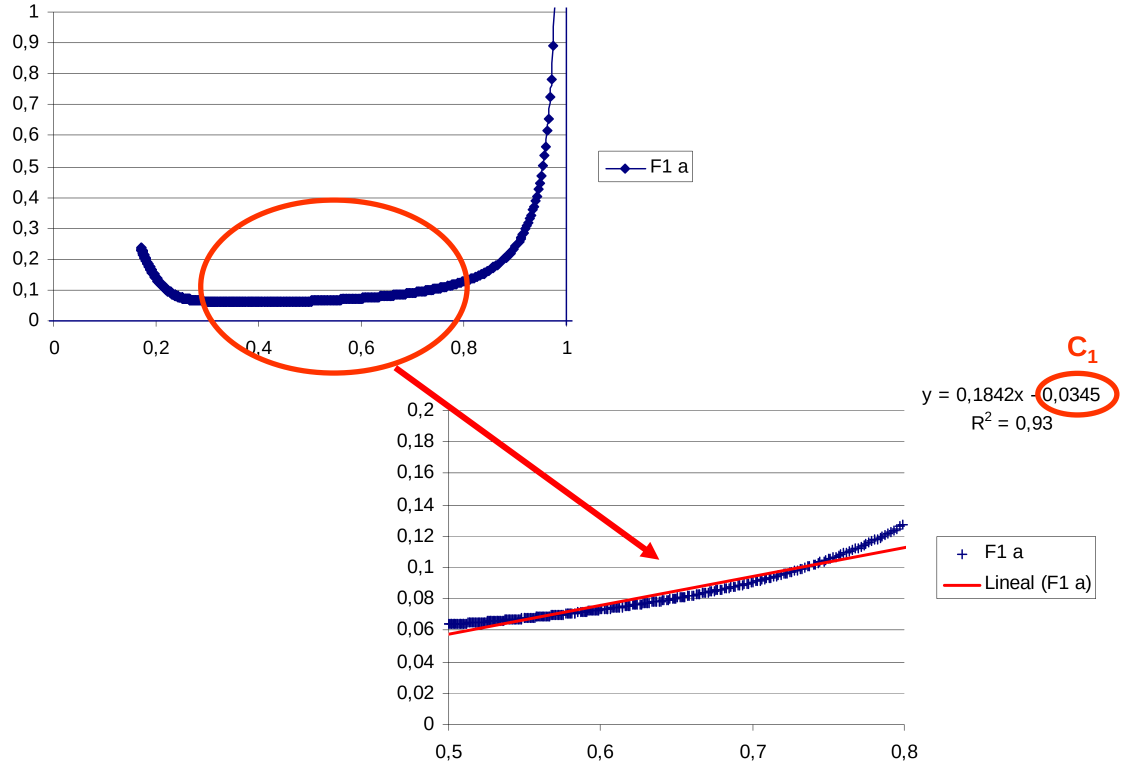


Figure 2.27. Mooney-Rivlin stress-strain curve.

2.4.5.4. SWELLING MEASUREMENTS (FLORY-REHNER) AND THIOL-AMINE CHEMICAL-PROBES

One of the methods more often employed to determine network chain density (ν_e) is based on the Flory-Rehner equation (Equation 2.11.). NR samples are swollen to equilibrium by inmersion in toluene at room temperature for at least 72 hours. Solvent is renewed after 24 hours and the swelling is performed under mild agitation and sheltering rubber specimens from light, to avoid UV degradation. Huggins interaction constant (χ) is characteristic of both, rubber and solvent. This constant is equal to 0.4 for (NR-Toluene) and to 0.48 for (EPDM-Toluene). The molar volume of toluene (V_0) is also required and it is equal to 106.26 $cm^3\ mol^{-1}$. For the volume fraction of rubber in a swollen network (ϕ_2) calculation (Equation 2.7.); densities of the different rubber types and solvents are also required. These values are 0.91 g cm^{-3} for NR, 0.86 g cm^{-3} for EPDM and 0.867 g cm^{-3} for Toluene. For swelling measurements specimens of 14mm diameter are cut from vulcanizated 1mm thickness sheets. Network chain density was calculated as an average of 3 measurements for each vulcanizate.

Thiol-amine chemical-probes

Saville and Watson[39] and Campbell[16] showed that the fraction of mono-, di- and polysulfidic crosslinks could be determined by selective decomposition; using thiols activated by an amine (see section 2.3.2.5.). Due to steric hindrance and a lower nucleophily, propane-2-thiol is less reactive than hexane-1-thiol. As stated before, treatment of NR vulcanizates of 1mm thickness with hexane-1-thiol cleaves disulfidic and polysulfidic crosslinks while treatment with propane-2-thiol cleaves only polysulfidic crossinks (Figure 2.6.).

Equilibrium swelling measurements yield:

- Before any treatment, the total crosslink density (S_1 + S_2 + S_X).
- After treatment with propane-2-thiol, the mono- and disulfidic crosslink density (S_1 + S_2).
- After treatment with hexane-1-thiol, the monosulfidic crosslink density (S_1).

Finally, the propane-2-thiol and the hexane-1-thiol detailed treatment methodologies will be following summarized:

PROPANE-2-THIOL

Specimens are pre-swollen in n-heptane under nitrogen overnight at room temperature, followed by a treatment with propane-2-thiol (0,4M) and piperidine (0,4M) in n-heptane for 2 hours. Before reaction n-heptane is evacuated under nitrogen atmosphere and substituted by 100mL of the reaction mixture. Reagents are stirred and maintained under nitrogen during the treatment. After the 2h reaction, the chemical probe is removed from the network by washing with 100 mL petroleum ether, also under nitrogen atmosphere. This washing step consists in 4 extractions with 100mL petroleum ether. The samples are kept under agitation: twice for 30 minutes and twice for 60 minutes. Specimens are then removed and dried overnight in vacuo (oil pump).

HEXANE-1-THIOL

Treatment with hexane-1-thiol (1M) in piperidine is carried out at room temperature under vacuum (water pump) for 72 hours. Specimens are sheltered from light and vacuum is renewed every 24h. No pre-swelling is carred out. After the reaction, the chemical probe is removed from the network by washing with 100 mL petroleum ether, also under nitrogen atmosphere. This washing step consists in 4 extractions with 100mL petroleum ether. The samples are kept under agitation: twice for 30 minutes and twice for 60 minutes. Specimens are then removed and dried overnight in vacuo (oil pump).

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Chapter 3

Study of the Influence of Microwaves on the Accelerator: Sulfenamides and Thiurams

The natural rubber (NR) vulcanization mechanism has been studied using microwaves (MW) as a heating source. The influence of such heating system on the mechanism reaction has been elucidated. In order to simplify the study of this process, squalene has been used as a Model Compound Vulcanization (MCV) for NR; and N-cyclohexyl-2-benzothiazolesulfenamide (CBS) and tetramethylthiuram disulfide (TMTD) as accelerators. The accelerator fading, the formation of the active sulfurating agents, the crosslink degree, the reversion process and the effect of the double bond have been studied and the results have been compared with results obtained by conventional heating (CH). As well as the expected reaction rate increase, a noticeable change in the crosslink degree has been observed. Furthermore, some differences have been detected in the amount of the intermediate compounds formed during the reaction and in the sulfur transfer to the squalene chain.

3.1. INTRODUCTION

As mentioned in section 2.1., the nature of the vulcanizing system has a considerably influence since this will determine the structure of the crosslinks and the extent to which the polymer chains are modified chemically during vulcanization. The accelerator system will be decisive primarily by the needed scorch delay and cure time, together with the modulus and other properties. In literature two reasons for scorch delay have been suggested: the thermal stability of the accelerator and alternatively exchange reactions between accelerator polysulfides and other reaction intermediates. Although the thermal stability of the accelerator clearly affects the scorch time, the exchange reactions involving the accelerator polysulfides are generally specified as the controlling mechanism. On the other hand, the modulus of a given vulcanizing system depends also on the accelerator and it has been found to vary with sulfur loading according to the relation,

$$\text{modulus} = (\text{phr sulfur} \cdot \text{phr accelerator})^n \text{ , where } n \approx 0.5$$

Different accelerator families have been presented in chapter 2 and although each accelerator family have different vulcanizing characteristics, it can be emphasized that all of them contain a common functionality (N=C-S). A graphic showing the vulcanizing characteristics (influence in the scorch time and the cure rate after scorch) of every accelerator type is presented in Figure 3.1. The fastest curing accelerators are the dithiocarbamates, being thiurams the mostly used group of this family. On the other hand, sulfenamides give excellent scorch delay and a reasonably rapid cure rate (delayed-action accelerators). General classification of accelerators describes thiurams as safe and fast curing accelerators, while sulfenamides are known for their safe processing and delayed action in the crosslink. In this chapter the study of the influence of microwaves in these two accelerator families will be discussed, just us the influence when working with the both together.

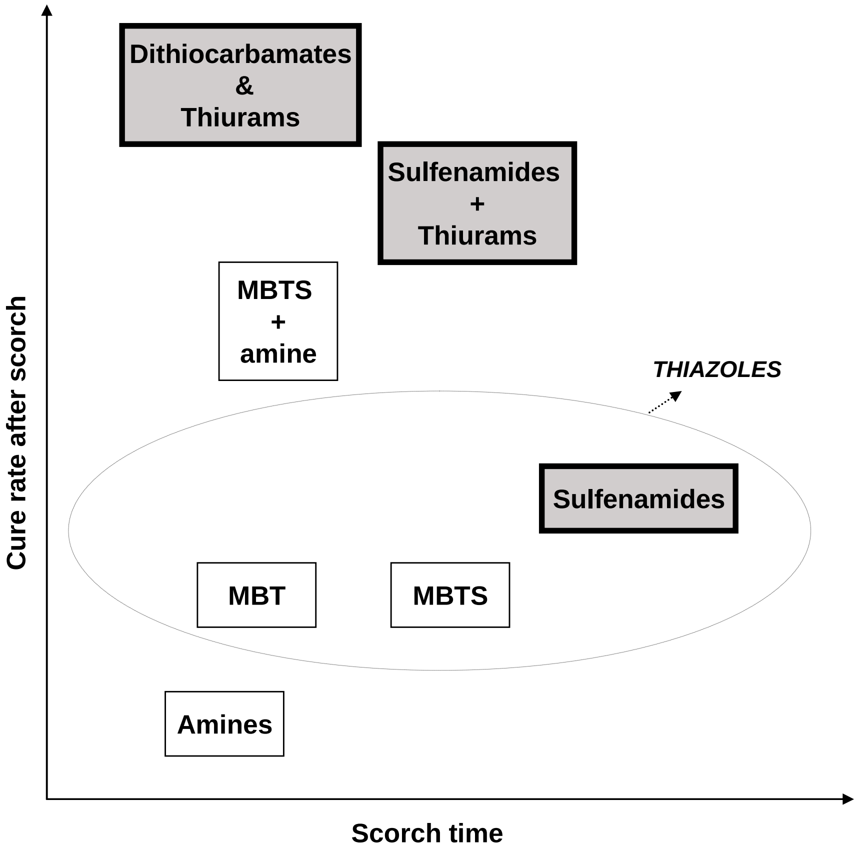


Figure 3.1. Vulcanizing characteristics of different accelerator systems[1].

A combination of zinc oxide and stearic acid is used as activator system with the various organic accelerator types. The zinc oxide activates the cure by complexing with the sulfur accelerator system to give a faster cure rate. Usually 2-5 phr of zinc oxide are added along with 1-3 phr of stearic acid. The stearic acid is needed to solubilize the zinc to give Zn^{2+} which can complex with the sulfur and accelerator[2]. Water is thus generated by the activator system.

$$ZnO + 2\ C_{17}H_{35}COOH \rightarrow Zn(OOCC_{17}H_{35})_2 + H_2O$$

The chemistry of accelerated vulcanization is extremely complex, especially when it is complicated by the usual practice of adding multiple accelerators and activators. If only the rubber-sulfur system is considered, the eight atom sulfur ring is broken down into free radicals and then the free radicals unite with an olefin like NR. Relations are:

$$S_8 \rightarrow \cdot S_x \cdot$$

$$\cdot S_x \cdot + 2R \rightarrow R\text{-}S_x\text{-}R$$

where R represents the rubber chain.

As explained in chapter 2, in an unaccelerated rubber-sulfur compound the sulfur linkages between chains may have one, two or more sulfur atoms (intermolecular crosslinks) but also intramolecular crosslinks and mono- and disulfidic cyclic structures, which are considered wasteful of sulfur. When accelerator and activators are added, broad changes can occur. Cure rate is increased, more intermolecular crosslinks are formed and there are less side reactions. Variation in the type of crosslinks and chain modifications are caused by the relative sulfur/accelerator ratio and this also correlates with vulcanizate properties. Concerning the mechanism of accelerated vulcanization there are some contradictory publications. Although the first studies supported a radical mechanism as when working without accelerator, some publications suggested a solute ionic process[3]. In addition, some other authors demonstrated that accelerated vulcanization is a process in which simultaneously ionic and radical reactions take place[4].

To evaluate the polar and/or the radical character of the reaction radical scavengers[5] and techniques such as Electron Spin Resonance (ESR)[6,7] have been used. Several researchers have concluded that both radical and ionic mechanisms are involved and that the precise nature is highly dependent on the formulation (Table 3.1.). These methods give general and qualitative information about the process. Before the 1960s the only thing investigators had, were proposed mechanisms which postulated that a number of intermediate compounds containing fragments of the accelerator are formed during the vulcanization cycle. However, although a number of workers had measured the change in initial accelerator and sulfur concentration in the rubber during the vulcanization; none had identified and determined the intermediate compounds which appear to be formed during the reaction. Campbell and Wise[8] were two of the first researchers that confirm the existence of these intermediates, and subsequently identified and quantitatively followed their concentrations throughout the process.

Table 3.1. Proposed mechanism for different vulcanizing systems.

MECHANISM	VULCANIZING SYSTEM
Radical	NR + CBS + S_8 NR + TMTD + S_8 NR + TMTD NR + S_8
Mixed radical-ionic	NR + CBS + S_8 + ZnO + Stearic acid
Ionic	NR + TMTD + S_8 + ZnO + Stearic acid NR + TMTD + ZnO

Next, the knowledge about the mechanism of sulfenamide and thiuram vulcanization, with conductive heating (CH), will briefly be reviewed as a base to understand the results of this chapter.

3.1.1. SULFENAMIDE VULCANIZATION CHEMISTRY

In the early 1900s the effectiveness of mercaptobenzothiazole (MBT) as an accelerator for vulcanization was discovered. The major contribution of MBT derivates to the process is the delayed action that they cause to the onset of the curing stage. Hereby providing increased process safety. This delayed action is needed to give reasonably long scorch times required for rubber processing. In 1934, Zaucher and Bogeman[9] discovered the effectiveness of sulfenamides, which are one of the most noteworthy MBT derivates providing various combinations of scorch delay and curing degree, and became of great importance. Sulfenamide type accelerators are by fast the most important commercially, and their large application stems for their ability to display a strongly retarded onset of vulcanization which increases the safety of the operation. Furthermore, they also promote rapid vulcanization and result in products with strong resistance to aging and good elasticity and tensile strength. They also appear to be less subjected to reversion than compounds cured by other systems.

There are three aspects of their structure that play a major role in the accelerator activity: (i) the basic strength and the steric hydrance of the amine group; (ii) the S-N bond strength and (iii) the mercaptobenzothiazole radical[10](Figure 3.2.).

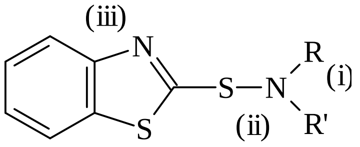


Figure 3.2. Sulfenamide structure, where R and R' are alkyl groups.

Since that time, work on accelerators has been concentrated primarily on the development of sulfenamides with more scorch delay. It was discovered that the final properties are affected by the amine involved. It is generally observed that the more basic the amine contained within the sulfenamide is, the shorter the scorch delay, but the faster the curing rate. Sterically hindered amines, however, result in longer delays and slow rates. One of the most widely used sulfenamide accelerator in rubber industry is N-cyclohexyl-2-benzothiazolesulfenamide (CBS), discovered by Harman[11] in 1937. It is a primarily amine-based accelerator which gives good scorch safety, a fast cure and good modulus development in a variety of general purpose elastomers.

Despite the progress in the development of this type of accelerators, the exact nature of the reactions taking place during the process is still quite unknown. An indication of the complexity of the subject may be the enormous amount of literature that can be found about it[12-15]. During the 1960s, the vulcanizing system based on CBS was studied by the structural characterization of the final vulcanizates[16] but it was not until the 1980s that researchers started studying the process itself. There seems to be a general agreement on the general course of vulcanization proposed by Morrison and Porter[17].

In agreement with the scheme showed in Figure 2.4., when using sulfenamides, the generally accepted reaction scheme is displayed in Figure 3.3. The sulfenamide decomposes to form amine and MBT which attacks the remaining sulfenamide to form dibenzothiazole disulfide (MBTS). It is these two reactions which give the nice scorch delay found with the MBT sulfenamides. Elemental sulfur then reacts with the MBTS giving a polysulfide (MBTP or active sulfurating agents) which attacks the allylic position of a rubber molecule to give a polythiomercaptobenzothiazyl group appended to the chain (pendant group), also known as rubber-bound intermediate compound or crosslink precursor. The CBS depletion is an autocatalytic process due to the formation of MBT. The rate of this decomposition is proportional to the amount of MBT present. In accelerated vulcanization sulfur becomes attached to the rubber hydrocarbon almost exclusively at allylic positions[18]. This is not the case with unaccelerated-sulfur vulcanization; crosslinks may form in other positions due to the radical mechanism. In the final step a second rubber molecule is attacked to the crosslink precursor by the MBT appendage, to form a sulfur crosslink containing 1, 2, 3 or more S atoms. Only the last step (crosslink formation) in the reaction sequence is detected by the rheometer curve. The above sequence of steps make clear a fact known for many years, namely, that sulfur is an effective crosslinking agent only for elastomers containing C-C unsaturation. Saturated chains cannot ordinarily be crosslinked by sulfur[2]. The initial formed crosslinks are usually polysulfidic and there is a post-crosslink chemistry or rearrangement to form the more stable mono- and disulfidic crosslinks. This involves desulfuration (crosslink shortening) and degradation, probably with concomitant main chain modifications, such as conjugated diene or triene structures, cyclic sulfide groups and final pendant groups that cannot act as crosslink precursors. During service, oxidative aging of the vulcanizates take place, as well as further maturing or reversion when the product is applied at elevated temperatures.

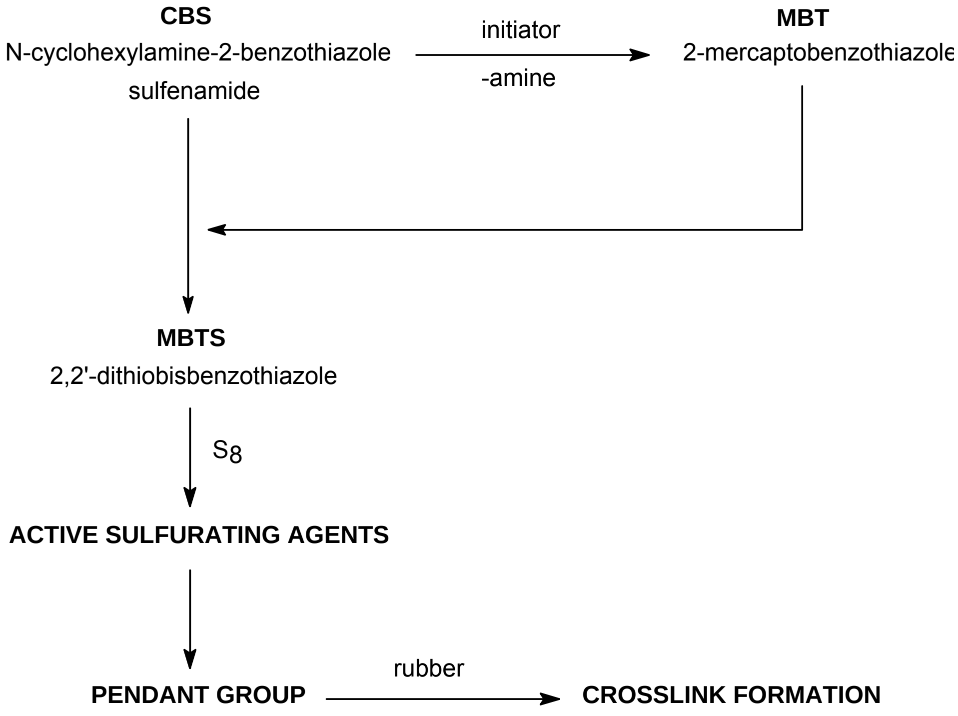


Figure 3.3. General accepted course for sulfenamide-sulfur vulcanization.

The discussion with more controversy concerns the nature of the active sulfurating agents, as to whether their contain zinc (Figure 3.4.). While some authors support the formation of a complex with zinc mercaptobenzothiazole salt making it soluble in the mixture and thereby available to react with the sulfur[19], others deny the occurrence of such a reaction of CBS or other MBT derivates[15].

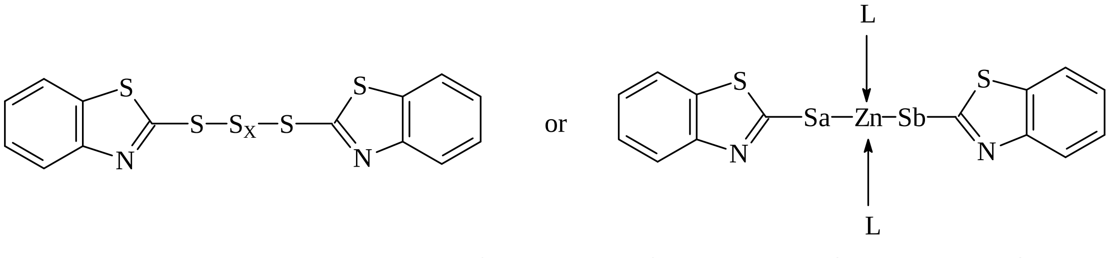


Figure 3.4. Postulated structures of the active sulfurating agents (L=amine group).

Coran[1] demonstrates that sulfenamide active sulfurating agents do not contain Zn (left structure in Figure 3.4.), although he described for dithiocarbamates that the presence of Zn^{2+} increases the rate of sulfurization through the formation of complexes with a similar structure to the one displayed in the right part of the figure above (see section 3.1.2.). For sulfenamide vulcanization he proposed a complex with a different structure. Next, the role of zinc and the intermediates formed in benzothiazole accelerated vulcanization will be presented. An increase in the concentration of fatty acid, and hence an increase in the concentration of available Zn^{2+}, causes an increased overall rate in the early reactions which lead to the formation of pendant group. However, it gives rise to a decrease in the rate of crosslink formation but an increase in the extent of crosslinking[20]. The increase in the rates of the early reactions has been explained by the formation of a complex intermediated (ZMBTS) displayed in Figure 3.5. This chelated form of the accelerator is more reactive than the free accelerator. Then, this ZMBTS is the specie which reacts with the ionized form of sulfur to form the active sulfurating agents (MBTP), with the structure showed in the figure below. This ionized form of sulfur could be rapidly formed in a reaction between sulfur and any of a number of initiating species. Agulló[21] also contributed substantially to gaining insight in all the reactions that take place during the scorch time.

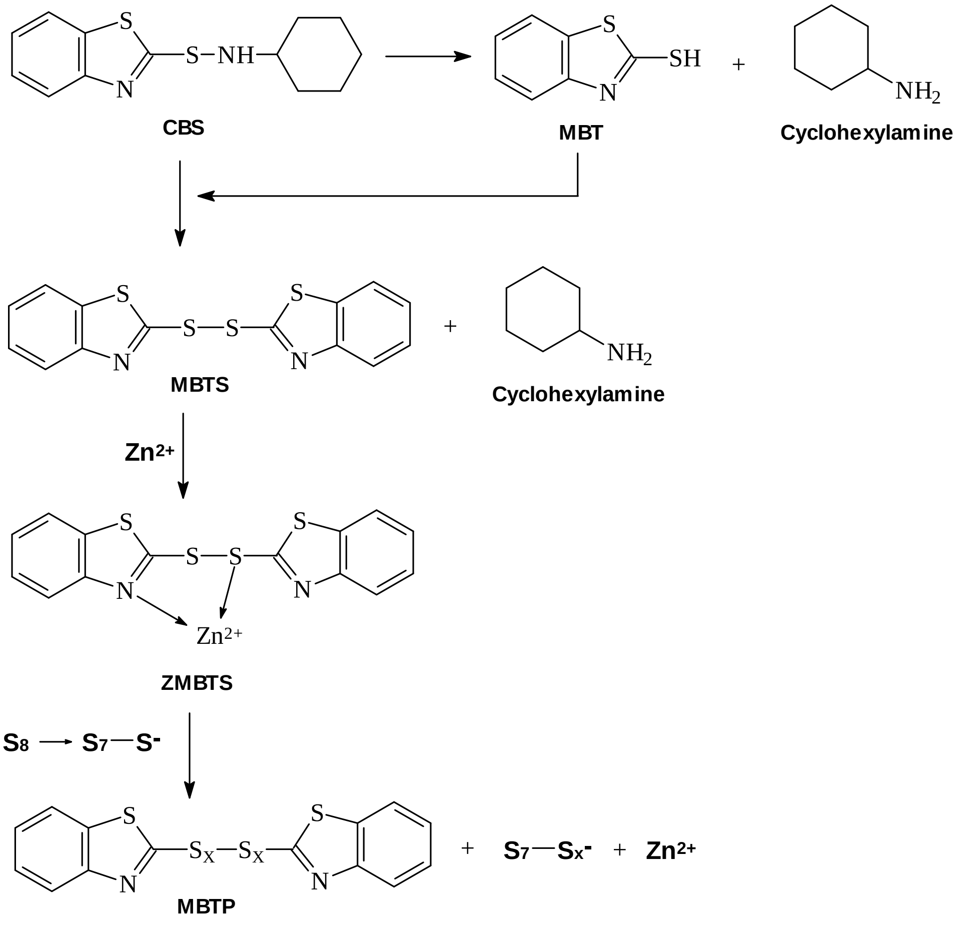


Figure 3.5. Course of the reactions taking place during the scorch time in sulfenamide accelerated vulcanization.

As stated before, the active sulfurating agents react with the double bonds present in the rubber chain giving rise to pendant group in the allylic position of a rubber molecule. Zn plays also a role in this step complexing with the accelerator polysulfides through a concerted mechanism involving a six-membered ring in the transition state[22]. The decreased specific rate of crosslink formation and the increased extent of crosslinking resulting from the presence of Zn^{2+} in benzothiazole accelerated vulcanization are explained in Figure 3.6. As listed in Table 3.1., sulfenamide accelerated vulcanization, when using ZnO as activator, passes through a mixed radical-ionic mechanism as displayed below. In the ionic pathway, zinc chelation changes the position of the S-S bond most likely to break. Since a stronger bond must break, the rate is slower. Though the rate of crosslinking is slower, the extent of crosslink formation is increased because less sulfur is used in each crosslink.

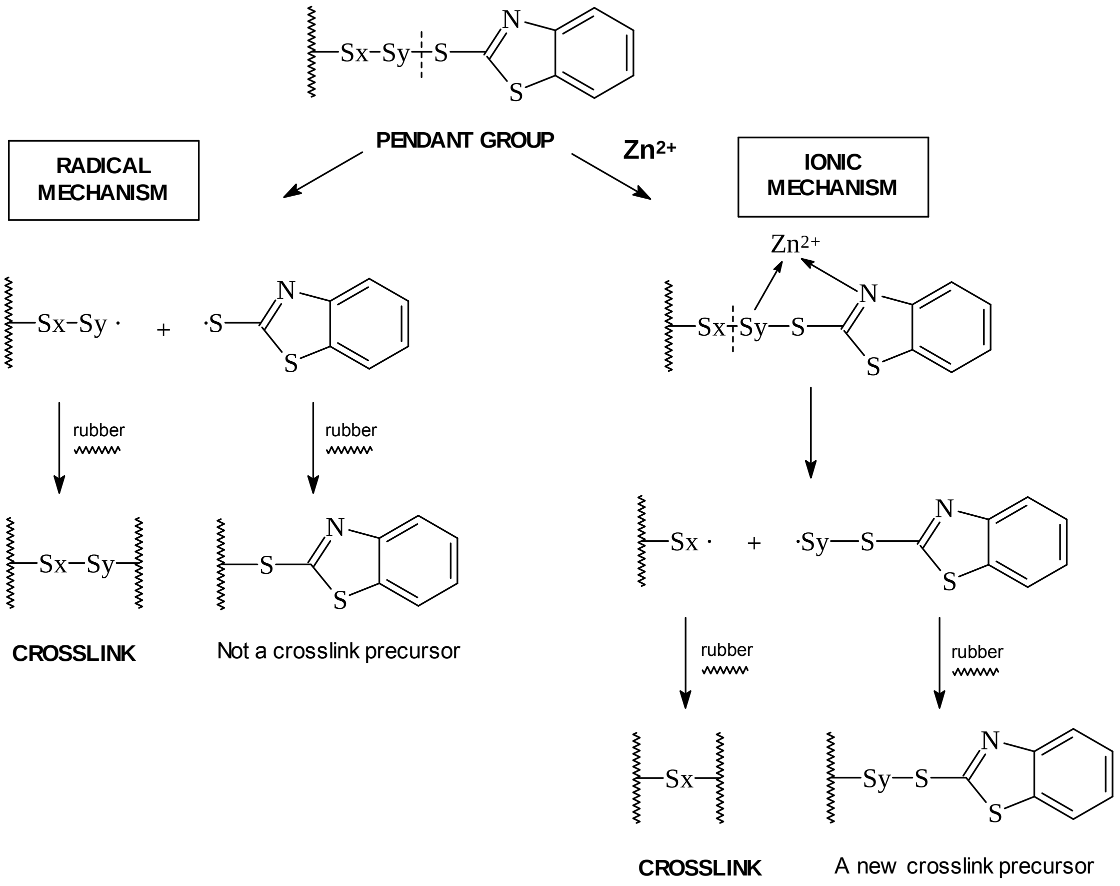


Figure 3.6. Crosslinking mechanism of sulfenamide accelerated vulcanization.

3.1.2. THIURAM VULCANIZATION CHEMISTRY

Thiuram sulfides were developed as successors of the dithiocarbamate accelerators. Because of their high curing rates, dithiocarbamates and their derivates are sometimes known as ultra-accelerators. Oxidation of dithiocarbamates results in the formation of thiuram disulfides. They came in use around 1918 and are reaction products from carbon disulfide and aliphatic amines[23]. These were, and still are, the most active accelerators with respect to both crosslinking rate and corsslinking degree. However, most of the thiuram accelerators give little or no scorch resistance and their use is impossible in many factory processing situations[24]. They are widely used for low-temperature and rapid high temperature vulcanization. The basic thiuram structure is presented in Figure 3.7. The most important products in this range though, are the tetraalkylthiuram disulfides. The vulcanizates obtained are characterized by a predominantly short crosslink network, a fact that explains their low reversion and good heat resistance. Within this group tetramethylthiuram disulfide (TMTD) is by far one of the most commonly used.

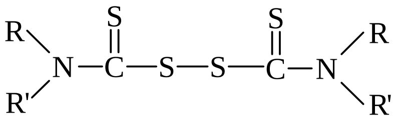


Figure 3.7. Thiuram structure, where R and R’ are alkyl groups.

Most of what is has been said about the general course of vulcanization using sulfenamides is applicable to thiurams accelerators (see Figure 2.4.). And in this case, again, there is a few clear evidence of the reaction paths that thiuram undergoes during the process. The major difficulty of studying these compounds is based on their ability to act both as accelerators and/or sulfur donors[25], i. e. they cure without the addition of sulfur since some of the sulfur in the compound is available for crosslinking. TMTD has 13,3% available sulfur for vulcanization[26].

Sulfur donation is considered to occur by predominantly radical mechanism, whereas the accelerator behavior is believed to follow the ionic/polar pathway. The overall character of a vulcanization reaction in which TMTD takes part, is highly dependent on the other ingredients of the vulcanizing system[27]. This fact might lead researchers to confusing conclusions when the reaction paths TMTD undergoes are generalized. The most widely accepted theory is that in the mechanism of thiuram accelerated sulfur vulcanization, ionic and radical reactions take place at the same time. Which one of them is predominating depends on both the other ingredients and the stage of the reaction[28]. For example, Geyser et al.[29] suggested a radical mechanism for the homollytic cleavage of TMTD leading to tetramethylthiuram monosulfide (TMTM) and tetramethylthiurea (TMTU). On the other hand, when ZnO is taken into account, a ionic mechanism seems to be predominant.

Reviewing literature published on thiuram accelerators[22], the complexity of theses systems and the apparently contradictory theories on the role of thiuram become clear. Considering for instance the role of ZnO, it is not clear in which stage of the reaction it acts. For years it has been believed that ZnO reacts directly with TMTD giving rise to zinc dimethylthiocarbamate and zinc dimethyldithiocarbamate (ZDMC), the latter, by reaction with a thiuram polysulfide or sulfur, being able to form zinc dimethylperthiocarbamate (ZDAC)[30] (Figure 3.8.).

Another point which generated controversy is the identity of the active sulfurating agents. Morrison[17] attributed this role to ZDAC complexes, whereas others assume that tetramethylthiuram polysulfides (TMTP) are the most important species[31]. Although both species are able to form the crosslink precursor, any ZDAC complex has been observed or proven, due to its short life transient state. Thus, generally TMTP are considered the responsible species of the formation of the crosslink precursor.

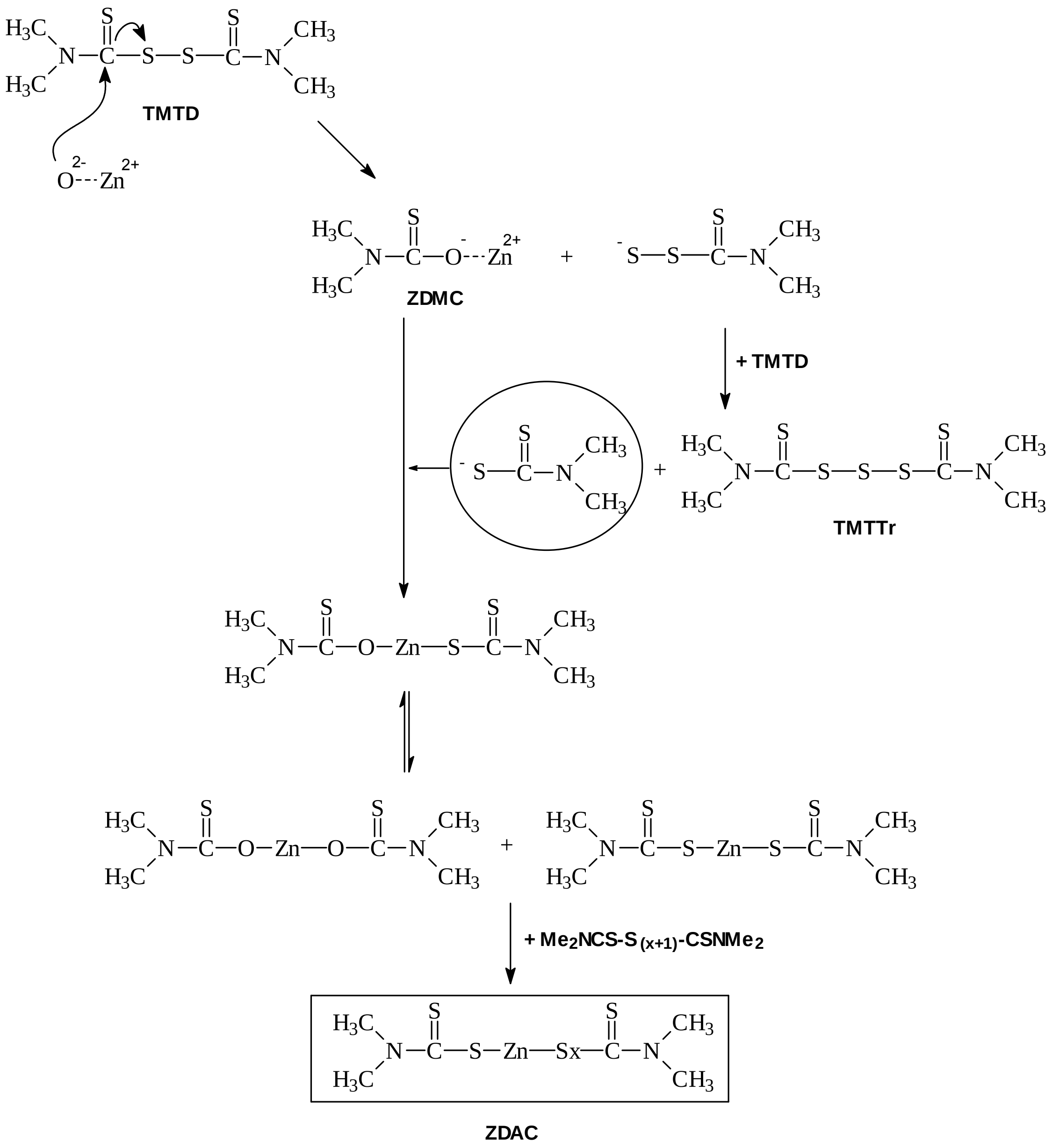


Figure 3.8. Postulated reaction between TMTD and ZnO.

Kruger and McGill[32] showed that the reaction between ZnO and TMTD, presented in Figure 3.8., is of negligible importance. They claim that the following occurs (Figure 3.9.):

(i) during thiuram accelerated vulcanization dimethyldithiocarbamic acid (DMDCA) is formed as a by-product

(ii) this acid is unstable and decomposes instantly to give Me_2NH and CS_2

(iii) Me_2NH then reacts readily with thiuram molecules thus demolishing accelerator molecules and pendant groups. Since these reactions do not involve ZnO, it was conclude that ZnO is imperative to specifically trap DMDCA forming ZDMC and water thereby preventing the detrimental reactions mentioned before.

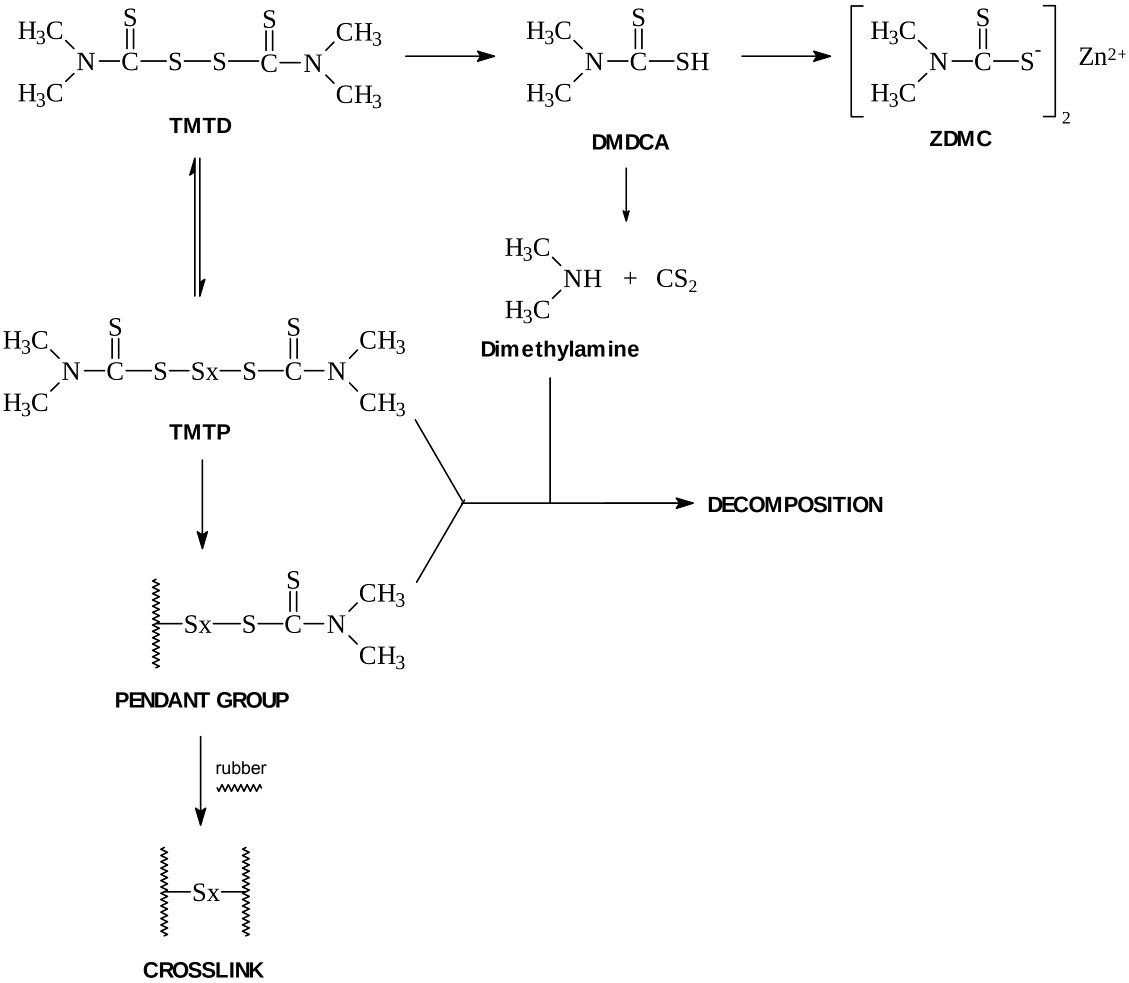


Figure 3.9. General scheme for thiuram-accelerated sulfur vulcanization.

Over the last three decades there has been a progressively growing concern over the hazard of certain organic chemicals employed in rubber vulcanization. Much focus has been on chemical compounds derived from secondary amines. N-nitrosamines with the structure R(R')N-NO (where R and R' are alkyl) have been found to be carcinogenic. Secondary amine residues from the vulcanization process could give rise to relatively stable N-nitrosamines and thus create a health and safety hazard.

Primary amine residues, as cyclohexylamine created in sulfenamide vulcanization, do not generate this concern since their N-Nitrosamines are much less stable than those from secondary amines. As a result of this concern, the use of vulcanization chemicals derived from secondary amines, i. e. thiuram accelerators, has decreased over the past two decades.

3.1.3. SECONDARY ACCELERATORS: SULFENAMIDE-THIURAM SYSTEMS

It is often necessary to speed up the cure of a stock having a specified cure system. This can be readily done through the use of a secondary accelerator, also called a “kicker”. Normally highly active accelerators, dithiocarbamates and diarylguanidines, are used to achieve this goal. The principal effects of the secondary accelerator[2] can be summarized in:

(i) a reduction in scorch delay
(ii) a faster rate of crosslink
(iii) and a lower overall cure time

In the case of TMTD an additional effect is obtained, namely a slightly higher modulus (torque) due to TMTD being also a sulfur-donor crosslinking agent as stated before. This can be corrected by a decrease in the primary accelerator. Many rubber technologists consider secondary accelerators to be activators because they “activate” the cure. Though secondary accelerators are cure activators in the general sense, the term “activator” is used specifically for those ingredients which “activate” the primary accelerator[2].

It is claimed that one effect of using mixture or two different types of accelerators can be that each one of them activates the other and better than expected crosslink rates are obtained as seen in Figure 3.1. On the other hand, mixing accelerators of the same type gives intermediate or average results[1]. The synergetic effect of such combinations has proved in terms of both processing characteristics and final product properties[33]. However, the exact interaction between the different accelerator types had not been described in detail until Agulló[21] performed a model compound study of the vulcanization process using sulfenamide and thiuram together, exploring the reactions taking place between both accelerator types and relating them to the improved process characteristics.

This chapter will discuss the effect of microwaves in the vulcanization of vulcanizing systems containing both accelerators, together and separated, using the MCV approach with squalene as a model molecule of NR. Since MW radiation is able to transfer energy to ions and radicals, as it has been explained in section 1.2.1., it is necessary to study its influence in the different accelerator systems.

3.2. RESULTS AND DISCUSSION

The experiments were performed using three different compounds (Table 3.2.). Mixture A is a vulcanizing system for studying sulfenamide vulcanization, Mixture B for studying thiuram curing and finally Mixture C was used to study the effect of the secondary accelerator in the different stages of the process. The three mixtures are conventional systems (CV) with a constant S/A ratio (1.67). All of them were vulcanized at 140ºC both using a silicon oil bath (CH) and a microwave oven (MW), as described in section 2.4.2. The obtained vulcanizates have been analyzed with different analytical methods as described in section 2.4.3. Comparing the evolution with the reaction time of the amounts of the different intermediates, the mechanism of reaction can be followed and the results of both heating methods can be compared.

Table 3.2. Composition of the mixtures studied.

INGREDIENTS	Mixture A, phr	Mixture B, phr	Mixture C, phr
Squalene	100	100	100
CBS	1.2	-	0.6
TMTD	-	1.2	0.6
Sulfur	2	2	2
ZnO	5	5	5
Stearic acid	2	2	2

Before starting presenting the differences observed in vulcanization mechanisms for every vulcanizing system, it was necessary to develop a microwave vulcanization method comparable with the conductive heating method. Basically, the only marked constraint was to develop a method (standard mode) maintaining the temperature constant at 140ºC during the whole reaction. As described in section 2.4.2., the problem of the standard mode methods is that they apply at the beginning a maximum power to achieve the desired temperature, but after and during the whole reaction they only produce little power peaks in order to maintain the bulk temperature constant at this desired value. This effect can be observed in Figure 2.8. and it was not desired since the goal of this work is exploring the effects of the microwave energy in the reactions. One possibility to increase the delivered microwave energy is to use simultaneous cooling during the microwave irradiation. This option consists in cooling the vessel cavity with compressed air during the reaction time (hold time) causing a decrease in the temperature. Therefore, the equipment is forced to apply a higher and continuous microwave supply during the reaction in order to maintain the temperature constant at the desired value. This allows a higher level of microwave power to be directly administered, but will also prevent overheating by continuously removing latent heat[34].

Thus, the influence of the simultaneous cooling process in the vulcanization has been studied. Two samples (Mixture A) were heated during 60 minutes, one with the cooling mode activated and the other without it. The results showed that the higher the microwave emission (cooling on), the more crosslink degree is achieved (Figure 3.10.). This is one of the first differences observed regarding the vulcanization mechanism in comparison with conventional vulcanization (CH). Although the bulk temperature was the same for both microwave experiments (140ºC), it has been demonstrated that the microwave power has an influence in the reaction yield. This suggests that microwave reaction mechanisms, due to the higher energy transfer efficiency, are less temperature dependent than the conductive heating processes. Differences in the reaction time were also detected, and again, the higher the power, the faster the reaction. Because of this, the cooling mode was used in all the experiments as indicated in Table 2.4.

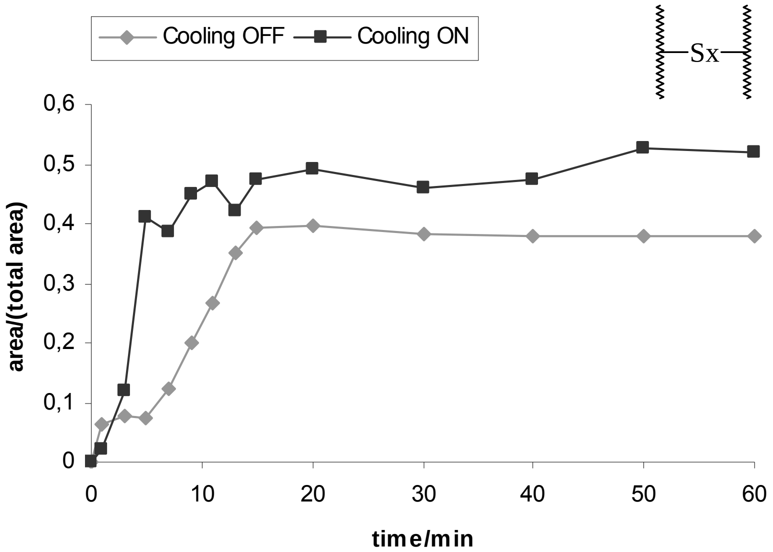


Figure 3.10. Crosslinked squalene evolution during microwave vulcanization, with and without simultaneous cooling.

Once the cooling mode was chosen, the presence of new products was checked by MALDI-ToF (Figure 2.17.) as explained in chapter 2. This technique permits the identification of some of all the species formed during vulcanization, using both conductive heating (CH) and microwave heating (MW). Comparing the intermediate compounds detected in both cases, their chemical nature seems to be independent of the heating source used, whereas the relative amounts are different, as we will see along this section. In relation to this, in all HPLC methods used in this work, no new chromatographic peaks were detected when analyzing microwave heating vulcanizates in comparison to conventional heating samples. However, although the chromatographic profiles were similar, significant differences in the resulting amounts of some species were detected and will be explained in the next sections.

3.2.1. ACCELERATOR DISSOCIATION AND ACTIVE SULFURATING AGENTS FORMATION

Although the analytical techniques do not show new intermediates formation, it should be noticed that, as it could be expected, there were enormous change in both: the set off of the reaction and its kinetic. Comparing the results obtained with microwave heating and conventional heating for the same formulation (Mixture A), it can be observed that, considering CBS degradation as a rate factor, the reaction of this compound becomes six-fold faster with microwaves heating (MW) in comparison with conductive heating (CH) under these conditions (Figure 3.11.).

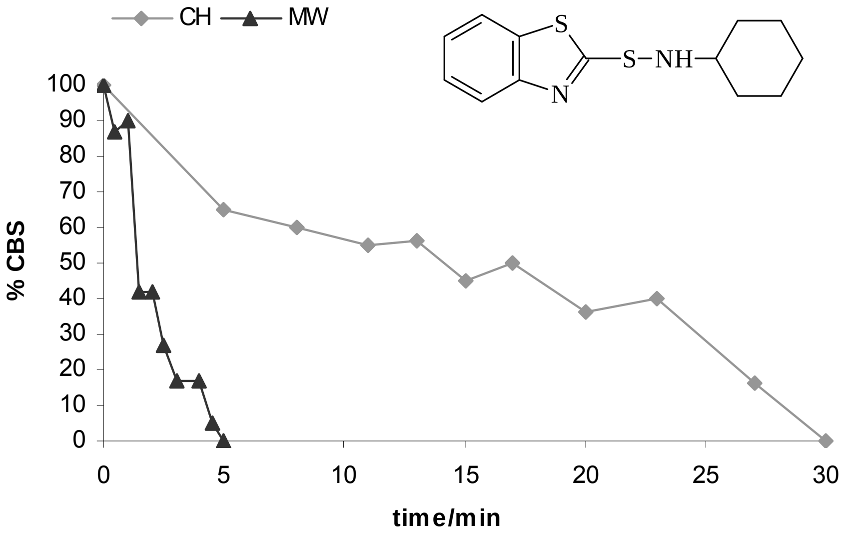


Figure 3.11. CBS degradation during vulcanization with MW and CH.

Figure 3.12. shows the same results for TMTD (Mixture B). Because this second is an ultra-accelerator, the accelerator fading is faster for both heating methods in comparison with CBS. As expected, MW are faster than CH to cleave TMTD, but this time the accelerator fading becomes ten-fold faster when using MW.

It should be emphasized that this rate factor is not a quantitative measurement of the reaction rate and that we may not conclude from these results that MW are more effective in activating thiuram accelerated vulcanization than sulfenamide vulcanization. With this rate factor measurement there is a time scale problem involved, because thiurams have faster cleavage kinetics in comparison with sulfenamides. Taking into account that after only 1 minute of vulcanization with MW method, there is complete TMTD degradation (Figure 3.12.), it is expected that this rate factor is difficult to measure, because working with such small sampling intervals causes an increase in the experimental error. Furthermore, it should be pointed out that before vulcanization, the amount of TMTD in the mixture it was 50% instead of 100%. That indicates the ability of this ultra-accelerator to break even at room temperature and with the interaction with solvents during the sample preparation. Thus, this rate factor is only a qualitative measurement of the reaction rate which helps to visualize MW activation for both systems in comparison with CH processes.

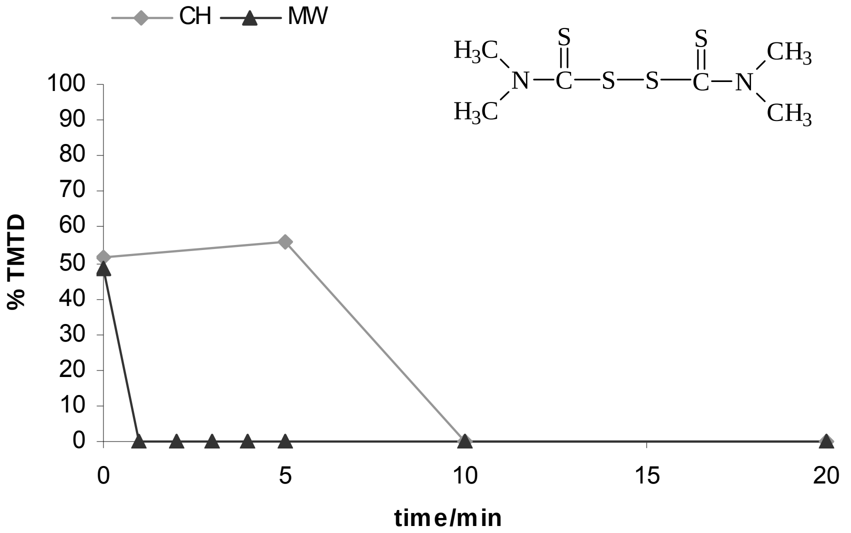


Figure 3.12. TMTD degradation during vulcanization with MW and CH.

Furthermore it is interesting to study the decomposition of the accelerator with respect to the evolution of sulfur and other intermediates in order to understand the reactions taking place during the scorch time and before the crosslink formation. Figure 3.13. shows the evolution of CBS, MBT, MBTS (as a representation of one active sulfurating agent) and sulfur with the two heating methods.

In addition to the acceleration of the reaction rate using microwave radiation (MW) as shown above, and although at first sight the profiles seem to be similar omitting the time scale, it seems that sulfur is consumed after CBS degradation when conductive heating (CH) is applied, whereas it happens simultaneously with microwaves. This consumption is due to the formation of the active sulfurating agents and consequently is related with the beginning of the crosslink process. Campbell and Wise[35] have found that in sulfenamide sulfur accelerated vulcanization with conductive heating, the sulfenamide concentration decreases rapidly in the induction period and crosslinking do not occur until the sulfenamide is totally consumed. This phenomenon can be also observed in CH results of squalene vulcanization (Figure 3.13.) looking at the sulfur consumption kinetics in comparison with CBS degradation, but not with MW vulcanization. From these results it could be concluded that, with microwave radiation differences are observed in the kinetics of formation of the active sulfurating agents with regard to CBS consumption and more significantly in the crosslinking rate in comparison with CBS degradation, as it will be seen in section 3.2.2.

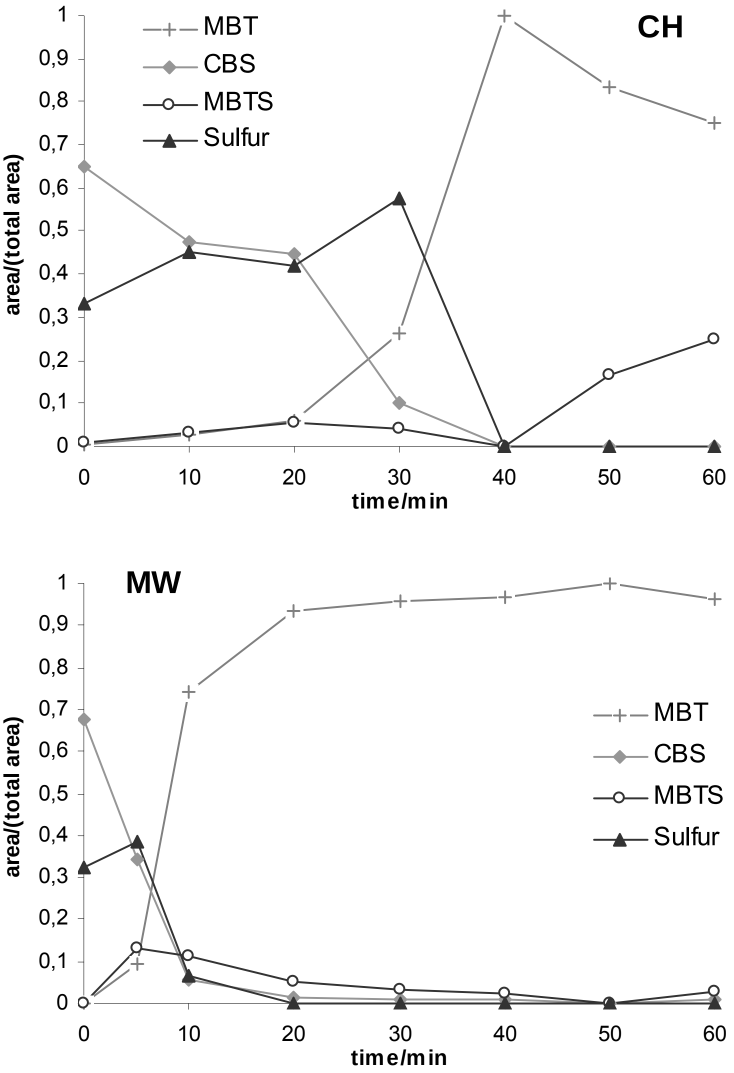
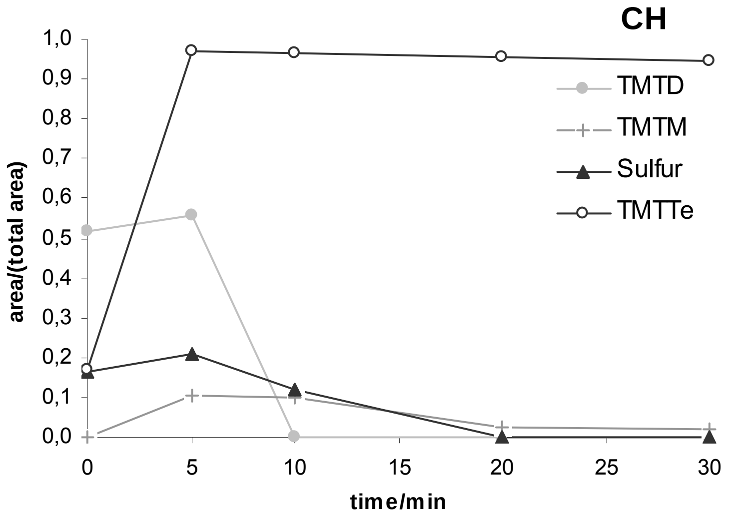


Figure 3.13. Relative amount of major compounds as a function of reaction time during squalene vulcanization with sulfur and CBS at 140ºC under CH (above) and MW (below).

In the same way, Figure 3.14. shows the evolution of TMTD, TMTM, tetramethylthiuram tetrasulfide (TMTTe) (as the active sulfurating agent mainly formed with this vulcanizing system) and sulfur with the two heating methods. For thiurams the difference in sulfur consumption with respect to TMTD degradation can not be observed when using MW. With CH TMTD is totally consumed at 10 minutes and the consumption of sulfur occurs mainly between 10 and 20 minutes. With MW vulcanization after 1 minute TMTD is completely consumed, whereas sulfur consumption takes 2 minutes. Therefore, on the contrary than sulfenamide vulcanization, no differences have been observed in the kinetics of formation of the active sulfurating agents (TMTP) with respect to TMTD degradation when using different heating sources.



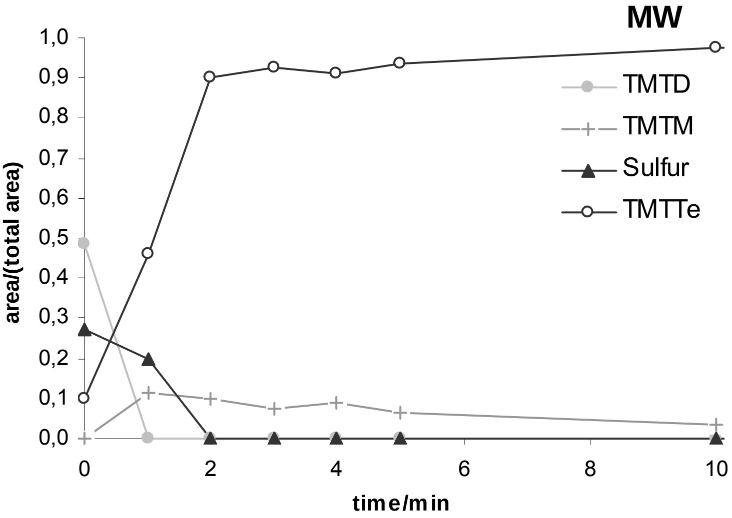


Figure 3.14. Relative amount of major compounds as a function of reaction time during squalene vulcanization with sulfur and TMTD at 140ºC under CH (above) and MW (below).

Another interesting point to study is the effect of microwaves in the first step of vulcanization process for the vulcanizing systems containing both accelerators (secondary accelerator). Figure 3.15. shows the evolution of CBS, TMTD and sulfur with the two heating methods and these results can be compared with the previously presented for the two vulcanizing systems containing one single accelerator (Figure 3.13. and 3.14.). The synergetic effect occurring when working wit a second accelerator can be observed with both heating methods. When vulcanizing Mixture A with CH, CBS is complete degrade at 30 minutes (Figure 3.11.), whereas this point occurs at 10 minutes when adding TMTD to this vulcanizing system (Mixure C) (Figure 3.15). TMTD cleavage kinetic is not affected by using a sulfenamide in the same vulcanizing system in CH vulcanization. On the other hand, and surprisingly, in MW vulcanization CBS degradation does not seem to be affected by the addition of TMTD to the mixture, whereas TMTD cleavage is working slower than when no sulfenamide is present in the vulcanizing mixture. Thus, it could be inferred, that MW seems to have more preference for sulfenamides than thiurams, although this radiation is able to activate both accelerators. On the other hand, it must be pointed out that there are few sampling points, due to the rapid reaction rate, to confirm this hypothesis and further experiments at lower time intervals during the first 10 minutes of reaction should be conducted.

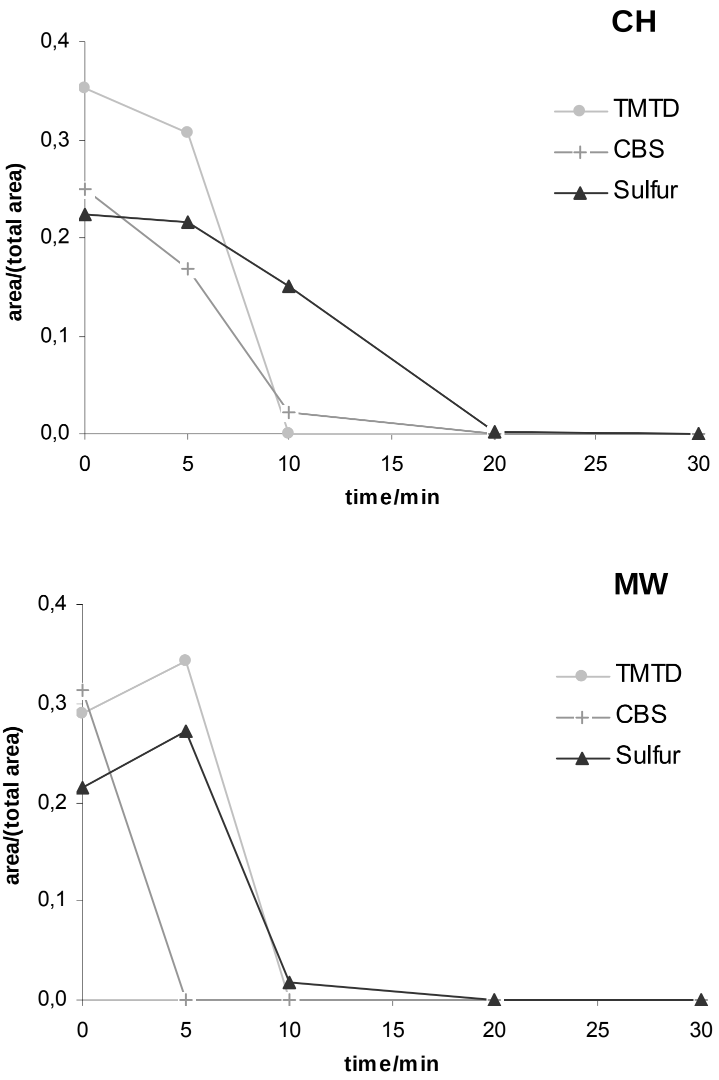


Figure 3.15. Relative amount of major compounds as a function of reaction time during squalene vulcanization with sulfur CBS and TMTD at 140ºC under CH (above) and MW (below).

Before finishing this discussion on the influence of microwaves in the reactions occurring during the scorch time, it should be remarked that although differences in the kinetics of some reactions have been detected when using MW; there are no significant differences in the amount of active sulfurating agents formed, when comparing vulcanizates of both heating methods for the three vulcanizing systems studied. As an example, Figure 3.16. displays the chromatograms of a CBS sample (Mixture A) vulcanized for 20 minutes with CH (above) and for 5 minutes with MW (below) and analyzed with the method for the characterization of the accelerator evolution described in section 2.4.3.1. Similar chromatographic profiles can be observed.

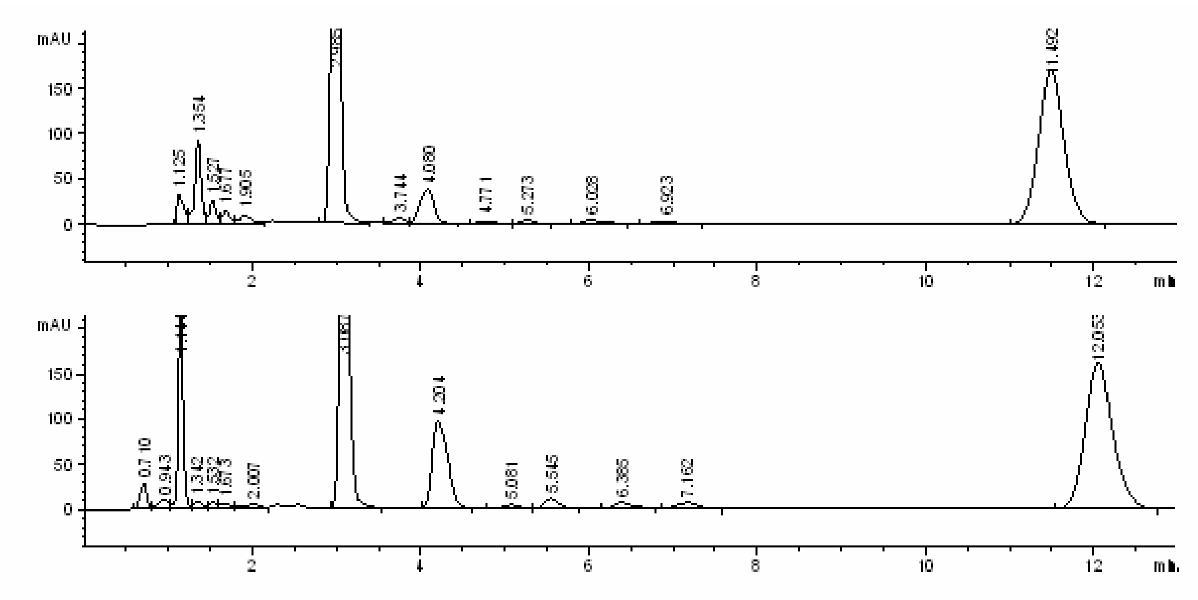


Figure 3.16. Chromatograms at 254nm of a CBS sample (Mixture A) vulcanized for 20 minutes with CH (above) and for 5 minutes with MW (below).

The last point of this section is an example, related with the accelerator, of the power of MW in comparison with CH to increase the reactivity of substances. As mentioned in the introductory chapter, one advantage that microwave energy (MW) presents over conventional heating (CH) is the capacity of overcoming high energetical barriers. This is possible due to microwaves transparency to non polar solvent, such as squalene (model molecule for natural rubber used in this study); therefore, all the energy is directed to the polar substances in the reaction media. In order to prove this hypothesis the following experiment was designed. Mixture A (Table 3.2.) was vulcanized substituting the model molecule squalene to squalane. Such change in the mixture was made with the aim of isolating the thermal degradation of the accelerator. Previous studies in our research group proved that the double bond of the model molecule catalyzes the breaking down of sulfenamide accelerator[31] and in absence of unsaturations no accelerator degradation was observed. In this study, the mixture was heated with both heating methods for 70 minutes and as it can be observed in Figure 3.17., complete dissociation of CBS occurred after 50 minutes of reaction. Thus, MW was able to thermally degrade the sulfenamide accelerator while conventional heating could not, proving the power of MW over the reactive sites on the active molecules.

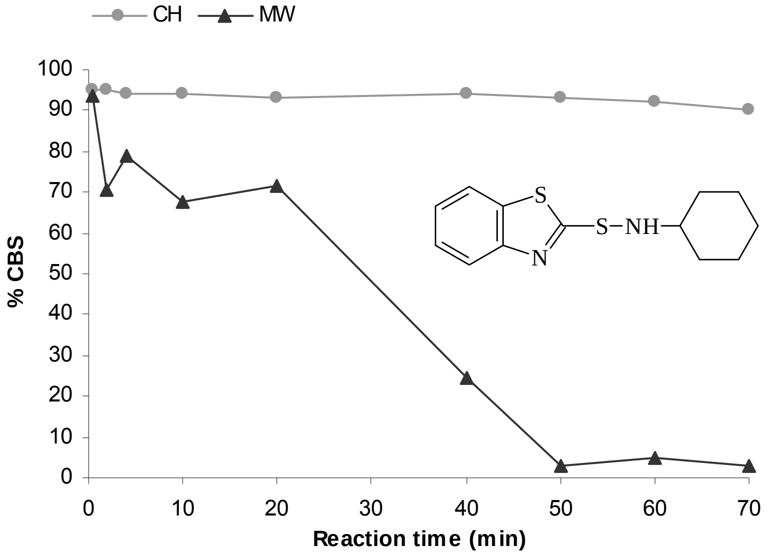


Figure 3.17. Comparison between the CBS dissociation using MW and CH and squalane instead of squalene.

3.2.2. CROSSLINK FORMATION

Regarding the second step of vulcanization process, it should be pointed out that when microwaves (MW) were used for the vulcanizing system containing sulfenamide (Mixture A); the formation of crosslinks seemed to be favored. As it can be seen in Figure 3.18., the crosslink degree achieved (calculated as the total amount of crosslinked squalene formed) was 20% much higher when MW was used and as it will be seen next, there were also differences in the crosslink structure.

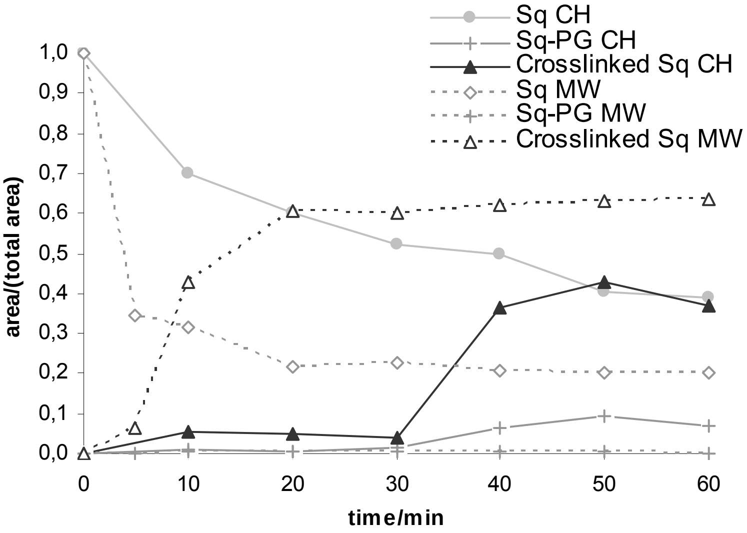


Figure 3.18. Evolution of crosslinked squalene (Crosslinked Sq), pendant group intermediate (Sq-PG) and unvulcanized squalene (Sq) in sulfenamide accelerated vulcanization with CH and MW.

Another explanation to justify the increase in the vulcanization yield caused by MW lies in the pendant group (Sq-PG) reactivity. Comparing the amount of pendant group at 60 minutes reaction with CH and with MW, it can be observed that with MW vulcanization the content of Sq-PG is very low. It could be conclude that when using MW the crosslink density is higher because all the pendant groups, formed during vulcanization, are crosslink precursors and they progress to crosslink formation; whereas most of them remain inactive when using CH. Thus, the sulfur transfer to the polymer chain is activated by MW when a sulfenamide is used as primary accelerator.

Moreover, as explained before, the crosslink process starts before with microwaves (MW) than with conventional heating (CH) with respect to CBS degradation, due to the changes in the kinetics of formation of the active sulfurating agents presented in the previous section. For CH vulcanization of squalene there is a scorch time of 30 minutes. During these 30 minutes CBS degradation occurs (Figure 3.13. (above)); and only when this process finishes, crosslink process starts (Figure 3.18.) as Campbell and Wise[35] and Agulló[21] proved. In MW vulcanization of squalene total degradation of CBS occurs at 10 minutes (Figure 3.13. (below)), but in this case it can be seen that the crosslink process starts from the beginning of the reaction (Figure 3.18.). This is evidence that MW curing works mechanistically in a different way than CH vulcanization. Campbell and Wise[34] observation is not valid for MW curing. On the one hand, the acceleration in the set off of crosslink process is patently obvious taking into account the already presented acceleration in the consumption of sulfur with respect to CBS degradation. Little amounts of active sulfurating agents are enough to start the sulfuration of the polymer chain when using MW. On the other hand, this premature vulcanization could also indicate that with MW radiation there is not only accelerated-vulcanization, but also unaccelerated curing, which is very slow process with CH. Said in other words, that MW radiation is able to increase sulfenamide accelerated vulcanization rate but also it speeds up the vulcanization of sulfur and rubber alone, and the improvement in the final results observed is the addition of both vulcanization processes taking place at the same time.

As stated before concerning the crosslink structure, some changes were also detected when working with MW in comparison with CH. Figure 3.19. displays the percentage of mono- (Sq-S-Sq), di- (Sq-S2-Sq), tri- (Sq-S3-Sq) and tetrasulfic (Sq-S4-Sq) crosslinks in three different samples: 60 minutes CH vulcanizate, 60 minutes MW vulcanizate and 30 minutes MW vulcanizate. This last sample has been included to this comparison because 60 minutes MW vulcanizate does not correspond exactly to 60 minutes CH sample due to the already commented changes in the kinetics of vulcanization when changing the heating source. MW curing is faster than CH vulcanization; as seen in Figure 3.18., MW curing reaches the Plateau at 30 minutes, whereas this point occurs at 60 minutes for the CH process. Therefore, 60 minutes CH vulcanizate is comparable with 30 minutes MW sample, but it would also be interesting to know what occurs to the network structure during the last 30 minutes of MW process (study the MW aging during Plateau). Disulfidic crosslinks were mainly formed when using MW (≈ 55%). This type of crosslink is also the most formed when using CH[36] (also ≈ 55%), although the absolute crosslink density value is higher for MW as it has been presented before (Figure 3.18.). The main effect of MW seems to be the increase in monosulfidic formation. Comparing the 60 minutes CH vulcanizate with the 30 minutes MW sample, it must be pointed out that disulfidic crosslink percentage remains equal whereas there is little decrease in polysulfidic crosslinks (from 44% in CH sample to 40% in MW sample) leading to the formation of 4% monosulfidic crosslinks. This trend is even more evident when comparing the samples of 60 minutes with both heating methods: there is only 1% monosulfidic crosslinks in CH sample (normal amount for a conventional system) whereas MW sample contains 15% of this crosslink type. These results indicate the dramatic effect of MW radiation in the crosslink distribution of the final vulcanizate and they highlight the MW ability to promote a more efficient vulcanization when working with sulfenamide systems. It seems that even when working with a conventional system (CV) (S/A =1.67), MW vulcanization lead to a final network that is more similar to an efficient system (EV) by increasing the number of monosulfidic crosslinks. The significant changes observed in the crosslink degree and in the crosslink structure for sulfenamide-accelerated vulcanization likely influence the final properties strongly.

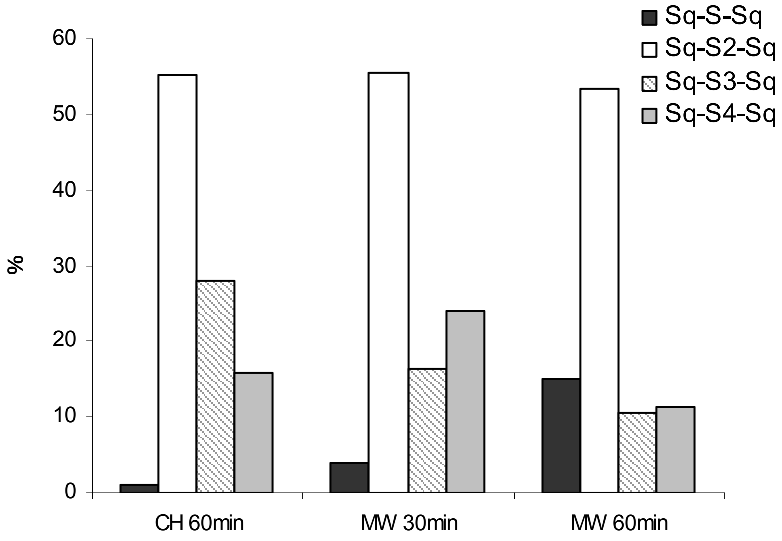


Figure 3.19. Distribution of sulfidic crosslinks (crosslink structure) in a CH 60 minutes vulcanizate, a MW 30 minutes vulcanizate and a MW 60 minutes sample (Mixture A).

The same study was performed for the vulcanizing system containing thiuram as primary accelerator (Mixture B). In this case the crosslink process is faster when using MW, but the crosslink formation does not seem to be as favored as in the sulfenamide system. As it can be seen in Figure 3.20., the crosslink degree achieved (calculated as the total amount of crosslinked squalene formed) was the same with both heating methods, with the difference that MW curing reaches Plateau at 5 minutes, whereas the same point takes about 30 minutes for the sample cured by CH method. Contrary to sulfenamide system, the pendant group content was always higher for MW curing than for CH vulcanization. Thus, it can be concluded that the higher reactivity of crosslink precursors (Sq-PG) observed in sulfenamide MW vulcanization does not occur in thiuram MW curing. Maybe this is one of the reasons for not enhancing the crosslink density when using MW in the thiuram accelerated-vulcanization.

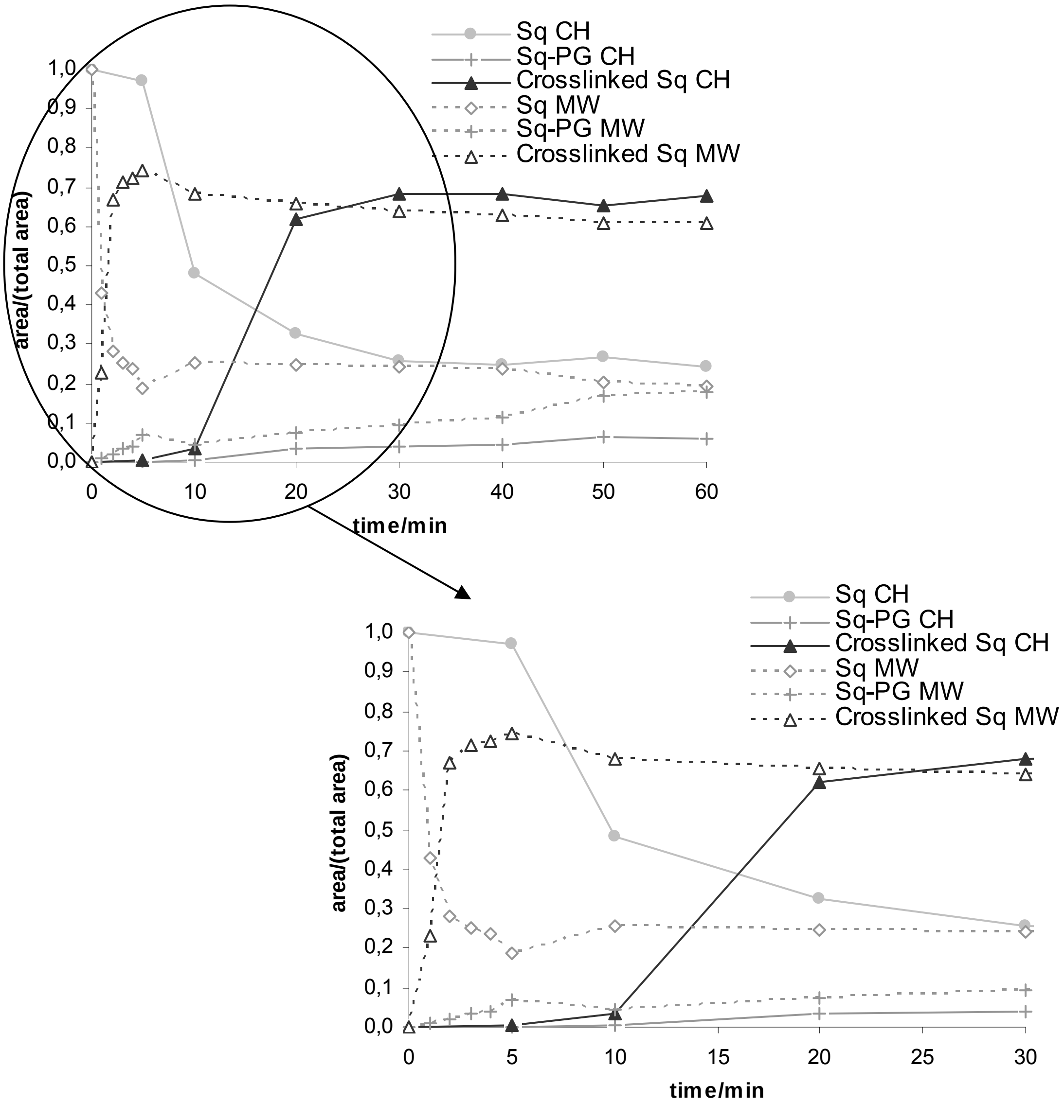


Figure 3.20. Evolution of crosslinked squalene (Crosslinked Sq), pendant group intermediate (Sq-PG) and unvulcanized squalene (Sq) in thiuram accelerated vulcanization with CH and MW.

Regarding the crosslink structure, only little changes were detected when working with MW in comparison with CH. In the same way than before, Figure 3.21. displays the percentage of mono- (Sq-S-Sq), di- (Sq-S2-Sq), tri- (Sq-S3-Sq) and tetrasulfic (Sq-S4-Sq) crosslinks in three different samples: 30 minutes CH vulcanizate, 30 minutes MW vulcanizate and 5 minutes MW vulcanizate. This last sample has been included to this comparison because 60 minutes MW vulcanizate does not correspond exactly to 60 minutes CH sample. MW curing is faster than CH vulcanization; as seen in Figure 3.20., MW curing reaches the Plateau at 5 minutes, whereas this point occurs at 30 minutes for the CH process. Therefore, 30 minutes CH vulcanizate is comparable with 5 minutes MW sample, but it would also be interesting to study the MW aging (overcuring) during Plateau (30 minutes MW vulcanizate). In this case no significant changes can be observed in the crosslink structure. For thiuram conventional system (Mixture B) disulfidic and polysulfidic crosslinks are the mainly formed with both heating sources. In addition, comparing both samples of 30 minutes reaction, it can be concluded that MW overcuring of thiuram vulcanizates promote a soft desulfuration of polysulfidic crosslinks giving rise to disulfidic crosslinks in this case, instead of the monosulfidic crosslinks formed with the MW aging of the sulfenamide system (Mixture A). From all these results it can be concluded that MW do not dramatically affect thiuram accelerated vulcanization.

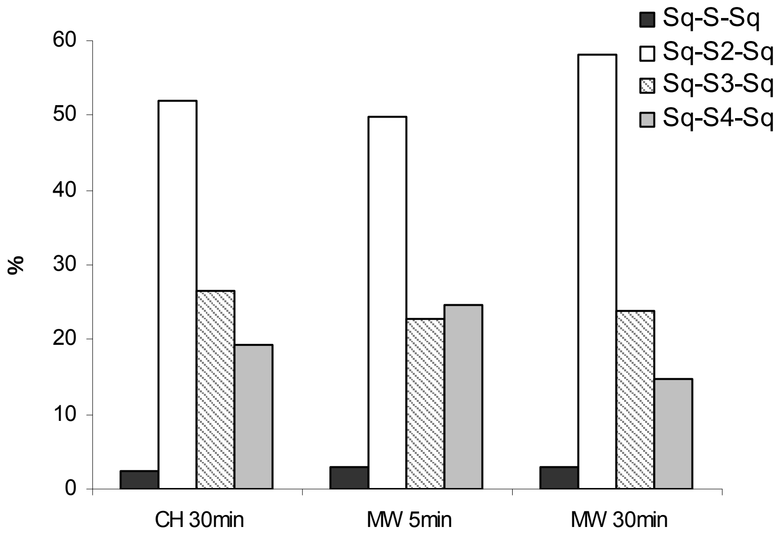


Figure 3.21. Distribution of sulfidic crosslinks (crosslink structure) in a CH 30 minutes vulcanizate, a MW 5 minutes vulcanizate and a MW 30 minutes vulcanizate (Mixture B).

Finally, the results obtained for the secondary accelerator system (Mixture C) will be next presented. Figure 3.22. displays the evolution of squalene (Sq), crosslink intermediate (Sq-PG) and crosslinked squalene during CH and MW vulcanization. The same conclusions as in thiuram accelerated vulcanization can be deduced. On one hand, MW promotes a faster reaction, but the same crosslink density is reached with both heating methods. Furthermore, the amount of pendant group is always higher when working with MW. On the other hand, Figure 3.23. shows the crosslink distribution of three different vulcanizates: 30 minutes CH vulcanizate, 30 minutes MW vulcanizate and 5 minutes MW vulcanizate. Comparing the crosslink nature of 30 minutes CH vulcanizate with the 5 minutes MW vulcanizate, it can be seen that although the main crosslink type is disulfidic in both samples, MW formes 10% less disulfidic crosslink than CH due to the formation of more polysulfidic and monosulfidic crosslinks. The MW aging of this sample leads to desulfuration forming a network rich in disulfidic crosslinks (60%). In this case it can be also concluded that MW do not dramatically affect the vulcanization of sulfenamide-thiurams systems as it does with sulfenamide systems.

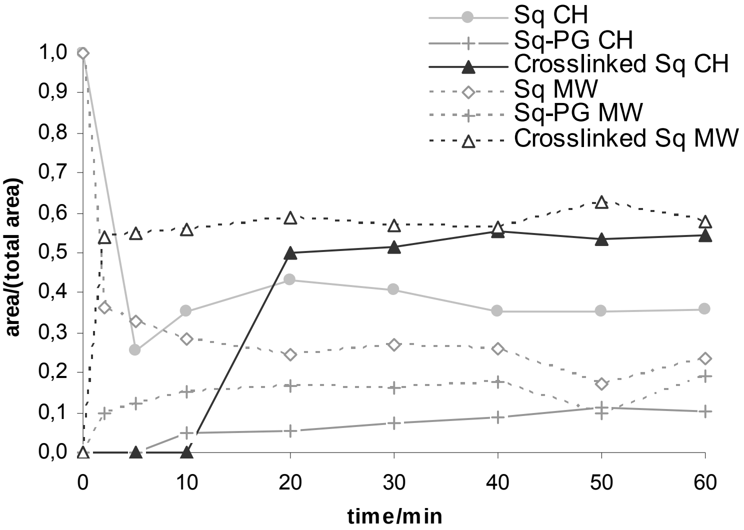


Figure 3.22. Evolution of crosslinked squalene (Crosslinked Sq), pendant group intermediate (Sq-PG) and unvulcanized squalene (Sq) in second accelerator vulcanization with CH and MW.

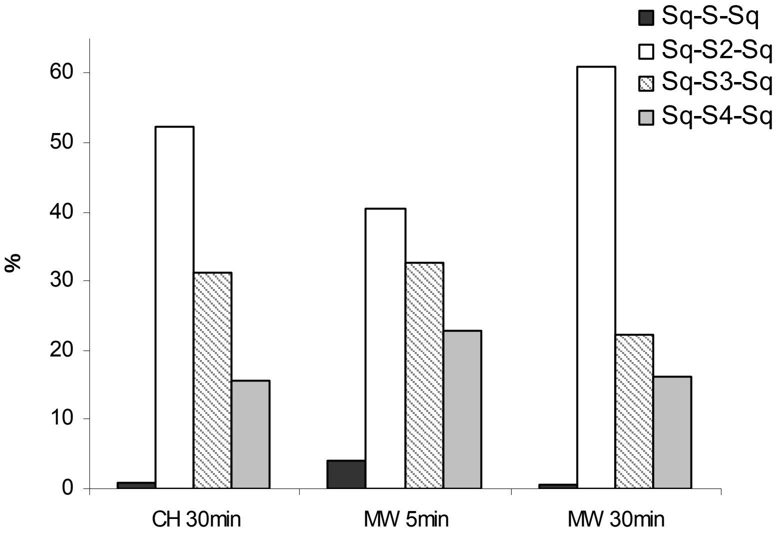


Figure 3.23. Distribution of sulfidic crosslinks (crosslink structure) in a CH 30 minutes vulcanizate, a MW 5 minutes vulcanizate and a MW 30 minutes vulcanizate (Mixture C).

Figure 3.24. summarizes the effect of microwave in the crosslink degree of the different accelerator systems presented in this section. It can be observed that MW always has an influence in the speed of the processes and also in the yield, although the highest effect has been detected for sulfenamide accelerated vulcanization. This increase in

the crosslink density caused by the use of MW when vulcanizing with CBS is also accompanied by enrichment in monosulfidic crosslinks in the final network. The role of activator has been also studied deeply in the different vulcanizing systems, but these results will be presented in the next chapter (Chapter 4).

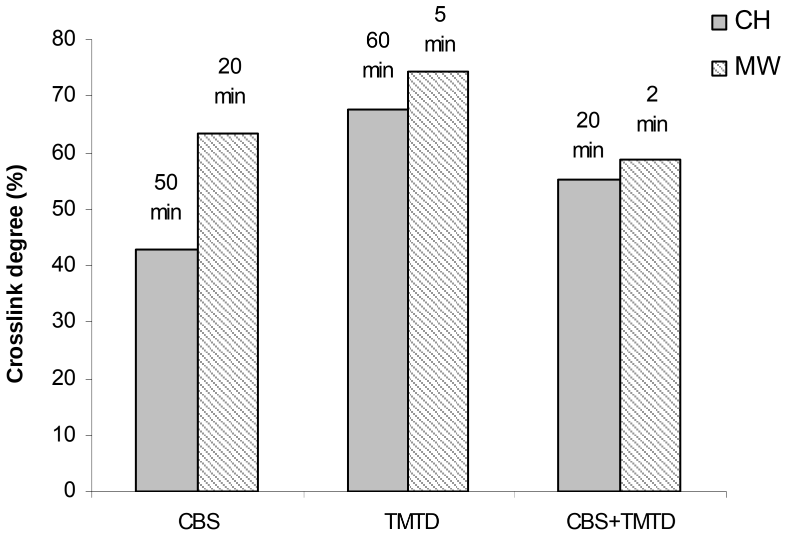


Figure 3.24. Effect of MW in the crosslink degree of the different accelerator systems.

3.2.3. TPhTD AS A NITROSAMINE-FREE THIURAM

There is no doubt about the efficiency of thiurams to vulcanize rubber. As it can be seen in the previous figure, the highest crosslink degree is reached with TMTD and also crosslink process is produced with good kinetics. However, as stated before, the use of these accelerators has decreased over the past two decades due to their environmental impact caused by the formation of nitrosamines derived from the secondary amines generated during the process.

Nitrosamines are considered a potential threat for human health since they are known to be cancirogenic, tertogenic and mutagenic. Existing legislation limits the maximum tolerated nitrosamine concentration for the rubber industry to 1μg/m^3 in the air. Studies on different thiuram based accelerators have shown that those accelerators derived from sterikally bulky amines are less likely to form nitrosamines[37]. On the contrary, even though they are more environmentally friendly than TMTD, normally they present very slow vulcanization kinetics which prevents their use at industrial scale. Since MW have been proved to enhance the vulcanization rate of different vulcanizing systems in the previous sections, the aim of this section is to improve the accelerator behavior of theses thiuram based accelerators containing sterikally bulky amines with the help of MW.

In this work Tetraphenylthiuram disulfide (TPhTD) has been studied as one possible substitute for TMTD as thiuram accelerator for rubber vulcanization. This study has been performed with CH, but also with MW. Figure 3.25. shows the molecular structure of TPhTD.

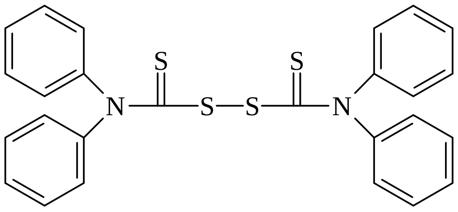


Figure 3.25. Perkacit® Tetraphenylthiuram disulfide (TPhTD).

Table 3.3. shows the model formulation prepared containing 1.2 phr TPhTD (Mixture D) instead of TMTD (Mixture B).

Table 3.3. Composition of TPhTD

INGREDIENTS	Mixture D, phr
Squalene	100
TPhTD	1.2
Sulfur	2
ZnO	5
Stearic acid	2

As it can be seen in Figure 3.26., the crosslink degree reached was 10% much higher when MW was used for Mixture D vulcanization and as it will be seen next; there were also differences in the crosslink structure.

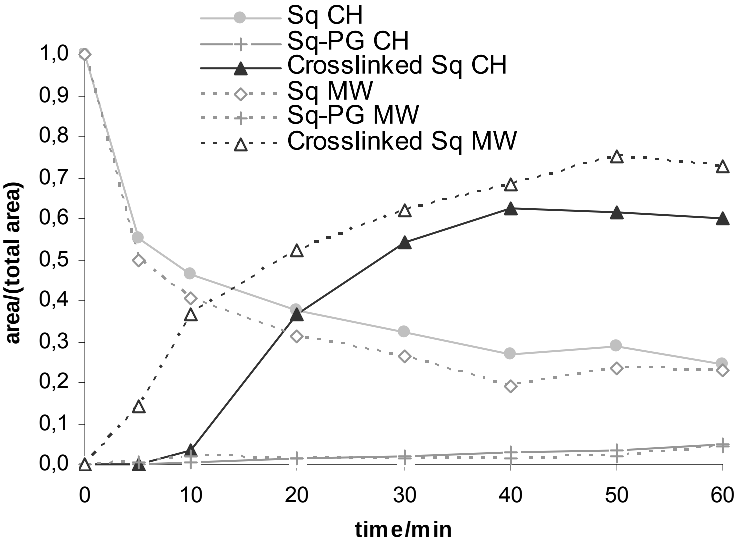


Figure 3.26. Evolution of crosslinked squalene (Crosslinked Sq), pendant group intermediate (Sq-PG) and unvulcanized squalene (Sq) in TPhTD accelerated vulcanization with CH and MW.

It should be pointed out that comparing with TMTD, the crosslink kinetics are very slow for both heating methods. Furthermore, TMTD vulcanization gave rise to 70% crosslinked squalene with CH and 75% with MW (Figure 3.20.), whereas TPhTD crosslinked only the 60% of squalene with CH and reached also the 75% crosslinked squalene with MW vulcanization. Finally, the crosslink structure of the two TPhTD vulcanizates afer 60 minutes (CH and MW) in reference to the results obtained for TMTD with CH is presented in Figure 3.27. It can be observed comparing both samples heated with conventional heating that TPhTD gives rise to a higher amount of disulfidic crosslinks than TMTD. This effect is even higher when using MW. Even when working with conventional systems (CV) (S/A=1.67), the resulting network when using TPhTD in MW vulcanization contains low amount of polysulfidic and monosulfidic crosslinks and a large amount of disulfidic crosslinks. This proves again that MW promotes a more efficient vulcanization than CH, independently of the vulcanizing system used (S/A ratio).

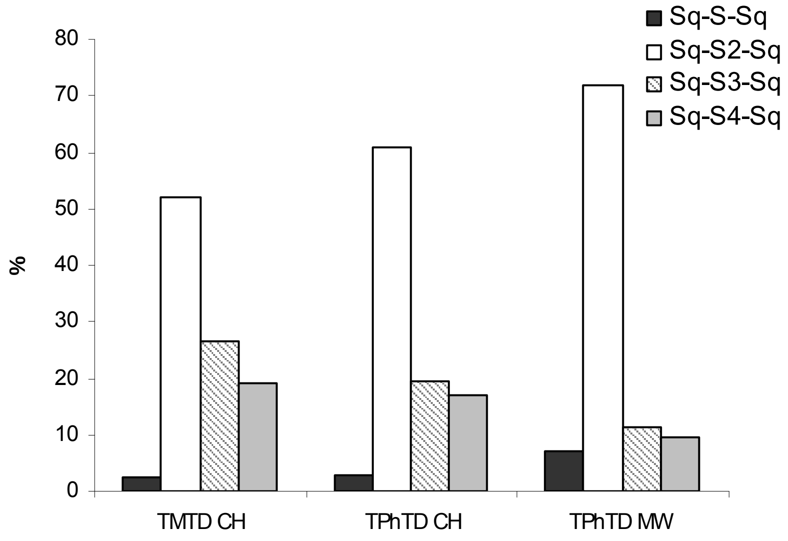


Figure 3.27. Distribution of sulfidic crosslinks (crosslink structure) in a TMTD reference (CH 60 minutes vulcanizate) and 2 samples of TPhTD (CH 60 minutes and MW 60 minutes).

To summarize the results discussed in this section, it has been proved that MW improves the accelerators behavior of TPhTD, increasing its crosslink yield and also its crosslink rate. Furthermore, it also affects the final crosslink structure. Since all these changes demonstrated could have strong consequences in the final properties of the vulcanizate, further experiments with natural rubber samples should be conducted.

3.3. REFERENCES

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Chapter 4

Study of the Influence of Microwaves on the Activator: substitutes for ZnO

The role of the activator in the mechanism of natural rubber (NR) sulfenamide-accelerated vulcanization has been studied using conductive heating (CH) and microwaves (MW) as heating sources. The original aim of this study was to explore the effect of microwaves on the activator system, as well as to the study of the influence of microwaves on the accelerator system already presented in Chapter 3. But in this case, a secondary objective was the reduction of the ZnO content of the activator system in order to minimize the environmental impact of the rubber goods. In the first approach, the influence of microwaves on the activator role has been elucidated and squalene has been used as a Model Compound Vulcanization (MCV) for NR. The results prove that the activator system is less critical when working with microwaves and that the metal oxide used has no influence in the crosslink density. The same study has been performed with NR samples, comparing the crosslink density and the crosslink structure of different formulations under both heating methods. Some synergetic effects between ZnO and MgO have been detected and discussed. Finally, a new family of activators has been synthesized in collaboration with the Department of Inorganic Chemistry of Universidad de Salamanca and tested as ZnO substitutes in our research group. These new activators consist of mixed oxides of Zn and Mg and have been developed to study the effect of the nanodispersion of these two metal oxides on the synergetic effect already commented.

4.1. INTRODUCTION

As it has been exposed in Chapter 3 the overall course of sulfur vulcanization is generally accepted, but there is still not general agreement in both the nature of the active sulfurating agents and the mechanism of their reaction with the rubber molecules, in particular as to whether or not zinc is involved[1]. Several mechanisms have been proposed, but fully elucidating the mechanisms remains difficult because of their complexity and the structural difficulty with analysis of vulcanizates.

From an historical point of view, the development of accelerators was paralleled by the development of activators systems. Significant has been the discovery that zinc oxide reduces the vulcanization time and has a reinforcing effect. Together with fatty acids, ZnO constitutes an activator system in which zinc becomes soluble. The combination not only improves the rate and the extent of crosslinking but also it improves many of the physical properties of the product[2].

Nowadays there is good evidence that zinc plays an important role in crosslinking, in particular in the efficiency of crosslinking. Although zinc is generally considered one of the least harmful of the heavy metals, is included on a priority list of substances which were suspected to have negative environmental effects[3]. Even though zinc is defined as a heavy metal, the statement that zinc is dangerous for the environment is not correct. Zinc is natural, recyclable and inherently part of our environment. It is the 17th most common element in the earth's crust and an essential element for humans, animals and plants[4], which is illustrated by the fact that for humans zinc deficiency can lead to adverse effects on growth, reproduction, cognition and immunity. Recently, the International Programme on Chemical Safety (IPCS) formed a Task Force on Zinc to establish Environmetal Health Criteria for Zinc. Among its conclusions, the Task Force states: "Zinc is an essential element in the environment. The possibility exists for both a deficiency and excess of this metal. For this reason it is important that regulatory criteria for zinc, while protecting against toxicity, are not set so low as to drive zinc levels into the deficiency area"[5].

Small quantities of zinc enter the environment during manufacturing processes through point source emissions to air or wastewater from ZnO producer or user industries. In addition, diffuse emissions of zinc from products, such as the wear of tires, run off from galvanized structures or roofing may enter the environment. Certain aquatic species have been shown to be sensitive to very low levels of zinc. Specifically soluble zinc compounds are therefore classified as ecotoxic to aquatic organisms. ZnO is also likely to be classified as such, which may lead to restrictions, in production or in applications of products in which it is contained. ZnO can be safely used in many applications as long as excess releases are controlled. However, if there is spillage into a watercourse then, as ZnO is in powder form, the dispersion rate is such that there would be an immediate localized toxic effect on algae in particular, because they are more sensitive to zinc than other organisms. Therefore, localized contamination sites, such as industrial plants, and diffuse sources require proper management.

Release of zinc into the environment from rubber occurs during production, during disposal and recycling of rubber products, for instance through leaching in land-fill sites. As it has been stated before, also during service conditions, e. g. through wear of tires. In view of the upcoming legislations and ecolabelling requirements for vehicle tires, for instance, it can be stated that it is desirable to keep the ZnO content in rubber compounds as low as possible, not only for environment but also for economical reasons. The increased attitude of protecting the environment, gives rise to a demand for products that entail the least amount of environmental pollution impact.

In rubber industry is well known that zinc species are the best activators for sulfur vulcanization. Over the years lower levels have been tried in order to decrease the environmental impact of the rubber goods and according to several researchers, it seems that ZnO levels can be reduced to a minimum of about 2 phr in tread compound without serious detrimental effects on properties[3,6]. A small reduction in modulus can be compensated by slightly increasing the level of accelerator. Complete elimination of zinc compounds would be rather ambitious. Domka[7] reported that with no ZnO, vulcanization of an unfilled NR compound did not occur at all. Morrison and coworkers used model compounds to analyze the behavior of several accelerator systems[8]. This work also concluded that ZnO plays a key role in the formation of the active sulfurating agents, in the formation of the crosslink precursor and in the conversion of the crosslink precursor to final network, just as in the absence of zinc little sulfurization and almost no crosslinking occurred.

ZnO reacts with most accelerators to form the highly active zinc complex. Complex formation of the zinc ion with different accelerators is critical to get efficient curing. Morgan et al[9] suggested that ZnO increases the rate of different reactions in the accelerator chemistry by facilitating the opening of the sulfur ring leading to faster sulfuration of the active sulfurating agents. The sulfur attached to the zinc in the sulfurating complex has a nucleophilic character due to the presence of zinc. Amines further increase the nucleophilicity of the sulfur in the complex and thereby increase the rate of precursor formation. Various mechanisms have been proposed for the conversion of crosslink precursor into crosslinks. In principle, any sulfur-sulfur bond in the crosslink precursor can break, but Coran et al.[10] have suggested that the weakest bond in the sulfur-sulfur bond adjacent to the benzothiazole group. Thus, without addition of ZnO this bond would break. However, in the presence of Zn^{2+}, the complex that is formed leads to a pathway, which changes the location of the split of the sulfur chain and decreases the rate of the actual croslinking. The zinc chelation stabilizes the other sulfur bonds and influences the position of the S-S bond most likely to break as shown in Figure 3.6. Without addition of ZnO this bond is unlikely to break as it could not be stabilized by resonance.

The complexity of the curing process becomes evident again in this section, when considering the role and action of the activators. The effects of ZnO can be summarized in[11]:

- Increase in vulcanization rate and crosslink efficiency.
- Improvement of abrasion resistance.
- Improvement of dynamic properties.

From the mechanistic point of view, and as stated before, several functions of ZnO in different stages of vulcanization are to be discerned:

- The initial scorch reactions proceed faster (breakdown of the accelerator, sulfur insertion in the zinc complex with the accelerator parts and crosslink precursor formation).
- The crosslinking reactions proceed with a better control and with a better distribution of sulfur in the polymer network.
- Change in crosslink distribution: the crosslinks contain less sulfur atoms, but the number of crosslinks is higher (crosslink density).

The multifunctional activity of ZnO in the accelerated sulfur vulcanization, as summarized above, clearly demonstrates the complexity of the problem of its substitution. The chances of finding a completely zinc-free curing system must be regarded rather small, and would involve a fundamental change in practice as well as chemistry of sulfur vulcanization. Nevertheless, alternative vulcanization systems without any zinc or metal species will improve the knowledge regarding the role of activators and mechanisms involved in vulcanization. Development of a new activator, which does contain only traces of zinc, but demonstrates effectiveness comparable to conventional systems, would be very interesting.

There have been a number of investigations comparing different metal oxides as vulcanization activators, mostly with TMTD in NR, with variable results. Rakhban et al.[12] analyzed the effect of various metals oxides on the extent of cure. Their work concluded that a variety of metal oxides can accelerate cure, but the degree of acceleration varies with the specific metal ion used. Duchacek[13] tested the effect of cooper, mercury, nickel, zinc, cadmium, indium, magnesium and calcium stearates on de course of CBS accelerated sulfur vulcanization of NR. Based on results and in accordance with Irving's and William's finding about the order of stability of metal complexes[14], the following order for stability of metal complexes with accelerators ligands was presented:

$$Cu^{2+}, Hg^{2+} > Ni^{2+}, Zn^{2+}, Cd^{2+}, In^{2+} > Mg^{2+}, Ca^{2+}$$

They concluded that nickel, zinc, cadmium and indium have a definite ability to form complexes, but they form significantly less strong coordination bonds than cooper and mercury. This is why zinc and cadmium form active sulfurating vulcanization intermediates. Magnesium and calcium have only a slight tendency to form these complexes.

In another research by Chapman[3], it was found that of metal oxides others than ZnO, cadmium oxide on average appears to be the best, followed by lead oxide and mercury oxide. However, in the investigation on the crosslinking of a model olefin, cupric oxide was found to give higher yields than ZnO, and nickel oxide was also quite effective[15].

Some metal oxides behave synergistically with ZnO. Replacement of half of the ZnO by an equivalent amount of CdO, PbO, Bi_2O_3, CaO, HgO or CuO in an efficient vulcanization system (EV) gave higher moduli. Other oxides gave moduli equal to or lower than with ZnO alone. Calcium oxide and magnesium oxide are apparently not so promising in conventional sulfur/sulfenamide cures, especially not in combination with ZnO. It has been reported that calcium oxide and magnesium oxide interfere with the efficient activation of ZnO[16].

Borros et al.[17-19] have studied the effect of the activator during the scorch time and during the curing time in squalene as a model of NR. ZnO, MgO, CaO and CdO were compared as activator of cure. The length of the scorch time was, amongst others, dependent on the ease of cleavage of the accelerator. To compare the amount of the intermediates formed, the reactions were carried out in squalene and squalane. Squalane does not have any double bonds and cannot react further, so there must be an accumulation of the intermediates. To determine the amount of CBS, HPLC was used. These reactions were first analyzed by measuring the amount of accelerator (CBS) as a function of time. If the activators work propertly, the amount of accelerator should decrease. After a certain reaction time, the mixture was quenched: the reaction stopped and the composition could be determined. CaO and CdO were found to be pour activators. MgO and ZnO were capable of ‘breaking’ the accelerator quite well. Gel Permeation Chromatography (GPC) was used to investigate crosslinked squalene concentration, since crosslinking increases the molecular weight of the reactants. The concentration of crosslinked squalene could be followed as a function of reaction time. ZnO performs better during curing stage than MgO.

Lautenschlaeger[16] has studied the effect of different metal oxides as activator in 2-methyl-2-pentene, as model olefin. The yield and types of products were compared from several metal oxides, like ZnO, CdO and CaO. Cadmium oxide was found to be the most effective oxide, it yielded the most monosulfidic products and hardly any byproduct were found. CaO was the worst activator. The effects of the activators were translated from the crosslink yield, the length of the sulfur bridges and the types of isomers.

In conclusion, although different approaches have been made to substitute ZnO for other environmentally friendly metal oxides, there is some controversy in the results obtained. This lack of agreement is mainly caused by changes in the vulcanizing system, since the role of ZnO changes depending on the accelerator used. However, some general conclusions can be drawn. On one hand, cadmium oxide (CdO) is the metal oxide which seems to have a better activating behavior in rubber vulcanization. Since its toxicity is even higher than ZnO, it could be concluded that CdO is not a good option to substitute ZnO. On the other hand, magnesium and calcium are the only non heavy metal oxides which form active sulfurating agents. However, their tendency to form these compounds is quite low and more important the sulfur transport to the polymeric chain is less efficient compared to ZnO. Previous studies carried comparing the activator potential of magnesium and calcium oxide in the vulcanization reaction using conventional heating[19,20], have shown that:

- When calcium oxide is used as an activator, kinetics is slower and very low crosslinking level is observed.
- When magnesium oxide is used as an activator, the accelerator reacts with good kinetics. This is due to the ability of magnesium oxide to activate sulfur[21]. However the crosslink level achieved is lower than that obtained with zinc oxide.
- Zinc oxide still remains as a better activator giving rise to a high crosslink degree.

All these studies have been performed using conventional vulcanization[21]. There is a lack of information about the influence that microwave could have on the role of the activator in rubber vulcanization. Thus, the aim of this chapter consists of improving the crosslink yield of vulcanization process using these non heavy-metal activators with the help of microwaves. The present work focused on the study of the influences of microwave radiation in the vulcanization of squalene with magnesium and calcium oxide in comparison to zinc oxide using a sulfenamide accelerator system. The initial hypothesis is based on the fact that, as seen in Chapter 3, microwaves are able to increase the crosslink density for ZnO mixtures. It would be logic that microwave could also increase the vulcanization yield when working with other metal oxides by increasing their tendency to form active sulfurating agents and improving the sulfur transport to the polymeric chain. Furthermore, taking into account that materials that absorb microwaves (as ZnO or other metal oxides) can display different rates of heating, according to their composition and the dimension of their particles, when solids. It has been proved that the inclusion of such materials in the form of powder or fibers within the mass of polymer can improve microwaves absorption and locally raise the temperature, thus increasing the hardening or improving the compaction of polymeric materials, indirectly acting as an adhesive[22]. Polymer chemistry will probably benefit greatly from the application of microwaves: in fact the presence of polar groups in the starting materials particularly favors the absorption of microwaves, allowing rapid and controlled synthesis, hardening and curing of the final products. In this manner, microwaves could contribute to improve the MgO and CaO activating behavior and to reduce the ZnO content without affecting the final properties of a vulcanizates

First of all, a Model Compound Vulcanization (MCV) study will be presented, following the MCV study presented in Chapter 3. Squalene was used as a model compound and some metal oxides were tested with conductive heating and with microwave radiation. In a second part of the study, the synergetic effects observed for the squalene study will be explored in natural rubber (NR) samples, also working with both heating methods. At the end of this chapter, and taking into account the knowledge obtained in these two studies, the development of new mixed oxides will be presented and the behavior of these new activators will be discussed in conventional and microwave vulcanization.

4.2. RESULTS AND DISCUSSION

4.2.1. MODEL COMPOUND VULCANIZATION (MCV)

The experiments were carried out using conventional vulcanizing systems with a constant S/A ratio (1.67) (see section 2.1.). The vulcanization recipes used are given in Table 4.1. Mixture A is the reference (contains 5 phr ZnO), and Mixture B and C substitute the activator for the same amount of magnesium and calcium oxides respectively. Mixture D contains both zinc and magnesium oxide as activators to study the synergetic effect between these two oxides detected in previous studies of our research group[19]. These 4 formulations were vulcanized under conductive heating (CH) and microwaves radiation (MW) following the protocols explained in section 2.4.2.

Table 4.1. Model Compound Vulcanization recipes.

INGREDIENTS(phr)	Mixture A	Mixture B	Mixture C	Mixture D
Squalene	100	100	100	100
CBS	1.2	1.2	1.2	1.2
Sulfur	2	2	2	2
ZnO	5	-	-	2.5
MgO	-	5	-	2.5
CaO	-	-	5	-
Stearic acid	2	2	2	2

The reactivity of CBS with the different activator systems is displayed in Figure 4.1. The rate of the accelerator degradation gives an idea of the ability of the system to form the active sulfurating agents. On the contrary to the conclusion inferred by Irving and Williams[14], who affirmed that magnesium and calcium oxides have only a slight tendency to form these complexes; it can be observed that when using CH, MgO is able to form these intermediates three-fold faster than ZnO. CaO degrades also CBS rapidly, but less than MgO. When working with Mixture D (50% ZnO and 50% MgO), the behavior is very similar in kinetics to the degradation obtained with 5phr of CaO. When working with MW, the same trend can be observed but in all cases reaction rate is higher as it could be expected. Furthermore, MW is able after 40 minutes to degrade completely CBS even when no activator is used.

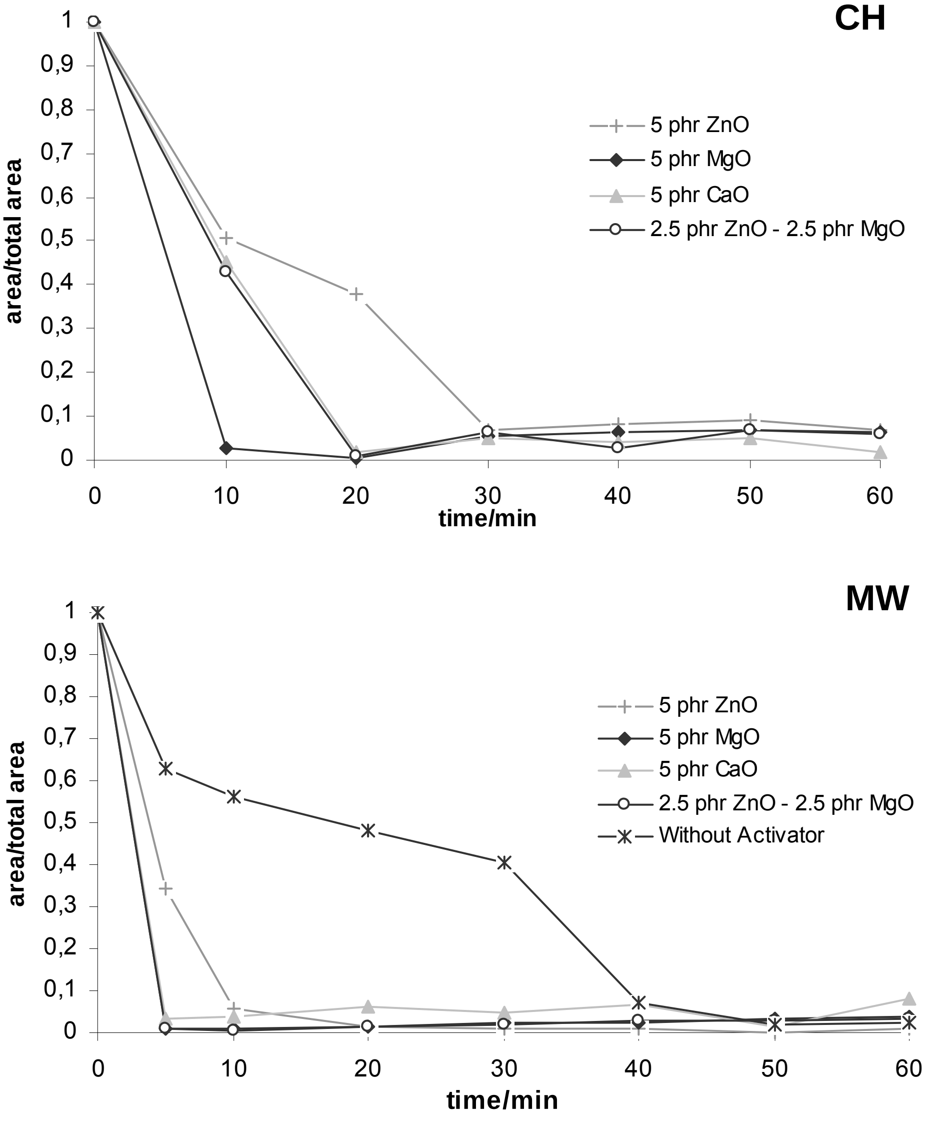

Figure 4.1. CBS degradation of different activator systems in conventional vulcanization (above) and microwave vulcanization (below).

Concerning the crosslink density and coinciding with the results previously published by our research group[19], when using CH any metal oxide is able to achieve the crosslink density obtained with ZnO (Figure 4.2. (above)). The crosslink kinetics is very similar for every activator system although the crosslink yield is different in whichever case. This is quite surprising taking into account that MgO and CaO were faster to form the active sulfurating agents, but for some reason, the formation of the crosslink precursors and the final crosslinks is more difficult when using MgO or CaO than when using ZnO. On the other hand, the experiments performed with MW proved that the same crosslink yield is achieved with all the oxides tested in this study, even when no activator was used, although different kinetics can be observed (Figure 4.2. (below)). The crosslink formation does not occur at all with conventional vulcanization when no activator is used as Domka[7] postulated. Thus, the formulation without activator was not included in CH graph (Figure 4.2. (above)), since the crosslink degree achieved was very low and the time needed to achieve Plateau was too long.

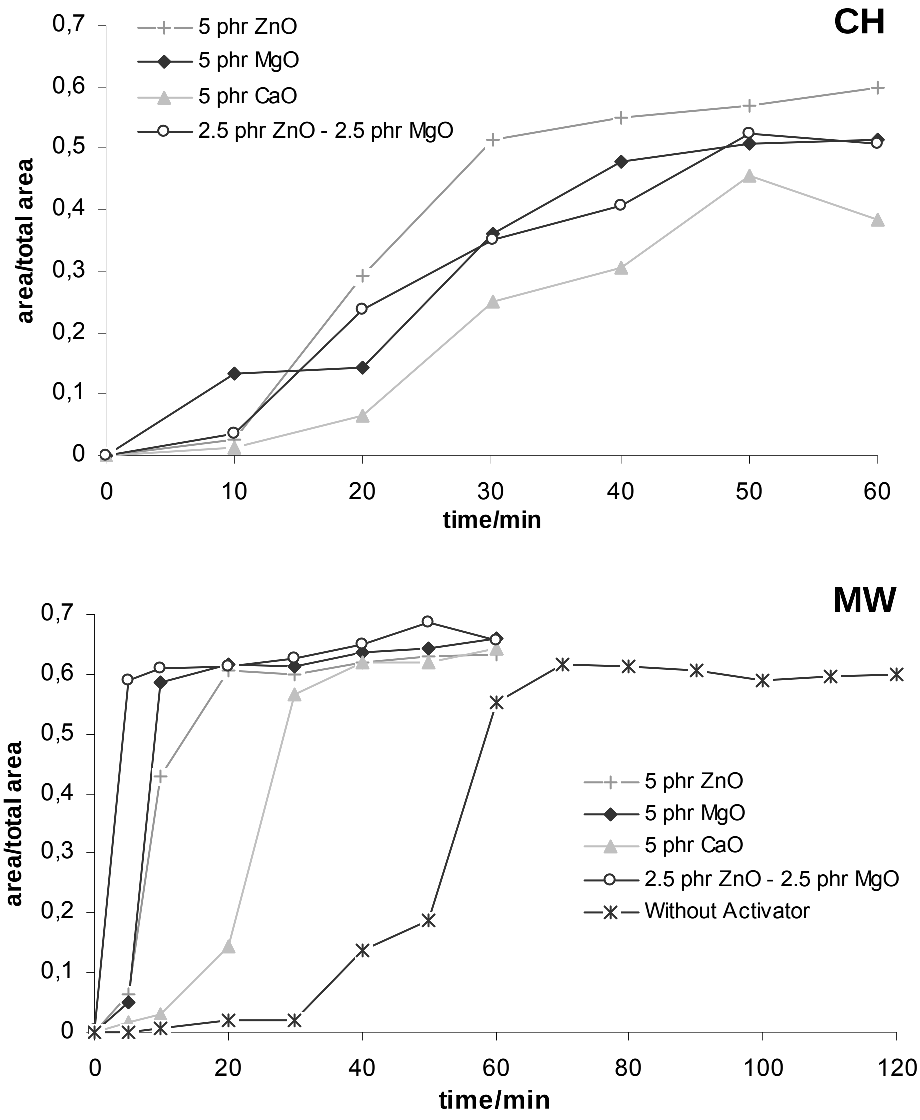

Figure 4.2. Formation of crosslinked squalene with different activator systems in conventional vulcanization (above) and microwave vulcanization (below).

This shows the ability of microwaves to increase the tendency of formation of the active sulfurating compounds and final crosslinks caused by the ability of microwaves to overcome high energetical barriers. Both zinc oxide and magnesium oxide react with similar kinetics when microwave emission is applied. This is not the case for calcium oxide, which presents slower kinetics and low crosslinking degree. A synergetic effect between magnesium and zinc oxides can be observed when using a mixture of them (Figure 4.2. (below)). This effect can also be observed with conventional heating[18], although it is enhanced when using microwaves. Previous studies have also shown this metal oxide synergism with zinc oxide and an increase in the modulus when half of the zinc oxide is replaced by an equivalent amount of other oxides in the formulation[16]. Although this result has been clearly observed with squalene studies, it is necessary to study deeply the behavior in NR samples when working with mixtures of ZnO and MgO with both heating methods to understand the effects of MW radiation on the activator in vulcanization. Therefore, in the study performed with NR samples, that will be presented in the next section, not only have mixtures of 50%ZnO-50%MgO been used, but also a range of ZnO-MgO mixtures to study deeply this synergetic effect. This in-depth study was not carried out with MCV samples, since all compounds had very similar and rapid vulcanization rates that made the slight differences between them more difficult to study.

4.2.2. NATURAL RUBBER

To study the synergetic effect already seen between ZnO and MgO five different formulations were prepared following the protocol described in section 2.4.5. Table 4.2. shows the content of these five non filled compounds which are very similar to the mixtures used for MCV. In this case, CBS was also used as accelerator system and the S/A ratio was maintained at 1.67 (conventional vulcanization). The only changing factor between the 5 recipes was the activator system: Mixture A' contains 100% ZnO; Mixtures B'-C'-D' correspond to mixtures of ZnO and MgO varying from 70%-30% to 50%-50% and to 30%-70% respectively. Finally, Mixture E' contains 100% MgO. These 5 materials were vulcanized at 140ºC with a conventional press and with a microwaves oven for rubber industry as reported in section 2.4.5.1. and the influence of the activator system on the crosslink density was studied by different methods with both heating sources.

Table 4.2. Natural Rubber recipes.

INGREDIENTS(phr)	**Mixture A'**	**Mixture B'**	**Mixture C'**	**Mixture D'**	**Mixture E'**
NR (creppe)	100	100	100	100	100
CBS	1.2	1.2	1.2	1.2	1.2
Sulfur	2	2	2	2	2
ZnO	5	3.5	2.5	1.5	-
MgO	-	1.5	2.5	3.5	5
Stearic acid	2	2	2	2	2

4.2.2.1. CONVENTIONAL VULCANIZATION

As stated in section 2.4.5.2. one of the most used and easiest ways to characterize a rubber compound is monitoring the curing process with a rheometer or curemeter. This curve permits to visualize the kinetics of the crosslink process and allows also to compare the crosslink yield through the maximum torque (M_H) of every mixture. Figure 4.3. displays the rheometer curves of the five compounds at 140ºC. Even though M_H gives an idea of the crosslink density, the parameter which is closely related to the crosslink density of the material is the difference between the maximum torque and the minimum torque (M_H – M_L). The curves were not only tested at 140ºC (vulcanization temperature used for vulcanization), but also at 130ºC, 150ºC, 160ºC and 170ºC to see the temperature effect in the different materials tested and in its reversion. Table 4.3. summarizes the differences between maximum and minimum torque (M_H – M_L) of the five compounds at the five temperature tested.

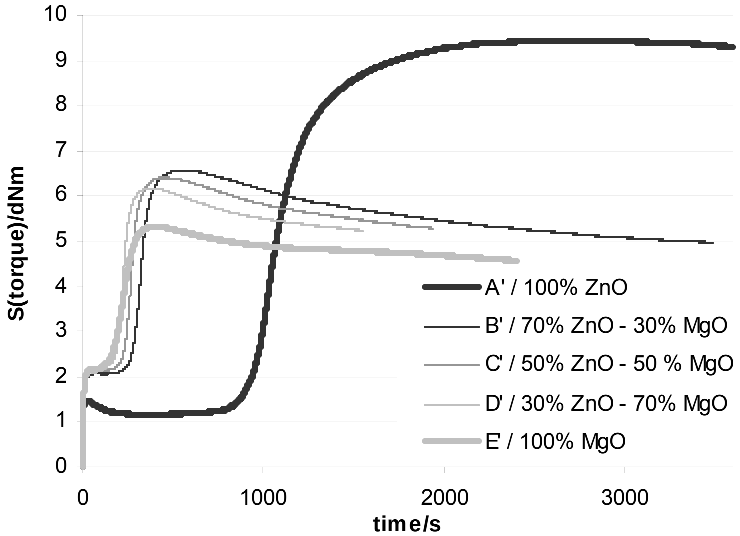

Figure 4.3. Rheometer curves at 140ºC of the mixtures A’, B’, C’, D’ and E’.

Table 4.3. (M_H – M_L) of the five compounds [dNm].

Temperature	Mixture A’	Mixture B’	Mixture C’	Mixture D’	Mixture E’
130ºC	8.55	5.42	5.35	5.13	4.17
140ºC	8.44	5.39	5.31	4.70	4.15
150ºC	8.08	5.51	5.06	4.87	4.15
160ºC	7.96	5.39	4.83	4.68	4.45
170ºC	6.92	4.99	4.84	4.56	4.05

From these data, comparing Mixture A’ and E’, it can be remarked that MgO cures with good kinetics in comparison with ZnO but the crosslink density obtained is much lower. These results are in agreement with the MCV results already shown in section 4.2.1.

($M_H - M_L$) values at 140ºC are 8.44 dNm for 100% ZnO and 4.15 dNm for 100% MgO. So, MgO reduces the crosslink density to the half. But what is more surprisingly, only 30% of MgO (Mixture B') affects dramatically the torque at all temperatures. ($M_H - M_L$) value at 140ºC goes from 8.44 dNm for Mixture A' to 5.39 dNm for Mixture B'. It could be concluded, that the presence of MgO affects strongly the crosslink density; but even though the higher amount of MgO, results in lower torque, the presence of MgO is more critical (even at low values) than the amount of MgO. The three materials with mixtures of both activators (Mixture B', C' and D') have similar values between 4.5 and 5.5 dNm. It should be also pointed out that ($M_H - M_L$) values, and consequently the crosslink density, are more affected by the temperature when using ZnO as activator than when using MgO.

Another parameter that can be studied is the reversion (equation 2.13.) and its dependence with the temperature. Figure 4.4. shows the evolution of the reversion with the temperature for these five compounds. The more MgO content, the higher the reversion and it increases with the temperature for all materials. It should be pointed out, that Mixture E' (100% MgO) only follows this rule up to 160ºC. At lower temperatures it behaves as good as the formulation containing 50% ZnO-50% MgO (Mixture C').

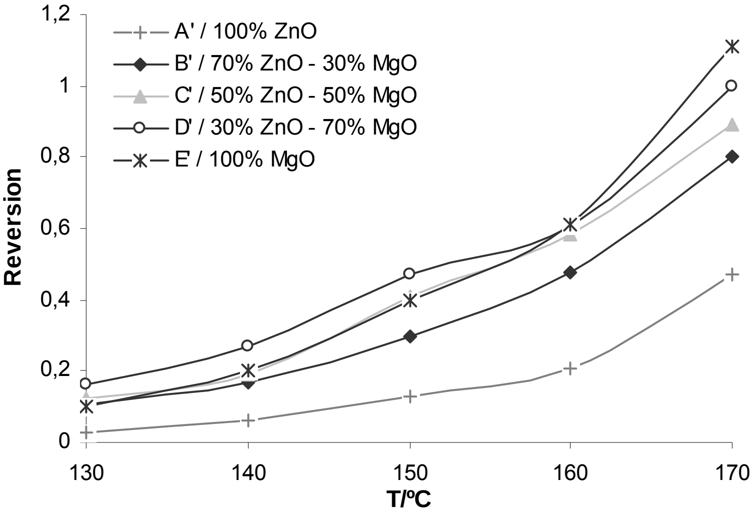

Figure 4.4. Evolution of reversion with temperatures for mixtures A', B', C', D' and E'.

All these results can be summarized in Figure 4.5. This figure contains two graphs with the rheometric curves of Mixtures A' (above) and E' (below) at the five temperatures tested. In this illustration it can be clearly seen that mixtures activated by ZnO experiment a higher decrease in maximum torque (~ crosslink density) when increasing the temperature than compounds activated by MgO. On the other hand, both activator systems suffer an increase in reversion with temperature as it could be espected, having always MgO systems higher reversion than ZnO systems.

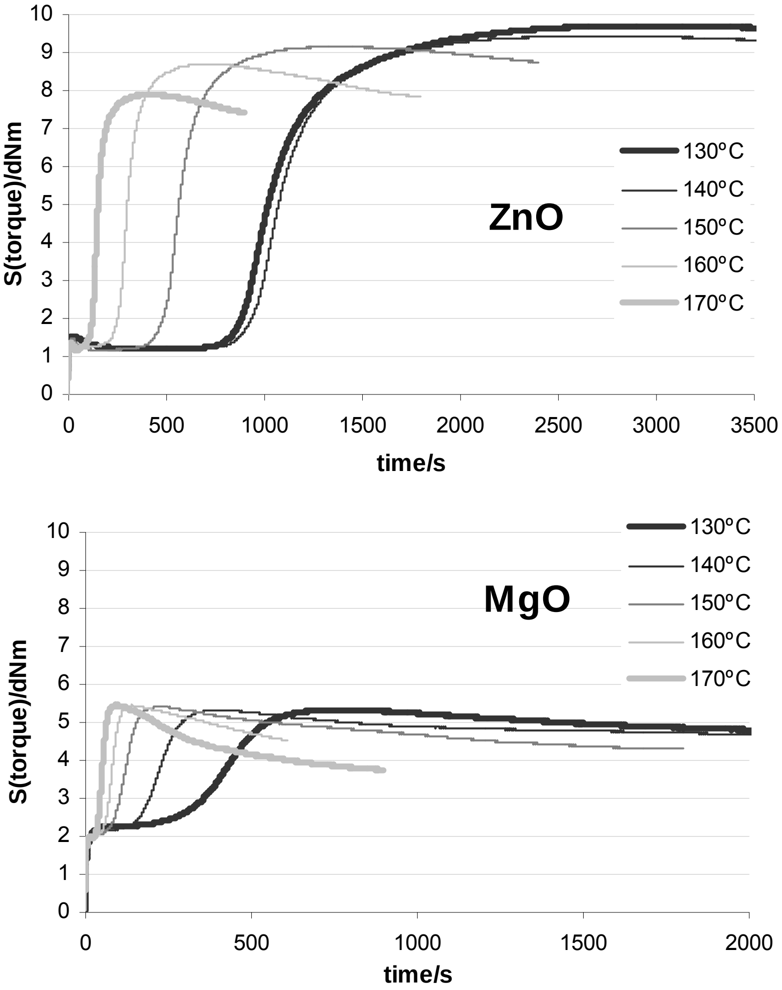

Figure 4.5. Rheometer curves of the mixtures A' and E' at different temperatures.

In order to evaluate the synergetic effect between these two activators, the following graph has been designed. Figure 4.6. shows five points corresponding to the maximum torque (M_H) at 140ºC with respect to the composition of ZnO and MgO for the five compounds. Thereby, the left point corresponds to Mixture E' (100% MgO) and the other extreme, the right point corresponds to Mixture A' (100% ZnO). Joining the five points it is evident the negative synergetic effect of the mixtures of ZnO and MgO in the maximum torque and consequently in the crosslink density.

On the contrary, a positive synergetic effect has been detected in the speed constant (k). In section 2.4.5.2. it has been explained how to calculate the speed constant (k) and the activation energy (Ea) from the rheometer curves. Figure 4.7. displays the speed constant (k) at every temperature with respect to the composition of ZnO and

MgO for the five compounds studied. As stated before, the left point corresponds to Mixture E' (100% MgO) and the right point corresponds to Mixture A' (100% ZnO). It can be clearly seen how this positive synergetic effect is enhance when increasing the temperature.

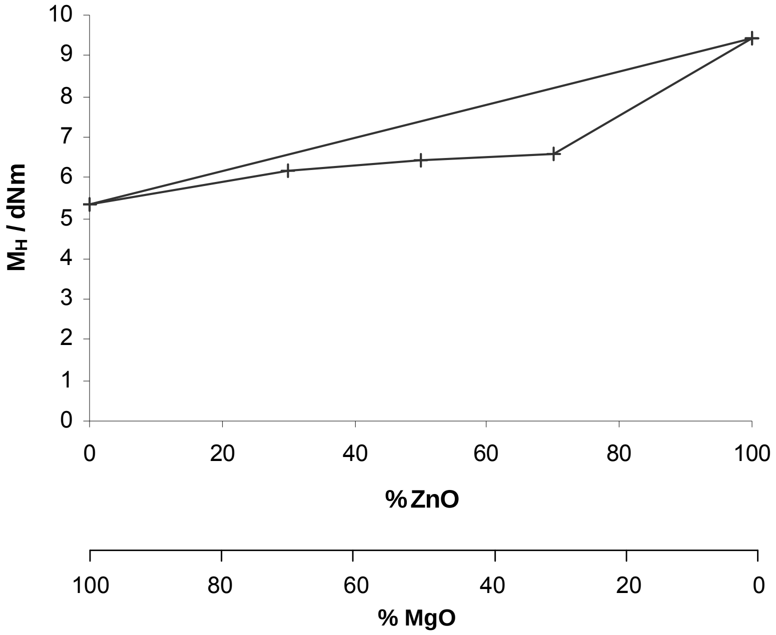

Figure 4.6. Maximum torque (M_H) at 140ºC with respect to the composition of ZnO and MgO for mixtures A', B', C', D' and E'.

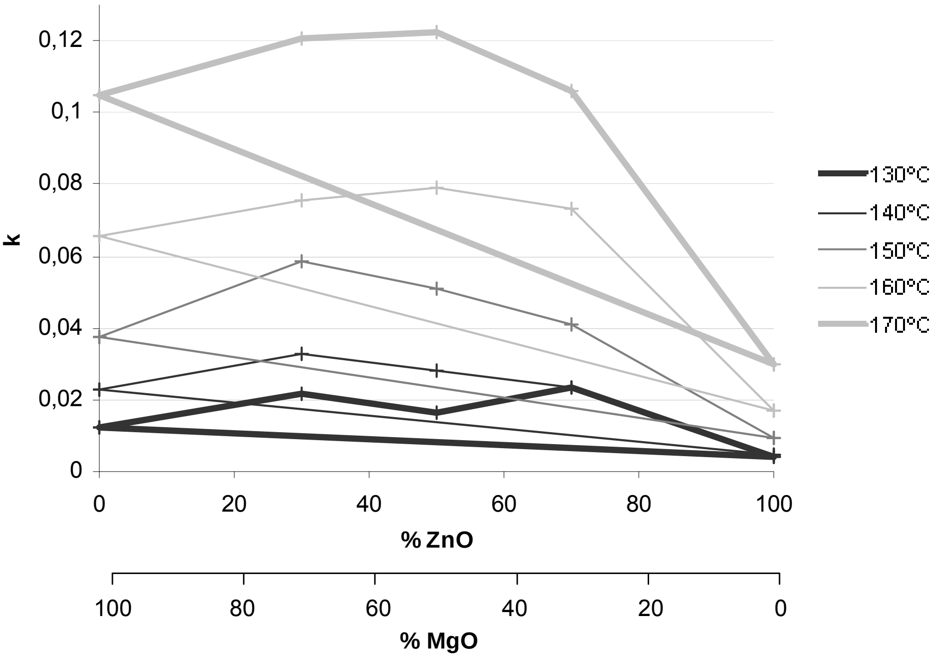

Figure 4.7. Speed constant (k) at different temperatures with respect to the composition of ZnO and MgO for mixtures A', B', C', D' and E'.

On the other hand, focusing on the activation energy (Ea) of every system, a positive synergetic effect has been also detected when working with both activators. Figure 4.8. shows the activation energy (Ea) with respect to the composition of ZnO and MgO for the five compounds studied. This positive synergetic effect seems to be much greater for Mixtures B' (70% ZnO and 30% MgO) and D' (30% ZnO and 70% MgO), than for mixture C' which consists in a mixture at 50% of both activators.

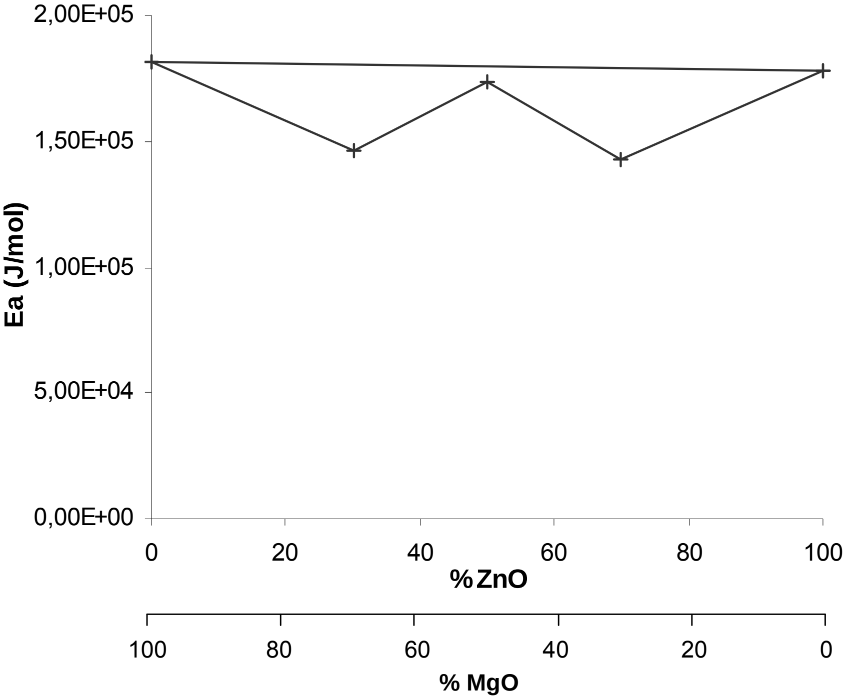

Figure 4.7. Activation energy (Ea) with respect to the composition of ZnO and MgO for mixtures A', B', C', D' and E'.

A surprising phenomenon that must be remarked is that both, Mixture A' and Mixture E', have the same activation energy (Ea). It has been seen that MgO reacts kinetically faster than ZnO and also, it is known, that Mg complexes are less stable than Zn as proven by Duchacek[13]. Therefore, what it was expected it was a lower Ea for the MgO system in comparison with ZnO activator system. This trend is followed by the systems containing a mixture of both oxides, but not by the system containing 100% of MgO (Mixture E'). A possible explanation to this fact is that the lower crosslink density obtained with systems activated by MgO is not only caused by the lower stability of Mg complexes or the ability of MgO to form active sulfurating agents, but also because for some reason these intermediates are not able to progress to final crosslinks as ZnO intermediates do. Said in other words, the problem of the lower crosslink yield obtained with MgO is not caused by the lower ability of this activator to form active sulfurating agents but by the ability of these intermediates to retain the sulfur instead of forming the final crosslinked network. Thus, the hypothesis at this point to explain these results was that MgO has more affinity for sulfur than ZnO due to its ability to form active sulfurating agents more quickly. The problem is that after, these MgO intermediates are not able to progress to final crosslinks. Therefore, when working with mixtures of both oxides, MgO competes with ZnO to react with sulfur, and due to the already commented higher affinity of MgO for sulfur, it takes up part of the sulfur which cannot react to form final crosslinks.

Then, the question posed was if the reduction in the crosslink density in mixtures C', D', E' and F' was really an effect of the MgO presence or a consequence of the ZnO absence. Therefore, four new mixtures were prepared and they are presented in Table 4.4. Mixture F',G' and H' contain only ZnO as activator with 50%, 70% and 130% respectively with respect to Mixture A'. Mixture F' and G' are analogous to Mixture C' and B' respectively but taking out the MgO content. Finally, Mixture I' contained no activator (w.a. = without activator) to see, in comparison with Mixture E', if MgO has a negative effect in the torque and consequently in the crosslink density.

Table 4.4. Natural Rubber recipes.

INGREDIENTS(phr)	Mixture A'	Mixture F'	Mixture G'	Mixture H'	Mixture I'
NR (creppe)	100	100	100	100	100
CBS	1.2	1.2	1.2	1.2	1.2
Sulfur	2	2	2	2	2
ZnO	5	2.5	3.5	6.5	-
Stearic acid	2	2	2	2	2

Figure 4.8. displays the rheometric curves of these five compounds at 140ºC. It can be seen that according to Chapman studies[3] there is no influence of the amount of ZnO in the crosslink density (maximum torque (M_H)). Thus, the rheometer curves of Mixtures A', F', G' and H' are very similar, only slight but not significant differences can be observed in the maximum torque achieved, even though the amount of ZnO varies.

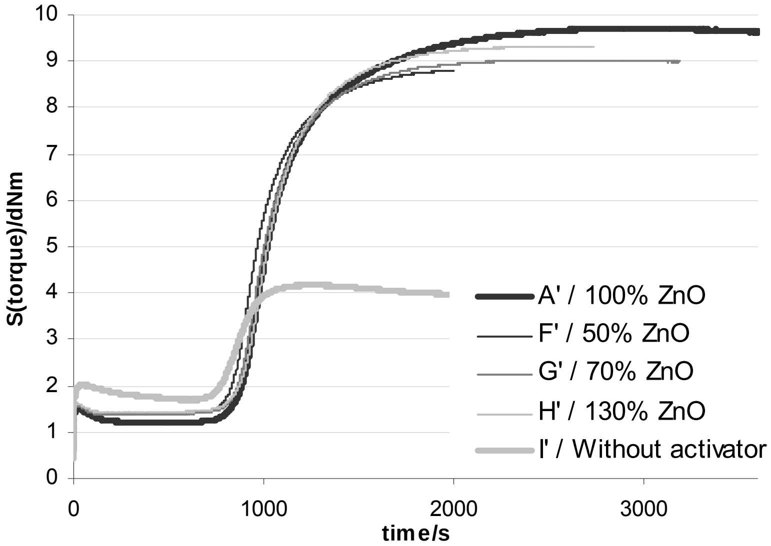

Figure 4.8. Rheometer curves at 140ºC of the mixtures A', F', G', H' and I'.

Furthermore, when comparing Mixtures F’ with C’ (both with 50%ZnO) and mixtures G’ with B’ (both with 70%ZnO) it is clear that the lower crosslink density achieved in Mixtures B’ and C’ is caused by the presence of MgO and not by the lower amount of ZnO in comparison to the reference (Mixture A’). On the other hand, Mixture I’ (without activator) has a very low maximum torque ($M_H \approx 4$), even lower than Mixture E’ ($M_H \approx 5.2$). It proves that even MgO has a negative synergetic effect in the crosslink density when working together with ZnO, it has a certain activator character when working alone and it generates higher crosslink density than when working with a system without activator.

These results supported the already suggested hypothesis of the MgO-ZnO competence for sulfur which causes a decrease in the crosslink density when working with mixtures of both oxides. In order to shift this equilibrium in ZnO benefit, some new experiments were developed. Five new compounds (Table 4.5.) were developed and tested. Mixture J’ (5phr ZnO – 2phr MgO) is analogous to Mixture B’ (3.5phr ZnO – 1.5phr MgO) both containing 70% ZnO and 30% MgO. The aim of this experiment was to see if the amount of activator is able to overcome this competence between the two metal oxides. On the other hand Mixtures K’, L’, M’ and N’ are very similar to Mixture A’, B’, C’ and D’, but containing more sulfur content (3phr instead of 2phr) in order to see if providing more sulfur to the system, ZnO is able to crosslink properly. These four last mixtures are also conventional vulcanizing systems although their S/A ratio is 2.5, instead of 1.67.

Table 4.5. Natural Rubber recipes.

INGREDIENTS(phr)	**Mixture J’**	**Mixture K’**	**Mixture L’**	**Mixture M’**	**Mixture N’**
NR (creppe)	100	100	100	100	100
CBS	1.2	1.2	1.2	1.2	1.2
Sulfur	2	3	3	3	3
ZnO	5	5	3.5	2.5	1.5
MgO	2	-	1.5	2.5	3.5
Stearic acid	2	2	2	2	2

Figure 4.9. displays the comparison between the rheometer curves at 140ºC of Mixture B’ and Mixture J’, both containing 70% ZnO and 30% MgO, with the reference Mixture A’ (100% ZnO). It can be clearly seen that the addition of more activator does no really increase the crosslink density, so this is not a solution to the competence problem between ZnO and MgO. On the other hand, Figure 4.10. shows the rheometric curves at 140ºC of Mixtures K’, L’, M’ and N’, that are analogous to Mixtures A’, B’, C’ and D’ but containing more sulfur. By comparing this figure with the Figure 4.3., it can be concluded that the addition of sulfur does not solve the competence problem between

ZnO and MgO. It must be pointed out that this conclusion is only valid for CBS, but different results could be expected for TMTD, due to its ability of acting as sulfur donor.

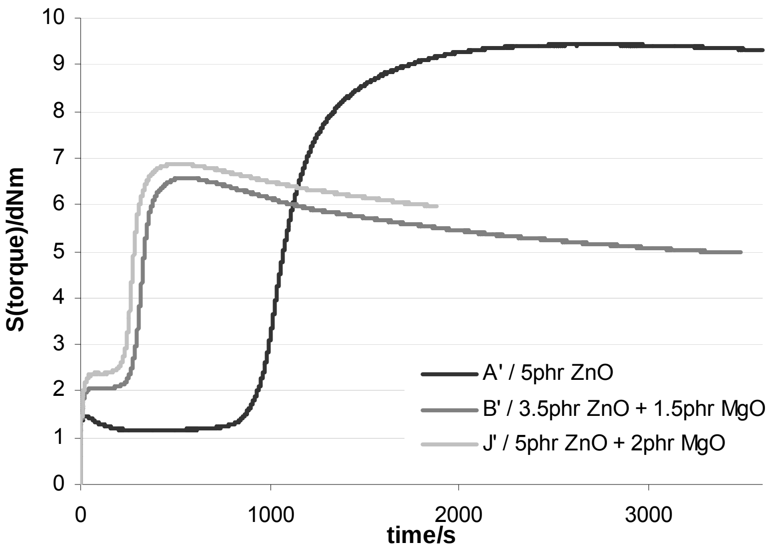

Figure 4.9. Rheometer curves at 140ºC of the mixtures A', B' and J'.

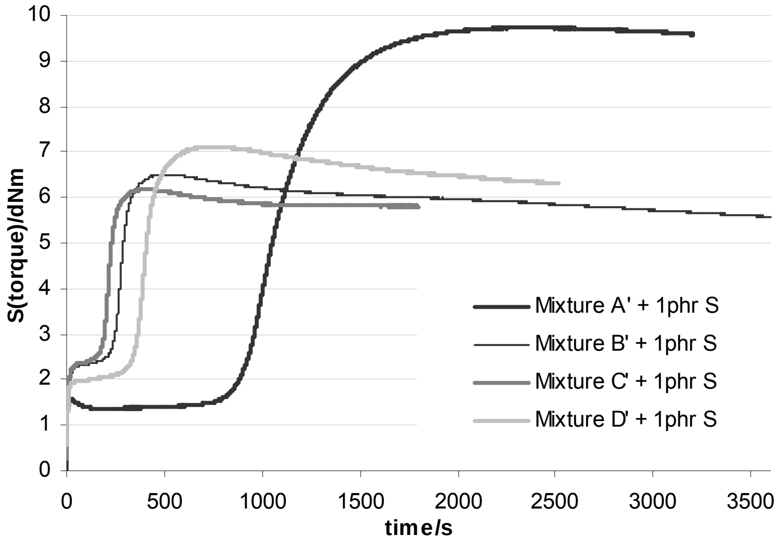

Figure 4.10. Rheometer curves at 140ºC of the mixtures K', L', M' and N'.

Although rheometer is a generally used technique that allows the qualitative evaluation of the crosslink density, it provides only rough results and there are other methods that permit to quantify this parameter. Even thought, until this point the conclusions drawn for NR conventional vulcanization are in agreement with MCV results presented in section 4.2.1. As explained in section 2.3.1., in this thesis two different approaches have been used to determine the crosslink density: the Mooney-Rivlin[23] empirical expression from stress-strain data and the Flory-Rehner[24] equation modified for tetrafunctional networks by using swelling measurement data. The latter permits also, with the help of thiolamine chemical-probes, the evaluation of the crosslink structure (see section 2.3.2.). Next, the network chain density (ν_e) results of all the mixtures will be presented and discussed, together with the crosslink distribution for every activator system. The term network chain density will be used from this point inter-changeably with the term crosslink density.

Before starting this discussion it is necessary to refresh the composition of the 14 mixtures studied (Table 4.2., Table 4.4. and Table 4.5.) to understand the following results.

- **Mixtures A'** to **E'** are the basic and initial compounds. The only variable factor between them is the activator composition having always a total amount of 5phr of activator: A' (100% ZnO), B' (70% ZnO + 30% MgO), C' (50% ZnO + 50% MgO), D' (30% ZnO + 70% MgO) and E' (100% MgO).
- **Mixtures F', G'** and **H'** only contain ZnO as activator and have to be compared with Mixture A'. They contain 50%, 70% and 130% of ZnO with respect to the reference (Mixture A'). They will be useful to study the effect of ZnO amount in the final properties.
- **Mixture I'** is a blank which does not contain any activator (**w.a.** = without activator).
- **Mixture J'** has to be compared with Mixture B'. Both contain the same proportion in the activator system (70% ZnO + 30% MgO) but Mixture J' has a total amount of 7phr of activator and Mixture B' has only 5phr of activator. Since Mixture J' was developed to study the effect of the amount of activator, it will be also called (**m.a.** = more activator).
- **Mixtures K'** to **M'** are comparable with Mixtures A' to D' respectively. The only difference is hat Mixtures K' to M' contain 3phr of sulfur whereas Mixture A' to D' contain only 2phr of sulfur.

Stress-strain data: Crosslink density (ν_e) by Mooney-Rivlin

As stated in section 2.4.5.3. the stress-strain data were acquired in % elongation (λ) and force (F) in MPa. From stress-strain curves the main parameters that can be extracted are tensile strength (the stress applied at the point when it fails) and the elongation at break. In Figure 4.11. it can be seen, from Mixtures A' to E', how the tensile strength decreases when increasing the MgO content. Comparing Mixture A' (100% ZnO) with Mixture E' (100% MgO) it is clear that with the same total activator amount, MgO needs only the half of the stress to break than ZnO. It can be also seen, comparing Mixture A', F', G' and H', how the ZnO amount has not a significant effect in the tensile strength. Mixture I' proves when comparing with Mixture E', that MgO has a real effect in the tensile strength, and that in some way it behaves as ZnO although his activating ability is lower. When comparing Mixtures B' and J', it can be seen that increasing the activator amount, the tensile strength increases and this could be a solution to solve the competence problem between ZnO and MgO already explained. Finally, increasing the sulfur content (Mixtures K’ to N’) it is also possible to enhance the tensile strength. Thus, it could be also a partial solution to improve the behavior of MgO as activator.

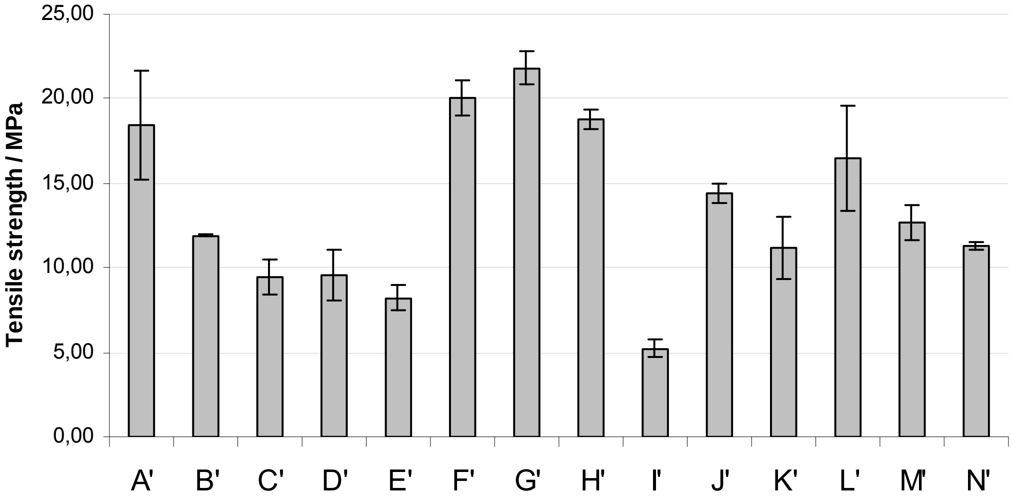

Figure 4.11.Tensile strength of the 14 compounds (**A’-E’:** ZnO-MgO mixtures by decreasing ZnO% / **F’-G’:** ZnO compounds by increasing ZnO% / **I’:** w.a. / **J’:** ZnO-MgO mixture with m.a. in comparison to B’ / **K’-N’:** Influence of sulfur addition in comparison to A’-D’ respectively).

Focusing in the results of elongation at break presented in Figure 4.12., it can be seen that the content or nature of activator do not seem to have a significant influence in this parameter. Mixture I’ is the only compound that seems to have a significant higher elongation and it is due to the low crosslink density caused by the lack of activator.

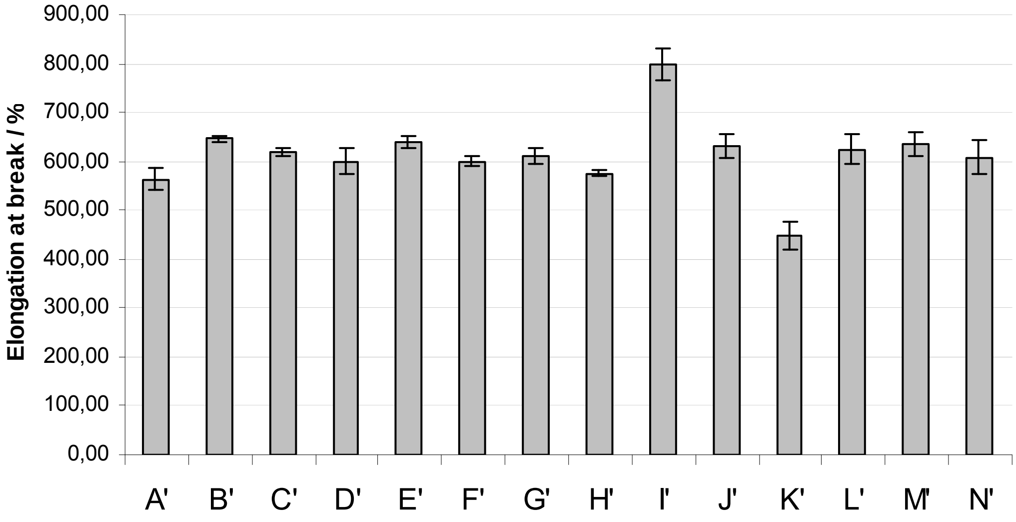

Figure 4.12. Elongation at break of the 14 compounds (**A’-E’:** ZnO-MgO mixtures by decreasing ZnO% / **F’-G’:** ZnO compounds by increasing ZnO% / **I’:** w.a. / **J’:** ZnO-MgO mixture with m.a. in comparison to B’ / **K’-N’:** Influence of sulfur addition in comparison to A’-D’ respectively).

In section 2.4.5.3. it has been explained how to determine the network chain density (ν_e) from the stress-strain data. Figure 4.13. shows the results obtained. The conclusions that can be extracted from the crosslink density results are very similar to the conclusions extracted from the tensile strength graph and also the conclusions already drawn with the rheometer results. On the one hand, it is clear that crosslink density is very affected by the presence of MgO. It decreases when increasing the MgO content. And as stated before, the key factor is the presence of MgO rather than the amount of this oxide in affecting the network chain density. On the other hand, it can be also seen, comparing Mixture A', F', G' and H', how the ZnO amount has not a significant effect in the crosslink density as found by Chapman[3]. In addition, in this case, surprisingly the same crosslink density, calculated by Mooney-Rivlin approach, was achieved by Mixtures E' (100% MgO) and I' (without activator). It suggests that MgO has no activating effect which is contradictory with the results obtained with rheometer. These results should be contrasted with the results obtained by Flory-Rehner approach which is a more robust method to calculate network chain density values. Finally, increasing the sulfur content (Mixtures K' to N') it is also possible to enhance the crosslink density. Thus, the addition of sulfur could be also in some way a partial solution to improve the behavior of MgO as activator.

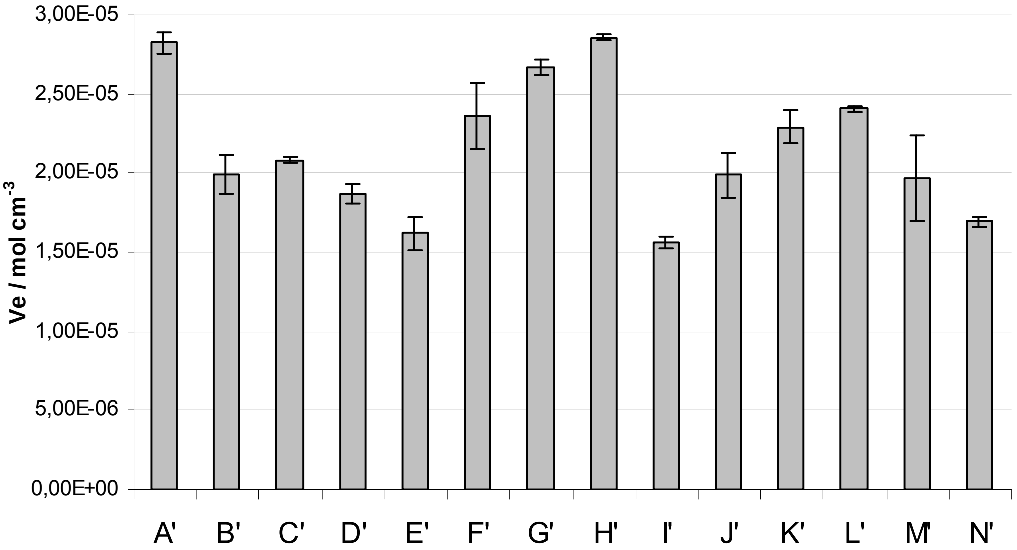

Figure 4.13. Network chain density (ν_e) of the 14 compounds calculated using Mooney-Rivlin approach (**A'-E':** ZnO-MgO mixtures by decreasing ZnO% / **F'-G':** ZnO compounds by increasing ZnO% / **I':** w.a. / **J':** ZnO-MgO mixture with m.a. in comparison to B' / **K'-N':** Influence of sulfur addition in comparison to A'-D' respectively).

Equilibrium sweeling data: Crosslink density (ν_e) by Flory-Rehner

In section 2.4.5.4. it has been explained how to determine the network chain density (ν_e) from the equilibrium swelling data. Figure 4.14. displays the results obtained. The trends observed between the 14 compounds are very similar to the showed in Figure 4.13. However, network chain density (ν_e) values are higher in Flory-Rehner approach than in Mooney-Rivlin. Despite of the differences in network chain density values (ν_e) between both methodologies, conclusions that can be extracted from the crosslink density results are very similar with both methods. Only two things must be pointed out. On one hand, the comparison between Mixtures E' and I' (w.a.) suggests that MgO has no activating effect at all, or not in the same way than ZnO, because when working without activator (Mixture I') the network chain density (ν_e) achieved is higher than when using MgO. On the other hand, with these results confirm that the addition of sulfur (Mixtures L' to N') helps the activator systems that combine both oxides (Mixtures B' to D') to overcome their lack of crosslink ability.

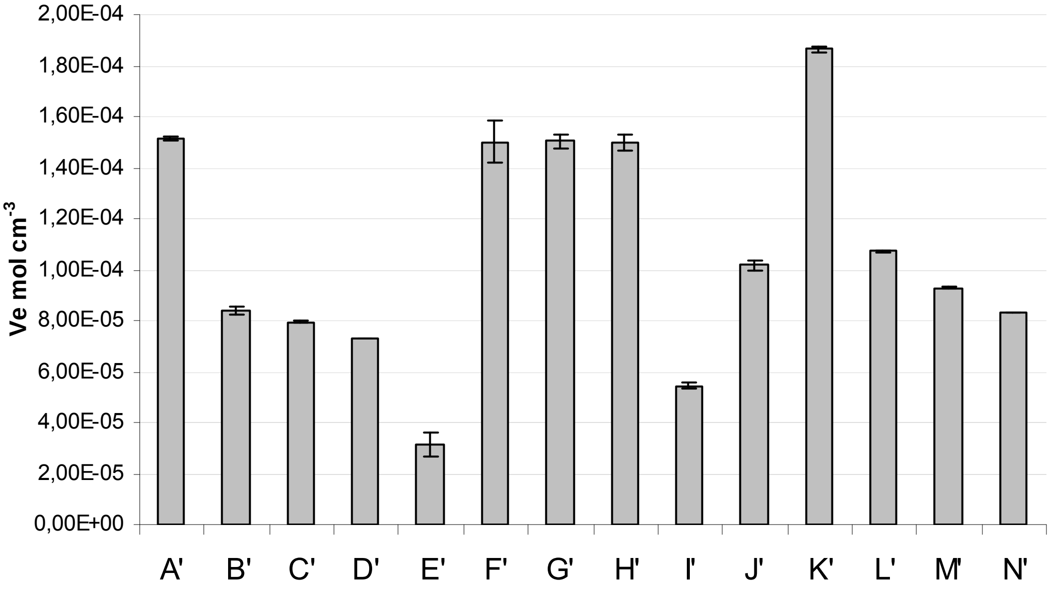

Figure 4.14. Network chain density (ν_e) of the 14 compounds calculated using Flory-Rehner approach (**A'-E':** ZnO-MgO mixtures by decreasing ZnO% / **F'-G':** ZnO compounds by increasing ZnO% / **I':** w.a. / **J':** ZnO-MgO mixture with m.a. in comparison to B' / **K'-N':** Influence of sulfur addition in comparison to A'-D' respectively).

The study of the synergetic effect between these two oxides have started with the rheometer results. A negative synergetic effect has been detected in the maximum torque (Figure 4.6.) whereas a positive synergetic effect has been discovered in the speed constant and activation energy. The same study has been developed with the Flory-Rehner results of network chain density (ν_e). In this case, a dual synergetic effect has been observed depending on the activator content when combining both oxides. At low ZnO content and high MgO content a positive synergetic effect has been detected and on the contrary, this synergetic effect becomes negative when there is more ZnO than MgO. This peculiar phenomenon is showed in Figure 4.15.

One of the advantages of swelling method, in comparison with stress-strain method, to determine the crosslink density is that, in combination with thiolamine chemical-probe method, it permits to study the crosslink distribution in the network. The thiolamine method was thoroughly explained in section 2.3.2.5. and 2.4.5.4.; but to make a long story short, through two selective reactions (hexane-1-thiol and propane-2-thiol), the method makes the analysis of the crosslink structure possible. The first one dissolve the polysulfidic and disulfidic crosslinks and the second one only the polysulfidic crosslinks. Performing swelling measurements and treating the data with Flory-Rehner expression, before an after the reactions, it is possible to determine the percentage of mono-, di- and polysulfidic crosslinks. All the compounds developed in this study were conventional systems. These kind of vulcanizing systems are known for containing mostly polysulfidic crosslinks with relatively high level of chain modification. Consequently, their monosulfidic network is very limited. Thus, in the experiments performed in this thesis all the treatments with hexane-1-thiol gave rise to a very weak gelatin of which crosslink density could not be determined by swelling measurements because the final drying process, after the hexane-1-thiol reaction, produced a very porous and unstable structure difficult to handle. Thus, the crosslink structure of these compounds could only be defined as the percentage of polysulfidic crosslinks and the percentage of the sum of mono- and disulfidic crosslinks. It can be remarked that most of this second percentage corresponds to disulfidic crosslinks since the monosulfidic network is very poor as explained before.

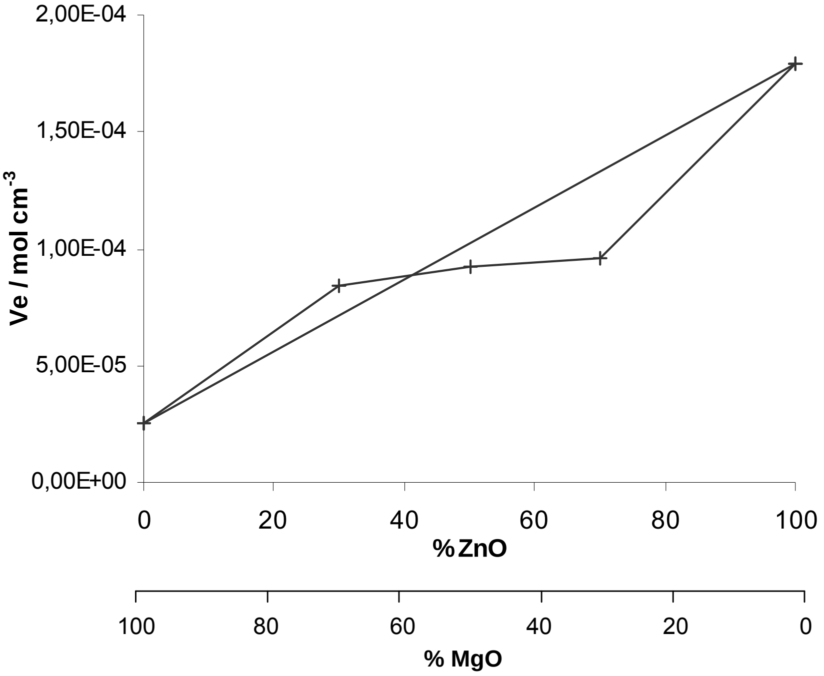

Figure 4.15. Network chain density (ν_e) calculated by Flory-Rehner approach as a function of the composition of ZnO and MgO of mixtures A', B', C', D' and E'.

Figure 4.16. displays the results of the crosslink structure for the 14 compounds studied. Some conclusions can be drawn. First of all, focusing in Mixtures A' to E', it is clear that when increasing the amount of MgO in the activating system, the percentage of mono- and disulfidic crosslink decreases, from 12% when working with 5phr ZnO to nearly 0% when using 5phr MgO. In addition, when comparing Mixtures A' (5phr ZnO), F' (2.5phr ZnO), G' (3.5phr ZnO) and H' (6.5phr ZnO), it can be concluded that the increase in the amount of ZnO produces also an increase in the mono- and disulfidic network, from a 10% in case of Mixture F' to a 17% in case of mixture H'.

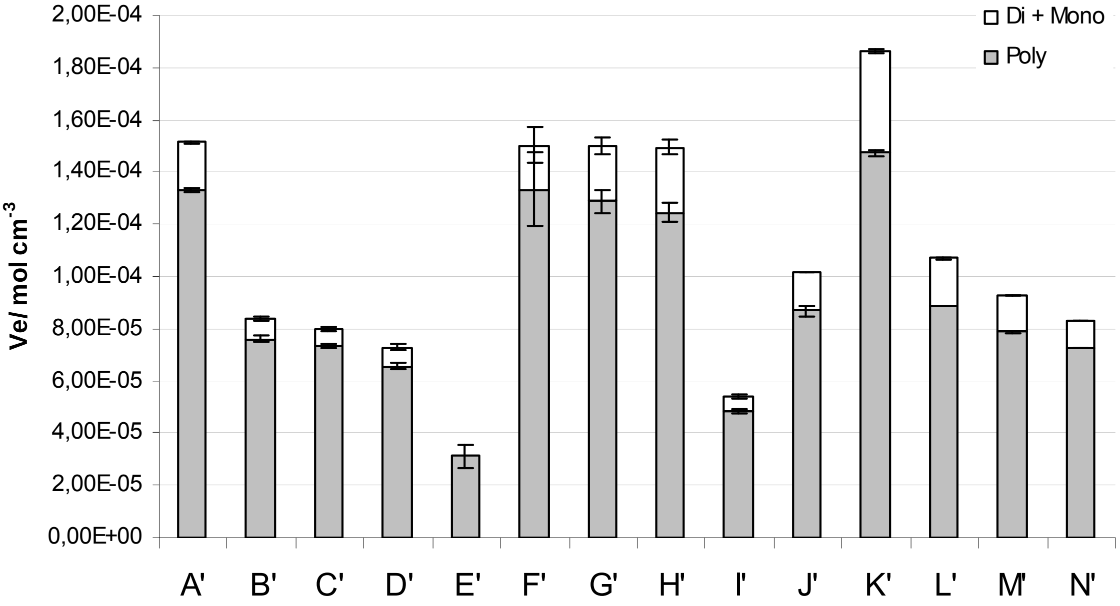

Figure 4.16. Crosslink structure expressed in network chain density (ν_e) of polysulfidic and (disulfidic + monosulfidic) crosslinks of the 14 compounds calculated using Flory-Rehner approach and using thiolamine chemical-probes (**A'-E':** ZnO-MgO mixtures by decreasing ZnO% / **F'-G':** ZnO compounds by increasing ZnO% / **I':** w.a. / **J':** ZnO-MgO mixture with m.a. in comparison to B' / **K'-N':** Influence of sulfur addition in comparison to A'-D' respectively).

Another point to emphasize is that when comparing Mixtures E' and I', not only the non activating effect of MgO is confirmed, since when working without activator (Mixture I') the network chain density (ν_e) achieved is higher than when using MgO. But also, it has been proved that MgO produces nearly any mono- and disulfidic crosslinks whereas around 11% of this type of crosslink is formed when using no activator. These changes in the crosslink structure will affect strongly the final properties and the aging behavior of the compounds as explained in section 2.1. Finally, the addition of sulfur (Mixtures L' to N') increases the crosslink density but also increases the amount of mono- and disulfidic crosslinks when comparing with Mixtures A' to D'.

Hardness

Hardness measurements have been performed following the protocol presented in section 2.4.5.2. Figure 4.17. shows the hardness of the 14 compounds tested in two different scales: Shore A and the International Rubber Hardness Durometer scale (IRHD). In both cases values are very similar and show the same trend. On the one hand the substitution of ZnO by MgO affects the hardness, but less strongly than the negative effect that it has been detected in the crosslink density. In this case, the amount of ZnO does not seem to have a significant effect on the hardness neither. Furthermore, in this case the hardness of the compound with 5phr ZnO (Mixture E') has a higher hardness than the compound without activator (Mixture I'). It can be seen that the IRDH value for Mixture I' (w.a.) is very low in comparison to Shore A value, which suggests an experimental error, but in any case both values are lower than the hardness measured for Mixture E' (100% MgO). Finally, the addition of sulfur increases slightly the hardness, but the effect is less significant than the effect detected in the crosslink density.

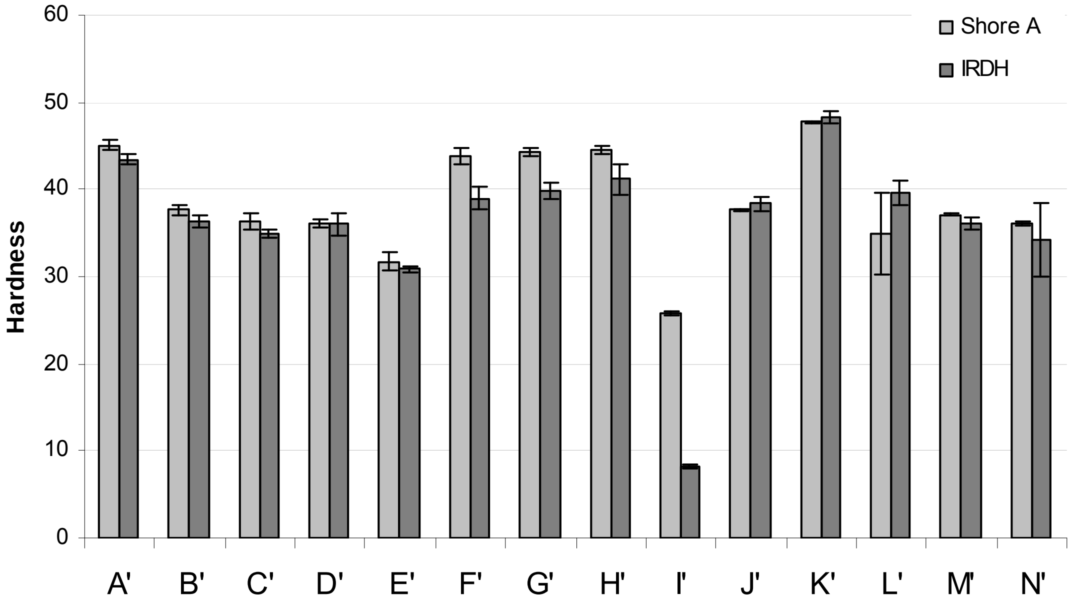

Figure 4.17. Hardness of the 14 compounds (**A'-E':** ZnO-MgO mixtures by decreasing ZnO% / **F'-G':** ZnO compounds by increasing ZnO% / **I':** w.a. / **J':** ZnO-MgO mixture with m.a. in comparison to B' / **K'-N':** Influence of sulfur addition in comparison to A'-D' respectively).

Compression set

The protocol followed for compression set measurements has been also presented in section 2.4.5.2. Figure 4.18. shows the compression set of the 14 compounds tested following the norm ISO 815.

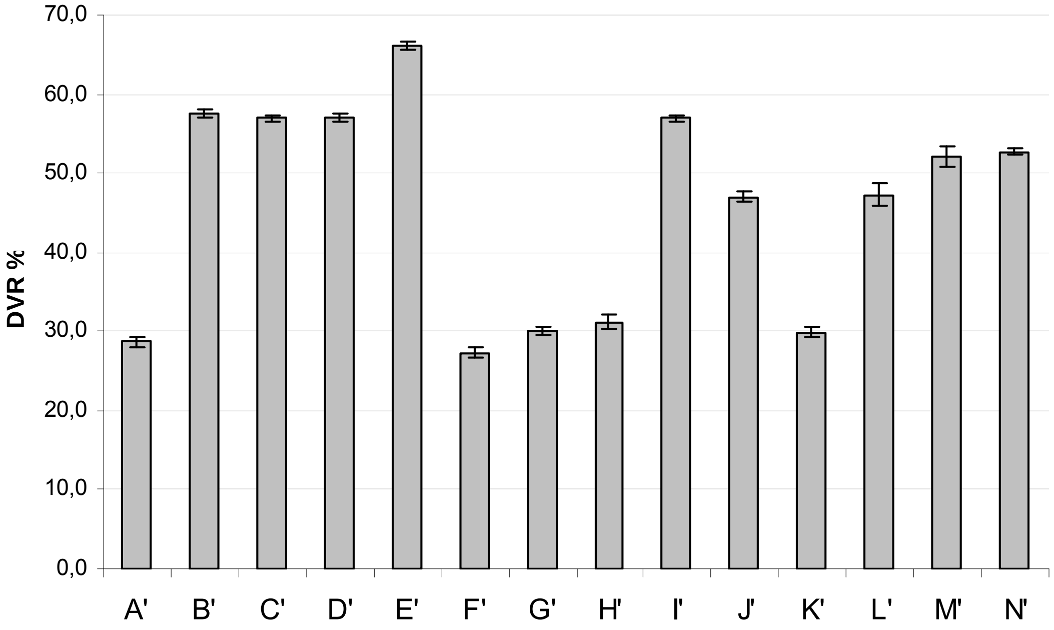

Figure 4.18. Compression set of the 14 compounds (**A'-E':** ZnO-MgO mixtures by decreasing ZnO% / **F'-G':** ZnO compounds by increasing ZnO% / **I':** w.a. / **J':** ZnO-MgO mixture with m.a. in comparison to B' / **K'-N':** Influence of sulfur addition in comparison to A'-D' respectively).

These results corroborate all the conclusions already drawn from the other properties measured about the systems activated by both, ZnO and MgO. Taking into account all the results presented in this section the following facts can be concluded:

- The MgO is, as expected, worst activator than ZnO in conventional vulcanization. It promotes a faster crosslink reaction but the crosslink density achieved is lower when using conventional heating. These results coincide with the MCV results presented in 4.2.1. Furthermore, MgO forms only polysulfidic crosslinks whereas ZnO give rise to the formation of 12% of mono- and disulfidic crosslinks. For this reason MgO has a bad aging behavior and higher reversion.
- The mixtures of MgO and ZnO have an intermediate behavior between the two extremes. It has been detected that little amounts of MgO are enough to cause a decrease in the crosslink density. Thus, it has been concluded that the key factor is the presence of MgO rather than the amount of this oxide in affecting the network chain density. Elongation at break is the only property measured which is not affected by the substitution of ZnO by MgO. In addition, hardness is only slightly affected by MgO. On the other hand, tensile strength and crosslink density are strongly affected by this activator change. MgO seems to have more affinity for sulfur than ZnO due to its ability to form active sulfurating agents more quickly. The problem is that after, these MgO intermediates are not able to progress to final crosslinks with the same ability than ZnO active sulfurating agents. Therefore, when

working with mixtures of both oxides, MgO competes with ZnO to react with sulfur, and due to the already commented higher affinity of MgO for sulfur, it takes up part of the sulfur which cannot react to form final crosslinks.

- Some strategies have been performed trying to shift the equilibrium of competence of ZnO and MgO for sulfur in ZnO benefit in order to increase the crosslink density. Increasing the amount of activator seems not to solve at all the problem whereas increasing the sulfur content promotes an improvement in crosslink density and the rest of final properties.
- As it could be expected, working without activator produces a lower torque in rheometer curve than working with 5phr MgO. That means that although MgO is a worst activator than ZnO, it has some activator behavior. MgO also presents a better tensile strength, compression set and hardness than the compound without activator whereas the elongation at break is better for the latest. It should be remarked, that surprisingly the crosslink density measured by Flory-Rehner is higher for the compound without activator whereas is slightly lower by Moonery-Rivlin. It could be concluded, that the effect of MgO as activator on the crosslink density is not very strong but it has an effect in other physical properties. Furthermore, the addition of sulfur helps to enhance the crosslink density and also improve the final properties.
- Some synergetic effects have been detected when using mixtures of ZnO and MgO. These synergetic effects are positive in the speed constant and the activation energy, but negative in the crosslink density when working at high ZnO levels.

In section 2.4.1. the ability of microwaves to increase the tendency of formation of the active sulfurating compounds and final crosslinks in MCV studies was proved. This increase was caused by the ability of microwaves to overcome high energetical barriers. Both zinc oxide and magnesium oxide reacted with similar kinetics when microwave emission was applied, but what is more important, MgO was able to form the same crosslink density than ZnO when working with microwaves. The synergetic effect between magnesium and zinc oxides could be observed with both heating methods although it was enhanced when using microwaves.

Taking into account MCV results presented in section 2.4.1., it would be logic to think that microwaves are a possible solution to overcome the limitations of MgO as an activator observed for conventional vulcanization. MgO interacts with sulfur and accelerates the formation of the actives sulfurating agents formation, but it affects significantly the crosslink degree, which disqualifies its use in conventional vulcanization. Microwave could increase the vulcanization yield of MgO mixtures, as it does with ZnO (Chapter 3), by increasing their tendency to form active sulfurating agents and improving the sulfur transport to the polymeric chain. In the next section the ability of microwaves to vulcanize natural rubber samples, activated by MgO and mixtures of ZnO and MgO, will be discussed.

4.2.2.2. MICROWAVES VULCANIZATION

As it has been explained in section 2.4.5.1. a multimode microwave oven for continuous vulcanization of rubber profiles was used to perform the first microwaves experiments. Usually this type of ovens is used for continuous vulcanization. A profile extruder is disposed just before the resonator entrance and the resonator is arranged in vertical position, to avoid the rubber profile to get in contact with the reactor walls. In this case samples are heated only for 5 to 10 seconds, the time that they pass through the resonator, and normally materials with high polarity are used to achieve high temperatures in short times. These ovens are used normally as pre-heaters in rubber industry to achieve the curing temperature as fast as possible and homogeneously in all the material. After this pre-heating a conventional curing system is used. This pre-heating is applied to obtain after the curing with conductive heating a vulcanizate as homogeneous as possible and also to safe production time. The aim of our study was to perform the whole vulcanization process using microwaves radiation in order to explore the effects of this energy in the vulcanizing system. Therefore, as showed in Figure 2.23., the geometry of the reactor was changed to work in batch instead of continuously.

Furthermore, and as explained in Chapter 2, there are two different working modes: Power-time and Standard mode. In the former, power and time are fixed whereas temperature changes during the reaction. In the later, temperature remains constant during the reaction time and power varies on time to maintain this temperature. This multimode microwave oven is designed to work only in a Power-time mode. There is no way to maintain the temperature constant during the reaction and also there is not a device to measure rubber temperature. In this study, a thermo-camera has been used, as explained in section 2.4.5.1., in order to control temperature. The input power has been set at a certain value in order to heat the sample approximately at 140ºC. This temperature has been controlled with the thermo-camera. The interest of our study to maintain this parameter constant during vulcanization resides in reproducing conventional vulcanization conditions in order to compare final results.

The development of the method was performed with the reference, Mixture A’ (Table 4.2.). The first problem detected was that in multimode ovens the radiation is not homogeneous in the entire cavity. This is not critical when working in continuous way, but it is in batch processes. Therefore, a study of the most active position in the resonator was performed and Figure 2.24., showed in Chapter 2, displays this zone. All the experiments have been performed in this part of the oven.

At the beginning of the study, it has been observed that at low power input, the reflection was very high. It means that the absorption was very low due to the low polarity of the compounds. It could also be concluded from the thermo-camera images, since the temperatures achieved were very low and the samples needed long times to heat up. When increasing the power input, the reflection was not decreasing at all and what it is worst, the vulcanization was taking place suddenly in some points giving rise to bubbles. It was caused by an overheating in certain points (hot spots). This is one of the drawbacks of the multimode ovens already commented in section 1.2. Trying to improve the heat distribution in the sample a little change in the recipe has been introduced. It is well known, that carbon black (CB) is a very good microwaves absorbent. Thus, 2phr of N550 were added to Mixture A' (Mixture A''). This very unreactive CB was chosen to improve the heat absorption of the material without interfering in the chemistry of the compound. The aim of this change was attained and the samples were able to heat at around 140ºC after 5 minutes with a power input of 60%. The samples were heated for 5, 10, 20, 30, 40, 50 and 60 minutes.

From all the methods for measuring crosslink density used for conventional heated vulcanizates, swelling measurements with Flory-Rehner approach was the only method which could be applied to microwaves vulcanizates. On the one hand, any rheometric study can be performed to calculate the kinetic of microwaves curing process, since there is any rheometer able to apply microwave radiation during the measurements. Furthermore, 2mm specimens are needed for stress-strain measurements and although it was possible to form 2mm pre-vulcanized sheets, the lack of pressure during microwaves vulcanization produced little changes in the samples thickness which could give problems in stress-strain measurements. Therefore, this technique was also rejected for microwaves samples characterization. Thus, swelling was chosen for microwaves samples characterization as the most reliable method and representing the evolution of the network chain density as a function of vulcanizing time, some kind of "rheometer curve" was obtained and the t_{90} for the microwaves process could be chosen to compare with the crosslink density of t_{90} of the conventional vulcanized sample.

Crosslink density was measured by swelling in toluene and using the Flory-Rehner equation, as explained in section 2.4.5.4. Samples after 5 minutes and 10 minutes microwave vulcanization were completely solved during swelling in toluene. It means that they were not vulcanized. Figure 4.19. displays the crosslink density of Mixture A'' vulcanized at 140ºC t_{90} (25 minutes) with conventional heating and the same compound vulcanized with this microwaves method at 20, 30, 40, 50 and 60 minutes. It can be seen how in this case, was sample A'' vulcanized with the microwaves method after 20 minutes. However, the crosslink density achieved with this microwave method was always lower than the maximum crosslink density achieved with conventional vulcanization.

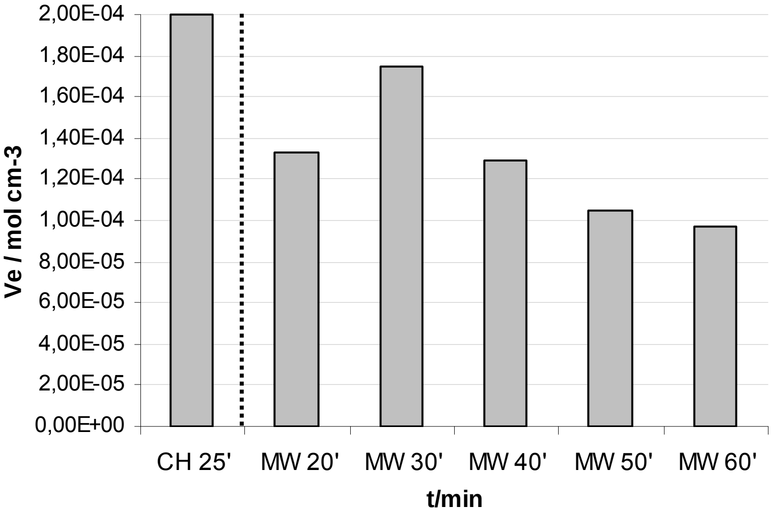

Figure 4.19. Network chain density (ν_e) calculated using Flory-Rehner approach of Mixture A'' heated at 140ºC during 25 minutes with conventional vulcanization and during 20-30-40-50-60 minutes with microwaves vulcanization.

In addition, it can be clearly seen that after 30 minutes MW process there is a strong decrease in network chain density (ν_e) when increasing the vulcanizing time. It seems to suggest that microwave vulcanization under these conditions produces a degradative process in the samples. This degradation is easy to detect in the surfaces of the samples. This degradation could be on the one hand, a high desulfuration of polysulfidic crosslinks to mono- and disulfidic crosslinks as the reversion that it can also be observed in a rheometer. On the other hand and more probably, this degradation could be an oxidative degradation caused by the extreme conditions present in the microwaves resonator: high temperatures and high concentration of O_2 (air) that is in contact with the surface of the sample and it is renewed constantly. This second case can not happen in an electric hot press or in a rheometer because the concentration of O_2 is very low, so it is like working in inert conditions. To corroborate this, Attenuated Total Reflectance (ATR) FTIR Spectroscopy has been performed in the samples surface and a signal at 1741 cm^{-1} corresponding to carbonyl has been detected after 30 minutes microwaves vulcanization. The signal appears in Figure 4.20. marked with a circle and its intensity increases with the vulcanizing time. Thus, an oxidative aging has been proved.

In order to confirm this oxidative degradation, a new receipt has been developed. This new compound (Mixture O'') is very similar to Mixture A'' but substituting NR by Ethylene Propylene Diene Monomer (EPDM), a saturated synthetic rubber that cannot be oxidized (Table 4.6.). It must be noted at this point that the development of this EPDM mixture is only a specific experiment designed with the aim of confirming the oxidative degradation problem of NR samples. This new compound has been studied with rheometer at 160ºC and t_{90} for CH has been determined at 32 minutes. The same compound has been vulcanized with the microwaves oven, but the power input must be increased to 80%, because of the difficiulty to achieve the desired temperature (160ºC). The samples were heated for 10, 20, 30, 40, 50 and 60 minutes. Figure 4.21. displays the crosslink density of Mixture O’’ vulcanized at 160ºC t_{90} (32 minutes) with conventional heating and the evolution of the crosslink density with the time of the same compound vulcanized with this microwaves method. Although in this case the crosslink density could not achieve the same value than conventional heating, any degradative process was observed in 60 minutes microwaves treatment and also, only 10 minutes of microwaves vulcanization were enough to achieve the maximum crosslink value showing the power of microwaves to increase the reaction speed.

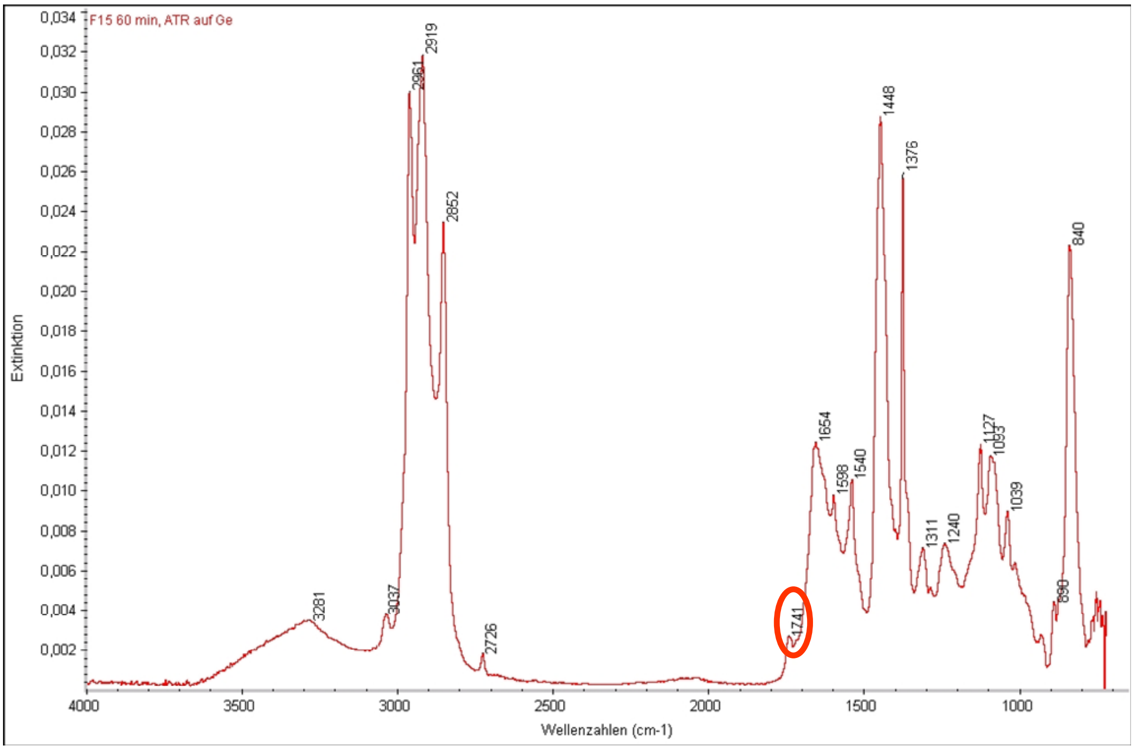

Figure 4.20. ATR FTIR of Mixture A’’ vulcanized 30 minutes with the microwaves multimode oven.

Table 4.6. Natural Rubber recipe.

INGREDIENTS(phr)	Mixture O’’
EPDM	100
CBS	1.2
Sulfur	2
ZnO	5
CB (N550)	2
Stearic acid	2

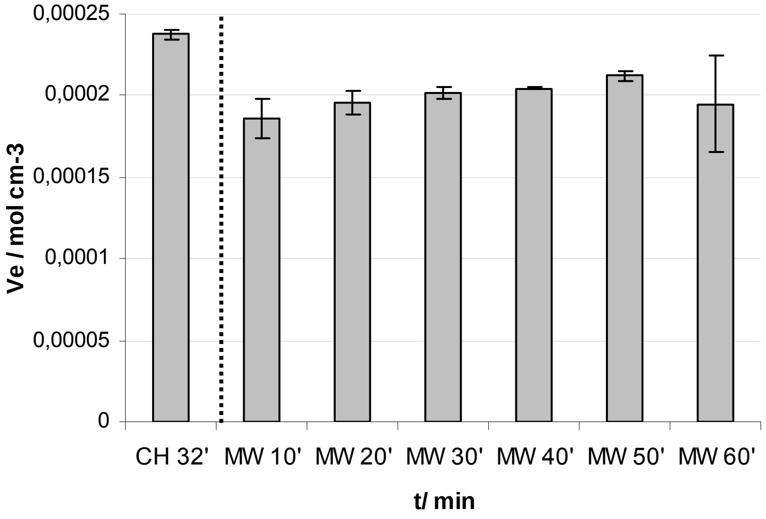

Figure 4.21. Network chain density (ν_e) calculated using Flory-Rehner approach of Mixture O'' heated at 140ºC during 32 minutes with conventional vulcanization and during 10-20-30-40-50-60 minutes with microwaves vulcanization.

Once confirmed the oxidative aging that the NR compounds suffer in this microwave treatment, a new change has been introduced in the method in order to reduce the contact between the rubber surface and the O_2 present in the air inside the resonator. In the industry powerful antioxidants are used for microwaves vulcanization to avoid oxidation, but in this case this possibility was rejected because it would have changed the chemistry of the vulcanizing system and it would have made the results not directly comparable with the ones obtained with conventional heating. Thus, a little glass press has been designed. The rubber sample was situated between two pieces of glass to avoid the oxidation of the surface, as Figure 4.22. shows, and this device was situated in the active zone over the Teflon® support. With this strategy the contact of the O_2 with the rubber sample was reduced and better crosslink densities with the microwaves method could be obtained.

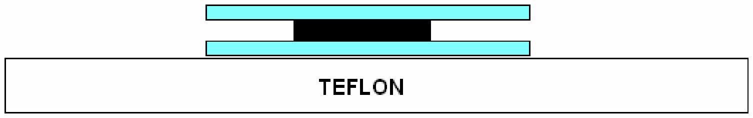

Figure 4.22. Glass press designed to reduce the contact between O_2 and the rubber surface.

Parallel mixtures to Mixtures A'' (containing 2phr of N550) were prepared as analogs of Mixtures B', C', D' and E' but adding the CB for a better dispersion. Mixtures A'' (5phr ZnO), B'' (3.5phr ZnO + 1.5phr MgO), C'' (2.5phr ZnO + 2.5phr MgO), D'' (1.5phr ZnO + 3.5phr MgO) and E'' (5phr MgO) were heated with this glass press at around 140ºC inside the microwaves oven with a power input of 20% and a reflection about 25%. The samples were heated for 2, 5, 10, 20 and 30 minutes. Figure 4.23. displays the maximum crosslink density achieved for these five NR compounds with both heating methods. Only mixture C'' (50% ZnO + 50% MgO) was able to achieve the same crosslink density than conventional vulcanization under these conditions.

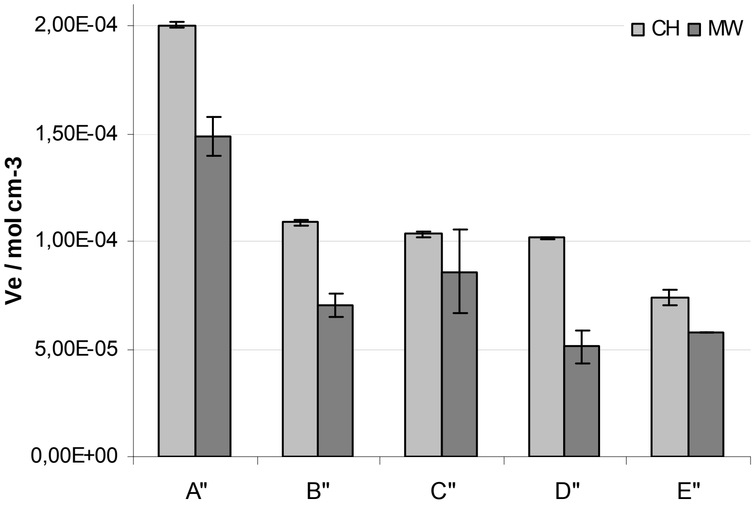

Figure 4.23. Maximum network chain density (ν_e) calculated using Flory-Rehner approach of Mixtures A'', B'', C'', D'' and E'' heated at 140ºC with conventional vulcanization and multimode microwaves vulcanization.

Although with this device the crosslink density has improved, there were still signals of oxidative degradation in the surface of the samples. Evidently, the microwaves method developed presented some obstacles that interfere in the correct performance of the microwaves curing and hamper the correct development of the study of the effect of this radiation in the role of the activator.

The main problem was caused by the design and nature of the microwaves oven used. This multimode oven was though for being used for the vulcanization of rubber profiles and in a continuous way. When working with larger sample sizes, the presence of the multiple areas of energy is not as significant; the sample moves around and is large enough to effectively absorb the existing microwave energy. However, with a single smaller sample, as in our case, the chance of the one sample of a few milliliters in volume within the cavity effectively absorbing the microwave energy moving around a big cavity is very low, resulting in slow or non-existent heating profiles and a significant amount of energy being wasted[25]. Thus, forcing a multimode microwaves oven to act as a single mode oven is not an optimum way to profit the microwaves radiation. And this is the reason to the bad results obtained with the method developed. In section 1.2. the differences between these two types of microwaves ovens have been presented. The basic drawback of multimode ovens is the lack of direction of the radiation field. This lack of control gives rise to multiple active modes and to reproducibility problems. One evidence of these reproducibility problems can be seen in the standard deviation presented in Figure 4.23. In this graph it is clear that for all the compounds tested, the reproducibility is always higher microwaves curing with the multimode oven than for conventional vulcanization. Furthermore, these ovens do not permit to control the temperature during the reaction what makes the control of the method difficult[26]. On the other hand, single mode ovens can not work continuously but they give an homogeneous energy distribution in the cavity that solves the reproducibility problems of multimode ovens. The microwaves oven used for MCV studies was a single mode oven. Therefore, NR experiments have been also performed in this single mode oven to explore the effects of microwaves in the role of the activator and improve the results obtained for the multimode method.

Pre-vulcanized sheets of 1mm of Mixtures A', B', C', D' and E' (Table 4.2.) were prepared as explained in section 2.4.5.1. In this case any CB was needed to improve the heat distribution since single mode ovens profit better the microwave energy due to a better and homogeneous distribution along the cavity of the oven forming a unique energy node. These compounds were treated as the MCV samples. On one hand, they were sealed under N_2 atmosphere and vulcanized at 140ºC in a silicon bath at 5, 10, 20, 30 and 60 minutes. On the other hand, the microwaves method developed for squalene, described in section 2.4.2., was used to vulcanize these NR compounds at 1, 2, 3, 4, 5, 10, 20 and 30 minutes. A CEM Focused Microwaves Synthesis System (Model Discover) was used and the conditions used have been already presented in Table 2.4. In this case the samples were also sealed under N_2 atmosphere, so any oxidative degradation could occur.

Figure 4.24. displays the maximum network chain density (ν_e) obtained for the five compounds with both heating methods. The crosslink densities achieved with the single mode microwaves method are higher than the values obtained for the multimode microwaves method (Figure 4.23.).

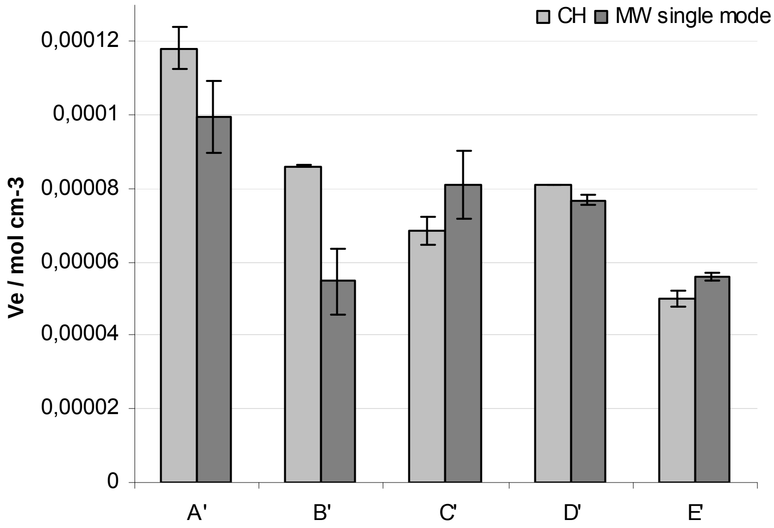

Figure 4.24. Maximum network chain density (ν_e) calculated using Flory-Rehner approach of Mixtures A', B', C', D' and E' heated at 140ºC with conventional vulcanization and single mode microwaves vulcanization.

An improvement in the crosslink density in comparison with the conventional vulcanization results has been obtained only for those compounds containing 50% or more of MgO (Mixtures C', D' and E'). Thus, the dual synergetic effect already displayed in Figure 4.15. for conventional vulcanization has been enhanced by microwaves (Figure 4.25). In this figure it is clear than the positive synergetic effect detected in conventional vulcanization (black line) at high MgO content has been enhanced in microwaves vulcanization (grey line), and also an increase in the negative synergetic effect at high ZnO content has been detected.

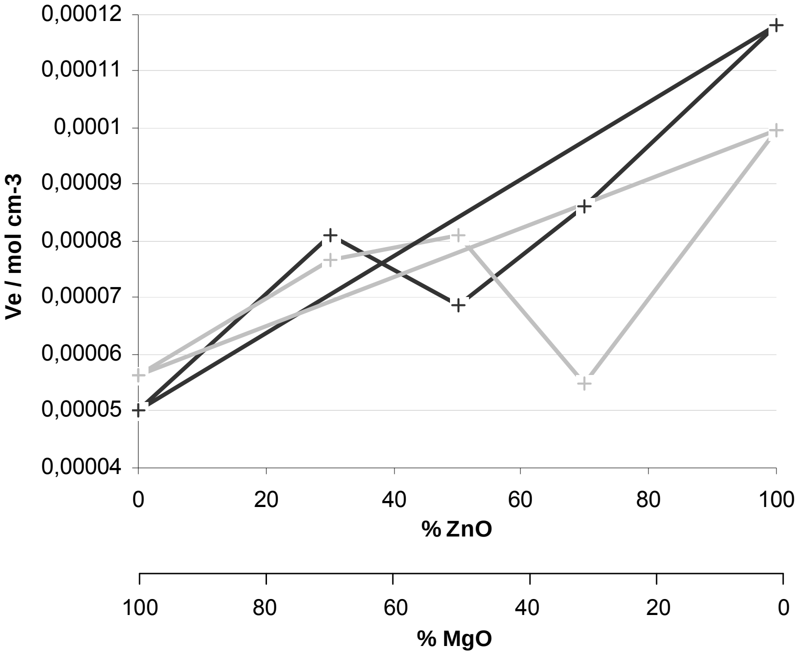

Figure 4.25. Network chain density (ν_e) calculated by Flory-Rehner as a function of the composition of ZnO and MgO of mixtures A', B', C', D' and E' vulcanized with CH (black) and MW (grey) at 140ºC.

Apparently the samples vulcanized with the single mode microwaves method seem to have an uniform curing or at least, better than in the case of the multimode oven. However, when cutting a sample and studying its section, it was easy to observe the presence of bubbles that suggest that although the macroscopic temperature was 140ºC, higher microscopic temperatures were achieved in some domains inside the material. This overheating of certain points could be the factor which caused the lower crosslink density observed in some compounds vulcanized with microwaves due to reversion processes and premature aging of the material. At the beginning of section 3.2., it has been exposed that in microwaves reactions is more important the power of microwaves applied than the global temperature created. An experiment has been presented in Figure 3.10., two samples of squalene (model compound) were vulcanized at 140ºC, but with different power input. It has been observed that the higher the power input, the higher the crosslink density achieved. It has been concluded that microwave reaction mechanisms, due to the higher energy transfer efficiency, are less macroscopic temperature dependent than the conductive heating processes. Thus, some experiments at lower macroscopic temperatures have been performed in order to minimize this localized overheating and study the effect of this macroscopic temperature reduction in the crosslink density of these five compounds. The idea is that maybe microwaves vulcanization could obtain the same crosslink density than conventional heating at lower temperatures and increasing anyway reaction speed. Figure 4.26. displays the maximum crosslink densities obtained for Mixtures A', B', C', D' and E' at 140ºC with the silicon bath (CH) and at 140ºC, 120ºC and 100ºC with the single mode microwaves oven (MW). In addition, Table 4.7. shows the times needed for all these methods to achieve these maximum crosslink densities.

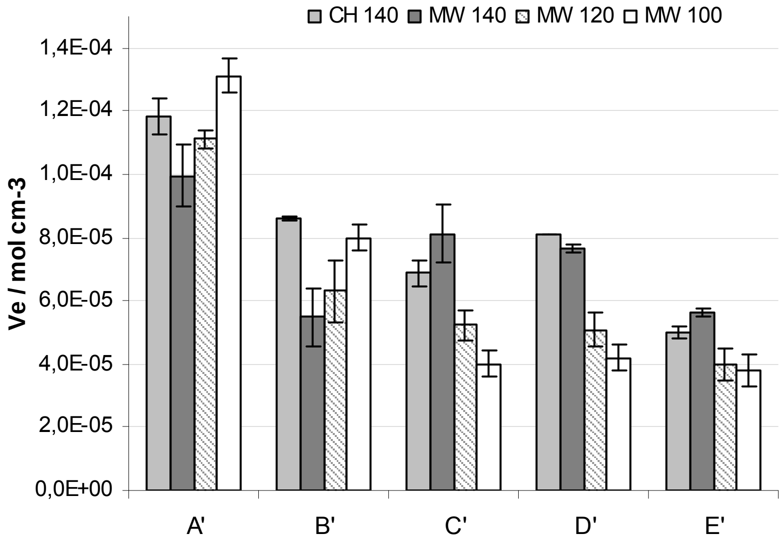

Figure 4.26. Maximum network chain density (ν_e) calculated using Flory-Rehner approach of Mixtures A', B', C', D' and E' heated at 140ºC with conventional vulcanization and at 140ºC, 120ºC and 100ºC with microwaves vulcanization.

Table 4.7. Times needed to achieve maximum crosslink density.

Heating Methods	Mixture A'	Mixture B'	Mixture C'	Mixture D'	Mixture E'
Silicon Bath (CH)	30 min	5 min	5 min	5 min	10 min
MW 140ºC	10 min	4 min	1 min	2 min	3 min
MW 120ºC	10 min	1 min	3 min	2 min	1 min
MW 100ºC	10 min	3 min	5 min	3 min	4 min

For Mixtures A' (100% ZnO) and B' (70% ZnO + 30% MgO) it is clear that the lower the macroscopic temperature, the higher the crosslink density. This proves that with microwaves it is possible to enhance the crosslink density obtained with conventional vulcanization in NR samples. And what it is more important, not only increasing the reaction speed but also decreasing the temperature of the process (30 minutes were needed with the silicon bath at 140ºC to achieve Plateau, whereas only 10 minutes where needed to achieve a higher Plateau with the single mode microwaves at 100ºC). This trend is not followed by Mixtures C', D' and E', which obtain better crosslink degree for the microwaves method at 140ºC. Thus, microwaves were able to increase the crosslink density of all this compounds although it seems that MgO needs higher temperatures to have a good behavior in microwaves vulcanization due to its lower polarity in comparison to ZnO.

To summarize the results discussed in this section, it can be concluded that it has been proved that microwaves have a higher ability to vulcanize rubber than conventional heating for all activator systems, although different conditions have been found to be optimal depending on the ZnO and MgO content. Furthermore, although crosslink densities of the compounds containing partially or totally MgO as activator have been improved in comparison to the values obtained with conventional vulcanization, this increase is lower as the increase obtained with squalene in the MCV studies and they are unable to achieve the crosslink density of the reference, Mixture A' (100% ZnO). The synergetic effect between ZnO and MgO seems to be enhanced in comparison with conventional vulcanization but also less than in MCV studies. On the other hand, it has been proven that good crosslink densities can be obtained in some cases working with microwaves at lower temperatures. This would minimize the overcrosslinked domains observed in microwaves vulcanization that could give problems of homogeneity in the final vulcanizate and also it would minimize energy costs when working at industrial scale.

In the next section, a new approach to face the competence problem between ZnO and MgO will be presented. It consists in the development of new activators based in the mixture of both mixed oxides at nanoscale. The effect of this mixture at nanoscale in the synergetic effect of both oxides will be discussed and compared with the results of mechanical mixture of ZnO and MgO.

4.2.3. DEVOLEPEMENT OF NEW ACTIVATORS

In collaboration with the Department of Inorganic Chemistry of Universidad de Salamanca some mixed oxides of Zn and Mg have been synthesized and tested as possible activators, substitutes for ZnO.

These mixed oxides have been obtained through the calcination of hydrocalcite compounds. The structure of these compounds (Figure 4.27.), also known as Layered Double Hydroxides, is similar to brucite, in which each magnesium is surrounded by six hydroxyl groups forming octahedrons. The different octahedrons share edges forming infinite sheets, joined by hydrogen bonding. If some Mg^{2+} cations are replaced isomorphicly by cations with more charge but similar radium. Therefore, sheets brucite type will be charged positively. In this case, Mg^{2+} was substituted by Al^{3+}. This excess of charge is compensated with the localization of anions in the intersheet space which coexist with water molecules. The chemical formula of this compound is,

$$[M_{1-X}^{II}\ M_{x}^{III}\ (OH)_2]\ (A_{x/m})^{m-} \cdot nH_2O$$

being M^{II} and M^{III} the divalent and trivalent cations respectively and A the intersheet anion.

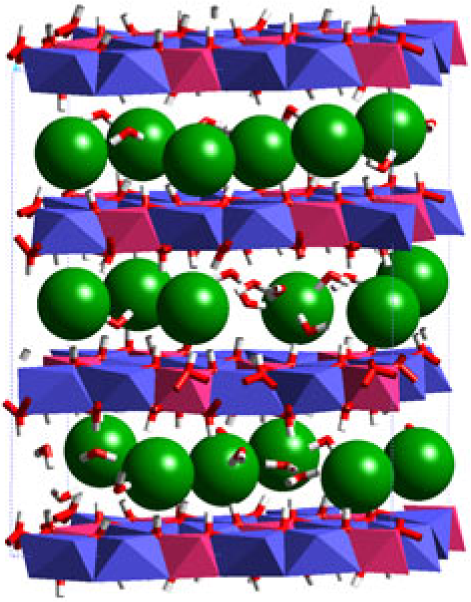

Figure 4.27. Hydrocalcite structure[27].

One of the applications of these compounds is the use as precursors of mixed oxides. The use of these precursors has suffered an increase in the last years due to the exceptional properties that they contribute to the mixed oxides:

- High specific surface area (100-300 m^2/g)
- Homogeneous interdispersion and thermally stable of the elements
- Synergetic effect between the elements
- Memory effect, with reconstruction of the structure in soft conditions

A parameter which is quoted to affect the activity of ZnO is the specific surface area[11]. In the so-called higly active zinc oxides the mean particle size is decreased and the specific surface area increased, which results in a easier and better dispersion and a higher reactivity[9]. ‘Active’ zinc oxides are normally prepared with BET specific surfaces ranging from 30 to 70 m^2/g compared to ~6 m^2/g for conventional red seal ZnO. The higher activity is probably due to the increased accessibility of Zn^{2+} ions at the surface compared to the conventional particle sizes. ZnO is a dense material which tend to compact and it is difficult to disperse. Thus, the homogeneity of dispersion of the ZnO in the rubber matrix is an important parameter, just as the contact surface between the ZnO particles and the accelerators. Said in other words, the key factors in this process are the particle size and the specific surface of the oxides. Therefore, it could be concluded that hydrocalcites have the suitable characteristics to act as a precursors of mixed oxides potentially active as activators for rubber vulcanization.

4.2.3.1. MIXED OXIDES SYNTHESIS AND CHARACTERIZATION

Five different hydrocalcite-type compounds have been synthesized with Zn^{2+} and Mg^{2+} as a divalent cations and Al^{3+} as the trivalent cation by the Department of Inorganic Chemistry of Universidad de Salamanca. The ratio (Zn+Mg)/Al has been maintained at a constant value 3. The ratio Zn^{2+}/Mg^{2+} has been modified from a 100% Zn content to 0%. Therefore, five different layered double hydroxides have been synthesized with general formula:

$$[Zn_{1-X}\, Mg_X\, Al_{0.25}\, (OH)_2]\, (CO_3)_{0.125} \cdot nH_2O$$

where x = 0, 0.19, 0.38, 0.55 and 0.75 (samples A(100%Zn), B, C, D and E(100%Mg)).

This syhthesis has been performed using a co-precipitation method[28], which consists of the addition drop by drop of a solution that contains salts of the cations ($ZnCl_2$, $MgCl_2$ and $AlCl_3$) in the desired proportions, into a Na_2CO_3 solution at room temperature. pH has been maintained constant at a value of 10 with the help of a pH Burete 24 (Crison) by adding if necessary a solution NaOH 1M. The precipitate was maintained under stirring for 20h, subsequently washed several times with bidistilled water and dried in an oven at 40ºC.

In order to enhance the crystallinity of the samples A, B, C and D, two types of hydrothermal treatments have been performed: the conventional hydrothermal treatment (CHT)[29] by using steel bombs with Teflon® coating, and the microwave hydrothermal treatment (MHT)[30] using in this case a microwave oven.

In the case of conventional hydrothermal treatment an aliquot of the samples was taken after 5 minutes stirring and were heated at 125ºC during 24h (samples ACHT, BCHT, CCHT, DCHT). With regard to microwave hydrothermal treatment, it was carried out at 100ºC during 180 minutes (samples AMHT, BMHT, CMHT and DMHT) in an Ethos Plus Microwave Oven with the help of Easyware software.

The mixed oxides were obtained by using a new calcinations system with a microwave-muffle, Milestone Pyro System, at 550ºC for 2h and a heating ramp of 5ºC/min. The nomenclature of these mixed oxides is the same than the one of their precursors but adding 550 at the end. The five mixed oxides synthesized have a general formula:

$$(ZnO)_{0.75-X}\ (Mg)_X\ (Al_2O_3)_{0.125}$$

where x = 0, 0.1875, 0.375, 0.5625 and 0.75 (samples A(100%Zn), B, C, D and E(100%Mg)). Table 4.8. summarizes the different mixed oxides synthesized.

Table 4.8. Mixed oxides synthesized.

Sample Name	% Zn	% Mg	Synthesis Type	Calcination Temperature	Calcination time
A550	100	0	Dried 40ºC	550ºC	2h
ACHT550	100	0	CHT	550ºC	2h
AMHT550	100	0	MHT	550ºC	2h
B550	75	25	Dried 40ºC	550ºC	2h
BCHT550	75	25	CHT	550ºC	2h
BMHT550	75	25	MHT	550ºC	2h
C550	50	50	Dried 40ºC	550ºC	2h
CCHT550	50	50	CHT	550ºC	2h
CMHT550	50	50	MHT	550ºC	2h
D550	25	75	Dried 40ºC	550ºC	2h
DCHT550	25	75	CHT	550ºC	2h
DMHT550	25	75	MHT	550ºC	2h
E550	0	100	Dried 40ºC	550ºC	2h

The precursors (hydrocalcites) and the mixed oxides were characterized with the following techniques:

- **Chemical Elemental Analysis** (Mark 2 EII-240 analyzer)
  The chemical elemental analysis was useful to prove that the experimental (Mg+Zn)/Al ratio is nearly 3 in all cases and that the Zn/Mg ratio is the desired for every sample.
- **X-Ray Diffraction** (Siemens D-500 diffractometer)
  This technique permitted to verify that ZnO crystallizes as *cincite* with an hexagonal system whereas MgO crystallizes as *periclase* with a structure type NaCl. The incorporation of MgO in the structure can be seen comparing the diffractograms of the different compounds.
- **IR spectrometry** (Perkin-Elmer FTIR 1600)
  This technique was useful to observe how the OH^- and CO_3^{2-} bands disappear in the transition from hydrocalcite to oxide.

- **TG** (Perkin-Elmer TGA-7) and **DTA** (Perkin-Elmer DTA-7)
  The thermal analysis was useful to determine that the higher the Mg^{2+} content in the compounds, the more intersheet water was found.
- **SEM** (Scanning Microscope Zeiss DSM 940 connected with a Scan Converter DSC-1024 G Sony, using MIP 4 Advanced for the data processing)
  SEM micrographies showed that with microwave hydrothermal treatment the surface of the oxides was more homogeneous.
- **BET** (Micromeritics Gemini v1.03. Degasification of the samples was carried out in an Micromeritics Flowprep 060 oven, at 150ºC for 2h)
  The Adsorption-Desorption Isothermes of N_2 were identified as type II, according to IUPAC classification, with hysteresis H3. The higher the Mg content, the higher the surface area, being this tendency much higher for the oxides obtained with microwave hydrothermal treatment.
- **Particle Size** (Saturn Digisizer 5200 v1.11)
  The general conclusion obtained with this technique was that when using microwave hydrothermal treatment, samples have smaller particle size, with higher porosity.

More details of the synthesis optimization and characterization of these mixed oxides can be found in the master thesis of Ivan Guinea[31]. In the next section only the BET and Particle Size results will be presented and related with the behavior of these mixed oxides as activators for rubber vulcanization.

4.2.3.2. MIXED OXIDES AS NEW ACTIVATORS FOR VULCANIZATION

A parallel MCV study to the developed in section 4.2.1. has been performed to test the behavior of these mixed oxides as activators for vulcanization. Two reference samples have been prepared with ZnO and MgO to have a reference value to make the comparisons. Table 4.9. shows the recipes of these two references and the recipe used to test the new activators developed.

Table 4.9. Model Compound Vulcanization recipes.

INGREDIENTS(phr)	Mixture ZnO	Mixture MgO	Mixture X
Squalene	100	100	100
CBS	1.2	1.2	1.2
Sulfur	2	2	2
ZnO	4.15	-	-
MgO	-	3.5	-
Al_2O_3	0.85	1.5	-
Mixed Oxide (X)	-	-	5
Stearic acid	2	2	2

In all cases 5phr of activator were used in the activator system. The two references contain ZnO or MgO and Al_2O_3 maintaining the atomic proportion Zn/Al and Mg/Al at a constant value 3, as the mixed oxides do. Therefore, the ZnO reference (Mixture ZnO) is similar to mixtures A550, ACHT550 and AMHT550 and the MgO reference (Mixture MgO) is similar to mixtures E550.

These model compound mixtures were sealed under N_2 atmosphere and vulcanized with the silicon bath and with the single mode microwaves oven as explained in section 2.4.2. Consequently, vulcanizates were analyzed with the methods described in sections 2.4.3.1. and 2.4.3.2. Before presenting the activating behavior of the different activators, the results of specific surface area and particle size of these oxides will be presented.

Specific Surface Area and Particle Size

As stated before, a parameter which is quoted to affect the activity of ZnO is the specific surface area[11]. The higher the specific surface area, the easier and better dispersion, and the higher reactivity[9]. Figure 4.28. displays the BET specific surfaces of the references, ZnO (grey quarter) and MgO (black quarter), and all the mixed oxides synthesized.

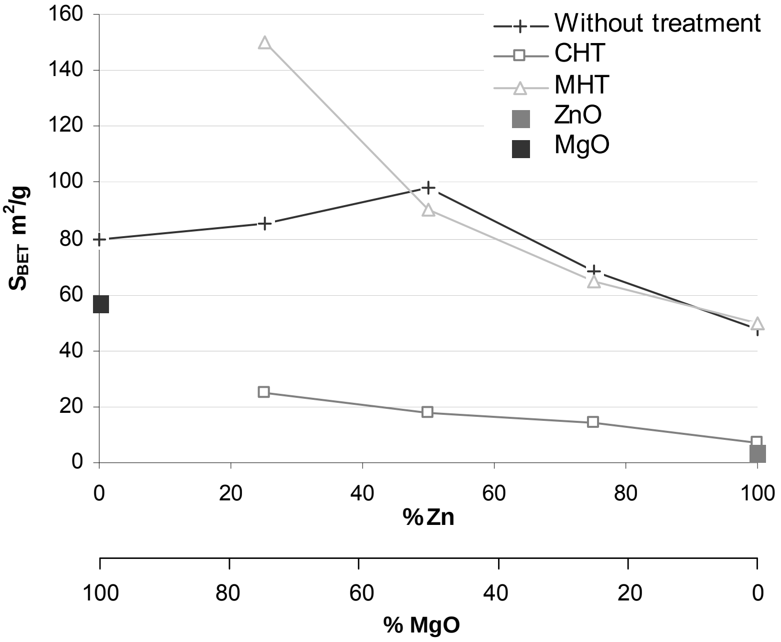

Figure 4.28. BET specific surface area of ZnO, MgO and the 13 new activators developed.

It is known that ZnO is a dense material which tends to compact and it is difficult to disperse. Thus, its specific surface area is lower than MgO. Furthermore, independently of the treatment used, the higher the MgO content, the higher the BET specific surface area. It can be clearly seen that the mixed oxides that come from the conventional hydrothermal treatment (CHT) present the lowest specific surface area. In the master thesis of Ivan Guinea[31] it was suggested that this low specific surface area could be caused by the fact that ZnO is crystallized before the calcination. On the other hand, samples treated with the microwaves hydrothermal treatment (MHT) present always the highest specific surface area, being the differences with other treating methods even higher when increasing the MgO content. At the beginning of section 4.2.3. it has been said that 'active' zinc oxides are normally prepared with BET specific surfaces ranging from 30 to 70 m^2/g compared to ~6 m^2/g for conventional red seal ZnO. Thus, concerning this factor these synthesized mixed oxides are expected to be good activators.

Another parameter that is known to condition the activating behavior in vulcanization is the particle size. Figure 4.29. displays the particle size distribution of the references, ZnO and MgO, and also of the Al_2O_3 used to reproduce the proportions of the mixed oxides synthesized. Al_2O_3 have a monomodal distribution centered in 100μm. ZnO and MgO have a broader multimodal distribution between 1-10μm for ZnO and 1-50μm for MgO.

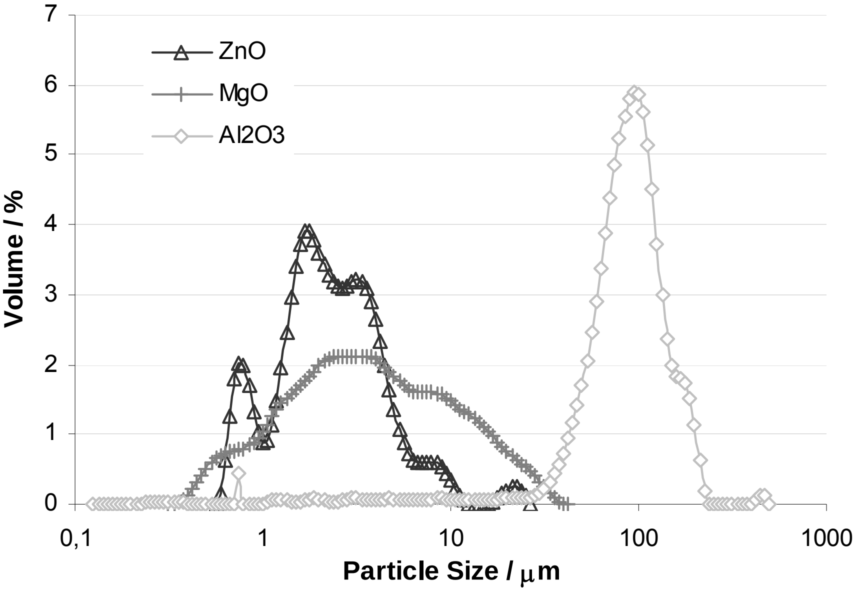

Figure 4.29. Particle size distribution of ZnO, MgO and Al_2O_3.

Figure 4.30. shows the particle size distribution of the mixed oxides treated with the conventional hydrothermal treatment (CHT). Regarding the BET specific surface area (Figure 4.28.), they were the mixed oxides with lower values. Their particle size distributions are very broad and multimodal, between 1 and 150μm. It seems that ACHT550 (100% ZnO) has the higher population of particles around 100μm and when increasing the MgO content, particles tend to be smaller, around 1 and 50μm.

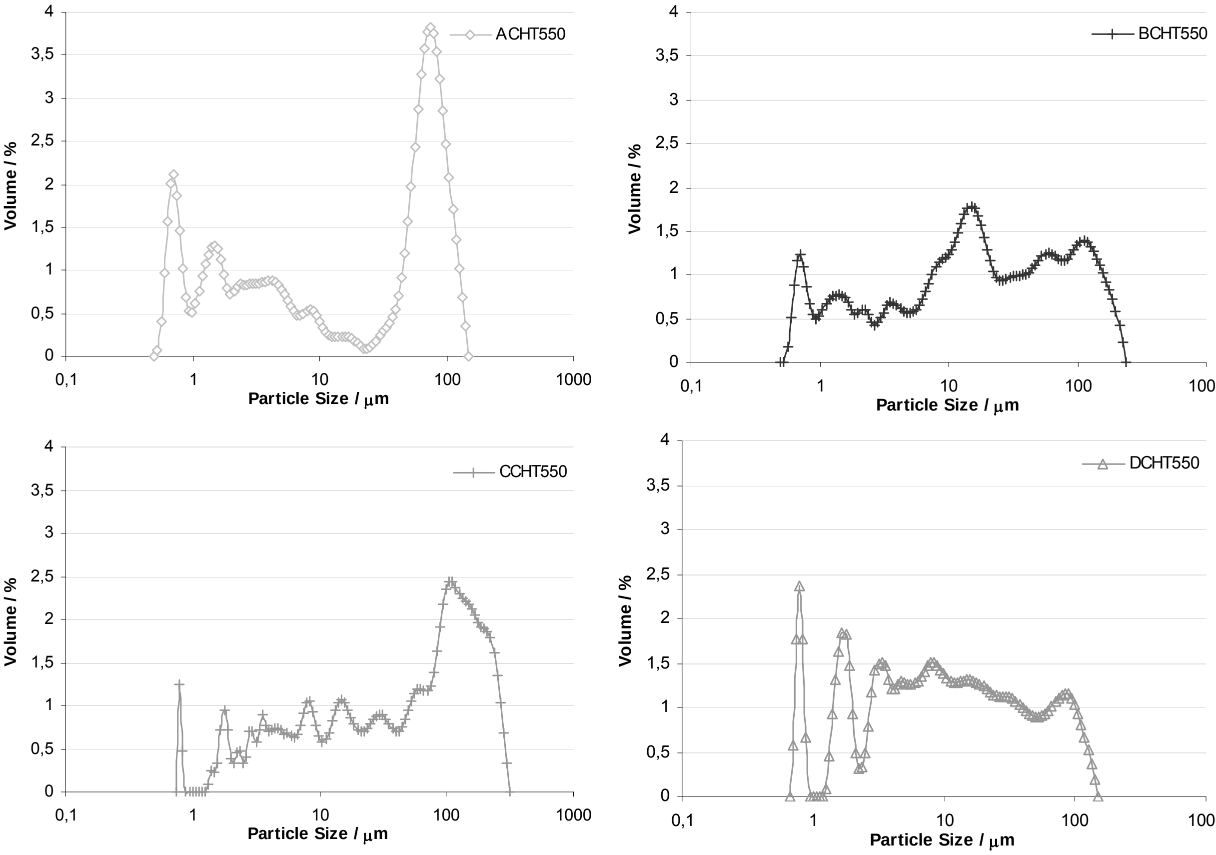

Figure 4.30. Particle size distribution of ACHT550, BCHT550, CCHT550 and DCHT550.

Figure 4.31. displays the same graphs for the mixed oxides synthesized without any treatment. In this case, samples had higher specific surface area and particle size distributions are also multimodal and broad, and the same trend presented for CHT samples can be observed: the higher the MgO content, the smaller the particles.

Finally, Figure 4.32. shows the particle size distribution of the mixed oxides treated with the microwaves hydrothermal treatment (MHT). Particle size distributions are also multimodal and broad, and the already commented trend presented for the rest of the samples can be also observed and it seems to be enhanced by the microwaves treatment. Thus, MHT are the samples with higher population of smaller particles, which could be the reason of the higher specific surface area presented in Figure 4.27.

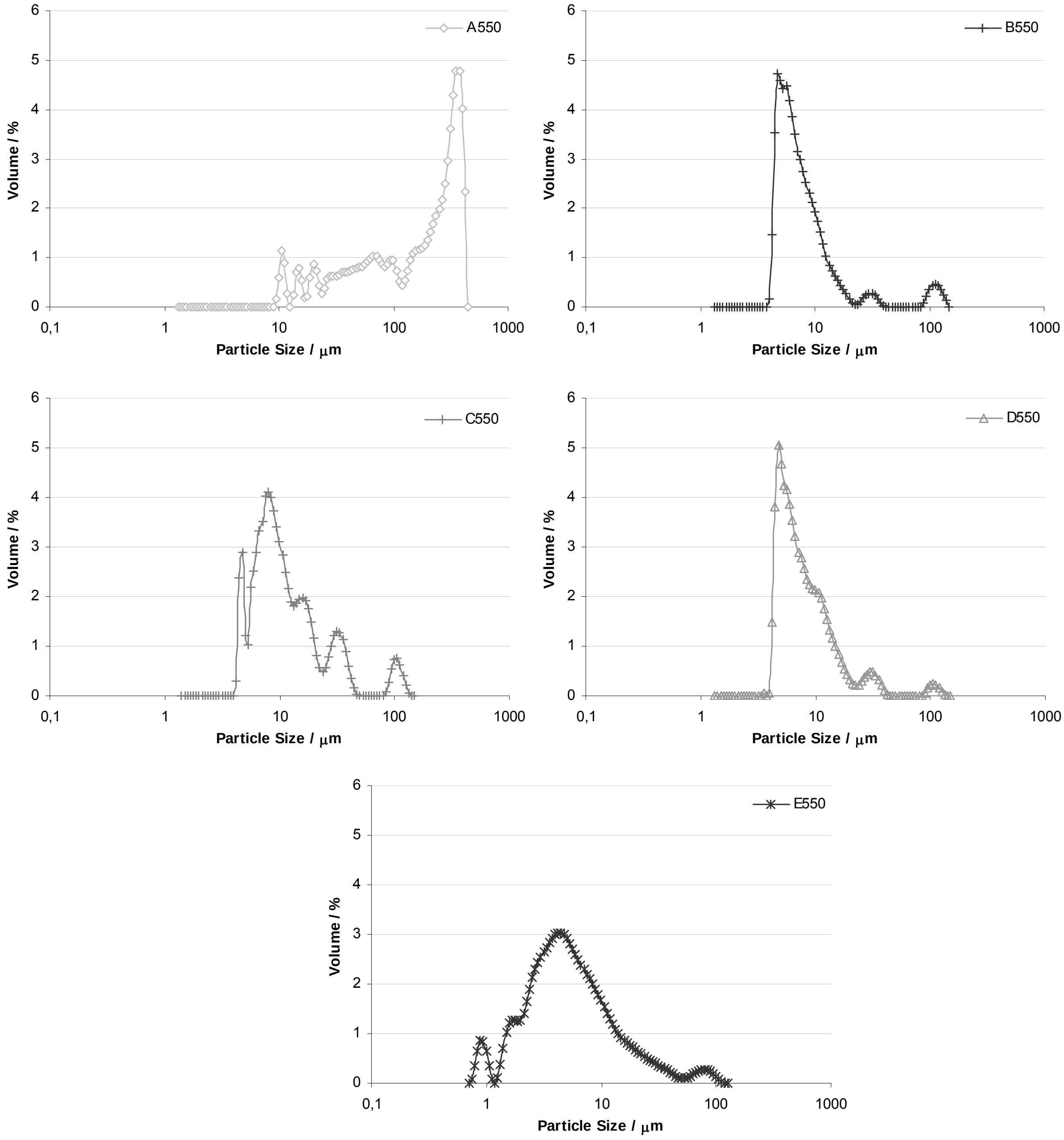

Figure 4.31. Particle size distribution of A550, B550, C550, D550 and E550.

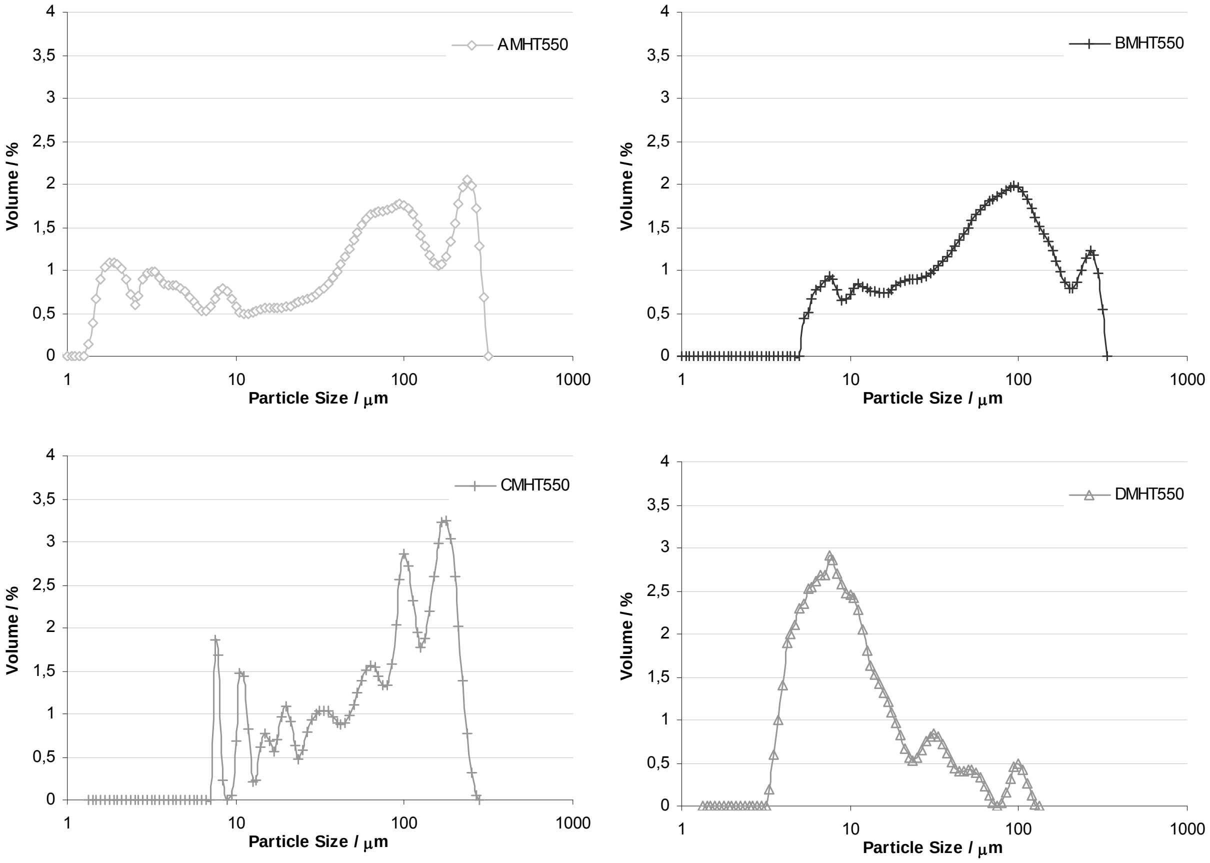

Figure 4.32. Particle size distribution of AMHT550, BMHT550, CMHT550 and DMHT550.

Conventional Vulcanization

As it has been seen along this chapter, MgO promotes a faster vulcanization kinetic than ZnO. Thus, the mixed oxides also follow this trend and they increase the kinetic of degradation of the sulfenamide, and also the kinetic of the crosslink formation, when increasing MgO content. It has to be pointed out, that although there are slight differences between them, after 30 minutes reaction all of them achieved Plateau (maximum crosslink density). More changes have been detected considering the degree of crosslink. Figure 4.33. displays the maximum crosslink density achieved with each activating system. The crosslink density has been expressed as the total area of crosslinked squalene (the sum of the areas of all crosslinked types detected with the HPLC method explained in section 2.4.3.2.) referred to the vulcanizate weight. The 13 mixed oxides developed have a positive effect in the crosslink degree. These good results are caused on one hand by the higher specific surface area of the synthesized oxides, in comparison with the references, already commented in this section. On the other hand, mixed oxides based on hydrocalcites are supposed to enhance the synergetic effects between the metals, as commented in section 4.2.3. It seems to be a positive synergetic effect with the samples B (70% ZnO – 30% MgO) and C (50% ZnO – 50% MgO) with all treatments.

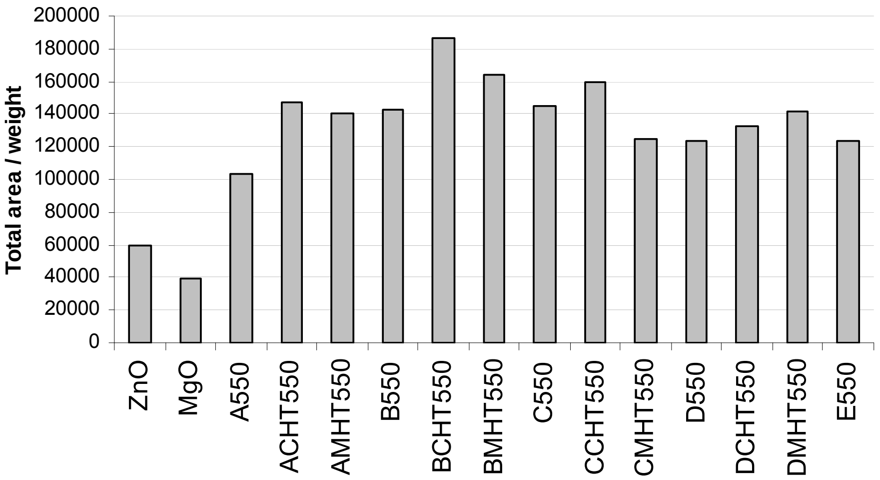

Figure 4.33. Crosslink density of ZnO, MgO and the 13 mixed oxides synthesized after 50 minutes conventional vulcanization.

To study this synergetic effect the following graph has been developed. Figure 4.34. displays the trend followed by the maximum crosslink density obtained by all the mixed oxides developed and also ZnO (grey square) and MgO (black square).

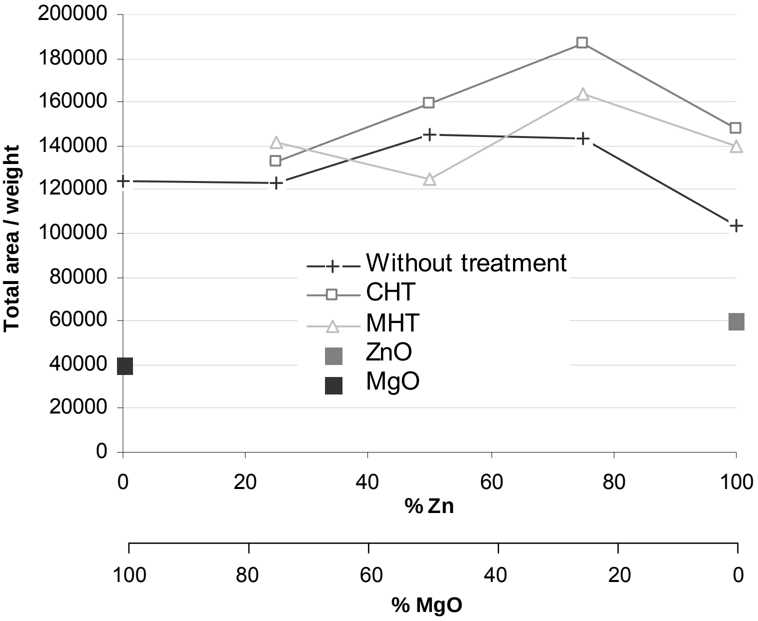

Figure 4.34. Crosslink density of ZnO, MgO and the 13 mixed oxides synthesized as a function of the composition of ZnO and MgO after 50 minutes conventional vulcanization.

The better crosslink density results have been achieved by the samples subjected to conventional hydrothermal treatment. This result does not fit with the specific surface area results, since conventional hydrothermal treated samples were the samples with lower specific surface area.

Regarding the crosslink structure, some changes have been detected between the different activating systems. Figure 4.34. displays the distribution of the different sulfidic crosslink types after 50 minutes conventional vulcanization at 140ºC. It can be seen, as proved for NR samples, that the MgO sample has a greater tendency to form long crosslinks than the ZnO sample for a given S/A ratio. The non treated mixed oxides follow this trend very clearly as it can be seen in the graph above in Figure 4.35.

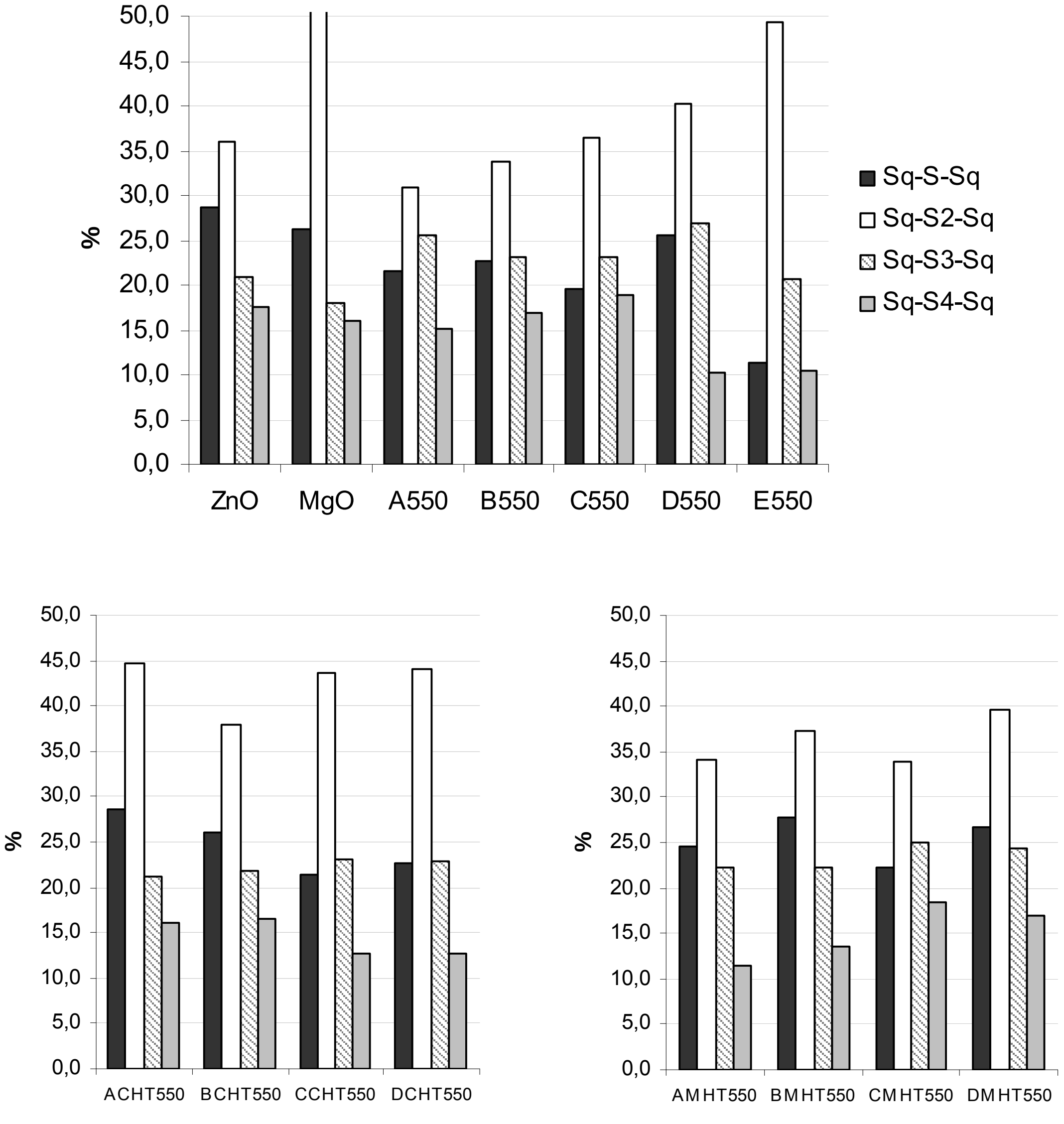

Figure 4.35. Distribution of sulfidic crosslinks (crosslink structure) in the two references and the 13 mixed oxides developed after 50 minutes conventional vulcanization.

On the other hand, samples subjected to conventional hydrothermal treatment (CHT) have a similar distribution of sulfidic crosslinks independently of the MgO and ZnO content, and it is very similar to the crosslink structure obtained to the MgO reference. Finally, samples subjected to microwaves hydrothermal treatment (MHT) have also a similar distribution of sulfidic crosslinks between them and it seems to be also independently of the MgO and ZnO content, but with a more similar crosslink structure to the ZnO reference in this case.

This preliminary MCV study shows promising results for this kind of mixed oxides as activators for vulcanization. Furthermore, they seem to be a solution to reduce ZnO contents in rubber goods without affecting the final properties. The next step to perform is to find a viable way to scale up the synthesis of these mixed oxides and perform real rubber tests.

Microwaves Vulcanization

The same MCV study has been performed with microwaves vulcanization. As it has been seen in Figure 4.2., MW is able to achieve the same crosslink density for ZnO and MgO, whereas MgO achieves a lower crosslink degree in conventional vulcanization, as showed in Figures 4.2. and 4.32. MW also enhances the kinetics of all vulcanizing systems, and in this case, it only took 5 minutes to achieve the maximum crosslink density. As for conventional vulcanization, it does not seem to be significant differences between the kinetics of the different activating systems. Figure 4.36. displays the maximum crosslink density achieved with each activating system when using MW. The crosslink density has been expressed as the total area of crosslinked squalene (the sum of the areas of all crosslinked types detected with the HPLC method explained in section 2.4.3.2.) referred to the vulcanizate weight. The 13 mixed oxides developed have also a positive effect in the crosslink degree.

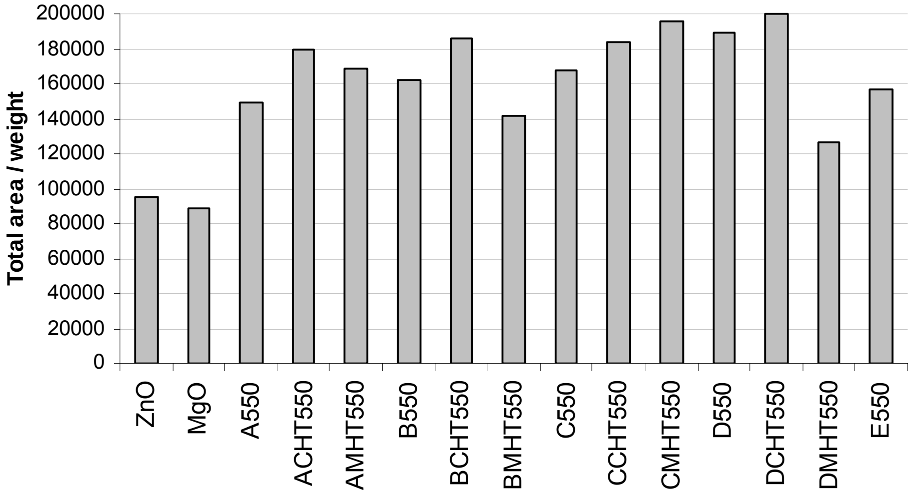

Figure 4.36. Crosslink density of ZnO, MgO and the 13 mixed oxides synthesized after 20 minutes microwaves vulcanization.

It does not seem to be a trend or explanation to correlate the treatment used with the crosslink density values. Furthermore, they do not seem to be related with the specific surface area neither. Figure 4.37. has been designed to evaluate the synergetic effects between the two metals. It displays the trend followed by the maximum crosslink density obtained by all the mixed oxides developed and also ZnO (grey square) and MgO (black square). It seems to be a slight positive synergetic effect but this is lower than the one observed in conventional vulcanization of these mixed oxides.

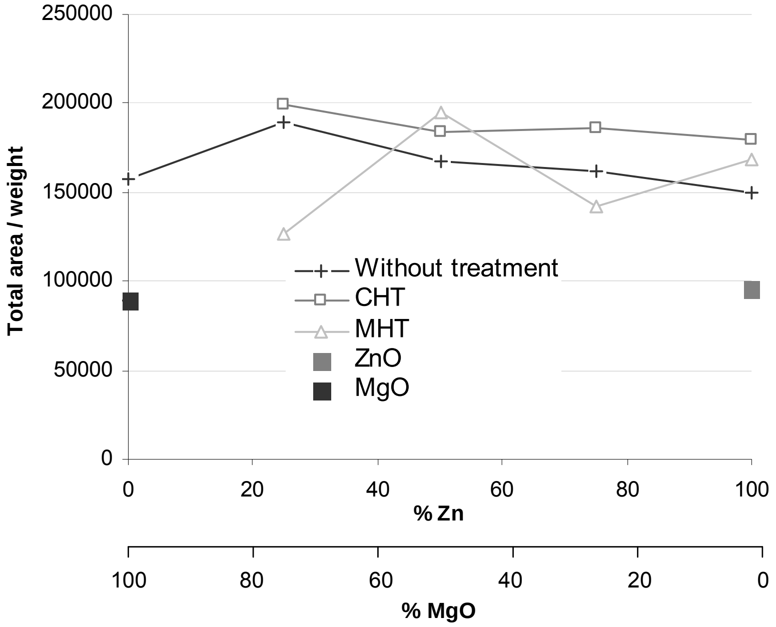

Figure 4.37. Crosslink density of ZnO, MgO and the 13 mixed oxides synthesized as a function of the composition of ZnO and MgO after 20 minutes conventional vulcanization.

However, what it is clear is that MW enhances the crosslink density more than conventional vulcanization for almost all the activating systems (Figure 4.38.). Only the microwaves hydrothermically treated samples BMHT550 (70%ZnO–30%MgO) and DMHT550 (30%ZnO–70%MgO) seem to have a slightly worst behavior with MW vulcanization than with CH curing. On the other hand, sample samples CMHT550 (50%ZnO–50%MgO) and DCHT550 (30%ZnO–70%MgO) are the samples with higher crosslink degree, which agrees with the positive synergetic effect that MW enhances at these proportions of ZnO and MgO, already plotted in Figure 4.25.

The last point to study is the effect of MW in the crosslink structure of the different activating systems. Figure 4.39. displays the distribution of the different sulfidic crosslink types after 20 minutes microwaves vulcanization at 140ºC. It can be also seen, as proved for NR samples, that the MgO sample has a greater tendency to form long crosslinks than the ZnO sample for a given S/A ratio as commented in conventional curing results. However, the crosslink distribution of the references is different than when using conventional vulcanization.

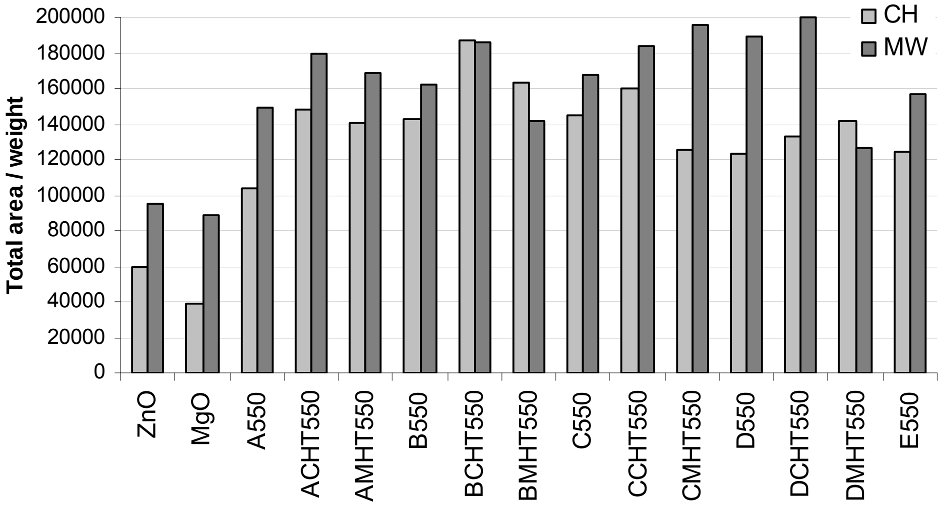

Figure 4.38. Comparison of the Maximum Crosslink density of ZnO, MgO and the 13 mixed oxides synthesized achieved with conventional and microwaves vulcanization.

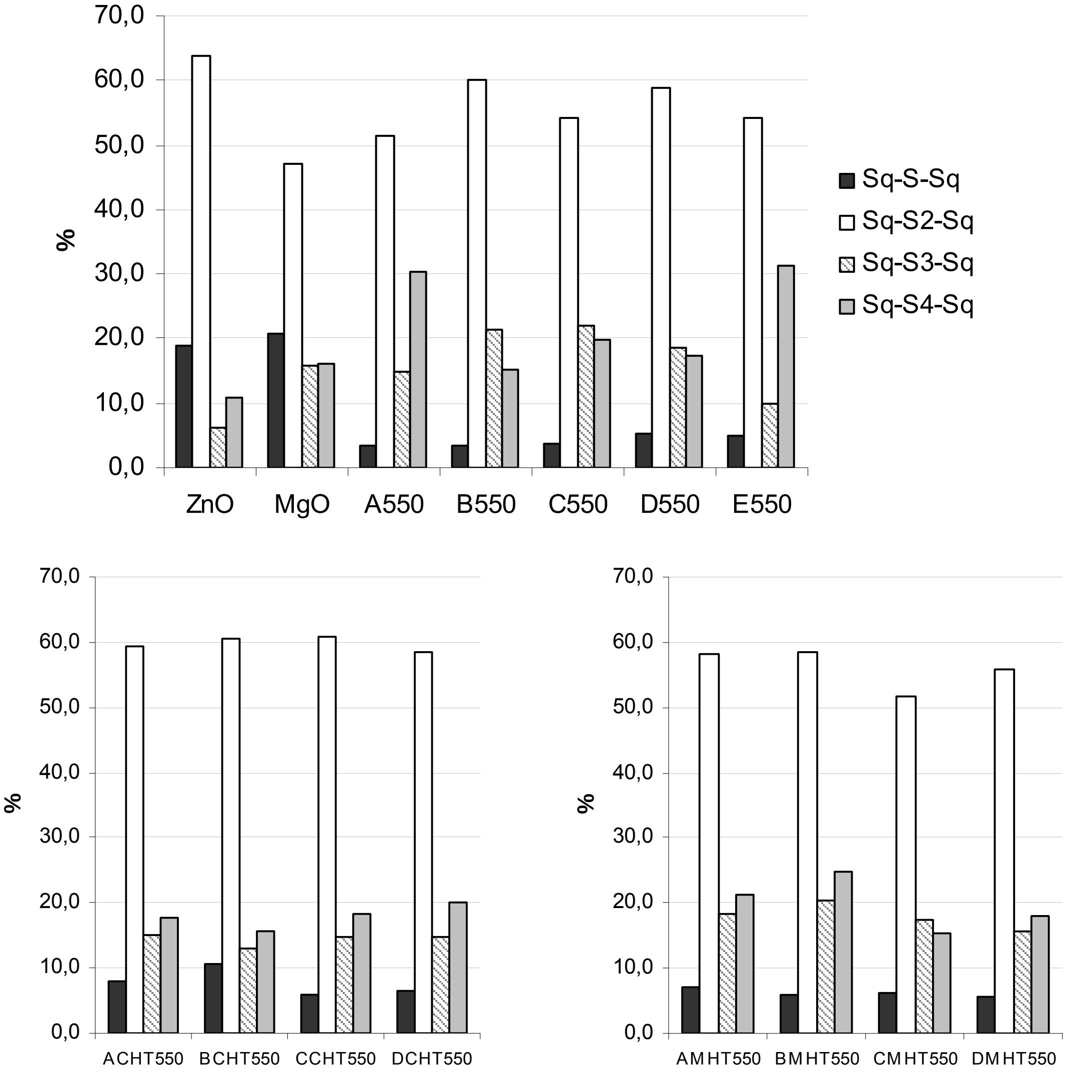

Figure 4.39. Distribution of sulfidic crosslinks (crosslink structure) in the two references and the 13 mixed oxides developed after 20 minutes microwaves vulcanization.

In this case all the mixed oxides synthesized have, more or less, the same distribution and it is different than the two references. This crosslink distribution is characterized by a predominance of polysulfidic crosslinks and a very low content in monosulfidic crosslinks. This crosslink structure will determine the final properties of the vulcanizates, giving bad aging behavior for all the mixed oxides independently of their ZnO and MgO contents. Thus, it may be recommended, to use these new activators for conventional curing, even though the crosslink density achieved with MW is higher. Conventional vulcanization of this mixed oxides gave better crosslink degrees than the references and they do not affect so much the crosslink structure.

To summarize the results discussed in this last section, it can be stated that the MCV study presented shows promising results for this kind of mixed oxides as activators for both conventional and microwaves vulcanization. All mixed oxides presented higher crosslink density than the references using CH due to their high specific surface area and the ability of hydrocalcites to increase the synergetic effect between metals. The vulcanization rates were very similar for all the activators and after 30 minutes all of them have achieved Plateau. The better crosslink density values were obtained when using the samples treated with conventional hydrothermal treatment although these results do not seem to be correlated with the specific surface area values. The crosslink structure also varies when changing the activator. On one hand, polysulfidic crosslinks seem to be favored when increasing MgO content in the mixed oxide for the untreated samples. On the other hand, the mixed oxides subjected to CHT tend to form a crosslink distribution more similar to MgO, while the activators subjected to MHT tend to form a crosslink distribution more similar to ZnO, independent of the MgO and ZnO content. As it could be expected, MW vulcanization of these activators increases the crosslink density of all the samples and reduces the time necessary to achieve the highest crosslink density to 5 minutes for all the activating systems tested. The synergetic effect between ZnO and MgO seems to be enhanced by MW for those samples containing 50% and 70% of MgO (B and C). Furthermore, the crosslink structure does not present significant differences between the different activators, in all cases being rich in polysulfidic crosslinks.

In conclusion, the mixed oxides developed seem to be a solution to reduce ZnO contents in rubber goods without affecting the final properties. The next step to perform is to find a viable way to scale up the synthesis of these mixed oxides and perform real rubber tests to evaluate the effect of these activators in the physical properties.

4.3. REFERENCES

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Chapter 5

Microwaves Devulcanization

The influence of microwaves in the devulcanization of NR using diphenyl disulfide (DPDS) as devulcanizing agent has been studied along this Chapter. Squalene has been used as a Model Compound Vulcanization (MCV) for NR. The results prove that DPDS in combination with MW increase the devulcanization yield of this devulcanizing agent, and what is more important, MW allow DPDS to be also effective to cleave disulfidic crosslinks, fact that does not occur with conventional heating (CH). Furthermore, it has been proven that DPDS reacts with the crosslinks giving rise to multiple pendant groups. A Reaction Stage Modeling (RSM) study has been also performed to study deeply the effect of the DPDS under MW on the most stable crosslinks: mono- and disulfidic crosslinks. Thus digeranyl monosulfide and digeranyl disulfide have been synthesized and their devulcanization under microwave radiation has been studied with and without DPDS at different temperatures.

5.1. INTRODUCTION

It has been estimated around one billion tyres are withdrawn from use in the world each year. The corresponding figure in Europe is around 250 million tyres. Of these tyres, around 60% are reused in some way and the rest end up in landfills. As recently as 1994 the figures were almost the other way round, with over 60% of tyres ending up in landfills. These statistics highlight that recycling has developed quickly due to the fact that legislation has become stricter[1].

Recycling of waste rubber has important implications as protection of the environment, conservation of energy, use as industrial raw material and reducing the costs, and improving the processing behavior of rubber compounds. There are basically four different levels of recycling[2]: Material recycling, monomer recycling, fuel recycling and energy recycling. In this study only material recycling will be taken into consideration.

The two principle methods to obtain a reusable recycling material are:

- Grinding of the rubber and reusing it in the form of a granulate or surface activated powder.
- Treating the material in a reclaiming process to generate a viscoelastic reclaim.

More formally, it could be said that the first method is a reuse process and the second one is strictly a recycling process. This chapter is focused in the recycling processes, and more precisely in the devulcanization, the attempt to make the vulcanization process reversible. Devulcanization of rubber is still an unsolved problem. The process of rubber devulcanization has a long history, but during the past ten years renewed interest in the subject has arisen, mainly because of the increased public and regulatory concerns for properly managing rubber wastes. This process should be understood as a potential method for recycling rubber wastes, i. e. making it possible to obtain rubber materials that can be vulcanized again and used for other applications[3]. Thus, it would be very important to gain insight in the reaction mechanisms occurring during the devulcanization process in order to be able to optimize and better understand it. The main difficulty in recycling rubber has been devulcanizing the rubber without compromising its desirable properties. The process of devulcanization involves treating rubber in granular form with heat and/or softening agents in order to restore its elastic qualities, in order to enable the rubber to be reused. The ideal goal is to break selectively the sulfidic crosslinks without affecting the polymeric chains but this aim is complicated as it will be seen thereupon.

First, it should be pointed out that the crosslink scission in sulfur vulcanizates during reclamation depends on the type and amount of sulfidic linkages. It is well known that the bond energy of the monosulfidic crosslinks is higher than that of poly- and disulfidic crosslinks[4] that implies that a sulfur vulcanizate with a lower percentage of monosulfidic crosslinks will reclaim easier. In Chapters 3 and 4 the influence of the crosslink structure in the vulcanizate properties has been exposed. This variation of the vulcanizate properties with the relative amounts of the various sulfides can best be understood in terms of the bond energy, the energy needed for hemolytic cleavage (each atom retaining one electron of the bonding pair), of the various bonds in the crosslinks. Table 5.1. gives a summary of the dissociation energies of the different types of chemical bonds found in sulfur crosslinks[5]. These data lead to the conclusion that the C-C bond is more stable than the C-S, which, in turn, is more stable than the S-S. Further, the stability of the S-S bond decreases as the number of sulfur atoms in the crosslink increases. Therefore, as stated before, the chemical stability of sulfur crosslinks should decrease in the order:

monosulfide > disulfide > trisulfide > tetrasulfide

Table 5.1. Dissociation Energy of bonds in rubber crosslinks[5].

Bond	Dissociation energy, kcal/mol
alkyl-**C-C**-alkyl	80
alkyl-C-**S-C**-alkyl	74
alkyl-C-S-**S-C**-alkyl	54
alkyl-C-$\mathbf{S_n}$**-**$\mathbf{S_m}$-C-alkyl	34

Therefore, di- and polysulfidic crosslinks are thermally fugitive species and increase susceptible to nucleophilic, electrophilic and free-radical attack[6]. Rubber stocks with a high proportion of polysulfidic crosslinks (conventional systems) are more susceptible to deterioration from heat and chemical attack. Consequently, on overcure they undergo much more reversion than those with high monosulfidic content (efficient systems). Further, their retention of properties on aging is diminished. This observation is due to the lower stability of polysulfidic crosslinks. Both the tensile strength and elasticity of NR have been found to be improved with polysulfidic content of crosslinks. They are poorest for C-C crosslinks. The improvement in tensile strength can be related to the greater flexibility and lability of the polysulfidic crosslinks. It appears that under tensile stress they can cleave and then reform. This process permits the relief of stress which would otherwise accumulate and lead to the initiation of failure.

The lability of polysulfidic linkages also serves to explain the improvement in fatigue cracking resulting from their presence. In fatigue cracking tests the rubber sample is repeatedly strained to a specific strain below the ultimate limit. After a certain large number of cycles failure will occur due to crack formation and its subsequent growth. In general, polysulfidic linkages will also favor resistance to abrasion, a property of basic importance in tire treads. A higher sulfur content in the crosslinks tends to increase the plasticity of the vulcanizate. Accordingly, the creep and compression set are greater for high polysulfidic stocks.

Returning to devulcanization, the problem lies in the selective cleavage of linkages. High energy supplies to the vulcanizates would cleave C-C, C-S and S-S indistinctly although they have different dissociation energies. On the other hand, the application of low energy to the system makes possible the cleavage of polysulfidic linkages through desulfuration pathways but this gives rise to the formation of more monosulfidic crosslinks, which are more difficult to break. Therefore, although some partial solutions have been found to devulcanize rubber, more research must be perform in this direction to solve this environmental problem.

When setting the status of the research and development for the devulcanization technologies, such methodologies can be grouped into the following categories: thermal processes, thermo-mechanical processes, mechano-chemical methods, microwave recycling, ultrasound recycling, chemical processes as the selective scission of crosslinks by chemical probes, biotechnological processes and devulcanization in supercritical carbon dioxide[7-9]. So far, most of the methodologies described in literature to devulcanize rubber have been applied only at laboratory and/or at pilot plant scale. In addition, nearly all the approaches studied showed some problems difficult to overcome: either the process is too slow, or is very inefficient, or it becomes too expensive to be implemented at an industrial scale, among others[10-11].

In the framework of this thesis, and based on the proved ability of microwaves to increase vulcanization yields, the goal of this chapter is to explore how microwaves can also help to devulcanize rubber more effectively and quickly, and what is more important, to study how microwaves can improve the devulcanizing behavior of the devulcanizing agents. Consequently, the idea is to combine two different kinds of already existing devulcanization technologies: ***chemical*** and ***microwaves***, creating a ***microwave-chemical process*** in order to increase the devulcanizing efficiency.

Diphenyl disulfide (DPDS) is a common agent used in devulcanization of sulfur-vulcanized goods[12-16]. It is the most prominent devulcanizing agent for NR[7]. Some studies have been published showing its effect on sulfidic crosslinks in real rubber samples, but always with conductive heating (CH) methods[17]. Model compound studies have also been conducted showing the ability of this devulcanization agent to break polysulfidic crosslinks and less efficiently, disulfidic crosslinks, whereas it leaves monosulfides intact due to its higher bond energy[18]. MCV is also been used in this thesis, using squalene as a model compound, to prove that microwaves (MW) can also improve the DPDS devulcanization behavior[19]. This modeling approach (MCV) provides a global idea of the effect of MW in the DPDS behavior by following simultaneously the evolution of the different crosslink types. This MCV study showed, as it will be seen in the next section, that DPDS in combination with MW were efficient not only for breaking polysulfidic crosslinks, but also disulfidic and monosulfidic crosslinks, unlike CH. Since monosulfidic and disulfidic crosslinks are more difficult to break, it would be interesting to study separately the devulcanization conditions of these more stable bonds. Therefore, a Reaction Stage Modeling (RSM) study[20] was also performed and it was focused on understading the effect of DPDS under microwave radiation on the monosulfidic and disulfidic crosslinks, using two separate molecular models: digeranyl monosulfide (monosulfidic) and digeranyl disulfide (disulfidic). Reaction Stage Modeling (RSM) is another modeling approach which permits the study of reactivity of certain intermediates compounds of polysulfidic crosslinks independently, as it has been explained in section 2.4.4. In the present work, digeranyl monosulfide and digeranyl disulfide were synthesized[21], as models of monosulfidic and disulfidic crossliks for RSM. These models have been used to understand deeply the effect of MW in these more stable crosslinks and also the influence of DPDS in combination with MW in monosulfidic and disulfidic crosslinks.

5.2. RESULTS AND DISCUSSION

The study of the ***microwave-chemical process*** has been divided into two parts: a MCV study and a RSM study that will be discussed separately in the next two sections.

5.2.1. MODEL COMPOUND VULCANIZATION (MCV)

In Chapter 3, it has been demonstrated that during the microwave-assisted squalene vulcanization, not only the reaction takes place in significantly less time, but also the vulcanization is more efficient. Such effect is deduced from the fact that a higher percentage of disulfidic and monosulfidic bonds are formed compared to the ones obtained using conventional heating (calculated as normalized area). Moreover, the role of the activator (ZnO) in the reaction is clearly less important when the heating is carried out using microwaves, as shown in Chapter 4. Considering the important changes regarding reactivity observed when microwaves are involved, before studying the effect of DPDS as devulcanizing agent, it would be interesting to know the effect of microwaves on the reactivity of such compound at 140ºC (vulcanization conditions). Thus, two different vulcanizing systems have been prepared: the first contained N-cyclohexylamine-2-benzothiazole sulfenamide (CBS) as the recipe given in Table 2.3. (1.2 phr of accelerator and any devulcanizing agent). The other compound has been prepared substituting CBS by the same amount of diphenyl disulphide (DPDS) in the reference recipe in order to test DPDS as a vulcanizing/devulcanizing agent and the results were compared with the mixture containing CBS. The aim of this experiment was to test the reactivity of DPDS at 140ºC (vulcanizing conditions) with both heating methods, since DPDS is known to be active as devulcanizing agent only up to 180ºC with CH[18].

Both formulations (containing CBS and DPDS) were heated for 60 minutes at 140ºC using both heating methods to study vulcanization behavior following the protocols already presented in section 2.4.2. After that, the resulting mixtures were heated for other 60 minutes at 200ºC for reversion studies. All the vulcanizates have been analyzed with the analytical methods described in section 2.4.3.1. to follow the evolution of CBS and DPDS and the formation of active sulfurating agents; and sections 2.4.3.2. and 2.4.3.3 to follow the crosslink process.

The evolution of the squalene, cross-linked squalene and squalene with pendant group is showed in Figure 5.1. for the reaction carried out with the DPDS systems using CH (above) and MW (below). As it can be seen, the crosslink of squalene using DPDS occurs at 140ºC in 5 minutes when microwave is the heating source used. This crosslink formation was almost not detected for 30 minutes when the reaction was carried out using conventional heating at 140ºC. During the second stage of the reaction, from minute 60 to 120, when the temperature is increased up to 200ºC, the crosslinks formed with microwaves seem to be reversed. Such reversion was not observed for the crosslinked squalene obtained when using conventional heating after 60min at 200ºC, as it can be seen in Figure 5.1. (above). It is a key point that the crosslink formation was obtained in a mixture that contained only DPDS and without any other accelerator compound.

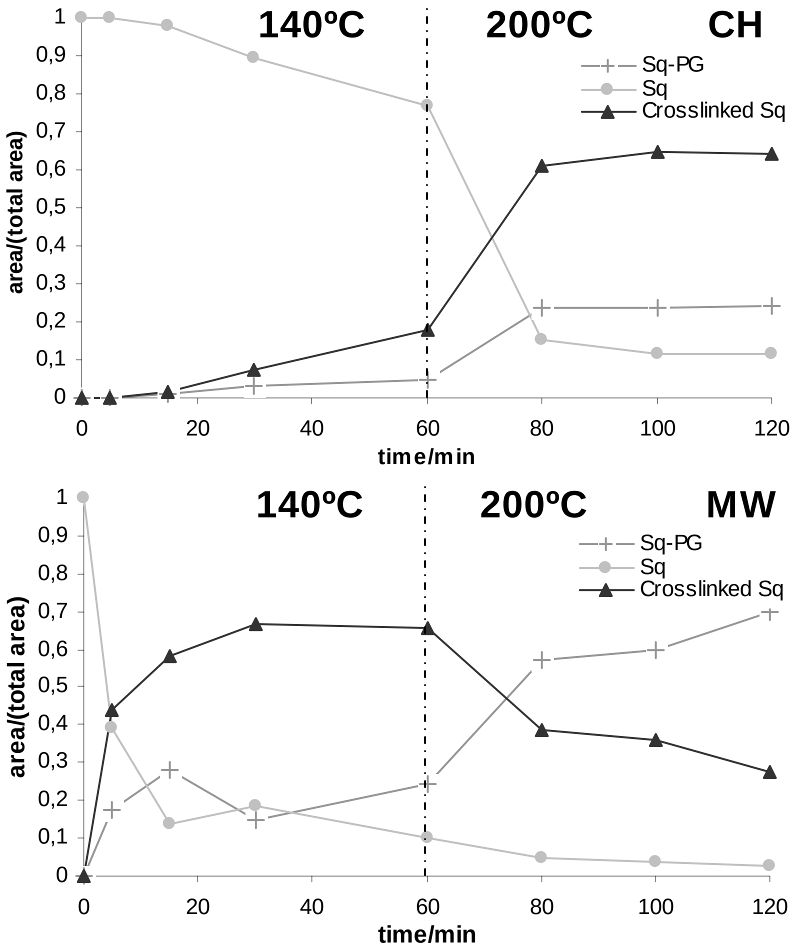

Figure 5.1. Evolution of crosslinked squalene (Crosslinked Sq), pendant group intermediate (Sq-PG) and unvulcanized squalene (Sq) in the DPDS system vulcanized 60 minutes at 140ºC and 60 minutes more at 200ºC with CH (above) and MW (below).

The chromatograms corresponding to the evolution of DPDS under microwaves heating at 0, 30 and 60 minutes are presented below in Figure 5.2. The peaks corresponding to DPDS and sulfur are marked in the figure. The other peaks between them have been identified as vulcanization intermediates similar to the active sulfurating agents. Obviously this evolution was not observed when conventional heating was used. This proves that DPDS, at 140ºC under MW radiation, is able to behave as an accelerator. In some way, its behavior could be compared to TMTD, due to its duality to behave as a sulfur donor whereas it is also able to incorporate sulfur in its structure.

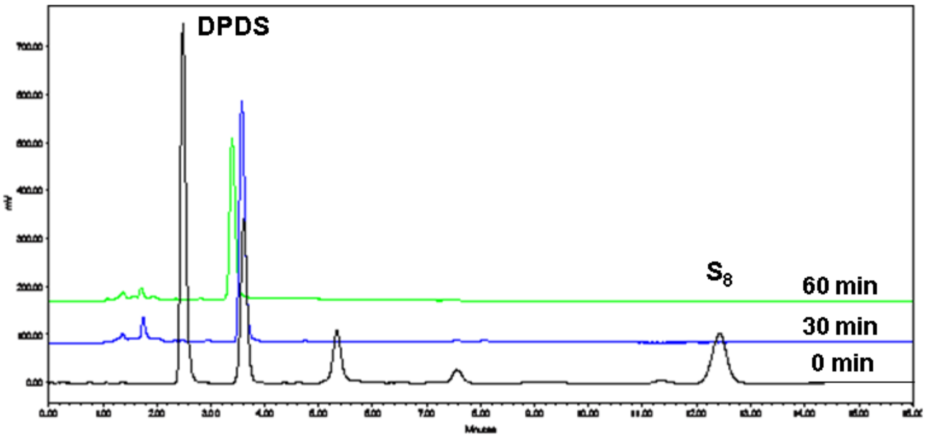

Figure 5.2. Chromatograms at 0, 30 ad 60 minutes of the DPDS mixture vulcanized with MW.

Concerning this accelerator behavior under MW heating, the crosslinking effect of DPDS was compared with the vulcanization degree obtained with a conventional sulfenamide accelerator such as CBS. This was done by vulcanizing the above described reaction mixtures both with microwaves (MW) and conventional heating (CH) at 140ºC for 60 minutes. The results obtained regarding the vulcanization degree compared with those obtained with DPDS are presented in Figure 5.3.

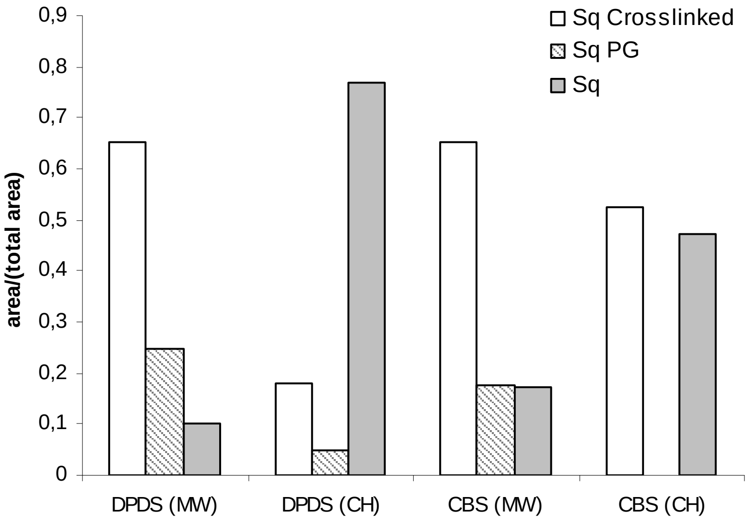

Figure 5.3. Distribution of crosslinked squalene (Crosslinked Sq), pendant group intermediate (Sq-PG) and unvulcanized squalene (Sq) in the DPDS Mixture and CBS Mixture after 60 minutes vulcanization at 140ºC with CH and MW.

As it can be seen the crosslink degree achieved with DPDS heated with MW was almost the same that the one corresponding with CBS, whereas DPDS showed a poor ability to promote the crosslinking of squalene when using CH. In order to explain this ability of DPDS to behave as a good accelerator at 140ºC when using MW, an experiment vulcanizing a recipe without accelerator was performed (squalene, ZnO, stearic acid and sulfur in the same amounts than the recipe displayed in Table 2.3.). It can be observed that MW allows the sulfur reaction with the polymer chain with good kinetics whereas this process is very slow an inefficient under CH. The presence of DPDS gives more control of the sulfur transfer to the polymer chain due to the ability of DPDS to form intermediates similar to the active sulfurating agents formed by conventional accelerators like CBS. Nevertheless, conventional heating only allowed acceptable crosslink degree when CBS was used. That means that the presence of sulfur is necessary at 140ºC to allow DPDS to behave as an accelerator when conventional heating is used. This compound by itself is only active up to 180ºC when its disulfidic bond cleavage starts. This can be supported by the fact that when a mixture of CBS and DPDS was heated using MW at 140ºC, only CBS reacted, remaining the DPDS unchanged during the reaction. This is caused by the fact that although DPDS has a certain accelerator behavior at 140ºC when using MW, CBS is a better accelerator, and when both are present DPDS does not need to develop its vulcanizing ability.

However, the interest on DPDS is its ability to produce devulcanization[18]. In order to bring some insights into this aspect, it is important to study the behavior of the mixtures after heating both with MW and CH at 200ºC. In Figure 5.4. the crosslinked squalene evolution as a function of time analyzed by the HPLC method presented in section 2.4.3.2. is presented for the DPDS mixture. This compound has reacted at 140ºC for 60 minutes and consequently at 200ºC for other 60 minutes using both heating methods.

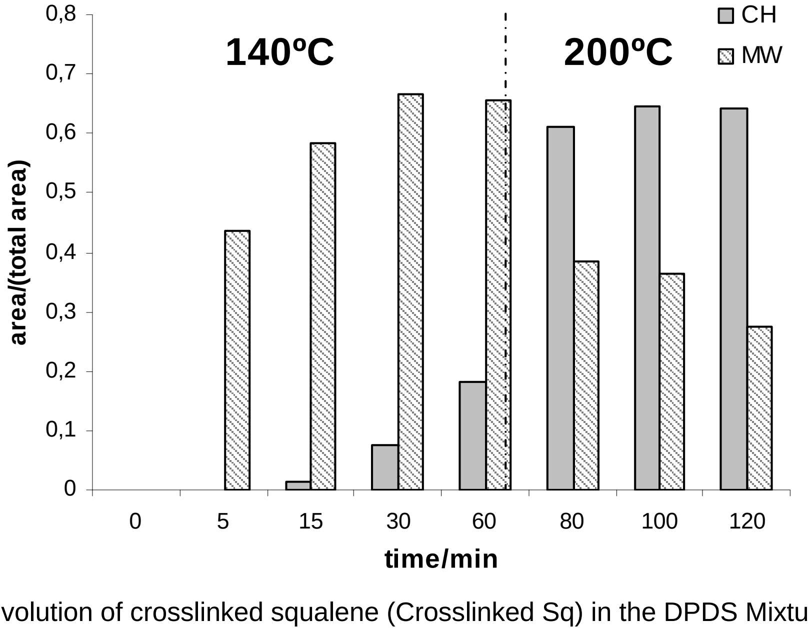

Figure 5.4. Evolution of crosslinked squalene (Crosslinked Sq) in the DPDS Mixture vulcanized at 140ºC for 60 minutes and devulcanized at 200ºC for other 60 minutes with CH and MW.

It seems that at 200ºC with microwaves the crosslink density decreased significantly. This proved the higher ability of MW in comparison to CH to activate DPDS as devulcanizing agent.

Figure 5.5. displays the crosslink structure of vulcanizates of DPDS Mixture after 60 minutes reaction (140ºC) and after 120 minutes reaction (60' vulcanization at 140ºC and 60' devulcanization at 200ºC) with both heating methods. The treatment with CH does not seem to have an important influence in the crosslink structure and it is clear that the increase in the crosslink density when applying 200ºC is mainly caused by the formation of monosulfidic linkages. On the other hand, the use of conventional heating in such conditions did not show any significant devulcanization. Moreover the temperature increase led to the formation of more crosslinks. Furthermore, even though CH is not able to cleave disulfidic crosslinks, as Noordermeer et al.[18] demonstrated also with MCV studies with other model molecule; it can also be seen that despite the known stability of disulfidic crosslinks, these are the most affected by the MW treatment developed.

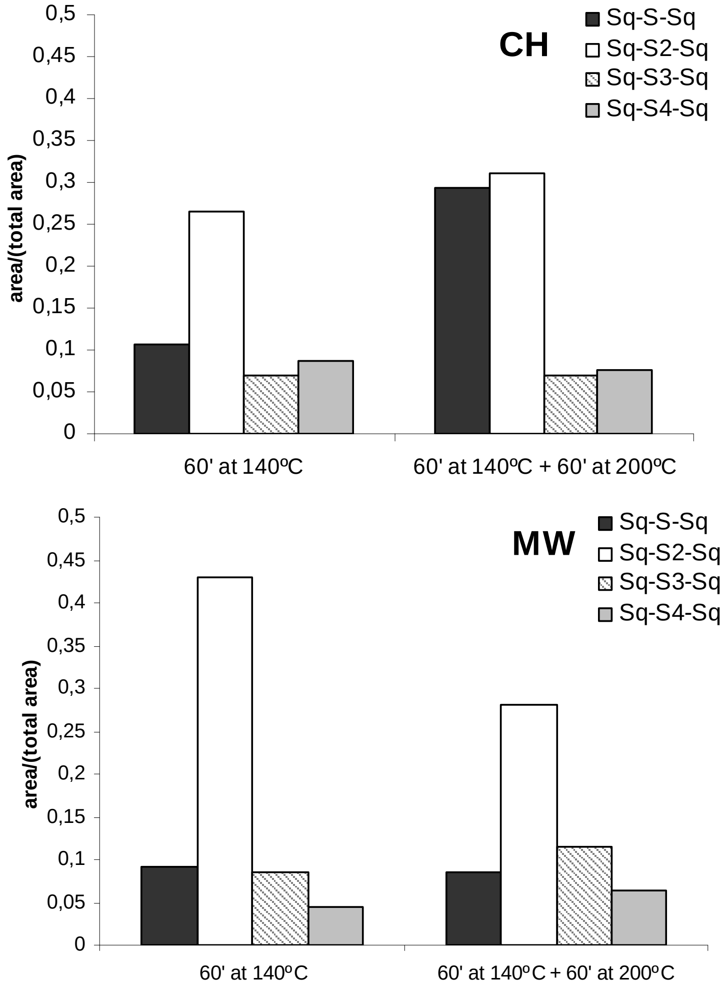

Figure 5.5. Distribution of sulfidic crosslinks (crosslink structure) in the DPDS Mixture after 60 minutes vulcanization at 140ºC and after 60 minutes vulcanization followed by 60 minutes devulcanization at 200ºC with CH (above) and MW (below).

When the squalene was vulcanized with CBS in absence of DPDS and then heated with microwaves at 200ºC for 60 min (Figure 5.6.), not significant changes were observed in the amount of crosslinks formed. This confirms that the devulcanization observed (Figure 5.1. (below)) is a result of the combination of DPDS with microwaves, instead of a devulcanization caused only by microwave radiation. And what is more important, it seems that this MW treatment not only improves the devulcanization degree, but also it makes DPDS effective to cleave disulfidic crosslinks, as it has been seen in Figure 5.5.

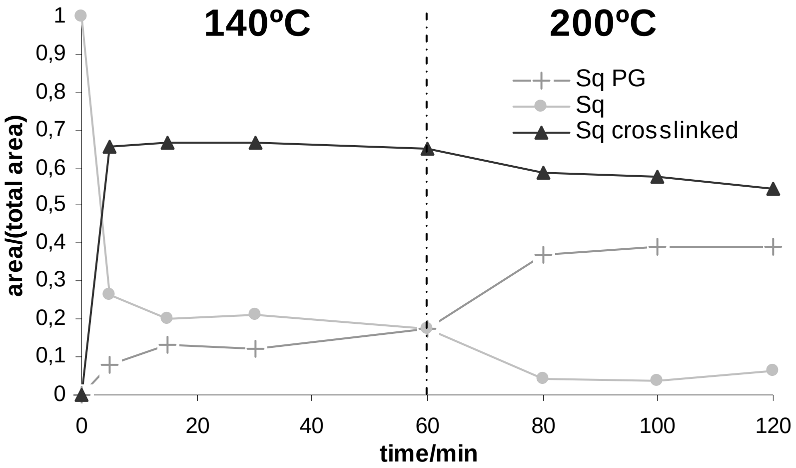

Figure 5.6. Evolution of crosslinked squalene (Crosslinked Sq), pendant group intermediate (Sq-PG) and unvulcanized squalene (Sq) in the CBS system vulcanized 60 minutes at 140ºC and 60 minutes more at 200ºC with MW.

A mechanism that is often proposed for the reaction of disulfides (DPDS) with sulfur vulcanizates is the opening of crosslinks and the scission of main polymer chains by heat and shearing forces and their reaction with disulfides, forming pendant groups, which prevents recombination[22]. The use of GPC permitted to confirm that DPDS promotes mainly the breaking of crosslinks, rather than the main chain scission, leading to the formation of pendant groups in the squalene chain. This ability is higher when working wit MW as shown in Figure 5.1. (below). DPDS acts as a radical scavenger and reacts with the sulfidic bonds through a radical mechanism[11], breaking the crosslinks and remained attached to the main chain of the polymer which avoids recombination (Figure 5.7.).

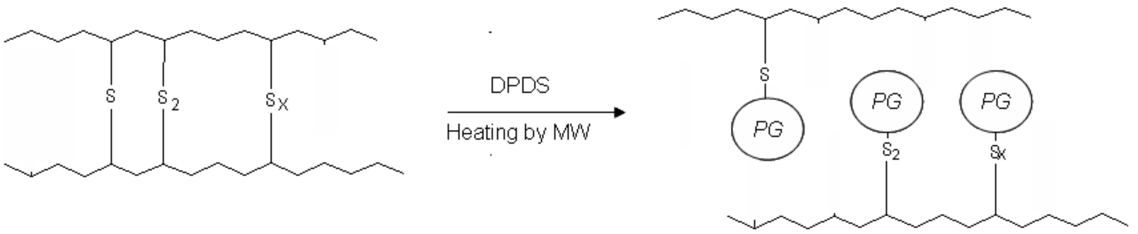

Figure 5.7. Pendant group formation.

Figure 5.8. displays the evolution of the squalene intermediate with pendant group (Sq-PG) along the reaction analyzed by the HPLC method presented in section 2.4.3.2. It is clear that MW forms more pendant group than CH, and when increasing the temperature to 200ºC, there is a big increase in the PG that corresponds to the final product of the already observed cleavage of the sulfidic crosslinks (Figure 5.4.).

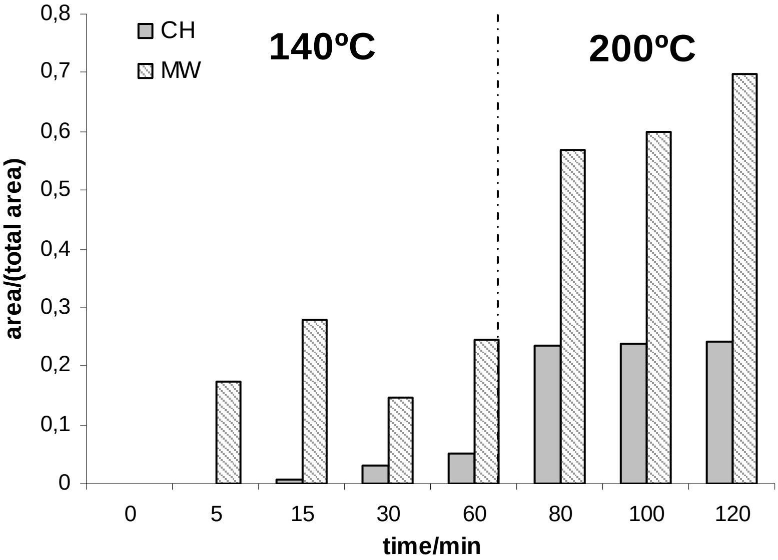

Figure 5.8. Evolution of pendant group intermediate (Sq-PG) in the DPDS Mixture vulcanized at 140ºC for 60 minutes and devulcanized at 200ºC for other 60 minutes with CH and MW.

A final question to be answered is that if it is possible to control the DPDS reactivity by changing the reaction temperature. In Figure 5.9. the evolution of crosslinked squalene, squalene with pendant group and unvulcanized squalene at three different temperatures (140ºC, 180ºC and 200ºC) is shown.

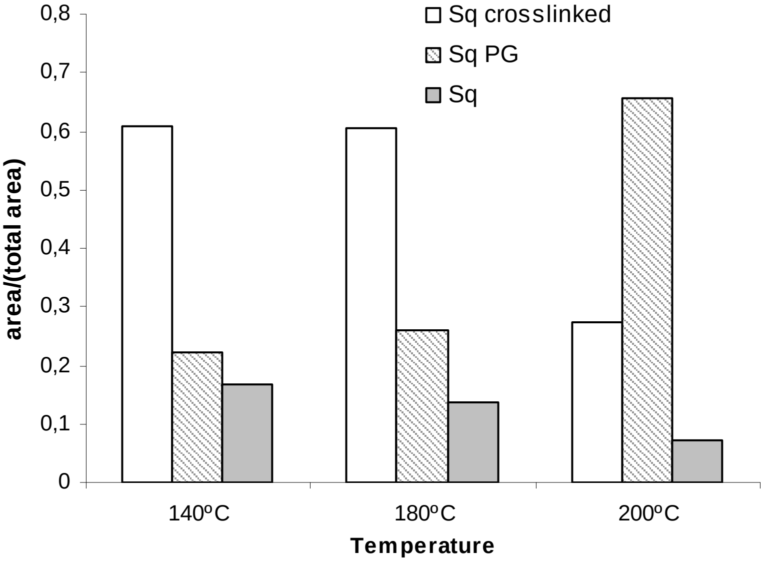

Figure 5.9. Distribution of crosslinked squalene (Crosslinked Sq), pendant group intermediate (Sq-PG) and unvulcanized squalene (Sq) in the DPDS Mixture after 60 minutes reaction at 140ºC, 180ºC and 200ºC with MW.

It can be clearly seen that the devulcanization reactions was performed only when the temperature arrived to 200ºC. This could be important in industrial devulcanizations because it seems possible to tune on the process choosing properly the temperature of the treatment.

In summary, the efficiency of microwaves heating in a devulcanization process with DPDS as devulcanizing agent has been proven using a Model Compound Vulcanization approach. The reaction can be tuned through the temperature set and microwave power control. Thus, it would be possible to introduce the DPDS during compounding, since it has been proven that in presence of other accelerator it remains unreactive at vulcanizations temperatures (140ºC) and activate its devulcanizing ability by controlling the temperature and power of the microwaves when required. The devulcanization mechanism seems to lead to the final formation of a pendant group of the devulcanizing agent on the squalene chain.

Noordermeer et al.[18] published a model compound study on the devulcanization of NR using 2,3-dimethyl-2-butene as model compound at different temperatures and they proved that DPDS was only effective to cleave polysulfidic crosslinks at temperatures higher than 180ºC. A similar work has been presented in this section using squalene as model compound of NR and the CH results supported the conclusions posted by Noordermeer research group. On the contrary, as stated before the combination of DPDS and MW improves significantly the devulcanization degree, but also it seems to make DPDS effective to cleave disulfidic crosslinks, as it has been showed in Figure 5.5. In order to study deeply the ability of DPDS in combination with MW to cleave the most stable crosslinks (mono- and disulfidic) a Reaction Stage Modeling study[20] is presented in the next section.

5.2.2. REACTION STAGE MODELING (RSM)

Digeranyl monosulfide (monosulfidic) and digeranyl disulfide (disulfidic) have been synthesized following the protocols presented in sections 2.4.4.1. and 2.4.4.2. In the same way, RSM procedure and the analytical methods developed to analyze the samples have been already presented in section 2.4.4.3. These models have been used to understand deeply the effect of MW in these more stable crosslinks and also the influence of DPDS in combination with MW in monosulfidic and disulfidic crosslinks.

First of all, a comparative study on the thermal degradation of the two crosslink models has been made, without using any devulcanizing agent, analyzing the use of CH and MW heating. This reversion study was performed at two different temperatures: 140ºC[19] (a standard vulcanization temperature) and 180ºC[18] (a temperature where DPDS is known to start being active as devulcanizing agent). Figure 5.10. shows that CH was not able to degrade digeranyl monosulfide, but degrades partially digeranyl disulfide after 90 minutes treatment at 140ºC. Figures 5.11. illustrates that with increasing the temperature to 180ºC, the disulfide model was completely degraded after 90 minutes, while the monosulfide model was still stable after 90 minutes of treatment. As it could be expected, MW showed better kinetics of degradation at both temperatures. MW was able to degrade completely digenaryl disulfide after 30 minutes at 140ºC while the treatment remains ineffective for digeranyl monosulfide at this temperature (Figure 5.10.). On the contrary, at 180ºC MW was able to break completely both crosslink models: monosufidic after 30 minutes and disulfidic after 3 minutes.

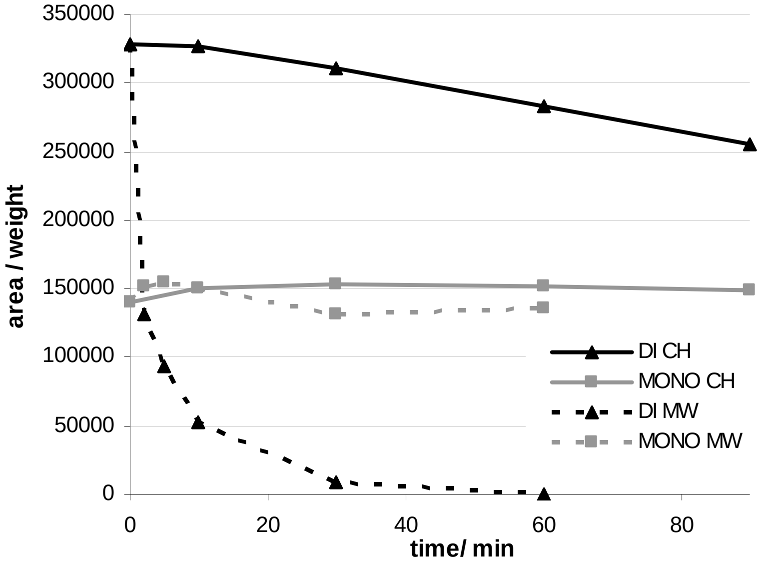

Figure 5.10. Degradation of digeranyl monosulfide and digeranyl disulfide at 140ºC with CH and with MW.

As stated before, although DPDS is not a good devulcanizing agent for monosulfidic and disulfidic crosslinks when working with CH, in previous studies performed using MCV[19] showed a higher ability to degrade these types of stable crosslinks in comparison with CH. The effect of DPDS in the digeranyl models degradation has also been studied with both heating methods. 2 phr of DPDS were mixed with the crosslink models, and the mixtures were treated with both heating methods at 180ºC. The aim of this experiment was to understand if the higher degradation observed for monosulfidic and disulfidic crosslinks in MCV studies was caused only by the MW effect or occurred due to the combination of DPDS+MW. No degradation of digeranyl monosulfide has been observed at 180ºC after 90 minutes when using CH, while complete degradation of this model was seen under these conditions after 20 minutes when using MW (Figure 5.12.). Digeranyl disulfide degraded completely at 180ºC when DPDS was present. This degradation occurred immediately with MW and after 60 minutes when using CH as a heating source. These results confirm the active role of DPDS in the sulfidic bond breaking and the improvement of its devulcanazing behavior when using MW. When comparing these results (Figure 5.12.), with the ones obtained from thermal degradation at 180ºC (Figure 5.11.), where no DPDS was used, it can be seen that the devulcanizing agent in combination with MW helps to degrade monosulfidic crosslinks with better kinetics. However it could be concluded that the improvement in degradation of short crosslinks is caused mainly by the effect of MW, instead of the effect of the devulcanizing agent.

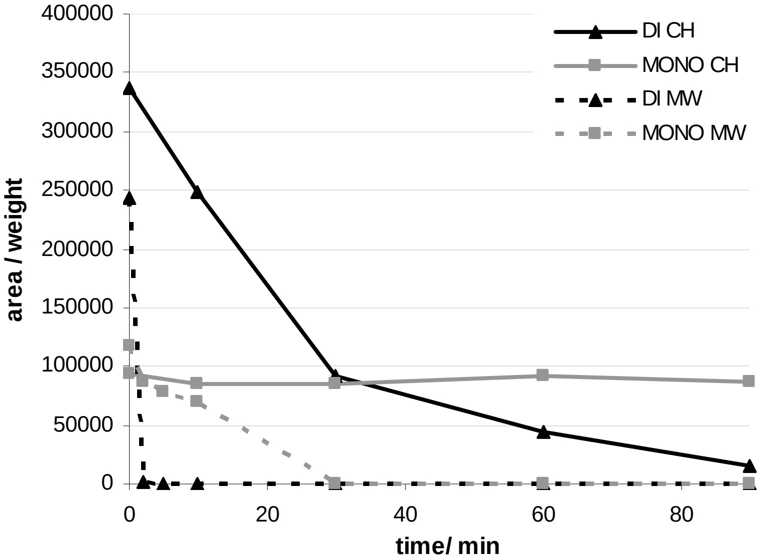

Figure 5.11. Degradation of digeranyl monosulfide and digeranyl disulfide at 180ºC with CH and with MW.

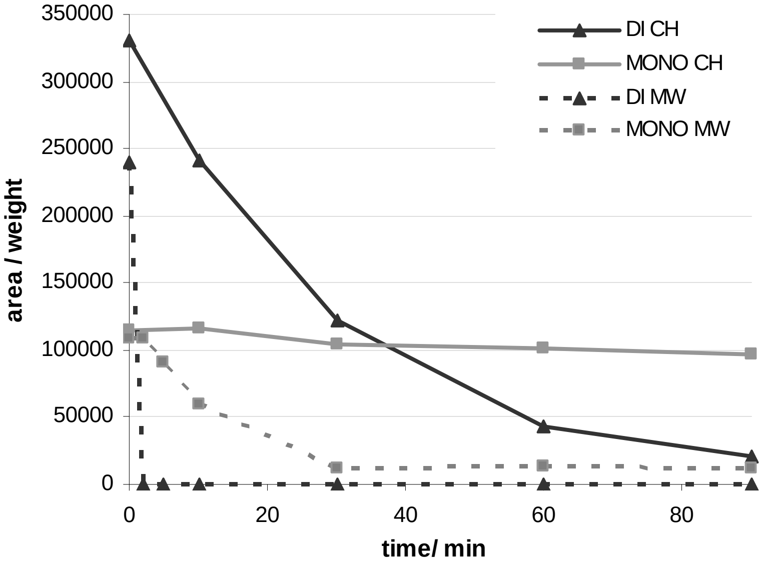

Figure 5.12. Degradation of digeranyl monosulfide and digeranyl disulfide at 180ºC with CH and with MW using 2 phr DPDS as devulcanizing agent.

Finally, since the activator (ZnO) has an important role in vulcanization it would be interesting to study if there is also an influence of ZnO in the devulcanizing effect of DPDS. 5 phr of ZnO were added to the mixture of 2 phr of DPDS and digeranyl model.

ZnO is known to have an active role in the transfer of sulfur to the polymer chain during vulcanization, through the formation of the active sulfurating agents[23]. It could be expected that ZnO may work also as an activator in the devulcanization mechanism, helping DPDS in the crosslink breakage. Figure 5.13. displays the degradation at 180ºC of the two models using both heating methods. No significant differences were observed from the results performed without ZnO (Figure 5.12.). Thus, although it could be concluded at this point that ZnO does not seem to have an important role in the devulcanization mechanism under the conditions studied in this work at 180ºC, further experiments on this topic are needed.

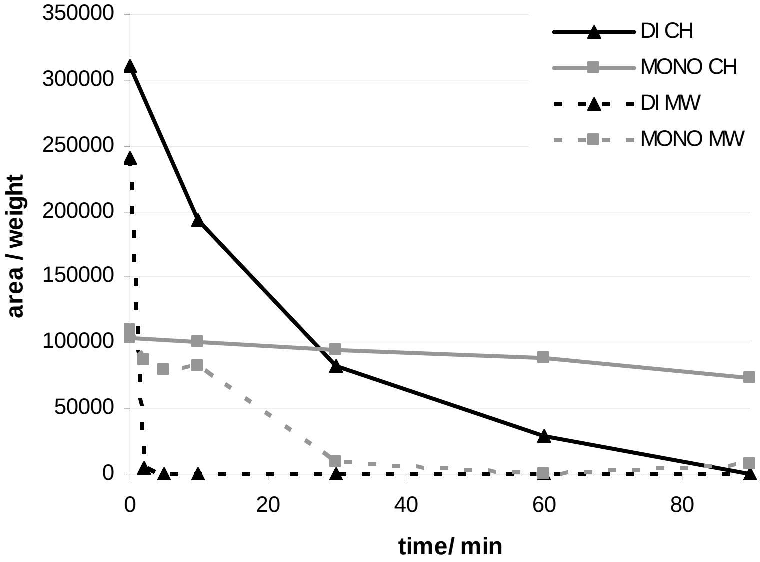

Figure 5.13. Degradation of digeranyl monosulfide and digeranyl disulfide at 180ºC with CH and MW using 2 phr DPDS as devulcanazing agent and 5 phr ZnO.

In conclusion, RSM in combination with HPLC techniques appear to be an effective tool to study the devulcanization effect on the different crosslink compounds. Thermal degradation of the models has been studied using CH and MW at 140ºC and at 180ºC. As it would be expected, the disulfidic model is always easier to break than the monosulfidic. MW increases the degradation rate of disulfidic crosslinks. Most importantly, CH is not able to degrade monosulfidic bonds at any temperature, while MW is able to do that at 180ºC. DPDS has been tested as a devulcanizing agent at 180ºC. The system has shown similar results in devulcanization rate as thermal degradation with CH and with MW. Therefore, the higher devulcanizing power obtained with MCV for monosulfidic and disulfidic crosslinks is mainly caused by MW and not by the combination of DPDS and MW. Said in other words, MW in combination with DPDS allows this devulcanizing agent to be more effective with polysulfidic crosslinks than when working with CH, but not to be an effective agent for monosulfidic and disulfidic crosslinks, even when using ZnO as an activator. The improvements detected in the cleavage of monosulfidic and disulfidic crosslinks is only caused by the MW thermal degradation.

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Chapter 6

Conclusions

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1. Regarding the study of the influence of MW on the accelerator, it has been proven that as expected MW cleave the accelerator faster than CH for both accelerator systems tested: sulfenamides (CBS) and thiurams (TMTD). In addition to the differences in the vulcanization kinetics, some mechanistic differences between conventional and microwaves vulcanization have also been observed:

    - In sulfenamide sulfur accelerated vulcanization with CH, the sulfenamide concentration decreases rapidly during the induction period and crosslinking does not occur until the sulfenamide is completely consumed. On the contrary, in MW vulcanization crosslinking starts from the very beginning of the reaction and both processes occur simultaneously. This phenomenon also involves the kinetic acceleration of formation of the active sulfurating agents with regard to CBS cleavage. These changes were not detected when working with thiurams or sulfenamide-thiurams systems. Thus, it could be inferred, that MW seems to have a preference for CBS over TMTD, although this radiation is able to activate both accelerators.
    - Crosslink formation is favored by the use of MW. Model Compound Vulcanization (MCV) studies using squalene as model molecule have shown that, when using CBS as accelerator, achieving Plateau requires 20 minutes of vulcanization at 140ºC when using MW, whereas it takes 50 minutes when using CH. The crosslink degree is found to be 20% higher with MW vulcanization. This increase can be explained by the higher reactivity of the crosslink precursors to evolve to crosslink formation and also by an additional crosslink process parallel to sulfenamide-accelerated vulcanization, caused by the acceleration of unaccelerated curing, a process that does not occur in

conventional vulcanization. Thiuram systems and systems combining sulfenamide and thiuram also become faster when working with MW, but the crosslink degree achieved, expressed by the addition of mono-,di -and polysulfidic crosslinks divided by the total area, are the same with both heating methods.

- Crosslink structure is also affected by the heating source. MW have been found to have an ability to promote a more efficient vulcanization by increasing the number of monosulfidic crosslinks when working with sulfenamide systems. Thiuram systems and systems combining sulfenamide and thiuram are less sensitive to MW radiation than sulfenamide systems, and no significant differences have been detected in the crosslink distribution.

2. Concerning the study of microwave influence on the activator in sulfenamide-accelerated vulcanization some relevant observations are presented:

- MCV studies have found that MgO is able to form the active sulfurating agents three-fold faster than ZnO in conventional vulcanization, however MgO has less tendency to form the crosslink precursor and the final crosslink. Furthermore, a synergetic effect between the two oxides has been detected. MW seems to enhance the crosslink ability of MgO, resulting in the same crosslink degree achieved by all activator systems tested; and what is more surprising, even when no activator was used, the same crosslink yield as with ZnO was achieved, although different kinetics could be observed. In addition, the synergetic effect between the two oxides is enhanced when using MW.
- MW have a higher ability than CH to vulcanize rubber than conventional heating for all activator systems (ZnO, MgO and mixtures of both), although different conditions have been found to be optimal depending on the ZnO and MgO content. Furthermore, although crosslink densities of the compounds containing partial or total MgO as the activator have been improved in comparison to the values obtained with conventional vulcanization, this increase is lower than the increase obtained with squalene in the MCV studies and these mixtures are unable to achieve the crosslink density of the reference (100% ZnO). The synergetic effect between ZnO and MgO seems to be greater than conventional vulcanization but also less than in MCV studies. On the other hand, good crosslink densities can be obtained in some cases working with microwaves at lower temperatures. This would minimize the overcrosslinked domains observed in microwaves vulcanization that could produce homogeneity problems in the final vulcanizate and also it could minimize energy costs when working at industrial scale.
- The test as activators of the mixed oxides, developed by the Department of Inorganic Chemistry of Universidad de Salamanca, shows promising results for both conventional and microwaves vulcanization. All mixed oxides presented

higher crosslink densities than the references (ZnO and MgO alone) using CH due to their high specific surface area and the ability of hydrocalcites to increase the synergetic effect between metals. The vulcanization rates were very similar for all the activators and after 30 minutes all had achieved Plateau. The better crosslink density values were obtained when using the samples treated with conventional hydrothermal treatment although these results do not seem to be correlated with the specific surface area values. The crosslink structure also varies when changing the activator. On one hand, polysulfidic crosslinks seem to be favored as MgO content increases in the mixed oxide for the untreated samples. On the other hand, the mixed oxides subjected to conventional hydrothermal treatment (CHT) tend to form a crosslink distribution more similar to MgO, while the activators subjected to microwave hydrothermal treatment (MHT) tend to form a crosslink distribution more similar to ZnO, independent of the MgO and ZnO content. As it could be expected, MW vulcanization of these activators increases the crosslink density of all the samples and reduces the time necessary to achieve the highest crosslink density to 5 minutes for all the activating systems tested. The synergetic effect between ZnO and MgO seems to be enhanced by MW for those samples containing 50% and 70% of MgO (B and C). Furthermore, the crosslink structure does not present significant differences between the different activators, with all cases being rich in polysulfidic crosslinks. In conclusion, the mixed oxides seem to be a possible solution to reduce ZnO contents in rubber goods without affecting the final properties. The next step to perform is to find a viable way to scale up the synthesis of these mixed oxides and perform real rubber tests to evaluate the effect of these activators in the physical properties.

3. As a conclusion for the MCV study on the microwave devulcanization of squalene as a model of NR, it has been proven that dyphenyl disulfide (DPDS) is an efficient reclaiming agent up to 180ºC for polysulfidic crosslinks. On the contrary, the combination of DPDS and MW significantly improves the devulcanization degree, but also seems to make DPDS effective in cleaving disulfidic crosslinks. Reaction Stage Modeling (RSM) has been used to study the thermal degradation of monosulfidic and disulfidic crosslinks separately. The study has been performed using CH and MW at 140ºC and at 180ºC. As it would be expected, the disulfidic model is always easier to break than the monosulfidic for both heating methods. MW increase the degradation rate of disulfidic crosslinks. Most importantly, CH is not able to degrade monosulfidic bonds at any temperature, while MW is able to do that at 180ºC. The addition of DPDS did not show a significant increase in the devulcanization degree, proving that the increase of the devulcanization effectiveness with disulfidic crosslinks detected in MCV studies was mainly caused by MW and not by the combination of DPDS and MW, on the contrary of what occurs with polysulfidic crosslinks.

4. It has been demonstrated that microwave (MW) power has a strong influence on the reaction yield and that in MW vulcanization this factor seems to be more deciding than the macroscopic temperature. The higher the power applied, the higher the reaction yield is, even when the bulk temperature is maintained constant. This phenomenon can be explained by the appearance of the microscopic temperature concept in MW reactions. This temperature is always higher than the macroscopic temperature and is caused by the formation of high localized temperatures (hot spots). Therefore, MW permit performance of chemical processes at lower macroscopic temperatures than conventional heating (CH), without affecting reaction yields. Thus, microwaves provide a potential way of saving time and energy at the industrial scale.

Appendix 1

How to Define the Polarity of a Substance in Microwave Synthesis

As stated in Chapter 1 the polarity of a substance will determine the ability to couple with the microwave energy. The more efficient a solvent is in coupling with the microwave energy, the faster the temperature of the reaction mixture increases. Many factors characterize the polarity of a substance. Intrinsically, there are five factors that contribute to the substance absorbing characteristics[1]:

- **Dielectric constant (ε'):** also known as the relative permittivity, measures the ability of the substance to store electric charges. Mathematically, it is the ratio of the electrical capacity of a capacitor filled with the solvent to the electrical capacity of the evacuated capacitor (Equation a1.1.). This value, when measured, is dependent of both temperature and frequency.

$$\varepsilon' = \frac{C_{filled}}{C_{evacuated}}$$

Equation a1.1.

- **Dipole moment (μ):** it is measured in Debye units (D) and it is also a mathematical entity. It is the product of the distance between the centers of the charge in the substance molecule multiplied by the magnitude of that charge $\mu = Qr$, where Q is the charge and r the distance between charges. Molecules with large dipole moments also have large dielectric constants. This is because polarization depends on dipole rotation (the ability of the dipole of a molecule to align with a rapidily changing electric field).

- **Dielectric loss (ε''):** or complexed permittivity is the amount of input microwave energy that is lost to the sample by being dissipated as heat.
- **Tangent delta (δ):** or loss tangent, shows the ability of a substance to convert electromagnetic energy into heat at a given frequency and temperature. It is defined by the ratio of the dielectric loss to the dielectric constant (Equation a1.2.). It is the dissipation factor of the sample or how efficiently microwave energy is converted into thermal energy.

$$\delta = \frac{\varepsilon''}{\varepsilon'}$$

Equation a1.2.

- **Molecular relaxation time:** the dielectric relaxation time is the time it takes a molecule to achieve 63% of its return to randomized disorder from an organized state after an applied microwave field is removed. Functional groups, temperature, frequency and volume will all influence the relaxation time of a solvent.

The three main dielectric parameters (tangent delta, dielectric constant and dielectric loss) are all related to the ability of a solvent to absorb microwave energy. Molecular relaxation time has a large effect on these parameters. Most commercial microwave systems are set to a frequency of 2450 MHz. At this frequency, the only thing that can change the three parameters is temperature. As the temperature of a substance increases, a decrease in its relaxation time and dielectric parameters will be seen, and hence, its coupling efficiency.

Microwave heating is the result of a direct transfer of energy from an electromagnetic field to the work. The transfer takes place directly without the necessity of an intermediate medium. Moreover, energy transfer occurs wherever the field penetrates. Because of this phenomenon, no limit is imposed on the speed of heating of the microwave energy or its intensity of concentration on the work.

As stated in Chapter 1, microwave heating offers far higher efficiencies because:

(i) it eliminates the inherent inefficiency of generating thermal energy at an outside source;
(ii) it eliminates the inefficiency of transferring heat from an external source to the system;
(iii) it reduces re-radiation loss from the surface of the system while the interior is being brought up to temperature.

The power developed in the system by a microwave electromagnetic field is governed by the basic power equation[2] which explains the partial dissipation of the electromagnetic field:

$$P_v = 1.41 \cdot E^2 \cdot f \cdot \varepsilon' \cdot \tan\delta \cdot 10^{-12} \text{ watts/in}^3$$

Equation a1.3.

where P_v is the power dissipated in the system per unit volume in watts/in^3,
E is the electric field strength in the system in volts per inch
f is the microwave frequency in cycles per second,
ε' is the relative dielectric constant of the system and
$\tan\delta$ is the loss tangent of the system.

The uniformity of energy transfer throughout the bulk of the work material is related to the dimensions of the work and the loss characteristics of the material. A standard way of reviewing this characteristic is to know the half power depth for a given material at a given frequency. The half power depth is that depth in the work where a molecule receives half of the energy that a molecule at the surface receives. Half power depth equation[2] is next shown,

$$x = \frac{3 \cdot \lambda_0}{8.686 \cdot \pi \cdot \sqrt{\varepsilon'} \cdot \tan\delta}$$

Equation a1.3.

where λ_0 is the wavelength in free space.

The amount of heat developed in the work material is a function of the intensity and frequency of the electromagnetic field and the electrical properties of the material. In general, $\tan\delta$ increases in proportion to the frequency. Consequently, power transfer occurs at the lowest field strength when the frequency is highest. However, generating very high frequency power for heating purposes is extremely costly and penetration difficulties are encountered. In microwave energy transfer for heating, the molecular characteristics of the work material are significant. Since the molecules are placed within an alternating field, they will exhibit a tendency to align themselves with the electric field generated by the microwaves particularly if they are dipolar. Each time the field reverses, the molecules tend to realign accordingly. The resulting inter-molecular friction acts to convert the electromagnetic energy to thermal energy. The nature of the electric dipole in the molecule and the rotation time of the molecule determine the magnitude of the loss tangent of the material. The loss tangent value and the dielectric constant value of any given material is a function of the frequency.

In determining the suitability of a product for microwave heating, the effective loss tangent of the material at the various microwave frequencies is measured. The physical size of the material is then related to the half power depth of the optimum frequency. The final step is the choice of the frequency which proves best for the required process. If several frequencies are equally effective, the choice is governed by the cost of the equipment.

REFERENCES

[1] B. Krieger, Microwave vulcanization: a lesson in business and technology. Materials Research Society Symposium Proceedings 347(Microwave Processing of Materials IV), (1994), 57.

[2] http://www.smecc.org/litton_-_for_heat,_tune_to_915_or_2450_megacycles.htm (18/06/08)

Appendix 2

Identification of TMTD intermediates by HPLC-APCI$^+$- MS

As it has been in figure 2.12., gradient method with acetonitrile: formic acid (0.1%) shown in Table 2.6. achieved a better separation of peaks from A to F than the initial isocratic method presented in Figure 2.11. Figure a2.1. displays the chromatogram and the mass spectrum of a TMTD vulcanizate where peaks A to G are labeled.

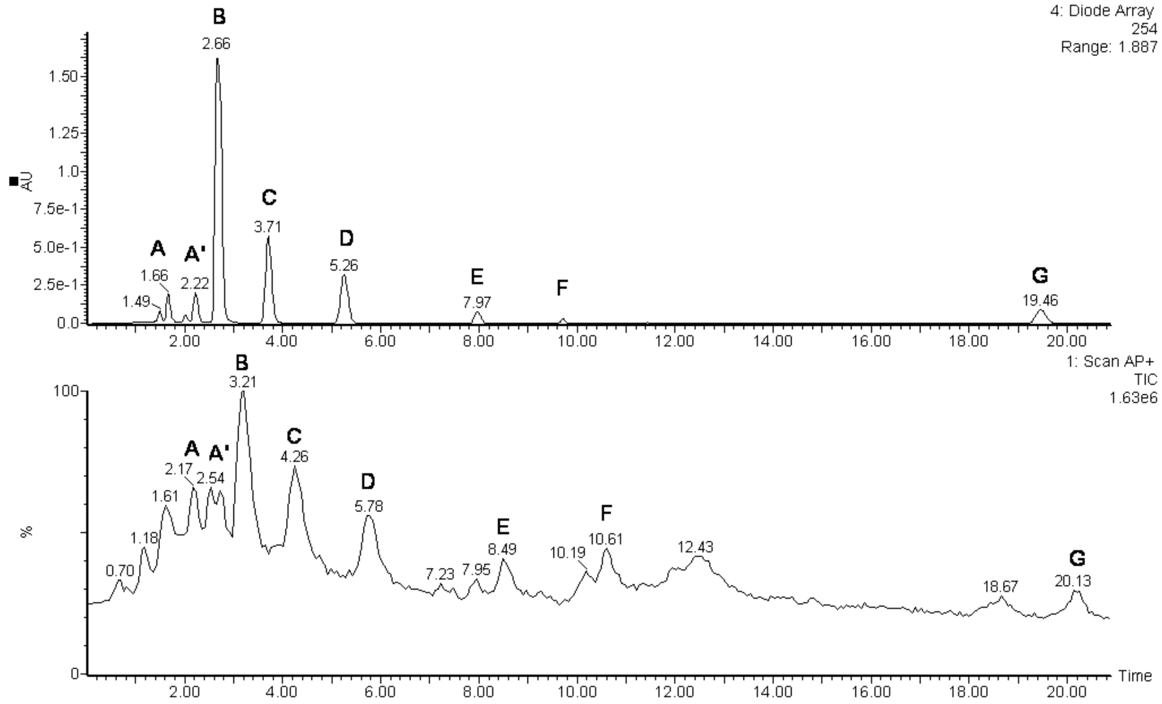


Figure a2.1. Chromatogram of a TMTD vulcanizate at 254nm (above),ans the Total Ion Chromatogram (TIC) for 20V cone voltage (below).

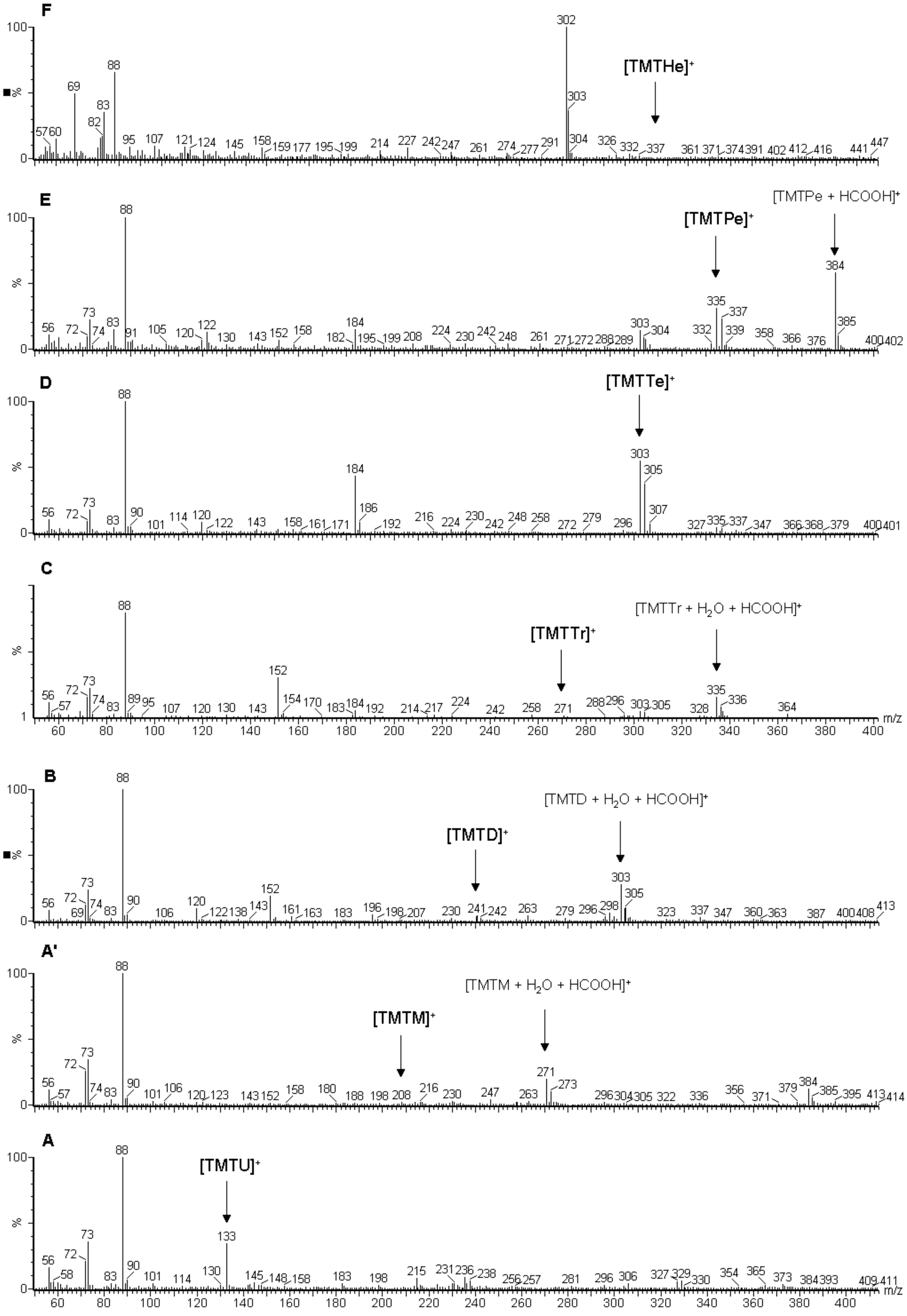
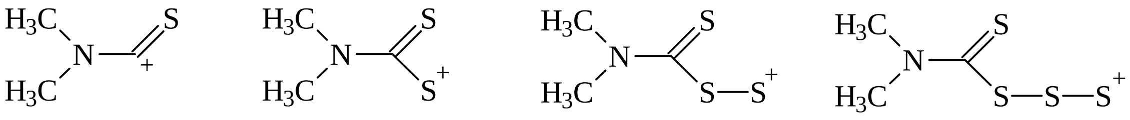


Figure a2.2. Mass spectra (m/z from 50 to 400) of peaks A to F.

The identification of these chromatographic peaks has been already shown in Table 2.5. in Chapter 2. Peak A’ has been also identified with this method as tetramethylthiuram monosulfide (TMTM) as it will be following shown. Peaks B and G could be identified using external standards as TMTD and sulfur respectively. Figure a2.2. displays the mass spectra of peaks A, A’, B, C, D, E and F. All these spectra contain common fragments of thiuram accelerated intermediate compounds. In Figure a2.3. some of them are presented.



m/z 88 m/z 120 m/z 152 m/z 184

Figure a2.3. MS fragments for thiuram accelerated intermediate compounds.

In **spectrum A** the molecular ion is at m/z 133, which corresponds to a protonated tetramethylthiourea molecule (TMTU$^+$). As stated before, **spectrum A’** has been identified as tetramethylthiuram monosulfide (TMTM$^+$). The molecular ion can be seen at m/z 209, but there is a more intense signal at m/z 273. This signal corresponds to the adduct formed by a TMTM molecule, a water molecule and a formic acid unit. Peak B has been identified as TMTD with an external standard. **Spectrum B** shows a signal at m/z 241 corresponding to the molecular ion and a signal at m/z 305 that corresponds to the adduct with a water molecule and a formic acid unit. **Spectrum C** has been identified as tetramethylthiuram trisulfide (TMTTr$^+$). Its molecular ion is at m/z 273 and there is also a signal at m/z 337 corresponding to the adduct with water and formic acid. **Spectrum D** has been identified as tetramethylthiuram tetrasulfide (TMTTe$^+$) (m/z 305). **Spectrum E** corresponds to tetramethylthiuram pentasulfide (TMTPe$^+$). Its molecular ion is at m/z 337, and there is also an intense signal at m/z 383 corresponding to the adduct of this molecule with a formic acid unit. Finally, **Spectrum F** presents the molecular ion at m/z 339 and has been identified as tetramethylthiuram hexasulfide (TMTHe$^+$).

Appendix 3

Identification of Squalene by-products by HPLC-ESI$^+$- MS with Silver Nitrate post-column Derivatization

First of all, and as stated in section 2.4.3.2. the original RP-HPLC method[1] to analyze squalene by-products has been modified in order to remove n-hexane, since ESI does not allow the use of non polar eluents. The original mobile phase, acetonitrile/2-propanol/n-hexane (72:17:11), was replaced by acetonitrile/2-propanol (70:30) obtaining a good resolution in the cross-linked squalenes peaks. However, the resolution of these peaks has been diminished in comparison with the one obtained with the original conditions, due to the polarity increase in the eluent. A drawback of the method developed, apart from the lack of resolution caused by the mobile phase polarity modification, is that the sulfur isotopic abundance (4% of the signal at M+2) is shielded by silver isotopic abundance. Therefore, in this method only the molecular weights are detected but no the isotopic abundances.

Before developing the post-column derivatization method, ESI and APCI where tried to ionize crosslinked squalenes (Sq-S$_x$-Sq). As it can be seen in Figure a3.1. a) samples did not present ionization between minutes 8 and 12 (times when these intermediates elute), neither with ESI nor with APCI, in none of the work modes (positive and negative) tested. For that reason this post-column method with silver nitrate derivatization has been developed to form silver adducts (ESI positive mode) in order to facilitate the ionization. Figure a3.1. b) displays the dramatic change in the ionization obtained with silver derivatization for all the crosslinked squalenes (from minute 8 to minute 12).

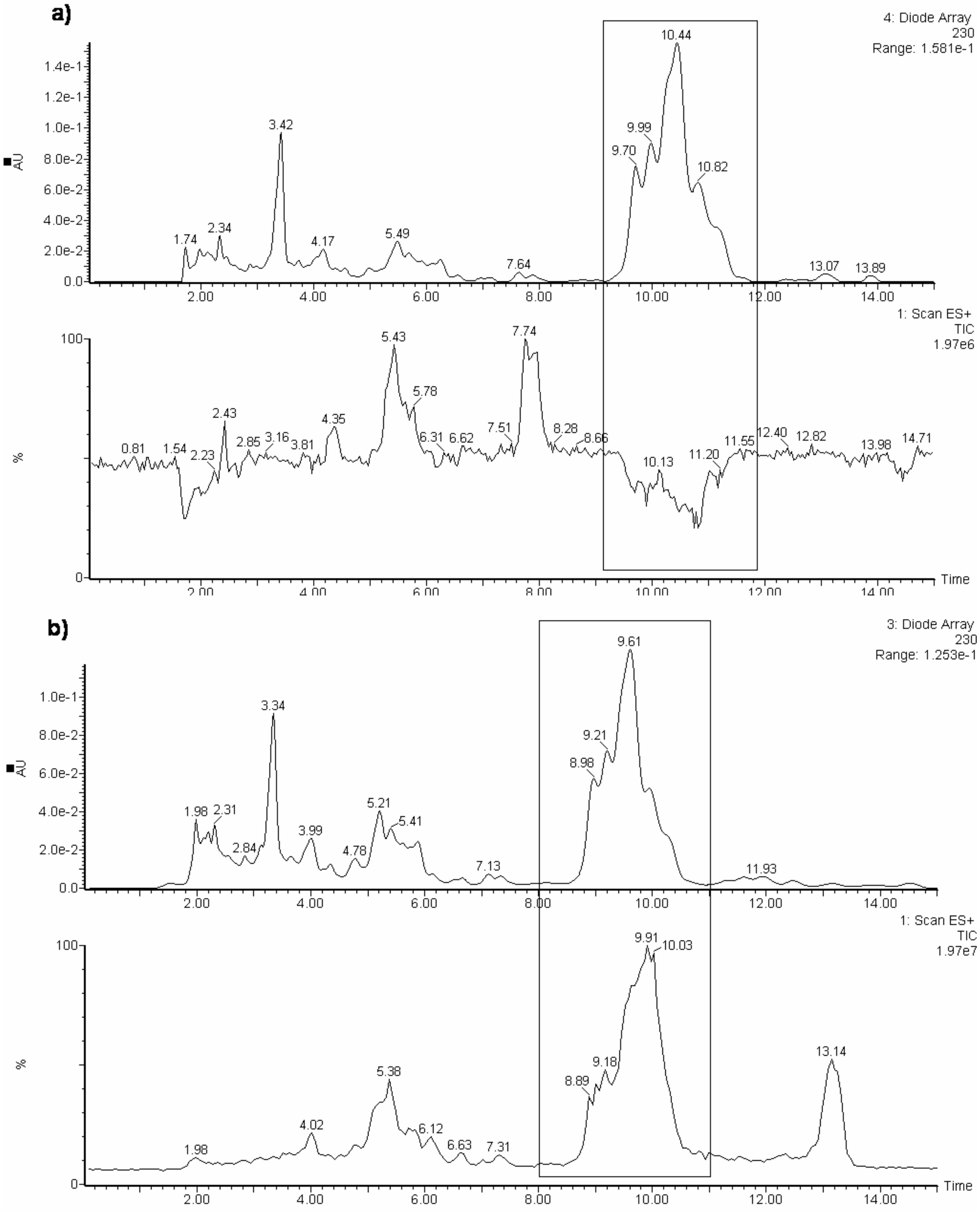


Figure a3.1. (a) Chromatogram at 230 nm (above) and mass spectrum in positive mode (below) without silver nitrate derivatization. (b) Chromatogram at 230 nm (above) and mass spectrum in positive mode (below) with silver nitrate derivatization. An outstanding increase of the ionization of the cross-linked squalens (peaks between peaks 9 and 11 minutes) can be observed.

As it has been displayed in Figure 2.15., the first peaks correspond to N-cyclohexylbenzothiazol-2-sulfenamide (CBS) and 2-mercaptobenzothiazole (MBT), product of CBS decomposition. They have been identified by external standards. The last peak at 15.4 minutes corresponds to squalene, which also has been identified by external standard. Figure a3.2. displays a chromatogram at 230nm and the mass spectrum obtained with silver nitrate derivatization (m/z between 400 and 1200). This mass spectrum was obtained using a cone voltage of 5V to obtain as less fragmentation as possible. In addition figure a3.2. shows the chromatographic peaks that have been identified with external standards (CBS, MBT, sulfur and squalene (Sq)) but also the peaks, or group of peaks, that present the same mass spectrum although their identification is not yet clear. The non identified peaks have been grouped in fractions a, b, c, d, e and f.

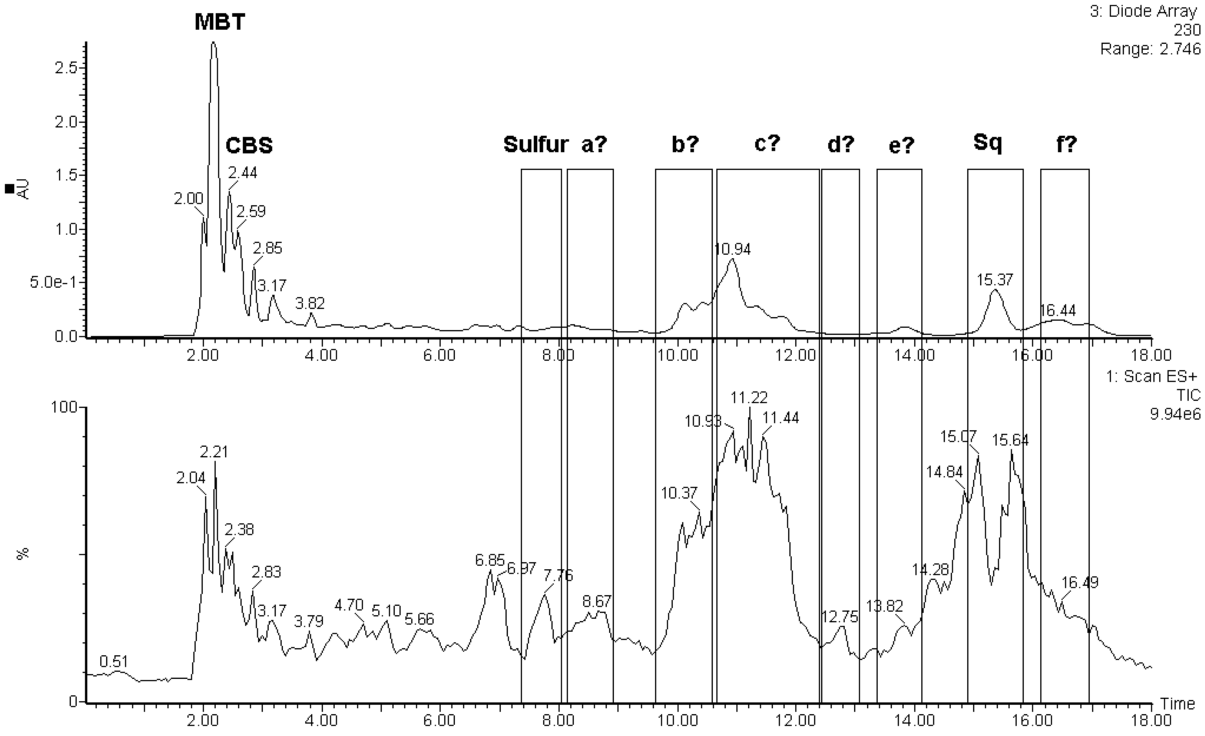


Figure a3.2. Chromatogram at 230 nm (above) and mass spectrum (below) of a sample vulcanized for 60 minutes in which cross-linked and modified squalenes can be seen.

Mass spectrum (m/z = 400-1200) of silver adduct of squalene is presented in figure a3.3. Squalene (Sq) has a molecular weight of 410 g/mol. His silver adduct $[Sq+Ag]^+$ corresponds to the peak at m/z=519. Some other peaks separated by a constant distance of m/z=169 can be clearly observed. They correspond to additions of silver nitrate molecules, present in the eluent ($[Sq+Ag+AgNO_3]^+$ m/z=688, $[Sq+Ag+2AgNO_3]^+$ m/z=857 and $[Sq+Ag+3AgNO_3]^+$ m/z=1028). Sometimes and depending on the solvent and the cone voltage it is normal to find solvent adduct ions as $[M+Ag+solvent]^+$ aside from the adduct $[M+Ag]^+$ [2]. Sometimes, as in this case, salt adducts ions from salts present in the mobile phase are formed instead of the solvent adducts ions[3]. Under these conditions some silver nitrate adducts ions have been formed.

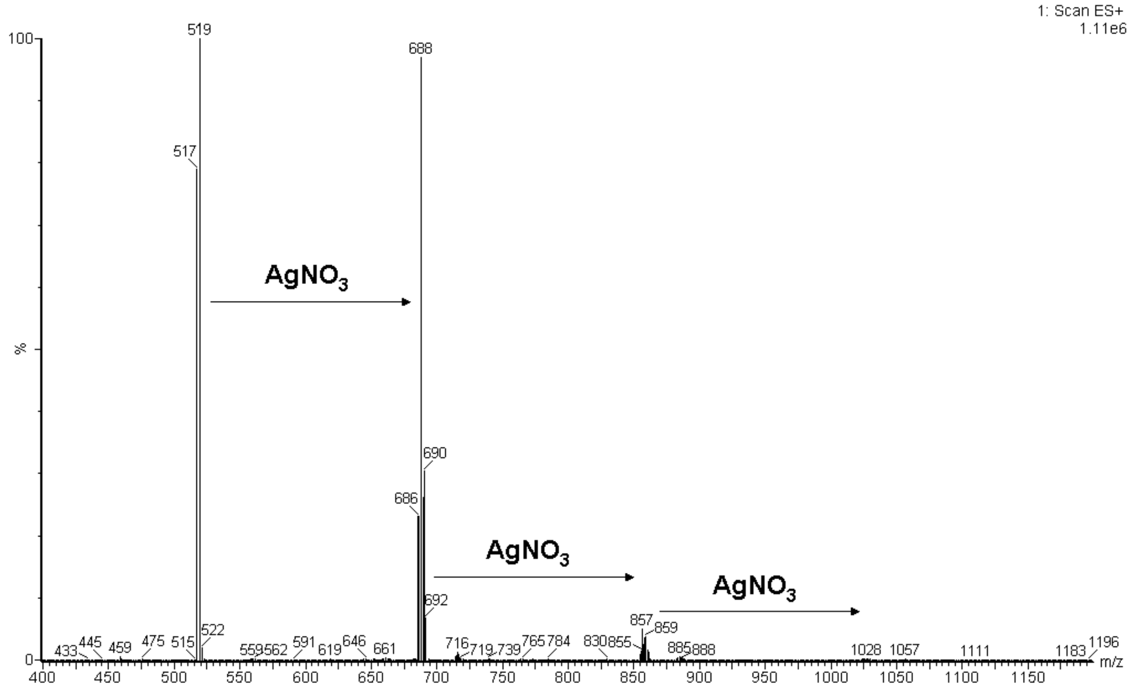


Figure a3.3. Mass spectrum of the silver adduct of squalene (Sq).

At 6.9 minutes appears the peak of sulfur (S_8). This peak has also been identified with an external standard. Figure a3.4. shows the mass spectrum (m/z=400-1200) of silver adduct of sulfur. It is very similar to the one of squalene (Figure a3.3.). Elementary sulfur (S_8) has a molecular weight of 256 g/mol. The signal m/z=535 in the mass spectrum corresponds to the adduct of sulfur with a silver molecule and a silver nitrate adittion $[S_8+Ag+AgNO_3]^+$. At a gap of m/z=169, and multiples of this distance, some intense peaks can be also observed corresponding to multiple additions of silver nitrate molecules, as we have observed in the squalene mass spectrum ($[S_8+Ag+2AgNO_3]^+$ m/z=703, $[S_8+Ag+3AgNO_3]^+$ m/z=875 and $[S_8+Ag+4AgNO_3]^+$ m/z=1044). Silver adduct ion of sulfur $[S_8+Ag]^+$ must appear at m/z=363, outside the analyzed region.

In the electronic impact method[1], **fraction a** was identified as cross-linked squalene with a tetrasulfídic sulfur bridge (Sq-S_4-Sq); **fraction b** was interpreted as modified squalene; **fraction c** formed by three peaks bad resolved were taken respectively as trisulfidic (Sq-S_3-Sq), disulfidic (Sq-S_2-Sq) and monosulfidic (Sq-S-Sq) cross-linked squalenes; **fraction d**, as it is seen in figure a3.2., is not detected at 230nm; **fraction e** was assigned as squalene with pendant group and **fraction f** was not detected either at 230nm. The pendant group is formed by a sulfur chain ended by a benzothiazole molecule (Bz). The development of this ESI$^+$-MS method has allowed the correct identification of the fractions. Now, we will focus on the mass spectra of the fractions with the ESI-MS method.

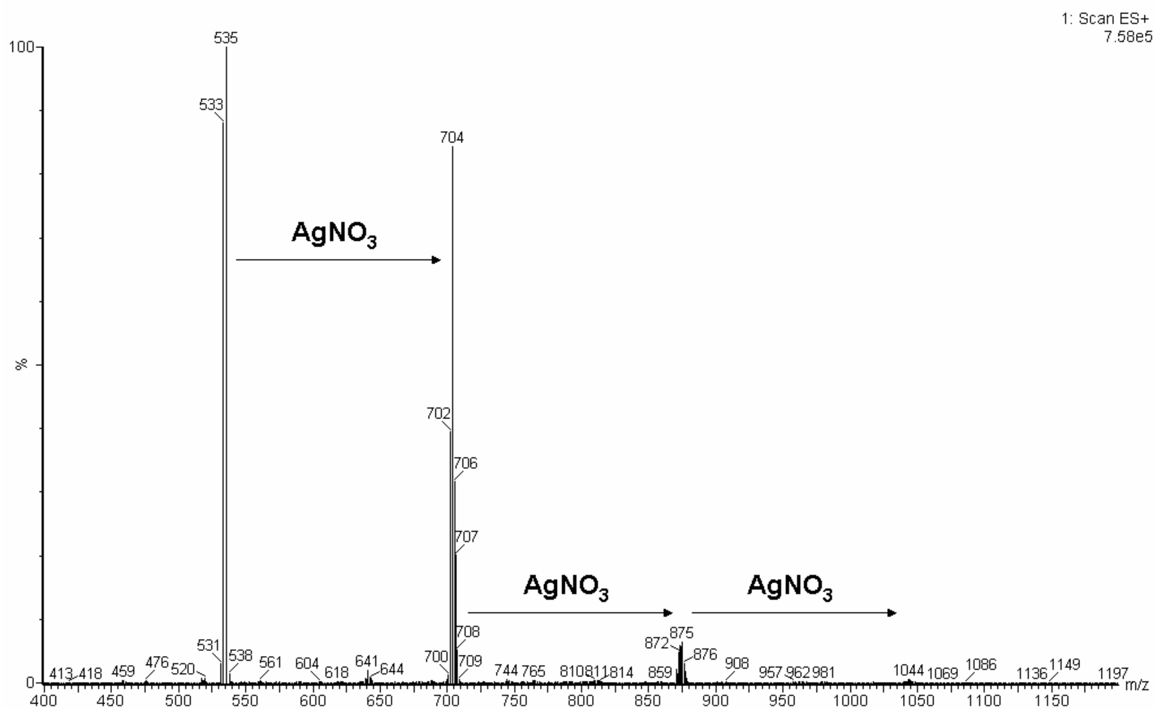


Figure a3.4. Mass spectrum of the silver adduct of sulfur.

In figure a3.5. the mass spectrum of **fraction a** is displayed, which corresponds to the tetrasulfidic cross-linked squalene (Sq-S_4-Sq). The molecular ion corresponding to the silver adduct $[M+Ag]^+$ is at m/z=1055. Furthermore, a low signal at m/z=519 can be also seen. As mentioned before, it corresponds to the silver adduct of squalene $[Sq+Ag]^+$. Another peaks at m/z=549, 583 and 515 corresponding to $[Sq\text{-}S+Ag]^+$, $[Sq\text{-}S_2+Ag]^+$ and $[Sq\text{-}S_3+Ag]^+$ respectively can also be detected. This gradation of squalenes bonded with a different sulfur chain bridges are fragmentation products of the molecular ion and this profile is repeated in the m/z zone between 700 and 800 with the signals corresponding to the ions $[Sq\text{-}S_x+Ag+AgNO_3]^+$.

Figure a3.6. shows the mass spectra of **fraction b** which has been identified as trisulfidic cross-linked squalene (Sq-S_3-Sq). In the EI method[1] this chromatographic peak had been interpreted as modified squalene, but this method of RP-HPLC-ESI$^+$-MS with silver nitrate post-column derivatization has allowed its correct identification. This fraction is formed by two chromatographic peaks, but both have the same mass spectrum. This is due to the formation of different isomers according to the position of the sulfur bridge that bind the two squalene chains. The molecular ion corresponding to the silver adduct $[M+Ag]^+$ is at m/z=1023. This signal does not appear in the mass spectrum, but at m/z=1195 the ion $[M+Ag+AgNO_3]^+$ is clearly detected. Besides, there are peaks at m/z=517 corresponding to the silver adduct of squalene $[Sq+Ag]^+$ and at m/z=549, 583 and 515 corresponding to $[Sq\text{-}S+Ag]^+$, $[Sq\text{-}S_2+Ag]^+$ and $[Sq\text{-}S_3+Ag]^+$ respectively. These signals have also appeared in the tetrasulfidic cross-linked squalene (Figure a3.5.), but the relation between their intensities is different. This gradation of squalenes bonded with a different sulfur chain bridges are fragmentation products of the molecular ion and this profile is repeated in the m/z zone between 700 and 800 with the signals corresponding to the ions $[Sq\text{-}S_x+Ag+AgNO_3]^+$.

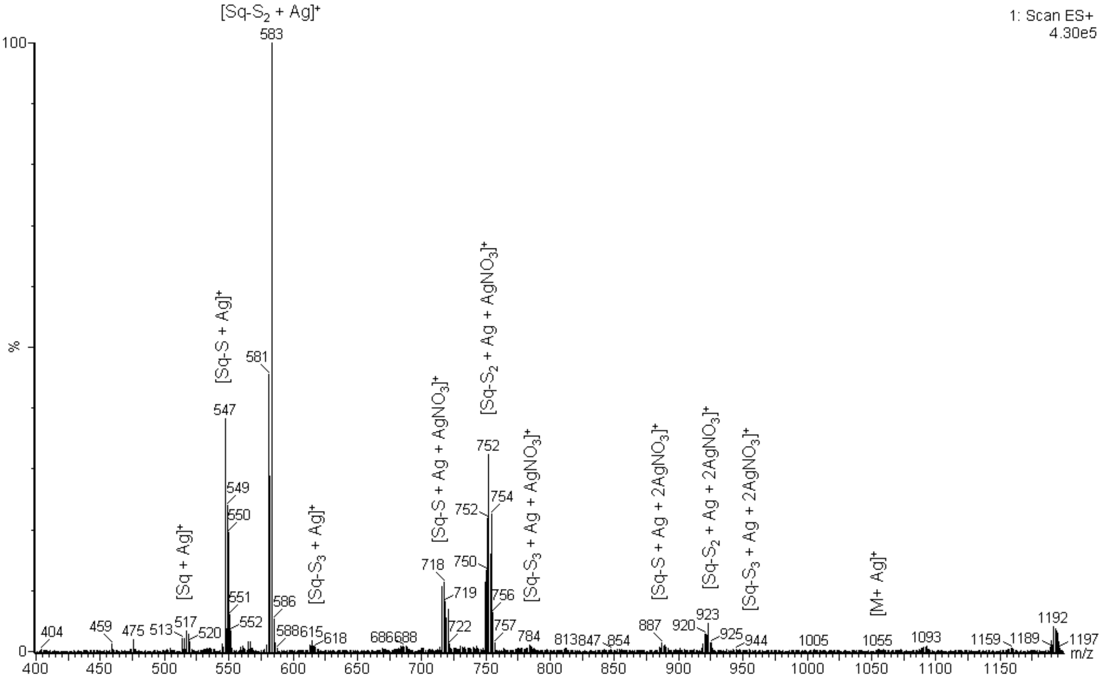


Figure a3.5. Mass spectrum of **fraction a** between m/z = 400-1200. It corresponds to two squalene molecules bonded with a tetrasulfidic bond ($Sq\text{-}S_4\text{-}Sq$).

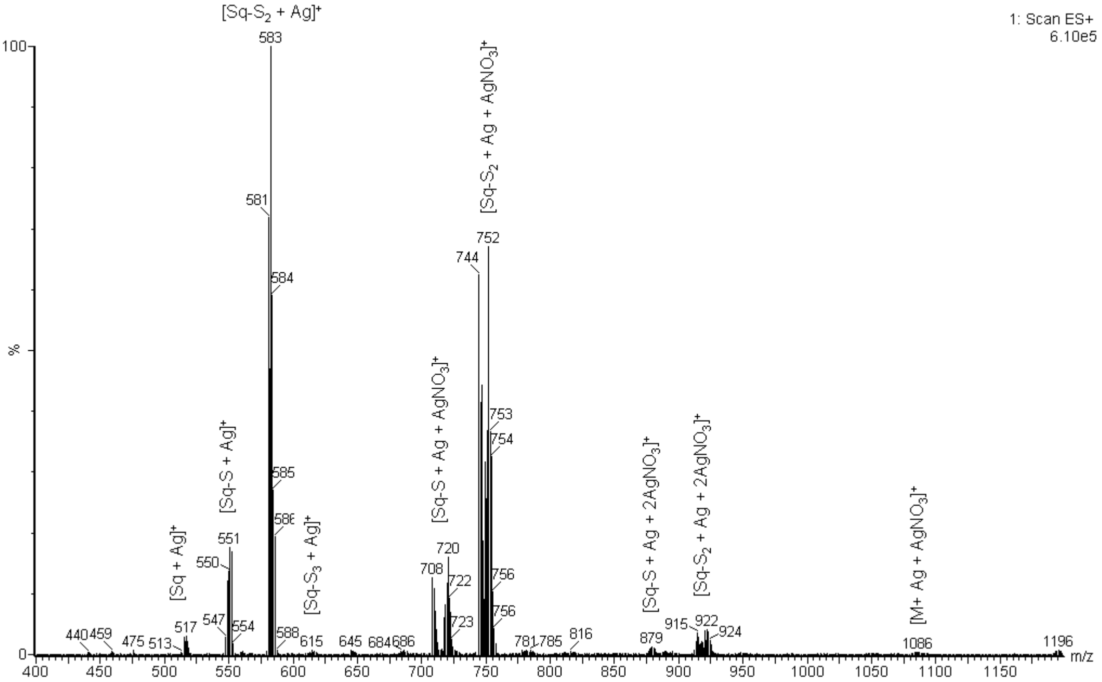


Figure a3.6. Mass spectrum of **fraction b** between m/z = 400-1200. It corresponds to two squalene molecules bonded with a trisulfidic bond ($Sq\text{-}S_3\text{-}Sq$).

In Figure a3.7. the mass spectra of the **fraction c** is seen and it has been identified as disulfidic cross-linked squalene (Sq-S_2-Sq). In the electronic impact method[1] this three chromatographic peaks had been interpreted as trisulfidic, disulfidic and monosulfidic cross-linked squalenes respectively, but this RP-HPLC-ESI-MS method with silver nitrate post-column derivatization has allowed its correct identification. These three peaks have the same mass spectrum, since they are different isomers according to the position of the sulfur bridge that bind the two squalene chains. The molecular ion corresponding to the silver adduct $[M+Ag]^+$ is at m/z=991. This signal is not in the mass spectra, but there is a peak at m/z=1162, which is the ion $[M+Ag+AgNO_3]^+$. In this case signal m/z=517 corresponding to the silver adduct of squalene is not observed $[Sq+Ag]^+$, but a very intense signal is seen at m/z=551, which corresponds to $[Sq\text{-}S+Ag]^+$. There is also a small signal at m/z=583 corresponding to the ion $[Sq\text{-}S_2+Ag]^+$. This can be explained due to the homolytic break of the disulfidic bridges (Sq-S_2-Sq), giving rise to a molecule of squalene connected to a sulfur (Sq-S), whose adduct with silver is m/z=551. At m/z=720 the peak of $[Sq\text{-}S+Ag+AgNO^3]^+$ can be seen.

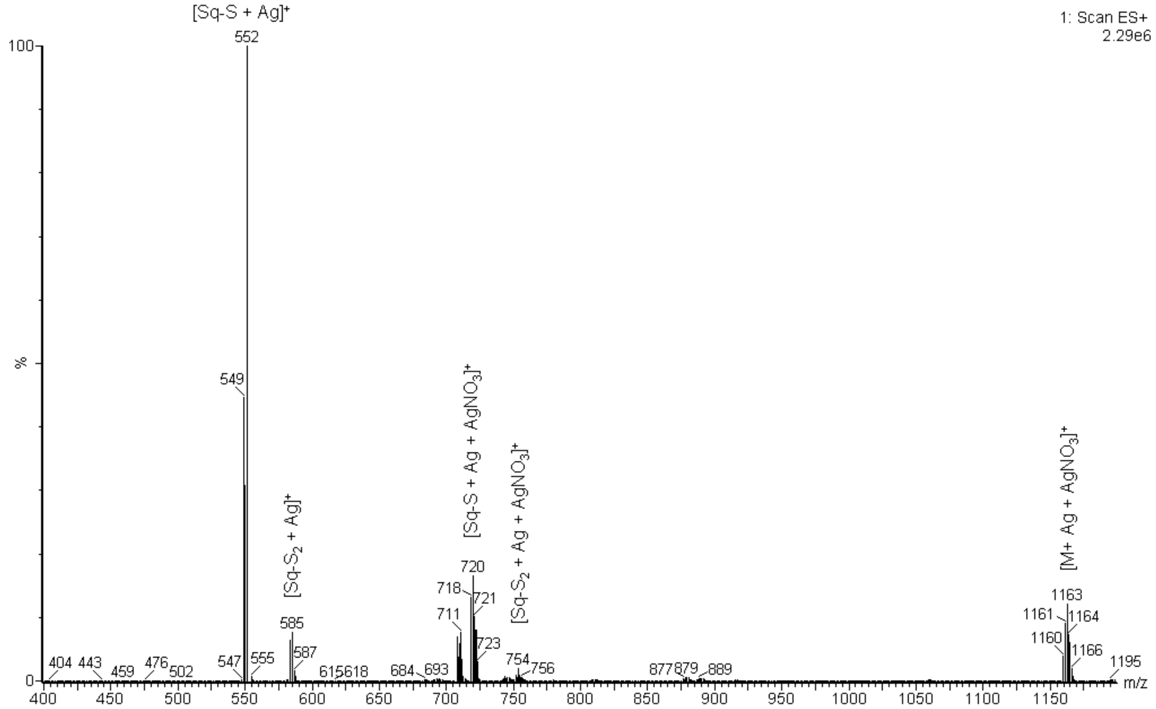


Figure a3.7. Mass spectrum of **fraction c** between m/z = 400-1200. It corresponds to two squalene molecules bonded with a disulfidic bond (Sq-S_3-Sq).

In figure a3.8. the mass spectrum of **fraction d** is presented and it is very similar to the disulfidic cross-linked squalene (Sq-S_2-Sq) (Figure a3.7.). This peak is detected by ionization in the mass spectrometer, but does not absorb at 230 nm, since it does not appear in the DAD signal. The signals are the same than in the Sq-S_2-Sq (Figure a3.7.), but the peaks of m/z=688, 720 and 750 appear with more intensity. This can be explained because they could correspond to the squalenes with pendant group (Sq-PG): [Sq-S-Bz+Ag]$^+$, [Sq-S$_2$-Bz+Ag]$^+$ and [Sq-S$_3$-Bz+Ag]$^+$ respectively.

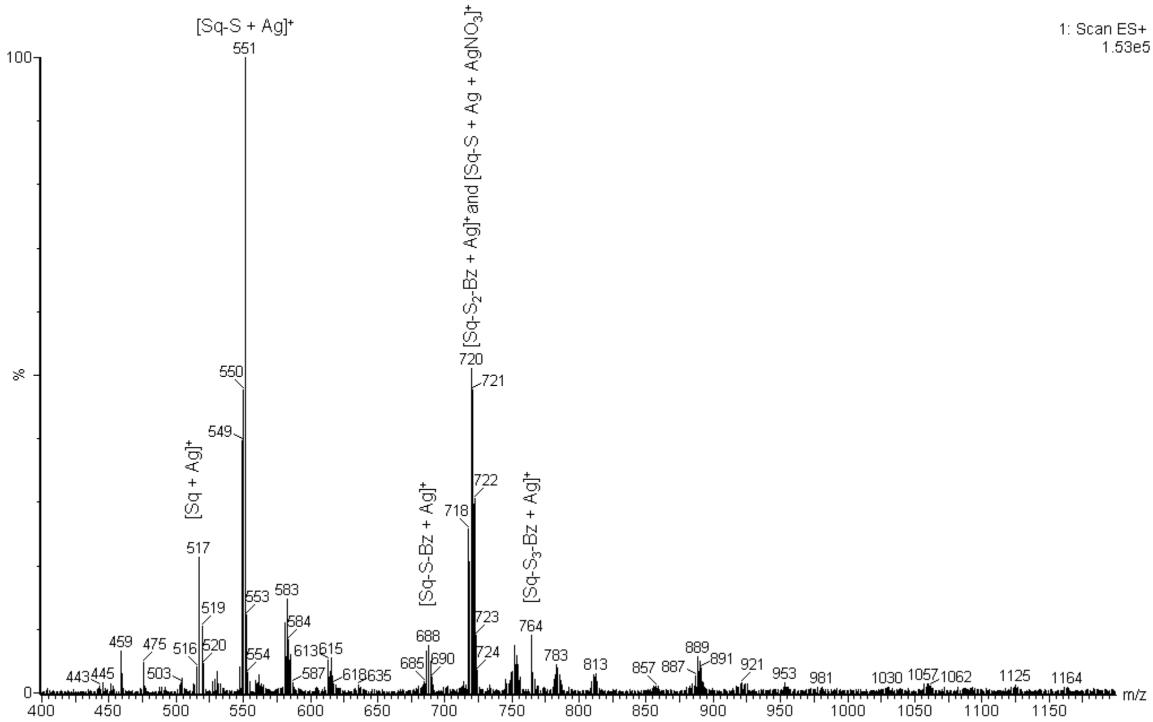


Figure a3.8. Mass spectrum of **fraction d** between m/z=400-1200. It corresponds to a squalene molecule bonded with a pendant group (Sq-PG).

Figure a3.9. shows the mass spectrum of **fraction e** and that corresponds to the monosulfidic cross-linked squalene (Sq-S-Sq). In the electronic impact method[1] this chromatographic peak had been interpreted as squalene with pendant group, but this method of HPLC-ESI$^+$-MS with silver nitrate post-column derivatization has allowed its correct identification. The molecular ion corresponding to the silver adduct [M+Ag]$^+$ is at m/z=953 and the salt adduct of the molecular ion [M+Ag+AgNO$_3$]$^+$ is at m/z=1123. In this case the signal m/z=517 corresponding to the silver adduct of squalene [Sq+Ag]$^+$ and the signal at m/z=551 corresponding to [Sq-S+Ag]$^+$ are observed. Both ions are fragmentation products of the breakage of the monosulfidic cross-linked squalene. At m/z=688 and 720 we find the adduct ions [Sq+Ag+AgNO$_3$]$^+$ and [Sq-S+Ag+AgNO$_3$]$^+$ respectively; and at m/z=859 and 885 the adduct ions [Sq+Ag+2AgNO$_3$]$^+$ and [Sq-S+Ag+2AgNO$_3$]$^+$ respectively.

Finally **fraction f** (Figure a3.10.) displays a mass spectrum very similar to the squalene mass spectrum (Figure a3.3.), but some intensities vary significantly, which could mean that this peak belongs to the modified squalene, with a similar structure to squalene.

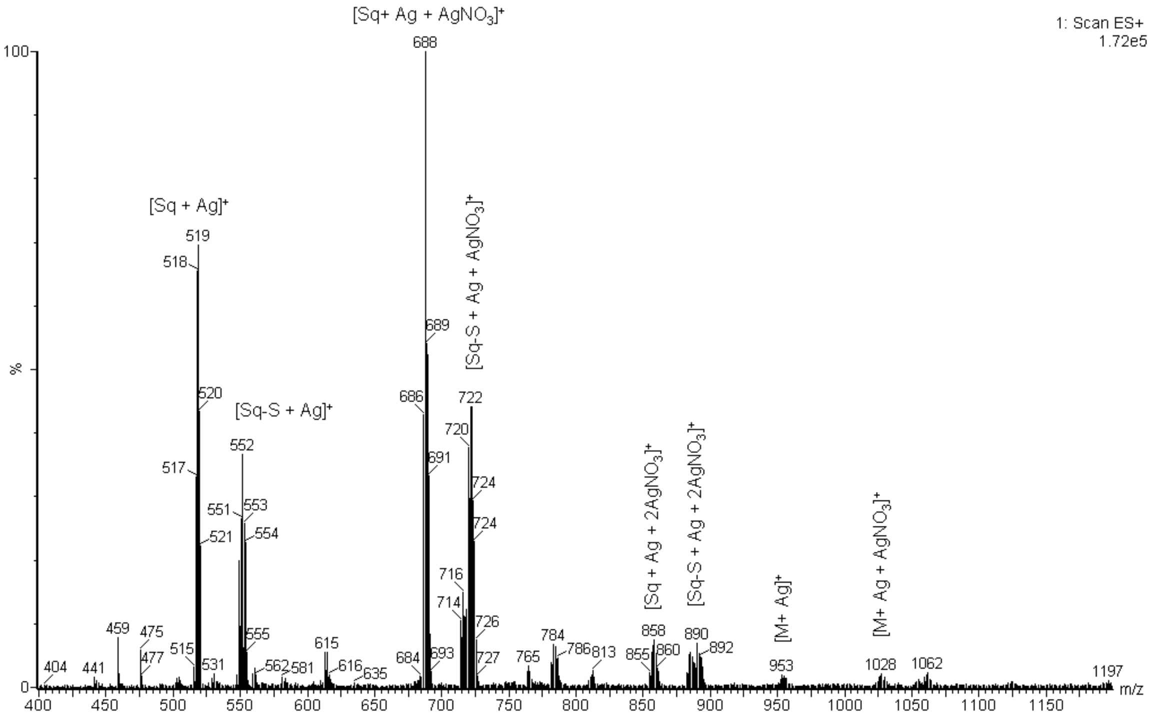


Figure a3.9. Mass spectrum of **fraction e** between m/z=400-1200. It corresponds to two squalene molecules bonded with a monosulfidic bond (Sq-S-Sq).

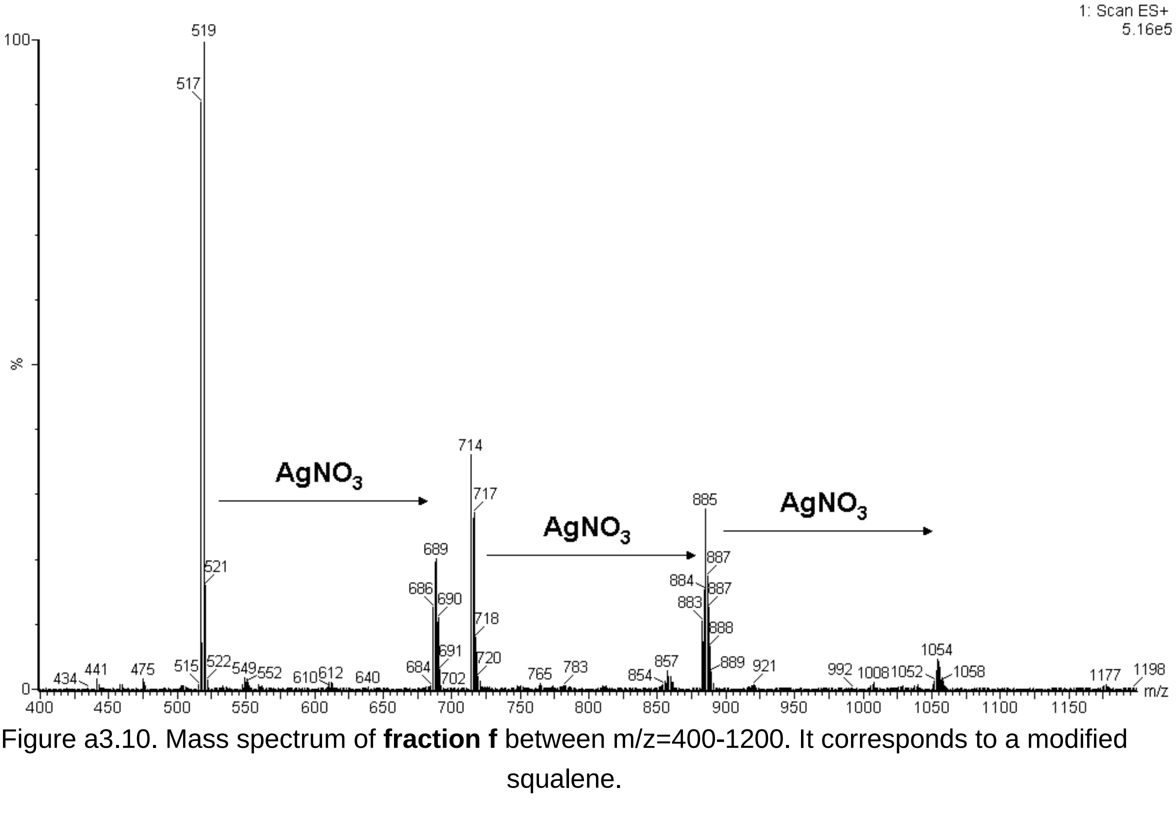


Figure a3.10. Mass spectrum of **fraction f** between m/z=400-1200. It corresponds to a modified squalene.

In order to finish determining the chromatographic peaks allocation, the m/z extraction of the most characteristic peaks of crosslinked squalenes have been performed. For that reason, in Figure a3.11. the result of this peak extraction is shown. The figure shows the extraction of m/z=688, 720, 752 and 784 (from top to bottom) where the rich zones of the chromatogram in these ions can be observed. Furthermore, some constant gaps between them can be observed due to the sulfur lost (m/z 32). In the graphic it is possible to observe that the elution order is Sq-S_4-Sq, Sq-S_3-Sq, Sq-S_2-Sq and Sq-S-Sq, from more polar to less polar, as it was said in the electronic impact method[1]. In addition, it is observed that the peak extractions results in a wide zone, that does not correspond only with the chromatographic peak. This is due to the formation of diverse isomers of the different types of cross-linked squalenes and also a consequence of the resolution decrease caused by the eluent change. Furthermore, it can be observed that some of these isomers do not absorb at 230nm, which shows that it is not possible to quantify completely the degree and nature of the crosslink process with HPLC-UV. The summery of all this identification work is displayed in Figure 2.15 (Chapter 2).

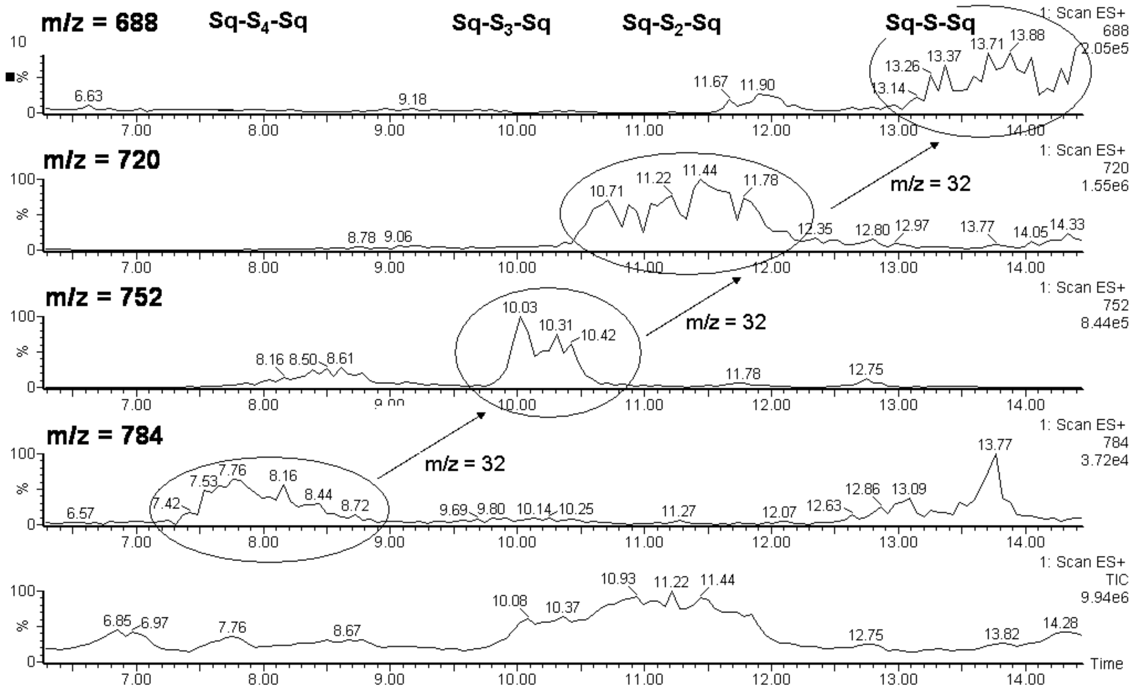


Figure a3.11. Mass spectrum between m/z=400-1200 of the chromatogram zone where the cross-linked squalenes are (7-14 minutes) (below). Extracts of m/z 688, 720, 752 y 784 (from above to below) where the zones of the chromatogram rich in these ions, and the gaps of m/z 32 corresponding to the sulfur lost, can be seen.

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AWARDS

- Finalist of Junior EUROMAT 2004, 1st award to the best poster of the session "Polymers, Ceramics and Nanomaterials", September 2004, Lausanne, Switzerland.
- 1st award to the best presentation of the Symposium “Materials i química de l’estat sòlid” of the IV Trobada de Joves Investigadors dels Països Catalans, January 2006, Lleida, Spain.
- Best Graduate Paper Award of the Student Colloquium of the 170th Fall Technical Meeting (Rubber Division, ACS), October 2006, Cincinnati (OH), USA.