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DOCTORAL THESIS

Title	NOVEL VULCANISING INGREDIENTS: TOWARDS GREENER RUBBER FORMULATIONS
Presented by	Manuel Guzmán Medrano
Centre	Escola Tècnica Superior IQS
Department	Industrial Engineering
Supervised by	Dr. Salvador Borrós Gómez and Dr. Núria Agulló Chaler

C. Claravall, 1-3
08022 Barcelona
Tel. 936 022 200
Fax 936 022 249
E-mail: urlsc@sec.url.es
www.url.es

A mi familia y a María

‘A man has cause for regret only when he sows and no one reaps.’
Charles Goodyear (1800 – 1860)

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SUMMARY

Zinc oxide is a widely used compound in rubber industry due to the excellent properties that shows as activator for sulphur vulcanisation. Despite its superior characteristics, there is an increased concern about its environmental effects and several research studies have been carried out in order to reduce the ZnO levels in rubber compounds or substitute it.

Between all the alternatives proposed to reduce the ZnO levels, the use of nano-sized ZnO particles with high surface area seems to be promising. Another approach to reduce the ZnO levels that has been studied by many authors is the use of alternative metal oxides, such us CaO, MgO, CdO, CuO, PbO and NiO.

In this work, novel activators with reduced zinc content have been developed in order to reduce the environmental impact of the rubber industry. Mixed metal oxides nanoparticles of zinc and other metal have been synthesised with the aim of profiting from its size and to take advantage of the behaviour of both ZnO and MgO in sulphur vulcanisation.

Another environmental problem related to the rubber industry is the management of end of life and waste rubber, especially tyres. The environmental impact of waste tyres, together with the economic problems related with the management and disposal, has led to a great variety of studies to develop technologies to re-use and recycle waste tyres.

The use of reclaimed or regenerated rubber in blends with virgin rubber has been investigated by different authors. However, the migration of chemicals between the crumb and the matrix has not been considered as an advantage in order to use tyre crumb as an activator and, therefore, reduce the zinc levels employed in rubber compounds and introducing new applications for the waste rubber from end of life tyres. This approach has been investigated in this thesis.

RESUMEN

El óxido de zinc es un compuesto ampliamente utilizado en la industria del caucho debido a las excelentes propiedades que muestra como activador para la vulcanización con azufre. A pesar de sus características superiores, existe una creciente preocupación acerca de sus efectos medioambientales y numerosos estudios han sido realizados con el fin de reducir los niveles de ZnO en los compuestos de caucho o para sustituirlo.

Entre todas las alternativas propuestas para reducir la cantidad de óxido de zinc, el empleo de nanopartículas de ZnO con una alta superficie específica parece ser prometedor. Otro propuesta para reducir los niveles de ZnO que ha sido estudiado por numerosos autores es el uso de otros óxidos metálicos, como el CaO, MgO, CdO, CuO, PbO y NiO.

En este trabajo, nuevos activadores con un reducido contenido de zinc han sido desarrollados con el fin de reducir el impacto ambiental de la industria del caucho. Nanopartículas de óxidos metálicos mixtos de zinc y otros metales han sido sintetizados con el fin de beneficiarse de su tamaño y aprovecharse del comportamiento tanto del ZnO como del MgO en la vulcanización con azufre.

Otro gran problema medioambiental relacionado con la industria del caucho es la gestión de los compuestos de caucho que han alcanzado el final de su vida útil, especialmente de neumáticos. El impacto medioambiental de los neumáticos, junto con los problemas económicos relacionados con su gestión y eliminación, ha dado lugar a una gran variedad de estudios para desarrollar tecnologías para reutilizar y reciclar los neumáticos fuera de uso.

El uso de caucho recuperado o regenerado en mezclas con caucho virgen ha sido investigado por diferentes autores. Sin embargo, la migración de las sustancias químicas entre el caucho triturado y la matriz virgen no ha sido considerada como una ventaja con el fin de utilizar el caucho de neumáticos fuera de uso como un activador y, por lo tanto, reducir los niveles de zinc empleadas en los compuestos de caucho e introducir nuevas aplicaciones para los neumáticos fuera de uso. Este enfoque ha sido investigado en esta tesis.

RESUM

L'òxid de zinc és un compost àmpliament utilitzat en la indústria del cautxú a causa de les excel·lents propietats que mostra com activador per a la vulcanització amb sofre. Malgrat les seves característiques superiors, hi ha una creixent preocupació sobre els seus efectes mediambientals i nombrosos estudis s'han portat a terme per tal de reduir els nivells de ZnO als compostos de cautxú o per a substituir-lo.

Entre totes les alternatives propostes per reduir la quantitat d'òxid de zinc, l'ús de nanopartícules de ZnO amb una alta superfície específica sembla prometedor. Una altra proposta per reduir els nivells de ZnO que ha estat estudiada per nombrosos autors és l'ús d'altres òxids metàl·lics, com el CaO, MgO, CdO, CuO, PbO i NiO.

En aquest treball, nous activadors amb un reduït contingut de zinc han estat desenvolupats per tal de reduir l'impacte ambiental de la indústria del cautxú. Nanopartícules d'òxids metàl·lics mixtes de zinc i altres metalls s'han sintetitzat per tal de beneficiar-se de la seva grandària i aprofitar-se del comportament tant del ZnO com del MgO a la vulcanització amb sofre.

Un altre gran problema mediambiental relacionat amb la indústria del cautxú és la gestió dels compostos de cautxú que han arribat al final de la seva vida útil, especialment de pneumàtics. L'impacte mediambiental dels pneumàtics, juntament amb els problemes econòmics relacionats amb la seva gestió i eliminació, ha donat lloc a una gran varietat d'estudis per desenvolupar tecnologies per a reutilitzar i reciclar els pneumàtics fora d'ús.

L'ús de cautxú recuperat o regenerat en mescles amb cautxú verge s'ha investigat per diferents autors. No obstant això, la migració de les substàncies químiques entre el cautxú triturat i la matriu verge no ha estat considerada com un avantatge per tal d'utilitzar el cautxú de pneumàtics fora d'ús com un activador i, per tant, reduir els nivells de zinc emprats en els compostos de cautxú i introduir noves aplicacions per als pneumàtics fora d'ús. Aquest enfocament ha estat investigat en aquesta tesi.

MAIN SYMBOLS AND ABBREVIATIONS

A_0	Compensation for a possible DC offset of the signal in relaxation time spectroscopy
A_1	Amplitude of the cross-linked fraction of the polymer in relaxation time spectroscopy [%]
A_2	Amplitude of the highly mobile fraction of the polymer in relaxation time spectroscopy [%]
APS	Aperiodic pulse sequence
A/S ratio	Accelerator/Sulphur ratio [-]
B	Non-coupled fraction of polymer chains [%]
BET	Brunauer-Emmett-Teller
Bi_2O_3	Bismuth Oxide
BIIR	Bromo-isobutylene-isoprene rubber
BR	Butadiene rubber
$CaCO_3$	Calcium carbonate
$Ca(NO_3)_2 \cdot 4H_2O$	Calcium nitrate tetrahydrate
CaO	Calcium oxide
CB	Carbon black
CBS	N-Cyclohexylbenzothiazole-2-sulphenamide
CdO	Cadmium oxide
CIIR	Chloro-isobutylene-isoprene rubber
CR	Chloroprene rubber
CRI	Cure rate index [%]
CuO	Copper oxide
DLS	Dynamic light scattering

d_p	Particle diameter [nm]
DPG	Diphenylguanidine
DQ	Double Quantum
D_{res}	Residual dipolar coupling constant [Hz]
DSC	Differential scanning calorimetry
DTG	Derivative thermogravimetry
E_a	Activation energy [J/mol]
E_b	Elongation at break [%]
EPDM	Ethylene-propylene-diene rubber
ESI	Electrospray ionisation
EV	Efficient vulcanisation
f	Cross-link functionality [-]
f_{ins}	Weight fraction of insoluble components
GC	Gas chromatography
HgO	Mercury oxide
HPLC	High performance liquid chromatography
I_{DQ}	Spectroscopic intensity build-up of DQ coherence [a.u.]
$I_{\sum DQ}$	Total spectroscopic intensity of the coupled segments that constitute the network [a.u.]
IGC	Inverse gas chromatography
IIR	Isobutylene-isoprene rubber (butyl rubber)
I_{nDQ}	Normalized DQ intensity [a.u.]
IR	Synthetic isoprene rubber
IRHD	International Rubber Hardness Degree
I_{ref}	Reference spectroscopic intensity [a.u.]
M_2	Second moment
M_{50}	Modulus at 50% elongation [MPa]
M_{100}	Modulus at 100% elongation [MPa]
M_{200}	Modulus at 200% elongation [MPa]
M_{300}	Modulus at 300% elongation [MPa]

M_{500}	Modulus at 500% elongation [MPa]
MALDI–TOFMS	Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry
MBT	2-mercaptobenzothiazole
MBTS	2,2’-bisbenzothiazole disulphide
M_C	Molecular weight between constrains [g/mol]
MCV	Model compound vulcanisation
MgO	Magnesium oxide
$Mg(NO_3)_2{\cdot}6H_2O$	Magnesium nitrate hexahydrate
M_H	Maxtimum torque [dN·m]
M_L	Minimum torque [dN·m]
MMO	Mixed metal oxide
$M_{(t)}$	Magnetization at time *t* in relaxation time spectroscopy
M_0	Magnetization at the thermal equilibrium state in relaxation time spectroscopy
MQ	Multiple Quantum
MS	Mass spectroscopy
NBR	Acrylonitrile-butadiene rubber
NiO	Nickel oxide
NMR	Nuclear magnetic resonance
NR	Natural rubber
NRPRA	Natural Rubber Producers' Research Association
P	Equilibrium pressure of adsorbates at the temperature of adsorption [Pa]
P_o	Saturation pressure of adsorbates at the temperature of adsorption [Pa]
PAA	Poly (acrylic acid)
PbO	Lead oxide
PEG	Polyethylene glycol
phr	Parts per hundred rubber
PPG	Polypropylene glycol

ϕ_r	Polymeric volume fraction at equilibrium degree of swelling [-]
q	Residual fraction of the non-to-zero averaged dipolar magnetic interaction of the interacting protons in relaxation time spectroscopy
ρ	Density [g/cm^3]
rf	Radio frecuency
RT	Reversion time [min]
S_b	Dynamic order parameter of the polymer backbone
S_{BET}	Brunauer-Emmett-Teller (BET) specific surface area [m^2/g]
SBR	Styrene-butadiene rubber
SEM–EDS	Scanning electron microscopy-energy dispersive spectroscopy
σ_G	Standard deviation of Gaussian distribution
TOF–SIMS	Time-of-flight secondary ion mass spectrometry
T_1	Longitudinal relaxation time or spin-lattice relaxation time [ms]
T_2	Transverse relaxation time or spin-spin relaxation time [ms]
t_{02}	Time to reach 2 % of maximum torque [min]
t_{s2}	Time to 2 dN·m rise above the minimum torque [min]
t_{90}	Time to achieve 90 % of maximum torque [min]
t_{97}	Time to achieve 97 % of maximum torque. [min]
TBBS	N-t-butylbenzothiazole-2-sulphenamide
TC	Tyre crumb
T_d	Decomposition temperature [°C]
τ_{DQ}	DQ evolution time [ms]
T_g	Glass transition temperature [°C]
TGA	Thermogravimetric analysis
TLC	Thin layer chromatography
TME	2,3-dimethyl-2-butene
TMTD	Tetramethylthiuram disulphide
TS	Tensile strength [MPa]
ν	Cross-link density [mol/g]
ν'	Cross-link density [mol/cm^3]

V_S	Molar volume of solvent [cm^3/mol]
χ	Flory-Huggins interaction parameter [-]
XRD	X-ray diffraction
ZMBT	Zinc benzothiazolyl mercaptide
ZDMC	Zinc dimethyldithiocarbamate
$Zn(NO_3)_2 \cdot 6H_2O$	Zinc nitrate hexahydrate
ZnO	Zinc oxide

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Chapter 1

SULPHUR VULCANISATION AND ENVIRONMENTAL CONCERNS: AN INTRODUCTION

> *'Perhaps nowhere in chemistry is there encountered a field which even in its literature alone shows so many uncertainties and (possibly only apparent) contradictions as that of the vulcanization of rubber.'*
> *Walter Scheele[1] (1906 - 1978)*

> *'Whilst it has long been appreciated, albeit intuitively, that sulfur vulcanization is a very complex chemical process, the actual complexity… is probably far in excess of what has ever been envisaged.'*
> *Leslie Clifford Bateman[2] (1915 - 2005)*

This chapter introduces the general outline of the topic of this thesis and provides some insights in the reasons to perform this research. The first part of the chapter focuses on the history of rubber vulcanisation and the environmental impact of rubber goods, principally of tyres. In the second part, the aims of this thesis are proposed and discussed.

1.1. HISTORICAL REVIEW

Vulcanisation is a specific curing process for rubber. It increases the retractile force and reduces the amount of permanent deformation after the removal of the deforming force[3], i.e. the vulcanisation process changes rubber from a plastic material to an elastic or hard material, it increases elasticity while decreases plasticity, greatly improves rubber strength and eliminates its deficiencies at temperature extremes. It is generally accomplished by the formation of a cross-linked molecular network with sulphur bridges, where a cross-link may be a sulphur atom or a short chain of sulphur atoms (Figure 1.1).

Vulcanisation describes not only the chemical cross-linking reaction but the overall process. Curing, vulcanisation and cross-linking are to a certain extend synonymous and are used interchangeably in this thesis.

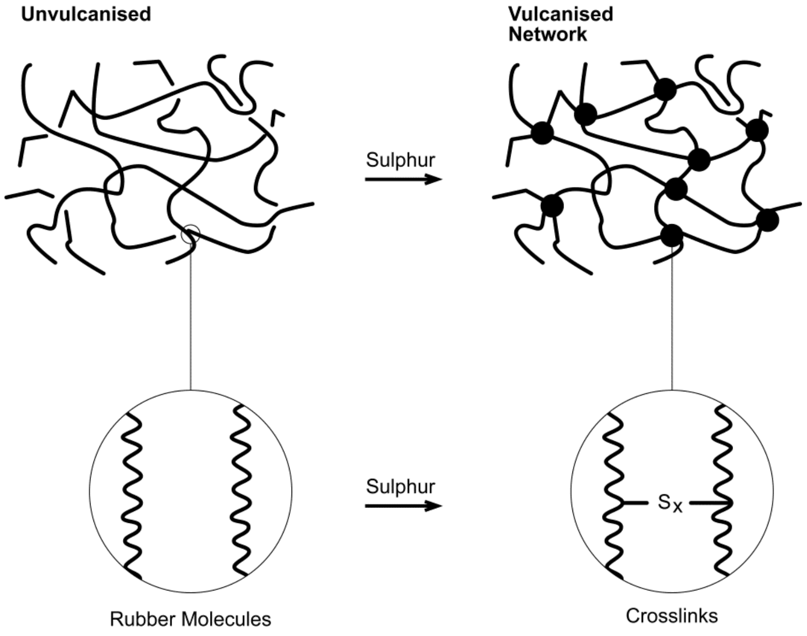

Figure 1.1. Vulcanisation process

The vulcanisation involves three stages: induction or scorch time, curing or cross-linking stage, and the post-cure region, where the modulus can increase, decrease or remain constant depending on the specific vulcanisation system and temperature (Figure 1.2). The induction period represents the time where no measurable cross-linking has occurred. Its duration determines the safety of the rubber against premature vulcanisation which reduces the plastic properties of the compound, becoming more difficult to process. There must be sufficient delay or scorch resistance to permit mixing, shaping, forming, and flowing in the mould before vulcanisation[3]. This induction period is defined by the processing and the additives used. During the scorch time a great variety of chemical reaction takes place, although no cross-links are formed.

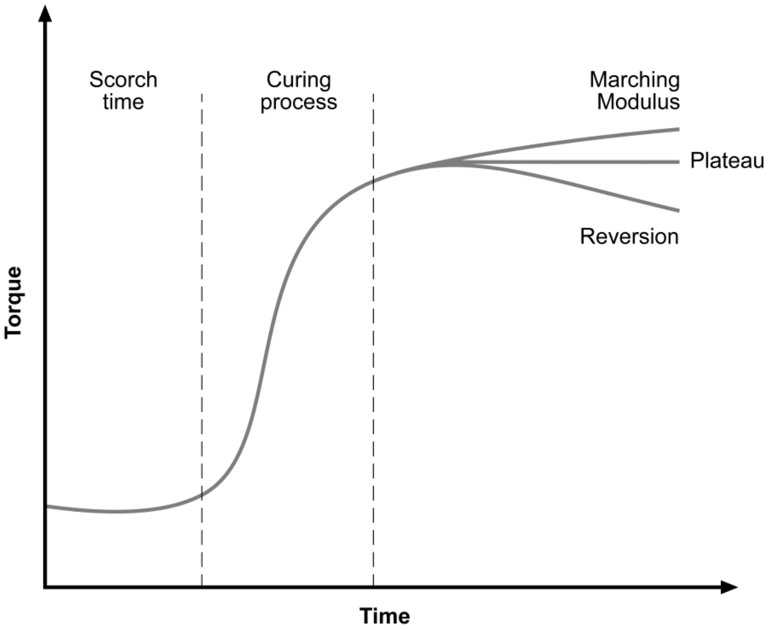

Figure 1.2. Different steps of the vulcanisation curve.

Following the induction period, the curing or cross-linking stage proceeds. The rate of cure, which is dependent on the temperature and the composition of the rubber compound, is the rate at which cross-linking and the development of the stiffness (modulus) of the compound occur. The material changes from a soft plastic to a tough elastic material. As vulcanisation progresses, the various properties developed by vulcanisation are not optimised simultaneously. The state of cure is a measure of the development of these properties. The cure time should be, therefore, the one that allows to reach a state of cure where the desired balance of properties has been attained[4].

When cross-linking proceeds to full cure, continued heating produces an overcure. For most elastomers it results either in a further stiffening of the compound, a long plateau or in a reversion, where there is a decrease of cross-links which lowers the mechanical properties.

The history of rubber commences with Christopher Columbus, who is thought to have been the first white man to become acquainted with rubber. It is related that on the occasion of his second voyage to America, 1493–96, he witnessed a game played by the inhabitants of Haiti using balls prepared from the gum of a tree. This story is open to question since there is no rubber–producing tree or shrub indigenous to Haiti. It is certain, however, that Spanish explorers found rubber in tropical Mexico about 1521. They saw it being used by the natives in various ways in the activities of their primitive lives[5].

Since Charles Goodyear and Thomas Hancock, in USA and England respectively, started to combine sulphur with rubber and using heat in the nineteenth century[6-8], there have been enormous progresses toward the improvement of the vulcanisation process. Sulphur alone was used as the vulcanising agent up to the discovery of organic accelerators at the beginning of the 20th century. It was quickly realised that the use of accelerators gave improved properties and significantly reduced the required cure times[9]. Acceleration was first discovered by adding aniline to the system which significantly decreased vulcanisation times. Dialkyl amines were also found to provide acceleration. Aniline led to guanidines, thiazoles, and sulphenamides, and the amines led to thiurams and dithiocarbamates[4].

By World War II the developments in organic chemistry provided an insight into the properties of natural rubber (NR) which led to chloroprene (CR), styrene–butadiene rubber (SBR), butadiene rubber (BR), acrylonitrile–butadiene rubber (NBR) and butyl rubber (IIR).

Parallel to the development of accelerators runs the discovery of activators. In the early 1920s it was found that metal oxides, combined with fatty acids, also reduce the vulcanisation time and improve rubber properties. The most common combination is ZnO and stearic acid, with the fatty acid solubilising the zinc in the elastomer. Although metal activated vulcanisation proceed faster than sulphur alone, it is not used to activate the sulphur itself but to activate the vulcanisation accelerators.

Zinc oxide, when used as activator for sulphur vulcanisation, improves the cross-link efficiency and the vulcanisate properties such as the abrasion resistance. It also induces the initial scorch reactions to proceed faster although the crosslinking reactions proceed slower[10]. It has a marked effect on the chemical pathways which leads to a network with a greater proportion of mono- and di-sulphidic cross-links and to reduced reversion[11].

In 2011 the global annual rubber consumption was 25.8 million tons as reported by the International Rubber Study Group[12]. Most of the rubber is used in the tyre industry, which also remains the largest single market for ZnO. According to the International Zinc Association[13] the tyre companies consume more than half of the total worldwide demand of 1,200,000 metric tons. A typical tyre contains around 100 g of ZnO[14]. Despite its superior characteristics there is an increased concern about its environmental effects.

ZnO has been classified by the European Union in the Commission Directive 2004/73/EC as “Dangerous for the environment” and “Very toxic to aquatic organisms, may cause long term adverse effects in the aquatic environment”. Release of zinc into the environment from rubber occurs during production, disposal and recycling of rubber products, for instance through leaching in land-fill sites[15]. Small quantities of zinc enter the environment 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 tyres, the run off from galvanized structures or roofing, and rubber granulates produced from end-of-life tyres used in the construction of artificial sports pitches may enter the environment[16, 17]. 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.

For all these reasons, it is desirable to keep the ZnO content in rubber compounds as low as possible, not only for environment but also for economic reasons, and several research studies have been carried out in order to reduce the ZnO levels in rubber compounds or substitute it.

Between all the alternatives proposed to reduce the ZnO levels, the use of nano-sized ZnO particles with high surface area seems to be promising. It has been found that the cross-link density could be increased compared with standard ZnO[18] and that the mechanical properties can be enhanced when ZnO nanoparticles were used[19]. It has been also obtained that small quantities of nano-sized ZnO have similar curing and mechanical properties as higher dosage of conventional ZnO[20]. Still, its major disadvantage is that nano-sized ZnO tends to agglomerate in rubber compounds[17]. However, it has also been reported[21, 22] that the same reductions could be also applied with standard zinc oxide.

Another approach to reduce the ZnO levels which has been studied by several authors[15, 23-25] is the use of alternative metal oxides. Several metal oxides have been investigated: CaO, MgO, CdO, CuO, PbO and NiO. Among them MgO, when is used, dissociates the accelerator very rapidly and a large amount of intermediate compounds that are active sulphurating species are formed. However, the main drawback of MgO is the low reticulation degree achieved[23, 26].

One of the most important environmental related problems in the rubber industry is the management of end of life and waste rubber, especially tyres. The environmental impact of waste tyres, together with the economic problems related with the management and disposal, has led to a great variety of studies to develop technologies to re-use and recycle waste tyres.

When tyres are taken off vehicles, in some cases they can be retreated allowing the tyre to start its new life cycle, but mainly the end of life tyre is non-reusable in its original form. Due to the chemical cross-linking, it is not possible to simply melt and reshape rubber materials, as can be done with thermoplastics. The most important applications of recycled tyre are as tyre-derived fuel[27], as rubberized asphalt concrete[28-30], for playgrounds and tracks surfaces[31] or for civil engineering applications such as noise and vibration damping on railway projects[32].

In 2009 usage rate of scrap tyre, the ratio between the scrap tyre generation and utilisation, in the U.S. was close to 85 %[33]. Although, the percentage has been growing since the 1990's[34], it was attributed to expanded markets for tyre-derived fuel.

Another application of main importance is the use of reclaimed or regenerated rubber in blends with virgin rubber. Diverse research studies have investigated the effect of adding ground rubber on the fresh rubber compounds[35, 36]. The most common methods to obtain the desulphurisation of vulcanised rubber are thermal process, thermomechanical process, mechanochemical process and chemical process[31].

When reclaimed rubber is mixed with virgin rubber, the properties of the final product depend strongly on the treatments that have been applied to the reclaim rubber i.e., the grinding procedure and the de-vulcanising system. It has been shown that the mixtures of reclaim and virgin rubber cure faster and show less reversion[37]. However, the physical properties are frequently deteriorated[37-39], particularly with increasing amounts of reclaimed powder.

1.2. AIM AND STRUCTURE OF THIS THESIS

As stated before, the reduction of the ZnO level in rubber compounds has become a major concern due to the harmful effect of soluble zinc compounds to aquatic organisms. Mainly two approaches have been studied to overcome this problem: the use of active ZnO having nano-metre sized and high surface area or the use of alternative metal oxides. However none of them has been able to fulfil the performance requirements to the extent of substituting ZnO.

For that reason, there is still a need to provide alternative activators for sulphur vulcanisation which reduce the ZnO levels and which could overcome at least some of the drawbacks of the other alternatives above mentioned. Therefore, the aim of this thesis is to provide new activators for sulphur vulcanisation which could lead to a reduction of the potential harmful environmental impact caused by rubber compounds.

In order to gain benefit from the two different approaches indicated before: the use of nano-ZnO and to take advantage of the behaviour of both ZnO and MgO in sulphur vulcanisation; mixed metal oxide nanoparticles of zinc and other metals will be synthesised and tested as activators.

In addition, it has been reported[40-42] that in blends of reclaimed or regenerated rubber with virgin rubber, sulphur and accelerator fragments migrate from the rubber matrix to the particles and vice versa. In this work, this exchange between the crumb and the matrix will be considered as an advantage in order to investigate the possibility of using tyre crumb as an activator and, therefore, reduce the zinc levels employed in the rubber compounds and introducing new applications for the waste rubber from end of life tyres.

Thus, the objectives of this thesis are:

- The study of the differences in the mechanism caused by the substitution of zinc oxide by magnesium oxide.
- The synthesis of novel activators which could reduce the zinc content in rubber compounds.
- The study of the influence of these novel activators on the vulcanisation of different rubbers.
- The evaluation of the use of tyre crumb as activator to reduce the zinc levels and moderate the environmental impact of end of life and waste rubber.

Therefore, the thesis is divided into 7 chapters, as outlined:

Chapter 2 of this thesis gives an overview about the vulcanisation of rubber. Special emphasis is given on the mechanism and particularly the role of the activator since this component of the recipe has been chosen to study different approaches to minimise the environmental effect of the rubber industry. Firstly, a summary of the mechanism occurring during the unaccelerated sulphur vulcanisation is presented. A detailed description for accelerators and the influence of the activator is discussed in following sections. Additionally, the experimental methods employed in this work are reviewed. The Model Compound Vulcanisation (MCV) approach is revised together with some of the different techniques used to study and characterise the rubber compounds.

In *Chapter 3* the role of MgO on the mechanism of accelerated sulphur vulcanisation is studied by MCV to gain a better understanding of the differences shown by this activator. Different recipes with squalene and squalane as model molecules, with and without sulphur, are vulcanised and analysed to investigate the influence of MgO in the different stages of vulcanisation.

In *Chapter 4*, all knowledge gained about ZnO and MgO as activators in the previous chapters is applied to develop a new activator for sulphur vulcanisation. A mixed metal oxide of zinc and magnesium is synthesised and characterised by different techniques. The model compound vulcanisation approach with squalene as a model molecule is employed to study the role of the mixed metal oxide along the reaction and explore the possibility of reducing the zinc content in rubber goods.

Another activator is developed in *Chapter 5*, a mixed metal oxide of zinc and calcium. These novel activators are tested in natural rubber, cis-butadiene rubber and solution styrene-butadiene rubber. Different mixtures with varying activator content are prepared and analysed employing classic and cutting edge techniques.

In *Chapter 6* a new approach to reduce the environmental effects of end of life and waste rubber and, at the same time, to minimise the ZnO levels in rubber compounds is presented. The use of tyre crumb as activator for sulphur vulcanisation is investigated. To give an insight into the reaction mechanism, the approach is firstly tested using MCV. Following, different tyre crumbs are mixed in natural rubber, cis-butadiene rubber and solution styrene-butadiene rubber without activator to study the cure characteristics and the mechanical properties of the compounds.

Chapter 7 shows a general summary and the final remarks. The final conclusions are given in *Chapter 8*.

Parts of this thesis have been published[43, 44] and others still have to be submitted for publication.

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Chapter 2

SULPHUR VULCANISATION OF RUBBER: BACKGROUND REMARKS AND EXPERIMENTAL METHODS

'Anyone who stops learning is old, whether at twenty or eighty.'
Henry Ford (1863 –1947)

This chapter provides an introduction about the vulcanisation of rubber. Special emphasis is given on the mechanism and particularly the role of the activator since this component of the recipe has been chosen to study different approaches to minimise the environmental effect of the rubber industry. Firstly, a summary of the mechanism occurring during the unaccelerated sulphur vulcanisation is given. A detailed description for accelerators and the influence of the activator is discussed in following sections. Additionally, the experimental methods employed in this work are reviewed. The Model Compound Vulcanisation (MCV) approach is reviewed together with some of the different techniques used to study and characterise the rubber compounds.

2.1. RUBBER VULCANISATION

Vulcanisation (or curing) is a process designed to reduce the effects of heat, cold, or solvents on the properties of a rubber compound and to create useful mechanical properties[1]. It involves the conversion of a raw rubber into a network due to the formation of cross-links, chemical bonds or bridges. Cross-linking can be achieved by several methods, chemical and physical. It is most often accomplished by heating with vulcanizing agents such as elemental sulphur, organic peroxides, organic resins, metal oxides, or urethanes[1]. This process converts a viscous entanglement of long chain molecules into a three dimensional elastic network by the insertion of cross-links, as shown in Figure 1.1.

The vulcanisation system is the collection of additives required to vulcanise an elastomer. Table 2.1 shows a typical compound formulation in the rubber industry for most unsaturated elastomers. In the rubber industry, all ingredients are given in amounts based on a total of 100 parts per hundred rubber (phr) or combination of rubbers; consequently the effects of varying any ingredient are easily distinguished.

Table 2.1. Typical compound formulation in the rubber industry[2-4].

Basic recipe	
Material	**phr**
Elastomer	100
Sulphur	0.5 – 4
Zinc oxide	2 – 10
Stearic acid	1 – 4
Accelerators	0.5 – 10
Antioxidant	0 – 4
Filler	0 – 150
Plasticizer	0 – 150
Miscellaneous	

In general, the materials used in the rubber industry can be classified as follows[1, 4-6]:

- Elastomers: The basic component of all rubber compounds. It may be in the form of rubber alone, "masterbatches" of rubber-oil, rubber-carbon black, or rubber-oil-carbon black, reclaimed rubber, or thermoplastic elastomers.

- Processing Aids: Materials used to modify rubber during the mixing or processing steps, to aid in a specific manner during extrusion, calendaring or moulding operations. Examples include petroleum oils, various ester plasticizers, and various soaps.

- Vulcanisation Agents: Sulphur is the most commonly used curing agent for elastomers with chemically unsaturated backbones, particularly the more common diene rubbers. Nevertheless, peroxides find extensive use in the rubber industry as vulcanising agents. Sulphur is available in two forms: amorphous and rhombic. The amorphous form or insoluble sulphur is a metastable high polymer that is insoluble in rubber and most solvents. Rhombic sulphur, a ring of eight sulphur atoms, is soluble in rubber.

- Accelerators: These materials reduce the vulcanisation time by increasing the rate of vulcanisation. In most cases, the physical properties are also improved.

- Activators: These products increase both the rate of cross-linking and cross-link density. These ingredients form chemical complexes with accelerators, and thus aid to obtain the maximum benefits from an acceleration system by increasing vulcanisation rates and improving the final properties. It is usually accomplished by a metal oxide plus fatty acid. The most common combination is zinc oxide and stearic acid, with the fatty acid solubilising the zinc into the elastomer.

- Age-Resistors (Antidegradants): Antioxidants, antiozonants and other materials used to reduce aging processes in vulcanisates. They are used to prevent the properties of the final product from changing during service. Deterioration occurs through reactions with materials that catalyse rubber failure. i.e., oxygen, ozone, light, heat, radiation, and so forth.

- Fillers: These materials are used to reinforce or modify physical properties, impart certain processing properties, or reduce cost. The most common fillers, or reinforcement aids, are carbon black, clays, and silica.

- Miscellaneous Ingredients: Materials that can be used for specific purposes but are not normally required in the majority of rubber compounds can be included in this group. It includes retarders, colours, blowing aids, abrasives, dusting agents, odorants, homogenizing agents, and so forth.

In the production of rubber compounds the first step is the selection of the elastomer, filler, cross-linking agents, and various additives. In order achieve sufficiently high and uniform properties, homogeneous distribution of all additives in the rubber matrix is necessary. The raw compounds need to be processed by mixing, milling, extrusion, or mastication. Then, it can be processed further and moulded by different procedures such as calendering, extrusion, pressing, injection moulding, or coating processes. These lead to the final step of vulcanisation or curing. Once it has been moulded into the desired shape, the compound needs to be vulcanised to obtain the strong and elastic material required for the end use. Processing is generally carried out in internal mixers, less frequently in open mills[4, 6].

For simplifying purposes and since the effect of the rest of the materials employed in the rubber recipe is out of the aim of this work, much of the discussion here will be focused on the accelerators and activators. Special importance is given to the effect of the activator since this component of the recipe has been chosen to study different approaches trying to minimise the environmental effect of the rubber industry.

Firstly, it will be described the mechanism of the unaccelerated sulphur vulcanisation. A detailed description for accelerators and the influence of the activator will be discussed in following sections. Although unaccelerated sulphur vulcanisation is no longer of much commercial impact, it is necessary to study the mechanism in order to understand how accelerators and activators interact and how it influences the chemistry of vulcanisation.

2.1.1. UNACCELERATED SULPHUR VULCANISATION

Although it would be expected a more easily understood behaviour with a system containing only sulphur in the formulation, many reactions have been found that either do not occur or occur to much lesser extents in accelerated systems. These reactions range from double bond migration, isomerization and saturation to chain cleavage, cyclisation and formation of vicinal cross-links[7].

The reaction mechanism of unaccelerated sulphur vulcanisation is controversial. The major debate lies in whether the predominant reaction is radical or ionic, due to rhombic sulphur, eight sulphur atoms ring, can undergo homolytic or heterolytic fission as shown in Figure 2.1.

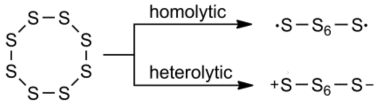


Figure 2.1. Homolytic and heterolytic fission of sulphur ring.

The proposed free-radical mechanism is shown in Figure 2.2 and Figure 2.3. In essence the mechanism predicts that there is a proton extraction by the radical and sulphur addition, which produces the propagating sulphurisation species8 (I). It has been proposed that the sulphenyl radical removes an allylic hydrogen forming a rubber radical which attacks sulphur producing a polysulphenyl radical9 (II). Isomeration and double bound migration of the rubber radical can also occur8 (III).

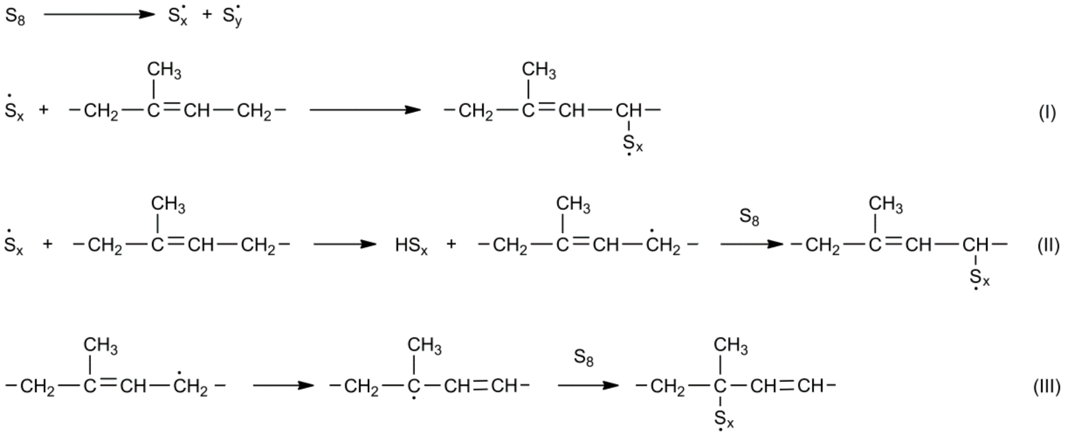


Figure 2.2. Proposed radical mechanism for unaccelerated sulphur vulcanisation. Formation of radicals[5, 7-11].

Then, these radicals abstract hydrogen from a second olefin molecule and the reaction propagates (Figure 2.3).

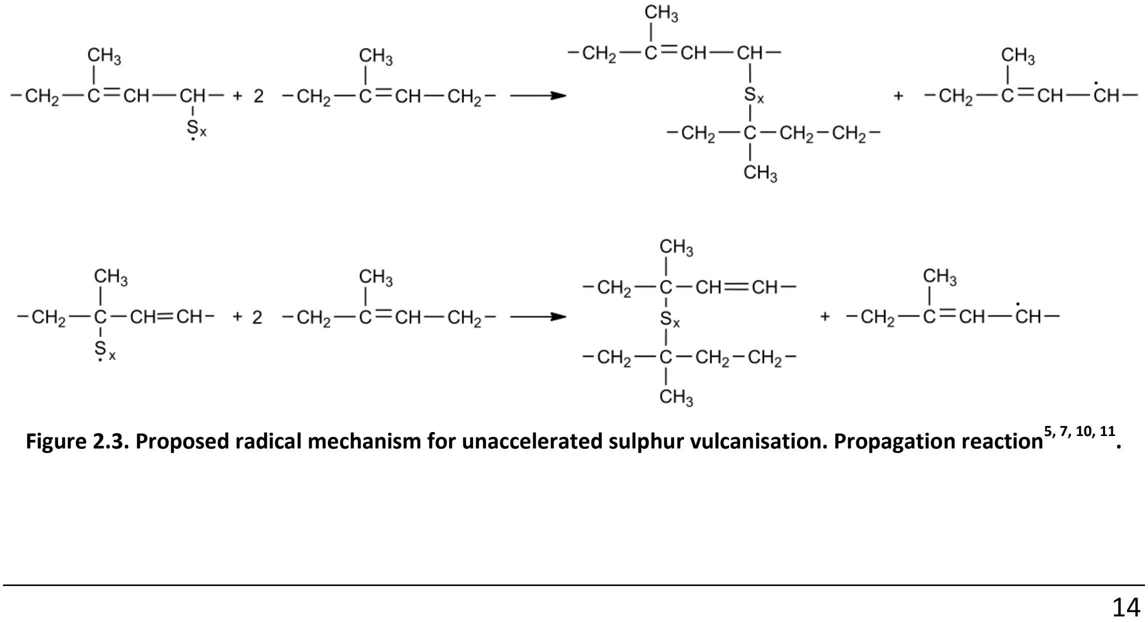
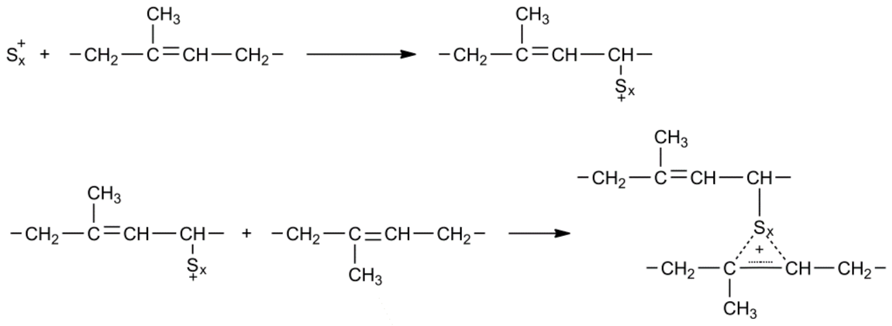


Figure 2.3. Proposed radical mechanism for unaccelerated sulphur vulcanisation. Propagation reaction[5, 7, 10, 11].

Although this free-radical mechanism has been strongly criticised[12], an advantage of this mechanistic scheme is its ability to account for alkenyl-alkyl products and double bond migration, and cis-trans isomerization[7].

As it has been explained, there is no general agreement regarding the nature of the mechanism. The radical mechanism is not the only explanation that has been elucidated by the rubber researchers; the ionic or polar route has also been supported by many. The initiation of the polar mechanism involves the heterolytic scission of sulphur. This heterolysis of the S-S bond in the initially formed polysulphides or in molecular sulphur to yield persulphenium ions which initiate the sulphuration reaction, and persulphenyl anions which act as terminator[13, 14]. The key step is the addition of S_x^+ to the hydrocarbon chain. The reaction can involve proton transfer or hydride transfer, Figure 2.4 *a)* and *b)* respectively.

a) via proton transfer



b) via hydride transfer

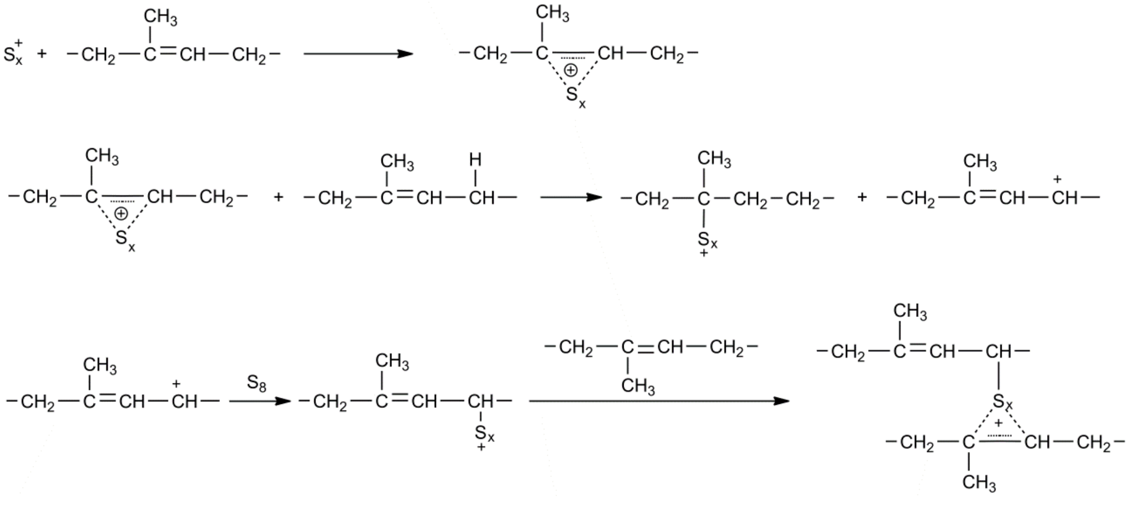


Figure 2.4. Proposed polar mechanism for unaccelerated sulphur vulcanisation[5, 8, 9, 13, 14].

Then, this sulphur-carbon charged ring may undergo a number of different reactions depending on its structure; an example is given in Figure 2.5.

This polar mechanism is able to predict the cyclic structures and conjugated species that are found on the sulphuration of some dienes[7, 9]. Nonetheless, some authors have rejected this mechanism and postulated that the reaction proceeds *via* a free radical chain involving polysulphenyl radicals accompanied by a secondary polar reaction[15].

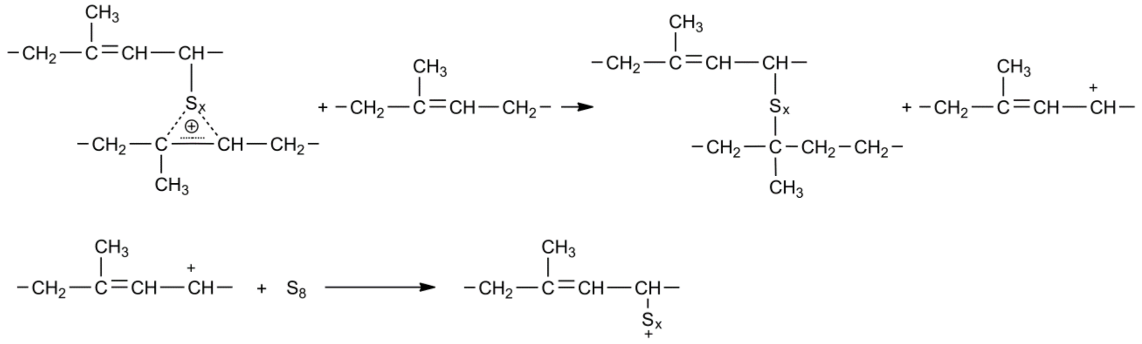


Figure 2.5. Proposed polar mechanism for unaccelerated sulphur vulcanisation. Propagation reaction[5, 8, 9, 13, 14].

Altogether, although the possibility of involvement of sulphenyl radicals cannot be completely eliminated due to the ability of sulphur to undergo radical reactions, it is believed that the mechanism is predominantly polar[8, 9].

2.1.2. ACCELERATED SULPHUR VULCANISATION

Sulphur alone at a concentration of 8 phr was used as the vulcanisation agent until the discovery of organic accelerator. It required 5 hours at 140 °C. The addition of zinc oxide reduced the time to 3 hours and the presence of accelerators, even at 0.5 phr, provoked a further reduction to as short as 1 to 3 minutes[8, 16]. It is very easy to understand why the use of accelerators and activators became essential in the rubber industry.

The discovery of organic accelerators is due to Oenslager who discovered the effect of aniline on sulphur vulcanisation in 1906[17, 18]. Aniline was used until 1907 when thiocarbanilide, its reaction product with carbon disulphide, was introduced due to its toxicity. Aniline led to guanidines. The most important guanidine is diphenylguanidine (DPG) which, although it was very popular, it is used now as secondary accelerator[9].

The dithiocarbamates, which show extremely rapid acceleration properties and exceptionally active cross-linking rate and extent of cross-link formation, came into use in 1919. However, most of the dithiocarbamate accelerators suffer from very short or no scorch resistance and their use is impossible in many factory processing situations[19]. From these accelerators thiuram sulphides were developed. They were the outcome of further experimentation designed to substitute the mercaptan sulphur of dithiocarbamic acid in order to obtain a more satisfactory cure rate. Thiuram sulphides have become very important accelerators[9].

The first delayed-action vulcanisation systems were introduced in 1925 with the use of 2-mercaptobenzothiazole (MBT) and 2,2'-bisbenzothiazole disulphide (MBTS)[16, 19]. Efforts to optimize the scorch delay properties of the MBT type accelerators led to the development, in 1937, of an important new subgroup of accelerators, the sulphenamides.

When the mercaptan sulphur of MBT is substituted by an amine, it produces N-Cyclohexylbenzothiazole-2-sulphenamide (CBS), which results in a retardation of the vulcanisation[9]. These materials, the last new accelerator class of great commercial significance to be introduced, proved to be very valuable and they are probably at present the most widely used accelerators.

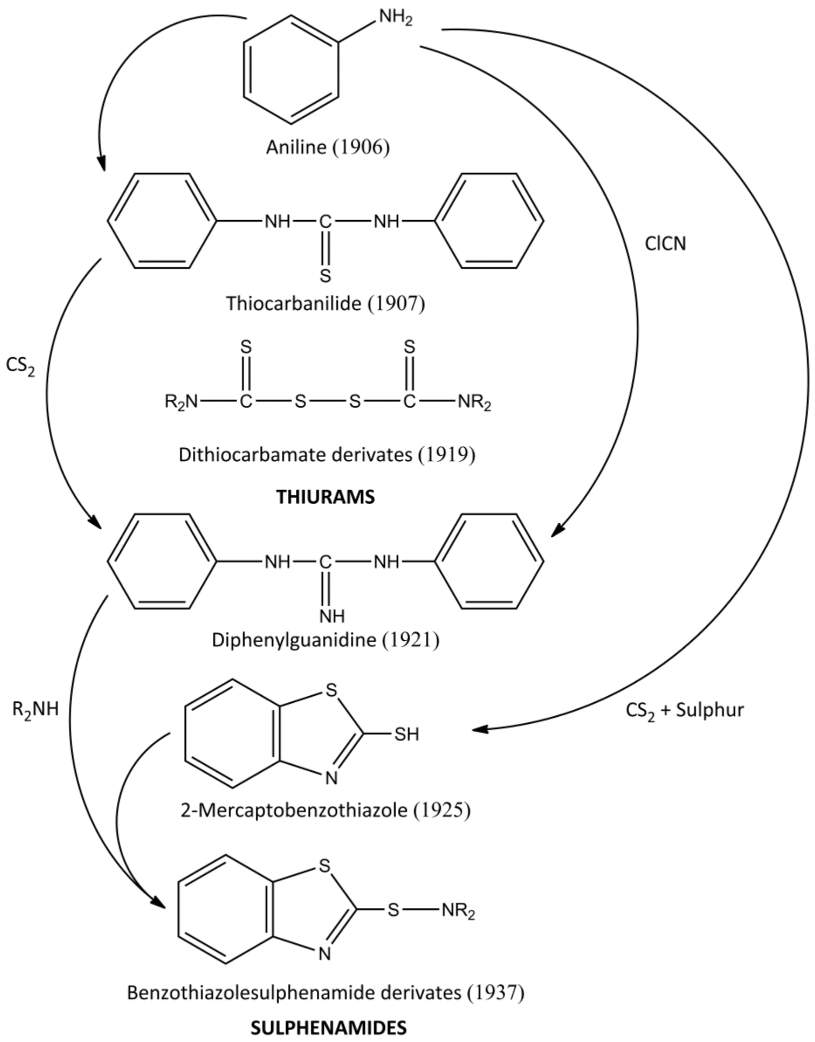
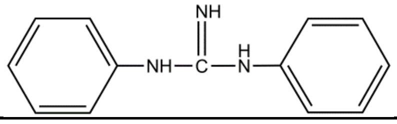
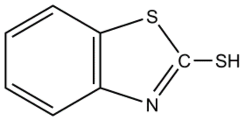
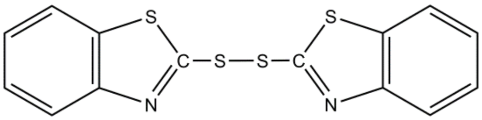
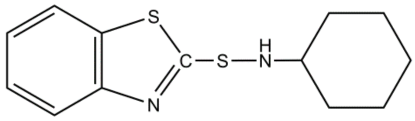
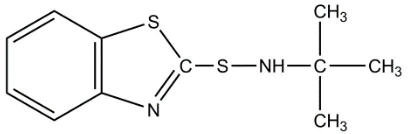
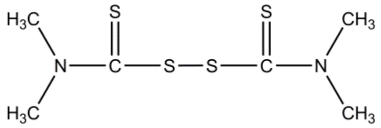
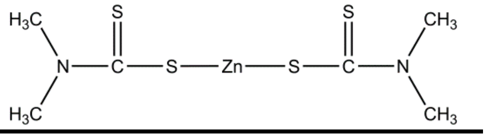


Figure 2.6. History of the chemistry of accelerator synthesis[16].

Delayed action and fast cure characteristics are important in the preparation of large components made of rubber, such as tyres. Large items require a great deal of processing to prepare the final form. Once in the final shape and in the curing press, vulcanisation should commence rapidly to allow for high productivity. The mechanical shaping and forming processes involve mixing, calendering and extrusion operations, each of which produces considerable heating due to the viscous nature of the rubber compound. The delayed action provided by the sulphenamide accelerators allows time for processing before the onset of vulcanisation[20]. Different types of accelerators produce vulcanisation characteristics which differ with respect to both scorch resistance and cross-linking rate. Table 2.2 shows a comparison between the subgroups of accelerators previously described and a list of typical representative accelerators.

Accelerators increase the rate of vulcanisation and allow the lowering of the vulcanisation temperature and the reduction of curing times. Therefore, the rubber is not subjected to drastic conditions during vulcanisation and the possibility of thermal and oxidative degradation is minimized. Furthermore, the sulphur content can be reduced resulting in a lower blooming, improving the appearance, and still retaining optimum physical and aging properties of the vulcanisate. Concerning the final network structure, accelerated sulphur vulcanisation form a higher sulphidic cross-link network (higher cross-link density), spreading homogeneously sulphur in the polymer matrix (better cross-link structure), and forming less main chain modifications[9].

Table 2.2. Common accelerators used in sulphur vulcanisation[4, 8, 9].

Compound	Scorch Safety	Cure Rate	Cross-link Length	Structure
None		very slow	very long	
Guanidines	moderate	moderate	medium-long	
Diphenylguanidine				DPG 
Benzothiazoles	moderate	moderate	medium	
2-Mercaptobenzothiazole				MBT 
2,2'-Dithiobenzothiazole				MBTS 
Sulphenamides	long	fast	short-medium	
N-Cyclohexylbenzothiazole-2-sulphenamide				CBS 
N-t-butylbenzothiazole-2-sulphenamide				TBBS 
Thiurams	short	very fast	short	
Tetramethylthiuram disulphide				TMTD 
Dithiocarbamates	least	very fast	short	
Zinc dimethyldithiocarbamate				ZDMC 

The study of sulphur accelerated vulcanisation has led to several publications which reveal the complexity of its mechanism since it is necessary to understand the interaction of the accelerators and activators and how these interactions influence the pathways of the reactions. Proposed mechanisms varied from radical to ionic, although now it is thought that in a complex mixture of rubber, ZnO, sulphur, fatty acids, and accelerators it is likely that both free radical and polar reactions are occurring simultaneously. The dominant mechanism is determined by a large number of variables such as the type and concentration of the accelerator, the concentration and stability of zinc complexes, etc. Therefore, depending on the vulcanizing system one or the other mechanism will predominate at different stages of the overall vulcanisation reaction[9].

The most widely accepted mechanism for accelerated sulphur vulcanisation is depicted in Figure 2.7, although this scheme changes in every particular case depending on the recipe.

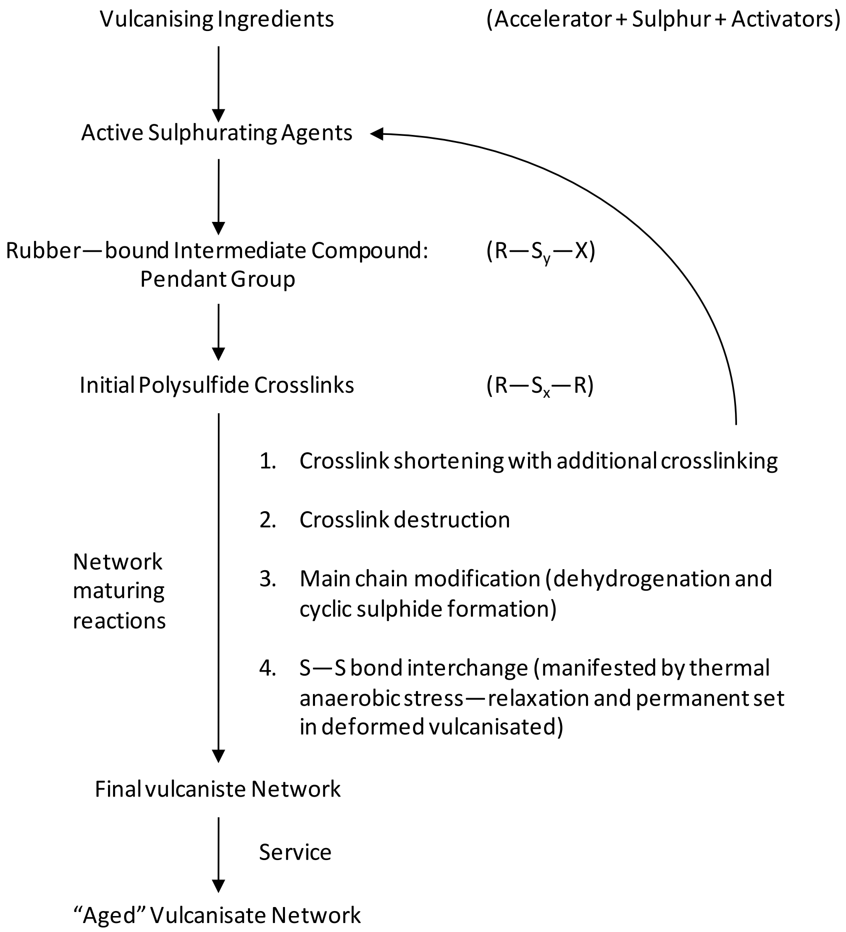


Figure 2.7. Outline reaction scheme for the sulphur vulcanisation of rubbers[21].
(R represents the rubber chain; X is the accelerator residue).

The final network structure of an accelerated sulphur vulcanisate of natural rubber is shown in Figure 2.8. It contains mono-, di- and polysulphidic cross-links, essentially between different polymer molecules, although mono- and disulphidic cyclic structures can also be formed in little amounts; pendant groups and rearranged isolated double bonds and conjugated diene and triene moieties products of dehydrogenation of the rubber may also be present.

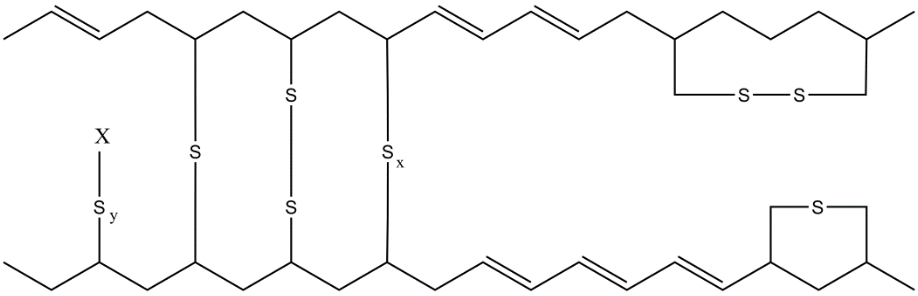


Figure 2.8. Structural features of an accelerated sulphur vulcanisate of natural rubber[21].
(X= accelerator fragment, y≥1, x≥3)

In the next sections the mechanism of vulcanisation with sulphenamides accelerators either with or without the presence of activator, ZnO, is deeply discussed. The chemical pathway of the reaction will be described using N-cyclohexylbenzothiazole-2-sulphenamide (CBS) since this sulphenamide was the molecule employed as accelerator in all the experiments carried out during this thesis.

2.1.2.1 ACCELERATED SULPHUR VULCANISATION IN THE ABSENCE OF AN ACTIVATOR

The first step consists on the reaction of the accelerator with sulphur to give active sulphurating agents, $\mathrm{Ac} - S_x - \mathrm{Ac}$, as shown in Figure 2.9. Initially, CBS decomposes and the $S - N$ bond of the accelerator is cleaved forming 2-mercaptobenzothiazole (MBT) and cyclohexylamine. Then, the reaction between MBT and another molecule of CBS results in the formation of 2,2'-dithiobenzothiazole (MBTS) which reacts with sulphur yielding in the active sulphurating agents.

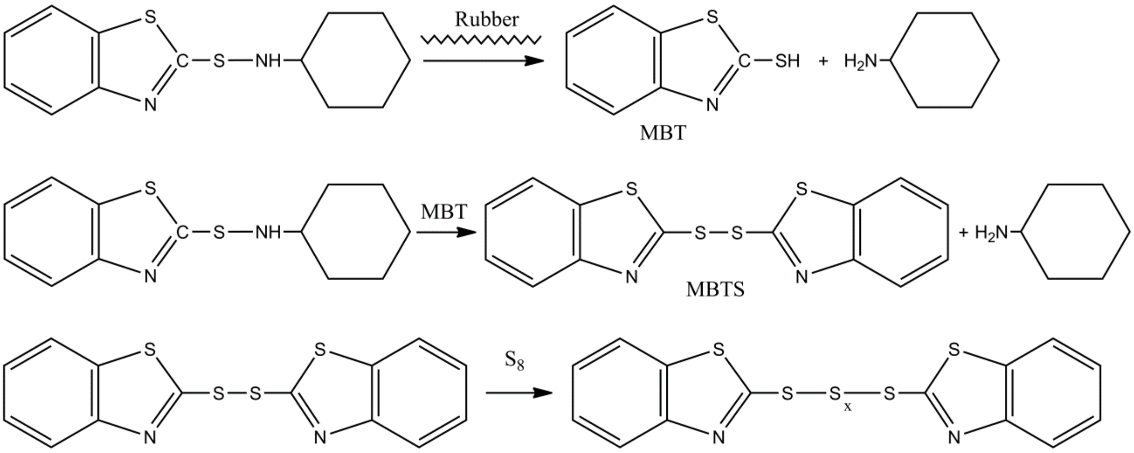


Figure 2.9. Formation of active sulphurating agents via a polar pathway.

It has been evidenced that first free MBT is formed from the direct interaction between the accelerator and the double bonds of the hydrocarbon chain22. Once the MBT is generated, its catalytic effect on CBS dissociation provokes the formation of the active sulphurating agents to be much faster. Following, the active sulphurating agents interact with rubber to form a rubber-bound polysulphidic pendant group, $R - S_x - Ac$.

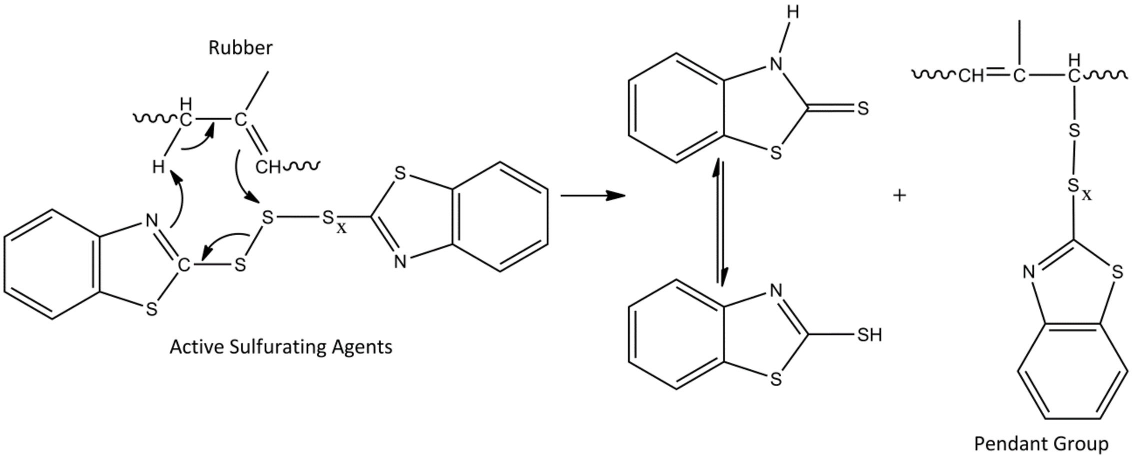


Figure 2.10. Formation of the rubber-bound intermediate via a polar pathway[16].

Finally, the rubber polysulphides react, either directly or through an intermediate, to give cross-links, $R - S_x - R$.

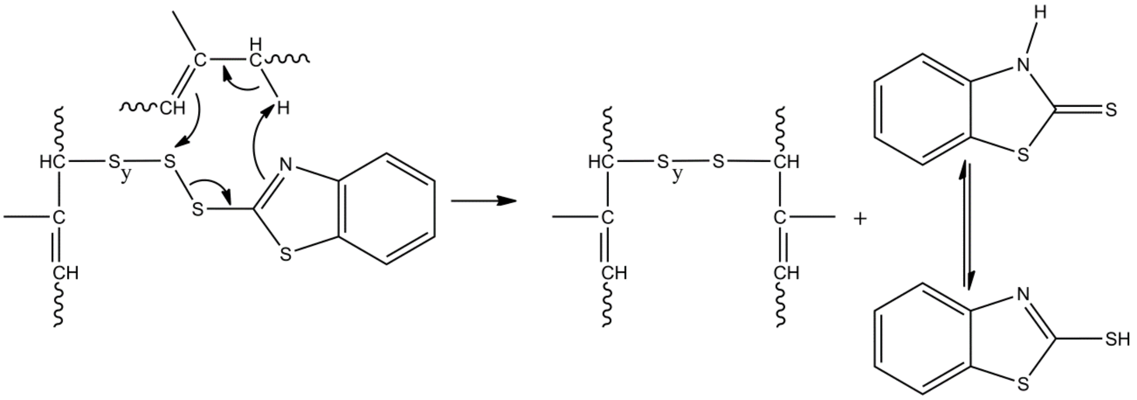


Figure 2.11. Formation of initial polysulphide cross-links via a polar pathway[16].

As stated before, vulcanisation is thought to occur via either a radical or a polar pathway. The radical mechanism for accelerated sulphur vulcanisation without activator follows the scheme presented in Figure 2.7. As in the polar path, first CBS is decomposed by breakage the S–N bond. The mercapto radical formed is stabilised by resonance23.

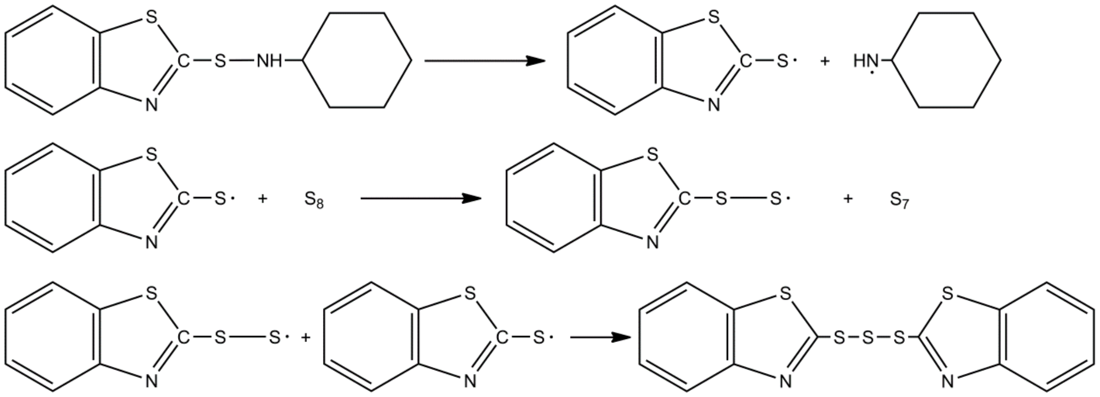


Figure 2.12. Formation of active sulphurating agents via a radical pathway.

From the active sulphurating agents, the rubber-bound polysulphidic pendant groups are formed as indicated in Figure 2.13.

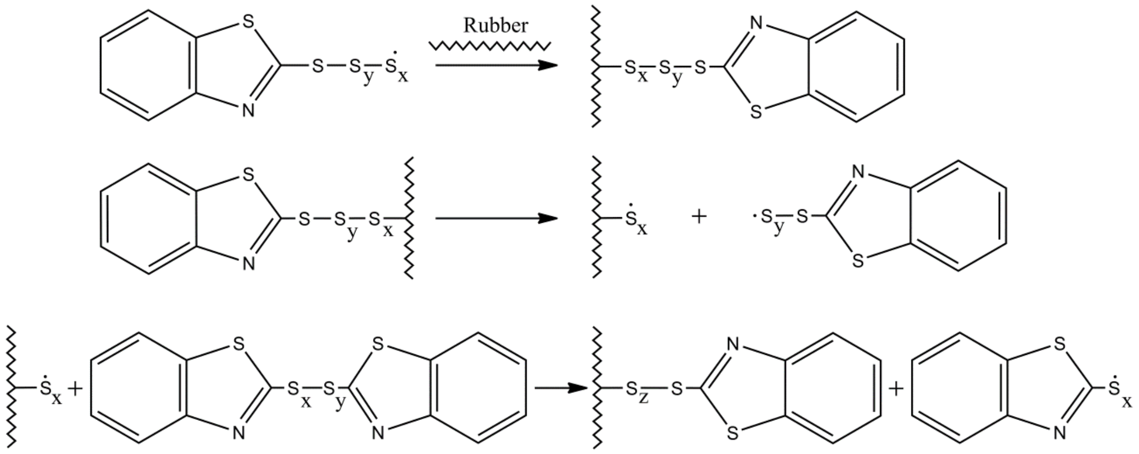


Figure 2.13. Formation of pendant groups via a radical pathway.

Then, these pendant groups yield to the formation of cross-links (Figure 2.14).

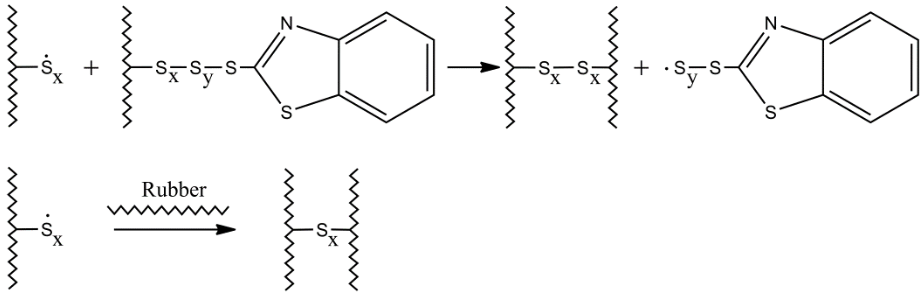


Figure 2.14. Formation of cross-link products via a radical pathway.

Figure 2.15 shows the types of structures that have been assigned to the attachment points of sulphur atoms to the rubber backbone by using solid-state 13C NMR spectroscopy24.

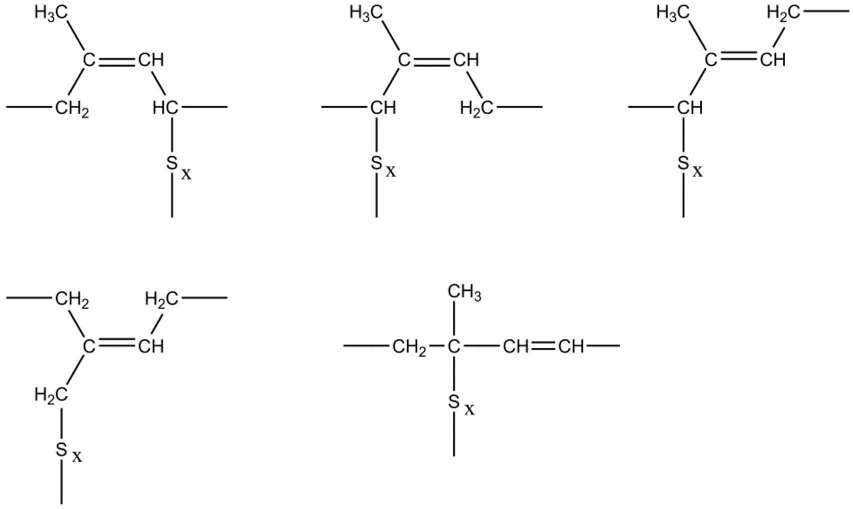


Figure 2.15. Sulphur attachment sites on *cis*-polyisoprene based on NMR measurements[24].

2.1.2.2 INFLUENCE OF ZINC OXIDE ON ACCELERATED SULPHUR VULCANISATION

As it has been stated before, the role of activators were discovered in the 1920s. ZnO was used before in the rubber industry as a reinforcing agent until it was substituted when the advantages of carbon black were known. Zinc oxide started to be added again to rubber compounds when it was found that metal oxides, combined with fatty acids, reduced the vulcanisation time and improved rubber properties, even when no accelerator is present. Although metal activated vulcanisation proceed faster than sulphur alone, it is not used to activate the sulphur itself but to activate the vulcanisation accelerators.

Traditionally, ZnO is used in rubber formulations in concentrations of 3-8 phr. The effect of zinc oxide in the number of cross-links produced in a natural rubber compound is shown in Figure 2.16. It can clearly be seen that ZnO along with stearic acid (compound #2) do not perform very differently from sulphur alone (compound #1). There is a slightly increase in the rheometer torque but they are ineffective to increase considerably the number of cross-links produced. Compound #3, with a sulphenamide accelerator, N-t-butylbenzothiazole-2-sulphenamide (TBBS), produces a significant increase of cross-links. When stearic acid (compound #4) is added to the mixture a further enhancement is achieved although not as large as when zinc oxide is present in the mixture (compound #5). The combination of ZnO and stearic acid with the accelerator (compound #6) yields to the higher rheometer torque, i.e. greatest number of cross-links.

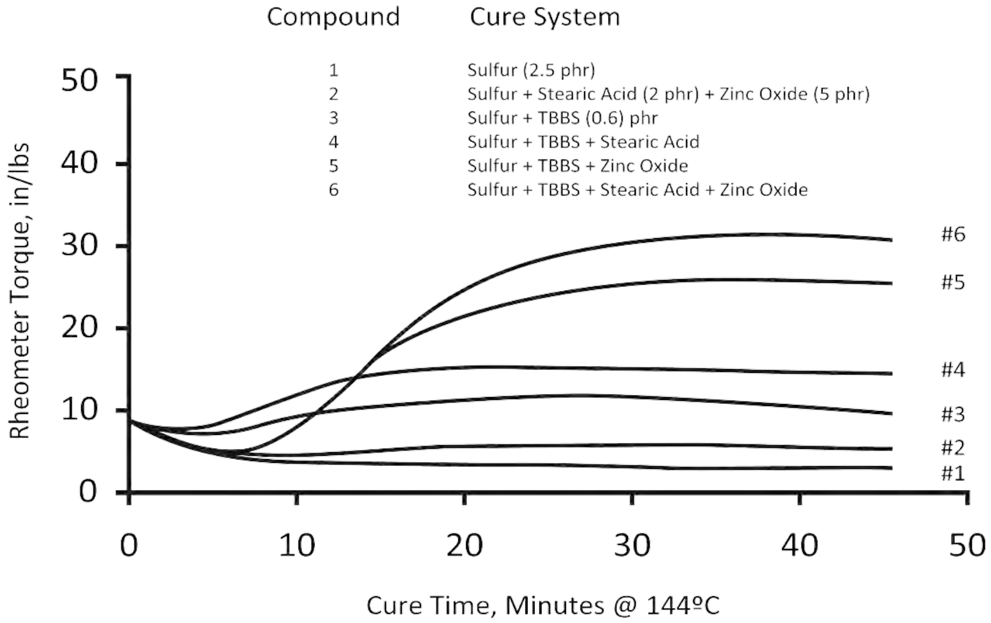


Figure 2.16. Effect of activator on cure rate of natural rubber[1].

The effects of ZnO can be summarised in[23]:

- Increase in vulcanisation rate and cross-link efficiency.
- Processing aid in uncured rubber.
- Improvement of abrasion resistance.

- Improvement of dynamic properties.

From the mechanistic point of view, and as it will be shown, several functions of ZnO in different stages of vulcanisation are as follows:

- The decomposition of sulphenamide accelerators proceed faster.
- The cross-linking reactions proceed with a better control and with a better distribution of sulphur in the polymer network.
- Change in cross-link distribution: the cross-links contain less sulphur atoms, but the number of cross-links is higher (cross-link density).

The overall course of accelerated sulphur vulcanisation in the presence of zinc oxide and stearic acid can be represented by the simplified reaction sequence shown in Figure 2.17. Although, the scheme presented is generally accepted, there is still not general agreement as to the nature of the active sulphurating agent and the mechanism of its reaction with the rubber molecule[21].

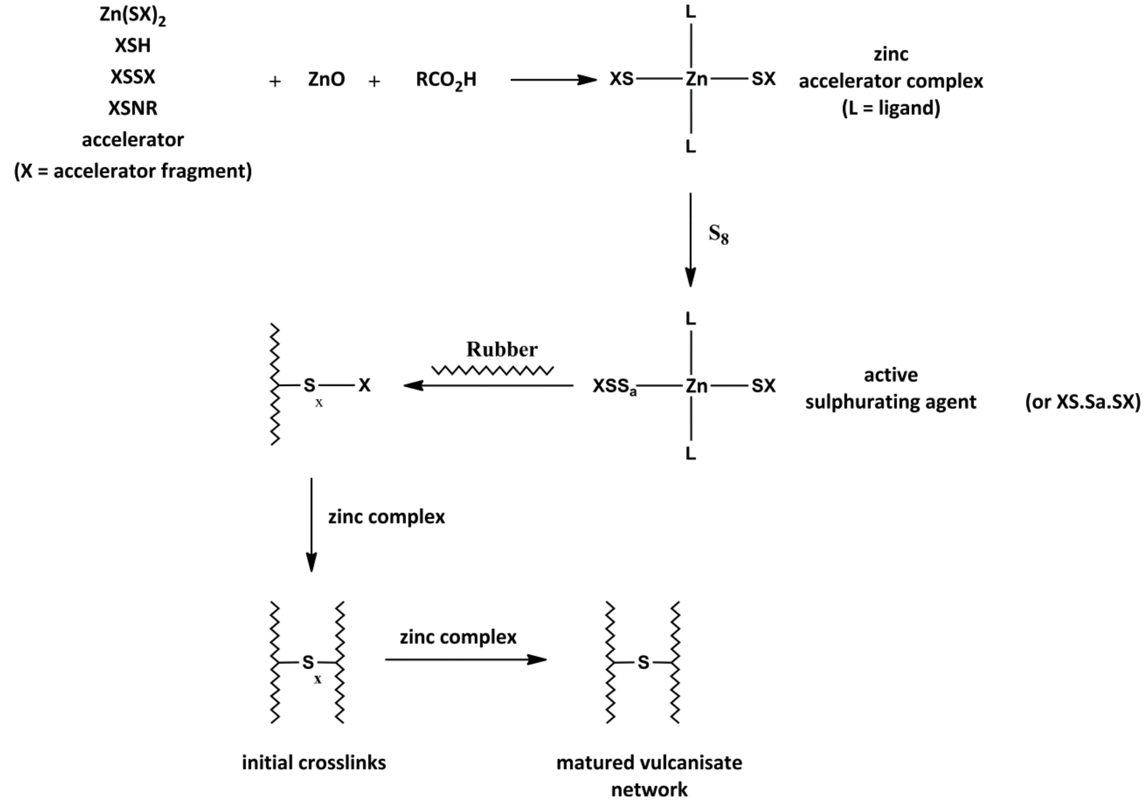


Figure 2.17. Overall course of accelerated sulphur vulcanisation in the presence of zinc oxide and stearic acid[25].

The initial step in vulcanisation using CBS is believed to be the reaction of ZnO with the accelerator to give zinc benzothiazolyl mercaptide (ZMBT), shown in Figure 2.18. The role of amines is thought to be the forming of coordination compounds with ZMBT[21, 26, 27]. These complexes, being more soluble in rubber than ZMBT itself, enhance the nucleophilic reaction of ZMBT with sulphur catalysing the insertion of sulphur to form active sulphurating agents[28].

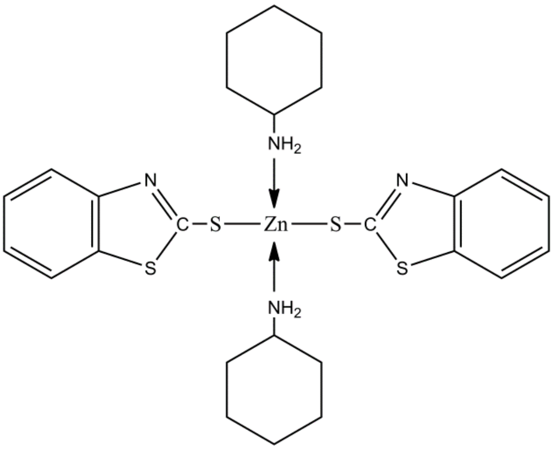


Figure 2.18. Zinc benzothiazolyl mercaptide (ZMBT).

The reaction of the zinc accelerator complex with sulphur to produce the active sulphurating agents is depicted in Figure 2.19. This reaction involves the nucleophilic attack of ZMBT to sulphur[28]. The average value of x in $Ac - S_x - Zn - S_x - Ac$ is controlled by the relative concentration of sulphur and soluble ZMBT[27].

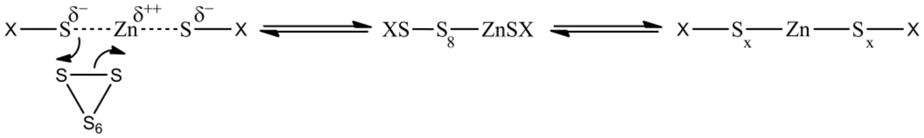


Figure 2.19. Reaction of the zinc accelerator complex with sulphur[27, 28].

Figure 2.18 shows a formalized structure and represents the stoichiometry, but it does not necessarily the actual structure of the complex[21]. Other researchers consider this complex to be as illustrated in Figure 2.20.

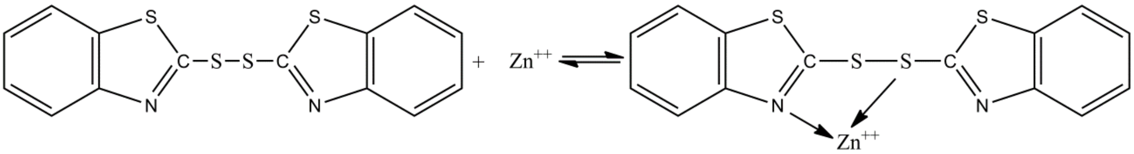


Figure 2.20. Postulated structures of the zinc accelerator complexes[29].

This chelated form of the accelerator is more reactive than the free accelerator. Then, this zinc accelerator complex reacts with the ionised form of sulphur to produce the active sulphurating agents, as shown in the figure below. This ionized form of sulphur could be rapidly formed in a reaction between sulphur and any of a number of initiating species[29].

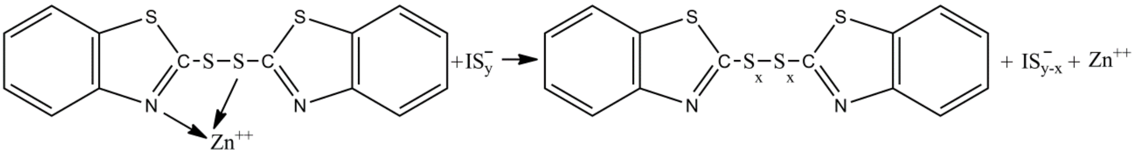


Figure 2.21. Reaction of the zinc accelerator complex with sulphur[29].

Ignatz-Hoover *et al.*[26] have proposed another structure for the active sulphurating agents (Figure 2.22). This structure resembles the complex depicted in Figure 2.18 having a sulphur polythiolate coordinated to the zinc ion producing either a five or six coordinate complex.

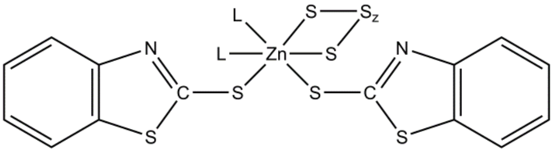


Figure 2.22. Active sulphurating agents proposed by Ignatz-Hoover *et al.*[26]

As stated previously, there is no general agreement about the role of zinc in the formation of the active sulphurating agents. It has been reported[28, 30] that ZMBT-amine complexes effectively catalyse sulphur insertion reactions. However, some authors have advocated that the active sulphurating agent is an accelerator polysulphide, $\mathrm{Ac} - S_x - \mathrm{Ac}$, instead of the zinc complex while others have proposed that both zinc complex and polysulphide may act as the active sulphurating agent, depending on the conditions and the extent of cure[25, 31]. Agulló[32] supported the structures depicted in Figure 2.20 and Figure 2.21. By synthesising and adding the structure shown in Figure 2.18 to a model recipe with squalene it was demonstrated that these complexes do not lead to cross-link formation.

Borrós et al.22 demonstrated that for sulphenamide accelerated vulcanisation, ZnO which is usually described as a catalyst for the breaking down of the accelerator, is necessary but not enough to cause the decomposition of the sulphenamide. These authors proved that small amounts of MBT are required for the formation of the active sulphurating agents and that this compound is formed from the direct interaction between the accelerator and the double bonds of the hydrocarbon.

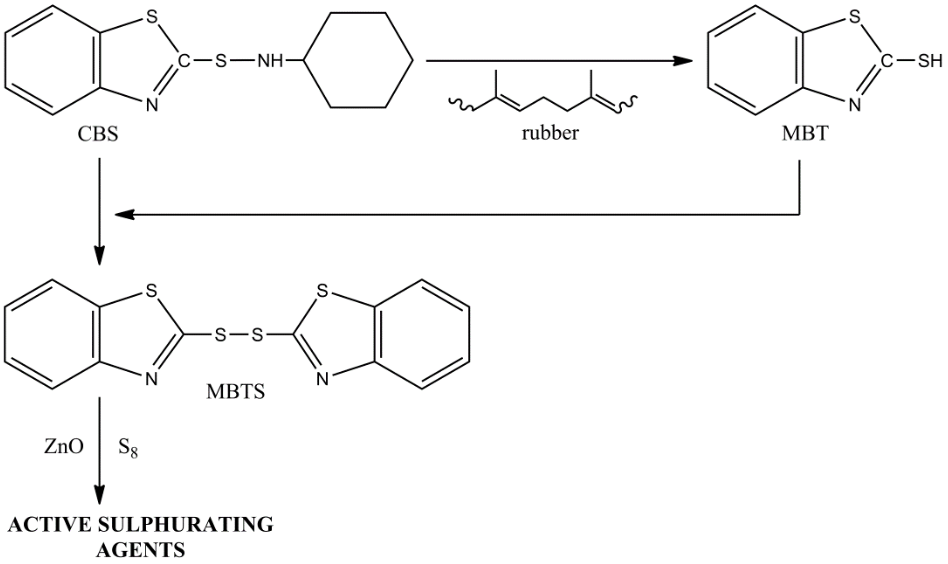


Figure 2.23. Active sulphurating agents' formation mechanism proposed by Borrós et al.[22]

The next step in the vulcanisation process is the formation of the rubber-bound intermediate compound by the reaction of the active sulphurating agents, whether they are $Ac - S_x - Ac$ or $Ac - S_x - Zn - S_x - Ac$ with the rubber hydrocarbon.

The mechanism by which the pendant group is formed from the active sulphurating agents is not known with certainty. Figure 2.24 shows a nucleophilic reaction displacement. This reaction involves the nucleophilic attack of a terminal sulphur atom on an α-methylenic or α-methylic carbon atom with a displacement of hydrogen as an hidryde ion and formation of zinc sulphide[26-28]. Another carbanionic mechanism with an addition-elimination process is illustrated in Figure 2.25.

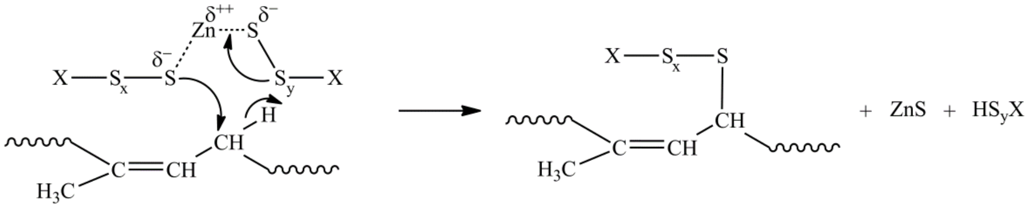


Figure 2.24. Nucleophilic hydride displacement[26-28].

The coordination of electron donating ligands, such as amines, to the zinc atom weakens the $Zn - S$ bond increasing the charge on the terminal sulphur atom making it more nucleophilic. Therefore, substitution at α-methyl groups will then be promoted over α-methylene groups[9].

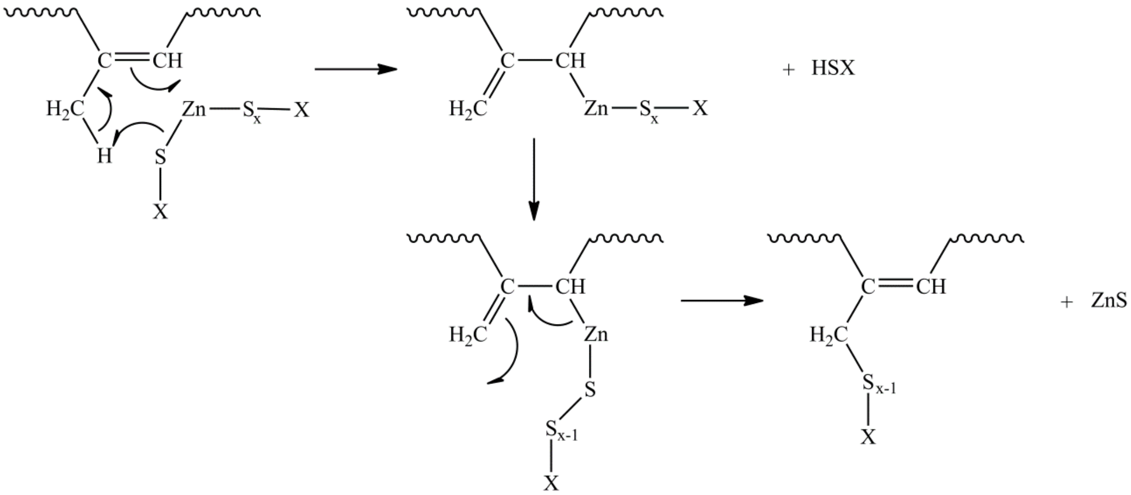


Figure 2.25. Carbanionic intermediate stepwise mechanism[26].

The possibility of homolysis of $Ac - S_x - Zn - S_x - Ac$ to yield persulphenyl radicals which could then react with the rubber to form the rubber-bound intermediate is shown in Figure 2.26. Albeit the mechanism depicted in Figure 2.17 is supported by formidable evidences and is generally accepted, some authors consider that free radicals cannot be ignored in the formation of the rubber-bound intermediate.[9] Other researchers concluded that although the reaction had some radical character the mechanism shown in Figure 2.26 could be ruled as insignificant[26].

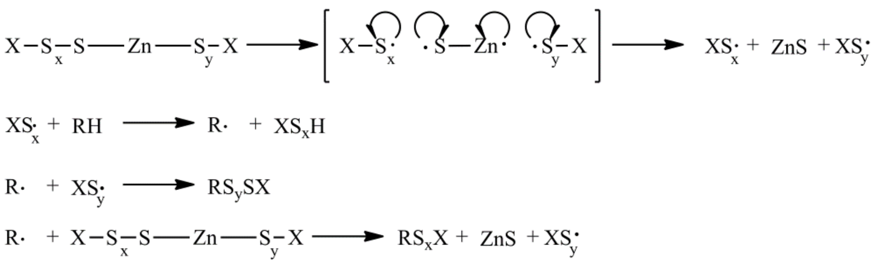


Figure 2.26. Radical intermediate mechanism[26].

In this sense, It has been argued[29] that the reaction yielding to pendant groups is ionic. On the contrary, the formation of initial polysulphide cross-links is not ionic but radical.

Pendant groups are the intermediate precursors to polysulphidic cross-links. Various mechanisms have been proposed for the conversion of cross-link precursors into cross-links. Some authors have suggested a mechanism for the cross-link formation by disproportionation with another pendant group or by the reaction between a precursor molecule and the rubber chain. Although these reactions are basically catalysed by zinc-accelerator complexes, they can also occur in the absence of zinc, albeit at significantly lower reaction rates[23].

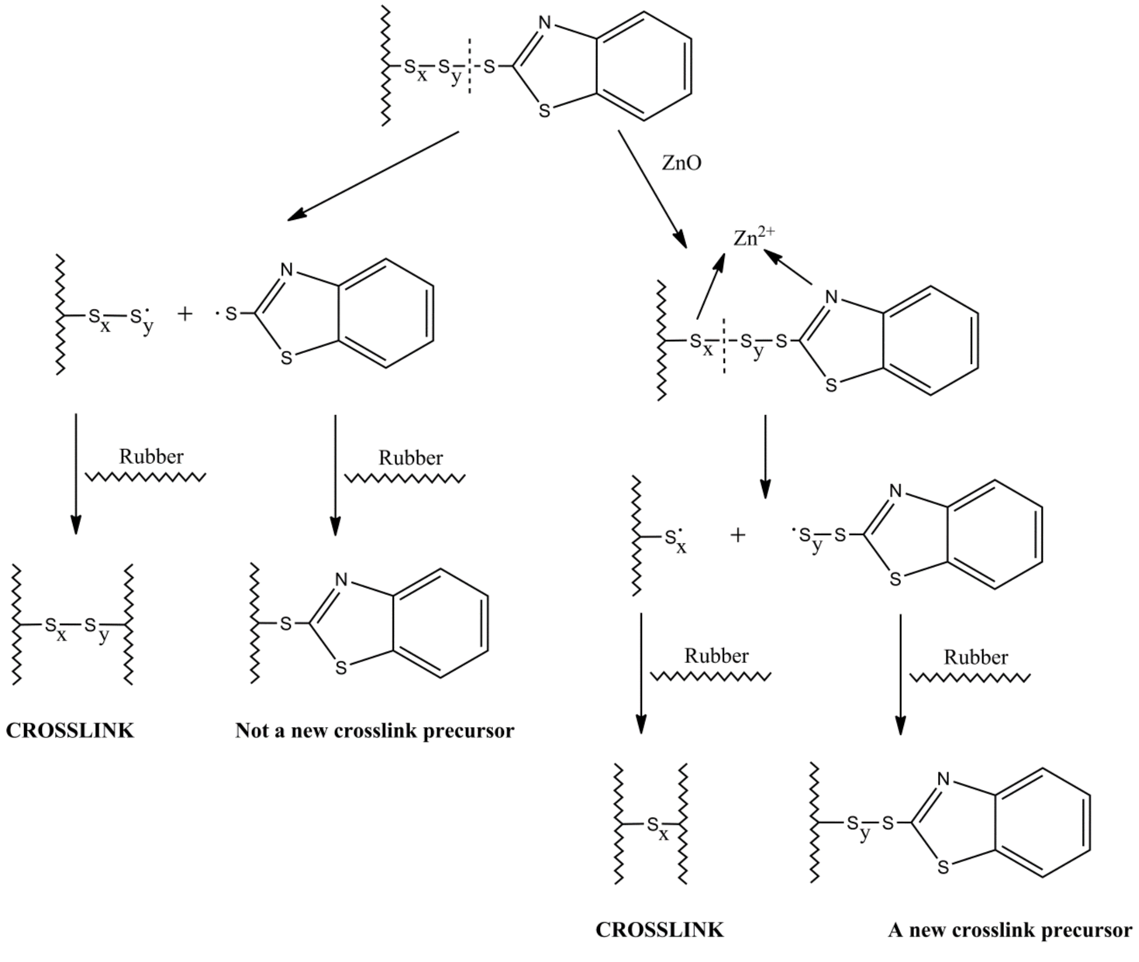


Figure 2.27. Cross-linking mechanism of sulphenamide accelerated vulcanisation[29, 33].

It has been found that the presence of Zn^{2+} in benzothiazole accelerated vulcanisation results in a decreased rate of cross-link formation and an increased extent of cross-linking. This has been attributed to the effect of zinc chelation, which changes the position of the S-S bond most likely to break. The weakest bond is the sulphur-sulphur bond adjacent to the benzothiazole group, but zinc stabilises this bond and the cleavage occurs at a stronger S-S bond closer to the rubber hydrocarbon chain. This leads to the formation of a polythiyl radical which then add to the rubber chain giving a new cross-link precursor. If the bond that breaks is the S-S bond contiguous to the benzothiazole group, most likely to occur when zinc is not present as it could not be stabilised by resonance, a monomeric thiyl radical would be produced and, when added to a rubber backbone, a polymeric monosulphide, and not a new cross-link precursor, would be formed[29, 33] (Figure 2.27).

This brief review of rubber vulcanisation is an indication that the mechanism is very complex and still open to question. Despite all the advances that have been made during the past years, there are still some details that remain unanswered. The complexity of studying the vulcanisation reaction makes it not possible to analyse each step of the reaction under general considerations. Each system, i.e. elastomer-activator-accelerator, presents differences on the reaction pathway that occurs during the vulcanisation of rubber goods. As a summary, the work of Banerjee *et al.*, who studied a large number of systems to elucidate whether the pathway was radical or polar and was collected later by Krejsa and Koenig[7], is presented in Table 2.3. Their approach consisted on the use of highly reactive peroxide radicals to interfere with radical reactions of the accelerator complexes. If the vulcanisation chemistry is ionic, then the radical does not interfere, and no effect is observed upon its addition.

Table 2.3. Proposed mechanism for different vulcanising systems[7].

Mechanism	System
Radical	NR/TMTD NR/TMTD/S NR/CBS/S SBR/MBT/S NR/MBT/S
Mixed Radical/Polar	NR/CBS/S/ZnO/Stearic Acid SBR/DPG/S/ZnO/Stearic Acid NR/MBT/TMTD/S SBR/CBS/S SBR/CBS/S/ZnO/Stearic Acid NR/MBT/DPG/S NR/DPG/S/ZnO/Stearic Acid
Polar	NR/TMTD/S/ZnO/Stearic Acid NR/MBT/TMTD/S/ZnO/Stearic Acid NR/MBT/DPG/S/ZnO/Stearic Acid NR/DPG/S SBR/DPG/S NR/MBT/S/ZnO/Stearic Acid SBR/MBT/S/ZnO/Stearic Acid NR/TMTD/ZnO

2.2. EXPERIMENTAL

The aim of this thesis is to explore new means to design rubber goods with lower environmental effects. Among the different approaches that might be applied to this affair it has been chosen to study how it can be accomplished by revising the activator system. Various substitutes for ZnO have been investigated through this work. Several techniques have been applied to study the vulcanisation process and the characteristics of the compounds vulcanised with the new activators. Model compound vulcanisation has been used to gain a better understanding of the mechanism of the different reactions that take place during vulcanisation and samples of different rubbers (NR, BR and SBR) have been also prepared and characterised using different methods.

In this section, the different procedures used to study and characterise the rubber compounds are reviewed. The specifics of the techniques and sample preparation will be explained on each chapter. Nonetheless, the basics of some methods and common techniques are described.

2.2.1. MODEL COMPOUND VULCANISATION

As it has been shown, although sulphur vulcanisation is a very old industrial process, and considerable research studies of this process have been carried out, there are still a lot of questions that remain unanswered. The variety of chemical reactions taking place simultaneously during vulcanisation together with the fact that by standard analytical and chemical methods it is generally difficult to analyse rubber due to the insolubility of the elastomer and the low concentrations and variety of cross-linked structures, researchers have attempted to simplify their task by using a modelling approach.

Model compound vulcanisation consists on altering the composition of a vulcanisation mixture by introducing a low molecular weight model as a substitute for the elastomer. The vulcanisation process is then simulated by reactions of models with curatives. This approach can cover the whole process depicted in Figure 2.7: the formation of the active sulphurating agents, the precursor formation, the cross-link shortening and the formation of the final network. MCV is widely used because it shows good agreement with real rubber systems and because model compound vulcanisates are relatively easy to analyse.

The first authors that employed MCV where Meyer and Hohenemser[34] who used in 1935 ciclohexene to investigate the mechanism of unaccelerated sulphur vulcanisation. In 1944 Amstrong *et al.*[35] performed a similar study using cyclohexene, 2-methyl-2-butene, 2-methyl-1-butene, 2-butene and 5-methyl-4-nonene as model molecules. In 1947 the Natural Rubber Producers' Research Association (NRPRA) started various research studies using olefinic substances instead of rubber. Their first publications[10, 36] dealt with the use of mono-olefins and di-isoprenes and in 1948 Bloomfield[37, 38] used squalene for the first time. In later reports by the NRPRA group[13, 14, 39-43] different model molecules including 1-octene, cyclohexene, 2-heptene, 2-methyl-2-pentene, and 2,6-dimethyl-2,6-octadiene were studied. In 1956 Scheele *et al.*[44] used geraniol, which has the disadvantage of containing an alcohol group which can lead to side reactions. In the early 1990's Versloot *et al.*[45-48] applied MCV with 2,3-dimethyl-2-butene (TME), a highly symmetric model molecule, to study the vulcanisation mechanism using TMTD as accelerator. In a later paper, these authors[49] compared the MCV results using different models: TME, 1-decene, 2,3-dimethyl- 1-butene, trans-2-hexene and trans-3-hexene.

Figure 2.28 summarises the different model molecules that have employed to investigate the mechanism of sulphur vulcanisation of natural rubber. MCV has been employed to study not only the vulcanisation of natural rubber but as well of EPDM, SBR, BR. For EPDM, the most commonly used model molecule is ethylidene norbornane[50-52]. To simulate SBR, *cis*-1,7-diphenyl-3-heptene and *cis*-1-phenyl-3-heptene have been used and, for BR cyclooctene, *cis*-3-hexene[53], *cis*-3-heptene, *trans*-4-octene and Polyoil 110, which is a butadiene oligormer of about 44 monomer units containing 74 % 1,4-*cis*, 27 % 1,4-*trans* and 1 % 1,2-vinylic structures[54]. To investigate the curing mechanism of the halobutyl rubbers like chloro-isobutylene-isoprene rubber (CIIR) and bromo-isobutylene-isoprene rubber (BIIR), 5-chloro-4-methylene-2,2,8,8-tetramethylnonane and 5-bromo-4-methylene-2,2,8,8-tetramethylnonane[55] and 3-chloro-2-methyl-1-pentene[56] have been employed as model molecules. Figure 2.29 shows some of the model compounds used in MCV of different elastomers.

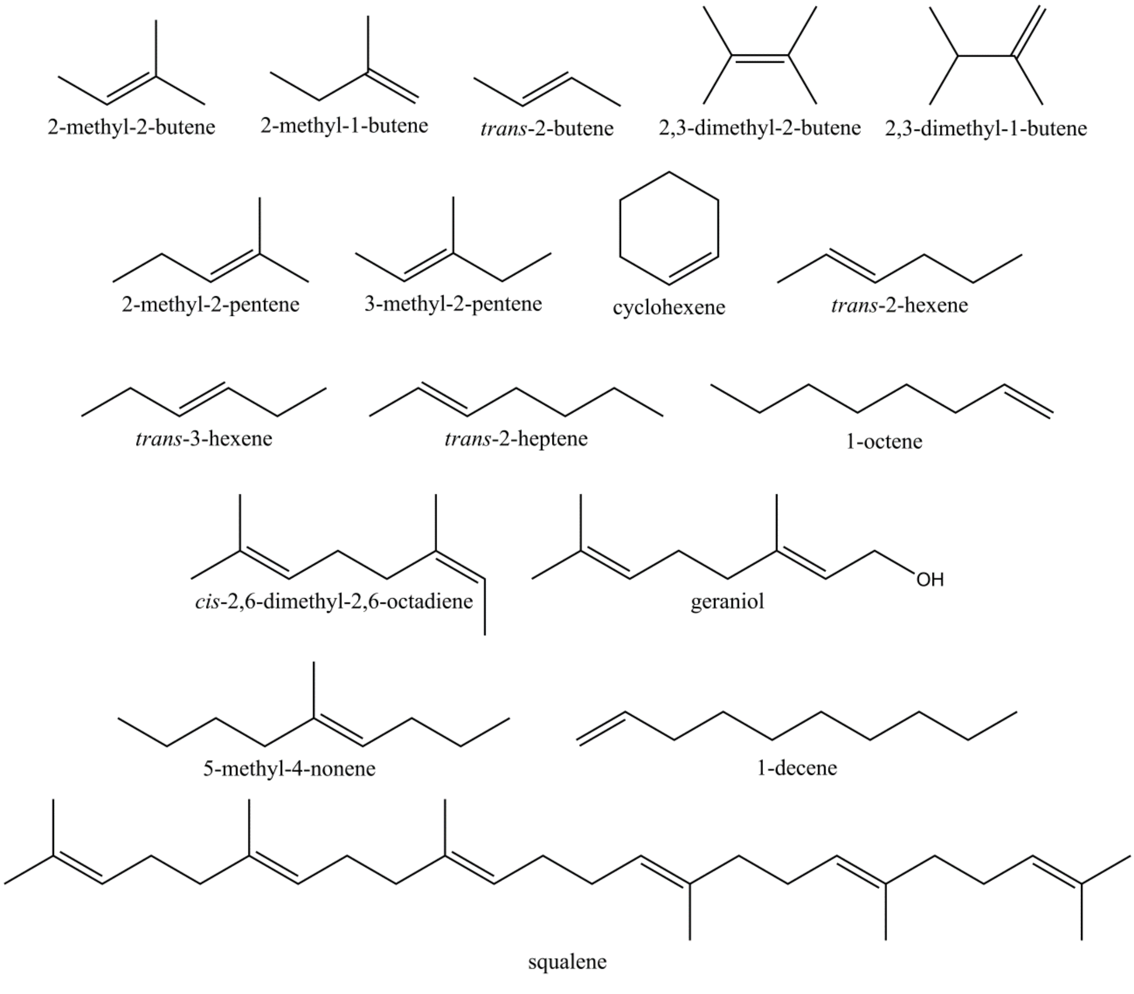
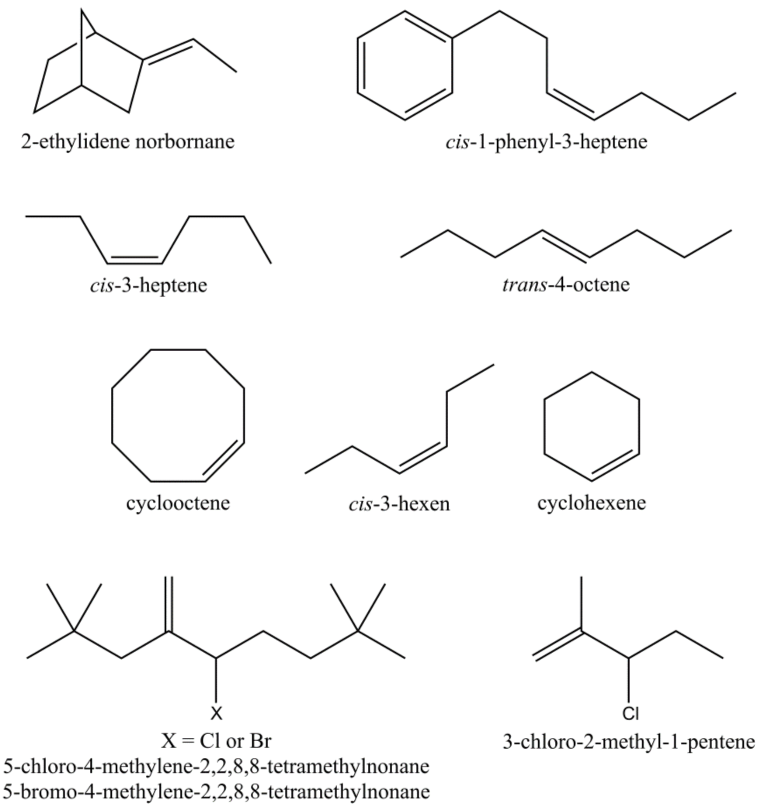


Figure 2.28. Compounds used as models molecules for natural rubber.



2-ethylidene norbornane

cis-1-phenyl-3-heptene

cis-3-heptene

trans-4-octene

cyclooctene

cis-3-hexen

cyclohexene

X = Cl or Br
5-chloro-4-methylene-2,2,8,8-tetramethylnonane
5-bromo-4-methylene-2,2,8,8-tetramethylnonane

3-chloro-2-methyl-1-pentene

Figure 2.29. Compounds used as models molecules for other different elastomers.

Once the reaction has been carried out, the samples should be analysed. When using MCV samples are still liquid after vulcanisation and still soluble in most of the common solvents, which permits better sample handling and the application of a wider range of analytical techniques. Furthermore, the vulcanised 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. The analytical techniques that have been applied to detect, identify, and if desired, quantify MCV products can generally be divided in chromatographic techniques, mainly Gas Chromatography (GC) and High Performance Liquid Chromatography (HPLC), and spectroscopic techniques, such as Infrared spectroscopy (IR), Nuclear Magnetic Resonance (NMR) and Raman spectroscopy.

Throughout literature, as it has been previously described, several models have been employed to study the vulcanisation process of different type of rubbers. One of the most used model is 2,3-dimethyl-2-butene (TME). Although it is not directly comparable with any specific rubber, it is a more general model compound. Squalene is another compound that has been extensively used to investigate the vulcanisation mechanism. As it can be seen from Figure 2.28, it consists of six units of isoprene and its molecular weight is relatively high; hence, its structure is more similar to natural rubber polymer chains than other smaller models that consist only of one isoprene unit. However, there is one important difference: in squalene all double bonds are *trans*, and not *cis* as in NR and IR.

One of the main disadvantages of using low-molecular-weight model compounds is the high concentration of end groups that are present. These end groups (mostly methyl groups) have a reactivity that differs from the methylene and methenyl groups, which form the majority of reactive groups in a polymeric rubber. Furthermore, low-molecular-weight models, such as TME, are monofunctional, i.e. they contain only one double bond, which might be a drawback. With the use of larger models, such as squalene, these disadvantages may be overcame[57].

In addition, not only the number of the double bonds is important, but also its configuration and exact position, and the double-bond shifts that may occur from that position. Since the number of substituents at a double bond determines the relative energy of an isomer, and since the distribution between isomeric cross-links is determined by the relative energy of allylic isomers, it is disadvantageous that in TME the double bond occupies a stable tetra-alkyl-substituted position. Such small model does not offer the possibility of isomerisation due to the double bond will have to shift from the tetra- to a less stabilized disubstituted position. The energy barrier involved must be overcome and this could make this model compound less reactive than other compounds[58].

The MCV methodology is often carried out under nitrogen environment in order to avoid the oxidation of the double bonds. It is also important to take into account the boiling point of the model molecule used. Vulcanisation of low molecular weight models requires not only closed but also pressurized vessels, since these models have a boiling point well below normal vulcanisation temperatures. In addition to evaporation, it should not be neglected the question as to whether the differences in the solubility of chemicals in high-molecular-weight rubber is simulated satisfactory by low-molecular-weight model compounds[57].

In our research group MCV with squalene has been extensively studied[59-64]. Different techniques have been employed in order to gain insight into the vulcanisation process: high performance liquid chromatography (HPLC), matrix-assisted laser desorption/Ionization time-of-flight mass spectrometry (MALDI-TOFMS), time-of-flight secondary ion mass spectrometry (TOF-SIMS) and inverse gas chromatography (IGC) was employed to characterise the vulcanisation products of squalene and to study influence of carbon black.

2.2.1.1 MODEL COMPOUND VULCANISATION METHODOLOGY

Model compound vulcanisation has been employed to study the role of various activators along the curing process. Different recipes with squalene and squalane as model molecules, with and without sulphur, were vulcanised and analysed. The basic vulcanisation recipe is given in Table 2.4.

Table 2.4. Model Compound Vulcanisation Recipe.

INGREDIENTS	CONCENTRATION, phr
Squalene/Squalane	100
Accelerator	1.2
Sulphur	0 – 2
Activator	0 – 5
Stearic acid	2

Squalane has also been used as model molecule because it has the same structure than squalene but it has no double bonds. This permits to investigate the mechanism that occurs when the new activator systems are used and compare it with the pathway followed by common formulations containing zinc oxide due to it is possible to study whether the double bonds of the hydrocarbon exert an influence on the vulcanisation process as it occurs when ZnO is the activator[22].

The reaction for all formulations was performed in a preheated thermostatic oil bath at 140 °C for 60 minutes. The vulcanisation reaction is carried out in different vessels under nitrogen environment in order to avoid the oxidation of the double bonds of squalene. The model mixtures are continuously stirred to assure its homogeneity. During the reaction, vessels are taken from the oil bath at different preset times and quickly cold quenched in dried ice to stop the reaction. After cooling, the vessels were covered to avoid any UV influence, and stored in a refrigerator.

All the MCV mixtures were characterized by two analytical methods of HPLC coupled to an UV detector to cover both aspects of the vulcanisation process process: the fading of the accelerator and the formation of cross-links between the model molecules (Squalene). 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 cross-linking. These methods have been developed and extensively studied by Borrós *et al.*[59, 60, 62-64].

One of the main advantages of the MCV approach is the simplification of sample preparation before analysis. In this thesis, 0.1 g of the cold quenched vulcanised mixture was dissolved for 5 minutes in an ultrasonic bath at room temperature in 5 ml acetonitrile or a mixture of acetonitrile/2-propanol/n-hexane (72:17:11), depending on whether the accelerator evolution or the cross-link formation is investigated. Before injection, samples were filtered with a 0.45 µm Nylon filter in order to remove insoluble particles that would damage the column.

A VWR International LaChrom Elite High Performance Liquid Chromatograph has been used. Data acquisition and treatment has been made using EZ Chrom Elite. To follow the accelerator evolution, the ultraviolet detector was set to 254 nm and the mobile phase was an isocratic mixture of acetonitile and water in proportion 90:10. When investigating the cross-link formation, the ultraviolet detector was set to 230 nm and the mobile phase was an isocratic mixture of acetonitile, 2-propanol and n-hexane in proportion 72:17:11. In both cases, the flux was set to 1 ml/min, the injected volume was 20 µl and the total time of the chromatogram was 15 minutes. A Teknokroma Kromasil 100 C-18 (5 µm, 15 x 0.4 cm) column has been used.

2.2.1.2 HPLC METHOD FOR THE CHARACTERISATION OF THE ACCELERATOR EVOLUTION

A representative chromatogram of a vulcanised sample is shown in Figure 2.30. The different intermediates were identified comparing the results with those obtained earlier in our research group. The presence of 2-mercaptobenzothiazole (MBT) (peak A), CBS (peak B), 2,2'-dithiobenzothiazole (MBTS) (peak C), and sulphur (peak H) can be seen at 1.4, 3.1, 4.3 and 11.6 minutes, respectively. Peaks with retention times of 5.0, 5.3, 6.1, and 7.2 minutes, peaks D, E, F and G respectively, correspond to active sulphurating agents. As expected, the elution time of these species increases as more sulphur atoms are present in the chain. The identification of these compounds was carried out earlier in our research group using different techniques such as mass spectroscopy (MS)[63-65], Matrix-Assisted Laser Desorption/Ionization time-of-flight mass spectrometry (MALDI-TOFMS)[59, 60] and time-of-flight secondary ion mass spectrometry (TOF-SIMS)[62].

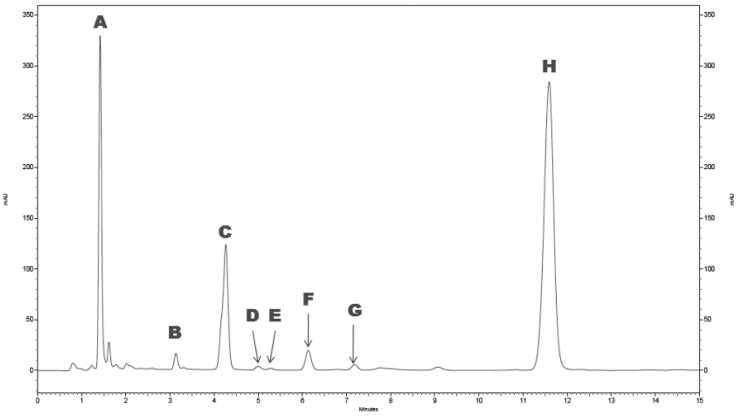


Figure 2.30. HPLC-UV analysis of squalene vulcanised at 30 min hold time, 254 nm, 20 µl injection volume, mobile phase acetonitrile/water (90:10).

2.2.1.3 HPLC METHOD FOR THE CROSS-LINK PROCESS MONITORING

This method was used to follow the polysulphidic cross-links (Sq cross-linked) and the evolution of squalene (Sq) and squalene with pendant group ($Sq-PG$). Once the active sulphurating agents are formed, they commence to interact with rubber to form a rubber-bound polysulphidic pendant group, $R-S_x-Bt$. Finally, the rubber polysulphides react, either directly or through an intermediate, to give cross-links, $R-S_x-R$. Since in this work squalene has been used as a substitute of NR, the pendant groups are $Sq-S_x-Bt$ and the cross-links $Sq-S_x-Sq$.

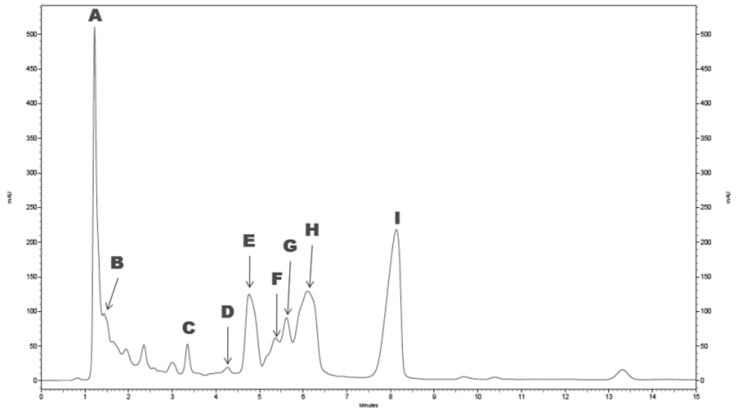


Figure 2.31. HPLC-UV analysis of squalene vulcanised at 60 min hold time, 230 nm, 20 µl injection volume, mobile phase acetonitrile/2-propanol/n-hexane (72:17:11).

A representative chromatogram of a vulcanised sample is shown in Figure 2.31. The different products were identified comparing the results with those obtained earlier in our research group. The presence of MBT (peak A), CBS (peak B), sulphur (peak C), and squalene (peak I) can be seen at 1.2, 1.5, 3.3, and 8.1 minutes, respectively. The identification of these compounds was carried out earlier in our research group using different techniques such as mass spectroscopy[63, 64], MALDI-TOFMS[59, 60] and TOF-SIMS[62].

Peaks with retention times between 4 and 6.3 minutes (peaks D, E, F, G and H) correspond to the cross-linked squalene products. The identification of the chromatographic peaks was carried out by comparing the results with those obtained earlier using a HPLC-ESI-MS method with silver nitrate derivatisation developed by our research group[65].

2.2.2. RUBBER MIXTURES

Samples of different rubbers have been prepared and characterised in this work. Natural rubber, butadiene rubber and styrene-butadiene rubber have been employed to study the different approaches to reduce the zinc oxide levels in the rubber compounds. In the next sections, the basics of some of the different experiments carried out with these rubbers are explained. The particulars of some common techniques that have also been applied to the rubber compounds such as mixing and vulcanisation procedures, monitoring the curing process with a rheometer, tensile-strain and hardness measurements, differential scanning calorimetry (DSC) analysis, etc. will not be reviewed.

2.2.2.1 EQUILIBRIUM SWELLING EXPERIMENTS

The cross-link degree and the distribution of cross-links in the rubber compounds are important factors because these parameters exert a major influence in the final properties of vulcanisates. The state of cure of the rubber can be obtained performing equilibrium swelling experiments. The technique allows the determination of the average molecular weight between cross-links, M_C. The cross-linking density (ν) is related to M_C by $1/2\, M_C$ in moles of cross-links per gram of rubber, or $\rho/2\, M_C$ in moles of cross-links per volume of rubber (ν'), assuming tetra-functional cross-links and that the network is free from chain ends[12].

The Flory-Rehner model[66-68] and the Frenkel-Flory-Rehner[69] treatment predicts the thermodynamics of swollen polymer networks. In these theories the terms for the free energy of mixing are equated to those for the elastic retraction energy of the network. The modified Flory-Rehner equation relating volume swelling to degree of cross-linking of a polymer molecule is

$$-\left[ln(1-\phi_r)+\phi_r+\chi\cdot{\phi_r}^2\right]=\frac{\rho_r}{M_C}\cdot V_S\cdot\left({\phi_r}^{1/3}-\frac{2\cdot\phi_r}{f}\right)$$

Equation 2.1

where ρ_r is the unswollen rubber density, f the functionality of the cross-links, ϕ_r the volume fraction of polymer at the equilibrium degree of swelling and V_S the molar volume of solvent; χ is an interaction parameter between the polymer and the solvent known as the Flory-Huggins interaction parameter. It should be noted that Equation 2.1 is strictly applicable only to a hypothetical network free from entanglements and chain ends.

By swelling experiments, the average molecular weights between cross-links are physical values of cross-linking ($M_{C,\,phys.}$) including the effect of chain ends and entanglements. The chemical estimates of the degree of cross-linking ($1/2\,M_{C,\,chem.}$) can be obtained using stress-strain measurements and applying the Mullins-Moore-Watson correlation[12, 70, 71]. The difference between the chemical cross-link density and the physical density, the former being lower than the later, has been attributed to the introduction into the network of physical entanglements. Such entanglements would serve as additional cross-links, and the magnitude of the divergence between the physical and the chemical estimates of $1/2\,M_C$ indicates that they make an important contribution to the elastically effective degree of cross-linking, especially at low extent of chemical cross-liking[12].

It is also important to remark that the parameters used to obtain the M_C values may cause a large uncertainty. In this sense, the Flory-Huggins interaction parameter is of great importance. Small changes in χ can lead to large changes in the calculated cross-link density. It is usually assumed to be constant for a given polymer-solvent pair but it varies with the chemical structure of the vulcanisate and therefore with the nature of the cure system. When a χ constant is used over a narrow ϕ_r range, good correlation is obtained, so long as the same curing chemistry was used most experimenters are satisfied[72]. However, some authors[72-76] have showed a dependence of χ on the volumetric fraction of polymer, the cross-link density and the extent of cure.

The determination of the volumetric fraction of rubber in the swollen state is another source of uncertainty. If swelling measurements are carried out gravimetrically, it is necessary to eliminate the fraction of insoluble components[77] and to take into account the amount of imbibed solvent at the interface between rubber and noninteracting filler particles[78].

For more details on this topic, the work by Valentín *et al.*[79] and the references therein are recommended.

2.2.2.2 DETERMINATION OF CROSS-LINK STRUCTURE

In order to determine the structure of rubber vulcanisates the chemical probe methodology is a very useful technique. This methodology allows the determination of the fraction of mono- (S_1), di- (S_2) and polysulphidic (S_x, 3 or more sulphur atoms) cross-links in the rubber samples by selective decomposition using thiols activated by amines.

The methodology has been thoroughly explained by Saville and Watson[80] and Campbell[81]. Basically the method involves of three steps. First, the total cross-links (S_1, S_2 and S_x cross-links) are measured by swelling. The fraction of S_1 and S_2 is obtained by a treating with 2-propanethiol and piperidine a heptane-swollen sample, due to this treatment cleaves only polysulphidic cross-links. Then, the S_1 contribution is obtained by destruction of all of S_2 and S_x, cross-links with 1-hexanethiol and piperidine.

The ν from S_1 is determined by swelling the sample treated with 1-hexanthiol. The ν attributed to S_2 is the difference between the ν measured by swelling the sample treated with 2-propanethiol and the ν from S_1. Finally, the cross-link density from S_x is calculated by subtracting the ν from S_1 and S_2 from the total cross-link density.

When the chemical probe methodology is applied together with equilibrium swelling experiments, it is important to notice that the χ values changes after the chemical probe treatment.

2.2.2.3 NMR FOR THE STUDY OF CHAIN DYNAMICS AND STRUCTURAL CONSTRAINTS

Nuclear magnetic resonance is a technique that probes molecular properties by interrogating atomic nuclei with magnetic fields and radio-frequency (rf) irradiation. NMR has been successfully applied to different elastomers and rubber samples for describing the relation between the cross-link density of the elastomer network and the NMR signal.

In this work two different types of NMR techniques have been applied to measure the cross-link density of rubber samples: ^{1}H NMR relaxation and ^{1}H double-quantum (DQ) (or more generally multiple-quantum, MQ) NMR experiments. A brief description of the these methodologies is given below but for a more detailed picture the work of Litvinov[82] and Saalwächter[83], respectively, is recommended.

2.2.2.3.1 ^{1}H NMR Relaxation Time Spectroscopy

Different types of NMR magnetisation relaxation experiments are used to analyse local and long-range spatial mobility of polymer chains. Since chain motion is closely coupled to the length of network chains, chemical information on network structure and network defects can be obtained in this way. The mobility of polymer chain units of different chemical origins can be determined by means of selective NMR magnetisation relaxation experiments. The application of this type of relaxation experiments is based on the high sensitivity of the relaxation process to chain dynamics involving large spatial-scale chain motion at temperatures well above the glass transition temperature (T_g)[84].

NMR magnetisation relaxation experiments are based on the measurement of T_1 and T_2, the longitudinal and transversal relaxation times. The longitudinal relaxation time T_1, also called the spin-lattice relaxation time, is the energy dissipation time characteristic for build-up of the magnetization parallel to the magnetic field. The transverse relaxation time T_2, also known as spin-spin relaxation time, is the time constant for disappearance of magnetisation components orthogonal to the magnetic field.[82]

The relaxation time T_1 is understood as the time describing the return of magnetization to thermal equilibrium after perturbation of the sample by radio frequency pulses, while T_2 is characterised as the time constant for signal decay. T_2 is generally shorter than the T_1. In liquids, T_2 is close to T_1 while in solids it can be orders of magnitude shorter.

T_1 is a relaxation parameter describing the build-up of magnetisation to a thermal equilibrium state after a 90° pulse. The T_1 relaxation obeys the function shown by Equation 2.2

$$M(t) = M_0 \cdot \left[1 - (1 - cos \propto) \cdot e^{-\frac{t}{T_1}}\right]$$

Equation 2.2

with M_0 representing magnetization at the thermal equilibrium state and α the pulse angle (which should be around 90°).

The T_2 curves can be analysed according to a Gaussian-exponential function[85, 86] shown in Equation 2.3

$$M(t) = A_0 + A_1 \cdot e^{-\frac{t}{T_2} - \frac{1}{2} \cdot qM_2 t^2} + A_2 \cdot e^{-\frac{t}{T_2}}$$

Equation 2.3

with $M(t)$ as the detected signal standing for the magnetization at time t, A_0 compensates for a possible DC offset of the signal, A_1 and A_2 are respective amplitudes of the cross-linked and highly mobile fractions of the polymer in [%] of the total signal, fractions of respective Gauss and exponential fractions (with A_0 + A_1 +A_2 = 100), qM_2 with q the residual fraction of the non-to-zero averaged dipolar magnetic interaction of the interacting protons, and M_2 the second moment, and T_2 the transversal relaxation time.

Equation 2.3 allows for a differentiation between the chain mobility of the actual polymer chains (movement of networks and cross-linked hydrocarbon chains) and that of low-molecular-weight constituents and dangling chain ends. The Gauss fraction (qM_2) in the earlier relaxation time range corresponds to polymer chains and the exponential fraction T_2 to the low molecular area[85-87].

The cross-link density can be extracted based on the model of residual dipolar couplings induced by permanent cross-linking. The factor qM_2 allows the determination of the average molecular weight between cross-links, (M_C)[86]. However, the results are very much dependent on the method and assumptions adopted. On the other hand, it has been shown that ν is directly proportional to qM_2 and inversely proportional to T_2[85, 87-90].

2.2.2.3.2 ^{1}H Double Quantum (DQ) Solid-State NMR Experiments

DQ spectroscopy is one of the most versatile and robust quantitative techniques to investigate not only the structure but also the dynamics of polymer networks[83, 91]. These experiments are based on the determination of partially averaged residual dipolar coupling constant (D_{res}) that persist because the presence of cross-links and other topological constrains provoke the non-isotropic segmental fluctuations[83, 91, 92].

The essential advantage of MQ spectroscopy as compared to more traditional NMR approaches such as Hahn or solid echoes is that, without invoking any specific model, effects of temperature independent network structure and temperature-dependent chain dynamics can be quantitatively separated, in the high temperature regime[78].

When MQ spectroscopy is used two qualitatively different sets of data are obtained in the same experiment as a function of the double-quantum evolution time (τ_{DQ}) that can be used to independently analyse residual couplings and the chain dynamics. On one hand, a build-up curve dominated by spin-pair double-quantum coherence (I_{DQ}) and on the other hand, a decay curve (I_{ref})[83, 91-93].

The sum of both components ($I_{DQ} + I_{ref}$) contains the full magnetisation of the sample including signal from dipolar coupled network segments and signal from non-coupled network defects like dangling chains and loops that do not participate in the elastic properties of the compound. Each segment show different relaxation behaviour. Coupled network segments relax faster and typically in a non-exponential manner, while the signal of non-coupled, elastically non-active defects show a slower exponential decay (T_2^* in Equation 2.4). Therefore, it is necessary to identify and subtract the exponential long-time contribution, the non-coupled fraction of polymer chains (B in Equation 2.4) to the total magnetisation[94], $I_{\sum MQ}$:

$$I_{\sum DQ} = I_{DQ} + I_{ref} - B \cdot e^{-2\cdot\tau_{DQ}/T_2^*}$$

Equation 2.4

The double-quantum signal must be normalized by the total intensity of the coupled segments that constitute the network ($I_{\sum MQ}$) in order to obtain a build-up curve (I_{nDQ}) independent of the timescale of the segmental motion; consequently it is only related to the network structure ($I_{nDQ} = I_{DQ}/I_{\sum nDQ}$)[79, 93, 94]. In the high temperature regime, the data from MQ experiments can be processed in such a way that the temperature-independent network structure effect can be separated from the temperature dependent segmental dynamics without invoking any specific model[94]. This involves a normalization procedure that was detailed previously by Saalwächter[83].

The most robust and general approach to analyse the I_{nDQ} build-up curve is to assume a Gaussian distribution of dipolar couplings[76, 83, 92] as shown in Equation 2.5, where D_{res} and σ_G are the average residual dipolar couplings and their standard deviations, respectively.

$$I_{nDQ}(D_{res}, \sigma_G) = \frac{1}{2}\left(1 - \frac{exp\left\{-\frac{\frac{2}{5}D_{res}\tau_{DQ}^2}{1+\frac{4}{5}\sigma_{res}^2\tau_{DQ}^2}\right\}}{\sqrt{1+\frac{4}{5}\sigma_G^2\tau_{DQ}^2}}\right)$$

Equation 2.5

It is well established that D_{res} is directly related to the dynamic order parameter of the polymer backbone, S_b, and therefore it is a direct measurement of the real cross-link density since it depends, not only on the chemical cross-links, but also on the entanglements[92].

For natural rubber, the molecular weight between constrains, M_C, is related to D_{res} via the following expression[79, 83, 94]

$$M_C^{(NR)} = \frac{617\ Hz}{D_{res}/2\pi} kg/mol$$

Equation 2.6

The approximate validity of the (model-dependent) reference values has recently been confirmed by comparison with results from equilibrium swelling experiments[79].

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Chapter 3

EFFECT OF METAL OXIDES AS ACTIVATORS: DISCUSSION ON THE DIFFERENT MECHANISMS OF RUBBER VULCANISATION ACTIVATED BY ZINC OXIDE AND MAGNESIUM OXIDE[#]

'Scientific discovery and scientific knowledge have been achieved only by those who have gone in pursuit of it without any practical purpose whatsoever in view.'
Max Planck (1858 - 1947)

Zinc oxide is a widely used compound in the rubber industry due to the excellent properties that it shows as an activator and, consequently, its role in the mechanism of accelerated sulphur vulcanisation has been extensively studied. Due to the increased concern about its environmental effects, several research studies have been carried out in order to substitute it with different metal oxides such us MgO. The aim of this chapter is to study by MCV the role of MgO on the mechanism to gain a better understanding of the differences shown by this activator. The model compound studies have shown that when MgO is the accelerator, its interaction with sulphur provokes a faster breakdown of the accelerator to form the active sulphurating agents. The presence of sulphur is a necessary condition for the breakdown of the accelerator and not the presence of unsaturations in the hydrocarbon chain as occurs with ZnO. Furthermore, the incapability of magnesium oxide to form complexes with the accelerator and the cross-link precursor's leads to a lower cross-linking degree due to less cross-link precursors are obtained after the cross-linked is formed. In addition, this lack of complexes formation protected the cross-links formed from desulphuration.

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3.1. INTRODUCTION

The overall course of sulphur vulcanisation shown in Figure 2.17 is generally accepted, but there is still not general agreement in both the nature of the active sulphurating agents and the mechanism of their reaction with the rubber molecules, in particular as to whether or not zinc is involved. As it have been shown in Chapter 2, several mechanisms have been proposed, but fully elucidating the mechanisms remains difficult because of their complexity and the structural difficulty with analysis of vulcanisates.

There is no general agreement about the role of zinc in the formation of the active sulphurating agents. Some authors have advocated that the active sulphurating agent is an accelerator polysulphide, $Ac - S_x - Ac$, instead of the zinc complex zinc benzothiazolyl mercaptide (ZMBT), while others have proposed that both zinc complex and polysulphide may act as the active sulphurating agent, depending on the conditions and the extent of cure[1].

Morrison[2] found that the zinc complex promoted a substantial yield of model cross-links from 2-methyl-2-pentene and MBTS-sulphur. On the contrary, Agulló[3], working with squalene, supported the structures depicted in Figure 2.20 and Figure 2.21. It was demonstrated that in the case that ZMBT could be actually formed, which is very unlikely, theses complexes do not lead to cross-link formation. It was also observed that they were not stable at the vulcanisation temperature. Kruger and McGill, using thermal techniques (DSC), found that there was no evidence for the formation of a sulphur/MBTS/ZnO compound[4] or of a zinc-accelerator complex with TMTD[5] of the type generally attributed the role of an active sulphurating agent in accelerated sulphur vulcanisation.

Borrós *et al.*[6] demonstrated that for sulphenamide accelerated vulcanisation, ZnO which is usually described as a catalyst for the breaking down of the accelerator, is necessary but not enough to cause the decomposition of the sulphenamide. These authors proved that small amounts of 2-mercaptobenzothiazole (MBT) are required for the formation of the active sulphurating agents and that this compound is formed from the direct interaction between the accelerator and the double bonds of the hydrocarbon (Figure 2.22).

Various mechanisms have been proposed for the conversion of cross-link precursor into cross-links. In principle, any *S–S* bond in the cross-link precursor can break, but Coran[7] have suggested that the weakest bond in the sulphur-sulphur 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 sulphur chain and decreases the rate of the actual croslinking. The zinc chelation stabilizes the other sulphur bonds and influences the position of the S-S bond most likely to break as shown in Scheme 3. Without addition of ZnO this bond is unlikely to break as it could not be stabilized by resonance.

There have been a number of investigations comparing different metal oxides as vulcanisation activators. Duchacek *et al.*[8] tested the effect of copper, mercury, nickel, zinc, cadmium, indium, magnesium and calcium stearates on the course of CBS accelerated sulphur vulcanisation of NR. Based on results 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 copper and mercury. This is why zinc and cadmium form active sulphurating vulcanisation intermediates. Magnesium and calcium have only a slight tendency to form these complexes.

In a review by Chapman[9], he concluded 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 cross-linking of a model olefin, cupric oxide was found to give higher yields than ZnO, and nickel oxide was also quite effective[10].

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 vulcanisation system (EV) gave higher moduli[11]. Other oxides gave moduli equal to or lower than with ZnO alone. Calcium oxide and magnesium oxide are apparently not so promising in conventional sulphur/sulphenamide cures, especially not in combination with ZnO. It has been reported that calcium oxide and magnesium oxide interfere with the efficient activation of ZnO[12].

Borros *et al.*[6, 13, 14] 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. CaO and CdO were found to be pour activators. MgO and ZnO were capable of ‘breaking’ the accelerator quite well. MgO seemed to have more affinity for sulphur than ZnO and the active sulphurating agents are formed more quickly. Nevertheless ZnO performs better during curing stage than MgO.

Lautenschlaeger and Edwards[12] have 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 monosulphidic products and hardly any by-products were found. CaO was the worst activator. The effects of the activators were translated from the cross-link yield, the length of the sulphur bridges and the types of isomers.

Noordermeer *et al.*[15] used squalene and 2,3-dimethyl-2-butene (TME) as model molecules and N-t-butylbenzothiazole-2-sulphenamide (TBBS) to study different metal oxides. They observed that when using MgO the accelerator dissociates very rapidly and cross-linked products are formed faster than with ZnO. However, the cross-links are formed to a higher extent with ZnO. The addition of CaO was also investigated but it was found that this metal oxide did not perform as a good activator.

In order to gain a better understanding of the mechanism and therefore to be able to explain the differences observed when vulcanising different formulations (see Borrós *et al.*[16]), model compound vulcanisation has been used to study the role of MgO. Different recipes with squalene and squalane as model molecules, with and without sulphur, were vulcanised and analysed.

Squalane has also been used as model molecule because it has the same structure than squalene but it has no double bonds and this permits study whether the double bonds of the hydrocarbon exert an influence on the vulcanisation process as it occurs when ZnO is the activator.

3.2. EXPERIMENTAL

3.2.1. MATERIALS

Squalene (Fluka, 97%) and squalane (Fluka, 95%) were used for the present study without further purification. Sulphur (CEPSA), N-cyclohexyl-2-benzothiazolesulphenamide (CBS) (Lanxess), zinc oxide (Silox), magnesium oxide (Silox), and stearic acid (Calià&Parés) were provided by IACP-JEVSA, (Castellbisbal, Barcelona, Spain) and used for the vulcanisation of the model compound. Solvents used in the investigation were all HPLC grade: Acetonitrile (J. T. Baker); 2-propanol and n-hexane (Panreac).

3.2.2. MODEL COMPOUND VULCANISATION (MCV)

Model compound vulcanisation has been chosen to study the role of the metal oxides along the reaction using CBS as accelerator. The vulcanisation recipes are given in Table 3.1.

Table 3.1. Model Compound Vulcanisation Recipes (phr).

Ingredients	Mixture A	Mixture B	Mixture C	Mixture D	Mixture E
Squalene	100	100	–	100	–
Squalane	–	–	100	–	100
CBS	1.2	1.2	1.2	1.2	1.2
Sulphur	2	2	2	–	–
ZnO	5	–	–	–	–
MgO	–	5	5	5	5
Stearic acid	2	2	2	2	2

The reaction for all formulations was performed in a preheated thermostatic oil bath at 140 °C for 60 minutes. The vulcanisation reaction is carried out in different vessels under nitrogen environment in order to avoid the oxidation of the double bonds of squalene. The model mixtures are continuously stirred to assure its homogeneity. During the reaction, vessels are taken from the oil bath at different pre-set times and quickly cold quenched in dry ice to stop the reaction. After cooling, the vessels were covered to avoid any UV influence, and stored in a refrigerator.

All the model compound vulcanisation mixtures were characterized by two analytical methods of HPLC coupled to an UV detector to cover both aspects of the process: the fading of the accelerator and the formation of cross-links between the model molecules. The identification of the different compounds (CBS, MBT, MBTS, sulphur, squalene and the different cross-linked squalenes) was carried out earlier in our research group using different techniques[14, 17-21].

3.3. RESULTS AND DISCUSSION

This study was performed in order to gain a better understanding of the mechanism when magnesium oxide is the activator. The role of ZnO in the mechanism of accelerated sulphur vulcanisation has been significantly studied and it is relatively well known due to it has been and is extensively used in the rubber industry.

Although different studies have been carried out using MgO as activator[8, 15], the role of MgO on the mechanism remains unclear. As it has been explained before, MgO seems to have more affinity for sulphur than ZnO which means that the active sulphurating agents are formed more quickly[13]. It has also been reported[6, 15] that the breakdown of the accelerator occurs faster when MgO substitutes ZnO as the activator. As it can be seen in Figure 3.1 (Mixtures A and B), when using squalene as a model molecule for natural rubber, the accelerator reacts faster if MgO is the activator. When MgO is used, CBS is completely degraded after 20 minutes while, with ZnO, there is around 40 % of unreacted CBS which does not disappear entirely until 30 minutes as reported earlier[6, 13, 17, 18].

As it can be seen in Figure 3.2, there are not significant differences in the formation of MBT when MgO or ZnO are used as activators. Since MBT is a decomposition product of the accelerator and the breakdown of the accelerator occurs faster when the activator is MgO, it is not surprising to observe that the formation of MBT commences earlier with MgO than ZnO. Nonetheless, at longer reaction times these differences disappear.

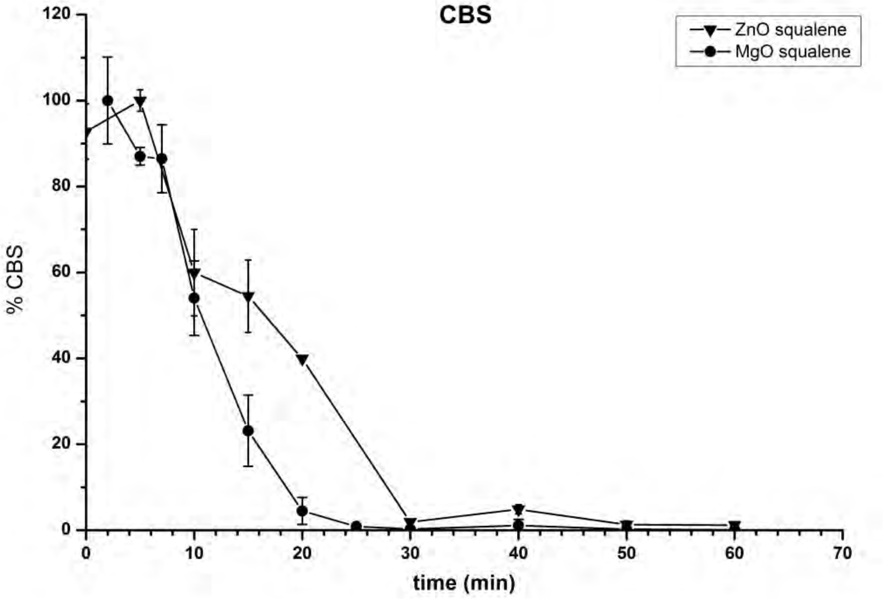

Figure 3.1. Breakdown of CBS as a function of the reaction time with ZnO and MgO as activators using squalene as model molecule.

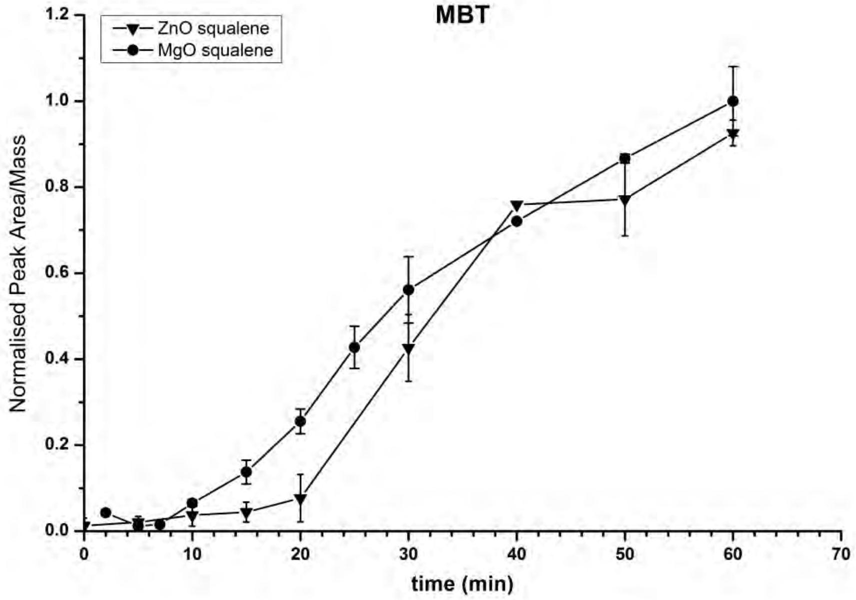

Figure 3.2. MBT concentration as a function of the reaction time with ZnO and MgO as activators using squalene as model molecule.

Figure 3.3 shows that sulphur has completely reacted in 50 minutes for both ZnO and MgO. However, it can be seen that the reaction begins earlier when MgO is used as the accelerator, as it was observed following the formation of MBT.

In order to check if the reaction follows the same path when MgO is the activator, that is to say, as shown in in Figure 2.22, a new reaction was carried with MgO but using squalane as the model molecule (Mixture C). Squalane has the same structure that squalene but it has no double bonds. Therefore, if with MgO the reaction follows the same path that it does with.

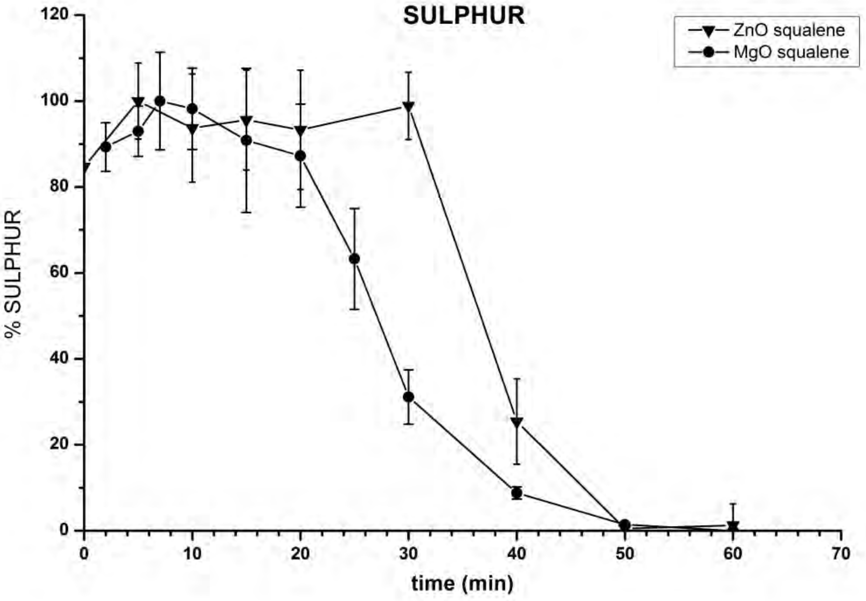

Figure 3.3. Degradation of sulphur during vulcanisation with ZnO and MgO as activators using squalene as model molecule.

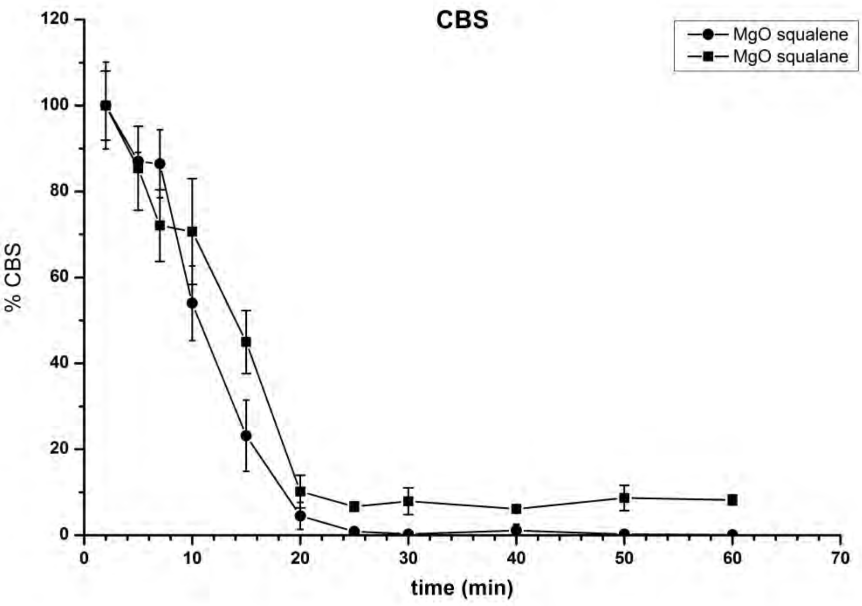

Figure 3.4 .Breakdown of CBS as a function of the reaction time with MgO as activators using squalene and squalane as model molecules.

ZnO, the breakdown of the accelerator would not occur until much longer reaction times as reported previously[6, 17].

As it can be seen in Figure 3.4 there are no differences when the reaction is carried out with squalene or squalane. This means that it is not the direct interaction between the accelerator and the double bonds of the hydrocarbon chains which produces enough amounts of MBT to act as catalyst to decompose CBS. The breakdown of the accelerator is caused by other route.

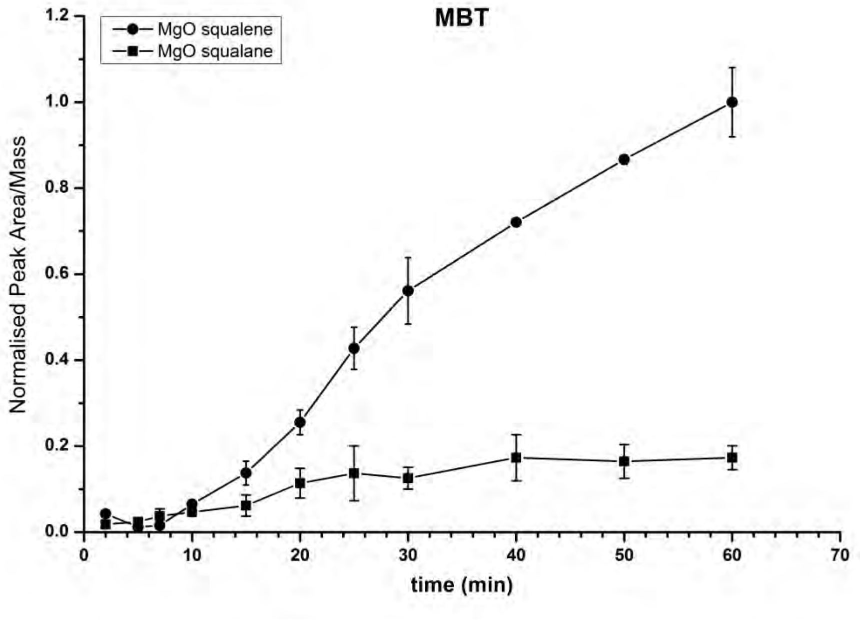

Figure 3.5. MBT concentration as a function of the reaction time with MgO as activators using squalene and squalane as model molecules.

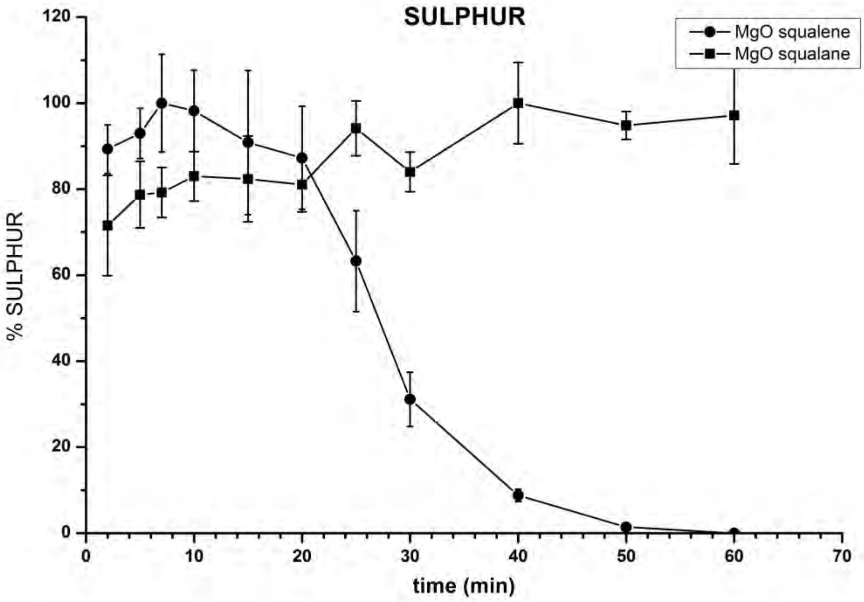

Figure 3.6. Degradation of sulphur during vulcanisation with MgO as activators using squalene and squalane as model molecules.

Figure 3.5 shows the formation of MBT and Figure 3.6 displays the consumption of sulphur, both for mixtures B and C. It can be seen that when squalane is used instead of squalene there is almost no formation of MBT and practically no reaction of sulphur. These results contrast with the fact that the breakdown of CBS occurs at the same rate in both cases. Since there are no double bonds in squalane, the intermediates and active sulphurating agents formed are not able to add sulphur into the hydrocarbon chain which leads to a low formation of MBT.

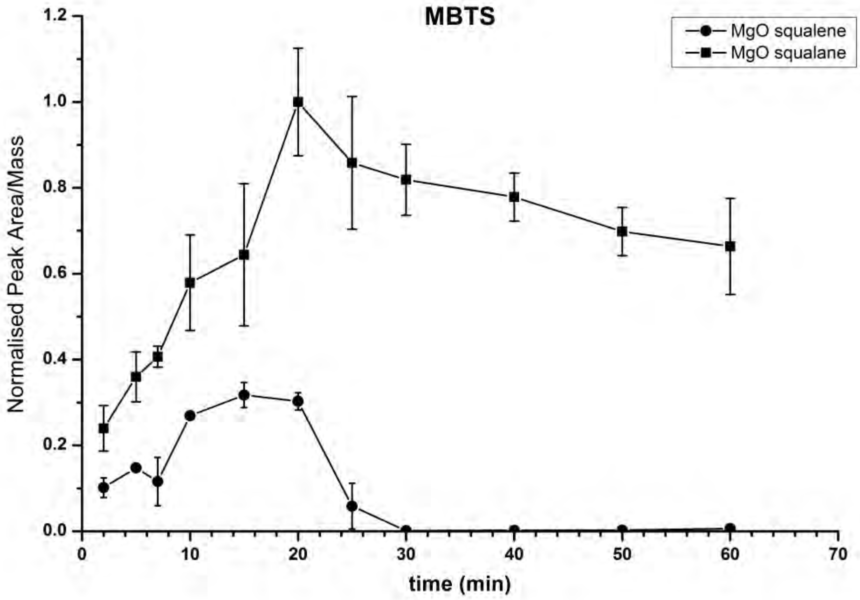

Figure 3.7. MBTS concentration as a function of the reaction time with MgO as activators using squalene and squalane as model molecules.

In Figure 3.7 it is shown the evolution of MBTS for mixtures B and C. As it has been explained, the intermediate compounds that are formed in the recipe containing squalane are not able to progress forming cross-links due to there are no double bonds in the hydrocarbon chain. That is why there is a higher concentration of MBTS when the model molecule is squalane and not squalene.

As it has been explained previously, MgO seems to have more affinity for sulphur than ZnO. In order to check if this difference may cause that breakdown of CBS follows a different path, two more mixtures where prepared (mixtures D and E). These two new recipes do not contain sulphur.

In Figure 3.8 it can be seen that there are very significant differences when sulphur is taken out of the reaction mixture. In the mixtures that do not contain sulphur, whether using squalene or squalane, the accelerator does not disappear. Figure 3.9 shows that, since the accelerator does not react, there is not MBT formed when sulphur is not present in the recipe.

These results mean that when the vulcanisation is carried out with MgO instead of ZnO the reaction does not follow the path presented in Figure 2.22. For the breakdown of the accelerator it is needed sulphur to be present in the recipe. As it has been shown, when sulphur is present the breakdown of the accelerator is faster with MgO than with ZnO, but CBS does not react if sulphur is taken out. From these results it can be deduced that the dissociation of CBS occurs via sulphur activation from magnesium oxide. Therefore, regarding the reaction taking place in the scorch time, the main difference in the mechanism of sulphenamide accelerated vulcanisation with MgO as the activator is that sulphur plays an important role in the decomposition of the accelerator and not just in the formation of the active sulphurating agent.

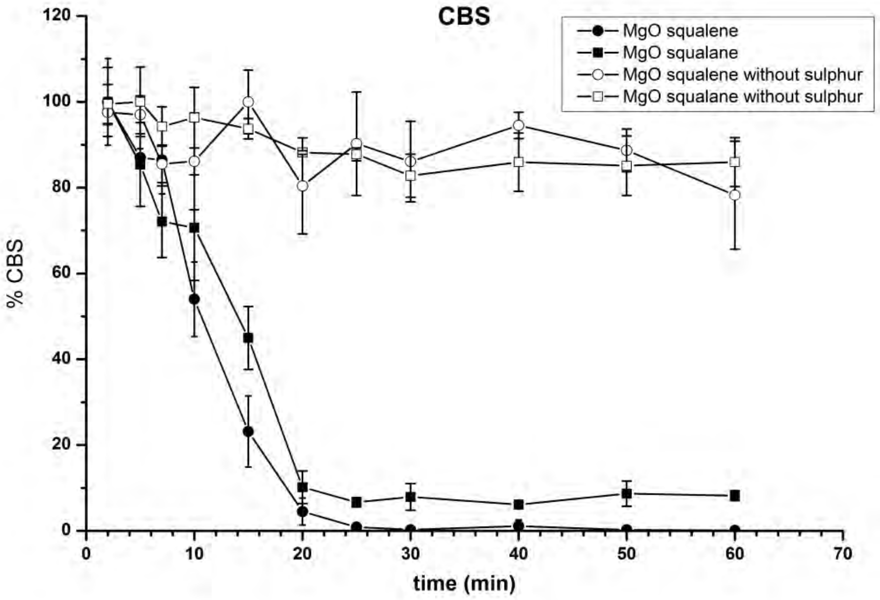

Figure 3.8. Breakdown of CBS as a function of the reaction time for mixtures B, C, D and E.

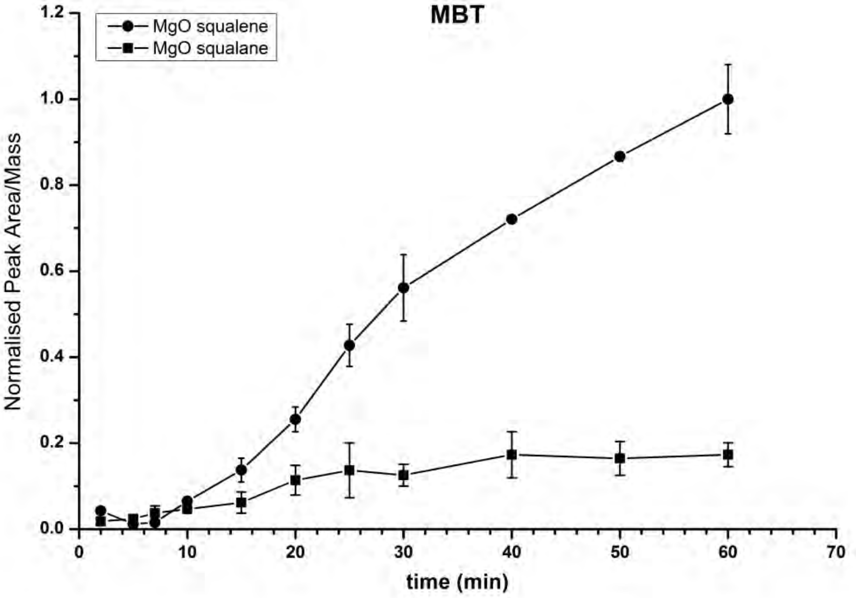

Figure 3.9. MBT concentration as a function of the reaction time for mixtures B, C, D and E.

It has been reported[8, 15, 22] that MgO has only a slight tendency to form complexes with the active sulphurating agents. That means that the route shown in Scheme 1, which illustrates the formation of the active sulphurating agents when ZnO is present in the vulcanisation mixture, does not occur for the case of MgO activated vulcanisation. In presence of MgO sulphur is consumed much faster compared to the systems with ZnO present and the active sulphurating species are formed via sulphur insertion in the active accelerator species due to the higher affinity of MgO for sulphur.

The main drawback is that these MgO intermediates are not able to progress to final cross-links with the same ability than ZnO active sulphurating agents, which leads to a lower cross-linking degree. In Figure 3.10 it can be seen that total amount of cross-link squalene obtained with ZnO (mixture A) is higher than with MgO (mixture B). However, when the model compound vulcanisation approach is employed the differences are not as significant as they are in NR vulcanisation as it has been reported by Borrós *et al.*[16]).

As it has been explained previously, MgO has only a slight tendency to form complexes with the active sulphurating agents. In the same way, MgO is not able to form complexes with the cross-link precursors. This provokes that the formation of the cross-linked products to occur more likely as it is shown in the left hand side of Figure 2.26.

The weakest bond of the cross-link precursors is the sulphur-sulphur bond adjacent to the benzothiazole group. If the bond that breaks is the S-S bond contiguous to the benzothiazole group, a monomeric thiyl radical would be produced and, when added to a rubber backbone, a polymeric monosulphide, and not a new cross-link precursor, would be formed[7, 23]. Previous studies have demonstrated that there is an increased formation of monosulphidic pendant groups in the absence of zinc[24]. This leads to a lower cross-linking degree, as it has been shown, due to less cross-link precursors are formed.

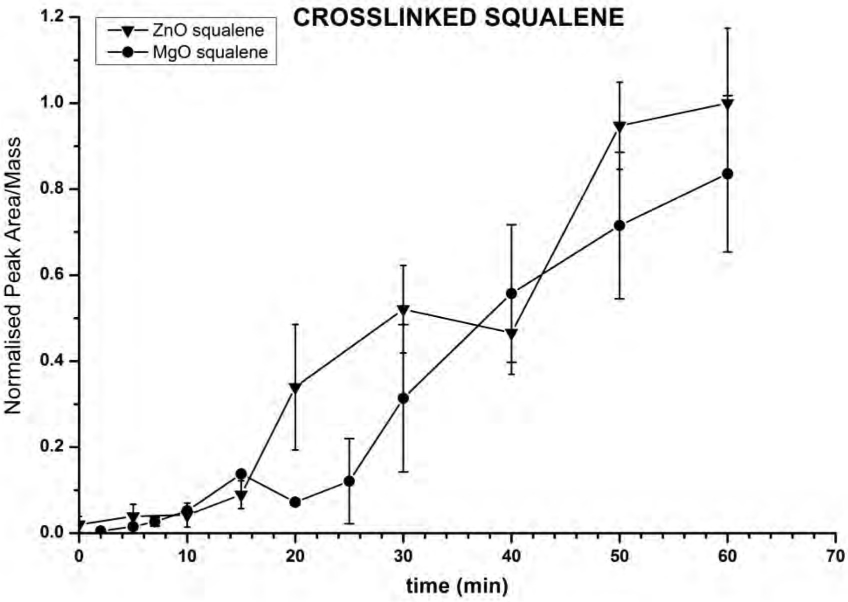

Figure 3.10. Evolution of total cross-linked squalene during vulcanisation with ZnO and MgO.

Furthermore, the fact that the bond that breaks is the $S-S$ bond contiguous to the benzothiazole group provokes that the cross-linked products formed contain longer sulphur chains. Figure 3.11 displays the percentage of mono- (*Sq–S–Sq*), di- (*Sq–S₂–Sq*), tri- (*Sq–S₃–Sq*) and tetrasulphidic (*Sq–S₄–Sq*) cross-links in the different samples tested. The main effect of magnesium oxide seems to be the decrease of monosulphidic cross-links by an increase in the formation of di- and tetrasulphidic cross-links. The proportion of trisulphidic cross-links is not modified.

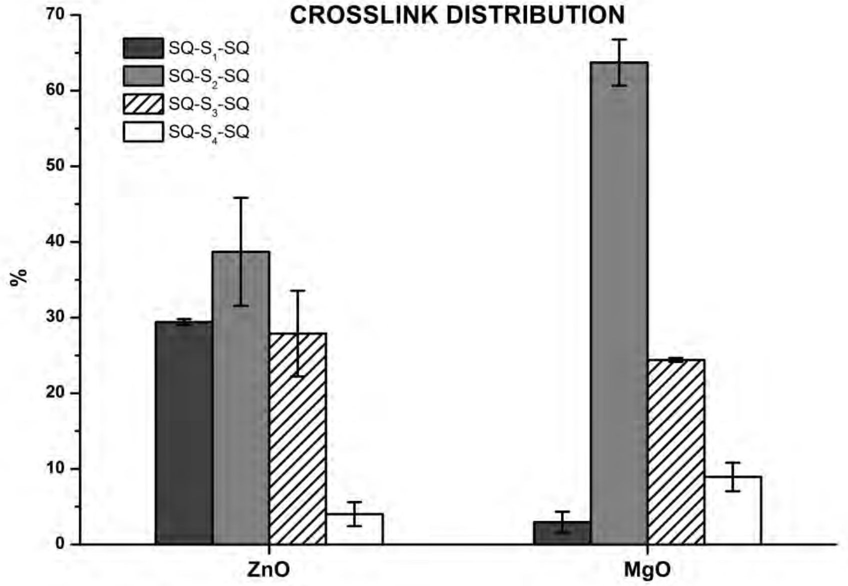

Figure 3.11. Distribution of sulphidic cross-links in 60 minutes vulcanisates with ZnO and MgO.

The longer sulphidic cross-links formed with MgO can also be attributable to the fact that MgO is limiting or preventing the desulphuration, presumably by restricting formation of accelerator complexes or other desulphurating agents that are formed in the absence of ZnO. On the contrary, ZnO shows shorter cross-links because, as it has been reported[25, 26], zinc accelerator complexes promote desulphuration of cross-links. The shortening of crosslink is often accompanied by changes in the positions of sulphur attachment to the chain. The polysulphide cross-links are initially mostly allylic attachments, but these structures can be gradually rearranged as the reaction progresses. Zinc accelerator complexes catalyses the cross-link shortening and the allylic rearrangements via nucleophilic reactions reactions[27, 28].

In summary, it has been shown that the mechanism of sulphenamide accelerated vulcanisation with MgO as the activator differs greatly with the route that it is followed when ZnO is the activator. The presence of sulphur is a necessary condition for the breakdown of the accelerator and not the presence of unsaturations in the hydrocarbon chain as occurs with ZnO. Furthermore, the incapability of magnesium oxide to form complexes with the accelerator and the cross-link precursors leads to a lower cross-linking degree due to less cross-link precursors are obtained after the cross-linked is formed. In addition, this lack of complexes formation protected the cross-links formed from desulphuration.

From the results, it is clear that MgO cannot be considered to substitute zinc oxide. In spite of this, it has been proven to be a potential substance to reduce ZnO. Its ability to form active sulphurating agents even faster than ZnO provides not only the possibility to reduce the zinc oxide levels in rubber compounds but to improve the cure characteristics. However, it has been reported that a mixture of ZnO and MgO has an intermediate behaviour between the two extremes and little amounts of MgO are enough to cause a decrease in the cross-link density[29].

In order to take advantage of the behaviour of both ZnO and MgO in sulphur vulcanisation and overcoming the disadvantages of the simple mixture, novel activators have been synthesised and tested. The methods employed to synthesise these pioneering activators and their performance in MCV and with different rubbers will be described in the following chapters.

3.4. SUMMARY

The model compound studies have demonstrated that the differences observed between ZnO and MgO are caused by the different mechanisms that the reaction follows.

When MgO is the accelerator, the breakdown of the accelerator and the consumption of sulphur occur faster, whether or not there are double bonds in the hydrocarbon chains. However, when sulphur is removed, the accelerator does not react. Therefore, it is the interaction of MgO with sulphur which provokes a faster breakdown of the accelerator to form the active sulphurating agents.

In spite of that, MgO does not form complexes with these species which causes a decrease of the cross-linking degree achieved. The cross-linked products formed contain longer sulphur chains because MgO does not form complexes with the cross-link precursors either. The sulphur-sulphur bond adjacent to the benzothiazole group in the cross-link precursor breaks leading to a polysulphidic cross-link and a pendant group that is not a new cross-link precursor and this produces a reduction of the cross-link density.

3.5. REFERENCES

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Chapter 4

MIXED METAL OXIDES AS ACTIVATORS FOR SULPHUR VULCANISATION: SYNTHESIS AND EVALUATION BY MODEL COMPOUND VULCANISATION[#]

'La verdadera ciencia enseña, por encima de todo, a dudar y a ser ignorante.'
(True science teaches, above all, to doubt and to be ignorant)
Miguel de Unamuno (1864 - 1936)

To reduce the ZnO levels in rubber compounds, mixed metal oxide nanoparticles of zinc and magnesium ($Zn_{1-x}Mg_xO$) have been synthesized and used as activator. The aim is to obtain better curing properties due to its nanosize and to take advantage of the different behaviour of both ZnO and MgO in sulphur vulcanisation that has been revealed in Chapter 3. The model compound vulcanisation approach with squalene as a model molecule for NR and CBS as accelerator has been used to study the role of the mixed metal oxide along the reaction. The results found show that with $Zn_{1-x}Mg_xO$ nanoparticles the reaction of CBS becomes faster, higher amounts of MBT are formed at shorter reaction times, and the consumption of sulphur occurs faster in comparison with standard ZnO. Furthermore and more important, an increased cross-link degree calculated as the total amount of cross-linked squalene is obtained. All these findings indicate that the mixed metal oxide $Zn_{1-x}Mg_xO$ is a promising candidate to reduce the ZnO levels in rubber compounds.

4.1. INTRODUCTION

Zinc oxide is a widely used compound in rubber industry due to the excellent properties that shows as activator for sulphur vulcanisation. The tyre industry remains the largest single market for ZnO, consuming more than half of the total worldwide demand of

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[#] Part of this work has been presented at the 176th Technical meeting - Rubber Division, ACS, October 13-15, 2009, in Pittsburgh, PA USA; and has been publsihed in the Journal of Applied Polymer Science: Guzmán, M.; Reyes, G.; Agulló, N.; Borrós, S. *J. Appl. Polym. Sci.* **2011**, 119, (4), 2048.

1,200,000 metric tons[1]. Traditionally, ZnO is used in rubber formulations in concentrations of 3-8 parts per hundred rubber (phr).

Over the years lower levels of zinc have been tried in order to decrease the environmental impact of the rubber goods and to minimise the production costs. Ducháček[2] studied the effect of zinc oxide concentration on the course of thiuram-accelerated sulphur vulcanisation of NR and concluded that the optimum zinc oxide content in the rubber mix corresponds generally to 2.5 phr. At this concentration, or even at 1.5 phr, the extent of vulcanisation was comparable to 5 phr but the extent of reversion is significant if the less than 2.5 phr are used, especially when sulphur is employed at 1.5 phr or higher proportions. These results are in very good agreement with the optimum values of ZnO concentration found for sulphenamides by others authors[3]. Any small reduction in modulus can be compensated by slightly increasing the level of accelerators.

Chapman *et al.*[4] found that 2 phr of ZnO could be used in ethylene-propylene-diene rubber (EPDM) without affecting properties. In NR, with CBS as accelerator, further reductions till 1.5 phr could be employed if antireversion agents are added to the mixture. The authors also suggested that in SBR/BR compounds the reduction could be even greater.

Noordermeer *et al.*[5] obtained very similar results with EPDM using TMTD as accelerator and MBT as secondary accelerator and with SBR using TBBS as accelerator. They found that the cure characteristics and physical properties of compounds do not change significantly with levels of 1 phr or more of ZnO in SBR and 2 phr or more in EPDM.

Furthermore, different approaches have been considered for reducing zinc levels. Between all the alternatives proposed, the use of nano-sized ZnO particles with high surface area seems to be promising. Bhowmick *et al.*[6, 7] studied the effect of ZnO nanoparticles (50 nm) as cure activator in natural rubber (NR), acrylonitrile-butadiene rubber (NBR) and polychloroprene rubber (CR). They found that the maximum torque value increased and the tensile strength was improved significantly. An increase in cross-linking density and a decrease in the swelling ratio were also found.

Joseph *et al.*[8] found that a low dosage of zinc oxide nanoparticles was enough to give equivalent curing and mechanical properties to NR compared to the one containing a higher dosage of conventional zinc oxide.

Parasiewicz *et al.*[9] investigated the effect of different concentrations of ZnO nanoparticles (100 nm) in isoprene rubber (IR) and styrene-butadiene rubber (SBR). They reported that the reduction of ZnO content to 2 phr resulted in shortening of scorch and optimal vulcanisation time but the extent of cure was on the same level. The mechanical properties did not vary significantly when using active or standard ZnO. They attributed the small differences between active ZnO and standard ZnO despite its nine times higher specific surface area to the poorer dispersion of the active ZnO and its tendency to form agglomerates.

Chapman[10] examined the impact of high surface area/small particle size zinc oxide in sulphur vulcanisation of NR, EPDM and SBR. It was found that the use of more active forms of zinc oxide did not substantially reduce further the minimum zinc content that can be achieved with conventional zinc oxide, contrary to other suggestions in the literature. However, the dispersion of high surface area ZnO during mixing was found to be significantly better, which could enable low levels of this zinc oxide to be used in industry with more confidence. It was also reported a slight increase of scorch delay.

Noordermeer *et al.*[5] studied the influence of active ZnO (0.1-0.4 µm) and nano-ZnO (20-40 nm) in SBR. Their results are similar to those mentioned above for active ZnO; it apparently had a negligible influence on the cure characteristics and physical properties. However, they concluded that only one-tenth of the amount of nano-ZnO is necessary to achieve the same cure characteristics in comparison with conventional ZnO.

Thus, the use of ZnO nanoparticles as activator for sulphur accelerated vulcanisation seems a good proposal for reducing the zinc levels despite some contradictory results previously explained.

Another approach considered for reducing zinc levels is the used of zinc complexes. Several proposals have been suggested: zinc complex with 18-crown-6-ether[9, 11], zinc monomethacrylate[12], the so called ZnClay[13, 14], zinc stearate, zinc-2-ethylhexanoate, zinc borate and zinc-m-glycerolate[15]. Although some proposals look very interesting, the limited amount of data available and their limitation in most cases only to some types of rubber compounds have restricted their industrial application.

Finally, using other oxides as activators for rubber vulcanisation was also studied as alternative to ZnO. Several metal oxides have been used, CaO, MgO, CdO, CuO, PbO and NiO. Among them, MgO is the most promising candidate.

Borrós *et al.*[16] studied the role of MgO using the model compound vulcanisation (MCV) approach with squalene as a model molecule for NR and CBS. They found that the breakdown of the accelerator occurs faster with MgO but higher cross-link degree is obtained with ZnO.

These results are in good agreement with those found by Noordermeer *et al.*[17] using model molecules and N-t-butylbenzothiazole-2-sulphenamide (TBBS). They observed that when using MgO the accelerator dissociates very rapidly and cross-linked products are formed faster. However, the cross-links are formed to a higher extent with ZnO.

These authors also compared the effect of different metal oxides with EPDM[5] and SBR[5, 14]. In EPDM with tetramethylthiuram disulphide (TMTD) as accelerator, none of the metal oxides studied was as active as ZnO. In SBR with TBBS as accelerator, the substitution of ZnO by MgO did not cause large effects on the cure and physical properties. The scorch times were comparable with the reference compound with ZnO, but the rates of cure were to a certain extent lower. The extent of cross-linking of the compounds was slightly lower although, in contrast with ZnO, at longer vulcanisation times no decrease or reversion was observed.

In another paper by Borrós *et al.*[18] the effect of different activators by MCV using microwave heating was studied. They concluded that both zinc oxide and magnesium oxide react with similar kinetics when microwave emission is applied. A synergetic effect between magnesium and zinc oxides was observed when using a mixture of them. This effect can also be observed with conventional heating, although they found it was enhanced when using microwaves.

In another report[19] it was found that when mixing ZnO and MgO in NR using CBS as accelerator, MgO cures with good kinetics in comparison with ZnO but the cross-link density obtained is much lower. MgO seemed to have more affinity for sulphur than ZnO due to its ability to form active sulphurating agents more quickly. However, these MgO intermediates were not able to progress to final cross-links with the same ability than ZnO active sulphurating agents. Therefore, when working with mixtures of both oxides, MgO competes with ZnO to react with sulphur, and due to the higher affinity of MgO for sulphur, it takes up part of the sulphur which cannot react to form final cross-links.

In summary, although there is a lack of agreement respect the effect of MgO, mainly caused by the differences in the vulcanising system, magnesium is a non-heavy metal oxide which forms active sulphurating agents. As detailed in Chapter 3, albeit it cannot be considered to substitute zinc oxide, it has been proven to be a potential substance to reduce ZnO. Its ability to form active sulphurating agents even faster than ZnO provides not only the possibility to reduce the zinc oxide levels in rubber compounds but to improve the cure characteristics. However, it affects significantly the cross-link degree, which prevents its use in vulcanisation.

In Chapter 3 it has been shown that the mechanism is different when ZnO or MgO are used as activators. The presence of sulphur is a necessary condition for the breakdown of the accelerator and not the presence of unsaturations in the hydrocarbon chain as occurs with ZnO. In spite of that, the incapability of magnesium oxide to form complexes with the accelerator and the cross-link precursors leads to a lower cross-linking.

In this work, a new approach to overcome the problems between ZnO and MgO is presented. It consists in the development of a new activator based in the mixture of both oxides at nanoscale. The new activator is nanometer-sized mixed metal oxide (MMO) of zinc and magnesium ($Zn_{1-x}Mg_xO$) with very precise stoichiometry prepared by a polymer-based method. In this activator, magnesium is incorporated into the ZnO structure and this inclusion is presumed to show a better performance. The aim is to gain benefit from the two different approaches indicated before: to obtain better curing properties due to its nano-size and to take advantage of the behaviour of both ZnO and MgO in sulphur vulcanisation.

4.2. EXPERIMENTAL

4.2.1. MATERIALS

Poly (acrylic acid) (PAA) (Poly (acrylic acid) partial sodium salt solution, average Mw ~5000, 50 wt. % in H_2O), magnesium nitrate hexahydrate, $Mg(NO_3)_2 \cdot 6H_2O$, zinc nitrate hexahydrate, $Zn(NO_3)_2 \cdot 6H_2O$, and ammonium hydroxide (30 wt %) were obtained from Sigma-Aldrich. Squalene (Fluka, 97 %), sulphur (Julio Cabrero & Cia, S.L.), CBS (Flexsys), zinc oxide (Zincsa), and stearic acid (Calià&Parés) were used for the model compound studies. Solvents used in the investigation were all HPLC grade: Acetonitrile (J. T. Baker); 2-propanol and n-hexane (Panreac).

4.2.2. SYNTHESIS OF ZINC/MAGNESIUM OXIDE ($Zn_{1-X}Mg_XO$) NANOPARTICLES

Zinc/magnesium oxide nanoparticles were prepared following the method reported by Wegner *et al.*[20]. Basically, the method consists on the preparation of a polymer/metal salt complex that is water-soluble, its purification by precipitation/redissolution cycles and finally the calcination of the dried purified complex to give nanosized particles.

The method for obtaining $Zn_{1-x}Mg_xO$ nanoparticles, depicted in Figure 4.1, is as follows. A certain amount of poly(acrylic acid) prepared by freeze drying and $Zn(NO_3)_2{\cdot}6H_2O$ to obtain at least a four-fold molar excess of carboxylic groups compared to zinc are dissolved in water.

Once it is dissolved, nitrogen is bubbled through the solution to remove carbon dioxide for about 10 min. Then, ammonium hydroxide is added dropwise to adjust the pH to 7. The reaction mixture is concentrated in a heating magnetic stirrer. The residual viscous liquid is dropped into acetone and a colourless precipitate is formed. This precipitate is collected by centrifugation, washed with acetone and dried at 40 °C in vacuum.

This material is redissolved in water and mixed with a solution of the desired amount of magnesium nitrate. The pH is also adjusted to 7 with ammonia. The mixed solution is concentrated and then poured dropwise into acetone. The precursor material, a polymer/metal salt complex, is collected by centrifugation, washed with acetone, and dried in vacuum.

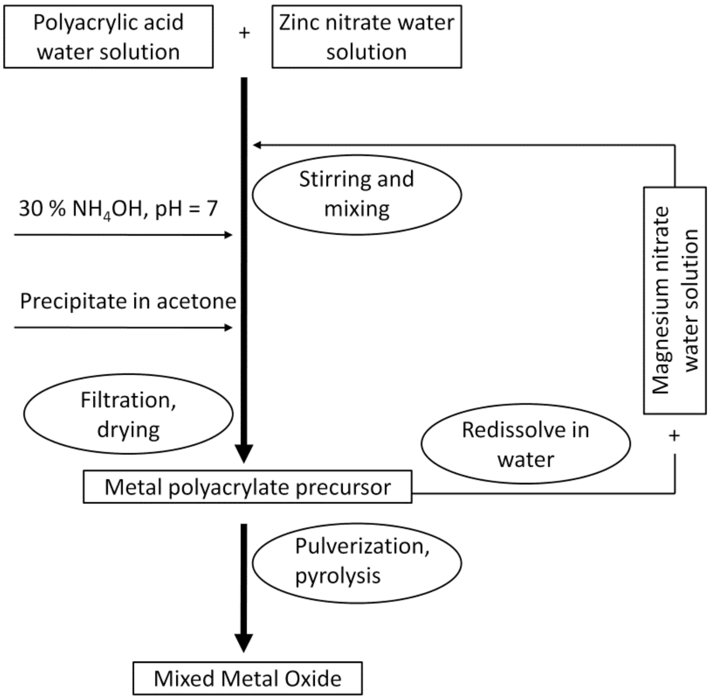

Figure 4.1. Synthesis mixed metal oxides powders of zinc/magnesium by pyrolysis of mixed metal polyacrylates[20].

Following, it is milled into a fine powder and then calcined in a temperature-controlled oven under air flow at a heating rate of 5 °C/min^{-1} to 550 °C. The sample is isothermally annealed for 1 h at this temperature.

$Zn_{1-x}Mg_xO$ nanoparticles with 20 % in weight of magnesium with respect to the total amount of metal (x of 0.40 in moles) were prepared.

4.2.3. CHARACTERISATION OF ZINC/MAGNESIUM OXIDE ($Zn_{1-x}Mg_xO$) NANOPARTICLES

Scanning Electron Microscope (Jeol JSM-5310), along with Energy Dispersive Spectroscopy, was used to measure the magnesium and zinc content in the mixed metal oxide. X-Ray diffraction (Philips X'Pert) was employed to elucidate the crystal structure of $Zn_{1-x}Mg_xO$. The data obtained was refined with CELREF[21] to determine the lattice parameters of $Zn_{1-x}Mg_xO$. In this work, Zetasizer Nano ZS™ (Malvern Instruments Ltd) was employed to measure the particle size of the $Zn_{1-x}Mg_xO$ particles. The Brunauer-Emmett-Teller (BET) specific surface areas (S_{BET}) were evaluated on the basis of nitrogen adsorption isotherms measured at 77 K using a nitrogen adsorption apparatus (BELSORP-max, BEL, Japan). All the samples were degassed at 150 °C before nitrogen adsorption measurements. The BET surface area was determined using the adsorption data in the relative pressure (P/P_0) range of 0.05-0.35.

4.2.4. MODEL COMPOUND VULCANISATION

Model compound vulcanisation with squalene as a model molecule for natural rubber has been chosen to study the role of the mixed metal oxide along the reaction using CBS as accelerator. The basic vulcanisation recipe is given in Table 4.1. The work was performed using the same concentration of ZnO and $Zn_{1-x}Mg_xO$, 5 phr.

Table 4.1. Model Compound Vulcanisation Recipes (phr).

Ingredients	Mixture A	Mixture F
Squalene	100	100
CBS	1.2	1.2
Sulphur	2	2
ZnO	5	–
$Zn_{1-x}Mg_xO$	–	5
Stearic acid	2	2

The reaction for all formulations was performed in a preheated thermostatic oil bath at 140 °C for 60 minutes. The reaction is carried out in different vessels under nitrogen environment in order to avoid the oxidation of the double bonds of squalene. The model mixtures are continuously stirred to assure its homogeneity. During the reaction, vessels are taken from the oil bath at different pre-set times and quickly cold quenched in dry ice to stop the reaction. After cooling, the vessels were covered to avoid any UV influence, and stored in a refrigerator.

All the model compound vulcanisation mixtures were characterized by two analytical methods of HPLC coupled to an UV detector to cover both aspects of the process: the fading of the accelerator and the formation of cross-links between the model molecules. The identification of the different compounds (CBS, MBT, MBTS, sulphur, squalene and the different cross-linked squalenes) was carried out earlier in our research group using different techniques[18, 22-26].

4.3. RESULTS AND DISCUSSION

4.3.1. SYNTHESIS AND CHARACTERISATION OF $Zn_{1-x}Mg_xO$ NANOPARTICLES

As it has been described previously, mixed metal oxides of zinc and magnesium have been synthesised using a polymer-based method. Energy Dispersive Spectroscopy has been employed to measure the actual content of zinc and magnesium in the oxide. The results indicate that there is a 24 % in weight of magnesium with respect to the total amount of metal (x equals to 0.46 in moles). The theoretical magnesium content is lower than the actual value achieved. This higher Mg content may be caused by the losses of material that occur during the precipitation and redissolution cycles. In the synthesis, poly(acrylic acid) and zinc nitrate are firstly dissolved in water and then purified by precipitation with acetone. This material is then dissolved again in water to be mixed afterwards with magnesium nitrate. During the first purification, where only Zn and not Mg is present, part of the material could not be recovered and, subsequently, the final content of magnesium is slightly higher than expected.

Dynamic Light Scattering was used to measure the particle size. $Zn_{1-x}Mg_xO$ has a particle size of 147 ± 32 nm. Nitrogen adsorption-desorption experiments show that $Zn_{1-x}Mg_xO$ particles exhibit a BET surface area of 27.2 ± 0.4 m^2/g.

X-Ray diffraction was employed to characterise the crystal structure of the mixed metal oxide particles. Figure 4.2 shows the X-ray diffraction patterns of the oxide products obtained in the synthesis. The patterns of the pure ZnO are indexed according to the known hexagonal phase (zincite)[27], and that of MgO is indexed according to its cubic phase (periclase)[28]. The vertical lines correspond to the standard reflections of the ZnO phase and the dashed vertical lines are the standard reflections of the MgO phase. The MgO planes are indicated with a star. Empty circles corresponds to the expected intensity of the ZnO peaks with respect to the maximum peak observed (1 0 1). Filled circles corresponds to the expected intensity of the MgO peaks with respect to the maximum peak observed (2 0 0).

The scans showed a weak (2 0 0) reflection of the MgO phase which is an indication that the material is mostly present in the hexagonal phase (zincite) and that magnesium has been incorporated into the ZnO structure. However, the presence of the (2 0 0) peak indicates the coexistence of the two phases, zincite and periclase; although the intensity of the peaks implies that the majority of the material was in the form of zincite.

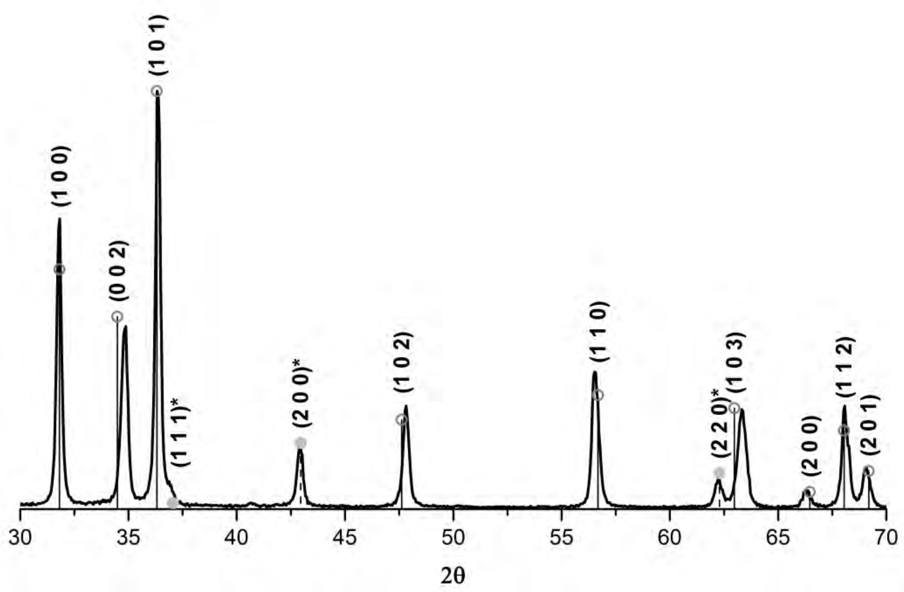

Figure 4.2. XRD patterns of $Zn_{1-x}Mg_xO$. Vertical lines correspond to the standard reflections of the ZnO phase and dashed vertical lines are the standard reflections of the MgO phase which planes are designated with a star. Empty circles indicate the expected intensity of the ZnO peaks regarding its maximum peak observed (1 0 1). Filled circles designate the expected intensity of the MgO peaks regarding its maximum peak observed (2 0 0).

The magnesium content at which the (2 0 0) and (2 2 0) diffraction peaks of the MgO cubic phase employing a polymer-based method seems be lower than the values reported on the literature by different authors using other methods. Geng *et al.*[29] found that for $x < 0.25$, only metastable $Zn_{1-x}Mg_xO$ was formed and Wang[30] reported a value of $x \leq 0.30$. Ohtomo *et al.*[31] and Zhang *et al.*[32] obtained that no cubic phase was formed if the magnesium content was lower than 0.33 and 0.39, respectively. Using the same polymer-based method, other authors[20] obtained that the cubic phase was formed if the magnesium content was higher than 0.21. In addition, it is worth noting that no data was reported for the range of $0.12 \leq x \leq 0.21$. These results could be due to the different preparation methods used and the adhesion to the substrate in the laser deposited films or in the thin films grown by metal-organic chemical vapour deposition. These deviations could also be caused by variations in the calcination process such as the air flow in the oven and the amount of powder annealed.

It can be seen in Figure 4.2 that the diffraction peaks (0 0 2), (1 0 2) and (1 0 3) have shifted to higher diffraction angles compared to those of the hexagonal structure of ZnO[27]. These shifts are caused by the substitution of Zn atoms by Mg atoms in the hexagonal phase and lead to a decrease of the *c*-axis lattice constant (5.1648 ± 0.0050 Å instead of 5.2066 Å). As magnesium replaces zinc in the hexagonal phase, due to the smaller radius of Mg^{2+} (0.57 Å) than Zn^{2+} (0.60 Å)[33], there is a shrinking of the lattice constant along the *c*-axis and a displacement of the diffraction peaks to higher angles.

On the contrary, as Mg incorporates into the structure, the *a*-axis lattice constant increases slightly (3.2533 ± 0.0023 Å instead of 3.2498 Å). The lattice parameters were calculated using CELREF[21]. These findings differ from the values reported by other researchers[30] but it should be noted that the variation from the standard values of the cell parameters zinc oxide is very small and that the same results were obtained by other authors[20, 31].

Figure 4.2 also shows that the diffraction peaks (2 0 0) and (2 2 0) have shifted to smaller diffraction angles compared to those of the cubic structure of MgO[28]. This is due to the incorporation of zinc into the MgO cubic phase and leads to an increase of the lattice parameter (4.2240 ± 0.0048 Å instead of 4.2112 Å).

4.3.2. $Zn_{1-x}Mg_xO$ NANOPARTICLES AS NEW ACTIVATORS FOR VULCANISATION

Model compound vulcanisation with squalene as a model molecule for natural rubber has been chosen to study the role of the mixed metal oxide along the reaction using CBS as accelerator. The basic vulcanisation recipe has been shown in Table 4.1.

The evolution of CBS, 2-mercaptobenzothiazole (MBT), 2,2'-bisbenzothiazole disulphide (MBTS) and sulphur when using ZnO and $Zn_{1-x}Mg_xO$ as activators is shown in Figure 4.3 and Figure 4.4, respectively. From these figures, it can be established some differences that occur when the new activator is used. $Zn_{1-x}Mg_xO$ nanoparticles provoke a faster consumption of CBS and sulphur, while in the case of ZnO it occurs in a more gradual manner.

The breakdown of the accelerator is one of the most used parameters to study what occurs during the scorch time since it has been demonstrated to be the bottle neck that determines the length of the scorch time[16]. In the case of acceleration by sulphenamides, the accelerator is depleted autocatalytically with the formation of MBT[34]. The MBT formed from the breakdown of CBS react with CBS to form the active sulphurating agents and the rate of the CBS depletion's is about proportional to the amount of MBT present.

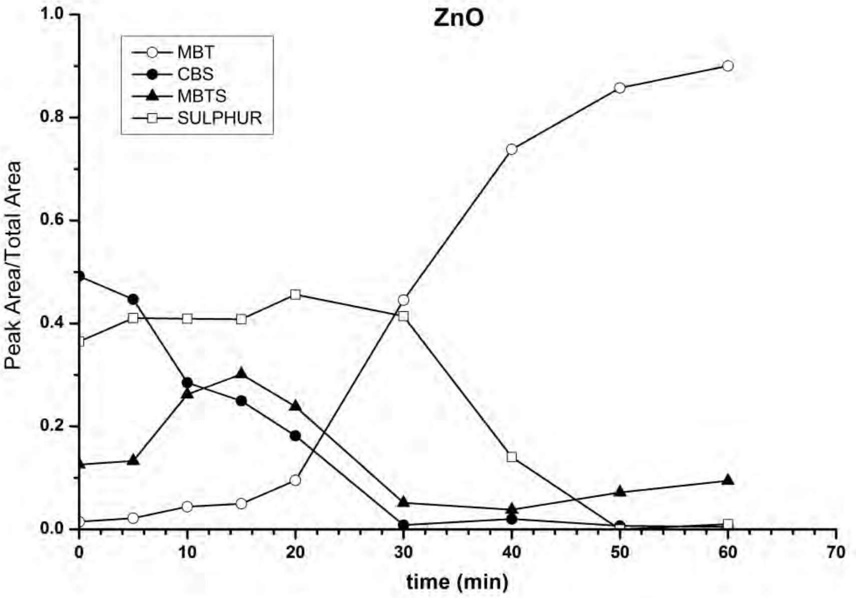

Figure 4.3. Relative amount of major compounds as a function of reaction time during squalene vulcanisation with sulphur and CBS at 140 °C using ZnO as activator.

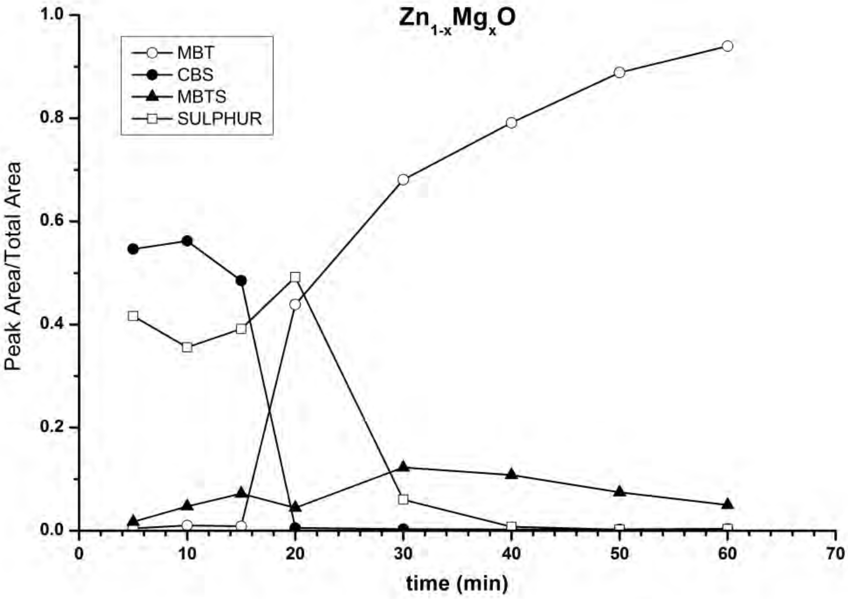

Figure 4.4. Relative amount of major compounds as a function of reaction time during squalene vulcanisation with sulphur and CBS at 140 °C using $Zn_{1-x}Mg_xO$ as activator.

Figure 4.5 shows the CBS concentration in the samples with ZnO and with $Zn_{1-x}Mg_xO$ as a function of the reaction time. It can clearly be seen, that the utilization of ZnO or $Zn_{1-x}Mg_xO$ as activators influences the breakdown of CBS differently. When $Zn_{1-x}Mg_xO$ nanoparticles are used, CBS is completely degraded after 20 minutes while, with standard ZnO, there is around 40 % of unreacted CBS which does not disappear entyrely until 30 minutes as reported earlier[16-18, 22, 35]. It can be seen that the breakdown of the accelerator does not commence very differently when using $Zn_{1-x}Mg_xO$ or zinc oxide but that the mixed metal oxide provokes a much faster disappearance of CBS.

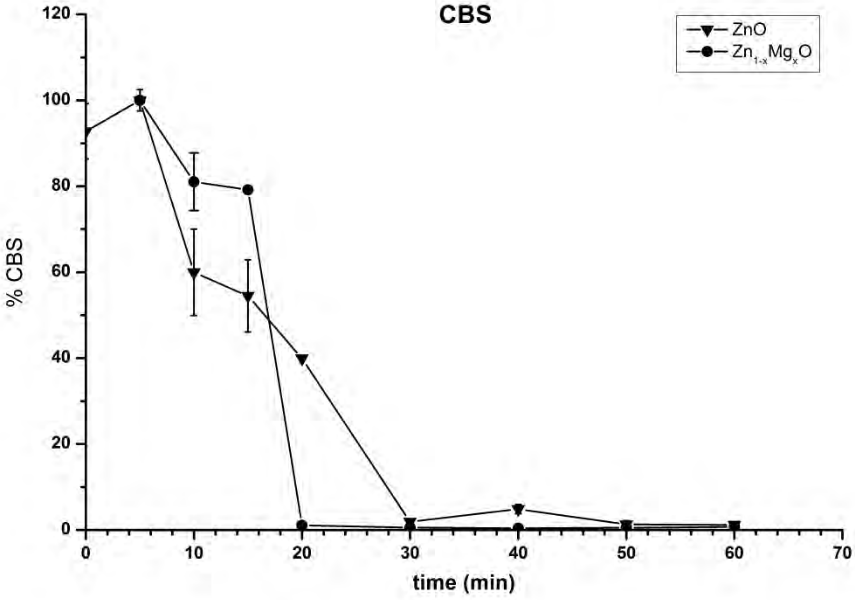

Figure 4.5. Breakdown of CBS as a function of the reaction time with $Zn_{1-x}Mg_xO$ and ZnO as activator.

Furthermore, it is interesting to study the decomposition of the accelerator with respect to the evolution of sulphur and MBT in order to understand the reactions taking place during the scorch time and before the cross-link formation. Decomposition of the accelerator and transformation of the cross-link precursor into a cross-link yields to MBT.

As it can be seen in Figure 4.6, $Zn_{1-x}Mg_xO$ nanoparticles lead to higher amounts of MBT at shorter reaction times. Since MBT is a decomposition product of the accelerator and the breakdown of the accelerator occurs faster when the activator are the mixed metal oxide nanoparticles, it is not surprising to observe that the formation of MBT is more rapidly with $Zn_{1-x}Mg_xO$ than zinc oxide.

Figure 4.7 shows that the consumption of sulphur occurs faster when $Zn_{1-x}Mg_xO$ nanoparticles are used as the accelerator. At 30 minutes it has almost disappeared. For standard ZnO, it is not until 50 minutes when it has been totally consumed. Furthermore, the fading of sulphur with $Zn_{1-x}Mg_xO$ is faster compared with the values that have been reported before with MgO[16] and seen in Chapter 3.

Previous researchers have described that, when ZnO is substituted by MgO, CBS is dissociated very rapidly and that MgO produces higher amount of MBT at shorter reaction times[16]. It has been proposed that the quicker dissociation of the accelerator is most likely to occur due to less complex formation between the magnesium ions and MBT occurs[17].

Another explanation to this behaviour has been postulated in Chapter 3. It has been found that when sulphur was not present in the reaction mixture, the breakdown of the accelerator is much slower. From these results it was concluded that the dissociation of CBS occurs via sulphur activation from magnesium oxide.

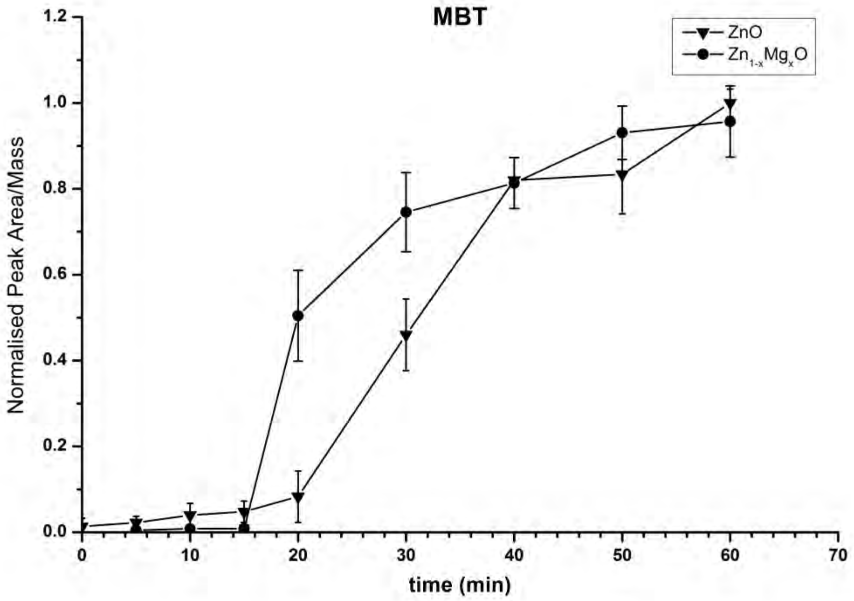

Figure 4.6. MBT concentration as a function of the reaction time with $Zn_{1-x}Mg_xO$ and ZnO as activator.

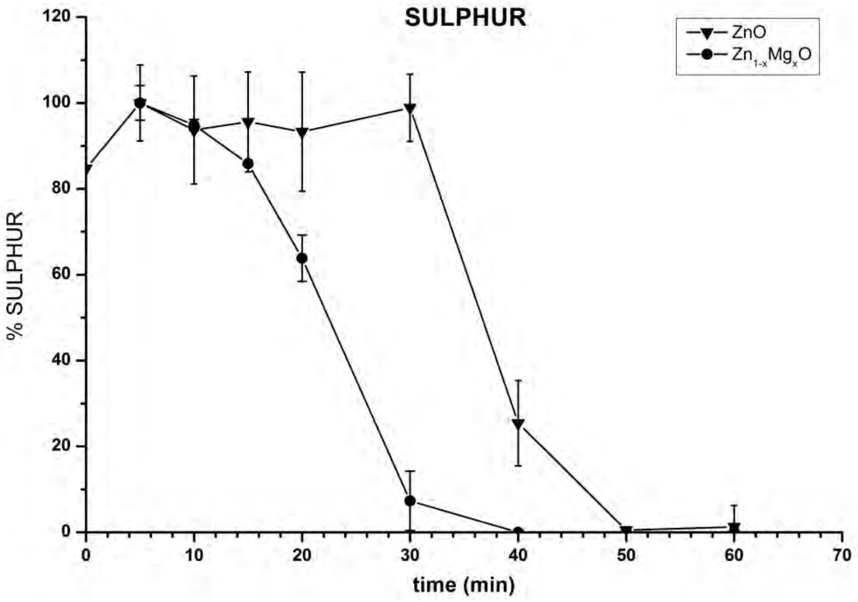

Figure 4.7. Degradation of sulphur during vulcanisation with standard ZnO and $Zn_{1-x}Mg_xO$.

The fact that $Zn_{1-x}Mg_xO$ nanoparticles dissociate CBS faster and produce higher amounts of MBT at shorter reaction times means that the CBS dissociation occurs by a different mechanism than with zinc oxide. Since the breakdown of the accelerator and the formation of MBT with $Zn_{1-x}Mg_xO$ is more similar to the manner that occurs when MgO is used, as it has been reported before[16, 17] and seen in Chapter 3, it can be deduced that the presence of magnesium into the zinc oxide structure alter ZnO performance. Furthermore, the consumption of sulphur takes place faster with $Zn_{1-x}Mg_xO$ than with ZnO or MgO indicating that $Zn_{1-x}Mg_xO$ nanoparticles provoke a faster reaction of sulphur with the accelerator.

The evolution of cross-linked squalene during vulcanisation with ZnO or $Zn_{1-x}Mg_xO$ as activator is shown in Figure 4.8. It can be noted that even though the formation of cross-linked squalene commences slightly later when $Zn_{1-x}Mg_xO$ nanoparticles are used, a higher cross-link degree, calculated as the total amount of cross-linked squalene formed, is attained. These findings are in agreement with the results reported before. Chapman[10] found that when high surface area/small-particle size zinc oxides were used scorch delay was increased a little; and Parasiewicz *et al.*[9] found that the use of ZnO nanoparticles resulted in a slightly longer scorch time. However, the curve reaches its maximum faster with $Zn_{1-x}Mg_xO$, which is an indication that in real rubber the reaction would be faster than with ZnO.

Regarding the cross-link degree achieved, it is worth noting that $Zn_{1-x}Mg_xO$ lead to around a 30 % higher cross-link degree than with standard zinc oxide. This effect can be partly attributed to the small particle size that $Zn_{1-x}Mg_xO$ particles show. Bhowmick *et al.*[6, 7] found that ZnO nanoparticles (30-70 nm) increased the cross-link degree by 15 % compared with standard ZnO. On the other hand, the fact that, even with bigger sizes, higher amounts of cross-linked products are formed suggests that $Zn_{1-x}Mg_xO$ nanoparticles are more active and more effective transporting sulphur into the hydrocarbon chain than ZnO nanoparticles. Furthermore, these results indicate that the incorporation of magnesium into the structure or the alteration of the network cause by this insertion is more important than the size.

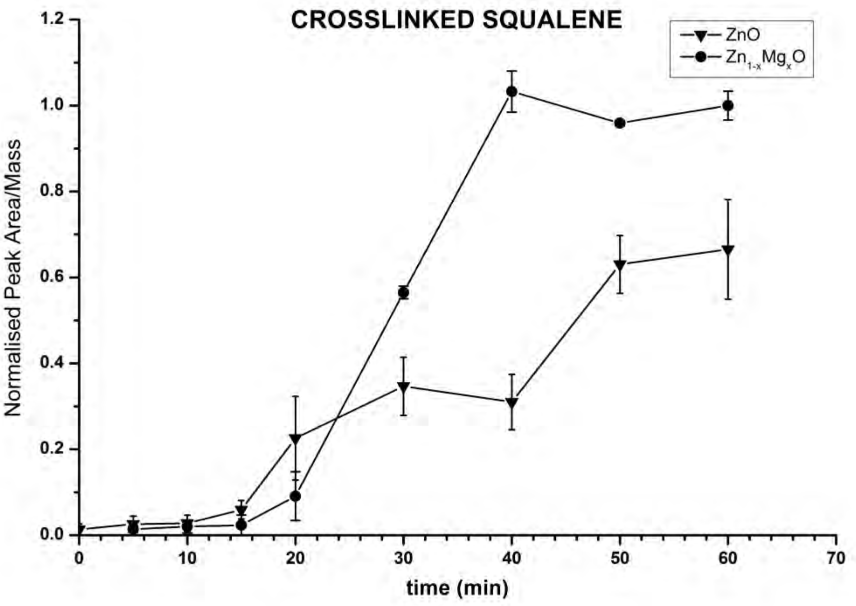

Figure 4.8. Evolution of total cross-linked squalene during vulcanisation with standard ZnO and $Zn_{1-x}Mg_xO$.

As stated before, when MgO is used as activator the accelerator is dissociated very rapidly and a large quantity of intermediate compounds are formed but its main drawback is the low reticulation degree achieved[16, 17]. The fact that the breakdown of the accelerator and the consumption of sulphur occur faster but cross-linked products appear later, indicate that larger amounts of intermediate compounds that are active sulphurating species are produced when the activator is $Zn_{1-x}Mg_xO$.

Concerning the cross-link structure, some changes were detected when working with $Zn_{1-x}Mg_xO$ in comparison with ZnO as it has been pointed out in previous sections. Figure 4.9 shows the different cross-linked products formed in 60 minutes vulcanisates: mono- (*Sq-S-Sq*), di- (*Sq-S₂-Sq*), tri- (*Sq-S₃-Sq*) and tetrasulphidic (*Sq-S₄-Sq*) cross-links. $Zn_{1-x}Mg_xO$ nanoparticles provoke that the major cross-linked products formed are disulphidic cross-links and that very little amount of monosulphidic cross-links are produced. The main effect of the mixed metal oxide seems to be the decrease of monosulphidic cross-links by an increase in the formation of disulphidic cross-links. However, the proportion of tri- and tetrasulphidic cross-links is not altered by the use of $Zn_{1-x}Mg_xO$ nanoparticles as activator.

In summary, the results obtained have shown that it is possible to take advantage of the behaviour of both ZnO and MgO in sulphur vulcanisation with $Zn_{1-x}Mg_xO$ nanoparticles. It has been seen that the reactions that take place during the scorch time, the breakdown of the accelerator and the formation of MBT, occur faster; fact that could be due to the presence of magnesium into the zinc oxide structure.

On the other hand, the formation of the cross-links start at longer reaction times, feature reported by other authors using zinc oxide nanoparticles. Nevertheless, the cross-link degree achieved is higher than those obtained with zinc oxide nanoparticles. Furthermore, the mixture of ZnO and MgO shows a cross-link degree similar to the one obtained with magnesium oxide[36]. Therefore, $Zn_{1-x}Mg_xO$ nanoparticles not only overcome the disadvantages of the mixture of ZnO and MgO but a better performance is achieved.

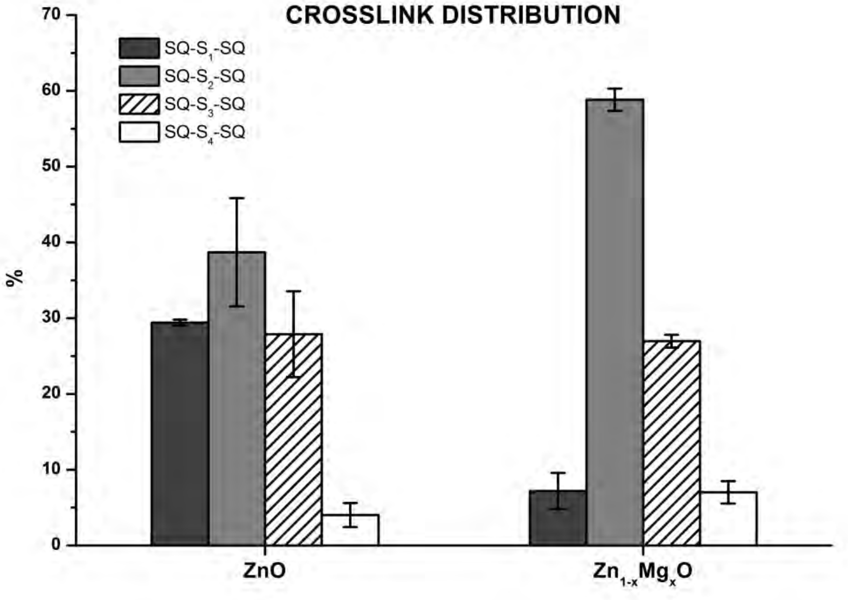

Figure 4.9. Distribution of cross-links (cross-link structure) in 60 minutes vulcanisates with ZnO and $Zn_{1-x}Mg_xO$.

Moreover, the use of $Zn_{1-x}Mg_xO$ nanoparticles as activator lead to a reduction of the total amount of zinc used in rubber compounds due to the presence of magnesium into the zinc oxide structure. This characteristic could minimise the environmental effect of rubber compounds, which is a major concern in the rubber industry.

4.4. SUMMARY

Mixed metal oxides nanoparticles of zinc and magnesium have been synthesised with a particle size of 147 ± 32 nm and a BET surface area of 27.2 ± 0.4 m^2/g. The X-ray diffraction patterns have proved that magnesium atoms incorporate into the zinc oxide structure altering the lattice parameters.

Model compound vulcanisation with squalene has been carried out to study the role of the mixed metal oxide along the reaction using CBS as accelerator. Concerning the reactions that take place during scorch time, it has been proved that the presence of magnesium into the zinc oxide structure modifies the manner that ZnO performs. The breakdown of the accelerator and the formation of MBT are faster with $Zn_{1-x}Mg_xO$ and more similar to the manner that occurs when MgO is used. The consumption of sulphur takes place faster with $Zn_{1-x}Mg_xO$ than with ZnO or MgO.

The formation of cross-linked squalene commences later when $Zn_{1-x}Mg_xO$ nanoparticles are used but a 30 % higher cross-link degree is attained. These results prove that $Zn_{1-x}Mg_xO$ nanoparticles are more active and more effective transporting sulphur into the hydrocarbon chain than ZnO. $Zn_{1-x}Mg_xO$ nanoparticles not only overcome the disadvantages of the mixture of ZnO and MgO but a better performance is achieved.

Regarding the cross-link structure, the mixed metal oxide produces a decrease of monosulphidic cross-links and an increase of disulphidic cross-links. The proportion of tri- and tetrasulphidic cross-links is not altered by the use of $Zn_{1-x}Mg_xO$ nanoparticles as activator.

In summary, the use of $Zn_{1-x}Mg_xO$ nanoparticles as activator leads to a reduction of the total amount of zinc used in rubber compounds which would reduce the environmental impact of the rubber industry.

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Chapter 5

EFFECT OF MIXED METAL OXIDES AS ACTIVATORS FOR SULPHUR VULCANISATION OF VARIOUS RUBBERS

> *'By all means let's be open-minded, but not so open-minded that our brains drop out.'*
> *Richard Dawkins (1941 –)*
> *"Science, Delusion and the Appetite for Wonder" (1996)*

In Chapter 4 it has been found that the mixed metal oxide $Zn_{1-x}Mg_xO$ is a promising candidate to substitute zinc oxide. In this chapter two mixed metal oxides are used as activator in conventional vulcanisation systems: $Zn_{1-x}Mg_xO$ and a new mixed metal oxide of zinc and calcium ($Zn_{1-x}Ca_xO$-like). The aim is to reduce the ZnO levels in natural rubber, cis-butadiene rubber and solution styrene-butadiene rubber compounds. The results found indicate that these oxides are good candidates to substitute ZnO. The use of $Zn_{1-x}Mg_xO$ not only drops the Zn content, but the cure characteristics are accelerated. Moreover, the mechanical properties and cross-link density of the compounds are not deteriorated and, in certain cases, even enhanced. With $Zn_{1-x}Ca_xO$-like it is also possible to use lower zinc loadings. The mechanical properties and cross-link density are not weakened, in some situations are improved, but the cure characteristics are not altered.

5.1. INTRODUCTION

As it has been explained previously, the use of ZnO nanoparticles as activator for sulphur accelerated vulcanisation of NR seems a good proposal for reducing the zinc levels. Several researchers have shown that it is possible to use lower amounts of activator if ZnO nanoparticles are used. Nevertheless, there are some contradictory results in the literature.

Chapman[1] examined the impact of high surface area/small particle size zinc oxide in sulphur vulcanisation of NR. It was found that the use of more active forms of zinc oxide did not substantially reduce further the minimum zinc content that can be achieved with conventional zinc oxide. However, other suggestions in the literature have indicated results contrary to these findings.

Bhowmick *et al*[2]. studied the effect of ZnO nanoparticles (50 nm) as cure activator in natural rubber. They found that the maximum torque value increased and there was substantial improvement in the tensile strength. An increase in cross-linking density and a decrease in the swelling ratio were also found. Joseph *et al.*[3] found that a low dosage of zinc oxide nanoparticles was enough to give equivalent curing and mechanical properties to natural rubber compared to conventional zinc oxide.

Other authors[4] have investigated the effect of modifying the zinc oxide surface using accelerators and fatty acids, which reduces agglomeration of nano particles of ZnO. It was found an improvement in cure and mechanical properties of NR compounds.

In the past years, different research studies have been carried out in order to explore the use of ZnO nanoparticles on SBR and BR with the aim of employing lower amounts of activator. In emulsion SBR compounds Parasiewicz *et al.*[5] found that low levels of zinc oxide can be used. It was reported that 1phr of zinc oxide (standard or active) is enough to vulcanise satisfactorily compounds.

Other authors[6] reported that the properties of carbon black-filled emulsion SBR cured with less than 1.5 phr of zinc oxide (also standard or active) were deteriorated. On the contrary, in solution SBR compounds much greater reductions of zinc oxide are possible, down to 0.5 or even less[1].

The application of active ZnO (0.1-0.4 µm) and nano-ZnO (20-40 nm) in solution SBR was studied by Noordermeer *et al*.[7]. It was found that high reductions could be obtained with nano-ZnO achieving the same cure characteristics in comparison with conventional ZnO. Unfortunately, no physical properties were reported.

Polyethylene glycol (PEG) and poly propylene glycol (PPG) have also been used to modify the surface of standard and nano zinc oxide[8]. It was found that nano-ZnO gave better curing and mechanical properties than standard ZnO in NR/SBR mixtures. PEG and PPG surface-modified ZnO and nano-ZnO produce also superior curing and mechanical characteristics. The improvement was considerably greater in PEG and PPG surface-modified standard ZnO in spite of the lower specific surface area compared to PEG and PPG surface-modified nano-ZnO or nano-ZnO.

Kim *et al*.[9] obtained that in unfilled NR/BR compounds it was possible to reduce significantly the zinc oxide content using ZnO nanoparticles (30–40 nm) with cure characteristics and mechanical properties of the same level. In silica-filled systems the effect was more pronounced. The authors attributed these effects to the increase in the specific surface area of nano-ZnO.

In BR compounds it has been reported[10] that ZnO nanoparticles cause a faster curing compared to the conventional commercial ZnO, improving also the mechanical properties. The enhancement was found to be better if PEG molecules were present on the surface of ZnO particles.

It has been proposed that the greater reductions of the zinc content that can be achieved in BR and SBR compared to NR is because of the differences on the chemistry of accelerated sulphur vulcanisation of these rubbers. In BR and SBR the mechanism seems to be closer to the pathway of unaccelerated sulphur vulcanisation, with less involvement of zinc-accelerator species and the appearance of radical reactions[6, 11].

In Chapter 4 it has been shown that zinc/magnesium oxide ($Zn_{1-x}Mg_xO$) has been proved to be a good candidate to substitute ZnO. Using 5 phr of this compound (25 % reduction of zinc content) a higher cross-link extent has been achieved and at shorter reaction times. The breakdown of the accelerator, the formation of MBT and the consumption of sulphur are faster with $Zn_{1-x}Mg_xO$ and more similar to the manner that occurs with MgO.

From MCV experiments it is clear that $Zn_{1-x}Mg_xO$ nanoparticles not only overcome the disadvantages of the mixture of ZnO and MgO but a better performance is achieved. In MCV the mixture of ZnO and MgO shows a cross-link degree similar to the one obtained with magnesium oxide[12], but in natural rubber the mixtures of MgO and ZnO have an intermediate behaviour between the two extremes. It has been detected that little amounts of MgO are enough to cause a decrease in the cross-link density. The key factor is the presence of MgO rather than the amount of this oxide in affecting the network chain density[13].

In this chapter $Zn_{1-x}Mg_xO$ is tested as activator for sulphur vulcanisation of natural rubber, cis-butadiene rubber and solution styrene-butadiene rubber. The aim is to take advantage of the behaviour of an intimate mixture of ZnO and MgO but eliminating their drawbacks as it has been seen in MCV. The different mixtures are cured with a conventional sulphur/sulphenamide system where the A/S ratio was maintained constant at 0.6. In order to have reference compounds to compare the effect of incorporating $Zn_{1-x}Mg_xO$ into the recipe, ZnO, MgO and a mixture of both have also been used as activators.

Additionally, a new mixed metal oxide is synthesised in this chapter. In this activator calcium is incorporated into the ZnO structure. The aim is to test if this inclusion leads also to a better performance. It will be investigated whether the alteration of the structure caused by the incorporation of another atom or the size and specific surface area of the oxide is the reason which causes the benefits seen. A mixed metal oxide of zinc and calcium has been chosen to carry out this study because CaO is not a good activator in conventional sulphur/sulphenamide cures[14, 15].

With the purpose of having a reference compound to compare the effect of adding zinc/calcium oxide into the recipe, a mixture of ZnO and $CaCO_3$ has also been used as activators. $CaCO_3$ and not calcium oxide has been chosen for the reference compound. As it will be explain in the following sections, in the synthesis of zinc/calcium oxide it has been observed that the calcium atoms that are not incorporated into the ZnO structure form $CaCO_3$.

In this work it will be studied the effects of the new activators in NR, BR and SBR. The cure characteristic and the physical properties will be analysed. Furthermore, the cross-link density will be examined by equilibrium swelling experiment and two different NMR spectroscopy techniques: ^1H NMR relaxation and ^1H double-quantum (DQ) (or more generally multiple-quantum, MQ) NMR experiments.

5.2. EXPERIMENTAL

5.2.1. MATERIALS

Poly (acrylic acid) (PAA) (Poly (acrylic acid) partial sodium salt solution, average Mw ~5000, 50 wt. % in H_2O), magnesium nitrate hexahydrate, $Mg(NO_3)_2{\cdot}6H_2O$, calcium nitrate tetrahydrate, $Ca(NO_3)_2{\cdot}4H_2O$, zinc nitrate hexahydrate, $Zn(NO_3)_2{\cdot}6H_2O$, and ammonium hydroxide (30 wt %) were obtained from Sigma-Aldrich and employed to synthesise the mixed metal oxides.

Natural rubber (Malaysian Rubber, SMR-CV60), Butadiene rubber (Buna CB 24, cis-1,4 content min. 96%, Lanxess), solution styrene-butadiene rubber (Buna VSL 2525-0, 25 % by wt. vinyl content, 25 % by wt. styrene content, Lanxess), sulphur (Mahlschwefel, Lanxess), CBS (Vulkacit CZ/C, Lanxess), zinc oxide (Red Seal, Numinor), magnesium oxide (Maglite DE, HallStar), calcium carbonate (Omya BSH), and stearic acid were used for rubber mixtures.

Toluene (Fluka, ≥99.0%), 1-hexanethiol (Fluka, ≥95.0%), 2-propanethiol (Fluka, ≥97.0%), heptane (Fluka, ≥99.0%), piperidine (Sigma-Aldrich ReagentPlus 99%) and petroleum ether (Sigma-Aldrich) were employed for the swelling and thiol-amine chemical-probe experiments.

5.2.2. SYNTHESIS OF MIXED METAL OXIDES

Zinc/magnesium oxide and zinc/calcium oxide nanoparticles were prepared following the method reported previously[16] and described in Chapter 4 (see section 4.2.2). As it has been explained, the method consists on the preparation of a polymer/metal salt complex that is water-soluble, its purification by precipitation and redissolution cycles and finally the calcination of the dried purified complex to give nanosized particles.

Zinc/magnesium oxide nanoparticles with 24 % in weight of magnesium with respect to the total amount of metal (x of 0.46 in moles) and zinc/calcium oxide nanoparticles with 20 % in weight of calcium with respect to the total amount of metal were prepared.

X-Ray diffraction (Philips X’Pert) was employed to characterize the crystal structure of the mixed metal oxides. The data obtained was refined with CELREF[17] to determine the lattice parameters of the oxides. Scanning Electron Microscope (Jeol JSM-5310), along with Energy Dispersive Spectroscopy, was used to measure the magnesium and calcium content in the mixed metal oxides. Zetasizer Nano ZS™ (Malvern Instruments Ltd) was employed to measure the particle size. The Brunauer-Emmett-Teller (BET) specific surface areas (S_{BET}) were evaluated on the basis of nitrogen adsorption isotherms measured at 77 K using a nitrogen adsorption apparatus (BELSORP-max, BEL, Japan). All the samples were degassed at 150 °C before nitrogen adsorption measurements. The BET surface area was determined using the adsorption data in the relative pressure (P/P_0) range of 0.05-0.35.

5.2.3. PREPARATION AND CHARACTERISATION OF THE RUBBER SAMPLES

5.2.3.1 NATURAL RUBBER SAMPLES

The studied compounds, based on standardised natural rubber (SMR-CV60), were prepared in an open two-roll mill. All the details about the composition of the different samples are showed in Table 5.1. The reaction mixtures were prepared by two steps. First, a 300 g masterbatch without activator was prepared in a two-roll mill using standard procedures. This masterbatch contains stearic acid (2 phr), CBS (1.2 phr) and sulphur (2 phr). Afterwards, the different activators systems were added to 20 g of masterbatch and mixed in a two-roll mill. Vulcanisation took place at 140 °C in a thermofluid-heated press at the optimum cure time (t_{97}), deduced from the rheometer curve (Alpha Technologies Rubber Process Analyser, model RPA2000) according to ASTM D2084.

Table 5.1. Composition of the NR Compounds.

	recipe[a] (phr)						**Zn content**	
sample	**ZnO**	**MgO**	**$CaCO_3$**	**$Zn_{1-x}Mg_xO$**	**$Zn_{1-x}Ca_xO$**		**Zn (mol × 10^3)**	**Zn reduction**
N0_5.0	5	–	–	–	–		11.7	–
N0_3.8		3.8	–	–	–	–	8.8	25%
N0_3.0		3	–	–	–	–	7	40%
N0_1.5		1.5	–	–	–	–	3.5	70%
N1_5.0	–	5	–	–	–		–	–
N2_5.0	4	1	–	–	–		9.3	21%
N3_6.7	–	–	–	6.7	–		11.7	–
N3_5.0	–	–	–	5	–		8.8	25%
N3_4.0	–	–	–	4	–		7	40%
N3_2.0	–	–	–	2	–		3.5	70%
N4_5.0	3.3	–	1.7	–	–		7.7	34%
N5_7.5	–	–	–	–	7.5		11.7	–
N5_5.0	–	–	–	–	5		7.7	34%
N5_4.0	–	–	–	–	4		6.2	47%

[a] Ingredients in parts per hundred rubber: natural rubber 100; stearic acid 2; CBS 1.2; sulphur 2; activator system.

The sample names, e.g., N0_5.0 encode the type of rubber (NR), the activator system (0 for ZnO, 1 for a MgO, 2 for a mixture of ZnO and MgO, 3 for $Zn_{1-x}Mg_xO$, 4 for a mixture of ZnO and $CaCO_3$, and 5 for $Zn_{1-x}Ca_xO$-like) and the amount of activator in phr (5.0 in this case).

Stress-strain measurements were performed on dumb-bell shaped specimens (Type 3) according to ISO 37 using an INSTRON 3366 at a traction rate of 200 mm/min. Five samples were used for the tensile test and an average of the five results was taken as the resultant value. A Bareiss digi test was used to perform micro International Rubber Hardness Degree (IRHD) measurements according to ISO 48.

The glass transition temperature (T_g) of the NR samples was measured by performing differential scanning calorimetry (DSC) analyses in a Mettler toledo DSC822^e. Nitrogen gas with a flow rate of about 20 ml/min was purged through the cell. Experiments started with an isothermal step (5 min) at 25 °C, and then samples were cooled down from 25 °C to -90 °C at a rate of 10 °C/min. After 10 min of equilibration at that temperature, far enough below T_g, a heating rate of 10 °C/min was applied up to 25 °C, and the glass transition temperature was taken from this heating run.

Proton double quantum solid-state NMR spectroscopy has been used to measure the cross-link density of the different samples and its distribution. Experiments were carried out at 353 K on a Bruker minispec mq20 spectrometer operating at 0.5 T with 90° pulses of 3 µs length and a dead time of 6 µs. As it has been shown in Chapter 2, the experiments are based on the determination of partially averaged residual dipolar coupling constant (D_{res}) that persist because the presence of cross-links and other topological constrains provokes the non-isotropic segmental fluctuations[18]. The molecular weight between constrains, M_C, is related to D_{res}, and the former is inversely proportional to the cross-link density[18-20].

5.2.3.2 BUTADIENE RUBBER AND STYRENE-BUTADIENE RUBBER SAMPLES

The studied compounds were prepared by two steps. The compositions of the different samples are showed in Table 5.2. First, approximately 1 kg masterbatch for each rubber without activator was prepared in a two-roll mill using standard procedures. These masterbatches contain stearic acid (2 phr), CBS (1.2 phr) and sulphur (2 phr). Afterwards, the different activators systems were added to the masterbatches in an internal mixer with Banbury rotors (Thermo Haake Polylab system Reocord/Rheomix 600 Type 557-9300), fill factor 0.75. The software PolyLab Monitor has been used for data acquisition. Every formulation was scaled-up to 50 g taking into account the density of every ingredient to avoid overpressure problems inside the internal mixer. Temperature was set at 40 °C for the cavity and it was controlled during the mixing process avoiding always to overcome 100 °C to prevent pre-vulcanisation of the material and the speed of the rotors was maintained at 50 Hz.

The sample names, e.g., B0_5.0 encode the type of rubber (B for BR and S for SBR), the activator system (0 for ZnO, 1 for a MgO, 2 for a mixture of ZnO and MgO, 3 for $Zn_{1-x}Mg_xO$, 4 for a mixture of ZnO and $CaCO_3$, and 5 for $Zn_{1-x}Ca_xO$-like) and the amount of activator in phr (5.0 in this case). Samples MB_SBR and MB_BR are the masterbatches employed to obtain each sample.

Vulcanisation was carried out at four different temperatures (140 °C, 150 °C, 160 °C and 170 °C) at 280 bar in an electric-heated press at the optimum cure time (t_{90}) plus 2 minutes. t_{90} was deduced from the rheometer curve (Monsanto Rubber Process Analyser, model RPA2000) according to ASTM D2084.

Norm DIN 53529 has been followed to measure the activation energy (E_a) with the different activators used in this work. The E_a is the specific constant determining the energy required to activate the reaction.

Stress-strain measurements were performed on dumb-bell shaped specimens (Type 3) according to ISO 37 in a Zwick/Roell Z010 at a traction rate of 200 mm/min. Five samples were used for the tensile test and an average of the five results was taken as the resultant value. A Zwick/Roell digi test was used to perform micro International Rubber Hardness Degree (IRHD) measurements according to ISO 48.

Table 5.2. Composition of the BR and SBR compounds.

samples		recipe[a] (phr)					Zn content	
SBR	**BR**	**ZnO**	**MgO**	**$CaCO_3$**	**$Zn_{1-x}Mg_xO$**	**$Zn_{1-x}Ca_xO$**	**Zn (mol × 10^3)**	**Zn reduction**
MB_SBR	MB_BR	–	–	–	–	–	–	–
S0_5.0	B0_5.0	5	–	–	–	–	28.2	–
S0_3.8	B0_3.8	3.8	–	–	–	–	21.2	25%
S0_3.0	B0_3.0	3	–	–	–	–	16.9	40%
S0_1.5	B0_1.5	1.5	–	–	–	–	8.4	70%
S1_5.0	B1_5.0	–	5	–	–	–	–	–
S2_5.0	B2_5.0	4	1	–	–	–	22.5	21%
S3_6.7	B3_6.7	–	–	–	6.7	–	28.2	–
S3_5.0	B3_5.0	–	–	–	5	–	21.2	25%
S3_4.0	B3_4.0	–	–	–	4	–	16.9	40%
S3_2.0	B3_2.0	–	–	–	2	–	8.4	70%
S4_5.0	B4_5.0	3.3	–	1.7	–	–	18.7	34%
S5_7.5	B5_7.5	–	–	–	–	7.5	28.2	–
S5_5.0	B5_5.0	–	–	–	–	5	18.7	34%
S5_4.0	B5_4.0	–	–	–	–	4	15.0	47%

[a] Ingredients in parts per hundred rubber: BR or SBR 100; stearic acid 2; CBS 1.2; sulphur 2; activator system.

Swelling measurements and the thiol–amine chemical probe methodology were employed to determine the cross-link density and the distribution of cross-links. The modified Flory-Rehner equation or affine model (Equation 2.1, see section 2.2.2.1) adapted for tetra-functional networks (f = 4) has been used to determine the cross-link density using swelling measurements which were carried out gravimetrically.

$$-\left[ln(1-\phi_r)+\phi_r+\chi\cdot{\phi_r}^{2}\right]=\frac{\rho_r}{M_C}\cdot V_S\cdot\left({\phi_r}^{1/3}-\frac{2\cdot\phi_r}{f}\right)$$

Equation 2.1

Network chain density was calculated as an average of three measurements for each vulcanisate. BR and SBR samples were swollen to equilibrium by immersion in toluene at room temperature for 72 h. Solvent was renewed after 24 h, and the swelling was performed under mild agitation and sheltering rubber specimens from light, to avoid UV degradation. Since the model is strictly applicable only to a hypothetical network free from entanglements and chain ends, the results obtained should only be considered as a qualitative comparison between samples.

The determination of the volumetric fraction of rubber (ϕ_r) in the swollen state is source of uncertainty. If swelling measurements are carried out gravimetrically, it is necessary to eliminate the fraction of insoluble components and to take into account the amount of imbibed solvent at the interface between rubber and non-interacting filler particles[21]. In this work the method described by Ellis and Welding[22, 23] have been employed (Equation 5.1). In this approach the volume fraction of rubber in a swollen network is calculated taking into account the rubber network and only the zinc oxide is considered insoluble.

$$\phi_r = \frac{\dfrac{w_d - f_{ins} \cdot w_i}{\rho_r}}{\dfrac{w_d - f_{ins} \cdot w_i}{\rho_r} + \dfrac{w_o^{sol}}{\rho_S}}$$

Equation 5.1

For calculation of ϕ_r the densities of the different rubber types and solvents are required. These values are 0.91 g·cm^{-3} for BR, 0.94 g·cm^{-3} for SBR. However, the density depends on the cross-link density in sulphur-vulcanised samples. For this reason, the Ellis and Welding[22, 23] modification was used (Equation 5.2). With this approach an estimated rubber density is calculated assuming that the volumes of polymer and sulphur are additive, with a fictitious density of 6 g·cm^{-3} for the combined sulphur. The density of toluene is 0.867 g·cm^{-3} and the molar volume of toluene, V_S, is equal to 106.26 cm^{3}·mol^{-1}.

$$\rho_r^{E-W} = \frac{w_r + w_{sulphur}}{\dfrac{w_r}{\rho_r} + \dfrac{w_{sulphur}}{6}}$$

Equation 5.2

The Flory-Huggins interaction parameter (χ) is of great importance because it is another source of uncertainty. Small changes in χ can lead to large variations in the calculated cross-link density. It is usually assumed to be constant for a given polymer-solvent pair but it varies with the chemical structure of the vulcanisate and therefore with the nature of the cure system. In this work χ was taken from the literature. For the BR/toluene pair χ is equal to 0.34[24] and for the SBR/toluene pair χ is equal to 0.21[25].

In order to determine the structure and cross-link distribution of the rubber vulcanisates the chemical probe methodology described in section 2.2.2.2 has been employed on the BR and SBR samples vulcanised at 140 °C. This methodology allows the determination of the fraction of mono-, di- and polysulphidic cross-links in the rubber samples by selective decomposition using thiols activated by amines.

NMR magnetisation relaxation experiments were performed on BR and SBR compounds vulcanised at 140 °C to measure the cross-link density of the elastomer network. The ^{1}H NMR relaxation times were determined on a XLOS-15 crosslink density spectrometer (IIC Innovative Imaging Corp. K. G.) at a proton resonance frequency of 15.214 MHz (0.35 T) at

80 °C. The T_1 times were measured using the aperiodic pulse sequence (APS) and T_2 times with the help of the Hahn echo. The T_1 measurement repetition times were 1 s and the τ times were 30 ms. The 90° and 180° pulses, determined for each compound prior testing, were between 2.79 and 2.91 µs for 90° pulses and between 4.71 and 4.92 µs for 180° pulses. The T_1 measurements were conducted as single experiment meanwhile the T_2 measurements as fourfold determination.

As it has been shown in Chapter 2, the experiments are based on the determination of the transverse relaxation time T_2, the spin-spin relaxation time, which is the time constant for disappearance of magnetisation components orthogonal to the magnetic field[26]. The T_2 curves can be analysed according to a Gaussian-exponential function shown in Equation 2.3 allowing the differentiation between the chain mobility of the actual polymer chains (movement of networks and cross-linked hydrocarbon chains) and that of low-molecular constituents and dangling chain ends. The Gauss fraction (qM_2) in the earlier relaxation time range corresponds to polymer chains and the exponential fraction T_2 to the low molecular area[27-29].

5.3. RESULTS

5.3.1. SYNTHESIS AND CHARACTERISATION OF MIXED METAL OXIDES

The characterisation of $Zn_{1-x}Mg_xO$ was detailed in Chapter 4 (see section 4.3.1). X-Ray diffraction was employed to characterise the crystal structure of the mixed metal oxide particles. The *c*-axis lattice constant of the ZnO hexagonal phase was found to be 5.1648 ± 0.0050 Å instead of 5.2066 Å and the *a*-axis lattice constant 3.2533 ± 0.0023 Å instead of 3.2498 Å[30]. The lattice parameter of the MgO cubic phase was found to be 4.2240 ± 0.0048 Å instead of 4.2112 Å[31].

Figure 5.1 shows the X-ray diffraction patterns of the oxide products obtained with zinc and calcium. Like in the other mixed metal oxide, two phases are formed. However, along with the ZnO phase, the calcium oxide phase is not present as one would expect. In this case calcium carbonate is formed as it can be noticed from the graph. The patterns of the pure ZnO are indexed according to the known hexagonal phase (zincite)[30], and that of $CaCO_3$ is indexed according to its rhombohedral phase[32]. The vertical lines correspond to the standard reflections of the ZnO phase and the dashed vertical lines are the standard reflections of the $CaCO_3$ phase. The $CaCO_3$ planes are indicated with a star. Empty circles represent the expected intensity of the ZnO peaks with respect to the maximum peak found (1 0 1). Filled circles indicate the expected intensity of the $CaCO_3$ peaks with respect to the maximum peak observed (1 1 3).

It can be seen in Figure 5.1 that the diffraction peaks (0 0 2), (1 0 2) and (1 0 3) have slightly shifted (much less than in the previous oxide) to lower diffraction angles compared to those of the hexagonal structure of ZnO[30]. These shifts are caused by the substitution of Zn atoms by Ca atoms in the hexagonal phase. As calcium replaces zinc in the structure, due to the greater radius of Ca^{2+} (1.00 Å) than Zn^{2+} (0.60 Å)[33], there is a very moderate increase of the lattice constant along the *c*-axis (5.2119 ± 0.0033 Å instead of 5.2066 Å) and a displacement of the diffraction peaks to lower angles. On the contrary, as Ca incorporates into the structure, the *a*-axis lattice constant is almost unaffected (3.2490 ± 0.0005 Å instead of 3.2498 Å). The lattice parameters were calculated using CELREF[17]. The fact that the changes in the lattice constants are very subtle, virtually non-existent, denotes that has been practically no incorporation of calcium into the zinc oxide structure. Therefore, the zinc/calcium oxide is basically a mixture of ZnO and $CaCo_3$ with a very small interchange of atoms between them and will be referred as $Zn_{1-x}Ca_xO$-like.

Figure 5.1 reveals that the calcium carbonate formed during the calcination process is not affected by zinc; there is no introduction of this atom into the $CaCO_3$ structure. The lattice constant along the *c*-axis is practically invariable (17.0699 ± 0.0135 Å instead of 17.0620 Å) as well as the lattice constant along the *a*-axis (4.9908 ± 0.0010 Å instead of 4.9890 Å).

The reason because there is not incorporation of calcium atoms is mainly caused by the calcination conditions used during the synthesis. The samples were isothermally annealed for 1 h at 550 °C and these conditions were optimised to incorporate magnesium[16]. However, difference of the radius between Ca^{2+} and Zn^{2+} is considerably higher than between Mg^{2+} and Zn^{2+}, and this could not be discarded.

Dynamic Light Scattering was employed to measure the particle size of the mixed metal oxides synthesised to use as activators in sulphur vulcanisation. $Zn_{1-x}Mg_xO$ has a particle size of 147 ± 32 nm and $Zn_{1-x}Ca_xO$-like has a particle size of 114 ± 33 nm. From the nitrogen adsorption-desorption results, $Zn_{1-x}Mg_xO$ particles exhibit a BET surface area of 27.2 ± 0.4 m²/g and $Zn_{1-x}Ca_xO$-like of 16.8 ± 0.2 m²/g. Energy Dispersive Spectroscopy indicates that there is a 24 % in weight of magnesium with respect to the total amount of metal in $Zn_{1-x}Mg_xO$ and a 18 % in weight of calcium with respect to the total amount of metal in $Zn_{1-x}Ca_xO$-like.

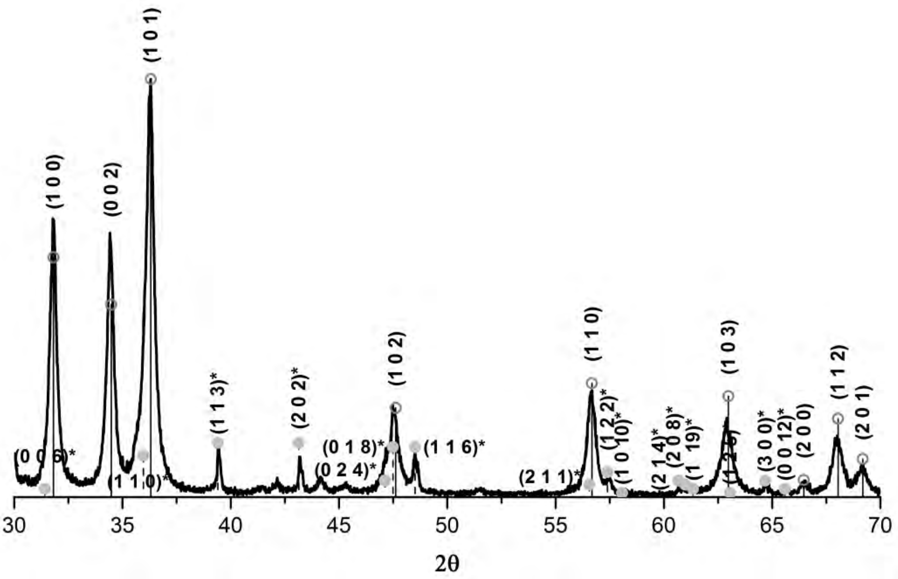

Figure 5.1. XRD patterns of $Zn_{1-x}Ca_xO$-like. Vertical lines correspond to the standard reflections of the ZnO phase and dashed vertical lines are the standard reflections of the $CaCO_3$ phase which planes are designated with a star. Empty circles indicate the expected intensity of the ZnO peaks regarding its maximum peak observed (1 0 1). Filled circles designate the expected intensity of the $CaCO_3$ peaks regarding its maximum peak observed (1 1 3).

5.3.2. NATURAL RUBBER SAMPLES

In order to study the effects already seen of the mixed metal oxides as activator for sulphur vulcanisation (see Chapter 4), fifteen different formulations were prepared following the protocol described in section 5.2.3.1. Table 5.1 shows the content of these eleven compounds. In all mixtures, CBS was used as accelerator with a constant A/S ratio of 0.6 (conventional vulcanisation) and the vulcanisation temperature was in all cases 140 °C.

5.3.2.1 CURE CHARACTERISTICS

Figure 5.2 shows the rheometric curves for the NR compounds with ZnO, MgO and a mixture of ZnO and MgO, and $Zn_{1-x}Mg_xO$. The scorch times for NR compounds with MgO and a mixture of ZnO and MgO (samples N1_5.0 and N2_5.0) are shorter than the reference compounds (samples N0). The extent of cross-linking ($M_H - M_L$), the difference between maximum torque (M_H) and the minimum torque (M_L), is lower for these compounds containing MgO. In addition, the reversion observed is more severe.

It is evident from these results that the presence of MgO affects strongly the cross-link density. As it has been reported earlier by Borrós *et al.*[13], the presence of MgO is more critical than the amount of MgO in affecting the network chain density.

Regarding the samples with different amounts of ZnO (samples N0), it can be observed that reducing the ZnO content to 3 phr does not produce significant differences on the vulcanisation curves. The $M_H - M_L$ values attained with the samples N0_3.8 and N0_3.0 are slightly slower than N0_5.0, but the rest of the properties are unaffected. However, when only 1.5 phr of ZnO are added to the recipe, the extent cure and the reversion resistance are reduced.

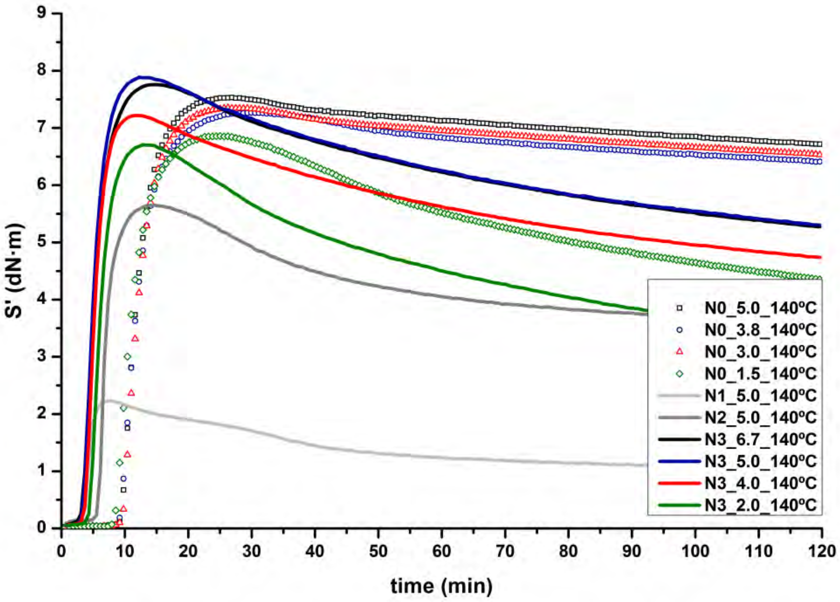

Figure 5.2 Cure characteristics of NR compounds with ZnO, MgO, a mixture of ZnO and MgO, and $Zn_{1-x}Mg_xO$.

In Figure 5.2 it can also be seen that samples containing $Zn_{1-x}Mg_xO$ show a superior performance than the compounds containing MgO. The scorch times for these compounds are comparable to those of N1_5.0 and slightly shorter than N2_5.0, but the extent of cross-linking is higher, especially in comparison to N1_5.

Comparing with the compounds containing ZnO (samples N0) it is observed that the cure characteristics are accelerated if $Zn_{1-x}Mg_xO$ is used as activator. The scorch and optimum vulcanisation times are shorter if the samples comprise $Zn_{1-x}Mg_xO$. Regarding the degree of cure, the $M_H - M_L$ values are similar, with the exception of the sample containing only 2 phr of $Zn_{1-x}Mg_xO$. Samples with 6.7 and 5 phr of $Zn_{1-x}Mg_xO$ exhibit, to some extent, a higher $M_H - M_L$ than the compound with 5 phr of ZnO. Sample N3_4.0 gives slightly lower values than N0_5.0 although on the same level than samples N0_3.8 and N0_3.0. When the zinc content is reduced by 70 % using 1.5 phr of ZnO (N0_1.5) or 2.0 of $Zn_{1-x}Mg_xO$ (N3_2.0) the same extent of cross-linking is achieved.

The percentage of reversion is shown in Figure 5.3. In the x-axis it is represented the time after reaching M_H. The percentage of reversion is defined as:

$$\% R = \frac{(M_H - M_t)}{(M_H - M_L)} \times 100$$

Equation 5.3

where M_t is torque at t minutes on the rheograph. It gives an indication of the quality of the compound regarding how long it will be able to retain its physical properties when subjected to heat ageing.

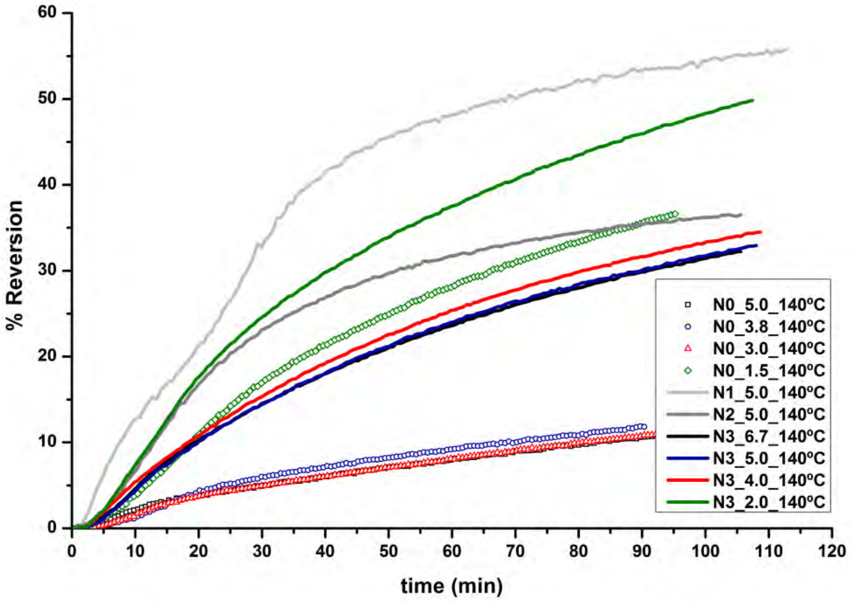

Figure 5.3. Evolution of reversion for mixtures with ZnO, MgO, a mixture of ZnO and MgO, and $Zn_{1-x}Mg_xO$.

In Figure 5.3 it can be seen that all compounds show higher reversion than the reference compounds with ZnO. The compound including MgO (N1_5.0) shows the most prominent reversion, with high percentages of reversion at short times. Samples containing $Zn_{1-x}Mg_xO$ as activator have a comparable behaviour than the sample containing 1.5 phr of ZnO (N0_1.5) at loading contents higher than 2 phr (N3_6.7, N3_5.0 and N3_4.0). Comparing the sample with a mixture of ZnO and MgO (N2_5.0) and with 2 phr of $Zn_{1-x}Mg_xO$ (N3_2.0) it is observed that the reversion is very similar until approximately 20 minutes, when the reversion raise is greater in N3_2.0. From Figure 5.3 it can clearly be understood that regarding reversion resistance ZnO shows the best performance. Samples with at least 3.0 phr of ZnO (N0_5.0, N0_3.8 and N0_3.0) present the lowest reversion.

Figure 5.4 shows the rheometric curves for the NR compounds with ZnO, a mixture of ZnO and $CaCO_3$, and $Zn_{1-x}Ca_xO$-like. The mixture of ZnO and $CaCO_3$ (sample N4_5.0) gives scorch times somewhat longer than the reference compound but t_{90} and t_{97} times shorter. In addition, the extent of cure is to a certain degree higher than in N0_5.0.

The scorch times for NR mixtures with $Zn_{1-x}Ca_xO$-like are on the same level than the samples containing ZnO (N0). The mixture with 7.5 phr (N5_7.5) gives a slightly shorter scorch time, although the differences are not as significant as it has been found with $Zn_{1-x}Mg_xO$. Regarding the extent of cure, the $M_H - M_L$ values of the compounds comprising $Zn_{1-x}Ca_xO$-like are slightly higher and, in addition, the reversion observed is comparatively similar. The sample containing a mixture of ZnO and $CacO_3$ exhibits a very similar behaviour to the samples with $Zn_{1-x}Ca_xO$-like, although the cross-linking degree is to some extent smaller, especially if at least 5 phr of $Zn_{1-x}Ca_xO$-like are used.

From Figure 5.5 it is evident that there are almost no differences concerning the reversion experienced by these samples, with the exception of N0_1.5, which has a limited reversion resistance. Only the sample containing 4 phr of $Zn_{1-x}Ca_xO$-like (sample N5_4.0) undergoes a higher reversion at long vulcanisation times.

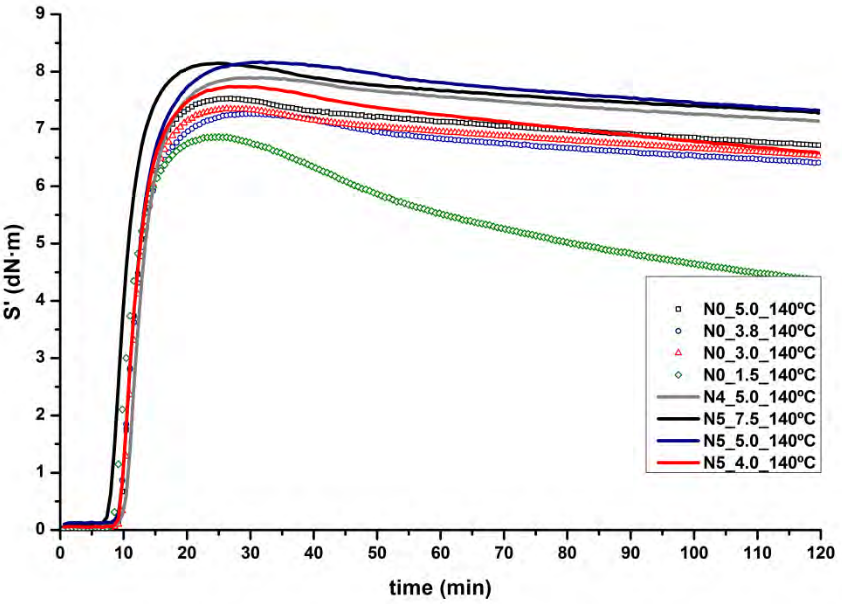

Figure 5.4 Cure characteristics of NR compounds with ZnO, a mixture of ZnO and $CaCO_3$, and $Zn_{1-x}Ca_xO$-like.

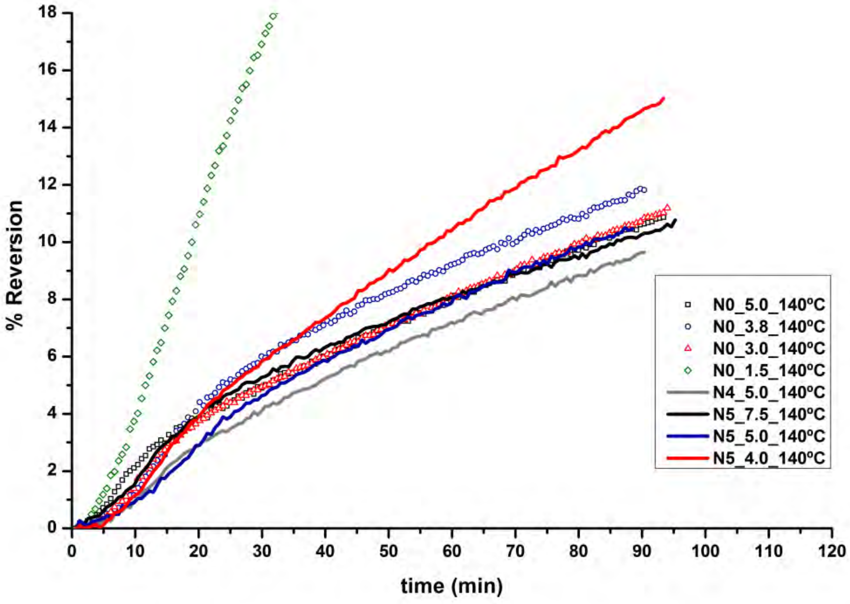

Figure 5.5. Evolution of reversion for mixtures with ZnO, a mixture of ZnO and $CaCO_3$, and $Zn_{1-x}Ca_xO$-like.

Table 5.3 summarises the vulcanisation parameters of the NR compounds mixed in this work. t_{02} is the time to 2 % of maximum torque, t_{s2} is the time to 2 dN·m rise above M_L, t_{90} is the time to 90 % of maximum torque, and t_{97} is the time to 97 % of maximum torque. The Cure Rate index (CRI) is calculated using Equation 5.4 and the reversion tax according to Equation 5.5. The reversion time (RT) is the time to reach 95 % M_H after passing M_H.

$$CRI = \frac{100}{t_{90} - t_{s2}}$$

Equation 5.4

$$Reversion\,Tax = \frac{M_H - M_{H+30\,min}}{M_H - M_L} \times 100$$

Equation 5.5

In Table 5.3 it can be observed that the compounds containing free MgO (samples N1_5.0 and N2_5.0) have the lowest reversion resistance. Reversion tax as well as reversion time are noticeably deteriorated by the presence of MgO. On the other hand, the reaction proceeds faster when it is added to the recipe.

The samples containing different amounts of ZnO have very similar cure characteristics. As it has been seen previously, the vulcanisation times and the CRI are very similar. The compound with 1.5 phr (N0_1.5) show a much lower reversion resistance, but the rest of the properties are very similar.

Mixed metal oxides of zinc and magnesium increase the vulcanisation rate. The CRI is remarkably high with $Zn_{1-x}Mg_xO$, independently of the amount of this compound, and scorch and cure times are shorter. As indicated before, the reversion resistance is inferior for the mixtures containing mixed metal oxides of zinc and magnesium. In general, the reversion times are shorter and the reversion taxes are higher for these compounds. However, there are no significant differences in the reversion tax when the loading is between 6.7 and 4 phr.

When $Zn_{1-x}Ca_xO$-like is used as activator for natural rubber, the reversion resistance is improved but, as already seen, the cure characteristics do not differ substantially from the reference compounds.

Table 5.3. Vulcanisation parameters of NR compounds vulcanised with different activators.

sample	t_{02} (min)	t_{s2} (min)	t_{90} (min)	t_{97} (min)	CRI (%)	RT (min)	Reversion Tax (%)	$M_H - M_L$ (dN·m)
N0_5.0	9.2	10.4	15.9	19.6	18.2	11.6	7.0	7.5
N0_3.8	8.6	10.4	16.5	21.4	16.4	7.9	7.8	7.2
N0_3.0	9.2	10.4	15.9	19.6	18.2	11.0	7.1	7.3
N0_1.5	8.0	9.2	15.3	18.3	16.4	11.0	17.3	6.8
N1_5.0	3.1	5.5	4.9	6.1	–	3.7	33.6	2.1
N2_5.0	4.9	6.1	9.2	11.0	32.8	7.6	23.3	5.6
N3_6.7	2.5	4.3	8.0	10.4	27.3	10.4	14.5	7.7
N3_5.0	3.1	3.7	7.4	9.2	27.3	10.4	14.6	7.8
N3_4.0	3.1	4.3	7.4	8.6	32.8	6.4	16.6	7.2
N3_2.0	3.7	4.9	8.6	9.8	27.3	7.3	24.8	6.7
N4_5.0	9.2	11.0	17.1	21.4	16.4	37.2	4.3	7.9
N5_7.5	7.4	8.6	14.1	17.7	18.2	26.2	5.3	8.1
N5_5.0	8.6	10.4	17.1	22.0	14.9	31.7	4.7	8.1
N5_4.0	8.6	10.4	16.5	20.2	16.4	23.2	6.1	7.7

Figure 5.6 shows the scorch and cure time and the $M_H - M_L$ values for the NR compounds studied in this chapter. Comparing the samples with different amounts of ZnO, it can be seen that a 40 % reduction does not cause a deterioration of the vulcanisation characteristics of the compounds. In

In Figure 5.6 it can also be appreciated that the cure times are reduced by half when $Zn_{1-x}Mg_xO$ is employed. Additionally, the cross-link degree is comparable (if not higher) when at least 4 phr are used. This means that a 40 % reduction of the zinc content is achievable by replacing zinc oxide with $Zn_{1-x}Mg_xO$ obtaining at the same time a decrease in the vulcanisation time. A further reduction to 70 % can be attained if 2.0 phr of $Zn_{1-x}Mg_xO$ or 1.5 phr of ZnO are used although the extent of cross-linking is lowered. The reversion resistance is the only characteristic that is visibly better with ZnO. Nonetheless, it should be noted that no anti-reversion agent was added to the recipe, which could reduce the differences considerably. Furthermore, conventional vulcanisation systems (in all mixtures the A/S ratio was kept at 0.6) contain less monosulphidic cross-links and more polysulphidic ones, which lead to low reversion resistance (resistance to non-oxidative thermal aging or overcure) and bad resistance to thermal-oxidative aging[34].

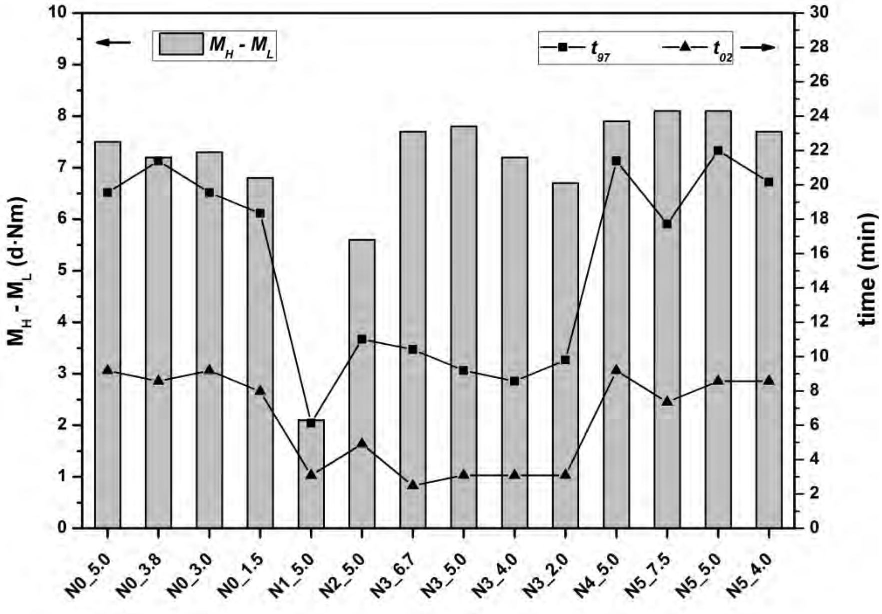

Figure 5.6. Scorch time (t_{02}), cure time (t_{97}), and extent of cure ($M_H - M_L$) for NR mixtures.

Using $Zn_{1-x}Ca_xO$-like the reduction in the cure times is not as marked as with $Zn_{1-x}Mg_xO$ but the cross-link density is also slightly higher. On the contrary, the reversion resistance is not affected, particularly if at least 5 phr are used. However, there are almost no differences between the sample with a mixture of ZnO and $CaCO_3$ (N4_5.0) and the mixtures containing $Zn_{1-x}Ca_xO$-like. Simply by adding 3.3 phr and 1.7 phr of $CaCO_3$ (34 % reduction of zinc content) the same cure properties are obtained. A higher reduction of the zinc content (47 %) can be obtained employing 4 phr of $Zn_{1-x}Ca_xO$-like.

In Chapter 4 (see Figure 4.8) it has been shown that when $Zn_{1-x}Mg_xO$ is used as activator the reactions that take place during scorch time are faster. The breakdown of the accelerator and the formation of MBT are faster with $Zn_{1-x}Mg_xO$ and more similar to the manner that occurs when MgO is used. The consumption of sulphur takes place faster with $Zn_{1-x}Mg_xO$ than with ZnO or MgO. The same behaviour has been observed in NR: scorch and cure time are faster. However, the cross-link degree achieved is very different if the study is carried out with squalene or with NR. In model compound vulcanisation it has been observed that when $Zn_{1-x}Mg_xO$ nanoparticles are used a 30 % higher cross-link degree is attained. On the contrary, in natural rubber compounds there are only small differences between $Zn_{1-x}Mg_xO$ and ZnO.

In order to understand the different behaviour of $Zn_{1-x}Mg_xO$ with squalene and NR it is important to take into account the discrepancies that are also obtained when MgO is the activator. In Chapter 3 (see Figure 3.10) it has been found that although the cross-link degree attained with MgO is lower than with ZnO, the variation is not as high as in NR. Similar results have been reported by other researchers using TME as model molecule[35]. Comparing the results attained in MCV and in NR it can be deduced that MgO does not produce the same detrimental effect. In real rubber mixtures the effects are more negative meanwhile in MCV are more unimportant.

In section 5.3.1 it has been shown that although almost all magnesium atoms incorporate into the zinc oxide structure, the cubic phase appeared. This indicates the coexistence of the two phases but in spite of that, the intensity of the cubic phase denotes that the majority of the material is in the form of modified zincite. The presence of the cubic phase is the key to understand the differences seen in MCV and in NR. In model compound vulcanisation, $Zn_{1-x}Mg_xO$ exhibits a higher cross-link degree than in natural rubber because the presence of a small fraction of $Mg_{1-y}Zn_yO$ does not affect as drastically as it does in NR. The negative effect of the appearance of the cubic phase is higher in natural rubber and that is the reason because the curves of $Zn_{1-x}Mg_xO$ shown in Figure 5.2 are very similar to the curve of ZnO regarding the difference between the minimum and the maximum torque. $Zn_{1-x}Mg_xO$ could show a higher cross-link degree provided that all magnesium was incorporated into the ZnO structure.

In addition, it can be deduced that the alteration of the zinc oxide structure caused by the substitution of zinc by magnesium atoms is the reason which causes the advantages seen in Chapter 4. As explained in section 4.3.2, rather than the size of the oxide or its specific surface area, the presence of magnesium into the ZnO crystal structure is the key factor for obtaining better curing characteristics. $Zn_{1-x}Mg_xO$ has a higher particle size and a lower specific surface area than $Zn_{1-x}Ca_xO$-like but, in spite of that, natural rubber compounds with $Zn_{1-x}Mg_xO$ as activator cure faster. Furthermore, standard ZnO has a much higher particle size and a much lower specific surface area than $Zn_{1-x}Ca_xO$-like and their cure characteristics presented in Figure 5.4 are very similar.

5.3.2.2 PHYSICAL PROPERTIES

Stress-strain measurements were performed to study the effect of the mixed metal oxides on the physical properties of the natural rubber compounds. Figure 5.7 shows the tensile strength (black, left y-axis) and the elongation at break (grey, right y-axis) of the natural rubber samples. The compound with MgO (sample N1_5.0) exhibits the lowest tensile strength (TS) of the compounds studied. Since in the previous section it has been seen that the extent of cross-linking of this sample is the smallest, it is not unexpected to find such a low tensile strength.

Surprisingly, there are not substantial differences between the other compounds regarding the tensile strength. Albeit some samples, particularly N0_1.5, N2_5.0 and N3_2.0, possess lower $M_H - M_L$ values, the tensile strength of the other natural rubber compounds is comparable. Decreasing the amount of $Zn_{1-x}Mg_xO$ produces a slight decrease in the tensile strength, although very minor. Lowering 70 % the amount of zinc using $Zn_{1-x}Mg_xO$ (N3_2.0) does not affect the TS significantly, the values are on the same level as 3.8 phr of ZnO (N0_3.8). A 70 % reduction employing only 1.5 phr of ZnO causes a moderate decrease, albeit not significant. On the contrary, as the content of $Zn_{1-x}Ca_xO$-like is reduced the tensile strength increases.

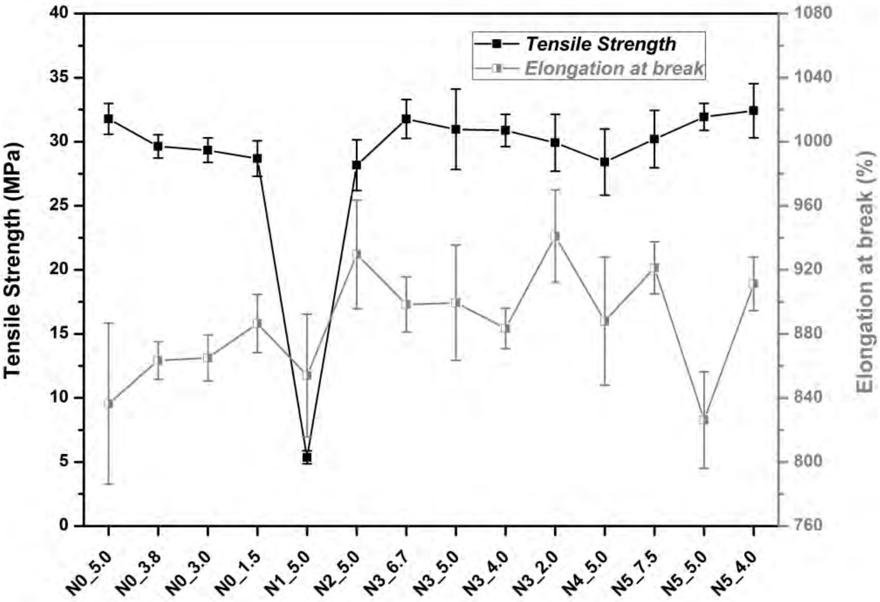

Figure 5.7. Effect of activator on tensile strength and elongation at break of natural rubber compounds.

These results found indicate that when the Zn content is to be reduced, mixed metal oxides are the only approach that would achieve the same tensile strength than ZnO. Replacing ZnO partially with MgO or calcium carbonate would not produce the same results.

Concerning the elongation at break (E_b), some differences are observed in Figure 5.7. Despite the fact that the tensile strength values are very similar in the samples with ZnO and $Zn_{1-x}Mg_xO$, E_b is higher for those compounds containing $Zn_{1-x}Mg_xO$. As the ZnO content is decreased, E_b raises. Reducing the loadings of $Zn_{1-x}Mg_xO$ from 6.7 to 4 phr does not alter the E_b.However, when only 2 phr are used E_b increases.

The samples including $Zn_{1-x}Ca_xO$-like do not show a clear correlation between the content and E_b. The vulcanisates containing 7.5 or 4 phr (N5_7.5 and N5_4.0, respectively) give the same elongation at break. However, the sample with 5 phr exhibit a much lower E_b. This outcome is unexpected since the tensile strength values are very similar.

Figure 5.8 shows the tensile moduli, M_{100} (modulus at 100% elongation), M_{300} (modulus at 300% elongation) and M_{500} (modulus at 500% elongation) of the NR compounds, which is a measure of stiffness of rubber compounds. It can be seen that sample with MgO as activator (N1_5.0) shows the lowest moduli and the mixture with ZnO (N0_5.0) the highest. When lower quantities of ZnO are added to the recipe only M_{500} is affected. There is a minor decrease in the M_{500} values achieved.

Samples containing $Zn_{1-x}Mg_xO$ and $Zn_{1-x}Ca_xO$-like show moduli alike, particularly at low elongation, but somewhat inferior to the samples with ZnO. From these results it can be deduced that using 2 phr of $Zn_{1-x}Mg_xO$ it is possible to reduce the zinc content by 70% obtaining comparable properties to 5 phr of ZnO. Tensile strength is unaffected meanwhile the elongation at break is higher. However, the tensile moduli are to some extent lower if ZnO is substituted by mixed metal oxides, particularly M_{300} and M_{500} .

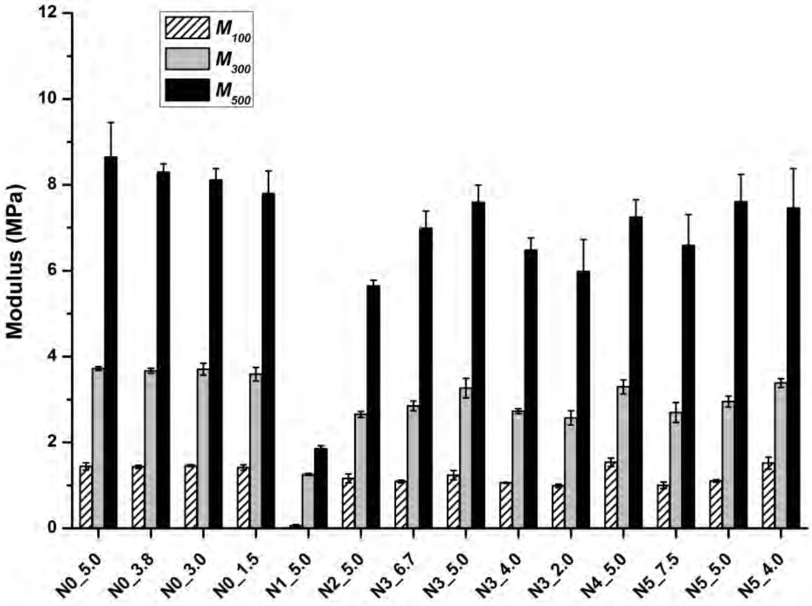

Figure 5.8. Effect of activator on modulus at 100%, 300% and 500% elongation of natural rubber compounds.

Figure 5.9 shows the micro IRHD measurements carried out on NR compounds. Sample N1_5.0 does not appear in the graph due to the hardness of this sample is out of the range of the scale. The mixture of ZnO and MgO (N2_5.0) gives the lowest hardness. The partial substitution of ZnO by MgO affects the hardness more strongly than the tensile strength. Decreasing the quantity of ZnO added to the mixture provokes that the IRDH values achieved are to some extent smaller, albeit the differences are not substantial.

Samples with a minimum $Zn_{1-x}Mg_xO$ content of 4 phr present hardness similar to 5 phr of ZnO. Furthermore, sample N3_6.7 exhibits a higher value. There are no differences between 5 and 4 phr of $Zn_{1-x}Mg_xO$, but an important decrease is found if only 2 phr are used (N3_2.0).

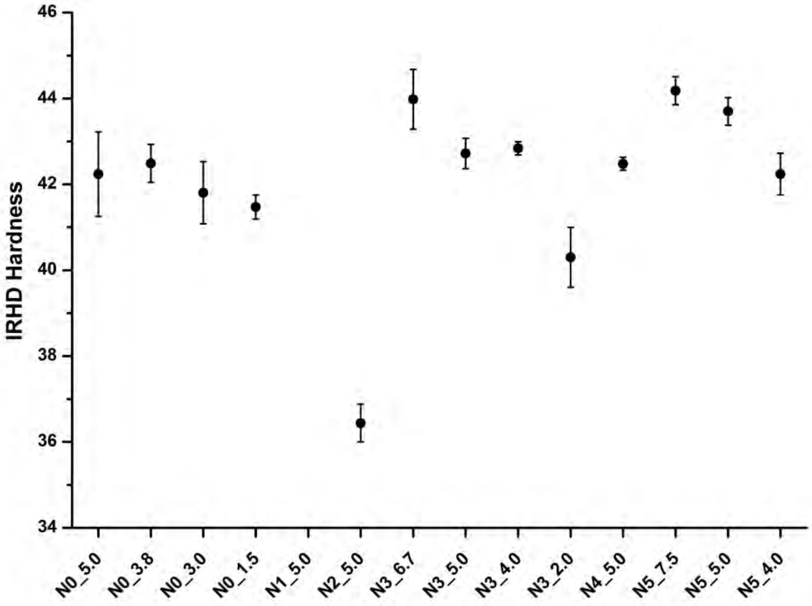

Figure 5.9. Effect of activator on micro IRHD of natural rubber compounds.

Mixtures containing at least 5 phr of $Zn_{1-x}Ca_xO$-like have greater IRHD than the compounds with ZnO or the mixture of ZnO and $CaCO_3$ (N4_5.0). Reducing to 4 phr the amount of $Zn_{1-x}Ca_xO$-like (N5_4.0) gives the same hardness than these compounds.

Taking into account the results found so far it can be seen that mixed metal oxides are good candidates to substitute ZnO as activator for sulphur vulcanisation of natural rubber. With mixed metal oxides of zinc and magnesium it is possible to obtain a 40 % reduction of the zinc content without affecting the properties of the compounds and accelerating the curing characteristics. On the other hand, the reversion observed is significant and it should be taken into account.

With $Zn_{1-x}Ca_xO$-like it is also possible to decrease the Zn content by 47 % without worsening of the properties of the sample. Care should also be taken concerning the reversion, although it is not as crucial as with $Zn_{1-x}Mg_xO$. Conversely, with $Zn_{1-x}Ca_xO$-like the cure characteristics are not enhanced and in both cases the tensile moduli are slightly deteriorated.

If the hardness of the material is not an important feature for the final application, a 70 % reduction of the Zn loading can be achieved with $Zn_{1-x}Mg_xO$ and the rest of the properties would be similar to higher loads. As it will be presented in the next sections, this reduction is also possible in BR and SBR compounds.

Reducing the zinc loadings by simply adding lower quantities of ZnO is also possible. However, there is no improvement of the mechanical properties and in some cases they are slightly worsened. Adding 3.0 phr of ZnO (40 % diminution) does not affect significantly the properties of the compounds. A 70 % reduction is also reachable incorporating 1.5 phr of ZnO but mechanical properties and especially the reversion resistance are worsened.

5.3.2.3 ^{1}H DOUBLE QUANTUM (DQ) SOLID-STATE NMR EXPERIMENTS

DQ NMR experiments allow obtaining a comprehensive description of the network structure. It is possible to differentiate the signal from dipolar coupled network segments and the signal from non-coupled network defects like dangling chains and loops that do not participate in the elastic properties of the compound. The distinction between the each segment is possible because they show different relaxation behaviour. Non-elastic network defects, number of cross-links (or the equivalent chain molecular weight between cross-links, M_C), their chemical nature and functionality, the spatial distribution of cross-links, and information about entanglements are some characteristics that can be extracted performing MQ NMR experiments.

In Table 5.4 it is collected the cross-link density (ν_{NMR}), the ratio between the standard deviation and the average value of the spatial distribution of local cross-link density (σ/D_{res}) in the studied networks (i.e., the distribution width), the non-coupled networks defects, and the glass transition temperature (T_g).

Table 5.4. Cross-link density (ν_{NMR}), distribution width (σ/D_{res}), non-coupled network defects and glass transition temperature (T_g) of the natural rubber compounds.

sample	$\nu_{NMR} \times 10^4$ (mol·g^{-1})		σ/D_{res}		Non-coupled network defects (%)		T_g (°C)	
	t_{97}	120 min	t_{97}	120 min	t_{97}	120 min	t_{97}	120 min
N0_5.0	1.99	1.79	0.23	0.26	9.6	11.0	-59.4	-56.2
N0_3.8	1.96	1.73	0.24	0.28	8.8	7.5	-59.2	-56.2
N0_3.0	1.86	1.75	0.27	0.29	6.6	7.5	-59.3	-54.2
N0_1.5	1.86	1.46	0.31	0.37	8.7	13.9	-59.0	-56.8
N1_5.0	0.97	0.89	0.48	0.67	37.1	44.1	-60.5	-55.5
N2_5.0	1.55	1.27	0.35	0.44	17.0	30.0	-60.2	-55.0
N3_6.7	2.00	1.55	0.22	0.23	8.5	16.1	-59.2	-56.5
N3_5.0	1.99	1.48	0.22	0.27	6.4	10.9	-58.9	-55.7
N3_4.0	1.99	1.50	0.25	0.26	9.4	16.1	-58.5	-55.7
N3_2.0	1.88	1.16	0.39	0.46	19.1	31.3	-60.0	-57.0
N4_5.0	1.93	1.74	0.38	0.37	16.2	19.8	-59.2	-57.4
N5_7.5	1.89	1.86	0.43	0.41	17.8	17.7	-58.7	-55.5
N5_5.0	2.07	1.88	0.19	0.22	9.0	9.1	-58.7	-56.0
N5_4.0	1.97	1.73	0.32	0.38	17.8	18.5	-59.7	-57.1

The table shows the results for the compounds vulcanised at two different times: t_{97} and 120 min. Samples cured at the optimum cure time (t_{97}) were vulcanised in a thermofluid-heated press meanwhile samples cured for 120 min were obtained from the specimen used to acquire the rheometer curve. ν_{NMR} and σ/D_{res} were obtained assuming tetra-functional cross-links and fitting experimental NMR data using a fast Tikhonov regularisation procedure (*ftikreg*) developed by Chassé *et al.*[36].

The cross-link density of the NR compounds is represented in Figure 5.10. Samples containing magnesium oxide (N1_5.0 and N2_5.0) have the lowest cross-link density. The substitution of ZnO by MgO (N1_5.0) produces a reduction of ν_{NMR} by half and replacing only 1 phr of ZnO by MgO (N2_5.0) causes a decrease around 25 %. These results are in accordance with those previously reported[13].

When the amount of ZnO added to the recipe is decreased, the cross-link density is also lowered. However, the diminution is not very severe. Samples containing mixed metal oxides of zinc and magnesium exhibit a ν_{NMR} similar to N0_5.0. If the content of $Zn_{1-x}Mg_xO$ is maintained between 6.7 and 4 phr, there are no differences in the ν_{NMR} achieved. Adding only 2 phr of $Zn_{1-x}Mg_xO$ (sample N3_2.0) presents a slightly smaller ν_{NMR}, but the values are nevertheless equivalent. The replacement of 1 phr of ZnO with $CaCO_3$ (N4_5.0) does not have any effect on the cross-link density attained and the use of $Zn_{1-x}Ca_xO$-like as activator produces samples with comparable ν_{NMR}.

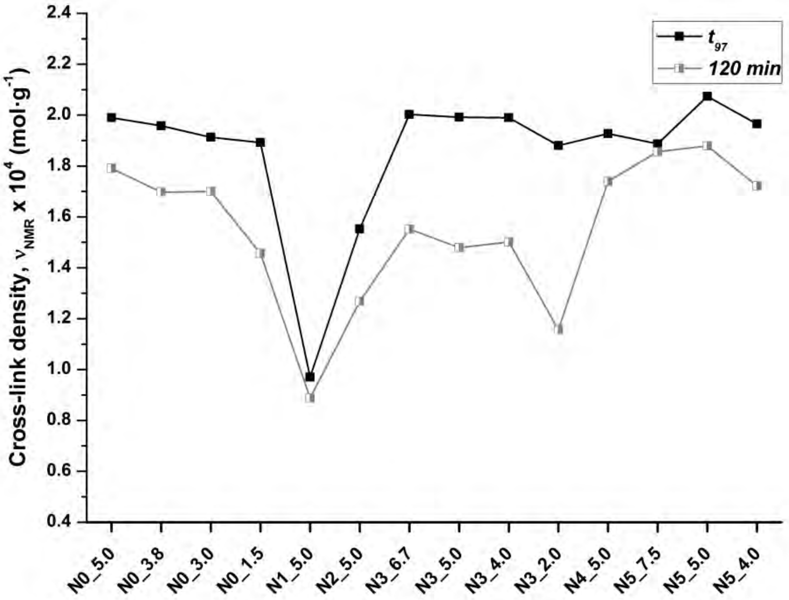

Figure 5.10. Cross-link density for different NR samples cured at t_{97} and 120 min. Results were obtained from NMR measurements at 80 °C fitting data using a fast Tikhonov regularisation procedure (*ftikreg*)[36].

Samples cured during 120 min show, as expected, lower cross-link densities. High decreases are obtained in the mixtures including $Zn_{1-x}Mg_xO$, around 25 %. Similar behaviour is found in sample N0_1.5. Since these compounds experience a high reversion it is not surprising to find that ν_{NMR} drops more significantly than in the other mixtures The lowest value is obtained by N3_2.0, which corresponds to a fall of about 37 %. When MgO replaces ZnO (N1_5.0) there is a decrease of nearly 10 %. When it substitutes partially ZnO (N2_5.0) a 17 % shrinkage of ν_{NMR}. Samples with at least 3 phr of ZnO, a mixture ZnO and $CaCO_3$ (N4_5.0) and $Zn_{1-x}Ca_xO$-like (N5_5.0 and N5_4.0) as activator undergo a reduction of approximately 10%. Sample N5_7.5 retains the same cross-link density when cured for 120 min.

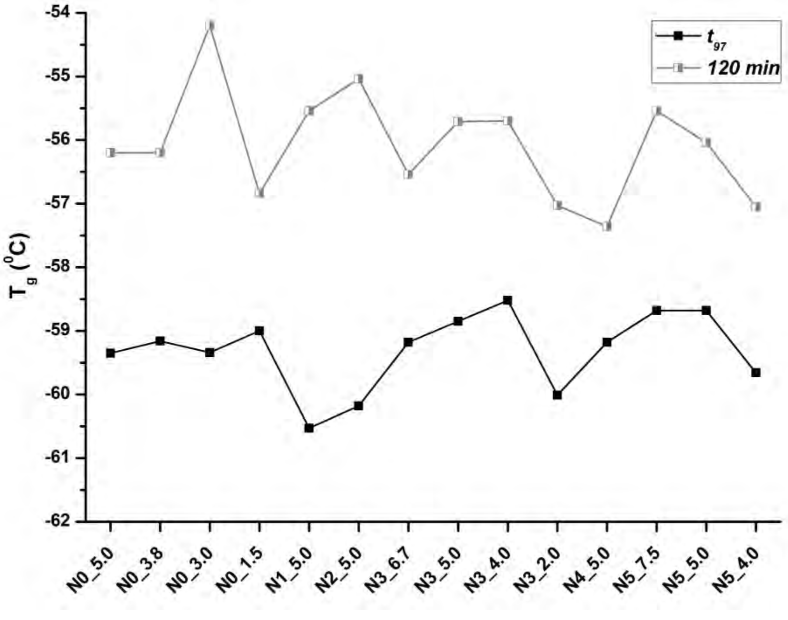

Figure 5.11. Glass transition temperature for different samples of natural rubber cured at t_{97} and 120 min.

Figure 5.11 shows the glass transition temperature of the NR samples vulcanised at t_{97} and 120 min. The T_{g} of the mixtures cured at t_{97} is dependent on cross-link density as it can be seen from the trends in Figure 5.10 and Figure 5.11. However, T_{g} is not dependent solely on cross-link density, the nature of the cure system plays a role[37] and therefore some discrepancies are obtained as a result of changing the activator. Mixtures cured for 120 minutes have higher T_{g} as a consequence of the changes suffered by the compounds during this additional vulcanisation time.

As it has been indicated previously, with MQ NMR experiments it is possible to differentiate and quantify the fraction of non-coupled defects. These defects include chain segments like dangling chains and loops which show slower relaxations and present isotropic motions that eventually average out the dipolar couplings. In contrast, the actual polymer networks are dipolar coupled because of the presence of permanent constraints and that lead to permanently non-isotropic segmental motions and faster relaxations[18, 20].

As it can be seen in Figure 5.12, in randomly cross-linked networks, the fraction of network defects depends on the cross-link density. Samples with higher ν_{NMR} values show a lower fraction of non-coupled defects. An increase of the number of linkages provokes a decrease of the molecular weight of end chains, and subsequently a reduction of the fraction of non-coupled defects. However, the fraction of network defects not only depends on ν_{NMR} and, consequently, some samples with similar ν_{NMR} contain higher fractions of defects.

It is noteworthy to observe the effect of prolonging the vulcanisation time on the fraction of non-coupled network defects which are elastically non-active. In Figure 5.12 it can be appreciated that the samples that experience a higher reversion show also a considerable increase in the fraction of defects.

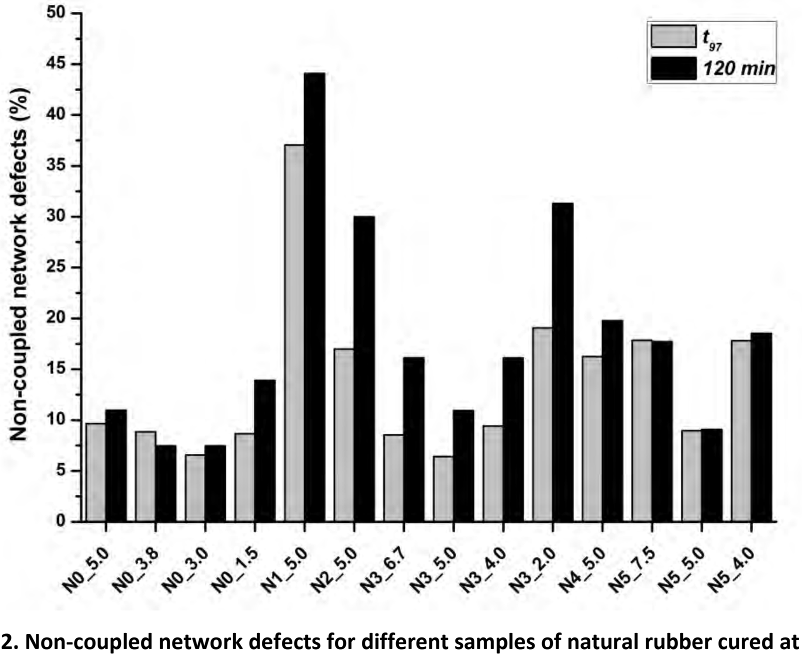

Figure 5.12. Non-coupled network defects for different samples of natural rubber cured at t_{97} and 120 min. Results are obtained from NMR measurements at 80 °C.

As it has been seen in Chapter 2 (see Figure 2.8) natural rubber, and in general diene rubbers, form not only mono-, di-, and polysulphidic cross-links, but pendant sulphidic groups terminated by an accelerator molecule, cyclic sulphides, conjugated diene and triene units, cis and trans-isomerized olefin units, and vicinal cross-links. Low A/S ratios produce polysulphidic cross-links that are more heat-labile and more likely to break and form cyclic chain modifications. Low A/S ratios give also more sulphur combined with the rubber chains to form sulphur-containing six-membered heterocyclic rings along the rubber molecular chains[38]. The cross-links formed during vulcanisation can undergo different reactions like cross-link shortening with additional cross-linking, cross-link destruction, main chain modification like dehydrogenation and cyclic sulphide formation, S-S bond interchange, etc.; that can produce a higher concentration of non-coupled network defects.

It should be pointed out that in order to obtain the proper order parameter (S_b) and then ν_{NMR}, the experiments should be carried out at temperatures far above the glass transition temperature (T_g) so that the dynamics are fast enough, principally for highly cross-linked samples. This could lead to an underestimation of the fraction of non-coupled network defects. However, even at 80 °C ($T > T_g + 150\,°C$), it is possible to extract quantitative information from the samples[20].

During sulphur vulcanisation of natural rubber several reactions take place as it has been explained. These reactions depend on many aspects, one being the vulcanisation system, i.e. the activator; and lead to variations in the cross-link density and also in their spatial distribution. The spatial cross-links distribution in the samples containing ZnO, MgO, a mixture of ZnO and MgO, and $Zn_{1-x}Mg_xO$ is represented in Figure 5.13. The curves were obtained using a fast Tikhonov regularisation procedure (*ftikreg*) developed by Chassé *et al.*[36].

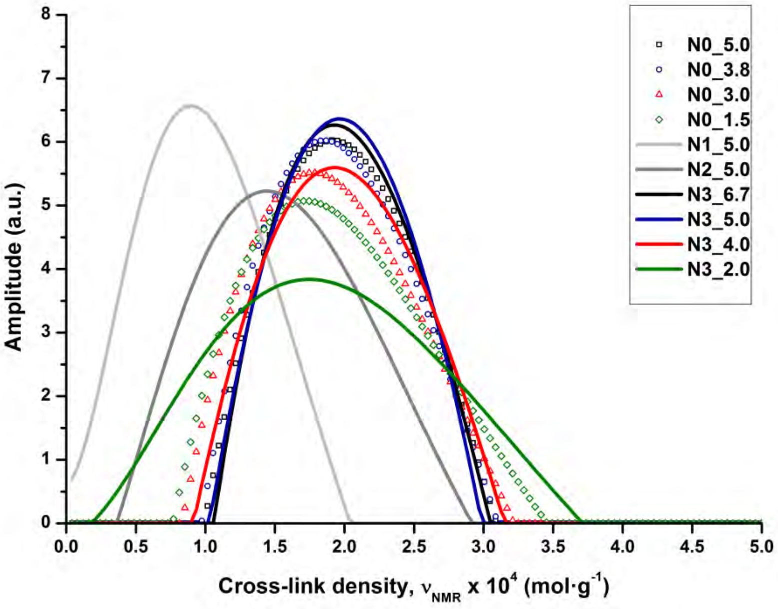

Figure 5.13. Effect of $Zn_{1-x}Mg_xO$ on cross-link distribution in NR samples. Results were obtained from NMR measurements at 80 °C fitting data using a fast Tikhonov regularisation procedure (*ftikreg*)[36].

From Figure 5.13 it can be seen the detrimental effect that the addition of MgO produces in NR samples. The compounds with ZnO (samples N0) are more homogeneous than the samples with MgO (N1_5.0) and a mixture of both (N2_5.0) because the distribution is narrower. It can be observed that samples containing MgO are characterised by Gaussian-like distributions of cross-links, although the symmetry seems to be less acute, indicating that MgO produces more heterogeneous samples.

Decreasing the amount of zinc oxide causes a broadening of the distribution, although the samples are still very homogeneous. There are no differences between the samples with 5 phr (N0_5.0) or 3.8 phr (N0_3.8) of ZnO, despite the fact the ν_{NMR} achieved is lower in the former. Further reductions to 3 phr (N0_3.0) cause a slight widening, although only sample N0_1.5 presents a cross-link distribution with a less precise Gaussian-like distribution.

Samples containing mixed metal oxides of zinc and magnesium show different behaviour depending on the loading. N3_6.7 has a very narrow distribution, very similar to N0_5.0, meaning that these samples are a random arrangement of cross-links forming very homogeneous networks. Reducing the content of $Zn_{1-x}Mg_xO$ to 5 phr (N3_5.0) or 4 phr (N3_4.0) produces again a narrow Gaussian-like distribution, although sample N3_4.0 is slightly broader. An additional diminution of $Zn_{1-x}Mg_xO$ to 2 phr (N3_2.0) broadens the cross-link distribution losing moderately the Gaussian-like aspect, although the cross-link density is very similar.

Figure 5.14 shows the spatial cross-links distribution in the samples containing ZnO, a mixture of ZnO and $CaCo_3$, and $Zn_{1-x}Ca_xO$-like obtained using *ftikreg*. The partial substitution of ZnO by $CaCo_3$ affects greatly the cross-link distribution. Sample N4_5.0 presents a broader distribution and the Gaussian-like aspect is not that evident.

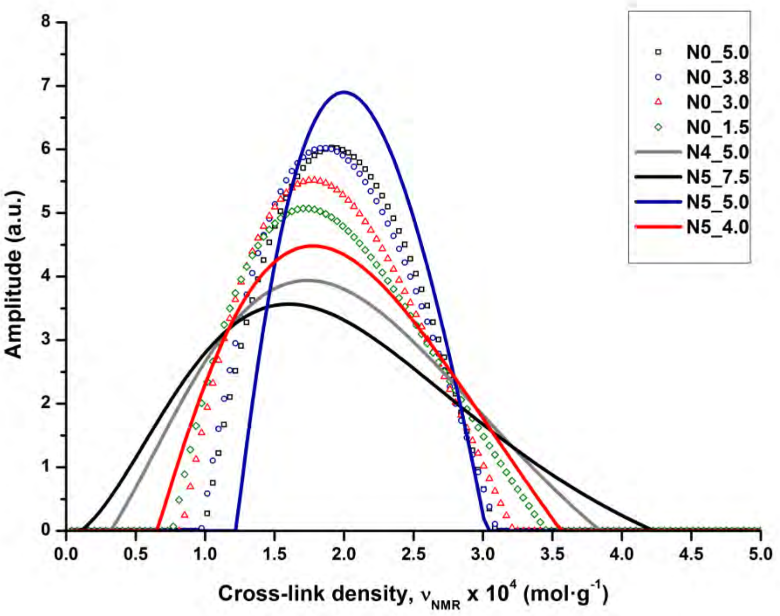

Figure 5.14. Effect of $Zn_{1-x}Ca_xO$-like on cross-link distribution in NR samples. Results were obtained from NMR measurements at 80 °C fitting data using a fast Tikhonov regularisation procedure (*ftikreg*)[36].

When $Zn_{1-x}Ca_xO$-like is used as activator an unexpected behaviour is observed depending on the loading. At high contents of $Zn_{1-x}Ca_xO$-like (N5_7.5) the distribution is particularly broad and not symmetric whatsoever. At low contents (N5_4.0) the distribution is also wide and asymmetric but less than N5_7.5 or N4_5.0. On the other hand, N5_5.0, with an intermediate loading content between N5_7.5 and N5_4.0, shows a very narrow Gaussian-like distribution, even narrower than N0_5.0.

It is important to note that the samples with $Zn_{1-x}Ca_xO$-like as activator and N0_5.0 have similar, nearly equal, cross-link density (see Table 5.4 and Figure 5.10). Once would expect N5_5.0 to show a broader distribution, similar to N4_5.0 and N5_4.0 and not to N0_5.0 since $Zn_{1-x}Ca_xO$-like is basically a mixture of ZnO and $CaCo_3$ and it has been seen that the presence of $CaCo_3$ affects greatly the cross-link distributions. In this sense, N5_5.0 also shows a rather unforeseen behaviour regarding the non-coupled network defects. The defects are more similar to the ones of N0_5.0 and not to those of N5_7.5, N5_4.0 and N4_5.0 (see Figure 5.12). Structural differences caused by side reactions during the cross-linking process are indeed one possible explanation, but it should be pointed out that the only difference in these samples is the $Zn_{1-x}Ca_xO$-like content, not the vulcanisation process or the sample preparation.

Figure 5.15 represents the ratio between the standard deviation and the average value of the spatial distribution of local cross-link density (σ/D_{res}) by fitting experimental NMR data using *ftikreg*. The effects of prolonging the vulcanisation time are very straightforward: when the samples are overcured σ/D_{res} is higher. However, the broadening of the cross-link distribution is not dependant on the reversion resistance. Samples N1_5.0 and N2_5.0 experience a high increase in σ/D_{res}, but in samples containing $Zn_{1-x}Mg_xO$ (which also experience a high reversion) the raise of σ/D_{res} is not that pronounced. In some samples (N3_6.7 and N3_4.0), it is even proportionally lower than in N0_5.0.

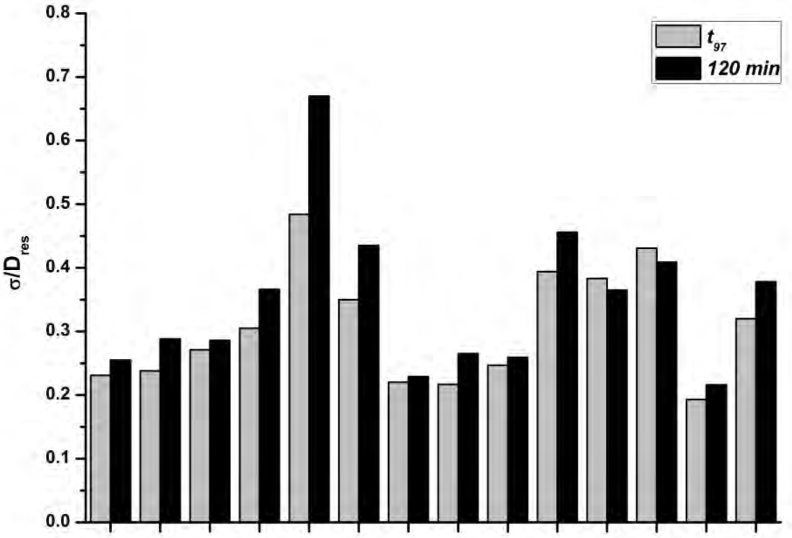

Figure 5.15. σ/D_{res} for different samples of NR cured at t_{97} and 120 min. Results were obtained from NMR measurements at 80 °C fitting data using a fast Tikhonov regularisation procedure (*ftikreg*)[36].

Two samples, N4_5.0 and N5_7.5, do not follow this trend. When they are vulcanised during 120 minutes σ/D_{res} is reduced. This unanticipated outcome could be the cause explaining the abnormal behaviour found when the $Zn_{1-x}Ca_xO$-like content is varied. Instead of assuming that sample N5_5.0 should present a broader distribution, samples N4_5.0 and N5_7.5 cured at t_{97} should have a lower σ/D_{res}, mainly smaller than when cured for 120 minutes and, therefore, the curves displayed in Figure 5.14 would be a narrower Gaussian-like distribution.

From the results obtained with the DQ NMR experiments it can be deduced that a large reduction of the Zn content in NR compounds can be safely reached. Employing 3 phr of ZnO a 40 % decrease can be attained without significant differences. Employing 1.5 phr (70 % diminution) provokes a lower cross-link density and a wider cross-link distribution, although the variations are not very remarkable.

Using $Zn_{1-x}Mg_xO$ a 70 % reduction can be achieved with N3_2.0 obtaining the same ν_{NMR}. However, an adverse increase in the fraction of non-coupled network defects and a broadening of the cross-link distribution is also obtained. Reducing 40 % the Zn content (sample N3_4.0) produces the same characteristics than the reference compound (N0_5.0).

With $Zn_{1-x}Ca_xO$-like it is also possible to reduce the Zn content achieving similar cross-link density. However, unusual results are obtained in the fraction of non-coupled network defects and the cross-link distribution depending on the amount added to the recipe.

5.3.3. BUTADIENE RUBBER SAMPLES

Fifteen formulations were prepared following the protocol described in section 5.2.3.2 to study the effect of mixed metal oxides as activator in BR compounds. In all mixtures, CBS was used as accelerator with a constant A/S ratio of 0.6 (conventional vulcanisation). The vulcanisation was carried out at four different temperatures: 140 °C, 150 °C, 160 °C and 170 °C.

5.3.3.1 CURE CHARACTERISTICS

Table 5.5 summarises the vulcanisation parameters of the different BR compounds mixed in this work. t_{02} is the time to reach 2 % of maximum torque, t_{s2} is the time to 2 dN·m rise above the minimum torque (M_L), and t_{90} is the time to achieve 90 % of M_H. The vulcanisation curves of the without activator is displayed in Figure 5.16.

Figure 5.17 shows the vulcanisation curves of the compounds containing different amounts of ZnO. In this figure it can be seen that reducing the ZnO content the cure characteristics of the samples are not affected substantially. t_{90} increases as the ZnO content is reduced, although at 140 °C sample B0_3.8 shows a shorter vulcanisation time. Nonetheless, at higher temperatures, especially at 160 °C and 170 °C, the differences are reduced.

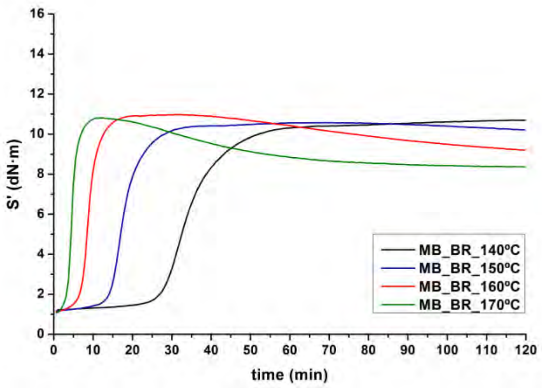

Figure 5.16. Cure characteristics of BR compounds without activator.

Table 5.5. Vulcanisation parameters of BR compounds vulcanised with different activators.

	t_{02} (min)				t_{s2} (min)				t_{90} (min)			
sample	**140°C**	**150°C**	**160°C**	**170°C**	**140°C**	**150°C**	**160°C**	**170°C**	**140°C**	**150°C**	**160°C**	**170°C**
MB_BR	17.4	8.0	3.1	1.3	29.9	15.6	7.6	3.8	49.6	25.5	12.6	6.6
B0_5.0	17.1	8.6	3.1	1.3	29.1	15.8	8.1	3.9	43.1	23.2	12.1	6.3
B0_3.8	16.5	8.0	3.1	1.3	23.3	17.1	8.7	4.3	37.2	25.5	13.2	6.7
B0_3.0	20.8	8.6	3.1	1.3	33.8	18.0	8.8	4.3	51.2	26.6	14.4	6.8
B0_1.5	22.6	8.6	3.1	1.3	33.4	18.7	9.0	4.5	50.3	27.3	13.6	7.2
B1_5.0	8.0	4.3	1.9	1.3	14.8	7.5	4.1	2.5	29.4	14.3	7.2	4.3
B2_5.0	13.5	6.8	3.1	1.3	17.4	8.9	4.8	2.7	25.4	13.1	7.2	4.2
B3_6.7	5.6	3.1	1.3	0.7	8.5	4.6	2.7	1.6	12.6	7.6	4.3	2.7
B3_5.0	5.6	3.7	1.9	0.7	8.9	5.2	2.9	1.7	14.1	8.2	4.7	2.8
B3_4.0	6.8	3.7	1.9	0.7	10.3	5.3	2.8	1.6	14.4	7.9	4.4	2.6
B3_2.0	8.6	3.7	1.9	0.7	12.2	5.7	3.0	1.8	16.9	8.1	5.1	2.6
B4_5.0	21.4	8.0	3.1	1.3	31.3	16.3	8.2	4.1	47.6	24.2	12.5	6.5
B5_7.5	14.7	6.8	2.5	1.3	21.5	10.7	5.2	2.7	34.0	16.8	8.5	4.6
B5_5.0	17.8	6.8	2.5	1.3	24.5	12.0	5.7	2.9	37.2	18.4	10.2	5.0
B5_4.0	14.7	8.6	2.5	1.3	22.4	11.3	5.3	2.8	32.5	16.6	8.8	4.4

Concerning the scorch time, Figure 5.17 shows that it is only slightly modified when the amount of activator is lowered. Generally, t_{s2} increases as lower quantities of ZnO are added into the recipe, although at 140 °C sample B0_3.8 shows a shorter t_{s2}. The variations are very small if the 3 or 1.5 phr are used and at 150 °C or higher temperatures even using 3.8 phr the compounds show similar scorch times than with lower amounts.

Correspondingly, the extent of cross-linking ($M_H - M_L$) of the compounds is lower for these compounds containing lower quantities of ZnO. Moreover, there are almost no differences between 5 phr and 3.8 phr, and further reductions down to 1.5 phr only produces a minor decrease.

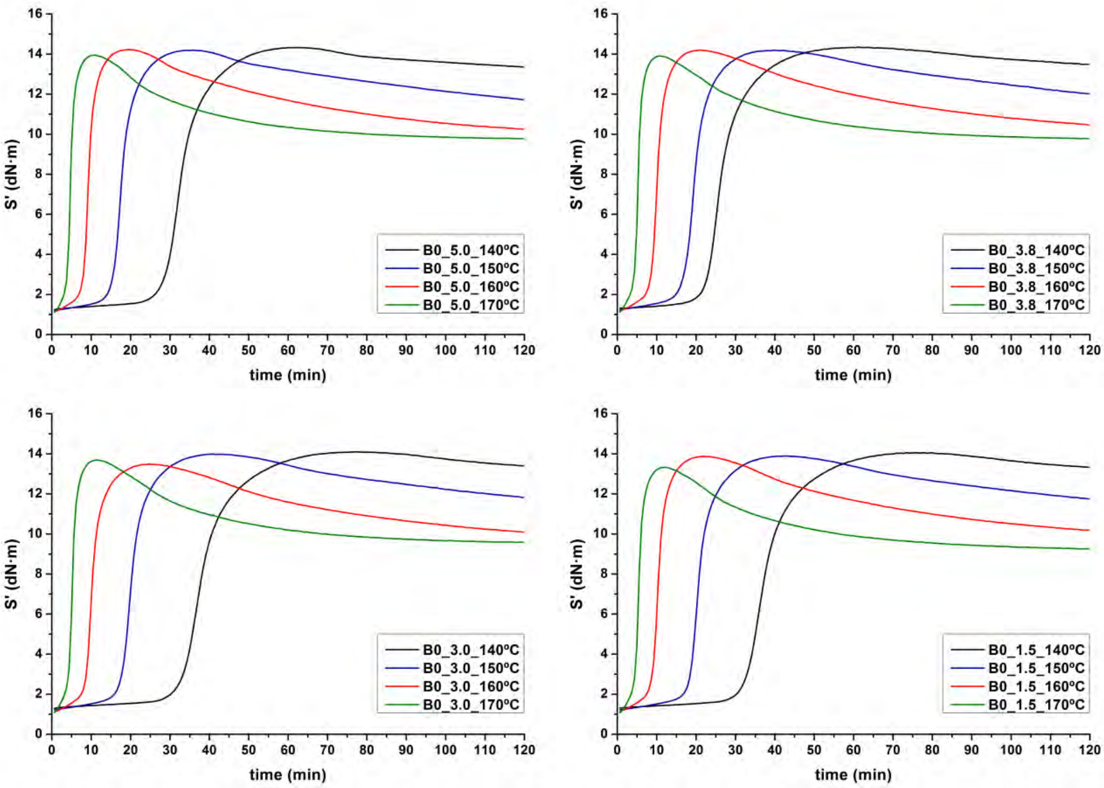

Figure 5.17. Cure characteristics of BR compounds with different amounts of ZnO.

Figure 5.18 shows the vulcanisation curves of the samples containing MgO (B1_5.0) and a mixture of ZnO and MgO (B2_5.0). Contrary to the results found in NR, MgO does not have that severe negative effect on the cure characteristics of BR. $M_H - M_L$ is lower when MgO substitutes ZnO but the decrease in torque is not as pronounced as it has been observed in NR. Replacing partially ZnO with MgO produces higher $M_H - M_L$ values. The adverse consequences of adding MgO to the recipe experienced in NR are not found in BR. In contrast, BR compounds profit from this replacement.

Regarding the vulcanisation times, in Figure 5.18 and in Table 5.5 it can be perceived that substituting partially or totally zinc oxide with magnesium oxide produces a diminution of scorch time and optimum vulcanisation time, although the reduction is higher in the latter case.

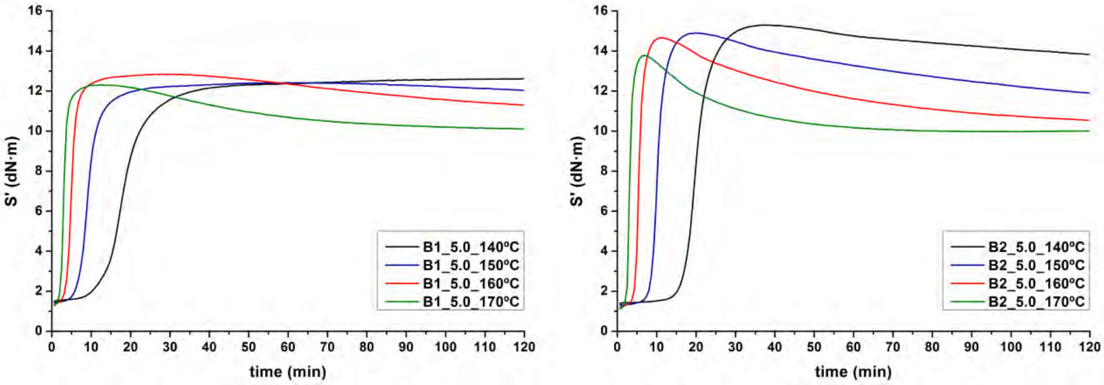

Figure 5.18. Cure characteristics of BR compounds with MgO and a mixture of ZnO and MgO.

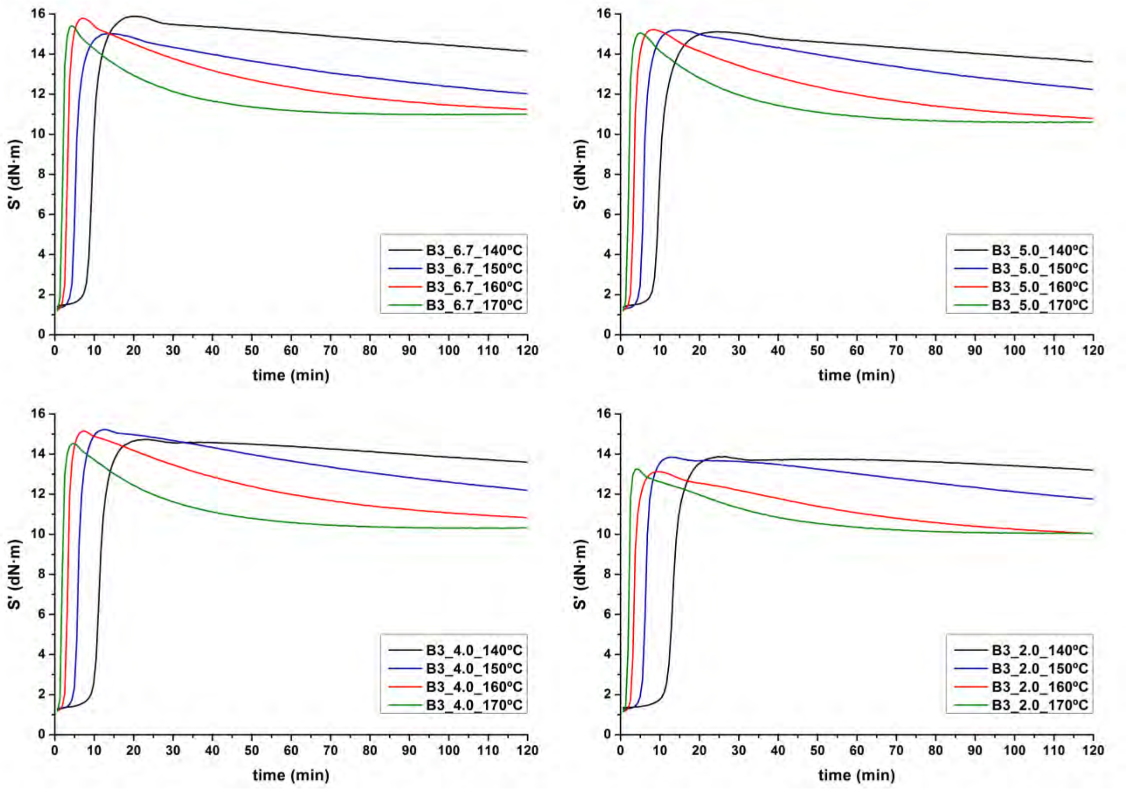

Figure 5.19. Cure characteristics of BR compounds with different amounts of $Zn_{1-x}Mg_xO$.

Figure 5.19 shows the vulcanisation curves of the compounds containing different amounts of $Zn_{1-x}Mg_xO$. As it has been observed in the compounds containing ZnO, when the zinc content is lowered both scorch time and t_{90} are reduced. However, in both cases the differences are reduced if higher vulcanisation temperatures are used.

Comparing the vulcanisation curves (Figure 5.17, Figure 5.18 and Figure 5.19) and the data shown in Table 5.5 it can be seen that the compounds including $Zn_{1-x}Mg_xO$ in the recipe show shorter scorch times than the compounds containing ZnO (samples B0) or MgO (samples B1_5.0 and B2_5.0). In general, the t_{90} times for the compounds containing $Zn_{1-x}Mg_xO$ are comparable to those of ZnO at higher temperatures, i.e. at 140 °C the t_{90} times of the B3 samples are similar to the t_{90} times of the B0 samples at 160 °C.

Regarding the extent of cure, from Figure 5.19 it can be seen that when the amount of activator is reduced there is a decrease in the $M_H - M_L$ values. The mixture containing 2 phr of $Zn_{1-x}Mg_xO$ (B3_2.0) shows a higher reduction in the extent of cure than the samples containing 5 or 4 phr (B3_5.0 and B3_4.0).

Figure 5.20 shows the rheometric curves for the BR compounds with a mixture of ZnO and $CaCO_3$, and $Zn_{1-x}Ca_xO$-like. The mixture of ZnO and $CaCO_3$ (sample B4_5.0) exhibits longer vulcanisation times and lower $M_H - M_L$ than the compounds containing $Zn_{1-x}Ca_xO$-like. The effect that the amount of $Zn_{1-x}Ca_xO$-like present in the recipe exerts on the vulcanisation times or in the extent of cure is not very significant. Figure 5.20 and Table 5.5 indicate that t_{90} and t_{s2} are almost unaffected if the content of $Zn_{1-x}Ca_xO$-like is reduced from 7.5 to 4 phr. The cross-link degree is also not influenced in a large degree when lower activator loads are used.

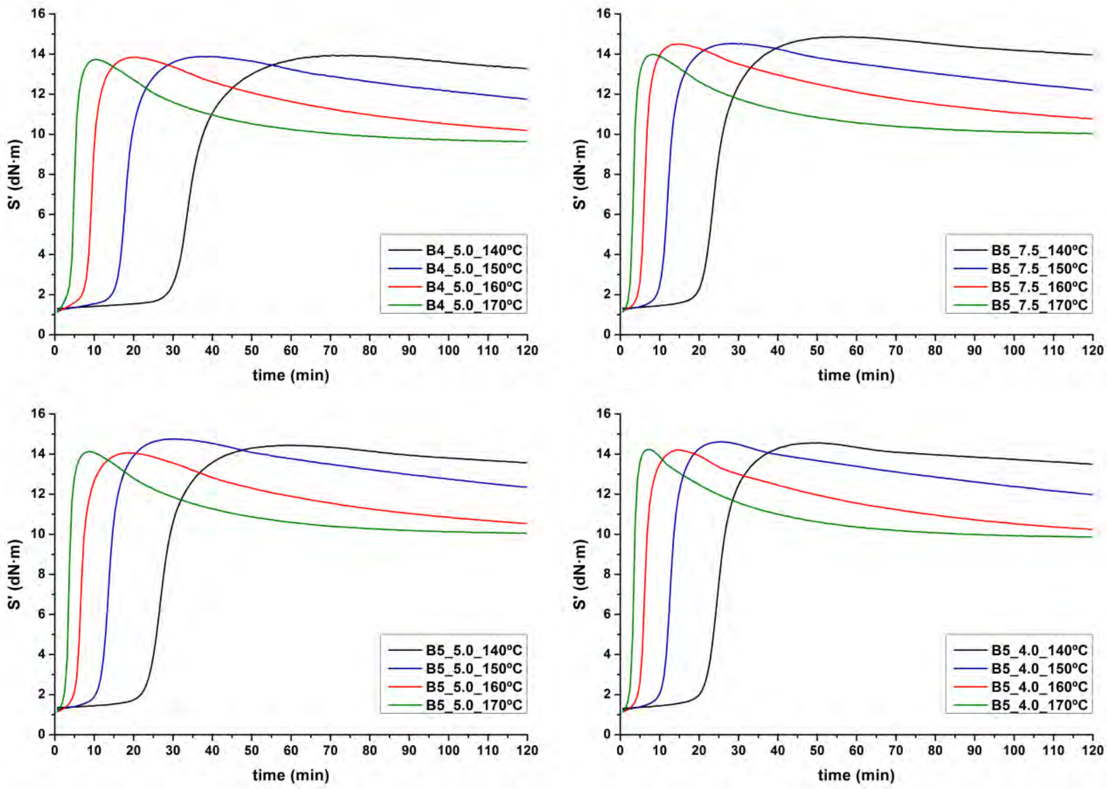

Figure 5.20. Cure characteristics of BR compounds with a mixture of ZnO and $CaCO_3$ and $Zn_{1-x}Ca_xO$-like.

Comparing the results obtained with the different activators it can be appreciated that the scorch times and t_{90} times for the BR compounds with $Zn_{1-x}Ca_xO$-like are shorter than the reference compounds (samples B0), although the differences are not as significant as it has been found with $Zn_{1-x}Mg_xO$.

Figure 5.21 displays the $M_H - M_L$ values for BR mixtures. In this figure it can be observed that lower amounts of ZnO produces a similar extent of cross-linking. Using only 1.5 phr of ZnO it is possible to obtain similar $M_H - M_L$ values. Contrary to what was found in NR compounds, the sample with a mixture of ZnO and MgO (B2_5.0) show a degree of cure higher than the mixtures containing only ZnO, especially if the vulcanisation temperature is low.

When $Zn_{1-x}Mg_xO$ is used $M_H - M_L$ is higher than when ZnO is the activator, with the exception of B3_2.0. Adding only 2 phr of $Zn_{1-x}Mg_xO$ produces lower $M_H - M_L$ values, but comparable to 1.5 phr of ZnO or even 3.0 phr at low temperatures. The extent of cross-linking of the compounds with $Zn_{1-x}Ca_xO$-like is slightly higher than those containing ZnO. In spite of that, $Zn_{1-x}Ca_xO$-like does not produce $M_H - M_L$ as high as $Zn_{1-x}Mg_xO$.

Table 5.6 shows the Cure Rate Index (CRI, calculated using Equation 5.2), the reversion time (RT, time to reach 95 % M_H after passing M_H), and the reversion tax (calculated according to Equation 5.3). It can be seen that the cure rate index is increased when ZnO is substituted by mixed metal oxides or MgO. Adding $CaCO_3$ to the recipe produces a slight reduction of the CRI. $Zn_{1-x}Mg_xO$ increases significantly the CRI wheras the effect of $Zn_{1-x}Ca_xO$-like is more moderate. Replacing partially ZnO with MgO (B2_5.0) improves also the CRI and the enhancement is comparable to $Zn_{1-x}Mg_xO$ when the temperature is 160 °C or higher.

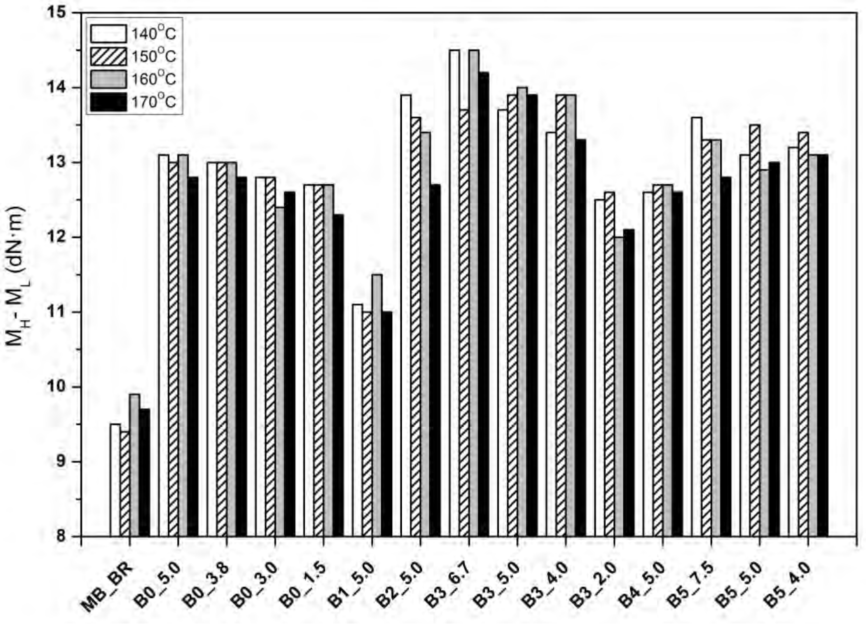

Figure 5.21. Extent of cure ($M_H - M_L$) for BR mixtures.

Table 5.6. Cure rate index (CRI), reversion time (RT), and reversion tax of BR compounds.

	CRI (%)				RT (min)				Reversion Tax (%)			
sample	140°C	150°C	160°C	170°C	140°C	150°C	160°C	170°C	140°C	150°C	160°C	170°C
MB_BR	5.0	9.1	16.4	41.0	–	–	28.1	14.0	–	1.8	5.3	13.9
B0_5.0	7.1	13.6	27.3	41.0	30.5	15.3	8.8	6.4	4.9	8.6	15.8	23.0
B0_3.8	7.5	11.7	23.4	54.6	41.5	21.4	12.2	7.3	3.5	7.4	13.9	21.8
B0_3.0	5.9	11.7	18.2	32.8	37.8	21.4	14.6	7.3	3.9	7.7	13.1	22.1
B0_1.5	5.9	11.7	20.5	41.0	39.7	20.1	12.8	6.7	3.7	7.9	14.2	22.7
B1_5.0	6.8	14.9	32.8	82.0	–	–	35.4	17.7	–	0.9	3.9	9.8
B2_5.0	12.6	23.4	41.0	82.0	30.5	14.6	7.9	4.9	4.8	9.5	16.9	23.7
B3_6.7	23.4	32.8	54.6	82.0	32.3	16.5	6.7	3.1	4.8	8.5	16.6	24.8
B3_5.0	18.2	32.8	54.6	82.0	38.4	19.5	6.7	4.0	4.1	7.3	16.4	24.4
B3_4.0	23.4	41.0	54.6	82.0	62.2	22.3	9.2	4.9	1.9	7.0	15.3	23.5
B3_2.0	20.5	41.0	40.8	82.0	89.1	39.1	11.6	4.9	1.2	3.5	10.9	17.9
B4_5.0	6.3	12.6	23.4	41.0	47.6	23.2	11.9	6.7	2.7	7.0	13.9	22.1
B5_7.5	8.2	16.4	32.8	54.6	43.3	20.8	10.1	6.7	3.5	7.2	13.5	20.8
B5_5.0	7.8	14.9	23.4	41.0	41.5	20.7	10.4	6.7	3.6	7.3	14.2	21.5
B5_4.0	9.6	20.5	27.3	54.3	37.2	15.9	9.2	4.0	4.3	8.1	15.0	23.7

Contrary to the behaviour of NR compounds, when $Zn_{1-x}Mg_xO$ is used as activator, the reversion time is increased and the reversion tax decreases in comparison to ZnO, predominantly at low temperatures or loadings. In general, the reversion resistance is not worsened if lower amounts of $Zn_{1-x}Mg_xO$ or ZnO are added to the recipe, rather the opposite behaviour is found, especially at 140 °C. On the other hand, if $Zn_{1-x}Ca_xO$-like is added, the reversion resistance is not enhanced, the RT and the reversion tax are comparable to ZnO. Surprisingly, the compounds with MgO show the highest RT and the lowest reversion tax.

Figure 5.22 shows the activation energy (E_a) of the mixtures containing the different activators used in this work. The E_a is the specific constant determining the energy required to activate the reaction and was calculated according to DIN 53529. The results displayed in Figure 5.22 indicate that the activation energy is drastically reduced when mixed metal oxides of zinc and magnesium are employed. On the contrary, $Zn_{1-x}Ca_xO$-like does not have an influence on E_a, the values attained are at the same level than with ZnO. MgO produces that the activation energy raises. However, when mixed with ZnO, E_a is moderated.

As it has been exposed before, lower amounts of ZnO produces similar extent of cure. A 70 % reduction of zinc content can be safely achieved by using only 1.5 phr of ZnO obtaining similar $M_H - M_L$ values and a higher reversion resistance. However, the vulcanisation times are longer and the cure rate index is reduced.

Using $Zn_{1-x}Mg_xO$ it is also possible to reduce significantly the Zn content in BR. Replacing ZnO with $Zn_{1-x}Mg_xO$ reduces the vulcanisation times and improves the reversion resistance and the CRI. Furthermore, the E_a is minimised. Reducing 40 % the zinc content with $Zn_{1-x}Mg_xO$ (B3_4.0) provokes also higher $M_H - M_L$ values. With 2 phr of $Zn_{1-x}Mg_xO$ (70 % reduction) there is a decrease in the extent of cure, but comparable to 1.5 phr of ZnO.

Using $Zn_{1-x}Ca_xO$-like the reduction in the cure times is not as marked as with $Zn_{1-x}Mg_xO$ but the cross-link extent is also higher. On the contrary, the reversion resistance is not improved, particularly if low loading are used. However, there are significant differences between sample B4_5.0 and the mixtures containing $Zn_{1-x}Ca_xO$-like. Adding 3.3 phr of ZnO and 1.7 phr of $CaCO_3$ (34 % reduction of zinc content) slower cure properties are obtained, even lower than when ZnO is the activator. A higher reduction of the zinc content (47 %) can be achieved employing 4 phr of $Zn_{1-x}Ca_xO$-like.

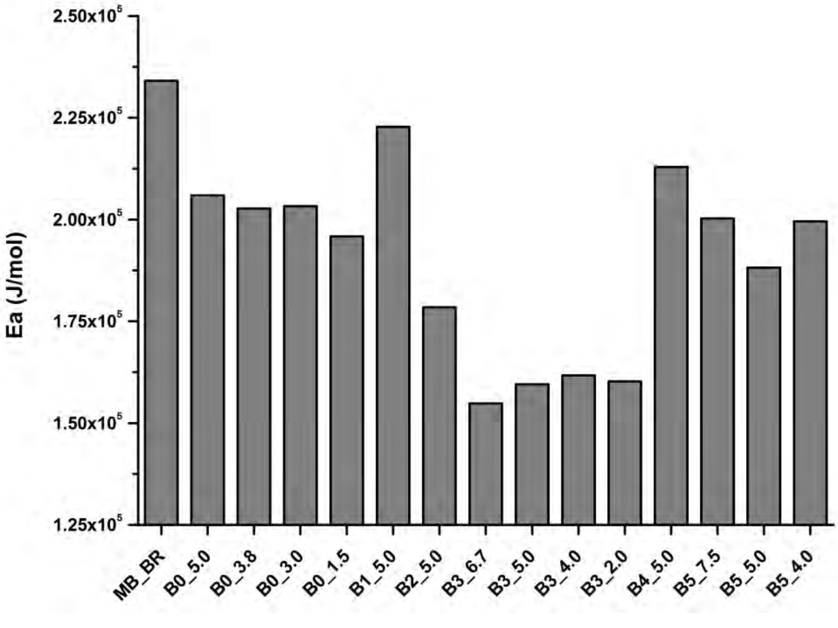

Figure 5.22. Effect of activator on activation energy (Ea) of butadiene rubber compounds.

It is worthwhile noting that MgO does not exert the same effect on the vulcanisation of natural rubber that on butadiene rubber. In spite of causing a lower extent of cure for BR compounds, the difference is not as substantial as in NR. Moreover, the mixture of MgO and ZnO possesses faster cure characteristics, higher extent of cross-linking and the reversion is not as severe as is NR.

5.3.3.2 PHYSICAL PROPERTIES

Stress-strain measurements were performed to study the effect of the mixed metal oxides on the physical properties of the rubber compounds. Figure 5.23 shows the tensile strength of the butadiene rubber samples vulcanised at different temperatures.

The mixtures containing ZnO in the recipe show similar tensile strength (TS) independently of the zinc content present in the mixture. From Figure 5.23 that there are no significant differences between samples vulcanised at 140 °C, 150 °C and 170 °C. At 160 °C the mixture containing 5 phr of ZnO (B0_5.0) is slightly different from the other mixtures. Since the $M_H - M_L$ values seen in the previous section are very similar for these samples, it is not unexpected to find equivalent tensile strength.

Surprisingly, when zinc oxide is substituted by MgO there are notable differences regarding the tensile strength. Albeit sample B1_5.0 possesses lower $M_H - M_L$ values at all the tested temperatures, TS is comparable (or rather higher) than for the compounds with ZnO. When ZnO is partially replaced by MgO (B2_5.0), the same behaviour is observed, especially at 140 °C and 150 °C. Nevertheless, this sample has shown a higher degree of cure at low temperatures.

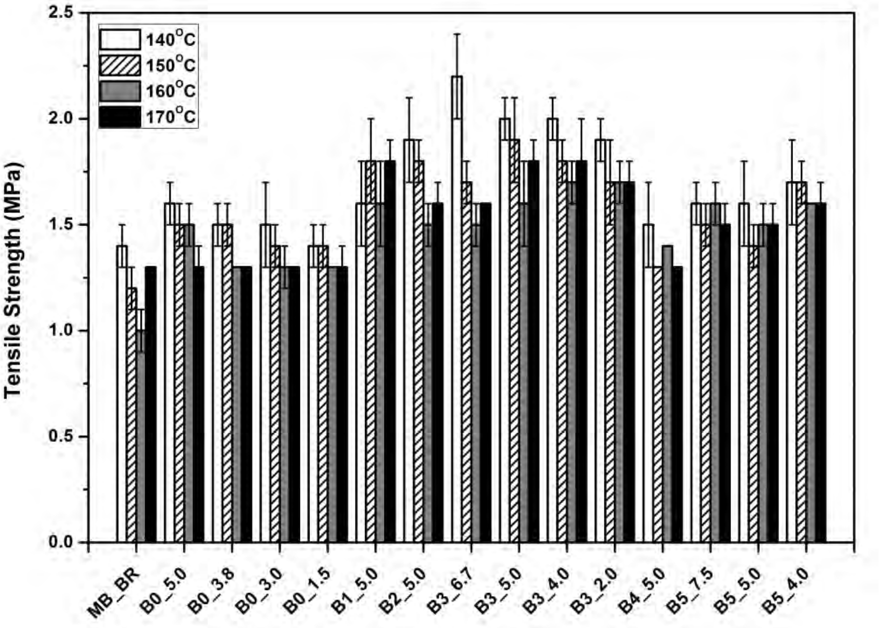

Figure 5.23. Effect of activator on tensile strength of butadiene rubber compounds.

When mixed metal oxides of zinc and magnesium are used as activator, the tensile strength of the compounds is not considerably affected if low amounts are used. B3_2.0 (2 phr of $Zn_{1-x}Mg_xO$) has the same TS than samples with 4, 5 phr or even 6.7 phr. Unexpectedly, B3_6.7 show low TS values at temperatures higher than 140 °C, not following the trend exhibited by the other compounds with lower amounts of activator.

In Figure 5.23 it can be seen that the mixtures containing $Zn_{1-x}Mg_xO$ show higher tensile strength than the mixtures with ZnO, especially at low temperatures. Even with only 2 phr of $Zn_{1-x}Mg_xO$, TS is higher than with 5 phr of ZnO. These results indicate that this activator is a good candidate to substitute ZnO reducing the zinc levels in the rubber industry.

Concerning the presence of $CaCO_3$ in the recipe, it can be observed from the findings displayed in Figure 5.23 that this compound does not have a strong influence in the tensile strength. Sample B4_5.0 shows TS similar to those shown by the samples containing ZnO. The mixtures including $Zn_{1-x}Ca_xO$-like possess slightly higher tensile strength than the samples with ZnO, although the enhancement is not comparable to $Zn_{1-x}Mg_xO$.

Furthermore, the different activator tested in this work show some differences regarding the elongation at break (E_b) as it can be appreciated in Figure 5.24. MgO produces an increase in the E_b values, whether it substitutes ZnO completely (B1_5.0) or partially (B2_5.0). However, the complete replacement gives higher values.

Regarding the compounds with ZnO on the recipe, Figure 5.24 shows that reducing the ZnO content or the variations in the vulcanisation temperature do not have an influence on the E_b. Mixtures comprising $CaCO_3$ or $Zn_{1-x}Ca_xO$-like have similar E_b than the samples with ZnO. On the contrary, when the BR compounds include $Zn_{1-x}Mg_xO$ instead of ZnO E_b is higher. Furthermore, reducing the amount of $Zn_{1-x}Mg_xO$ does not produce values significantly different.

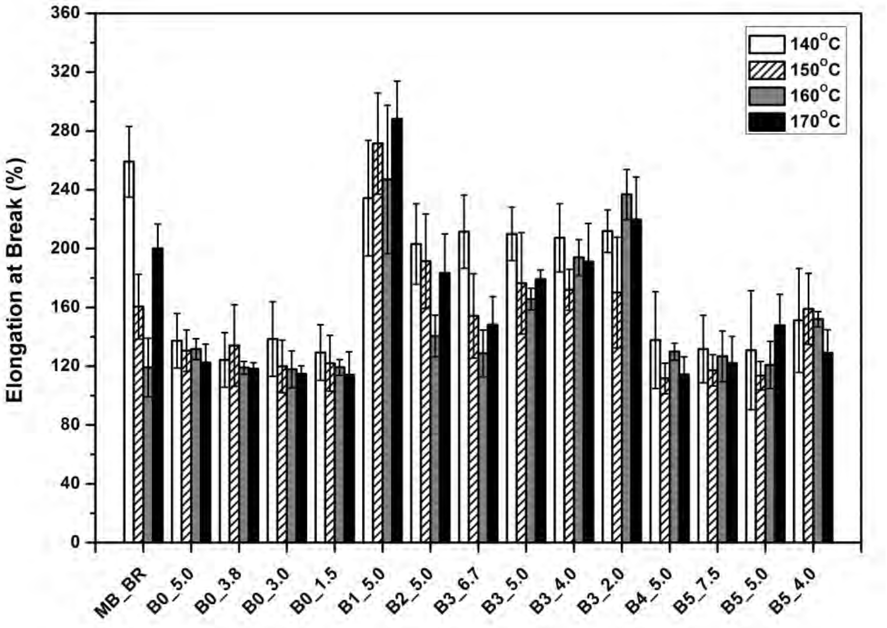

Figure 5.24. Effect of activator on elongation at break of butadiene rubber compounds.

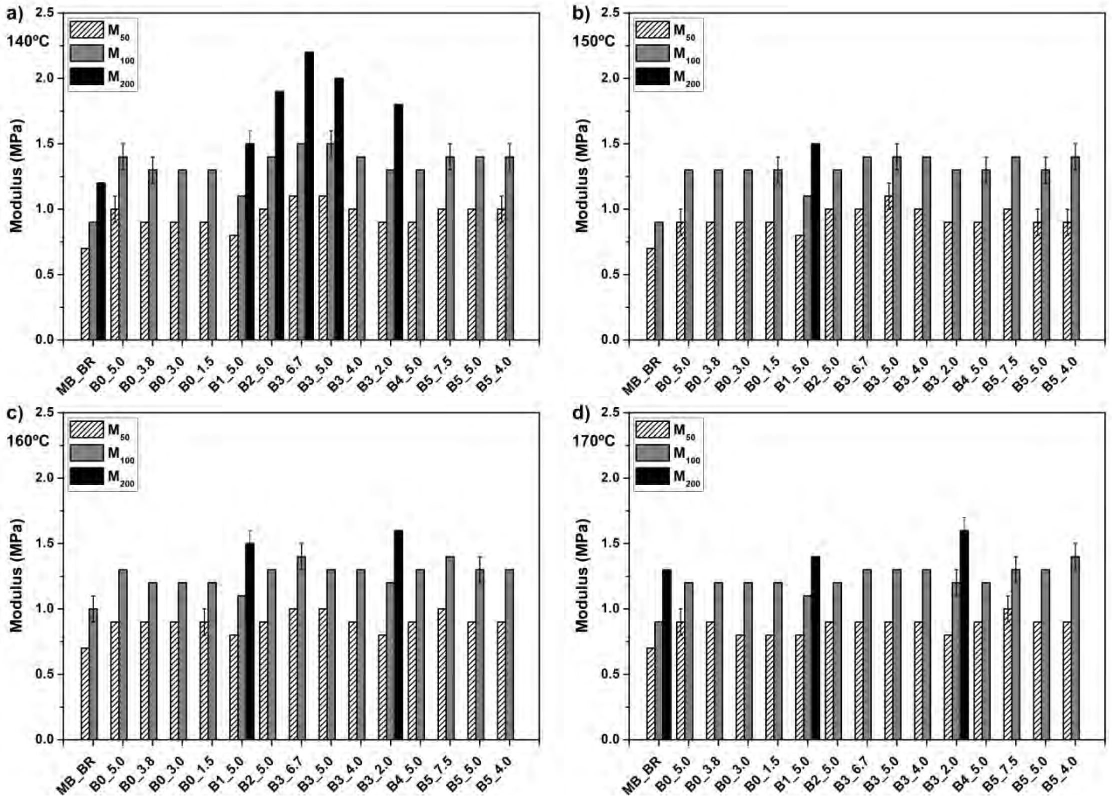

Figure 5.25. Modulus at 50%, 100% and 200% elongation for BR at a) 140°C, b) 150°C, c) 160°C and d) 170°C.

In Figure 5.25 it is represented the tensile moduli, M_{50} (modulus at 50% elongation), M_{100} (modulus at 100% elongation) and M_{200} (modulus at 200% elongation) for the butadiene rubber compounds vulcanised at the different temperatures tested in this work. In this figure it can be observed that the highest moduli are obtained when $Zn_{1-x}Mg_xO$ is employed as activator. However, the differences between the different compounds are not very significant.

From the results shown in Figure 5.25 it can be deduced that reducing the zinc levels in butadiene rubber compounds does not yield to lower tensile moduli. The mixtures with lower amount of ZnO, $Zn_{1-x}Mg_xO$ or $Zn_{1-x}Ca_xO$-like give moduli alike to those obtained employing higher loads of these activators.

Figure 5.26 shows the micro International Rubber Hardness Degree (IRHD) results from measurements according to ISO 48. In general, it can be seen that when the mixtures are vulcanised at higher temperatures the hardness decreases. The mixtures containing zinc oxide show similar IRHD, although there is a slight decrease as the zinc content in the mixture is reduced.

When MgO substitutes ZnO as activator (B1_5.0), the hardness is lowered. Although this sample show a higher tensile strength, the low extent of cure achieved provokes that the hardness of this compound is decreased. On the contrary, when MgO replaces ZnO partially (B2_5.0), the hardness achieved is comparable, if not higher in some cases, than the samples comprising only ZnO.

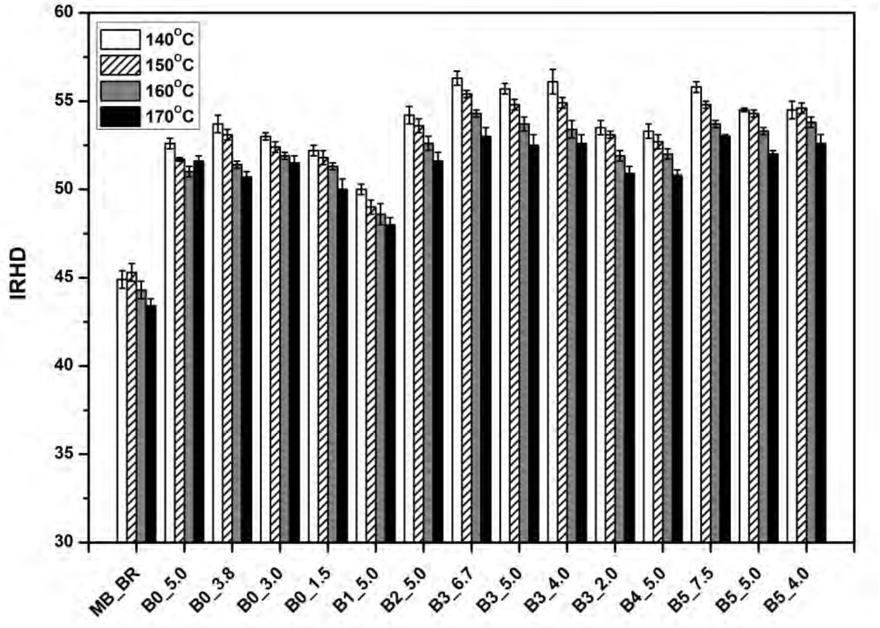

Figure 5.26. Effect of activator on IRHD of butadiene rubber compounds.

The compounds with $Zn_{1-x}Mg_xO$ exhibit the highest hardness. The mixtures containing between 6.7 and 4 phr present no differences regarding the IRHD. When only 2 phr are used, the hardness yielded is to some extent lower. In spite of that, this sample (B3_2.0) shows a hardness on the same level than those comprising ZnO with loadings as high as 5 phr.

Regarding the effect of $CaCO_3$, it can be observed from Figure 5.26 that this compound does not have a strong influence in the hardness. Sample B4_5.0 possesses an IRHD similar to those shown by the samples containing ZnO. The mixtures including $Zn_{1-x}Ca_xO$-like produce in some measure higher hardness than the samples with ZnO. Although the enhancement is not as significant as with $Zn_{1-x}Mg_xO$, it is nevertheless comparable.

From the results found in this section, it can be deduced that the use of mixed metal oxide of zinc and magnesium allows not only the reduction of the zinc level in BR compounds but also the achievement of higher mechanical properties. Adding to the recipe only 2 phr of $Zn_{1-x}Mg_xO$ (70 % reduction of the zinc levels) it is possible to obtain compounds with higher tensile strength and elongation at break than the compounds with higher amounts of ZnO. In addition, the tensile moduli and the hardness are not diminished.

The use of $Zn_{1-x}Ca_xO$-like also allows the production BR compounds with lower zinc levels. Using 4 phr (47 % reduction) the properties studied up to this point are not deteriorated in comparison with the use of ZnO. However, the improvement is not comparable as it is achieved with $Zn_{1-x}Mg_xO$, even with higher reductions.

Surprisingly and contrary to the results found working with natural rubber, MgO is not as bad activator as expected. The hardness is lower and the elongation at break is higher. Since the extent of cure achieved by this sample is inferior, the behaviour of these characteristics is not unexpected. However, the tensile strength and the tensile moduli are very similar. This may lead to consider that for certain specific application MgO could be used as activator.

Reducing the zinc loadings by simply adding lower quantities of ZnO is also possible. However, there is no improvement of the mechanical properties and in some cases they are slightly worsened. A 70 % reduction is also reachable incorporating 1.5 phr of ZnO but the hardness would have lower values.

5.3.3.3 EQUILIBRIUM SWELLING EXPERIMENTS

Figure 5.27 displays the cross-link density ($\nu_{phys.}$) obtained from the equilibrium swelling data of the BR compounds. The effect that the vulcanisation temperature exerts on the cross-link density of the samples can be easily extracted from the results presented in Figure 5.27. As the vulcanisation temperature is increased $\nu_{phys.}$ diminishes and, furthermore, the reduction is greater when higher temperatures are applied.

The swelling degree is shown in Figure 5.28. Contrary to the cross-link density, it can be seen that as the temperature is raised, the same behaviour is found in the swelling degree. When the temperature increases, there is a reduction in the cross-link density and, therefore, the samples are able to attain a higher swelling degree.

The mixtures with ZnO show similar $\nu_{phys.}$. When the amount of activator present in the mixture is minimised there is a slight decrease although, altogether, $\nu_{phys.}$ is maintained at the same level when the reduction is between 5 and 3.8 phr or between 3 and 1.5 phr.

When MgO substitutes ZnO as activator (B1_5.0), $\nu_{phys.}$ is largely diminished and, on the contrary, this sample has the highest swelling degree. Since it has been found that sample B1_5.0 shows the lowest $M_H - M_L$, it is not unexpected to find that the cross-link density is very low. When MgO replaces ZnO partially (B2_5.0), the $\nu_{phys.}$ achieved is comparable, if not higher at soft temperatures, than the samples comprising only ZnO.

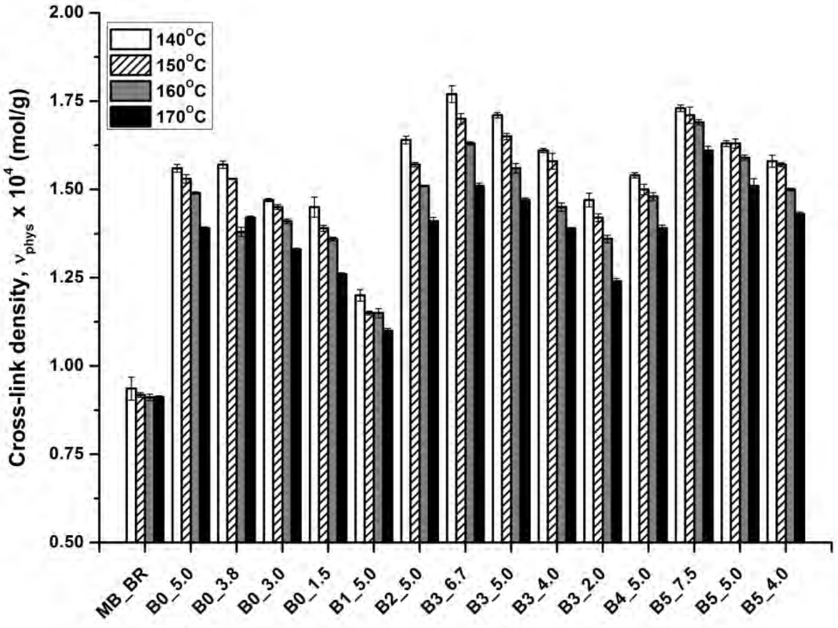

Figure 5.27. Cross-link density for the different BR compounds calculated using the Flory–Rehner approach.

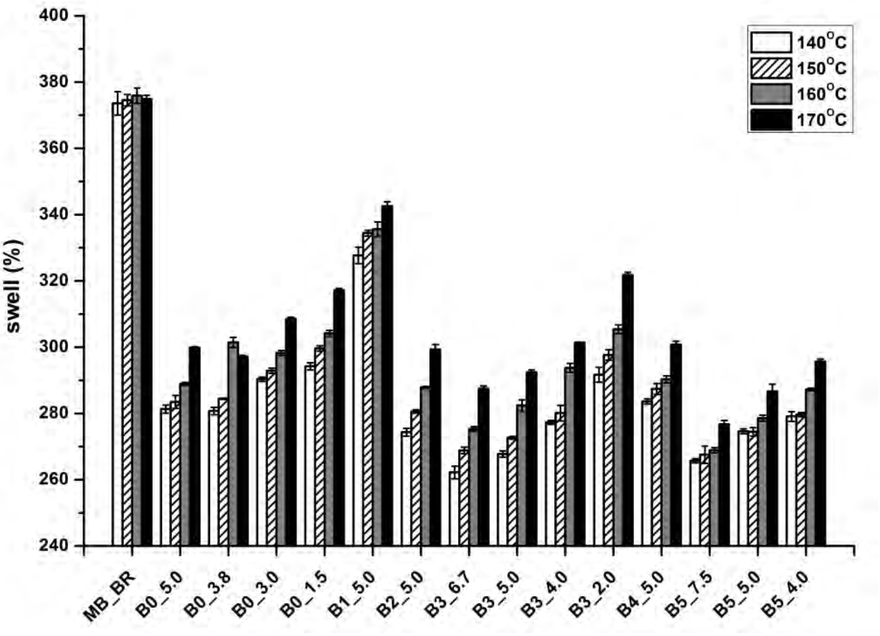

Figure 5.28. Swelling degree for the different BR compounds.

The use of mixed metal oxides of zinc and magnesium causes an enhancement on the cross-link density. As it has been observed with ZnO, when the zinc levels are reduced there is a slight decrease on the $\nu_{phys.}$. The addition of 6.7 or 5 phr of $Zn_{1-x}Mg_xO$ yields to a higher $\nu_{phys.}$ than the compounds with ZnO. The sample with 4 phr (B3_4.0) gives a $\nu_{phys.}$ comparable to samples with higher amounts of ZnO. A further reduction to 2 phr (B3_2.0) produces a compound with a cross-link density on the same level than 1.5 phr of ZnO or even 3.0 phr at low temperatures.

From the findings displayed in Figure 5.27 and Figure 5.28, it can be noticed that the presence of $CaCO_3$ does not have a strong influence in the cross-link density. Sample B4_5.0 shows $\nu_{phys.}$ and swelling degree similar to those shown by the samples containing ZnO.

The mixtures including $Zn_{1-x}Ca_xO$-like possess a higher $\nu_{phys.}$ than the samples with ZnO. Although the enhancement is not comparable to $Zn_{1-x}Mg_xO$ at low temperatures, as it is increased, $Zn_{1-x}Ca_xO$-like yields to cross-link densities higher than $Zn_{1-x}Mg_xO$. The detrimental effect of increasing the temperature is minimised when $Zn_{1-x}Ca_xO$-like is used as activator.

One of the advantages of the swelling method in determining the cross-link density is that, in combination with thiol–amine chemical probes, it is possible to study the cross-link distribution. Figure 5.29 shows the distribution of poly- and di- and monosulphidic cross-links in BR compounds vulcanised at 140 °C calculated using the Flory–Rehner approach together with the thiol–amine chemical probes.

All the compounds in this study were produced using conventional systems. These kinds of vulcanising systems are known for containing mostly polysulphidic cross-links with relatively high level of chain modification. Consequently, their monosulphidic network is very limited. For that reason, in the experiments performed in this work all the treatments with hexane-1-thiol generated a very weak gel. The cross-link density of these materials could not be determined by swelling measurements because the final drying process produced a very porous and unstable structure difficult to handle. Thus, the cross-link structure of these compounds could only be defined as the percentage of polysulphidic cross-links and the percentage of the sum of mono- and disulphidic cross-links. It should be remarked that most of this second percentage corresponds to disulphidic cross-links since the monosulphidic network is very poor as explained before.

In Figure 5.29 it can be seen that, as explained before, most of the samples contain mostly polysulphidic cross-links. Since the system is conventional and the cure was stopped at t_{90}, one would expected the network to be mainly polysulphidic as was found. However, it is surprising to find that the samples containing no activator exhibit a proportion of mono- and disulphudic cross-links very similar to the compounds with activator.

This behaviour is caused by the different mechanism that the reaction follows in the presence of ZnO depending on the rubber. For natural rubber it has been reported[39] that ZnO shows shorter cross-links because zinc accelerator complexes promote desulphuration of cross-links. Zinc accelerator complexes catalyses the cross-link shortening and the allylic rearrangements via nucleophilic reactions reactions[40]. In the case on BR it has been found that shows a much reduced response to zinc compounds in vulcanization, being able, unlike NR, to achieve substantial degrees of crosslinking in the absence of zinc[41]. It has been proposed that in BR the mechanism seems to be closer to the pathway of unaccelerated sulphur vulcanisation, with less involvement of zinc-accelerator species and the appearance of radical reactions[6].

However, it is surprising to find that the samples containing MgO exhibit a higher proportion of mono- and disulphudic cross-links. Contrary to has been found in NR, where MgO forms only polysulphidic cross-links, in BR compounds MgO seems to promote the formation of mono- and disulphudic cross-links.

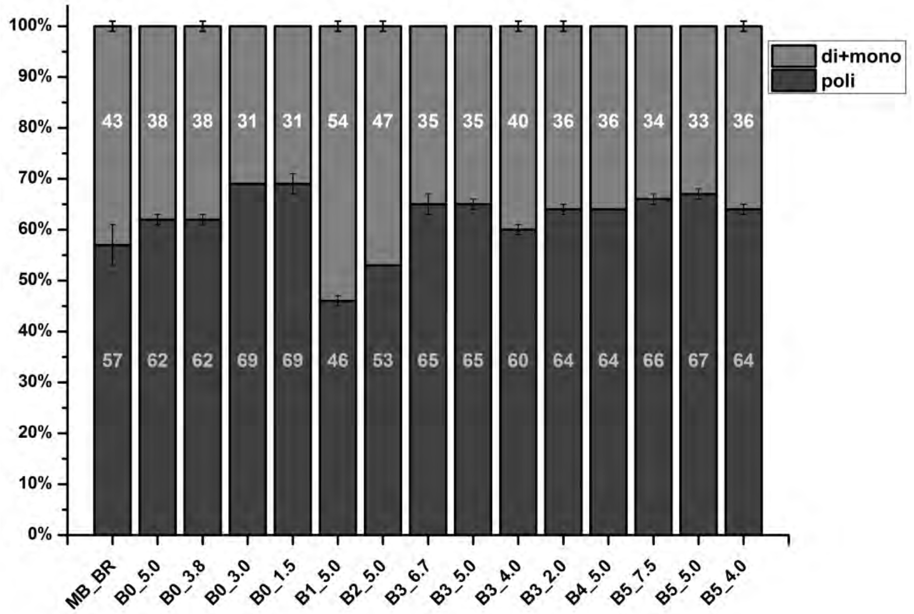

Figure 5.29. Cross-link distribution of polysulphidic and (disulphidic + monosulphidic) cross-links in BR compounds vulcanised at 140 °C calculated using the Flory–Rehner approach together with the thiol–amine chemical probes.

Concerning the other samples, in Figure 5.29 no significant differences are found in the cross-link distribution. Reducing the amount of activator does not cause important variations in the fractions of sulphidic cross-links. Only the mixtures activated with ZnO present a slight increase on the fraction of polysulphidic cross-links.

In summary, the equilibrium swelling experiments have shown that it is possible to reduce the zinc content in BR compounds. Using 4 phr of $Zn_{1-x}Mg_xO$ it is possible to reduce by 40 % the zinc levels obtaining the same cross-link distribution and higher cross-link density than with ZnO. A 70 % reduction is also attainable employing 2 phr of $Zn_{1-x}Mg_xO$, although there is a slight decrease of $\nu_{phys.}$. With 4 phr of $Zn_{1-x}Ca_xO$-like, the zinc levels can be decreased by 47% obtaining also the same cross-link distribution and higher $\nu_{phys.}$ than with ZnO.

However, the results obtained with equilibrium swelling experiments, especially those in combination with thiol–amine chemical probes, should be taken carefully due to all the uncertainties of the method. The Flory-Huggins interaction parameter, the effect of the fraction of insoluble components in the determination of the volumetric fraction of rubber and other assumptions of the model may lead to large changes in the calculated cross-link density. This may be the reason why there is a higher fraction of mono- and disulphidic cross-links in the samples containing MgO or no activator. Swelling experiments only yield a qualitative approximation to the real cross-link density of the sample, in particular when highly cross-linked samples are considered[19]. In spite of that, the results obtained can be safely used as a qualitative comparison between the different samples.

5.3.3.4 ^{1}H NMR RELAXATION TIME SPECTROSCOPY

NMR magnetisation relaxation experiments were performed on BR compounds vulcanised at 140 °C to measure the cross-link density. As it has been explained in Chapter 2 (see section 2.2.2.3.1), the cross-link density can be conveniently extracted analysing the T_2 curves according to a Gaussian-exponential function shown in Equation 2.3. The factor qM_2 allows the determination of the average molecular weight between cross-links, (M_C)[27]. However, the results are very much dependent on the method and assumptions adopted. On the other hand, it has been shown that the cross-link density is directly proportional to qM_2 and inversely proportional to T_2[28, 29]. For these reasons, only qM_2 and T_2 will be used in this section as indicators of the cross-linked density of the different compounds prepared.

Figure 5.30 shows the T_2 times (black, left y-axis) and the Gaussian fraction qM_2 (grey, right y-axis) of the BR compounds cured at 140 °C. It can be seen that the sample containing MgO gives the longest T_2 and the lowest qM_2 of the samples with activator because, as it has been found in the previous sections, it has a low cross-link density and extent of cure.

In the samples containing ZnO, the T_2 times increase and qM_2 decrease as the amount of activator in the recipe is reduced. The T_2 times and the Gaussian fraction qM_2 of the compounds with $Zn_{1-x}Mg_xO$ are on the same level that the mixtures with ZnO, although there are small differences. The qM_2 values are slightly smaller but the T_2 times are also shorter.

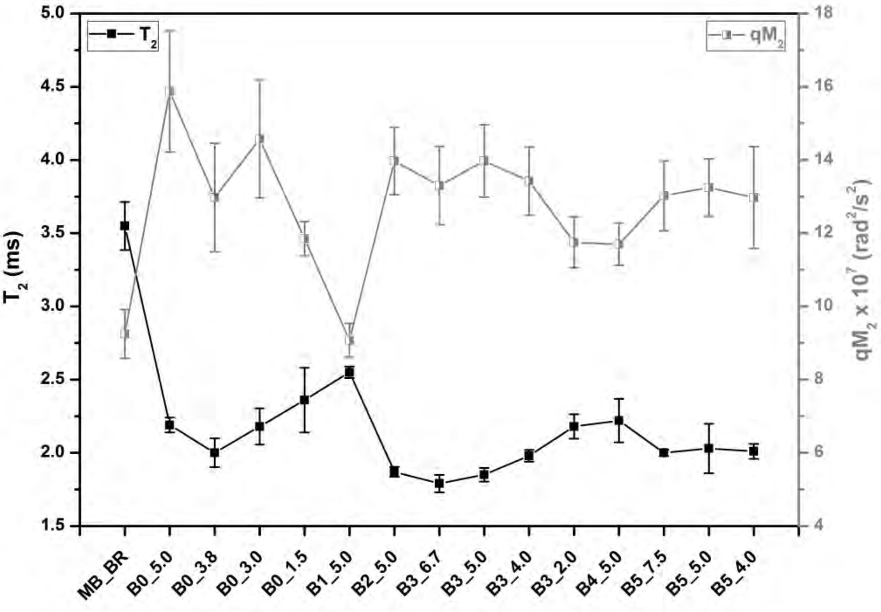

Figure 5.30. T_2 **and** qM_2 **of BR compounds cured at 140 °C from NMR magnetisation relaxation experiments.**

Additionally, the same behaviour is observed with $Zn_{1-x}Mg_xO$ regarding the diminution of the amount of activator. As minor quantities are employed T_2 increases and qM_2 decreases. When $Zn_{1-x}Ca_xO$-like is employed, the NMR magnetisation relaxation experiments indicate almost no difference in comparison with $Zn_{1-x}Mg_xO$.

Albeit transverse relaxation time measurements have been criticised[18, 42] due to the serious limitations inherent to the use of Equation 2.3 and the fitting ambiguities resulting from parameter interdependencies, it is still a very used technique[29, 43, 44] since it is simple and quick and the results are in good agreement with other methods such as swelling experiments.

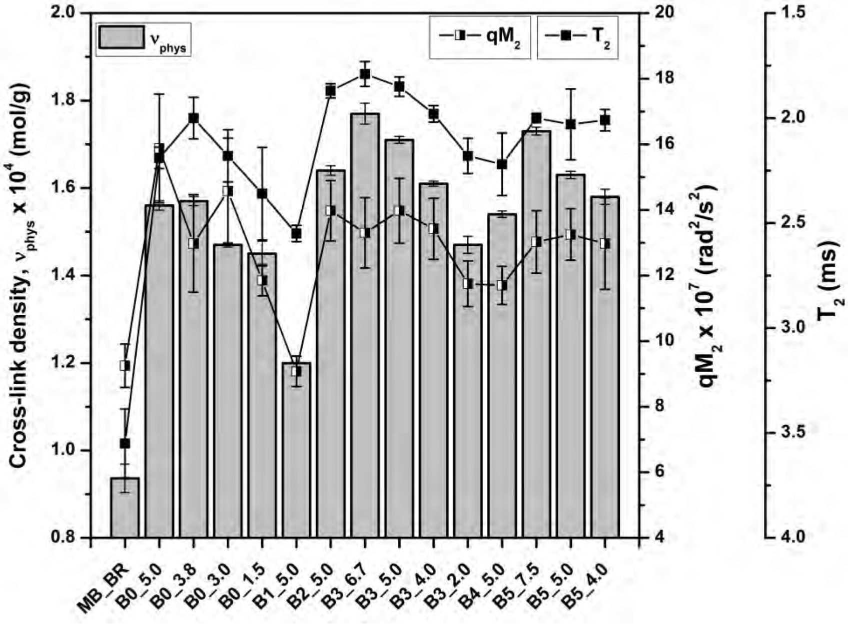

Figure 5.31. Comparison between $\nu_{phys.}$ **calculated using the Flory–Rehner approach (left** y**-axis) and** T_2 **and** qM_2 **from NMR magnetisation relaxation experiments (right** y**-axis) of BR compounds cured at 140 °C.**

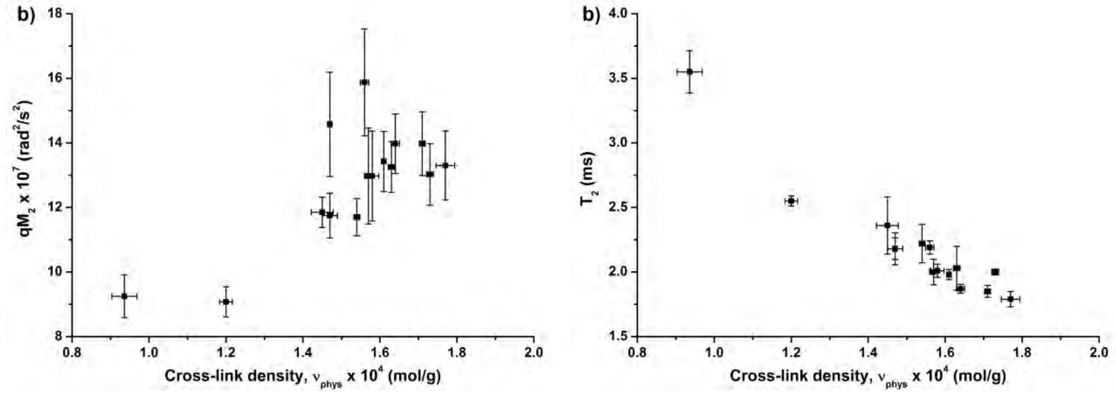

Figure 5.32. Relationship between v_e' calculated using the Flory–Rehner approach and a) qM_2 and b) T_2 from NMR magnetisation relaxation experiments of BR compounds cured at 140 °C.

Figure 5.31 shows the comparison between $v_{phys.}$ calculated using the Flory–Rehner approach and T_2 and qM_2 from NMR magnetisation relaxation experiments of BR compounds cured at 140 °C. This figure illustrates that the $v_{phys.}$ is directly proportional to qM_2 and inversely proportional to T_2. Although there are small discrepancies between the two techniques, it can be seen that for comparative purposes NMR magnetisation relaxation experiments is a very convenient practise.

In Figure 5.32 it is presented the relationship between cross-link density calculated using the Flory–Rehner approach and qM_2 and T_2 from NMR magnetisation relaxation experiments of BR compounds cured at 140 °C. It can be appreciated that there is a rather reliable linear relationship between $v_{phys.}$ and T_2. On the other hand, the relationship between $v_{phys.}$ and qM_2 is not as well defined, particularly at high cross-link densities, due to the error in qM_2 is increased. Nonetheless, it should be reminded that the Flory–Rehner approach contains also a great number of uncertainties and this could lead to the deviations observed.

5.3.4. STYRENE-BUTADIENE RUBBER SAMPLES

Analogous to the previous section, to study the effect of the mixed metal oxides as activator for sulphur vulcanisation in styrene-butadiene rubber, different formulations were prepared following the protocol described in section 5.2.3.2. Table 5.2 shows the content of these fifteen compounds. In all mixtures, CBS was used as accelerator with a constant A/S ratio of 0.6 (conventional vulcanisation). The vulcanisation was carried out at four different temperatures: 140 °C, 150 °C, 160 °C and 170 °C.

5.3.4.1 CURE CHARACTERISTICS

Table 5.7 summarises the vulcanisation parameters of the different SBR compounds. t_{02} is the time to reach 2 % of maximum torque, t_{s2} is the time to 2 dN·m rise above the minimum torque (M_L), and t_{90} is the time to achieve 90 % of maximum torque (M_H). The vulcanisation curves of the without activator is displayed in Figure 5.33.

Table 5.7. Vulcanisation parameters of SBR compounds vulcanised with different activators.

	t_{02} (min)				t_{s2} (min)				t_{90} (min)			
sample	**140°C**	**150°C**	**160°C**	**170°C**	**140°C**	**150°C**	**160°C**	**170°C**	**140°C**	**150°C**	**160°C**	**170°C**
MB_SBR	27.5	14.1	5.6	2.5	41.6	20.2	9.2	4.9	89.3	60.3	29.2	13.8
S0_5.0	34.8	15.9	6.8	3.1	47.0	23.2	12.3	6.2	68.7	35.1	18.9	10.2
S0_3.8	33.6	15.9	6.8	3.1	46.5	23.9	12.3	6.2	69.0	35.2	19.2	10.7
S0_3.0	30.0	15.3	6.8	3.1	40.9	22.6	11.7	6.2	62.2	35.7	18.6	9.7
S0_1.5	36.7	14.1	7.4	3.1	47.1	23.2	12.9	6.2	69.0	36.5	19.6	10.1
S1_5.0	11.7	7.4	3.7	1.9	28.7	14.7	7.4	4.3	84.1	58.0	29.2	14.7
S2_5.0	13.5	8.0	3.7	1.9	21.4	11.0	6.2	3.1	33.0	17.3	9.6	5.5
S3_6.7	11.0	5.6	2.5	1.3	17.1	8.6	4.3	2.5	26.5	15.8	8.1	5.0
S3_5.0	6.2	6.2	2.5	1.3	9.2	9.2	5.0	2.5	29.2	15.5	8.7	5.4
S3_4.0	11.7	6.2	3.1	1.3	19.0	9.8	4.9	2.5	27.8	15.9	8.9	5.3
S3_2.0	15.3	6.8	3.1	1.3	22.6	11.7	5.6	3.1	30.9	17.0	9.8	5.6
S4_5.0	26.9	16.5	3.1	3.1	39.1	22.6	6.2	6.2	61.3	34.6	18.5	9.9
S5_7.5	20.2	9.8	4.3	1.9	27.5	14.1	7.4	3.7	43.5	23.2	12.9	7.1
S5_5.0	20.2	8.6	4.3	1.9	28.1	12.9	6.8	3.7	43.9	22.4	12.0	6.8
S5_4.0	22.6	10.4	4.3	1.9	28.7	14.7	6.8	3.7	41.1	21.9	10.8	6.0

Figure 5.34 shows the rheometric curves for the SBR compounds cured with different amounts of ZnO. It can be seen that reducing the ZnO content does not affect significantly the cure characteristics of the samples. There is not a clear trend regarding the vulcanisation times and the amount of activator. Both scorch and optimum vulcanisation time do not show remarkable differences and as the temperature is increased the variations are diminished. However, there seems to be a slight decrease in the cure times when the ZnO content is reduced from 5 phr to 3 phr. When the quantity of activator present in the recipe is additionally reduced, the vulcanisation times are increased again.

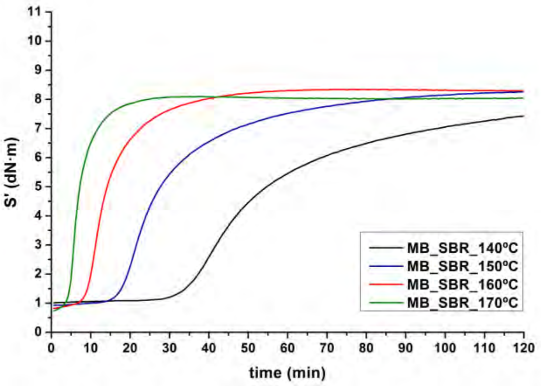

Figure 5.33. Cure characteristics of SBR compounds without activator

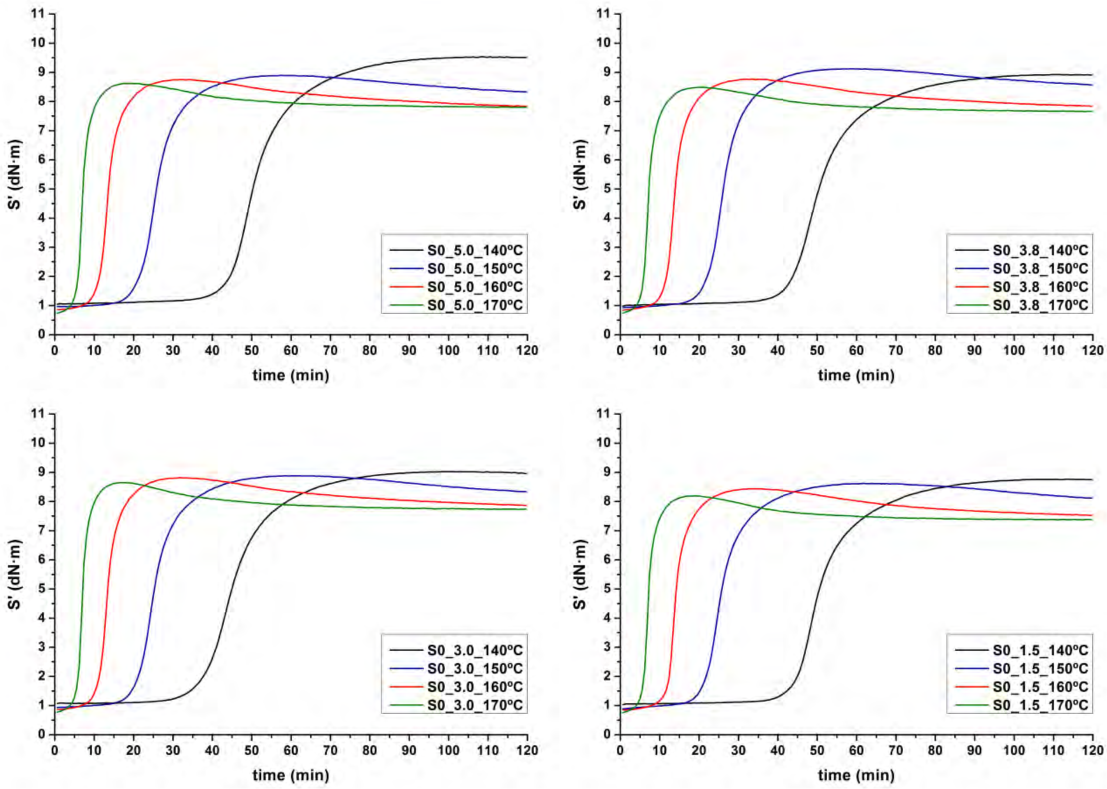

Figure 5.34. Cure characteristics of SBR compounds with different amounts of ZnO.

The extent of cure ($M_H - M_L$) of the styrene-butadiene compounds does not seem to be affected drastically by the different quantities of ZnO used. At 140 °C, the mixture containing 5.0 phr (S0_5.0) shows a higher $M_H - M_L$. Nonetheless, there are almost no differences between 5 and 3 phr at higher temperatures. Moreover, further reductions down to 1.5 phr of ZnO only produce a minor decrease, principally if the samples are vulcanised at low temperatures.

Figure 5.35 shows the vulcanisation curves of the samples containing MgO (S1_5.0) and a mixture of ZnO and MgO (S2_5.0). As it was found for BR and opposite to the results found in NR, MgO does not have an intense negative effect on the cure characteristics of SBR. $M_H - M_L$ is higher when MgO substitutes ZnO. When the mixtures are vulcanised at 140 °C the extent of cure is lower but it should be noted that the curve exhibits marching modulus. This behaviour is also evident at higher temperatures, but it is minimised as the temperature increases. Replacing partially ZnO with MgO produces higher $M_H - M_L$ values. The adverse consequences of adding MgO to the recipe experienced in NR are not found in SBR. As it occurred in BR and in contrast to NR, SBR compounds profit from the partial replacement of ZnO with MgO.

It is interesting to compare the curves without activator (Figure 5.33) and with MgO. When MgO is added to the mixture, the maximum torque achieved is higher than without activator. However, the curves are very similar. At 140 °C and 150 °C both the masterbatch and the sample with MgO show marching modulus. In Table 5.7 can be observed that, although the scorch time are shorter for S1_5.0, particularly at 140 °C, the t_{90} times are almost the same.

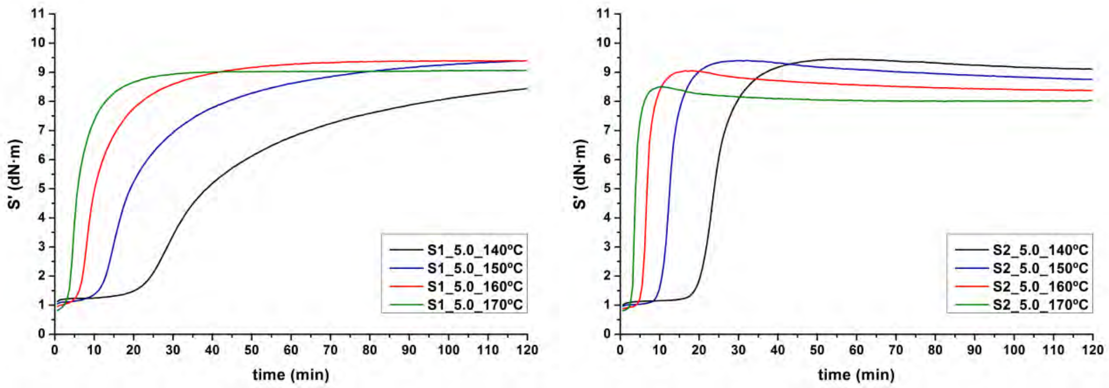

Figure 5.35. Cure characteristics of SBR compounds with MgO and a mixture of ZnO and MgO.

As it can be seen from Figure 5.35 and Table 5.7, when ZnO has been replaced partly with MgO (S2_5.0), there is a remarkable diminution of scorch time and t_{90}. When it is completely substituted, the scorch time is also reduced but t_{90} is enlarged, chiefly at low vulcanisation temperatures. The fact that the curves present marching modulus, predominantly at soft temperatures, is the reason behind the much longer t_{90} times.

Figure 5.36 shows the vulcanisation curves of the compounds containing different loads of the mixed metal oxide of zinc and magnesium. The scorch times of these mixtures are decreased when 5 phr of $Zn_{1-x}Mg_xO$ are used instead of 6.7 phr. Conversely, further reductions to 2 phr or just 4 phr provoke that t_{s2} grows.

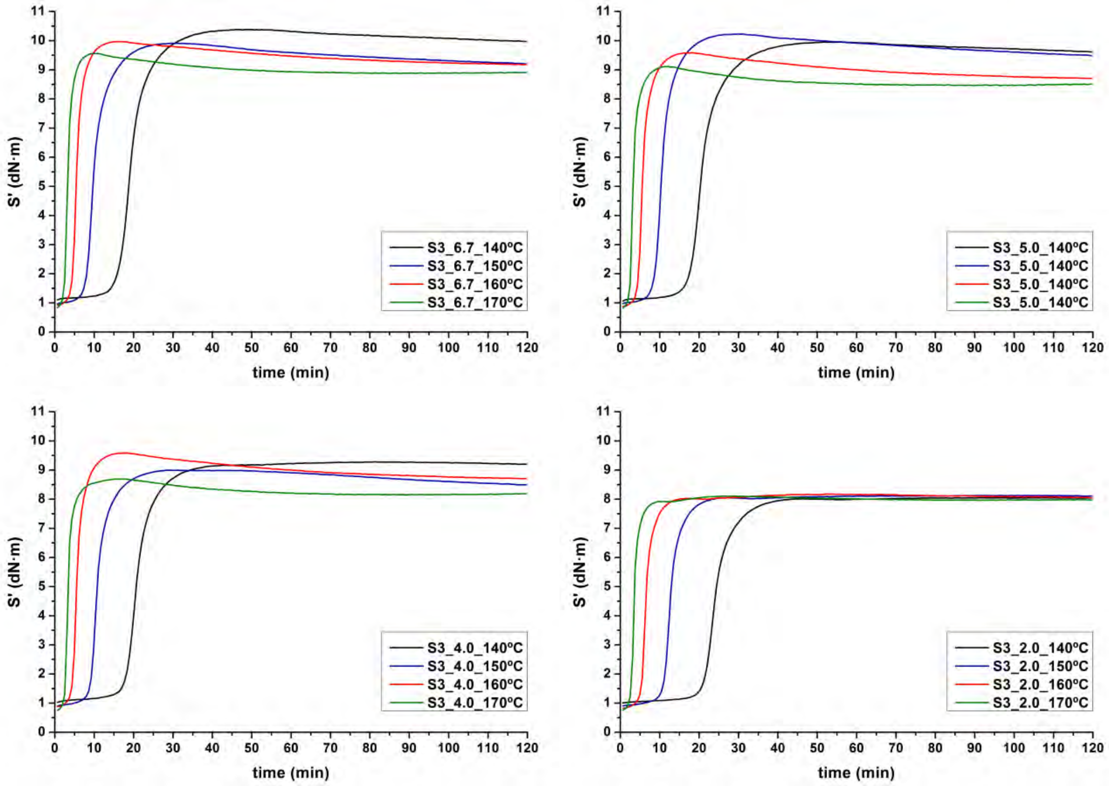

Figure 5.36. Cure characteristics of SBR compounds with different amounts of $Zn_{1-x}Mg_xO$.

The optimum vulcanisation time is not altered when the amount of $Zn_{1-x}Mg_xO$ added to the recipe is between 6.7 and 4 phr. When lower quantities are used t_{90} increases. Nevertheless, from the results displayed in Figure 5.36 and collected in Table 5.7 it can be noticed that the differences observed in the vulcanisation times are lowered if the vulcanisation takes place at high temperatures.

Comparing the vulcanisation curves (Figure 5.34, Figure 5.35 and Figure 5.36) and the data compiled in Table 5.7 it can be seen that the t_{90} times for the samples with $Zn_{1-x}Mg_xO$ are shorter than those of ZnO even at higher temperatures. In BR it was found that samples with $Zn_{1-x}Mg_xO$ have t_{90} times similar to the compounds with ZnO cured at a temperature 20 °C higher. For the SBR compounds t_{90} times are analogous to those obtained with compounds including ZnO cured at a temperature 10 °C higher. In addition, the scorch times of the compounds comprising $Zn_{1-x}Mg_xO$ are shorter than the compounds containing ZnO (samples S0) or MgO (samples S1_5.0 and S2_5.0).

With respect to the extent of cross-linking it can be appreciated in Figure 5.36 that the content of $Zn_{1-x}Mg_xO$ exerts an important influence. Samples with 6.7 and 5 phr exhibit a substantially higher extent of cure, especially at low temperatures. These mixtures present minor differences regarding $M_H - M_L$, but when lower activator loadings are used, the degree of cure is reduced substantially, especially if only 2 phr of $Zn_{1-x}Mg_xO$ are added to the recipe.

Figure 5.37 shows the rheometric curves for the SBR compounds with a mixture of ZnO and $CaCO_3$, and $Zn_{1-x}Ca_xO$-like. The mixture of ZnO and $CaCO_3$ (sample S4_5.0) presents longer vulcanisation times and lower $M_H - M_L$ than the compounds containing $Zn_{1-x}Ca_xO$-like, although at 140 °C the extent of cross-linking of this sample is similar to sample S5_7.5. The amount of $Zn_{1-x}Ca_xO$-like present in the recipe does not cause a very remarkable effect on the vulcanisation times or in the degree of cure. Figure 5.37 and Table 5.7 reveal that t_{90} and t_{s2} are almost unaltered if the content of $Zn_{1-x}Ca_xO$-like present in the recipe is lowered from 7.5 to 4 phr. The extent of cross-linking is also not influenced in a large degree when lower activator loads are used.

Comparing the results obtained using $Zn_{1-x}Ca_xO$-like with the other activators tested in this work it can be realised that the scorch and t_{90} times are shorter than the reference compounds (samples S0), although the differences are not as significant as it has been found with $Zn_{1-x}Mg_xO$.

Figure 5.38 displays the $M_H - M_L$ values for SBR mixtures. As it has been exposed before, lower amounts of ZnO produces similar extent of cross-linking. 1.5 phr of ZnO yields slightly lower but equivalent $M_H - M_L$ values than higher ZnO content.

Evaluating the impact of the presence of MgO in the SBR samples, it can be seen that MgO does not have the same effect on the vulcanisation of NR, or even BR, that on SBR. If the vulcanisation temperature is higher than 140 °C, the degree of cure is higher. Opposed to the behaviour seen in NR and parallel to what has been seen in BR, the compound containing a mixture of ZnO and MgO (S2_5.0) shows $M_H - M_L$ values higher to a certain degree than the compounds containing ZnO (samples S0).

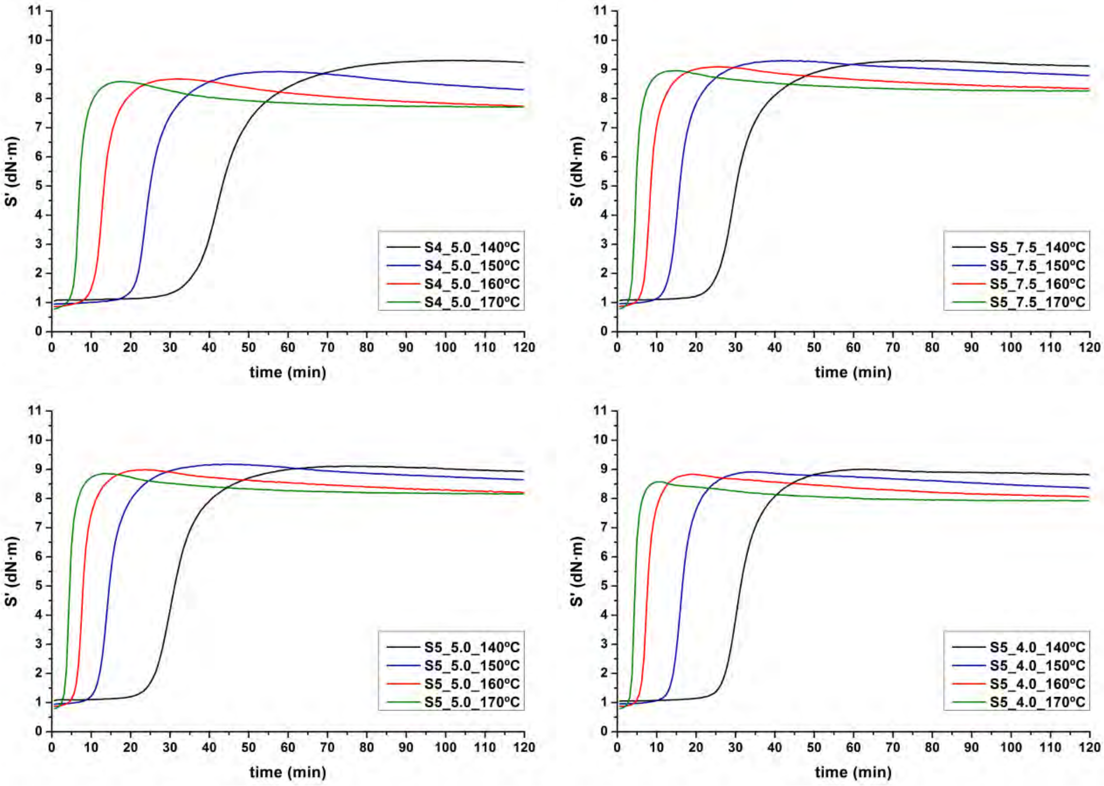

Figure 5.37. Cure characteristics of SBR compounds with a mixture of ZnO and $CaCO_3$ and $Zn_{1-x}Ca_xO$-like.

Samples including $Zn_{1-x}Mg_xO$ show a superior performance in comparison to the other SBR compounds tested regarding the extent of cure. The mixtures with 6.7 phr (S3_6.7) and 5 phr (S3_5.0) of $Zn_{1-x}Mg_xO$ give the maximum extent of cross-linking. Sample S3_4.0 (4 phr of $Zn_{1-x}Mg_xO$) produces similar $M_H - M_L$ values than the mixtures with ZnO. Adding only 2 phr of $Zn_{1-x}Mg_xO$ produces lower $M_H - M_L$, but comparable to 1.5 phr of ZnO, particularly at high temperatures.

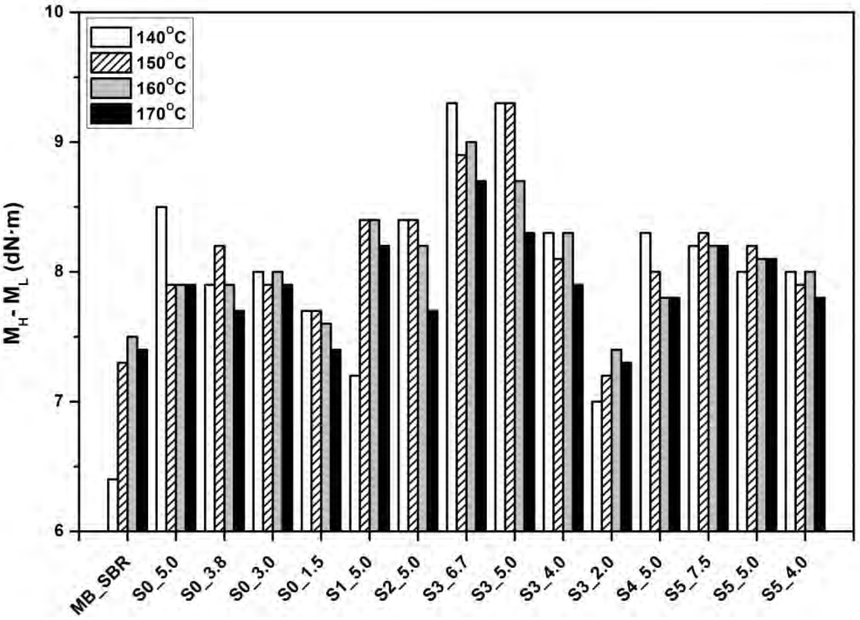

Figure 5.38. Extent of cure ($M_H - M_L$) for SBR mixtures.

From Figure 5.38 it can be noticed that the mixture of ZnO and $CaCO_3$ (sample S4_5.0) and the compounds containing $Zn_{1-x}Ca_xO$-like produce slightly higher $M_H - M_L$ than those containing zinc oxide. In spite of that, $Zn_{1-x}Ca_xO$-like does not produce $M_H - M_L$ values as high as $Zn_{1-x}Mg_xO$.

Table 5.8 shows the Cure Rate Index (CRI, calculated using Equation 5.2), the reversion time (RT, the time to reach 95 % M_H after passing M_H), and the reversion tax (calculated according to Equation 5.3). The results compiled in Table 5.8 indicate that the cure rate index is raised when ZnO is substituted by mixed metal oxides or MgO. Adding $CaCO_3$ to the recipe does not produce a modification of the CRI. $Zn_{1-x}Mg_xO$ increases significantly the CRI meanwhile the effect of $Zn_{1-x}Ca_xO$-like is more moderate. Replacing partially ZnO with MgO (S2_5.0) improves also the CRI and the enhancement is comparable to $Zn_{1-x}Mg_xO$.

Table 5.8 reveals that reversion tax of all the SBR compounds is very low, even at temperatures as high as 170 °C. The compounds containing MgO show the lowest reversion tax and no reversion time, but it is worth noticing that these compounds exhibit marching modulus. When $Zn_{1-x}Mg_xO$ is used as activator the reversion time increases and the reversion tax decreases in comparison to ZnO, especially at high temperatures and at low $Zn_{1-x}Mg_xO$ content. It should be noted that at 140 °C the samples containing ZnO present sort of marching modulus. On the other hand, if $Zn_{1-x}Ca_xO$-like is added to the mixture, the reversion resistance is also slightly improved, the RT is longer and the reversion tax is smaller compared to ZnO.

Table 5.8. Cure rate index (CRI), reversion time (RT), and reversion tax of SBR compounds.

	CRI (%)				RT (min)				Reversion Tax (%)			
sample	**140°C**	**150°C**	**160°C**	**170°C**	**140°C**	**150°C**	**160°C**	**170°C**	**140°C**	**150°C**	**160°C**	**170°C**
MB_SBR	2.1	2.5	5.1	11.7	–	–	–	-37.3	0.0	0.0	0.7	0.8
S0_5.0	4.7	8.6	16.4	27.3	–	40.3	25.0	19.5	0.4	3.5	5.8	7.2
S0_3.8	4.6	9.1	14.9	23.4	–	44.5	23.8	19.5	0.2	3.1	6.3	7.3
S0_3.0	4.8	7.8	14.9	32.8	–	43.3	23.2	14.3	0.9	3.0	6.4	8.4
S0_1.5	4.6	7.8	14.9	27.3	–	44.5	23.8	15.9	0.2	2.7	6.5	8.1
S1_5.0	1.8	2.3	4.7	10.2	–	–	–	–	0.0	0.0	0.0	0.1
S2_5.0	9.1	16.4	32.8	54.6	–	45.8	32.4	26.9	1.9	3.5	4.9	5.2
S3_6.7	10.9	14.9	27.3	41.0	–	45.8	39.1	26.2	1.9	3.6	3.8	5.4
S3_5.0	16.4	16.4	27.3	–	–	47.6	28.4	15.9	0.3	3.3	5.2	6.6
S3_4.0	11.7	18.2	27.3	41.0	–	73.8	38.4	30.5	0.8	1.0	4.1	5.1
S3_2.0	12.6	20.5	27.3	54.6	–	–	–	–	0.1	0.2	0.9	1.1
S4_5.0	4.6	8.6	27.3	27.3	–	37.2	15.3	15.3	0.8	4.0	8.0	8.0
S5_7.5	6.3	11.7	20.5	32.8	–	61.0	33.0	23.8	1.5	2.7	4.6	5.7
S5_5.0	6.6	10.9	20.4	32.8	–	53.1	30.5	23.2	1.5	3.3	4.7	5.8
S5_4.0	8.2	14.9	27.3	54.6	–	59.8	34.2	23.2	1.5	2.4	4.4	5.8

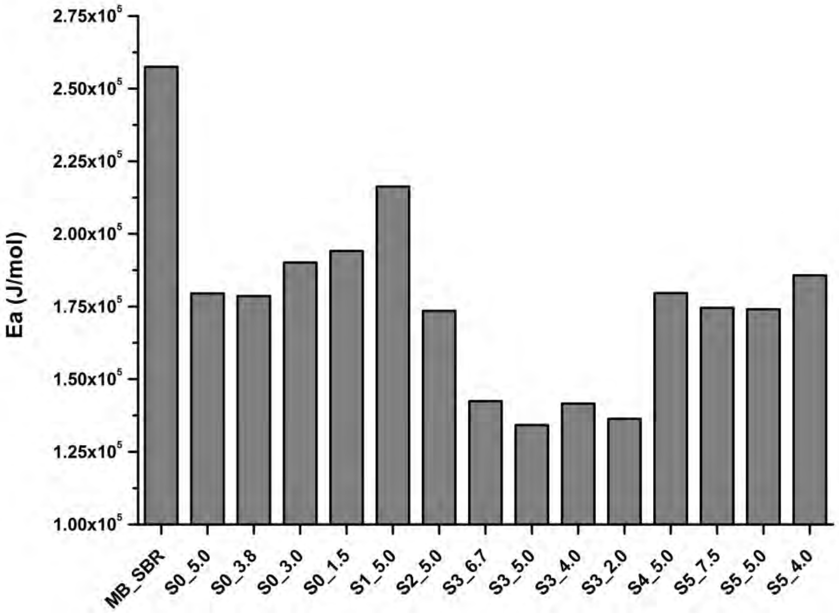

Figure 5.39. Effect of activator on activation energy (Ea) of styrene-butadiene rubber compounds.

Figure 5.39 displays the activation energy (E_a) of the SBR compounds. It can be observed that the E_a is substantially reduced when $Zn_{1-x}Mg_xO$ is added to the recipe. On the other hand, $Zn_{1-x}Ca_xO$-like does not produce different E_a compared to ZnO. When ZnO is substituted by MgO the activation energy is increased. In addition and opposed to the behaviour found in BR, when MgO is mixed with ZnO, E_a is not different than employing only ZnO.

Reviewing the results discussed previously, it can be recognised that it is possible to reduce the zinc levels in SBR compounds employing lower quantities of ZnO. A 40 % reduction can be accomplished confidently by using 3 phr of ZnO obtaining similar $M_H - M_L$ values, reversion resistance, and vulcanisation times. A further diminution to 70 % (1.5 phr of ZnO) produces slightly lower extent of cross-linking; however the other characteristics studied to this point are not modified to a great extent.

By means of $Zn_{1-x}Mg_xO$ it is also possible to decrease significantly the zinc content in SBR. Replacing ZnO with $Zn_{1-x}Mg_xO$ shortens the vulcanisation times and improves the reversion resistance and the CRI. Furthermore, the activation energy is notably minimised. Reducing 40 % the zinc content with $Zn_{1-x}Mg_xO$ (S3_4.0) causes also higher $M_H - M_L$ values (except at 140 °C). With 2 phr of $Zn_{1-x}Mg_xO$ (70 % reduction) there is a decrease in the extent of cure, but nearly comparable to 1.5 phr of ZnO at high temperatures.

$Zn_{1-x}Ca_xO$-like allows also to minimise the zinc levels. With this activator the reduction in the cure times and the raise of the CRI are not as marked as with $Zn_{1-x}Mg_xO$ and furthermore the degree of cure is not affected. Nevertheless, the reversion resistance is slightly improved. The samples with a mixture of ZnO and $CaCO_3$ (S4_5.0) and the mixtures containing $Zn_{1-x}Ca_xO$-like show significant differences. Substituting ZnO partially by adding to the recipe 3.3 phr of ZnO and 1.7 phr of $CaCO_3$ (34 % reduction of zinc content) causes that slower cure properties are obtained, similar to those seen when ZnO is the activator. A higher diminution of the zinc content (47 %) can be attained employing 4 phr of $Zn_{1-x}Ca_xO$-like.

Regarding the replacement of ZnO by MgO it should be remarked that, as it has been found for BR compounds, MgO does not exert the same effect on the vulcanisation of natural rubber than on SBR. Contrary to the results found in NR and BR, there is a higher extent of cure for SBR compounds; nonetheless, the difference is not exceptionally significant. In addition, the vulcanisation times are very slow and the cure rate index very low. The compound containing a mixture of ZnO and MgO does not show different $M_H - M_L$ values, although the vulcanisation times are reduced and the CRI is improved compared to MgO. This behaviour was also reported by other researchers[35].

5.3.4.2 PHYSICAL PROPERTIES

Stress-strain measurements were performed to study the effect of the mixed metal oxides on the physical properties of the rubber compounds. Figure 5.40 shows the tensile strength of the styrene-butadiene rubber samples vulcanised at different temperatures. In the figure it can be appreciated that the SBR compounds exhibit increasing tensile strength (TS) as the temperature is raised. However, it is worth stating that only some samples show remarkable differences. The mixtures containing ZnO in the recipe show similar TS independently of the zinc content present in the mixture. 3.8 phr of ZnO (S0_3.8) give slightly higher TS than the other mixtures, nevertheless even 1.5 phr (S0_1.5) produce similar values.

As it has been described in BR samples, when MgO substitutes ZnO as activator in SBR the effect on the tensile strength is not consonant to what has been seen in NR. When MgO is used (S1_5.0), TS is equivalent to the values given by samples containing ZnO. Furthermore, is ZnO is partially replace by MgO (S2_5.0), the tensile strength achieved is higher.

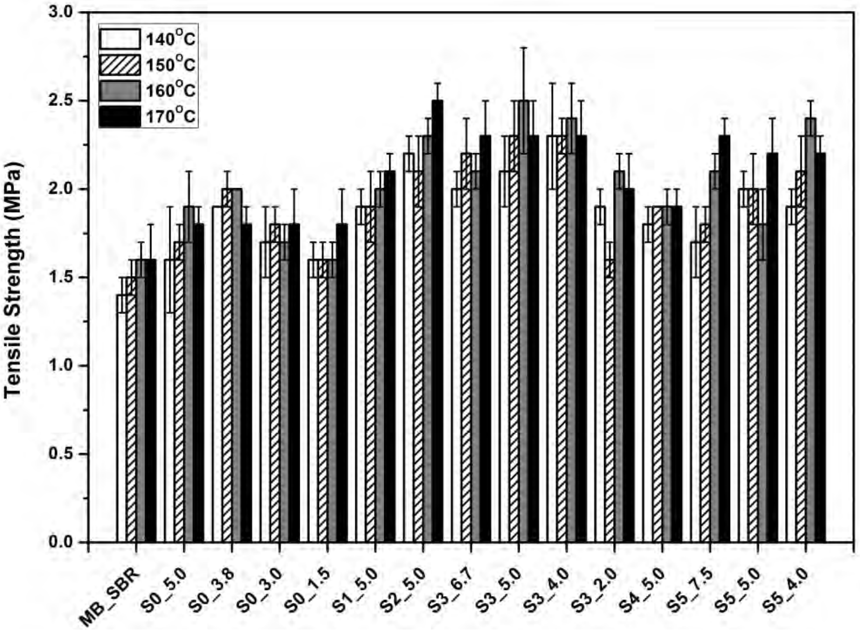

Figure 5.40. Effect of activator on tensile strength of styrene-butadiene rubber compounds.

The results displayed in Figure 5.40 indicate that the mixtures containing mixed metal oxides of zinc and magnesium are a good alternative to ZnO. The tensile strength of the samples including between 6.7 and 4 phr of $Zn_{1-x}Mg_xO$ is above the values obtained if ZnO is the activator. When 2 phr of $Zn_{1-x}Mg_xO$ are added (S3_2.0), TS is at the same level as when ZnO is used. At 150 °C the tensile strength is below the values obtained with samples containing at least 3 phr of ZnO. However, it is at the same level to the value reached by the sample with 1.5 phr of ZnO.

Concerning the presence of $CaCO_3$ in the recipe, it can be observed from the findings displayed in Figure 5.40 that this compound does not have a strong influence in the tensile strength. Sample S4_5.0 gives TS similar to those shown by the samples containing ZnO. The mixtures including $Zn_{1-x}Ca_xO$-like possess higher tensile strength than the samples with ZnO, and the enhancement is comparable to $Zn_{1-x}Mg_xO$, principally at high temperatures.

The different activators tested in this work show some differences regarding the elongation at break (E_b) as it is represented in Figure 5.41. However, these differences are not as significant as in BR. MgO produces an increase in the E_b values, when it substitutes ZnO partially (S2_5.0). The complete replacement (S1_5.0) does not cause remarkable variations, although as the temperature increases E_b is reduced.

In relation to the compounds with ZnO on the recipe Figure 5.41 shows that reducing the ZnO content does not have an influence on the E_b. The sample comprising $CaCO_3$ have similar E_b than the samples with ZnO. The SBR compounds including $Zn_{1-x}Ca_xO$-like instead of ZnO yield higher E_b as the activator loading is reduced. Nonetheless, these differences are minimised at high temperatures. Comparing with the mixtures enclosing ZnO, $Zn_{1-x}Ca_xO$-like causes low E_b if low temperatures are used. Furthermore, reducing the amount of $Zn_{1-x}Mg_xO$ does not produce values significantly different with respect to the samples with ZnO. Nevertheless, when 4 phr of $Zn_{1-x}Mg_xO$ are added to the mixture E_b is above the samples with ZnO, mainly at low temperatures.

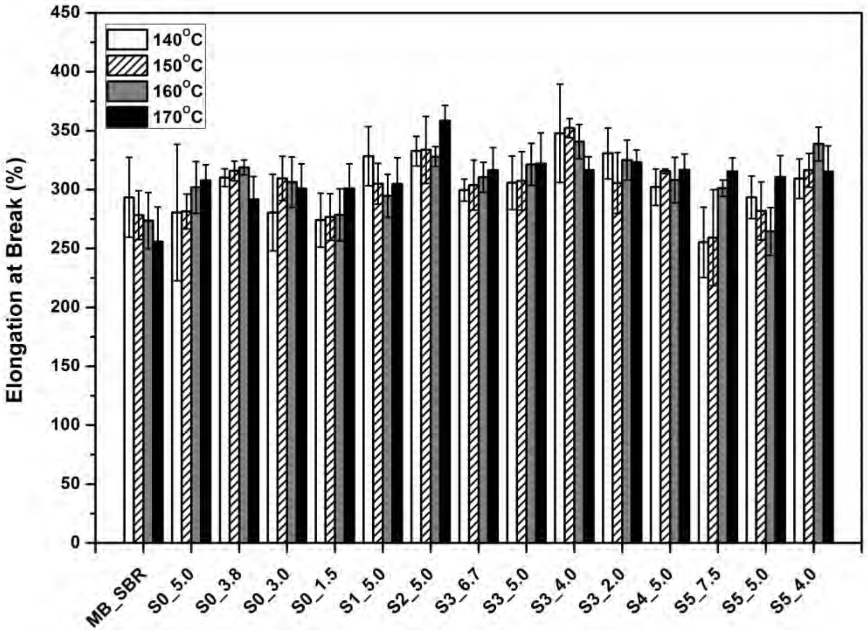

Figure 5.41. Effect of activator on elongation at break of styrene-butadiene rubber compounds.

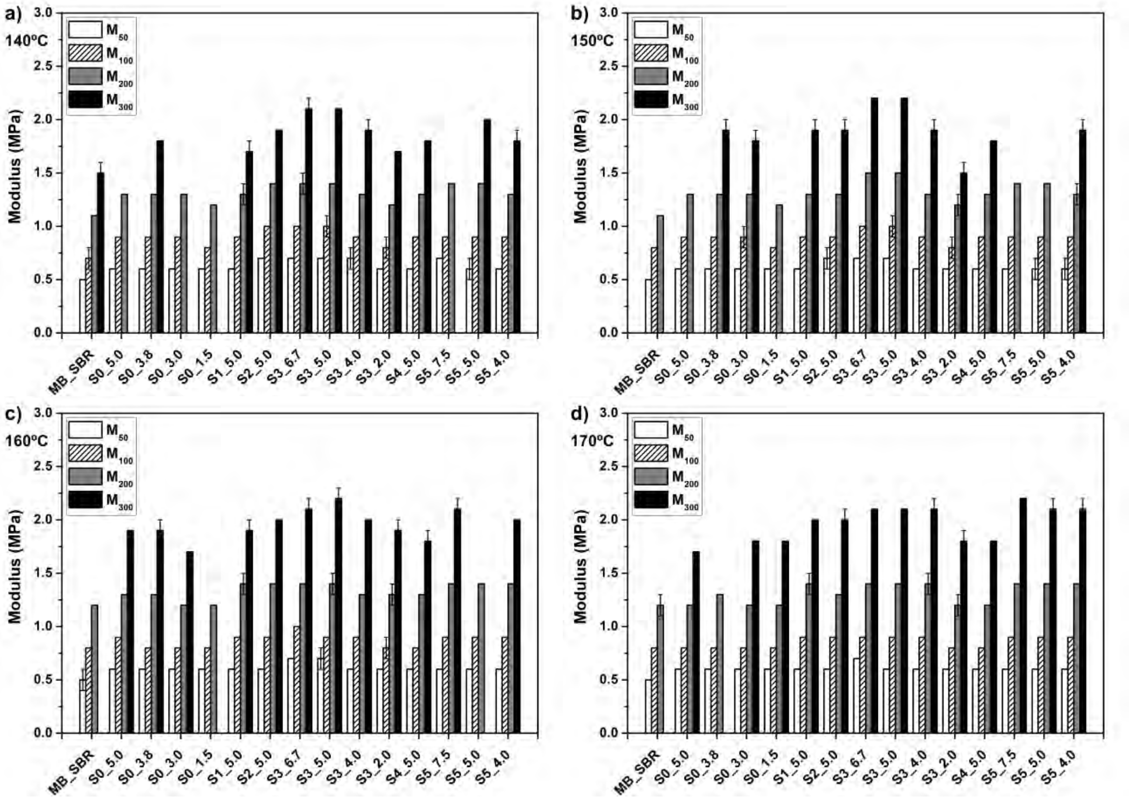

Figure 5.42. Modulus at 50%, 100%, 200% and 300% elongation for styrene-butadiene rubber compounds at a) 140 °C, b) 150 °C, c) 160 °C and d) 170

Figure 5.42 displays the tensile moduli, M_{50} (modulus at 50% elongation), M_{100} (modulus at 100% elongation), M_{200} (modulus at 200% elongation) and M_{300} (modulus at 300% elongation) for the SBR samples vulcanised at the different temperatures tested in this work. In this figure it can be seen that the highest moduli are obtained when $Zn_{1-x}Mg_xO$ and $Zn_{1-x}Ca_xO$-like are the activators, mostly at high elongations. The differences between the compounds including these activators are not very extensive.

From the results shown in Figure 5.42 it can be deduced that reducing the zinc levels in butadiene rubber compounds yield to slightly lower tensile moduli, mainly M_{200} and M_{300}. The mixtures with lower amount of ZnO or $Zn_{1-x}Mg_xO$ give moduli inferior to some extent than those obtained employing higher loads of these activators. Using $Zn_{1-x}Ca_xO$-like this effect is not as significant as with ZnO or $Zn_{1-x}Mg_xO$.

Figure 5.43 illustrates the micro International Rubber Hardness Degree (IRHD) results from measurements according to ISO 48. As it has been already seen in the BR compounds, when the mixtures are vulcanised at higher temperatures it can be seen that the hardness decreases. The mixtures containing ZnO in the recipe show similar IRHD when the amount of this activator is between 5 and 3 phr. When the mixture contains lower amounts (S0_1.5) there is a slight decrease.

When MgO substitutes ZnO as activator (S1_5.0), the hardness is on the same level as with ZnO. At 140 °C and 150 °C is somewhat lower but at 150 °C and 160 °C is slightly higher. On the contrary, when MgO replaces ZnO partially (S2_5.0), the hardness achieved is above the values obtained with samples comprising only ZnO.

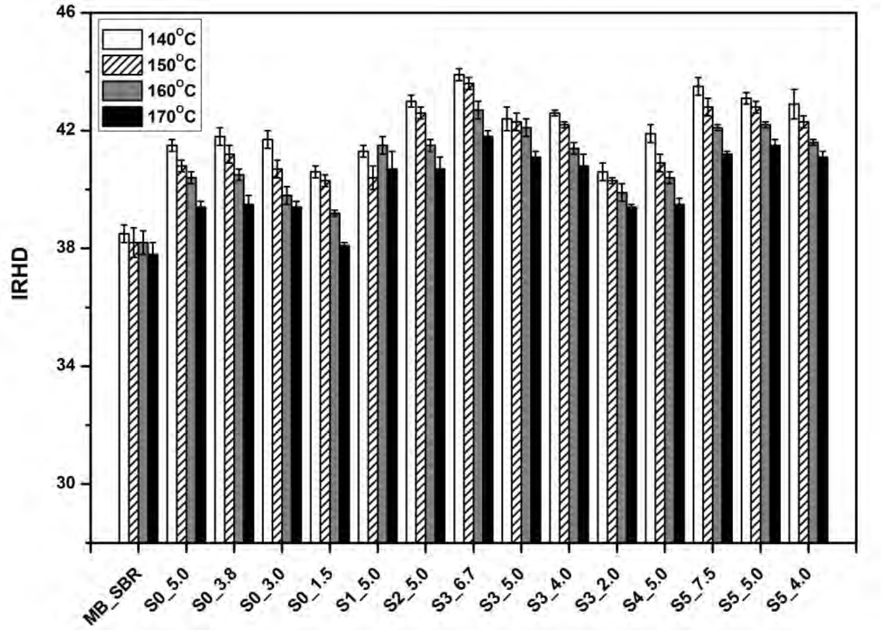

Figure 5.43. Effect of activator on IRHD of styrene-butadiene rubber compounds.

The compounds with $Zn_{1-x}Mg_xO$ present in the recipe exhibits the highest hardness when the $Zn_{1-x}Mg_xO$ content is between 6.7 and 4 phr. The mixtures containing between 5 and 4 phr of $Zn_{1-x}Mg_xO$ present no differences regarding the IRHD. When only 2 phr are used, the hardness reached is to some extent lower. In spite of that, this sample (S3_2.0) shows hardness on the same level than those comprising ZnO with loadings of 1.5 phr, or even 3.0 phr at high temperatures.

Regarding the effect of $CaCO_3$ in the recipe, it can be observed from Figure 5.43 that this compound does not affect the hardness. Sample S4_5.0 shows an IRHD similar the ZnO samples. The incorporation of $Zn_{1-x}Ca_xO$-like produces higher hardness than the samples with ZnO. Furthermore, the improvement is as remarkable as with $Zn_{1-x}Mg_xO$.

Taking into account all the results found in this section, it can be reasoned that the use of mixed metal oxide of zinc and magnesium allows not only the reduction of the zinc level in SBR compounds but also the achievement of higher mechanical properties. Adding 4 phr of $Zn_{1-x}Mg_xO$ (40 % reduction of the zinc levels) it is possible to obtain compounds with higher tensile strength, elongation at break, tensile moduli and hardness than the compounds with ZnO. Adding to the recipe only 2 phr of $Zn_{1-x}Mg_xO$ (70 % reduction) gives similar tensile strength and elongation at break although tensile moduli and hardness are lightly diminished.

$Zn_{1-x}Ca_xO$-like also allows the reduction of zinc levels in SBR compounds obtaining an enhancement of some of the properties studied in this section. Using 4 phr (47 % reduction), there is an improvement on the tensile strength, tensile moduli and hardness. In addition, the elongation at break is not reduced in comparison with the use of ZnO.

Reducing the zinc loadings by simply adding lower quantities of ZnO is also possible. A 70 % reduction is attainable employing 1.5 phr of ZnO; however, there is small deterioration of the mechanical properties.

As it has been found working with BR and contrary to natural rubber, MgO is not as bad activator as expected. When MgO replace ZnO as activator, whether partially or totally, the properties achieved are comparable to the properties given by ZnO. This may lead to consider that for certain specific application MgO could be used as activator in SBR, as reasoned for BR.

5.3.4.3 EQUILIBRIUM SWELLING EXPERIMENTS

In Figure 5.44 it is presented the cross-link density ($\nu_{phys.}$) obtained from the equilibrium swelling data of the SBR compounds. As it has been observed in the BR samples, when the vulcanisation temperature is increased $\nu_{phys.}$ decreases. However, opposed to what has been found in BR, when higher temperatures (170 °C) are applied, the reduction is on the same levels. As it can be seen in Figure 5.45, as the temperature is raised the swelling degree is also increased.

When ZnO is used as activator, the mixtures show similar $\nu_{phys.}$. From Figure 5.44 it can be deduced that whenever the amount of ZnO is reduced the cross-link degree of the samples is decreased. When only 1.5 phr are employed, the reduction is more important.

In the samples with MgO replacing ZnO as activator (S1_5.0), $\nu_{phys.}$ is lower but on the same levels as S0_1.5. In BR compounds it has been found that the sample activated with MgO gives the lowest cross-link density. On the contrary, although it is relatively inferior and the swelling degree is higher, especially at low temperatures, altogether, the cross-link density is not greatly worsened if MgO substitutes ZnO. In addition, it should be noted that the mixtures with MgO showed marching modulus when the vulcanisation temperature was mild. Furthermore, when MgO replaces ZnO partially (S2_5.0), the $\nu_{phys.}$ achieved is comparable to the samples comprising only ZnO.

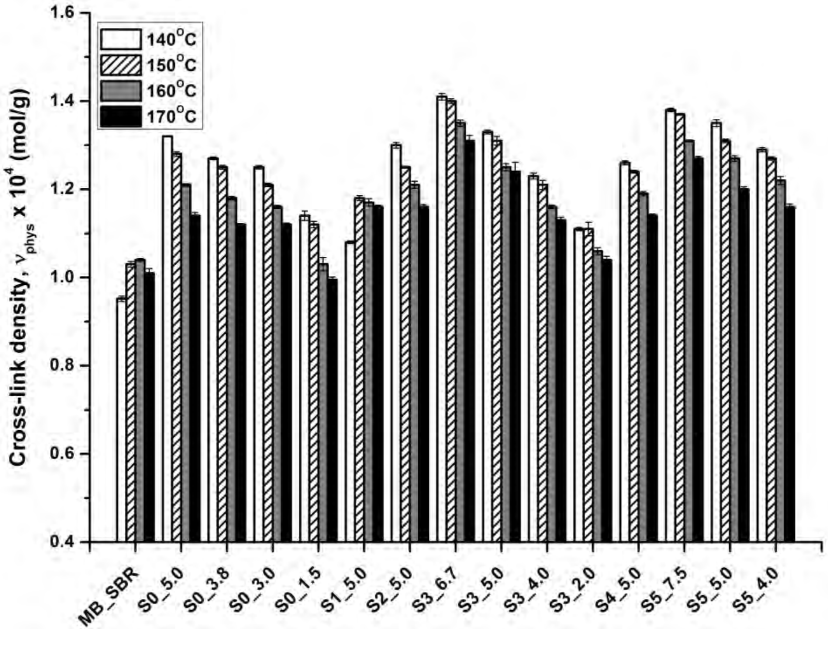

Figure 5.44. Cross-link density for the different SBR compounds calculated using the Flory–Rehner approach.

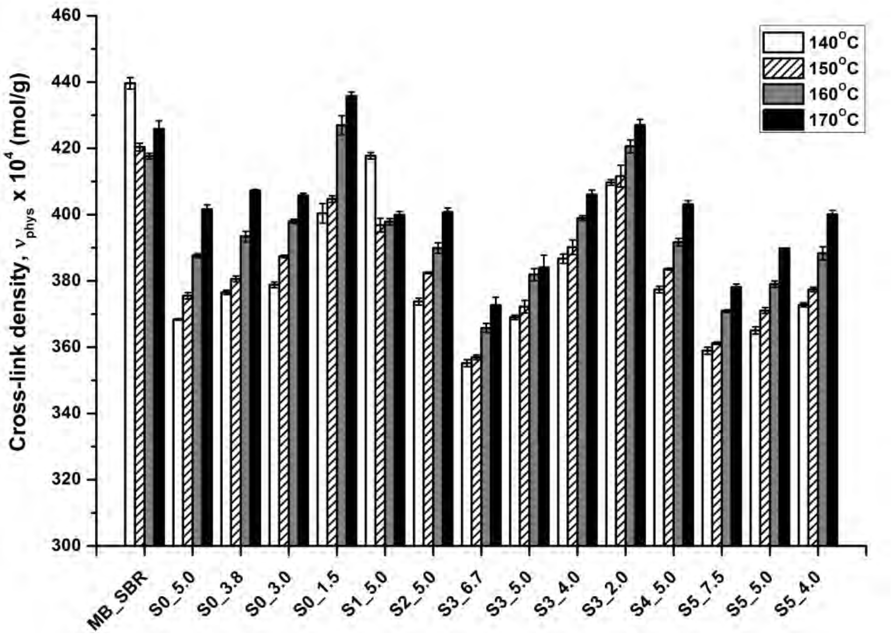

Figure 5.45. Swelling degree for the different SBR compounds.

The use mixed metal oxides of zinc and magnesium causes an enhancement on the cross-link density when normal zinc levels are used. Reducing the zinc levels causes a decrease on the $\nu_{phys.}$ as it has been observed with ZnO. The addition of 6.7 or 5 phr of $Zn_{1-x}Mg_xO$ yields to a higher $\nu_{phys.}$ than the compounds with ZnO. An additional reduction to 2 phr (S3_2.0) produces a compound with a cross-link density on the same level than 1.5 phr of ZnO.

Figure 5.44 and Figure 5.45 indicate that $CaCO_3$ does not affect the cross-link density of the mixtures. Sample S4_5.0 shows $\nu_{phys.}$ and swelling degree similar to those containing ZnO. On the other hand, the mixtures including $Zn_{1-x}Ca_xO$-like produces a higher $\nu_{phys.}$ than the samples with ZnO. Furthermore, the enhancement is equivalent to $Zn_{1-x}Mg_xO$. As expected, when the amount of $Zn_{1-x}Ca_xO$-like is reduced, $\nu_{phys.}$ decreases. However, this adverse effect is less harmful with $Zn_{1-x}Ca_xO$-like than when $Zn_{1-x}Mg_xO$ is used as activator.

Figure 5.46 shows the distribution of poly-, di- and monosulphidic cross-links in SBR compounds vulcanised at 140 °C calculated using the Flory–Rehner approach together with the thiol–amine chemical probes. In Figure 5.46 it can be seen that the samples contain mostly polysulphidic cross-links. As it has been explained in previous sections, since all the mixtures were cured with a conventional vulcanisation system and the cure was stopped at t_{90}, it is expected that the networks contain mainly polysulphidic cross-links.

On the contrary to what occurred with the BR compounds, in the experiments performed with SBR samples it was possible to measure the cross-link structure of these compounds after the treatments with hexane-1-thiol. This treatment generated a very weak gel but it was stronger than in BR compounds and swelling measurements could be performed. However, it is important to mention that this could lead to a higher error in the measurement than in the samples treated with 2-propanethiol or without treatment.

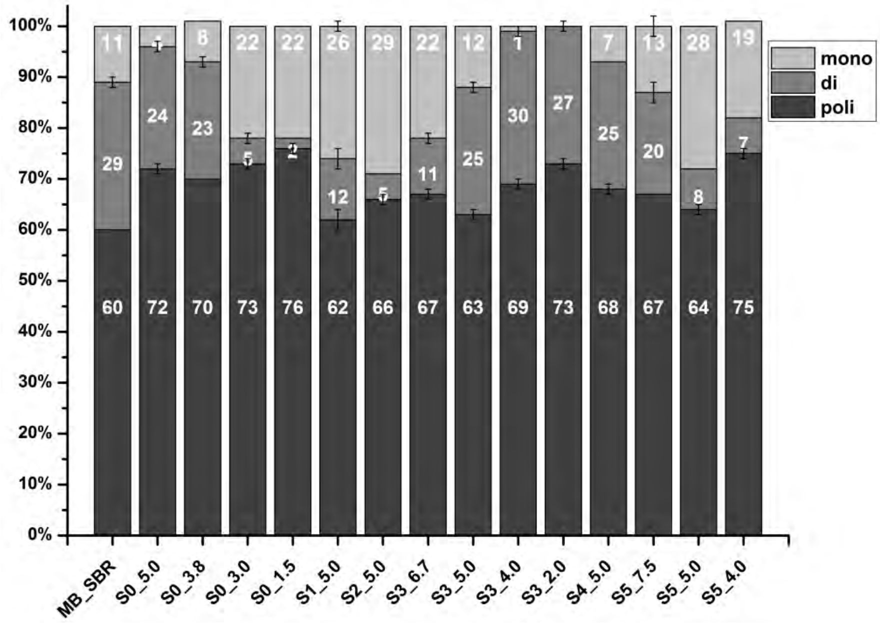

Figure 5.46. Cross-link distribution of polysulphidic, disulphidic and monosulphidic cross-links in SBR compounds vulcanised at 140 °C calculated using the Flory–Rehner approach together with the thiol–amine chemical probes.

In Figure 5.46 it can be perceived that in all the SBR mixtures the biggest fraction corresponds to the polysulphidic cross-links. The mixtures activated with ZnO present the largest ratio of polysulphidic cross-links and, in addition, there is a slight increase on this percentage when the amount of ZnO is reduced. When $Zn_{1-x}Mg_xO$ is added to the mixture, the same behaviour is observed. The lower the amount of $Zn_{1-x}Mg_xO$ present, the higher the polysulphidics. Concerning the proportion of monosulphidics, from Figure 5.46 it is noticed that it is enlarged with reducing quantities of ZnO whereas, on the contrary, this fraction is minimised as the samples comprise less $Zn_{1-x}Mg_xO$.

It has been reported[1, 45, 46] that in SBR compounds more desulphuration, converting poly- to disulphidic cross-links, occurs at high levels of zinc oxide but very little monosulphidic fraction was found. On the contrary, in the absence of ZnO there was a slow formation of monosulphidic cross-links. However, Figure 5.46 shows that there are no significant differences between the sample without activator and 5 or 3.8 phr of ZnO. In addition, employing 3 or 1.5 phr of ZnO increases the monosulphidic cross-links reducing the disulphidics.

When MgO substitutes ZnO partially (S2_5.0) or completely (S1_5.0), a large fraction of monosulphidic cross-links is detected. In BR samples it was also found that the proportion of mono- and disulphidic cross-links was higher employing MgO. As it has been explained formerly, these results are unexpected. Contrary to has been found in NR, where MgO forms only polysulphidic cross-links, in SBR compounds MgO seems to promote the formation of monosulphudic cross-links.

Employing $Zn_{1-x}Ca_xO$-like produces mixtures with an important fraction of monosulphidic cross-links. When $Zn_{1-x}Ca_xO$-like is reduced from 7.5 (S5_7.5) to 5 phr (S5_5.0), the percentage of monosulphidics is increased but the ratio of polysulphidics is maintained and, therefore, the number of disulphidics decreases. Lowering the amount of $Zn_{1-x}Ca_xO$-like from 5 to 4 phr (S5_4.0) causes a rise of the polysulphidic portion but the disulphidics are not affected and this provokes a drop on the monosulphidics. In spite of this, this fraction is bigger in S5_4.0 than in S5_7.5.

In this section it has been demonstrated that it is feasible to reduce the zinc content in SBR compounds. Using 5.0 phr of $Zn_{1-x}Mg_xO$ (25 % reduction) the cross-link density is higher and the network has a higher proportion of monosulphidic cross-link. Using 3.8 phr of ZnO or 4 phr of $Zn_{1-x}Mg_xO$ it is possible to reduce by 40 % the zinc levels although $\nu_{phys.}$ is slightly lower. However, with 3.8 phr of ZnO the fraction of monosulphidics is higher compared to 4 phr of $Zn_{1-x}Mg_xO$. With 4 phr of $Zn_{1-x}Ca_xO$-like, the zinc levels can be decreased by 47% obtaining also a higher $\nu_{phys.}$ than with ZnO and a larger fraction of monosulphidics.

Nevertheless, as it was explained previously, equilibrium swelling experiments are subject to a large number of uncertainties, especially those in combination with thiol–amine chemical probes, and should be examined prudently.

5.3.4.4 ^{1}H NMR RELAXATION TIME SPECTROSCOPY

Figure 5.47 shows the T_2 times (left y-axis) and the Gaussian fraction qM_2 (right y-axis) of the SBR compounds cured at 140 °C. It can be seen that the samples containing at least 5 phr of $Zn_{1-x}Mg_xO$ or $Zn_{1-x}Ca_xO$-like causes the shortest T_2 times and the highest qM_2 of the samples with activator because, as it has been found in the previous sections, these samples have a high $\nu_{phys.}$ and $M_H - M_L$.

In the samples containing ZnO, the T_2 and qM_2 are almost constant, reducing the amount of ZnO do not alter significantly the relaxation behaviour of the compounds. Sample S0_3.0 shows a short T_2 but qM_2 is approximately on the same level.

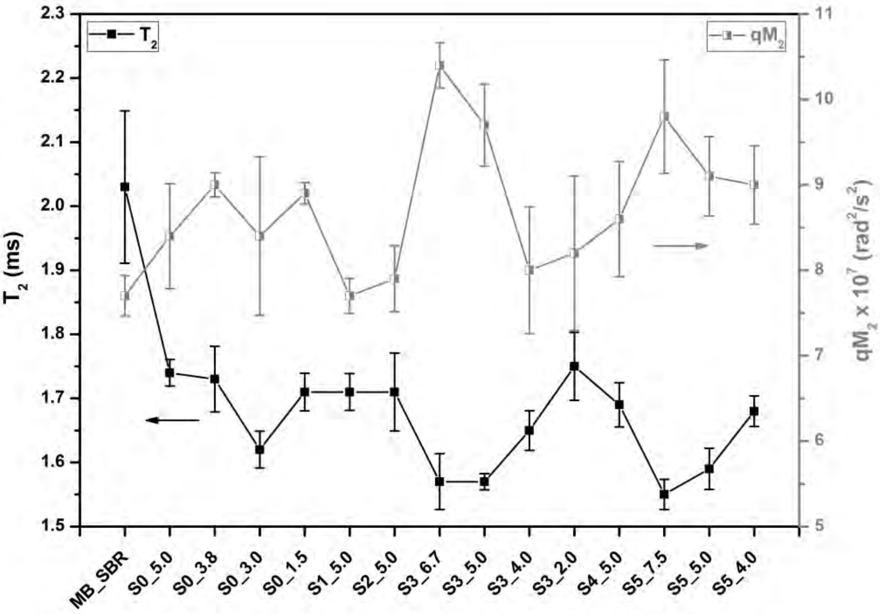

Figure 5.47. T_2 and qM_2 of SBR compounds cured at 140 °C from NMR magnetisation relaxation experiments.

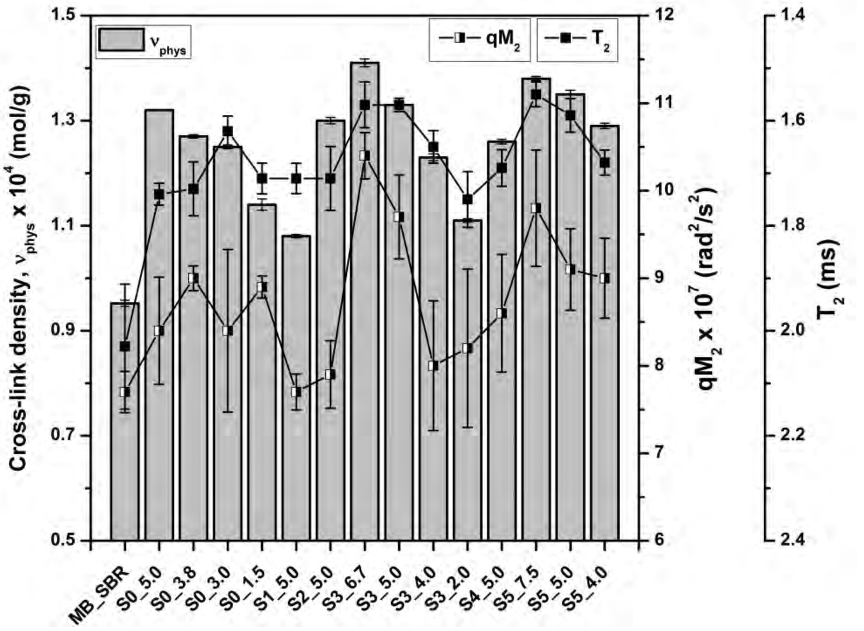

Figure 5.48. Comparison between $\nu_{phys.}$ calculated using the Flory–Rehner approach (left y-axis) and T_2 and qM_2 from NMR magnetisation relaxation experiments (right y-axis) of SBR compounds cured at 140 °C.

As lower quantities of mixed metal oxides of zinc and magnesium or $Zn_{1-x}Ca_xO$-like are employed T_2 increases and qM_2 decreases, indicating a lower cross-link density. In the case of $Zn_{1-x}Mg_xO$, the reduction of qM_2 is more important than in $Zn_{1-x}Ca_xO$-like.

When a mixture of ZnO and MgO (S2_5.0) is added to the recipe, the T_2 time and qM_2 are similar to the values obtained with the sample comprising only MgO (S1_5.0). However, swelling measurements have shown that the cross-link density attained is higher in the case of S2_5.0.

Figure 5.48 displays the comparison between $\nu_{phys.}$ calculated using the Flory–Rehner approach and T_2 and qM_2 from NMR magnetisation relaxation experiments of SBR compounds cured at 140 °C. This figure illustrates that the $\nu_{phys.}$ is directly proportional to qM_2 and inversely proportional to T_2. However, in the case of SBR the discrepancies between the two techniques are greater than in the case of BR, especially in the case of qM_2.

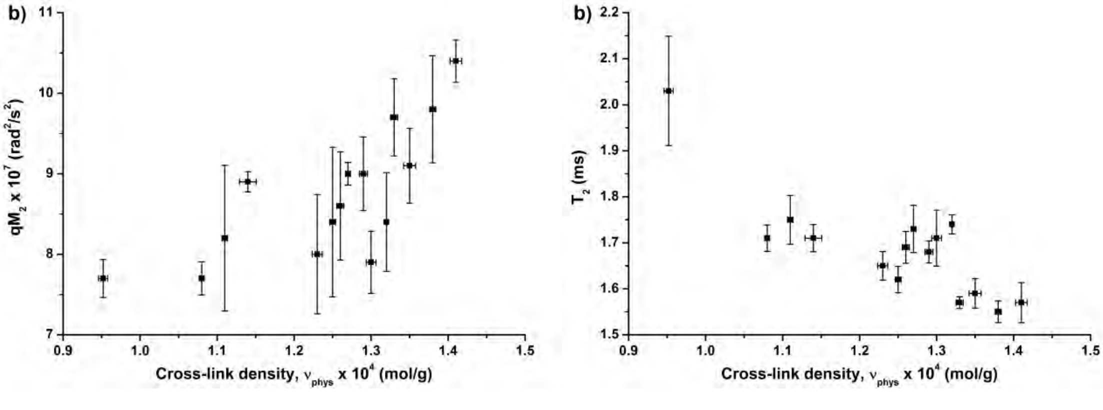

Figure 5.49. Relationship between $\nu_{phys.}$ calculated using the Flory–Rehner approach and a) T_2 and b) qM_2 from NMR magnetisation relaxation experiments of SBR compounds cured at 140 °C.

In Figure 5.49 it is presented the relationship between $\nu_{phys.}$ calculated using the Flory–Rehner approach and qM_2 and T_2 from NMR magnetisation relaxation experiments of SBR compounds cured at 140 °C. AS it has been exposed before, the relationship between $\nu_{phys.}$ and T_2 is stronger than between $\nu_{phys.}$ and qM_2. Due to the high error of qM_2, the correlation between $\nu_{phys.}$ and qM_2 is not as well defined. Nonetheless, for comparative purposes NMR magnetisation relaxation experiments is an appropriate methodology.

5.4. SUMMARY

From the XRD experiments that have been carried out in this work and in previous chapters, it has been evidenced that $Zn_{1-x}Mg_xO$ particles can be obtained by a polymer-based method. The results indicate that the hexagonal phase coexistences with a minor cubic phase, but that almost all magnesium is incorporated into the zinc oxide structure forming $Zn_{1-x}Mg_xO$. Furthermore, the lattice parameters of the small cubic phase formed reveal that zinc atoms have been introduced into this phase forming as well a mixed metal oxide, $Mg_{1-y}Zn_yO$. On the other hand, it is not possible to introduce calcium into the structure of zinc oxide using the same conditions employed to produce $Zn_{1-x}Mg_xO$. The oxide denoted as $Zn_{1-x}Ca_xO$-like is mainly a mixture of ZnO and $CaCO_3$ with a very small interchange of atoms between them.

The results found using mixed metal oxides as activators for sulphur vulcanisation of NR indicate that these oxides are good candidates to substitute ZnO. The use of $Zn_{1-x}Mg_xO$ drops the zinc content hardly affecting the properties of the compound and accelerating the cure characteristics. The reversion resistance is the only feature that is diminished.

With $Zn_{1-x}Ca_xO$-like it is also possible to use lower zinc loadings in NR compounds. The mechanical properties and the cross-link density are not modified but the cure characteristics are not altered. On the other hand, the fraction of non-elastic defects is increased and the homogeneity of the cross-link distribution is worsened.

As it has been seen when MgO is present in the recipe, the negative effect of the appearance of the cubic phase is higher in natural rubber than in MCV. The rheometric curves of the compounds containing $Zn_{1-x}Mg_xO$ could show a higher difference between the minimum and the maximum torque provided that all magnesium is incorporated into the ZnO structure. Moreover, it has been seen that the alteration of the zinc oxide structure caused by the substitution of zinc by magnesium atoms is the reason which causes the advantages seen employing $Zn_{1-x}Mg_xO$ rather than the size or the specific surface area of the oxide.

The results obtained studying the butadiene rubber mixtures have demonstrated that it is possible to reduce safely the zinc levels of BR compounds. A reduction of zinc content can be achieved by using lower amounts of ZnO obtaining similar $M_H - M_L$ values and a higher reversion resistance. However, the vulcanisation times are longer and the cure rate index is reduced. Furthermore, the mechanical properties are, in some cases, slightly worsened and, in addition, the equilibrium swelling and the NMR magnetisation relaxation experiments have shown that the cross-link density has fallen down.

By the means of $Zn_{1-x}Mg_xO$ it is possible to reduce significantly the zinc content in BR. Replacing ZnO with $Zn_{1-x}Mg_xO$ reduces the vulcanisation times and improves the reversion resistance and the CRI. Moreover, the activation energy is minimised. It is possible to obtain compounds with higher tensile strength and elongation at break than compounds with higher amounts of ZnO. In addition, the tensile moduli and the hardness are not diminished. Higher extent of cure and cross-link density can be attained depending on the reduction applied.

Using $Zn_{1-x}Ca_xO$-like the reduction in the cure times and the increase of the CRI are not as marked as with $Zn_{1-x}Mg_xO$ but the cross-link extent is also higher. On the contrary, the reversion resistance is not improved, particularly if low loading are used. The mechanical properties are not deteriorated in comparison with the use of ZnO and higher cross-link density is obtained. However, the improvement in elongation at break and tensile at break is not comparable as it is achieved with $Zn_{1-x}Mg_xO$, even with higher reductions.

In SBR mixtures, it is also possible to achieve a diminution of the zinc levels employing lower amounts of ZnO maintaining comparatively the same properties. When high reductions are applied there is a slightly lower extent of cross-linking but the curing characteristics are not modified. Nevertheless, the mechanical properties are somewhat deteriorated. Tensile strength, tensile moduli and hardness are lowered. Furthermore, the cross-link degree is also reduced.

$Zn_{1-x}Mg_xO$ is an appropriate candidate to substitute ZnO and to reduce the zinc content in SBR. Replacing ZnO with $Zn_{1-x}Mg_xO$ reduces the vulcanisation times and improves the reversion resistance and the CRI. Additionally, the activation energy is substantially minimised. However, the cross-link density is slightly lower, although not in a great extent. In spite of that, it gives similar tensile strength and elongation at break but, on the other hand, tensile moduli and hardness are lightly diminished.

$Zn_{1-x}Ca_xO$-like allows also to minimise the zinc levels. With this activator the reduction in the cure times and the raise of the CRI are not as marked as with $Zn_{1-x}Mg_xO$. Furthermore, , the reversion resistance is only moderately improved and the extent of cure and the activation energy are not enhanced. There is an improvement on the tensile strength, tensile moduli and hardness. In addition, the elongation at break and the cross-link density are not reduced in comparison with the use of ZnO.

Regarding the replacement of ZnO by MgO it is worth noting that, contrary to the results found in NR, for certain specific application MgO could be considered as activator in BR and SBR. In these rubbers there is less involvement of zinc-accelerator species. It is also interesting to remark that, contrary to has been found in NR, where MgO forms only polysulphidic cross-links, in BR and SBR compounds MgO seems to promote the formation of monosulphudic cross-links.

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Chapter 6

EXPLORING TYRE CRUMB AS AN ACTIVATOR FOR SULPHUR VULCANISATION[#]

'"But my lord, when we addressed this issue a few years ago, didn't you argue the other side?"
He said, "That's true, but when I get more evidence I sometimes change my mind. What do you do?"'
John Maynard Keynes (1883 – 1943)

In this chapter a new approach to reduce the environmental effects of end of life and waste rubber and, at the same time, to minimise the ZnO levels in rubber compounds is presented. The use of tyre crumb as activator for sulphur vulcanisation is investigated. To give an insight into the reaction mechanism, the approach is tested using MCV with squalene as a model molecule for natural rubber and CBS. The results showed that the use of the new recipe does not alter the kinetics of the vulcanisation and that the cross-link degree achieved is nearly equivalent to ZnO. However, in real rubber mixtures (NR, BR and SBR), there is not a correlation between the promising characteristics seen in MCV and the actual performance of tyre crumb. The extent of cross-linking is significantly lower, comparable to the mixtures without activator, and the mechanical properties are worsened in most of the cases.

6.1. INTRODUCTION

One of the most important environmental related problems in the rubber industry is the management of end of life and waste rubber, especially tyres. When tyres are taken off vehicles, in some cases they can be retreated allowing the tyre to start its new life cycle, but mainly the end of life tyre is non-reusable in its original form. Due to the chemical cross-linking, it is not possible to simply melt and reshape rubber materials, as can be done with thermoplastics. Furthermore, these materials cannot return to the ecological environment through natural biological degradation, hydrolysation or decomposition, like plants or animals, because they degrade very slowly[1].

[#] Part of this work has been presented at the 176th Technical meeting - Rubber Division, ACS, October 13-15, 2009, in Pittsburgh, PA USA.

Landfill was one of the early ways of disposal for discarded rubber products. Landfilling with waste tyres is of great concern due to environmental problems caused by leaching of small molecular weight additives that are not eco-friendly and may kill advantageous bacteria of soil and, in addition, the risks from fires and mosquitoes. Nonetheless, disposal of tyres in landfills has no future because of the increasingly restrictive legislations[2].

The tyres can be reused after being processed in different applications such as reinforcing agent in roads[3, 4] and in concrete[5-9], particleboard panels[10], different flooring and play surfaces[11], shoe soles, and so on.

The most common methods to obtain the desulphurisation of vulcanised rubber are thermal process, thermomechanical process, mechanochemical process and chemical process. However, various researches have investigated the possibility of microbial devulcanisation processes using different microorganisms[12-15]. Several reviews available in the literature cover aspects out of the scope of this work such as reclaiming methodologies, grinding and size reduction procedures and regeneration or devulcanisation techniques. From these, the works of Myhre and MacKillop[11], Adhikari *et al.*[2], Zhan *et al.*[16], Noordermeer *et al.*[17] and De, Isayev and Khait[18] are recommended.

Another application of main importance is the use of reclaimed or regenerated rubber in blends with virgin rubber. Diverse research studies have investigated the effect of adding ground rubber on the fresh rubber compounds and have been collected by other authors[19, 20]. In addition, collaborative projects have been carried out by suppliers of waste tyre rubber crumb and research institutes[21].

A blend of reclaim and virgin rubber would exhibit different properties depending on the grinding procedure and the de-vulcanising system. In general, these blends cure faster than virgin rubber compound and show less reversion and even antiaging characteristics[2]. Furthermore, deterioration of the physical properties has been found frequently[2, 21, 22], particularly with increasing amounts of powder. For this reason, it is technically unlikely that the use of scrap tyre crumb in new tyre compounds could exceed about 10% of the rubber compounds required[11].

Nonetheless, it has been reported that the change in scorch time is less in the case of filled compounds[19]. Other studies have shown that the tensile strength and elongation at break of the blends with ultrasonically devulcanised NR were much better than those with the ground rubber[20]. It has also been found that the aging conditions of the tyre crumbs affect the final properties of the blends[19].

In summary, although there are some contradictory results due to the enormous number of parameters affecting the performance, the use of tyre crumb in rubber mixtures is a very important approach to minimise the environmental effect of the rubber industry.

Although several research studies have been carried out with the aim of mixing tyre crumb and virgin rubber, no references have been found in the literature regarding the possibility of profiting from the migration of chemicals between the crumb and the matrix to reduce another environmental problem related to the tyre industry: the effect of ZnO.

It has been reported[23-25] that sulphur and accelerator fragments migrate from the matrix to the particles and vice versa. In this work, this exchange between the crumb and the matrix will be considered as an advantage in order to investigate the possibility of using tyre crumb as an activator and, therefore, reduce the zinc levels employed in the rubber compounds.

In order to test this new approach, different techniques will be applied. First model compound vulcanisation with squalene will be employed to investigate the reaction pathway when tyre crumb is used as activator. Afterwards, different tyre crumbs will be mixed with natural rubber, butadiene rubber and styrene-butadiene rubber to study the cure characteristics and the mechanical properties of the vulcanisates. Prior to these tests, different tyre crumbs will be characterised.

6.2. EXPERIMENTAL

6.2.1. MATERIALS

Squalene (Fluka, 97 %), sulphur (Julio Cabrero & Cia, S.L.), CBS (Flexsys), and stearic acid (Calià&Parés) were used for the model compound studies. Solvents used in the investigation were all HPLC grade: Acetonitrile (J. T. Baker); 2-propanol and n-hexane (Panreac).

Natural rubber (Malaysian Rubber, SMR-CV60), butadiene rubber (Buna CB 24, cis-1,4 content min. 96%, Lanxess), solution styrene-butadiene rubber (Buna VSL 2525-0, 25 % by wt. vinyl content, 25 % by wt. styrene content, Lanxess), sulphur (Mahlschwefel, lanxess), CBS (Vulkacit CZ/C, Lanxess), and stearic acid were used for rubber mixtures.

Tyre crumb was provided by two different suppliers, each of them delivering four different tyre crumbs. The first supplier contributed with two different rubber reclaims (TC1 and TC2) in the form of slabs and two rubber powders (TC3 and TC4), both obtained from truck tyre treads. The second supplier delivered four rubber powders (TC5, TC6, TC7 and TC8) from unspecified sources.

6.2.2. CHARACTERISATION OF TYRE CRUMB

The different tyre crumbs were characterised and analysed by different techniques. Thermogravimetric analysis (TGA) was performed in a Mettler TG30 (Mettler-Toledo) in order to determine the composition of the tyre crumb. Furthermore, from the decomposition temperature (T_d) it is possible to obtain information for the identification of the polymer type. The TGA method consists of two steps. In the first one, the sample is heated up to 550 °C in a nitrogen atmosphere at 10 $°C\cdot min^{-1}$ with a gas flow of 50 $ml\cdot min^{-1}$ to obtain information about the polymer and other volatile additives. The second step gives information about the fillers present in the mixture. In this part of the analysis, which is carried out in an oxidant atmosphere (air), the sample is heated up to 1000 °C at 10 $°C\cdot min^{-1}$ with a gas flow of 50 ml·min^{-1}. Between these two steps, there is a cool-down step to 300 °C at 30 °C·min^{-1} with a gas flow of 50 ml·min^{-1} in a nitrogen atmosphere.

Proton double quantum solid-state NMR spectroscopy has been used to measure the cross-link density of the different tyre crumbs. Experiments were carried out at 353 K on a Bruker minispec mq20 spectrometer operating at 0.5 T with 90° pulses of 1.7 µs length and a dead time of 12 µs.

6.2.3. MODEL COMPOUND VULCANISATION

Model compound vulcanisation with squalene as a model molecule for natural rubber has been chosen to study the role of the tyre crumb along the reaction using CBS as accelerator. The basic vulcanisation recipe is given in Table 6.1. The work was performed using the same concentration of ZnO and tyre crumb, 5 phr.

Table 6.1. Model Compound Vulcanisation Recipes (phr).

Ingredients	Mixture A	Mixture G
Squalene	100	100
CBS	1.2	1.2
Sulphur	2	2
ZnO	5	–
TC3	–	5
Stearic acid	2	2

The reaction for all formulations was performed in a preheated thermostatic oil bath at 140°C for 60 minutes. The vulcanisation reaction is carried out in different vessels under nitrogen environment in order to avoid the oxidation of the double bonds of squalene. The model mixtures are continuously stirred to assure its homogeneity. During the reaction, vessels are taken from the oil bath at different pre-set times and quickly cold quenched in dry ice to stop the reaction. After cooling, the vessels were covered to avoid any UV influence, and stored in a refrigerator.

All the model compound vulcanisation mixtures were characterized by two analytical methods of HPLC coupled to an UV detector to cover both aspects of the process: the fading of the accelerator and the formation of cross-links between the model molecules. The identification of the different compounds (CBS, MBT, MBTS, sulphur, squalene and the different cross-linked squalenes) was carried out earlier in our research group using different techniques[26-31].

6.2.4. PREPARATION AND CHARACTERISATION OF RUBBER SAMPLES

The studied compounds were prepared by two steps. The compositions of the different samples are showed in Table 6.2. First, approximately 500 g masterbatch for each rubber without activator was prepared in a two-roll mill using standard procedures. These masterbatches contain stearic acid (2 phr), CBS (1.2 phr) and sulphur (2 phr). Afterwards, the different activators systems were added to the masterbatches in an internal mixer with Banbury rotors (Thermo Haake Polylab system Reocord/Rheomix 600 Type 557-9300), fill factor 0.75. The software PolyLab Monitor has been used for data acquisition. Every formulation was scaled-up to 50 g taking into account the density of every ingredient to avoid overpressure problems inside the internal mixer. Temperature was set at 40 ^{o}C for the cavity and it was controlled during the mixing process avoiding always to overcome 100 ^{o}C to prevent pre-vulcanisation of the material and the speed of the rotors was maintained at 50 Hz.

Table 6.2. Composition of the NR, BR and SBR compounds.

samples			recipe[a] (phr)								
NR	**BR**	**SBR**	**ZnO**	**TC1**	**TC2**	**TC3**	**TC4**	**TC5**	**TC6**	**TC7**	**TC8**
MB_NR	MB_BR	MB_SBR	–	–	–	–	–	–	–	–	–
NZNO_5	BZNO_5	SZNO_5	5	–	–	–	–	–	–	–	–
NTC1_5	BTC1_5	STC1_5	–	5	–	–	–	–	–	–	–
NTC2_5	BTC2_5	STC2_5	–	–	5	–	–	–	–	–	–
NTC3_5	BTC3_5	STC3_5	–	–	–	5	–	–	–	–	–
NTC4_5	BTC4_5	STC4_5	–	–	–	–	5	–	–	–	–
NTC5_5	BTC5_5	STC5_5	–	–	–	–	–	5	–	–	–
NTC6_5	BTC6_5	STC6_5	–	–	–	–	–	–	5	–	–
NTC7_5	BTC7_5	STC7_5	–	–	–	–	–	–	–	5	–
NTC8_5	BTC8_5	STC8_5	–	–	–	–	–	–	–	–	5

[a] Ingredients in parts per hundred rubber: NR, BR or SBR 100; stearic acid 2; CBS 1.2; sulphur 2; activator system.

The sample names, e.g., NTC1_5 encode the type of rubber (N for NR, B for BR and S for SBR), the activator system (TCx for each different tyre crumb, ZNO for ZnO) and the amount of tyre crumb or ZnO in phr (5.0 in all cases). Samples MB_NR, MB_SBR and MB_BR are the masterbatches employed to obtain each sample.

Vulcanisation took place at 280 bar in an electric-heated press at the optimum cure time (t_{90}) plus 2 minutes. t_{90} was deduced from the rheometer curve (Monsanto Rubber Process Analyser, model RPA2000) according to ASTM D2084. The vulcanisation temperature was 140 ^{o}C for natural rubber and 160 ^{o}C for butadiene rubber and styrene-butadiene rubber.

Stress-strain measurements were performed on dumb-bell shaped specimens (Type 3) according to ISO 37 in a Zwick/Roell Z010 at a traction rate of 200 mm/min. Five samples were used for the tensile test and an average of the five results was taken as the resultant value. A Zwick/Roell digi test was used to perform Shore A measurements according to ASTM D 2240.

6.3. RESULTS

In order to test the effect of substituting ZnO with tyre crumb, different approaches will be applied. First model compound vulcanisation with squalene will be carried out to investigate the reaction pathway when tyre crumb is used as activator. Afterwards, different tyre crumbs will be mixed with natural rubber, butadiene rubber and styrene-butadiene rubber and the cure characteristics and the mechanical properties of the vulcanisates will be analysed. Prior to these tests, the different tyre crumbs used in this work will be characterised.

6.3.1. CHARACTERISATION OF TYRE CRUMB

A standard tyre formulation for trucks as well as cars incorporates a precise blend of different rubbers. However, the polymer blend also contains a relatively high number of substances like fillers, (carbon black, silica), organic substances as plasticizers, lubricants, antioxidants, vulcanisation agents, etc., being each formulation designed for a specific application. This complexity causes the identification and quantification of each component to be a laborious task.

Nonetheless, themogravimetrical analysis is a reliable method to obtain an approximate composition of the tyre. From the TG and the derivative thermogravimetry (DTG) procedure, the rubber types in tyres can be determined. As it is shown in Figure 6.1, when a sample is heated in a nitrogen atmosphere there is first the emission of volatile compounds (of processing oil or any other low boiling-point component), and then two mass losses. The DTG peaks at temperatures around 380 °C (T_{d1}) and 440 °C (T_{d2}) correspond to the polymers present in the blend. When the sample is further heated in air, there is a peak around 570 °C (T_{d3}) that is associated with the decomposition of carbon black. The non-volatile residue (ashes) corresponds mainly to inorganic fillers (ZnO, silica or other inorganic components).

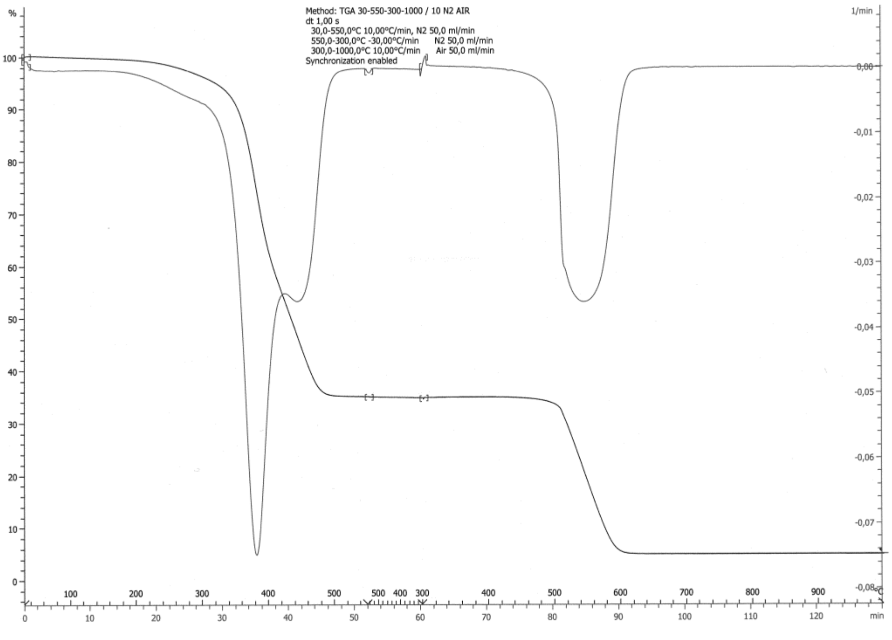

Figure 6.1. TGA thermogram and DTG curve of tyre crumb.

Although the tyre crumbs were provided by two suppliers, the samples are not very different. The decomposition temperatures of the tyre crumbs were very similar. T_{d1} was found to be 377.7±3.5 °C, T_{d2} 442.2±5.9 °C and T_{d3} 573.8±9.7 °C.

Figure 6.2 shows the composition of the different tyre crumbs studied. All the samples have around 63 wt. % of polymer, 30 wt. % of carbon black and 5 wt. % of ashes. There are some differences between the samples, the polymer content of TC4 is slightly lower than the rest of the samples and the ash content is higher, but overall the samples are very similar.

The identification of the types of polymers by the use of the T_d of the DTG curves has been extensively studied by several researchers[32-36]. The two marked peaks of the DTG curve under N_2 atmosphere in Figure 6.1 have been identified with the decomposition of NR and synthetic rubber, BR or SBR.

NR can be clearly distinguished from the other rubbers because it is decomposed at lower temperatures, far from that of SBR and BR. However, the identification between BR and SBR is more complicated because their decomposition temperatures are more similar. BR and SBR exhibit a two stage degradation mechanism[32, 37]. In SBR this first degradation step overlaps with the peak of NR[38] or even with the region where the thermal decomposition of the mixture of oil, plasticizer and additives takes place[39]. BR exhibits also a flat peak before the main weight loss and it also overlaps with the peak of NR[40]. Therefore, since it is very complex to distinguish the type of synthetic rubber in a tyre, the second peak found in the TC samples will be referred merely as synthetic rubber (SR). However, since TC1, TC2, TC3 and TC4 are allegedly obtained from truck tyre treads, it is reasonable to assume that the samples are NR/BR mixtures.

Figure 6.3 depicts the relative composition of natural and synthetic rubber. The relation between NR and SR is 70/30 in most of the samples. TC4, TC5 and TC7 show a higher NR content and TC8 a slightly higher SR content.

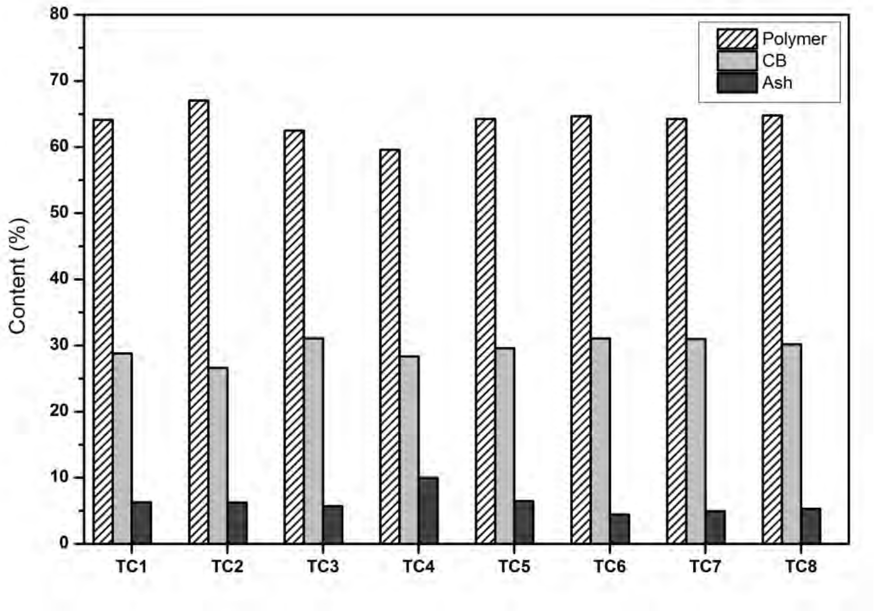

Figure 6.2. Composition of tyre crumb

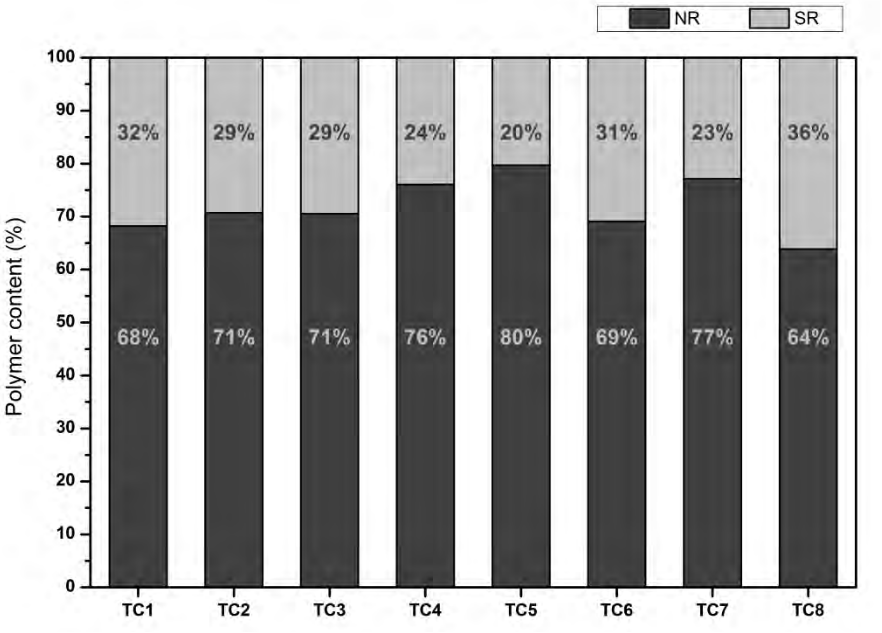

Figure 6.3. Polymer composition of tyre crumb.

The results found previously have indicated that there are almost no differences between the different tyre crumbs, despite the fact they come from two suppliers which, allegedly, perform different treatments to the samples. The first supplier has provided two rubber reclaims (TC1 and TC2) in the form of slabs and two rubber powders (TC3 and TC4). The second supplier delivered four rubber powders (TC5, TC6, TC7 and TC8). MQ NMR experiments were performed to measure the (de)vulcanisation degree of the tyre crumbs in order to find whether the treatments applied cause any difference. Since TC1 and TC2 are (supposedly) rubber reclaims, it is expected that these samples exhibit a low cross-link degree. However, the second supplier maintains that the process applied causes the devulcanisation of the sample and, therefore, it is anticipated to detect differences between these samples and TC3 and TC4.

As it has been explained in Chapter 2 (see section 2.2.2.3.2), the molecular weight between constrains, M_C, is related to D_{res}. For NR and cis-BR, the following expressions[41] can be used:

$$M_C^{(NR)} = \frac{617\ Hz}{D_{res}/2\pi} kg/mol$$

Equation 2.6

$$M_C^{(cis-BR)} = \frac{656\ Hz}{D_{res}/2\pi} kg/mol$$

Equation 6.1

However, since the samples contain a mixture of NR and BR and/or SBR and for SBR there is not yet an expression relating D_{res} and M_C, the fitted D_{res} will not be converted into actual values of cross-link density. In spite of that and since D_{res} and M_C are proportional ($D_{res} \sim 1/M_C$), D_{res} will be taken as a measure of the cross-link density.

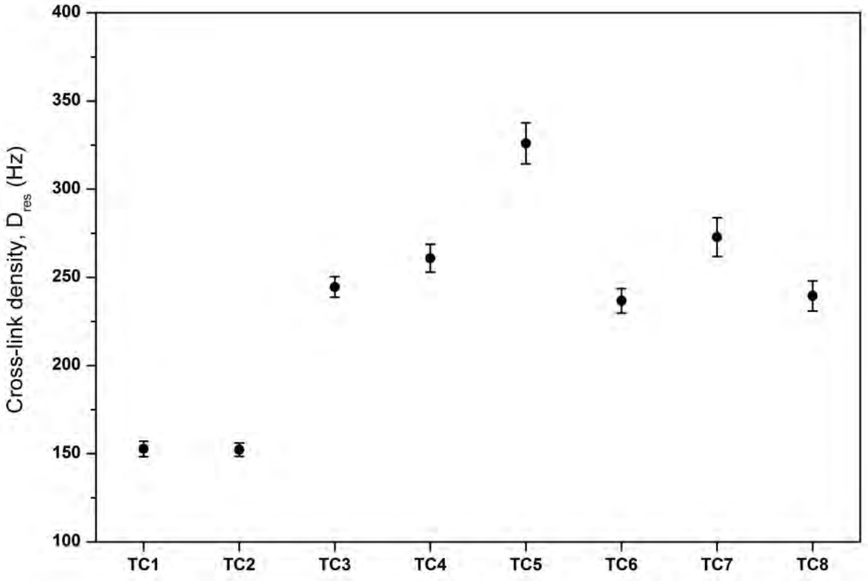

Figure 6.4. Cross-link density, expressed as the residual dipolar coupling constant (D_{res}), of tyre crumb.

Figure 6.4 shows the cross-link density of the tyre crumb samples. As expected, TC1 and TC2 have the lowest vulcanisation degree. TC3 and TC4 have a similar cure extent, higher than TC1 and TC2. Contrary to what was suggested by the second supplier, their samples have not been devulcanised as much as TC1 or TC2. There are no significant differences compared to the other rubber powders with the exception of TC5, which has the lowest devulcanistion degree of the specimens studied.

In summary, the analyses performed in this section have shown that the tyre crumbs obtained for this study are very similar, particularly the rubber powders. In order to perform the model compounds vulcanisation studies, TC3 has been chosen. This sample has, in average, the same content of polymer, carbon black and ashes than the rest of the samples. In addition, devulcanisation degree is at the same level than the average of the rest of rubber powders.

6.3.2. MODEL COMPOUND VULCANISATION

Model compound vulcanisation with squalene as a model molecule for natural rubber has been chosen to study the role of tyre crumb along the reaction using CBS as accelerator. The basic vulcanisation recipe is given in Table 6.1. The work was performed using the same concentration of tyre crumb and ZnO, 5 phr.

In Figure 6.5 it is represented the evolution of the accelerator along the reaction. Comparing the results obtained with standard ZnO and TC3, it can be observed that the reaction rate of this compound is the same in the mixtures with TC3 and standard ZnO. The application of ZnO or TC3 as activators does not influence the breakdown of CBS differently. When TC3 are used, CBS is completely degraded after 25 minutes while with standard ZnO it does not disappear entirely until 30 minutes. However, it should be noted the lack of values at 25 minutes for the mixture with ZnO.

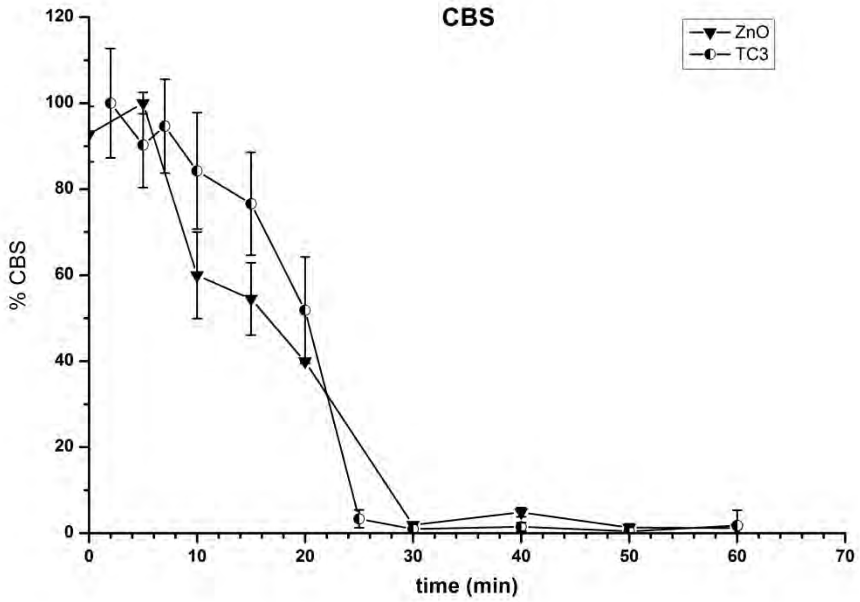

Figure 6.5. Breakdown of CBS as a function of the reaction time with tyre crumb and ZnO as activator.

To study further the decomposition of the accelerator, the formation of MBT is depicted in Figure 6.6. As it can be seen, the use of ZnO or TC3 does not cause significant differences. When TC3 is used, the formation of MBT commences faster, there are higher amounts of MBT at 30 minutes. At longer reaction times these differences disappear and the levels of MBT are harmonised.

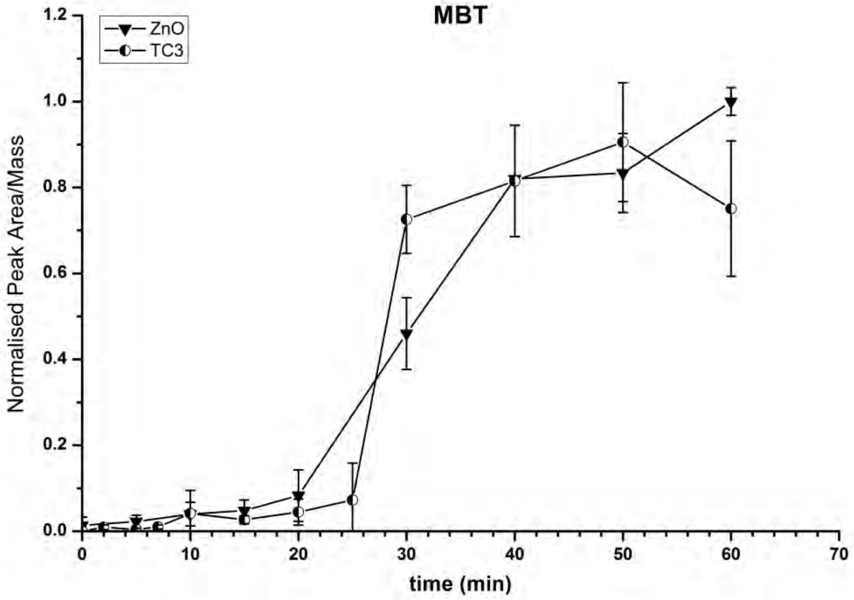

Figure 6.6. MBT concentration as a function of the reaction time with tyre crumb and ZnO as activator.

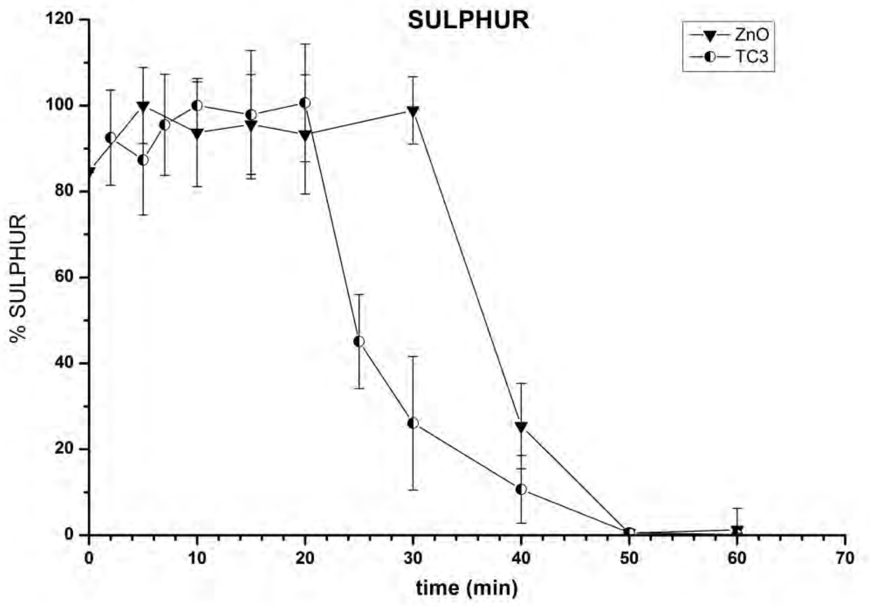

Figure 6.7. Degradation of sulphur during vulcanisation with tyre crumb and ZnO.

Figure 6.7 shows that the consumption of sulphur starts earlier when TC3 is used as the accelerator. Sulphur starts to react after 20 minutes with TC3 and after 30 minutes with ZnO. Nevertheless, once sulphur has begun to react, the depletion is sharper with ZnO. It takes 20 minutes for the complete reaction and 30 minutes with TC3. In both cases, at 50 minutes there is no more free sulphur present in the mixture.

The evolution of cross-linked squalene is displayed in Figure 6.8. When TC3 is used instead of ZnO, it can be appreciated that formation of the cross-linked products commences later and that the cross-link degree attained is reduced. However, the differences in the extent of cure achieved are smaller than working with MgO (see Chapter 3, Figure 3.10).

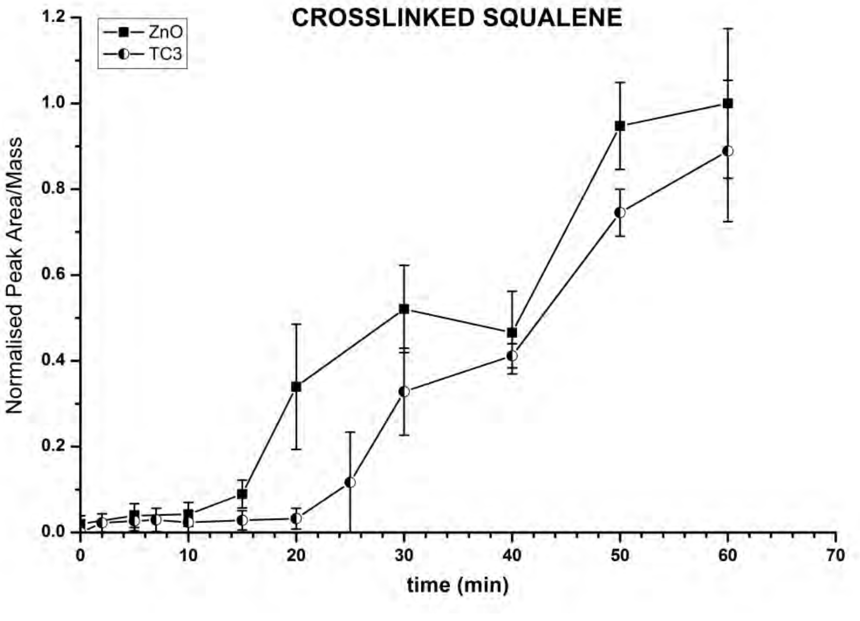

Figure 6.8. Evolution of total cross-linked squalene during vulcanisation with standard ZnO and tyre crumb.

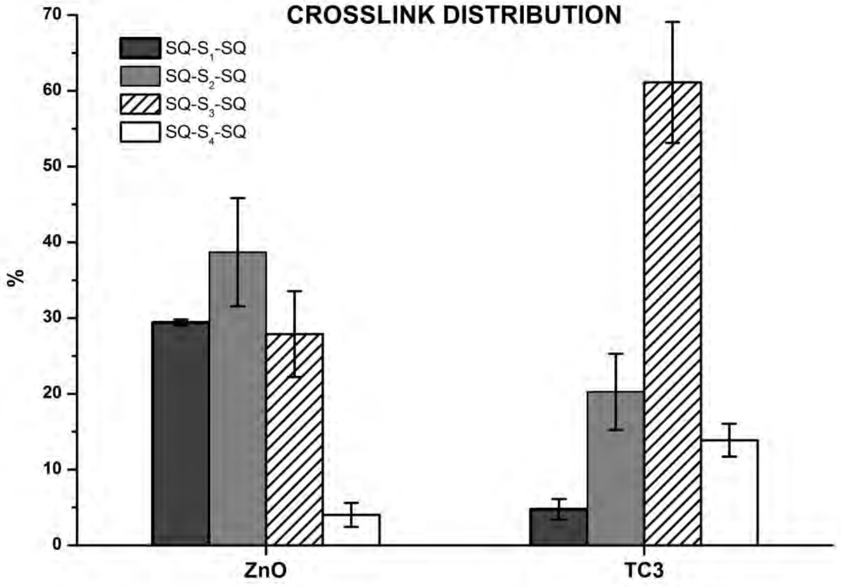

Figure 6.9. Distribution of cross-links (cross-link structure) in 60 minutes vulcanisates with ZnO and tyre crumb.

Regarding the cross-link structure, some changes are observed when TC3 is used. Figure 6.9 presents the percentage of mono- ($Sq - S - Sq$), di- ($Sq - S_2 - Sq$), tri- ($Sq - S_3 - Sq$) and tetrasulphidic ($Sq - S_4 - Sq$) cross-links in 60 minutes vulcanisates. The presence of TC3 in the recipe decreases the fraction of mono- and disulphidic cross-links. The reduction of monosulphidic cross-links is more acute, there is a fall from 30 % with ZnO to 5 % with TC3. On the contrary, the proportion of tri- and tetrasulphidic cross-links is increased, particularly significant in the case of trisulphidic cross-links, which rise from 30 % to more than 60 %.

This could be explained by the fact that the amount of zinc oxide present in the system containing tyre crumb is very small. Zinc accelerator complexes are thought to be responsible for the desulphuration of the polysulphidic cross-links[42, 43]. Due to the amount of ZnO is very limited in the recipe with TC, these species are not formed in enough quantities to promote desulphuration and cross-link shortening.

The results found performing model compound vulcanisation indicate that tyre crumb could be used as activator for sulphur vulcanisation and minimise or eliminate completely the ZnO levels in rubber compounds. Through this section it has been demonstrated that tyre crumb have some activator character. It has been seen that TC is able to cause the breakdown of the accelerator in the same way that ZnO does. Previous research studies[44] have proved that the breakdown of CBS in MCV with squalene occurs later if no activator is present in the recipe. Accordingly, the fact that CBS reacts similarly with ZnO or TC (Figure 6.5) indicates that tyre crumb possesses some characteristics to perform as an activator. Furthermore, other studies[45] have shown that MBT is not formed during the vulcanisation process in the absence of an activator despite the fact that CBS disappears.

Two main reasons may be the cause of the results found; the presence of ZnO and/or the presence of amines or accelerator residues in the tyre crumbs. TG experiments have shown that there is around 6 % of non-volatile residue or ashes present in the tyre crumb. This fraction corresponds mainly to inorganic fillers such us ZnO, silica or other inorganic components. If high levels of ashes were found, it could have been taken as an indication of silica. However, silica is usually added to the recipe in higher quantities and finding only round 6 % of ashes suggests that silica is not present in the tyre crumbs. Therefore, the non-volatile residue could be considered as ZnO plus other inorganic components. Consequently, the presence of ZnO might be the origin of the activator characteristics shown by tyre crumb.

On the other hand, guanidines and secondary amines in general are sometimes used as secondary accelerators because they increase the vulcanisation rate and cross-link density of the primary accelerator. The role of amines is thought to be the formation of coordination compounds with the zinc accelerator complexes[46-48]. These complexes, being more soluble in rubber, enhance the reactions with sulphur catalysing the insertion of sulphur to form active sulphurating agents[49]. The most important guanidine is diphenylguanidine (DPG) which is used mainly as secondary accelerator[50]. DPG is employed as an activator for sulphenamides and as secondary accelerator in tyre tread compounds[51], although more commonly in passenger tyre treads than in truck tyre treads. Furthermore, amines could also be present in the tyre crumb as a result of the decomposition of accelerators. Sulphenamides such us CBS or TBBS produce amines when they react to form the active sulphurating agents. For that reasons, the presence of amines could also be the cause of the performance shown by tyre crumb.

Moreover, sulphenamide accelerators also dissociate to form MBT, which is known for catalysing the decomposition of CBS[44]. It has been reported that the migration of sulphur into the crumb triggers the release of bound accelerator fragments from the crumb that diffuse into the matrix speeding vulcanisation[23].

The reactions of the accelerator and sulphur are very similar whether tyre crumb or ZnO is added to the recipe. However, the formation of cross-link products is slightly higher and the cross-link distribution of the final vulcanisate is more efficient with ZnO. In spite of this, it should be noted that apart from the variation in the distribution of cross-link, the rest of the parameters studied remains very similar. The cross-link degree attained is even slightly higher than with MgO (see Chapter 3, section 3.3). Thus, this is an indication that TC could replace ZnO as activator, especially in BR and SBR compounds where, as it has been seen in the previous chapter, the differences between MCV and rubber mixtures are not that significant.

In order to investigate if tyre crumb might replace or substitute ZnO as activator for sulphur vulcanisation, different real rubber mixtures containing TC will be prepared to check if the results found with model compound vulcanisation are also obtained with actual rubbers.

6.3.3. RUBBER MIXTURES

Three rubbers have been chosen to study the effect of tyre crumb as activator: NR, *cis*-BR and solution SBR. A masterbatch without activator was prepared with each rubber. Afterwards, 5 phr of the different tyre crumbs were added to the mixture obtaining 8 samples for each rubber. The compounds were vulcanised according to their optimum vulcanisation time and their physical properties were tested. In the following section the cure characteristics and the physical properties of the mixtures will be presented and discussed.

6.3.3.1 CURE CHARACTERISTICS

Figure 6.10 shows the rheometric curves for the NR compounds with tyre crumb vulcanised at 140 °C. The curves of the mixtures with tyre crumb are very similar, the scorch and optimal vulcanisation times are almost the same. Furthermore, these times are shorter than the compounds without activator or with ZnO. Regarding the extent of cure, tyre crumb produces very low $M_H - M_L$ values, on the same level than the masterbatch.

The minimum torque shows a slight increase with TC compare to ZnO-containing samples. This is an indication that the samples are more complicated to process. The increase might be due the rubber powders tend to agglomerate in the matrix although TC1 and TC2 are not rubber powder but rubber reclaims in the form of slabs.

It is clear from Figure 6.10 that the effect of tyre crumb as activator is not as it has been detected in model compound vulcanisation. Working with squalene it has been found that the reactions of the accelerator and sulphur are faster. This could explain why the scorch times of the mixtures with TC are shorter. Some authors[23-25, 52] have suggested that the presence of cross-linked precursors and unreacted curatives accelerators in the rubber powders is the cause of the shortening of the scorch times and optimum vulcanisation times. It has been reported that using peroxide-cured particles no reduction in scorch time is detected[18].

On the other hand, in MCV the total amount of cross-linked squalene was very similar comparing TC and ZnO, but the extent of cure in natural rubber is very different. The samples with TC give $M_H - M_L$ values equivalent to working without activator. These results suggest that the ZnO present in the tyre crumb is not able to interact with the accelerator in the same manner as it occurs in MCV.

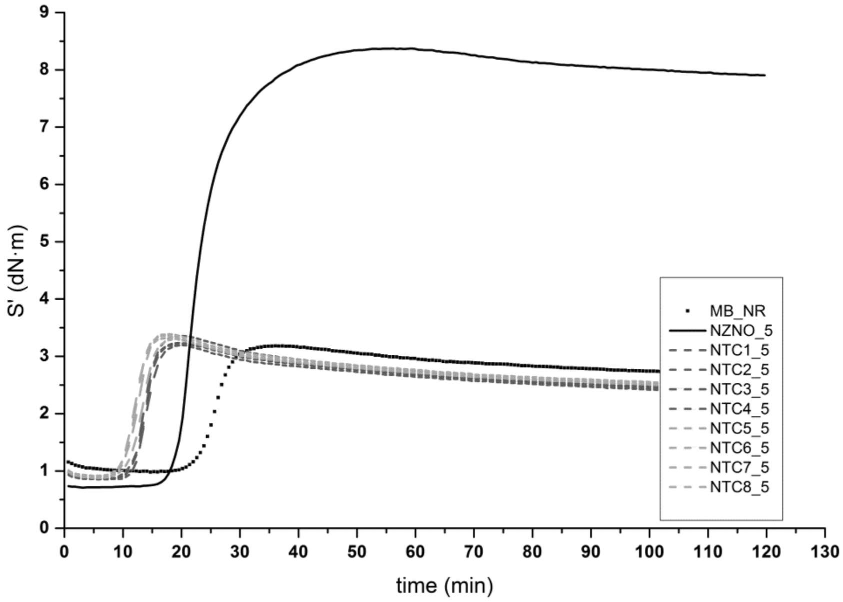

Figure 6.10. Cure characteristics of NR compounds with tyre crumb and ZnO at 140 °C.

As it has been explained previously, the presence of amines in the tyre crumbs enhances the cross-link degree. However, it is important to notice that the role of the amines have been associated to the coordination with zinc complexes[42, 43]. Therefore if zinc oxide is not able to assist in the formation of active sulphurating agents or cross-link precursors, the amines will not cause an increase in the extent of cure.

Table 6.3 summarises the vulcanisation parameters of the natural rubber mixtures. Concerning the reversion resistance, from the data collected in Table 6.3, it can be perceived that tyre crumb deteriorates the reversion behaviour in NR compounds. The reversion times and the reversion tax are similar for the different tyre crumbs tested. The reversion time is shorter when TC is used compared to the masterbatch without activator or with ZnO. In addition, the reversion tax is increased.

Table 6.3. Vulcanisation parameters of NR compounds vulcanised with different tyre crumbs.

sample	t_{02} (min)	t_{s2} (min)	t_{90} (min)	CRI (%)	RT (min)	Reversion Tax (%)	$M_H - M_L$ (dN·m)
MB_NR	19.6	29.3	29.2	–	12.2	12.4	2.2
NZNO_5	17.1	21.0	33.31	11.7	45.2	3.8	7.7
NTC1_5	9.8	15.1	15.8	–	5.5	19.6	2.4
NTC2_5	9.2	15.4	15.8	–	5.5	19.5	2.3
NTC3_5	9.2	16.0	16.4	–	6.7	18.3	2.3
NTC4_5	10.4	15.3	16.1	–	5.2	21.0	2.5
NTC5_5	8.0	14.0	14.7	–	4.9	21.0	2.5
NTC6_5	8.6	15.0	15.6	–	4.6	20.8	2.4
NTC7_5	8.6	13.5	14.2	–	4.3	21.3	2.5
NTC8_5	7.4	13.5	14.2	–	5.5	20.7	2.4

In relation to the different types of tyre crumb used as activator, it is worth stating that there are no significant changes in the results. The main important variation between the samples is the devulcanisation degree. It has been reported[52] that there is a weak interaction and bonding between the rubber powder particles and the natural rubber matrix due to little formation of interfacial sulphur cross-links. TC1 and TC2 have a lower cross-link density and this was thought to cause an improvement of the interaction between the rubber matrix and the tyre crumb. It has been reported that blends with ultrasonically devulcanised natural rubber produce better properties than those with the ground rubber[20]. Conversely, no improvement has been observed.

In Figure 6.11 are represented the rheometric curves for the BR compounds with tyre crumb vulcanised at 160 °C. As it has been found in the case of NR, there are almost no differences between the curves of the mixtures with TC. The scorch and t_{90} times of these mixtures are virtually the same and slightly shorter than the compounds without activator or with ZnO. In the case of BR, the extent of cure is even reduced compared to the masterbatch.

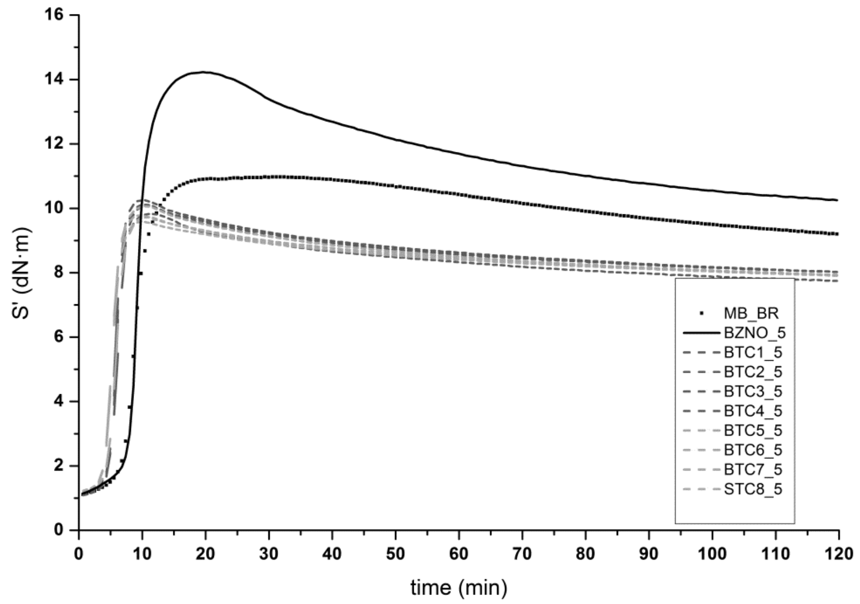

Figure 6.11. Cure characteristics of BR compounds with tyre crumb and ZnO.

The vulcanisation parameters of the BR mixtures are compiled in Table 6.4. The data displayed reveals that the cure rate index is enhanced if tyre crumb is added to the recipe. Considering the reversion exhibited by the BR compounds tested in this work it is interesting to notice the different behaviour observed in the reversion times and the reversion tax. The samples with TC give shorter reversion times but also lower reversion taxes compared to the compound with ZnO. This indicates that when the samples are overcured, those containing tyre crumb present a decay of torque very rapidly. Nevertheless, this decrease is moderated if samples are exposed to overcuring for longer time. On the contrary, the mixture with ZnO has a longer reversion time and a higher reversion tax.

Table 6.4. Vulcanisation parameters of BR compounds vulcanised with different tyre crumbs.

sample	t_{02} (min)	t_{s2} (min)	t_{90} (min)	CRI (%)	RT (min)	Reversion Tax (%)	$M_H - M_L$ (dN·m)
MB_BR	3.1	7.6	12.6	20.1	28.1	5.3	9.9
BZNO_5	3.1	8.1	12.1	27.3	8.8	15.8	13.1
BTC1_5	2.5	5.2	7.5	43.5	6.7	13.5	8.7
BTC2_5	2.5	5.3	7.2	52.6	6.1	14.0	9.1
BTC3_5	2.5	5.4	7.7	44.1	8.5	13.0	8.9
BTC4_5	3.1	5.3	7.3	49.8	6.1	14.1	8.9
BTC5_5	2.5	4.6	6.9	43.1	6.7	13.7	8.8
BTC6_5	2.5	5.1	7.5	42.2	8.5	12.2	8.5
BTC7_5	2.5	4.6	6.9	43.1	11.0	10.7	8.4
BTC8_5	2.5	4.5	6.7	45.9	8.9	11.8	8.6

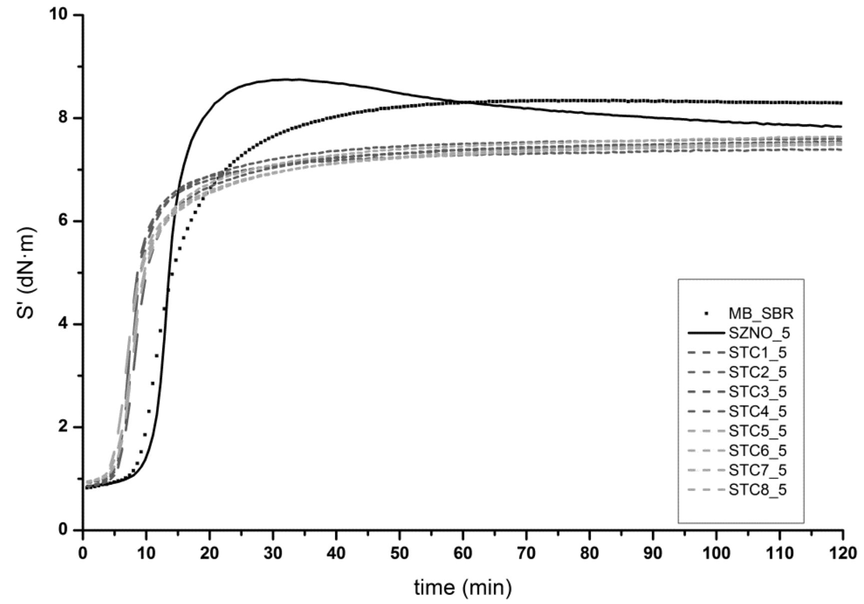

Figure 6.12. Cure characteristics of SBR compounds with tyre crumb and ZnO.

Figure 6.12 shows the vulcanisation curves of the SBR with TC vulcanised at 160 °C. As it was observed with the other kind of rubber tested in this chapter, tyre crumb causes an increase in the vulcanisation times. Both scorch and t_{90} times are longer. Regarding the extent of cross-linking, SBR mixtures containing TC have smaller $M_H - M_L$ and, as in the case of BR, lower than the masterbatch.

Table 6.5 summarises the vulcanisation parameters of the SBR mixtures. Concerning the reversion resistance, since the masterbatch and the compounds with TC show marching modulus, the reversion times and the reversion tax are not shown. The fact that the rheometric curves for the SBR samples with TC exhibit marching modulus also causes that the CRI is reduced in comparison to the samples with ZnO.

Table 6.5. Vulcanisation parameters of SBR compounds vulcanised with different tyre crumbs.

sample	t_{02} (min)	t_{s2} (min)	t_{90} (min)	CRI (%)	RT (min)	Reversion Tax (%)	$M_H - M_L$ (dN·m)
MB_SBR	5.6	11.0	29.2	5.5	–	0.5	7.5
SZNO_5	6.8	12.3	18.9	16.4	13.4	25.0	7.9
STC1_5	3.7	7.1	16.9	10.2	–	–	6.5
STC2_5	3.7	7.4	21.1	7.3	–	–	6.7
STC3_5	3.7	7.8	25.1	5.8	–	–	6.6
STC4_5	3.7	7.3	25.7	5.4	–	–	6.6
STC5_5	3.1	7.0	21.5	6.9	–	–	6.7
STC6_5	3.7	7.5	26.0	5.4	–	–	6.6
STC7_5	3.1	6.6	27.7	4.7	–	–	6.6
STC8_5	3.1	6.7	26.1	5.2	–	–	6.6

6.3.3.2 PHYSICAL PROPERTIES

Stress-strain measurements were performed on the mixtures of natural rubber vulcanised at 140 °C. Figure 6.13 displays the tensile strength, the elongation at break and the tensile moduli of the NR compounds. The tensile strength and elongation at break values of the samples containing TC are lower than the masterbatch indicating that the mechanical properties are deteriorated by the presence of tyre crumb. On the other hand, the tensile moduli are slightly higher if TC is present in the mixture, especially in the modulus at 500 % elongation.

The different types of tyre crumb do not cause significant differences in the values of TS and E_b indicating that neither the composition nor the devulcanisation degree exert an influence. However, minor differences are found in the tensile moduli. NTC1_5 and NTC2_5 have lower M_{500} than the other samples. As it has been explained previously, TC1 and TC2 have a higher devulcanisation degree than the rest of the TC. Therefore, from Figure 6.13 it can be deduced that when reclaim crumbs are used the tensile moduli at high elongations are slightly lowered.

In Figure 6.13 it can also be seen that the sample containing ZnO (NZNO_5) in the mixture exhibit much higher moduli and tensile strength. Since the cross-linking degree values are greater for the sample containing ZnO as activator this behaviour is not unexpected. The differences in the tensile moduli are especially greater at high elongations. Regarding the E_b, it can be observed that when ZnO is used as activator the elongation at break reached is significantly lower.

The tensile strength, the elongation at break and the tensile moduli of the BR compounds vulcanised at 160 °C are shown in Figure 6.14. Tensile strength and elongation at break are higher for the mixtures comprising TC, contrary to what has been found in NR samples. On the contrary, the tensile moduli are basically equivalent to the masterbatch. When ZnO is present in the mixture, the tensile moduli are higher than the rest of the compounds. The TS is higher if ZnO is added to the compound, however, the differences with respect the TC samples are not as significant as it has been found in NR. The E_b attained is similar to the masterbatch.

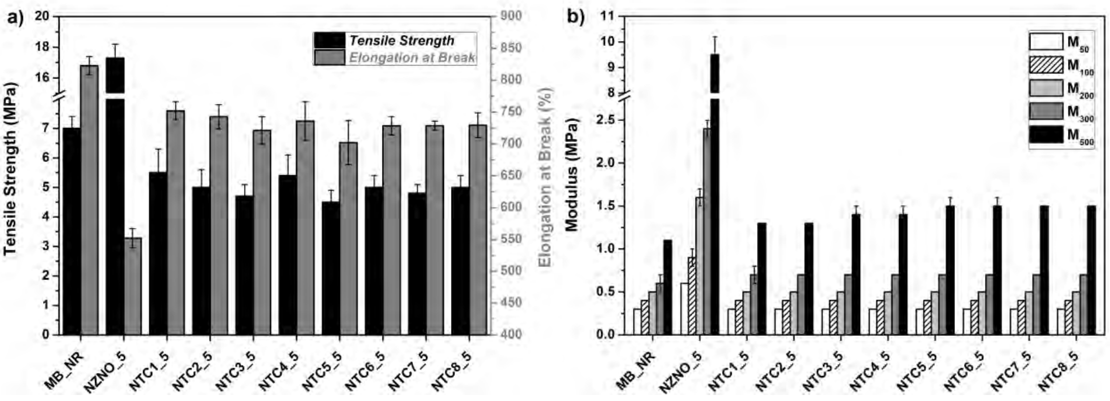

Figure 6.13. Effect of tyre crumb on a) tensile strength and elongation at break, and b) tensile moduli in NR compounds vulcanised at 140 °C.

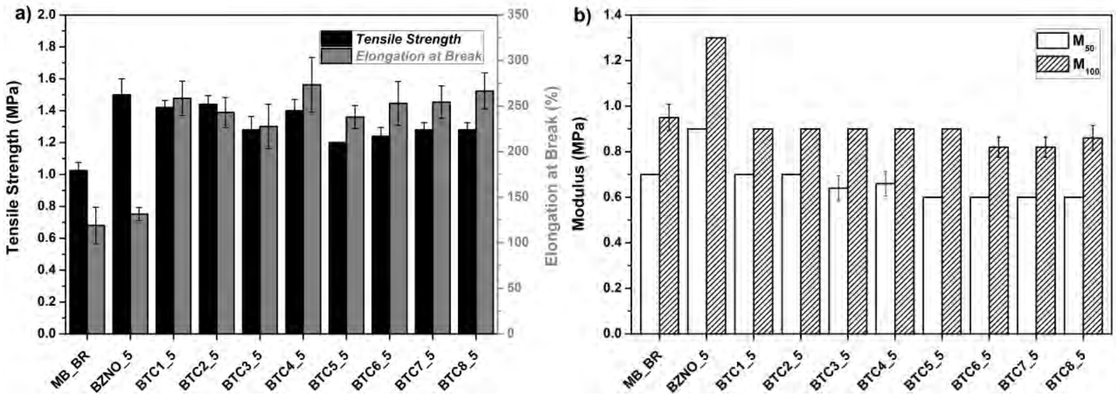

Figure 6.14. Effect of tyre crumb on a) tensile strength and elongation at break, and b) tensile moduli in BR compounds vulcanised at 160 °C.

In SBR mixtures vulcanised at 160 °C, tensile strength and elongation at break are worsened in comparison to the compound without activator as it can be perceived in Figure 6.15. Nevertheless, no remarkable differences are appreciated in the tensile moduli. In comparison with sample with 5 phr of ZnO (SZNO_5), the differences in the tensile moduli and in the elongation at break reached are not very pronounced although the tensile strength is higher.

Figure 6.16 shows the Shore A hardness of the rubber compounds studied in this section. It can be seen that tyre crumb does not have a significant influence on the hardness of the mixtures. In all cases, the samples without activator and the compounds containing tyre crumb have very similar hardness. Nonetheless, the rubber samples containing ZnO as activator possess higher hardness, especially the natural rubber and the *cis*-butadiene rubber samples.

The results found in this section indicate that the use tyre crumb as activator in real rubber mixtures is not as effective as it has been observed in model compound vulcanisation. The scorch times are shorter in all the rubber samples tested and the optimum vulcanisation times are shorter for natural and cis-butadiene mixtures. However, it is worth noting that if longer scorch safety is an important parameter to take into consideration, filled compounds would show a minor change in scorch times[19].

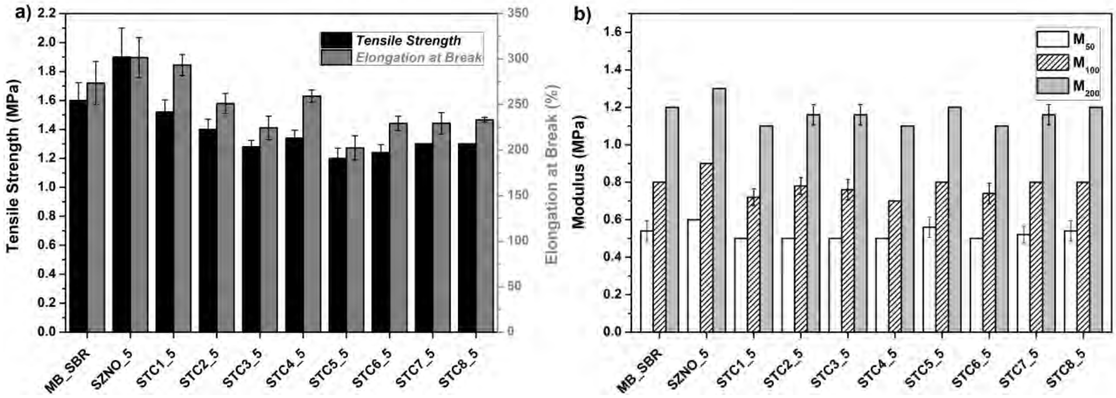

Figure 6.15. Effect of tyre crumb on a) tensile strength and elongation at break, and b) tensile moduli in SBR compounds vulcanised at 160 °C.

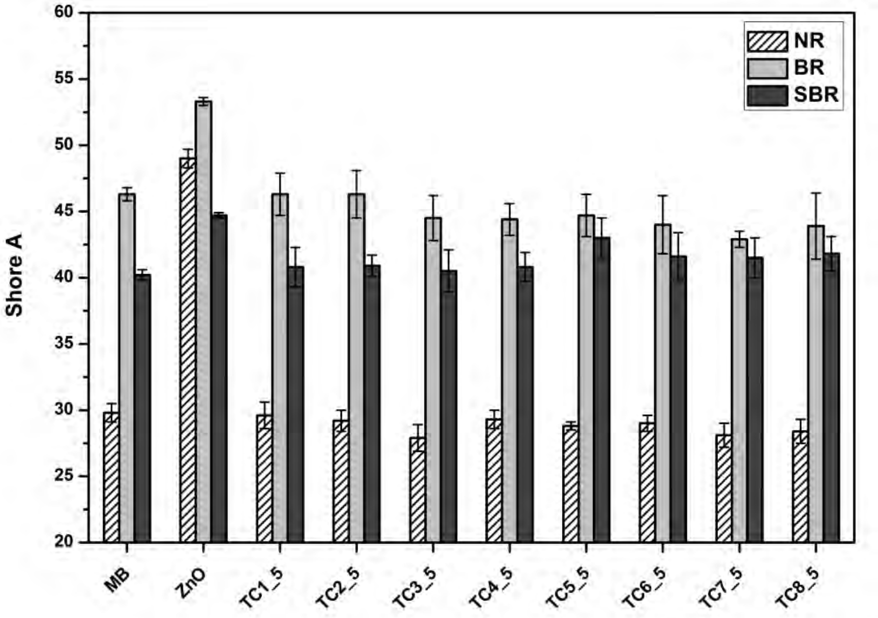

Figure 6.16. Effect of tyre crumb on shore A of NR compounds vulcanised at 140 °C and BR and SBR compounds vulcanised at 160 °C.

The most remarkable drawback found in the vulcanisation curves is the extent of cure achieved, which is significantly lower. This outcome is more considerable working with NR. In spite of this, in BR and SBR the difference between the masterbatches and the recipes with ZnO is not as important as in NR.

These divergences between MCV and real rubber samples might arise because the ZnO present in the tyre crumb is not able to interact with the accelerator in the same manner as it occurs in MCV. As it has been stated before, there is a weak interaction and bonding between the rubber powder particles and the rubber matrix. In MCV, since there are no problems such as agglomeration or dispersion in the matrix, the interaction between the curatives present in the tyre crumbs and the accelerator is higher and, therefore, the extent of cure achieved is not as worsened as it occurs with the various rubbers tested.

Regarding the mechanical properties, it has been seen that the effect of adding tyre crumb to the recipe is detrimental in most of the cases. Only the tensile strength of the BR compounds has been slightly improved. Comparing with the results found with ZnO as activator, it is clear that the physical properties of the compounds containing TC are not comparable to standard formulations with ZnO, especially for NR. Different researchers[22] have shown that adding tyre crumb to the recipes produces a decrease in the mechanical properties of NR compounds containing ZnO. The properties of the mixtures with tyre crumb were not expected to be on the same levels as with ZnO. However, taking into account the results obtained in the MCV studies, it was not anticipated to find no differences with the compounds without activator.

6.4. SUMMARY

Different tyre crumbs from two suppliers have been analysed and characterised employing various techniques. The composition of all samples is very similar. There is around 63 wt. % of polymer, 30 wt. % of carbon black and 5 wt. % of ashes. The polymer fraction consists on a blend of natural rubber and synthetic rubber (presumably BR) with a ratio of approximately 70/30.

MQ NMR experiments have shown that the samples labelled as rubber reclaims by the first supplier have the lowest vulcanisation degree. On the other hand, the tyre crumbs provided by the second supplier have a similar extent of cure than the rubber powders of the first supplier, contrary to what was indicated.

Model compound vulcanisation studies have suggested that tyre crumb could be used as activator for sulphur vulcanisation and minimise the ZnO levels in rubber compounds. The breakdown of the accelerator and the consumption of sulphur occur in the same way that when ZnO is used. The cross-link degree achieved, calculated as the total amount of cross-liked squalene, is slightly higher with ZnO and the cross-link distribution in the final product is more efficient. Nevertheless, the differences, especially in the extent of cure, are not significant enough to prevent the use of tyre crumb as activator.

In NR, BR or SBR compounds there is not a correlation between the promising characteristics observed in MCV and the actual performance of tyre crumb. The scorch and optimum vulcanisation times are shorter but the extent of cross-linking is significantly lower, comparable to the mixtures without activator. In the case of natural rubber, the effect on the degree of cure is more prominent. In addition, the mechanical properties are worsened in most of the cases.

Zinc oxide is very difficult to eliminate from NR compounds because it plays an essential role in the three key steps of the vulcanisation process. It is an important substance for the formation of the active sulphurating agents and the cross-links and, in addition, in the reactions that lead to cross-link shortening and cross-link degradation.

In rubber mixture containing only a synthetic rubber, such as styrene-butadiene rubber or butadiene rubber, the effects of cure-system changes may not be as pronounced as they are in the case of natural rubber[53]. It has been proposed that in BR and SBR the mechanism seems to be closer to the pathway of unaccelerated sulphur vulcanisation, with less involvement of zinc-accelerator species and the appearance of radical reactions[54]. For that reason the substitution of ZnO by tyre crumb is more detrimental in the case of natural rubber.

However, the results found in MCV suggest that further research should be carried out in order to try to take advantage of the features observed by improving or facilitating the interaction between the chemicals present in the tyre crumb (ZnO, amines, cross-linked precursors, unreacted curatives accelerators…) and the ingredients added to the rubber matrix.

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Chapter 7

GENERAL SUMMARY AND FINAL REMARKS

'Science is a wonderful thing if one does not have to earn one's living at it'
Albert Einstein (1879 – 1955)

The model compound vulcanisation approach has been employed to study the effect of magnesium oxide as activator for sulphur vulcanisation. It has been demonstrated that the differences observed between ZnO and MgO are caused by the different mechanisms that the reaction follows.

Regarding the reactions taking place during the scorch time, it has been seen that when MgO is the activator the breakdown of the accelerator and the consumption of sulphur occur faster. In addition and contrary to the behaviour reported with ZnO, the decomposition of the accelerator occurs whether or not double bonds are present in the hydrocarbon chains. Studies with squalene and squalane have shown that there are no differences in the reaction rate of the accelerator. However, when sulphur is removed from the recipe, the accelerator does not react. Therefore, it is the interaction of MgO with sulphur which provokes a faster formation of the active sulphurating agents from the accelerator. The presence of sulphur is a necessary condition for the breakdown of the accelerator and not the presence of unsaturations in the hydrocarbon chain as occurs with ZnO.

The cross-link degree achieved with MgO is lower in comparison to ZnO. MgO does not form complexes with the active sulphurating agents or the cross-link precursors and this causes a decrease of the cross-linking degree attained and that the cross-linked products formed contain longer sulphur chains.

In this work novel activators have been developed to minimise the environmental impact of rubber goods by reducing the ZnO levels employed in the rubber industry. A mixed metal oxide of zinc and magnesium has been synthesised in order to take advantage of the behaviour of ZnO and MgO but overcoming the problems of the mixture of them.

Mixed metal oxides of zinc and magnesium with a ratio Mg/Zn is 24/76 in weight weight were prepared. The particle size was found to be 147 ± 32 nm and the BET surface area 27.2 ± 0.4 m^2/g. The X-ray diffraction patterns have proved that magnesium atoms incorporate into the zinc oxide structure altering the lattice parameters. The results indicate that the hexagonal phase coexistences with a minor cubic phase, but that almost all magnesium is incorporated into the zinc oxide structure forming $Zn_{1-x}Mg_xO$. Furthermore, the lattice parameters of the small cubic phase formed reveal that zinc atoms have been introduced into this phase forming as well a mixed metal oxide, $Mg_{1-y}Zn_yO$.

Model compound vulcanisation with squalene has been carried out to study the role of the mixed metal oxide along the reaction. The results indicate that the use of $Zn_{1-x}Mg_xO$ nanoparticles as activator leads to a reduction of the total amount of zinc used in rubber compounds.

From a mechanistic point of view, the reaction of the accelerator is faster and more similar to the manner that occurs when MgO is used. Moreover, the consumption of sulphur takes place faster than with ZnO or MgO. Concerning the cross-link formation, a 30 % higher cross-link degree is attained but there is a decrease of monosulphidic cross-links and an increase of disulphidic cross-links. Overall, $Zn_{1-x}Mg_xO$ nanoparticles not only overcome the disadvantages of the mixture of ZnO and MgO but a better performance is achieved.

The effect of these mixed metal oxides in natural rubber, cis-butadiene rubber and solution styrene-butadiene rubber was investigated. In addition, a mixed metal oxide of zinc and calcium has been chosen to study whether the alteration of the structure caused by the incorporation of another atom or the size and specific surface area of the oxide are the reason which causes the performance seen in model compound vulcanisation.

From the XRD experiments that have been carried out it has been evidenced that it is not possible to introduce calcium into the structure of zinc oxide using the same conditions employed to produce $Zn_{1-x}Mg_xO$. The oxide denoted as $Zn_{1-x}Ca_xO$-like is mainly a mixture of ZnO and $CaCO_3$ with a very small substitution of atoms between them. The particle size was found to be 114 ± 33 nm and the BET surface area is 16.8 ± 0.2 m^2/g. The ratio Ca/Zn is 18/82 in weight.

The results obtained using mixed metal oxides as activators for the vulcanisation of NR, BR and SBR have demonstrated that it is possible to reduce safely the zinc levels of rubber compounds using these oxides.

The use of $Zn_{1-x}Mg_xO$ allows using lower quantities of Zn in NR without affecting significantly the properties of the compounds and accelerating the cure characteristics. The reversion resistance is the only feature that is diminished. In BR and SBR, the vulcanisation times are reduced and the reversion resistance and the CRI are enhanced. Moreover, the activation energy is minimised. The cross-link density is not reduced in NR mixtures and only slightly in BR and SBR at low loadings of $Zn_{1-x}Mg_xO$.

A 40 % reduction of zinc using $Zn_{1-x}Mg_xO$ does not deteriorate the mechanical properties of NR mixtures and in BR and SBR causes an enhancement. A further reduction to 70 % produces a slightly negative effect on the hardness of NR compounds. In BR, the tensile moduli and the hardness are not diminished and tensile strength and elongation at break are higher. In SBR, it gives similar tensile strength and elongation at break but the tensile moduli and hardness are slightly lower.

With $Zn_{1-x}Ca_xO$-like it is also possible to use lower zinc loadings in rubber compounds. The mechanical properties are not modified, in some cases are even improved, with reductions of 47 %. On the other hand, the reduction in the cure times and the increase of the cure rate index are not as marked as with $Zn_{1-x}Mg_xO$. Furthermore, the activation energy is not enhanced in BR and SBR. The reversion resistance is not improved in BR and only slightly in SBR.

The zinc levels of BR and SBR can be lowered adding less amount of ZnO into the recipe. However, the decreases are not as important as using mixed metal oxides, especially in BR. If comparable cross-link densities and hardness are required it is only possible to obtain a 25% reduction in BR by using lower quantities of ZnO. In SBR mixtures, it is possible to achieve a diminution of 40 % on the zinc levels maintaining comparatively the same properties.

In natural rubber mixtures, when MgO is present in the recipe the properties of the compounds are greatly deteriorated. However, for certain specific applications, MgO could be considered as activator in BR and SBR because in these rubbers there is less involvement of zinc-accelerator species. In addition, in BR and SBR compounds MgO seems to promote the formation of monosulphudic cross-links, whereas its formation is inhibited in NR.

In order to reduce the zinc levels employed in the rubber compounds and introducing new applications for the waste rubber from end of life tyres, the possibility of using tyre crumb as an activator has been investigated.

Model compound vulcanisation studies have suggested that tyre crumb could substitute ZnO as activator for sulphur vulcanisation. The reactions of the accelerator and sulphur take place in the same manner that when ZnO is used. The cross-link degree achieved and the cross-link distribution are slightly worsened although the differences, especially in the extent of cure, are not significant enough to prevent the use of tyre crumb as activator.

However, the promising characteristics observed in MCV are not reached in NR, BR or SBR. The vulcanisation times are shorter but the extent of cross-linking is significantly lower, comparable to the mixtures without activator, and the mechanical properties are worsened in most of the cases. The differences in the devulcanisation degree of the tyre crumbs do not exert an influence in the characteristics of the compounds.

It has been demonstrated that the negative effect of MgO or the appearance of the cubic phase in $Zn_{1-x}Mg_xO$ is higher in natural rubber than in MCV. Further research should be carried out in order to obtained mixed metal oxides were all the magnesium is incorporated in the structure of zinc oxide. The rheometric curves of the compounds containing $Zn_{1-x}Mg_xO$ could show a higher difference between the minimum and the maximum torque provided that all magnesium is incorporated into the ZnO structure. However, synthesising oxides with a lower content of magnesium is not appropriate. It has been shown that the alteration of the structure caused by the substitution of zinc by magnesium atoms is the reason which causes the advantages rather than the size or the specific surface area of the oxide. Decreasing the magnesium content will not altered the lattice parameters that much and, furthermore, the reduction of the zinc present in the compounds will be inferior.

Another aspect that should be further studied is the exploitation of the chemicals remaining in the in the tyre crumb. In waste rubber there are present substances such as ZnO, amines, cross-linked precursors, unreacted curatives accelerators… that could be beneficial to minimise the content of ZnO added to the rubber recipes. It would be very interesting to try to take advantage of the features observed in MCV by improving or facilitating the interaction between the chemicals present in the tyre crumb and the ingredients added to the rubber matrix.

Chapter 8

CONCLUSIONS

From the results presented and discussed in the previous chapters, the following conclusions can be extracted:

1. Concerning the study of the influence of magnesium oxide as activator, some relevant observations were presented:

    - The breakdown of the accelerator and the consumption of sulphur occur faster than with ZnO. However, the cross-link degree achieved with MgO is lower because it does not form complexes with the active sulphurating agents or the cross-link precursors.

    - The presence of sulphur is a necessary condition for the breakdown of the accelerator and not the presence of unsaturations in the hydrocarbon chain as it is needed with ZnO.

2. Regarding the novel activators with reduced zinc content that have been developed to minimise the environmental impact of rubber goods, some significant remarks are worth stating:

    - In relation to the synthesis, it has been obtained that it is not possible to introduce calcium into the structure of zinc oxide using the same conditions employed to produce mixed metal oxides of zinc and magnesium.

    - Model compound vulcanisation has indicated that the use of $Zn_{1-x}Mg_xO$ nanoparticles leads to a reduction of the total amount of zinc used in rubber compounds. Not only they overcome the disadvantages of the mixture of ZnO and MgO, but a better performance is achieved. The reactions of the accelerator and sulphur are faster, and a higher cross-link degree is attained.

    - The results obtained using mixed metal oxides as activators for the vulcanisation of NR, BR and SBR have demonstrated that it is possible to reduce safely the zinc levels using these oxides.

    - The use of $Zn_{1-x}Mg_xO$ allows using lower quantities of Zn in NR without affecting significantly the properties and accelerating the cure characteristics. The reversion resistance is the only feature that is diminished. In BR and SBR, the vulcanisation times are reduced and the reversion resistance and the CRI are enhanced.

Moreover, the activation energy is minimised. The cross-link density is not reduced in NR mixtures and only slightly in BR and SBR at low loadings.

- With $Zn_{1-x}Ca_xO$-like it is also possible to use lower zinc loadings. The mechanical properties are not modified and, in some cases, are even improved. On the other hand, the reduction in the cure times and the increase of the cure rate index are not as significant as with $Zn_{1-x}Mg_xO$. Furthermore, the activation energy is not enhanced in BR and SBR. The reversion resistance is not improved in BR and only slightly in SBR.

3. Referring to the possibility of using tyre crumb as activator, model compound vulcanisation studies have suggested that tyre crumb could substitute ZnO as activator for sulphur vulcanisation. However, the promising characteristics observed in MCV are not reached in NR, BR or SBR because the interaction between the chemicals present in the tyre crumb and the ingredients added to the rubber matrix is lower in rubber mixtures than in MCV.

CONCLUSIONES

A partir de los resultados presentados y discutidos en los capítulos anteriores, se pueden extraer las siguientes conclusiones:

1. En relación al estudio de la influencia de óxido de magnesio como activador, se obtuvieron resultados relevantes.

    - La descomposición del acelerador y el consumo de azufre se producen más rápido que con ZnO. Sin embargo, el grado de entrecruzamiento es menor con MgO, ya que no forma complejos con los agentes sulfurantes activos o con los precursores de entrecruzamiento.

    - La presencia de azufre es una condición necesaria para la descomposición del acelerador y no la presencia de insaturaciones en la cadena hidrocarbonada, tal y como se necesita cuando se emplea ZnO.

2. En cuanto a los nuevos activadores con un reducido contenido de zinc que se han desarrollado para minimizar el impacto medioambiental de los productos de caucho, algunas observaciones importantes son destacables:

    - En relación con la síntesis, se ha obtenido que no es posible introducir calcio en la estructura de óxido de zinc utilizando las mismas condiciones empleadas para producir óxidos mixtos de zinc y magnesio.

    - Los estudios realizados empleando MCV (model compound vulcanisation) han indicado que el uso de nanopartículas de $Zn_{1-x}Mg_xO$ produce una reducción de la cantidad total de zinc usado en compuestos de caucho. No sólo es posible superar las desventajas de la mezcla de ZnO y MgO, sino que se logra un mejor rendimiento. Las reacciones del acelerador y el azufre son más rápidas, y se alcanza un mayor grado de entrecruzamiento.

    - Los resultados obtenidos utilizando los óxidos metálicos mixtos como activadores para la vulcanización de NR, BR y SBR han demostrado que es posible reducir de manera segura los niveles de zinc utilizando estos óxidos.

    - La aplicación de $Zn_{1-x}Mg_xO$ permite el uso de menores cantidades de Zn en NR, sin afectar significativamente las propiedades y acelerando el proceso de curado. La resistencia a la reversión es la única característica que es disminuida. En BR y SBR, los tiempos de vulcanización se reducen y la resistencia a la reversión y el CRI son mejorados. Además, la energía de activación se reduce significativamente. La densidad de entrecruzamiento no se reduce en mezclas de NR y sólo ligeramente en BR y SBR cuando se emplean bajas cantidades de activador.

- Con el óxido mixto de zinc y calcio también es posible utilizar menores cantidades de zinc. Las propiedades mecánicas no son modificadas y, en algunos casos, son mejoradas. La reducción en los tiempos de curado y el aumento del CRI no son tan importantes como con $Zn_{1-x}Mg_xO$. Además, la energía de activación no se ha modificado en BR y SBR y la resistencia a la reversión no es mejorada en BR y sólo ligeramente en SBR.

3. Con referencia a la posibilidad de utilizar el caucho de los neumáticos fuera de uso como activador, los estudios con MCV han sugerido que el caucho triturado podría sustituir al ZnO como activador para la vulcanización con azufre. Sin embargo, las prometedoras características observadas en MCV no se obtienen en NR, BR o SBR porque la interacción entre los productos químicos presentes en el caucho triturado y los ingredientes añadidos a la matriz de caucho es menor en mezclas de caucho que en MCV.

CONCLUSIONS

A partir dels resultats presentats i discutits en els capítols anteriors, es poden extreure les següents conclusions:

1. En relació a l'estudi de la influència d'òxid de magnesi com a activador, es van obtenir resultats rellevants.

    - La descomposició de l'accelerador i el consum de sofre es produeixen més ràpid que amb ZnO. No obstant això, el grau d'entrecreuament és menor amb MgO, ja que no forma complexos amb els agents sulfurants actius o amb els precursors d'entrecreuament.

    - La presència de sofre és una condició necessària per a la descomposició de l'accelerador i no la presència de insaturacions a la cadena hidrocarbonada, tal com es necessita quan s'empra ZnO.

2. Pel que fa als nous activadors amb un reduït contingut de zinc que s'han desenvolupat per minimitzar l'impacte mediambiental dels productes de cautxú, algunes observacions importants són destacables:

    - En relació amb la síntesi, s'ha obtingut que no és possible introduir calci en l'estructura d'òxid de zinc utilitzant les mateixes condicions emprades per produir òxids mixtos de zinc i magnesi.

    - Els estudis realitzats utilitzant MCV (model compound vulcanisation) han indicat que l'ús de nanopartícules d'$Zn_{1-x}Mg_xO$ produeix una reducció de la quantitat total de zinc utilitzat en compostos de cautxú. No només és possible superar els desavantatges de la barreja de ZnO i MgO, sinó que s'aconsegueix un millor rendiment. Les reaccions de l'accelerador i el sofre són més ràpides, i s'assoleix un major grau d'entrecreuament.

    - Els resultats obtinguts utilitzant els òxids metàl·lics mixtes com a activadors per a la vulcanització de NR, BR i SBR han demostrat que és possible reduir de manera segura els nivells de zinc utilitzant aquests òxids.

    - L'aplicació de $Zn_{1-x}Mg_xO$ permet l'ús de menors quantitats de Zn en NR, sense afectar significativament les propietats i accelerant el procés de curat. La resistència a la reversió és l'única característica que és disminuïda. En BR i SBR, els temps de vulcanització es redueixen i la resistència a la reversió i el CRI són millorats. A més, l'energia d'activació es redueix significativament. La densitat d'entrecreuament no es redueix en barreges de NR i només lleugerament en BR i SBR quan s'utilitzen baixes quantitats d’activador.

- Amb l'òxid mixt de zinc i calci també és possible utilitzar menors quantitats de zinc. Les propietats mecàniques no són modificades i, en alguns casos, són millorades. La reducció en els temps de curat i l'augment del CRI no són tan importants com amb $Zn_{1-x}Mg_xO$. A més, la resistència a la reversió no s'ha modificat en BR i SBR i l'energia d'activació no s’ha millorat en BR i només lleugerament en SBR.

3. Amb referència a la possibilitat d'utilitzar el cautxú dels pneumàtics fora d'ús com activador, els estudis amb MCV han suggerit que el cautxú triturat podria substituir al ZnO com activador per a la vulcanització amb sofre. No obstant això, les prometedores característiques observades en MCV no s'obtenen en NR, BR o SBR perquè la interacció entre els productes químics presents en el cautxú triturat i els ingredients afegits a la matriu de cautxú és menor en mescles de cautxú que en MCV.

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