NOVEL CO-AGENTS FOR IMPROVED PROPERTIES IN PEROXIDE CURE OF SATURATED ELASTOMERS

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Novel Co-agents for Improved Properties in Peroxide Cure of Saturated Elastomers.

By M.M. Alvarez Grima

Cover design by Thijs Brilleman.
Front cover illustration: The springs represent the flexibility that the novel co-agents described in this thesis bring into the peroxide vulcanisation systems.

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DISSERTATION

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by

Maria Montserrat Alvarez Grima

born on the 6th of April 1978
in Barcelona, Spain

This dissertation has been approved by:

Promotor   : prof. dr. ir. J.W.M. Noordermeer
Assistant promotor   : dr. A.G. Talma

"Cada libro, cada tomo que ves, tiene alma. El alma de quien lo escribió, y el alma de quienes lo leyeron y vivieron y soñaron con él. Cada vez que un libro cambia de manos, cada vez que alguien desliza la mirada por sus páginas, su espiritu crece y se hace fuerte."

Carlos Ruiz Zafón *La Sombra del Viento*

"Every book, every volume you see here, has a soul. The soul of the person who wrote it and of those who read it and lived and dreamed with it. Every time a book changes hands, every time someone runs his eyes down its pages, its spirit grows and strengthens …"

Carlos Ruiz Zafón *The Shadow of the Wind*

"Enjoy the little things, for one day you may look back and realize they were the big things."

Robert Brault

A mis padres
y a mi hermano

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Chapter 1

Introduction:

Rubber and the Vulcanisation Process

"*Most of the fundamental ideas of science are essentially simple, and may, as a rule, be expressed in a language comprehensible to everyone.*"

Albert Einstein (1879-1955)

This first chapter provides an introduction into the research described in this thesis by giving a general view of vulcanisation. The vulcanisation process is defined and the two most important vulcanisation systems are briefly compared: sulphur and peroxide. A short definition of the term co-agent is given. The aim of the thesis is described and a summary of the structure of this thesis is provided.

1.1   RUBBER AND VULCANISATION

Rubbers or Elastomers are a highly interesting class of materials with main characteristic their ability to return to their original shape after being submitted to deformation; this property is called elasticity.

Rubber was first brought to Europe in the early sixteenth century by the Spanish explorers, who brought it from the recently discovered American continent. There the rubber, unvulcanised natural rubber (NR), was tapped from the *Hevea Brasiliensis* tree and was used to make rubber balls, used in a cultural ball game by the local Mesoamerican natives.[1] Recently it has been discovered that these balls were most probably crosslinked to some extent, by vegetable organic additives that they mixed in during the making of the balls; more precisely, a liquid extracted from a type of vine called *Ipomoea alba*.[2] Otherwise the balls would not have been form-stable and they would have been very sticky. In Europe, the first application of rubber was in fact as a "rubber", to erase pencil marks.[3] Later on it was also used as isolating waterproof layer. However, the performance of this material was very sensitive to temperature changes: it hardened at low temperature and softened at high temperature; additional problems were, for instance, surface tackiness and creep under stress.

The discovery of vulcanisation made rubber a much more interesting material. Both Goodyear, in the US in 1839, and Thomas Hancock, in the UK in 1843, discovered the vulcanisation process independently.[4, 5] They found that when natural rubber was heated in the presence of sulphur, the elasticity and strength of the material increased largely. At the same time, the material became insoluble and waterproof. The later discovery, in the early twentieth century, of the reinforcing effect of carbon black[6-8] together with the discovery of organic accelerators and antioxidants[9] broadened the range of applications of cured rubber articles, since its mechanical properties and durability were significantly improved.

Vulcanisation is the process by which rubber is changed from essentially a plastic material to either an elastic or a hard material.[10] In this process, an elastomer is transformed from a 'plastic', 'formable' material into an 'elastic' material by the formation of a three-dimensional network with different types of junctions. The word vulcanisation derives from *Vulcan*, the Roman God of fire. Not accidentally, it also means volcano, a hot place where quite some sulphur species can be found. The term vulcanisation was therefore originally exclusively applied to the crosslinking reaction achieved by sulphur at high temperatures. Nowadays this term is also applied to refer to other crosslinking processes, such as peroxide cure.

There are several possibilities for the crosslinking of rubber. The already mentioned sulphur vulcanisation was the first to be discovered and still is today's most common cure system. The sulphur vulcanisation process requires the presence of carbon-carbon unsaturation in the polymer and it leads to a three-dimensional rubber network in which the polymer chains are linked to each other by sulphur bridges. As a result, sulphur cured articles have good tensile and tear strength, good dynamic properties, but poor high temperature properties like ageing, for instance.[11]

Other vulcanisation systems, i.e. peroxides, ultraviolet light, resins, etc. were later discovered and gained more importance with the progressive development of synthetic rubbers. The use of organic peroxides as crosslinking agents for rubber was first reported by Ostromislenski in 1915[12] and at present it is the only vulcanisation method that can compete with accelerated sulphur cure, with respect to vulcanisation rate. Interest in the industrial use of peroxides as curing agents increased with the introduction of a number of fully saturated elastomers, such as ethylene-propylene polymethylene rubber (EPM), fluoro elastomers (FKM), etc., which cannot be cured by sulphur vulcanisation.[13]

In order to improve peroxide efficiency, certain additives named co-agents, are very often added to the cure system. Co-agents are polyfunctional molecules which are added to the peroxide vulcanisation system in order to boost the yield of peroxide-initiated radical reactions.[14, 15] Owing to the use of co-agents, a significantly higher crosslink density can be achieved with consequent response in mechanical properties, like tensile strength, modulus and hardness, amongst others. Scorch time is usually shortened when co-agents are used; that can result sometimes a disadvantage, since scorch safety is worsened.

Peroxide vulcanisation leads to a rubber network in which the polymer chains are linked to each other by very stable covalent carbon-carbon bonds. Peroxide cured vulcanisates have therefore good high temperature properties, like heat ageing and compression set, compared to sulphur cured articles.[11, 16] In addition, peroxide cure allows vulcanisation of both unsaturated and saturated polymers, which is not possible with sulphur vulcanisation. On the other hand, some mechanical properties of peroxide cured articles are inferior to those achieved by sulphur cure, i.e. tensile strength, dynamic properties, and therefore entail a limitation on the use of this vulcanisation system. Another serious problem with peroxides is the lack of sufficient scorch time. Scorch time: the time elapsed until vulcanisation starts, is of major importance in order to control the vulcanisation reaction. The term scorch safety refers to a certain scorch time which is enough to provide good processing of the material before it starts vulcanising; this is of great importance especially in industry. Upon reaching the typical

dissociation temperature of a peroxide, the crosslinking reaction immediately proceeds at full speed, leaving the processor little or no time for shaping of the rubber article. The addition of certain scorch-retarders is sometimes of help, but this usually goes at the expense of crosslink density obtained: a waste of money.

Of the entire rubber production, 45% is NR. Most of NR is used in the automobile industry, in tyres. The rest of the rubber production consists of synthetic rubbers (SR). The main application of rubber articles is in the automotive industry in the form of door seals, radiator hoses, engine mounts, fuel- and air- conditioning tubing, shock absorbers, etc. Nevertheless, other applications are also important, like footwear, belting, hose, wire and cable.

1.2 AIM OF THIS THESIS

The aim of this thesis is to develop new co-agents for peroxide vulcanisation, which can improve particular mechanical properties of peroxide vulcanisates, such as tensile strength and moduli, to reach the levels typically achieved with sulphur cure, while maintaining the excellent high temperature properties typical for peroxide curing. At the same time, scorch safety should be improved, if possible. A synergistic combination of peroxide and sulphur cure is thus sought, and the approach is to achieve it by using new co-agents.

The first approach to fulfil this goal is to synthesise new co-agents, which would perform in a better manner than the co-agents used nowadays. Another approach to reach the aim is to use a combination of already existing co-agents with other common chemicals, to find a synergistic effect of both chemicals in peroxide cure.

1.3 STRUCTURE OF THIS THESIS

A literature survey on peroxide vulcanisation is presented in **Chapter 2**. Peroxide cure is described with special emphasis on the classification, mechanism and performance of different co-agents. The scorch safety issue in peroxide cure is described. Several solutions reported in literature to improve the fast scorch problem of peroxides are reported. Finally, an overview of attempts and/or suggestions found in literature to improve mechanical properties of peroxide vulcanisates is described, to reach an improvement in those mechanical properties which are typically better in sulphur cure systems.

In **Chapter 3** the effect of several commercially available co-agents in an EPM peroxide cure system is investigated. The influence of peroxide and co-agent concentration is also addressed.

Chapter 4 introduces a series of new co-agents which are synthesised and tested. These co-agents have the common characteristic of containing either mono- or di-functional sulphur linkages in their molecular structure. They can be classified in two groups: sulphur-containing co-agents analogous to acrylate and methacrylate types of co-agents and sulphur-containing co-agents analogous to bismaleimide and biscitraconamide types of co-agents. The synthesis of these new materials is disclosed as well as their performance as co-agents in the peroxide cure of EPM rubber. The results obtained are compared to those obtained with equivalent commercially available co-agents.

In **Chaper 5** a new concept of co-agents for peroxide vulcanisation is introduced, which provides scorch safety and mechanical property improvement at the same time. This consists of the combination of a co-agent and a sulphur spender in the peroxide cure of EPM rubber. The effect of some traditional scorch retarders and elemental sulphur is explored. Several co-agents are combined with the sulphur

spender and tested, the results obtained are compared to those obtained in the absence of the sulphur spender in the formulation.

Chapter 6 provides a deeper insight into the phenomena described in Chapter 5. The performance of different sulphur spending compounds in combination with a bismaleimide co-agent is explored. Also a different peroxide is tested in the system. The influence of co-agent and sulphur spender concentration is investigated. The mechanical properties obtained with the combination of a bismaleimide co-agent and the sulphur spender dipentamethylenethiuram tetrasulphide (DPTT) are further studied, with special emphasis on high temperature properties like ageing and compression set at high temperature. Crosslink density measurements are also reported. Finally, the effect of this new system is studied in EPDM rubber.

A mechanistic study of the phenomena reported in Chapter 5, and further studied in Chapter 6, is reported in **Chapter 7**. The results of Infrared Spectroscopy and Nuclear Magnetic Resonance measurements are described. Model Compound Vulcanisation of the peroxide cure reaction is the main subject of this chapter. Vulcanisation experiments of a model olefine, using the new concept of co-agents, and analysis by Liquid Chromatography-Mass Spectromety are described. The results are interpreted in terms of a possible reaction mechanism, which could explain the physical phenomena observed in the "real" rubber system, viz. improved mechanical properties and scorch safety.

Finally, the most remarkable aspects of this thesis as well as some suggestions for interesting future work are evaluated in **Chapter 8**.

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14.	R.C. Keller, *Rubber Chem. Technol.* **61**, 238 (1988).
15.	W. Hofmann, *Kautsch. Gummi Kunstst.* **40** (4), 308 (1987).
16.	J. Class, *Rubber World* **220** (5), 35 (1999).

Chapter 2

Literature Survey:

Improving Properties in Peroxide Vulcanisation

by the use of Co-agents

"I never desire to converse with a man who has written more than he has read."

Samuel Johnson (1709-1784)

The present chapter provides an overview of the literature published on peroxide vulcanisation. Special emphasis is put on the literature concerning the use of co-agents in peroxide vulcanisation. The effect of co-agents on the vulcanisate properties as well as the chemistry that takes place in the presence of co-agents is addressed. Further the importance of scorch safety and several approaches to improve this issue are described in this chapter. Finally, several attempts found in literature in order to obtain sulphur-like properties in peroxide vulcanisation are described.

2.1 PEROXIDE VULCANISATION

2.1.1 Introduction

Peroxide vulcanisation consists of a radical process initiated by peroxide decomposition that leads to the crosslinking of rubber. Crosslinking elastomers with peroxides was first studied by Ostromislenski in 1915[1]. Later on it gained importance when synthetic saturated elastomers were developed[2] and, definitely, with the commercial introduction of dicumyl peroxide (DCP) in the late 1950s.[3]

Peroxide cure can be used to vulcanise both unsaturated and saturated elastomers. The latter is not possible by sulphur vulcanisation. Nevertheless, there are some polymers which cannot be crosslinked by peroxide vulcanisation. The following table shows the polymers which can/cannot be crosslinked by peroxide vulcanisation:

Table 1.1 Polymers which are possible/not possible to cure with peroxide.[2]

Polymers	Blends	Polymers
POSSIBLE		**NOT POSSIBLE**
Polymers	**Blends**	**Polymers**
NR (Natural rubber)	NBR/EPDM	ACM (polyacrylate rubber)
IR (Polyisoprene rubber)	SBR/EPDM	IIR (Butyl rubber)
BR (Polybutadiene rubber)	PE/EPDM	CIIR (Chlorobutyl rubber)
CR (Polychloroprene rubber)	PE/EVA	CO (Epichlorohydrin rubber)
SBR (Styrene butadiene rubber)	NBR/EVA	PP (Polypropylene)
NBR (Butadiene acrylonitrile rubber)	EPDM/PP	PB (Polybutene-1)
HNBR (Hydrogenated butadiene acrylonitril rubber)		ECO (Epichlorohydrin copolymer)
Q (Silicone rubber)		PIB (Polyisobutene)
AU/EU (Polyurethane rubber)		PVC (Polyvinylchloride)
EPM (Ethylene propylene polymethylene rubber)		
EPDM (Ethylene propylene diene polymethylene rubber)		
T (Polysulphide rubber)		
PE (Polyethylene)		
CM (Chlorinated polyethylene)		
CSM (Chlorosulphonated polyethylene)		
EVA (Ethylene vinylacetate copolymer)		
ABS (Acrylonitrile butadiene styrene copolymer)		
Ethylene acrylic rubber		
EBA (Ethylene butylacrylate copolymer)		
FPM (Fluor rubber)		

Peroxide vulcanisation is typically used in rubber applications which require good ageing resistance, high processing temperature, good compression set at elevated temperature or colour stability.[4-7] The main applications of peroxide vulcanisation are: automotive, construction and building (i.e. window profiles), wire and cable, etc.

2.1.2 Mechanism: initiation, propagation and termination

Peroxide vulcanisation, like all radical reactions, consists of three steps: initiation, propagation and termination.[8] Initiation is induced by homolytic decomposition of a peroxide species, which engenders the radical reaction, see Figure 2.1. The peroxide decomposition is normally triggered by heat.[9] The initiation step follows first order reaction kinetics,[6, 9] therefore the cleavage of the peroxide molecule is only proportional to the concentration of peroxide at any time.

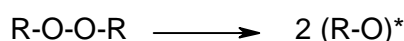$$R\text{-}O\text{-}O\text{-}R \longrightarrow 2\ (R\text{-}O)^*$$

Figure 2.1 – Initiation by homolytic decomposition of peroxide.

Normally, the time and temperature of the vulcanisation reaction are related to the half-life time of the peroxide. The half-life time ($t_{1/2}$) of a peroxide is defined as the time required to decompose one half of the initial amount of peroxide at a certain reaction temperature. It is a parameter characteristic of each peroxide at a given temperature. For the typical peroxides $t_{1/2}$ drops to about 1/3 of its value for each 10°C increase of temperature.[10] Normally, the rubber is vulcanised for the equivalent of at least five half-live times to ensure that only a trace of unreacted peroxide remains (less than 5% of the initial amount), since residual peroxide could lead to oxidation and chain scission or formation of additional crosslinks, depending on temperature, during product service.

During the propagation step, the alkoxy radical abstracts a hydrogen atom from a polymer chain leading to a radical on the polymer molecule, as shown in Figure 2.2. This reaction is bimolecular, because two species are involved: the alkoxy radical and the polymer chain. However, it is not a second order reaction, because the amount of hydrogen atoms is considerably large and thus their concentration does not vary significantly as the reaction proceeds.[3] Then, the propagation step is a first order reaction, due to the fact that the kinetics of the reaction are determined only by the concentration of alkoxy radicals. The concentration of alkoxy radicals is very low, since they are very energetic species and therefore react immediately after their generation. Accordingly, the extent of polymer radicals formed, and therefore the extent of crosslinking, is directly proportional to the amount of peroxide consumed.[10]
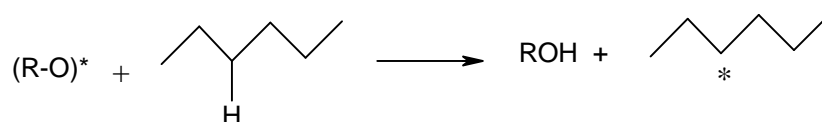

Figure 2.2 – Propagation by hydrogen abstraction from the polymer chain.

In case of unsaturated rubber the alkoxy radical can also add to the unsaturation, although that happens to a lesser extent than hydrogen abstraction.[11-15] Loan[16] and Dluzneski[6] provided detailed information about these reactions.

An alkoxy radical can abstract a hydrogen atom not only from the polymer chain but also from any other available source. The order of lability of hydrogen atoms is shown in Figure 2.3.[3, 17]
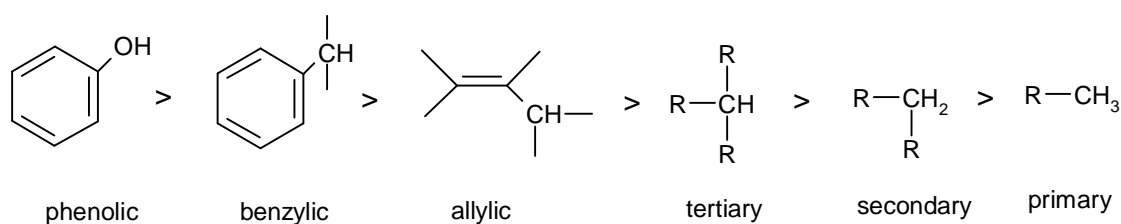

Figure 2.3 – Order of hydrogen lability.

Due to the high lability of benzylic and allylic hydrogen atoms the use of aromatic oils, which contain a significant concentration of these two kinds of hydrogen atoms, should be avoided in rubber compounding in order to avoid the consumption of peroxide radicals from their part. Paraffinic plasticisers consume less alkoxy radicals than aromatic and naphthenic oils.

The alkoxy radical can also initiate polymerisation by reacting with ethylenic unsaturation. Due to this fact polyfunctional reactive additives, known as co-agents,

are often added to the formulation in order to vary curing characteristics. These are further explained in paragraph 2.3.

Finally, in the termination step two radicals on adjacent polymer chains couple to form a carbon-carbon covalent crosslink, see Figure 2.4.
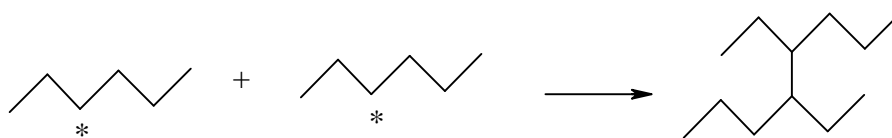

Figure 2.4 – Termination by coupling of two polymer radicals.

According to this mechanism, one crosslink is formed per two polymer radicals. As mentioned before, the amount of polymer radicals formed is proportional to the amount of peroxide molecules decomposed: two polymer radicals per peroxide bond.

The term "peroxide efficiency" or "crosslink efficiency" refers to the molar amount of crosslinks formed per initial mole of peroxide. Theoretically, one crosslink should be expected per each peroxide molecule; however, it is normally lower in real practice due to the occurrence of side reactions, which consume radicals.[9, 18] For instance, if oxygen molecules are present during the vulcanisation they can couple to the radical in the polymer backbone to yield a hydroperoxide radical, which leads to polymer degradation instead of a crosslink. Because of this, peroxide cure must always be performed in the absence of oxygen. Other non-productive, and therefore undesirable, side reactions that can occur to the polymer radical are chain scission and disproportionation, shown in Figures 2.5 and 2.6, respectively. These reactions are favoured by the presence of tertiary radicals and they contribute to lowering of the peroxide efficiency.
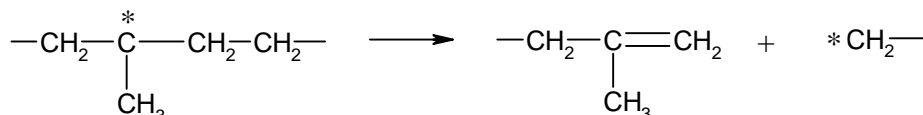

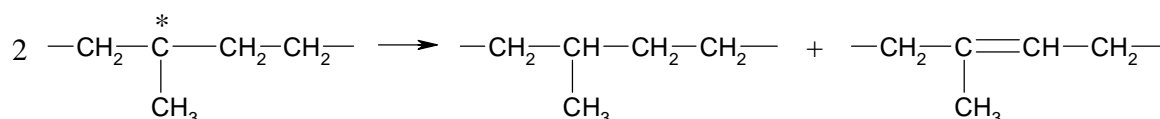**Figure 2.5** – Chain Scission in the polymer backbone.

Figure 2.6 – Disproportionation of the polymer radical.

Next to chain scission and disproportionation there are other side reactions that can influence the vulcanisation in a negative manner, such as metal catalysed decomposition of the peroxide, radical transfer, dehydrohalogenation, oxygenation, etc.[6, 19] Another example is the presence of acidic substances, which causes heterolytic or ionic decomposition of the peroxide molecule, as shown in Figure 2.7. As a consequence no radicals are formed, so crosslinking does not occur.[3] Accordingly, the crosslinking efficiency is reduced by the presence of acidic substances, such as caused by some fillers. For this reason, the fillers used in peroxide vulcanisation may not be acidic of nature. To sum up, a proper selection of the formulation ingredients is of crucial importance in order to minimise the occurrence of the negative side reactions and boost the more efficient reactions.[6]
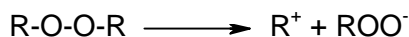
$$R\text{-}O\text{-}O\text{-}R \longrightarrow R^+ + ROO^-$$

Figure 2.7 – Ionic decomposition of the peroxide molecule.

2.1.3 Peroxide selection

A wide range of peroxides for crosslinking of rubber is available on the market. Some of the typically used peroxides are shown in Figure 2.8. Normally, for rubber vulcanisation relatively stable peroxides are selected, since they should be stable at storage temperature and also at compounding temperature, which can be rather high. However, they should be labile enough to quickly yield the radical species at the vulcanisation temperature yet providing proper scorch safety. The reactivity of the peroxide is mainly determined by its molecular structure.[6]

2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane (DTBPH)

Dicumyl peroxide (DCP)

Di(tert-butylperoxyisopropyl)benzene (DTBPIB)
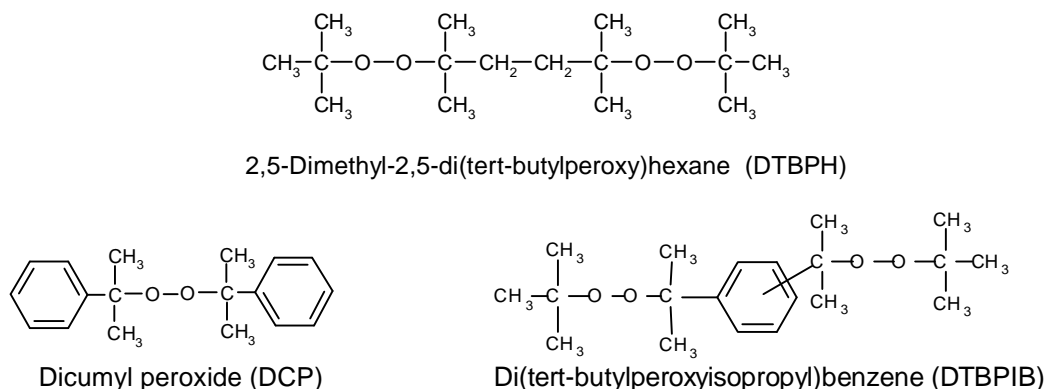
Figure 2.8 – Example of commonly used peroxides for rubber crosslinking.

Several authors agree upon the fact that the following are very important factors to take into account in order to select a proper peroxide: [4, 6, 9, 16, 20, 21]

- Good efficiency in vulcanising the rubber.
- Decomposition temperature: should be high enough to avoid scorch during processing and low enough to provide fast curing at the vulcanisation temperature.
- Harmless decomposition products.
- Effect of additives on efficiency and stability.
- Vulnerability to side reactions that lower efficiency.
- Non-volatility: to prevent loss during compounding and mixing.
- Possible generation of odour.
- Safety: It should be non-irritant and non-toxic, safe to store and handle, at storage and at processing temperature.
- Blooming of the decomposition products.

A very important factor to consider in peroxide selection is the nature of the radicals formed by its decomposition. Depending on the reactivity of these radicals, subsequent rearranging reactions take place leading to new radical species. These new radicals are sometimes reactive but in other cases they loose reactivity compared to the initial radical and that will negatively reflect in the peroxide efficiency. For instance, when using DCP, one of the most used crosslinking peroxides,[16] the decomposition yields methyl radicals, see Figure 2.9. These radicals are still very reactive and at the same time they are less sterically hindered than the initial cumyloxy radicals. Therefore they will easily react further and provide good crosslink efficiency. The best radicals for peroxide crosslinking are those which are good abstractors, like for instance methyl and cumyloxy radicals, and poor in addition to double bonds.
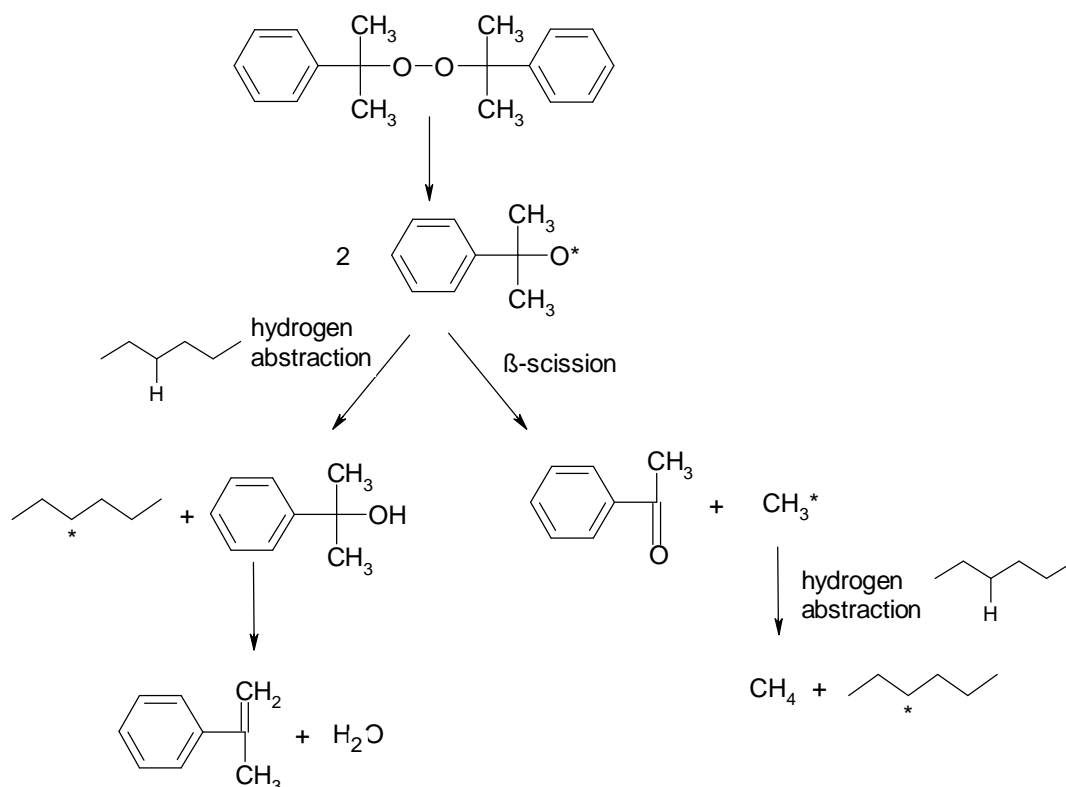
Figure 2.9 – Decomposition of dicumylperoxide.

2.1.4 Comparison between peroxide and sulphur vulcanisation

As a result of peroxide vulcanisation the crosslinks formed consist of carbon-carbon bonds between the polymer chains, while in sulphur vulcanisation the crosslinks between the chains consist of sulphur bridges: carbon-sulphur and sulphur-sulphur bonds.[6] The carbon-carbon bond is more rigid and stable (351 kJ/mol bond energy) than the carbon-sulphur (285 kJ/mol) and sulphur-sulphur (267 kJ/mol) bonds. This difference in network structure gives the two vulcanisation systems their different characteristic properties, since the lower the bond energy the easier the bonds break under influence of mechanical or thermal energy.[6] This wil be reflected, for instance, in ageing properties: peroxide vulcanisates have much better heat ageing characteristics than sulphur cured elastomers, due to the fact that the carbon-carbon bonds are more stable than the sulphur bridges. The main advantages of peroxide vulcanisation over sulphur vulcanisation are:[2, 4, 22-25]

- Simple formulation.
- Storage, under peroxide decomposition temperature, of the peroxide-containing compound over a long time period without risk of scorch.
- Rapid vulcanisation without reversion.
- Good compression set at elevated temperatures.
- Excellent heat ageing properties.
- Good electrical properties.
- No staining of the finished parts.
- No discolouration of crosslinked product in contact with metals and PVC.
- Possibility to co-vulcanise saturated and unsaturated rubbers and blends.
- Possibility to co-polymerise with polymerisable plasticisers or co-agents to give controlled hardness and stiffness, coupled with easy processing.
- No formation of N-nitrosamine by-products.

- Possibility to obtain transparent products.

While the main disadvantages of peroxide crosslinking compared to sulphur crosslinking are: [4, 22-25]

- Sensitivity to elemental oxygen under curing conditions, which gives tackiness.
- Certain components of the rubber compound, such as extender oils, antioxidants and resins, consume peroxide radicals.
- Usually, tensile and tear strength properties are reduced by about 15% in comparison with a conventional sulphur based crosslinking system.
- Lower abrasion resistance.
- Low scorch safety.
- Generally higher costs.

These differences between peroxide and sulphur cure should be properly evaluated when selecting a cure system for a specific material and application. The processing conditions, as well as the final properties that the material should meet according to the application, should be taken into account.
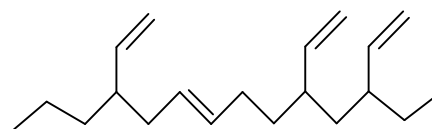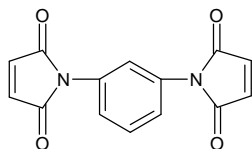
2.2 CO-AGENTS

2.2.1 Definition

Co-agents are multi-functional organic molecules which are highly reactive towards free radicals.[6] They are used as reactive additives to boost peroxide vulcanisation efficiency.[22, 26-28] Examples of co-agents are given in Figure 2.10. The most used co-agents are molecules with maleimide groups, (meth)acrylate groups, or allylic groups,[9, 29-33] but polymeric materials with a high vinyl content, i.e. 1,2-polybutadiene, can also act as co-agents. Some authors have even studied the action of sulphur, or sulphur donors as co-agents.[18, 34-43]
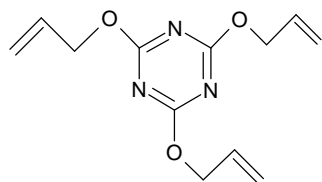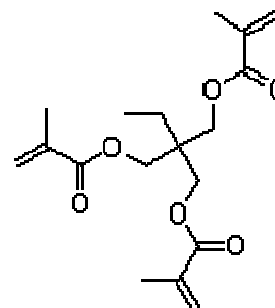

Triallylcyanurate (TAC)

1,2-polybutadiene (1,2-BR)

N,N'-m-phenylenedimaleimide (BMI-MP)

Trimethylolpropane trimethacrylate (TMPTM)

Figure 2.10 – Examples of commercially available co-agents.

The efficiency of peroxide cure in the absence of co-agents is rather low due to the occurrence of side reactions which consume radicals. Co-agents can improve the peroxide efficiency by suppressing inefficient side reactions to a large extent, like chain scission and disproportionation, as reported in literature.[9, 18, 28, 40, 44-52] This is, according to some authors, the main reason why co-agents increase crosslinking efficiency. However, later it has been reported that the reason why co-agents increase crosslinking efficiency is mainly because of the formation of co-agent bridges between polymer chains as extra crosslinks.[53] More detailed information about the co-agent chemistry can be found in paragraph 2.2.3.

When co-agents are added to a peroxide cure formulation the following improvements are achieved relative to the formulation with no co-agent:[6, 22]

- Improved peroxide efficiency.
- Lower compression set.
- Higher resilience.
- Higher modulus.
- Higher hardness.
- Lower compound viscosity.
- Improved resistance to oils and fuels.
- Improved heat ageing.
- Improved rubber to metal adhesion (in the case of zinc salts).
- Higher tensile strength.
- Better room temperature and hot tear.
- Improved dynamic flexibility.

Therefore, when a peroxide/co-agent system is compared to a conventional sulphur cure system, the following advantages and disadvantages result:[22]

Advantages of peroxide/co-agent cure system vs. sulphur:

- Excellent heat stability.
- Excellent compression set at elevated temperature.
- No reversion.
- Good shelf life stability.
- Simple compounding.
- No contact discoloration.
- Possibility to vulcanise saturated polymers.
- Possibility to co-vulcanisation blends: saturated and unsaturated polymers.

Disadvantages of peroxide/co-agent cure system vs. sulphur:

- Higher cost of raw materials.
- Interference with antidegradants.
- Surface tackiness in presence of elemental oxygen.
- Poor tensile and tear strength.
- Inferior dynamic properties.

2.2.2 Classification of co-agents

Depending on their chemical nature, co-agents can react in the peroxide cure of unsaturated rubber by addition and hydrogen abstraction, or by addition reactions only. In the case of saturated polymers, mainly addition reactions take place.[28] According to their different reactivity, a classification of co-agents can be found in literature. They can be divided into two groups: Type I and Type II co-agents.[4, 6, 9, 22, 54, 55] Table 1.2

shows a classification according to the reactivity of some commercially available co-agents:

-        Type I: Addition and hydrogen abstraction reactions: these co-agents consist of rather polar molecules with a low molecular weight and activated double bonds. Their main characteristic is, that they are highly reactive towards radicals, so scorch takes place very fast, which sometimes can be a disadvantage.[56] By using this kind of co-agents not only the rate of cure is increased but also the crosslink density or state of cure. A disadvantage that may be present when using this type of co-agents is that, due to polarity, the compatibility of these co-agents with the polymer matrix is limited.[57] Some examples of Type I co-agents are: acrylates, methacrylates, bismaleimides and zinc salts.

-        Type II: Addition reactions: these co-agents are, in general, less polar molecules, which form more stable free radicals, so scorch does not take place as fast as with the previous type of co-agents. The use of these co-agents leads to an increase in crosslink density of the vulcanisate but, unlike Type I, they are not capable of increasing the cure rate. Due to their low polarity, these co-agents have a good compatibility with many elastomers. Some examples are: high-vinyl 1,2-polybutadiene, divinylbenzene, allyl esters of cyanurates, isocyanurates and sulphur.

Table 1.2 Classification of several commercially available co-agents.

Type I
N,N-m-phenylenedimaleimide (BMI-MP)
Ethylene dimethacrylate (EDMA)
Trimethylolpropane trimethacrylate (TMPTM)

Type II
Cis-1,2-polybutadiene (1,2-BR)
Diallylterephthalate (DATP)
Divinylbenzene (DVB)
Triallylcyanurate (TAC)
Triallylisocyanurate (TAIC)
Triallylphosphate (TAP)

2.2.3 Mechanism

As mentioned in the previous paragraph, Type I and II co-agents differ in their reactivity during vulcanisation. Accordingly, the reaction mechanism that they follow differs. Figure 2.11 shows a possible reaction mechanism for Type II co-agents, viz. addition reaction, suggested by Endstra.[28] This mechanism explains how an allyl-containing co-agent incorporates into the polymer network.
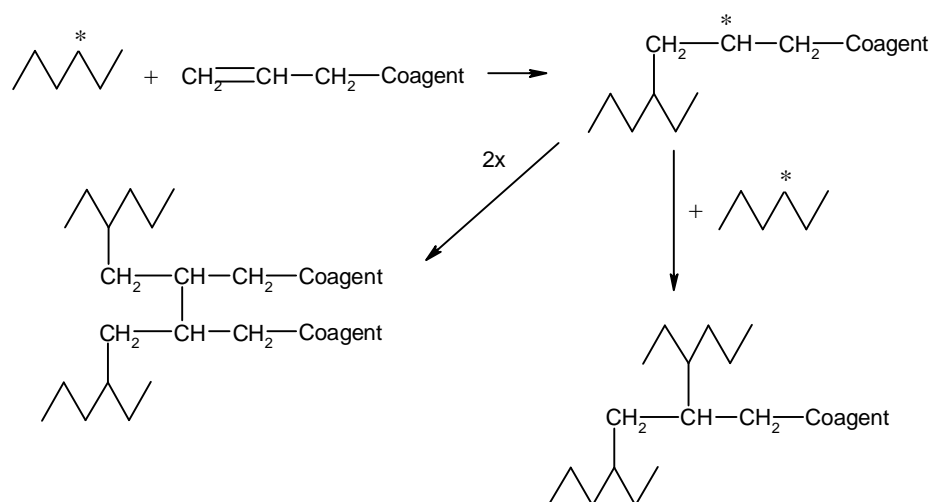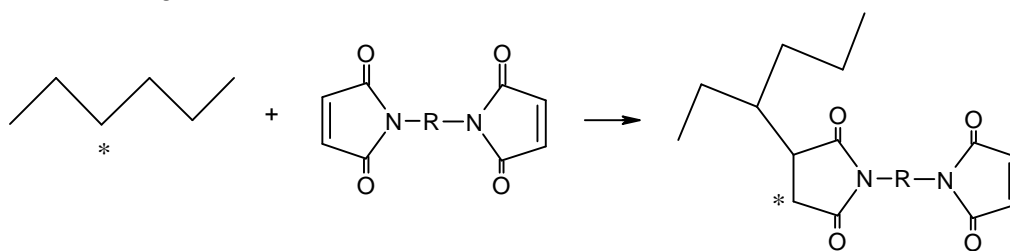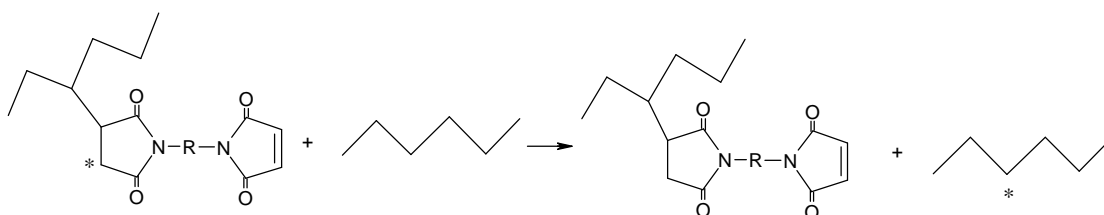
Figure 2.11 – Possible reaction mechanism of Type II co-agents suggested by Endstra.[28]

Kovacic and Hein[58] presented a mechanism for the Type I co-agent, N,N'-m-phenylenedimaleimide in which, once the macroradical in the polymer chain is formed, the co-agent adds very fast, giving little chance for scission to take place. As a result, a radical on the co-agent is formed. Afterwards, a chain transfer reaction takes place leading to the formation of a new polymer radical. Finally, the same sequence takes place on the other maleimide site of the co-agent, leading to a co-agent containing crosslink, as shown in Figure 2.12. The termination reaction can be either disproportionation or combination of radical intermediates, and can also lead to crosslink structures. This mechanism explains how the co-agent incorporates into the network, via the maleimide functionalities of the co-agent.

Formation of co-agent radical:

Chain transfer reaction, formation of polymer radical:

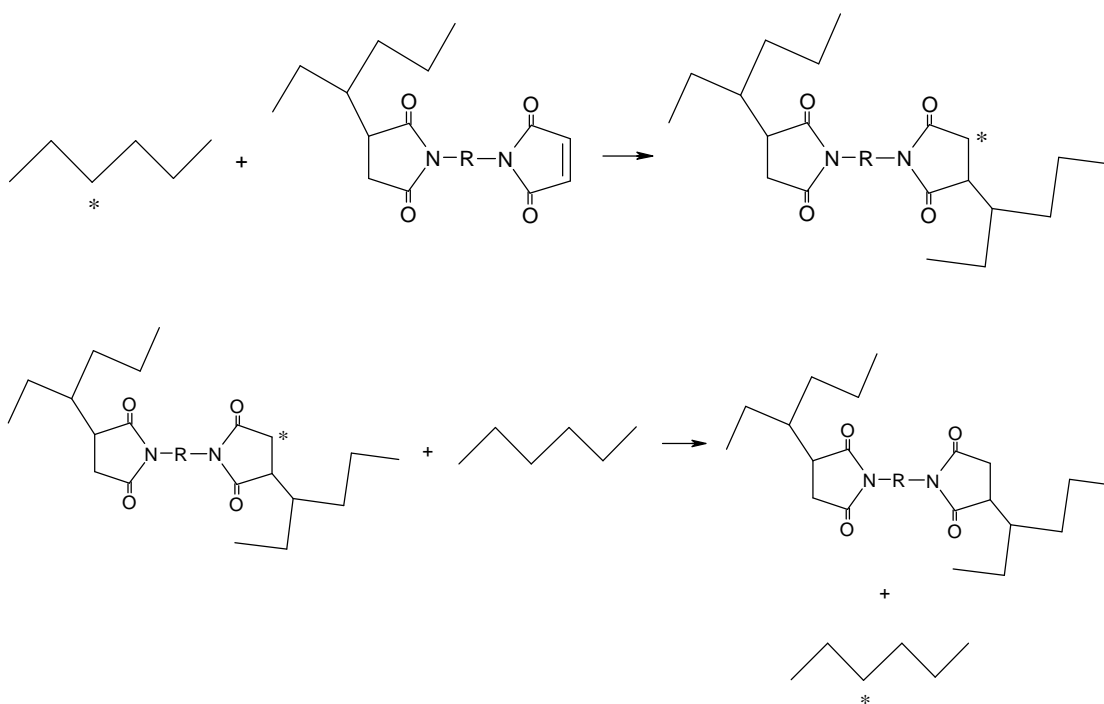Analogous sequence of the other maleimide unit, formation of crosslink:

Figure 2.12 – Reaction mechanism of Type I co-agent BMI-MP, suggested by Kovacic and Hein.[58]

Despite the fact that the mechanism of co-agent reaction during vulcanisation is still being investigated, it has been proven that co-agents get incorporated into the polymer network, [24, 28, 53] as explained by the mechanisms above. They create bridges between polymer chains, thus contributing to an increase in crosslinking efficiency by generating extra crosslinks. Further, since they have a major affinity for radicals, they help to minimise chain scission and disproportionation reactions.

From a morphological point of view, there can be two ways for the co-agent to incorporate into the polymer network. Either by polymerisation: forming an interpenetrating network by homopolymerisation of co-agent molecules; or by being grafted onto the polymer backbone.[3, 6, 10] Figure 2.13 shows these two options.
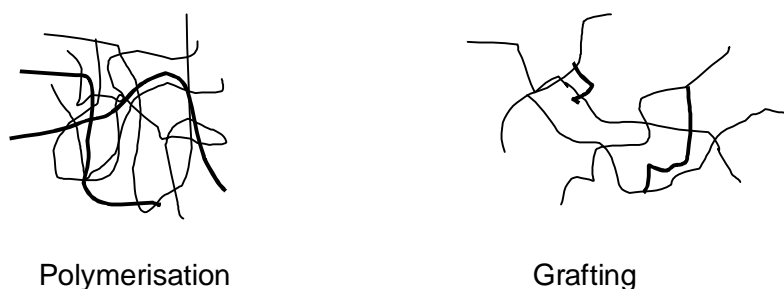

Polymerisation   Grafting

Figure 2.13 – Incorporation of the co-agent into the rubber network.[6, 10]

Probably, what takes place in real practice is a combination of the two mechanisms. Co-agents are in general rather polar materials, especially Type I co-agents. This means that they are not very miscible with the non-polar rubber and will tend to phase separate and homopolymerise.[57, 59, 60] These phase separated domains will also be covalently attached to the rubber network.[60, 61] Ultimately, the extent of homopolymerisation compared to grafting will depend on several factors, such as the readiness of the co-agent to homopolymerise, the co-agent concentration, the difference in polarity between the co-agent and the rubber matrix, viz. solubility, and the adequacy of mixing.[6, 62] Therefore, in the generic structure of a co-agent crosslink shown in Figure 2.14, the value of n will depend on the above mentioned factors.
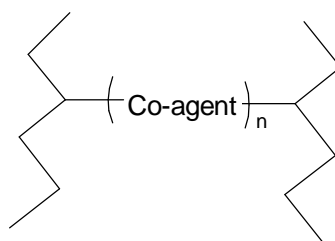

Figure 2.14 – Generic structure of a co-agent crosslink.

In an extensive study by Dikland et al. it was reported that the co-agents TAC and DATP, of Type II, form co-agent domains during vulcanisation, which co-vulcanise with the polymer matrix. These domains are therefore covalently bound to the rubber matrix and behave as filler particles.[59] The effect on mechanical properties of these co-agent domains depends on the rigidity of the co-agent molecules. Rigid co-agent molecules lead to hard domains, which concentrate the stress around the domains upon extension and, eventually, cavitation will take place, followed by tear. On the other hand, less rigid co-agent molecules will lead to softer co-agent domains, which may have a reinforcing effect and may therefore improve mechanical properties.[53]

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2.3   SCORCH SAFETY

2.3.1 Introduction

As a result of vulcanisation crosslinks are formed, due to which the polymer molecular weight increases and, as a consequence, the viscosity of the compound also increases.   When the vulcanisation process is studied by means of a curemeter (commonly called a "rheometer"), the occurrence of crosslinking, viz. increase in compound viscosity, is reflected in an increase in rheometer torque measured. Figure 2.15 shows a typical cure curve obtained from a rheometer, where torque is plotted against vulcanisation time. There are three important parameters of the vulcanisation process that are monitored and recorded by the rheometer: torque, scorch time or t_{s2} and t_{90}.
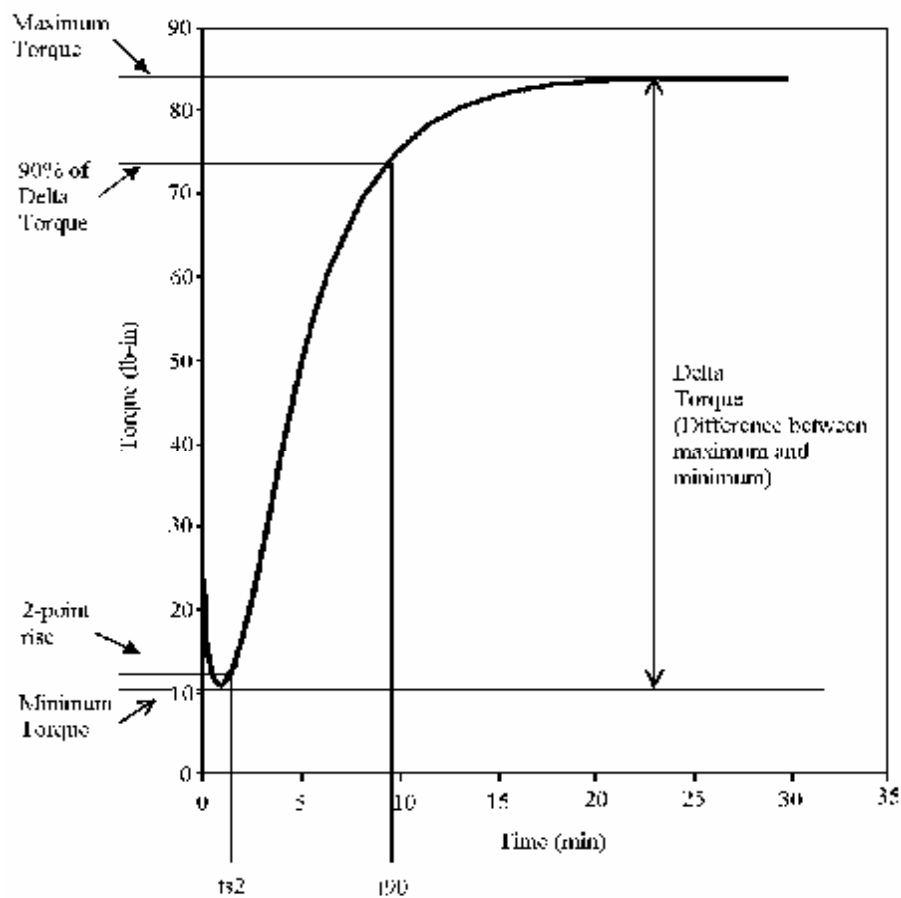

Figure 2.15 – Typical cure curve obtained from a rheometer: torque versus time.

The torque is measured as a function of time that the compound is subjected to the vulcanisation temperature. As time proceeds, the rubber becomes more and more crosslinked, as a result of which the viscosity and later modulus of the compound increases as reflected in an increasing value of the torque. The delta torque is defined as the maximum torque value achieved minus the minimum value of torque.

The scorch time, t_{s2}, is the time elapsed until the torque level raises 2 units above its minimum value.[63] In real practice, this increase in torque may take place very rapidly, before the material is fully processed. If this occurs, the partially crosslinked polymer cannot properly flow anymore, which makes processing of this material impossible. This phenomenon is called premature scorch and is related to low t_{s2} values. The term scorch safety refers to the ability of a compound, under given

processing conditions, to avoid the occurrence of premature scorch. For instance, in an injection moulding application, a lack of scorch safety due to premature scorch does not allow the material to flow to completely fill de mould; ergo it will be vulcanised before it has achieved the desired shape.

Finally, t_{90} is the time elapsed until 90% of the final delta torque value is achieved. This parameter is important in order to define the optimal vulcanisation time for a compound.

The slope of the cure curve between t_{s2} and t_{90} is defined as cure rate, and represents the speed of the vulcanisation reaction: high cure rate means fast vulcanisation. For most applications, the best processing conditions are achieved when t_{s2} has a high value. This is needed to provide scorch safety, thus enough time to process the still unvulcanised material. But once the material starts vulcanising, it should quickly vulcanise, to make the process faster, which means high cure rate and therefore low t_{90} value.

In peroxide vulcanisation, the scorch time and cure rate are mainly determined by the half-life time of the peroxide.[2] Therefore, peroxide cure cannot be accelerated by adding accelerators to the formulation, like is the case in sulphur cure. The only way to achieve a faster cure is by increasing the temperature, which lowers the half-life time of the peroxide.[4] However, this should be done carefully, since a peroxide with a rapid cure can also generate scorch too quickly, which sacrifices scorch safety.

As a matter of fact, a very common problem in peroxide crosslinking is premature scorch. There are several methods described in literature in order to obtain longer t_{s2} to improve scorch safety. One option is to lower the peroxide half-life time by lowering the temperature or to choose a peroxide with a higher half-life time. However, this approach often results in very high t_{90} values which is economically not favourable. Another approach to solve the premature scorch problem is to add a so-called "scorch retarder" or "scorch delay agent" to the formulation.

2.3.2 Scorch retarders
A scorch retarder is a chemical compound, which consumes peroxide radicals in the first stage of the vulcanisation process. The polymer radicals have a larger tendency to react with the scorch retarder molecules than to recombine to form a crosslink.[64, 65] This reaction of radicals with the retarder prevents the immediate initiation of crosslinking. The main disadvantage of using a scorch retarder is that the efficiency of the crosslinking reaction is lowered due to the consumption of peroxide radicals prior to crosslinking. This results in a lower final cure state of the product and reflects in the eventual properties of the material: inferior to those obtained without the scorch retarder. This problem can be overcome by adding more peroxide to the formulation, but that results in an economically less favourable process.

Several chemicals are commercially available as scorch retarders. Some of the scorch retarders were protected by patents[66-70] and no detailed studies are reported in literature about their chemical behaviour and retarding mechanism. Some examples are: derivatives from 4-tert-Butylcatechol (TBC)[69], methyl substituted amino alkyl phenols[68] and hydroperoxides.[66] Some scorch retarding systems have been reported in literature in more detail, like is the case for multifunctional acrylic monomers[71-73] and phenolic antioxidants.[74] Other scorch retarders have also been studied in order to understand the scorch retarding mechanism. This is the case for 2,6-Di-tert-butyl-4-methylphenol (BHT)[75-77] and α-methylstyrene dimer (MSD),[78-80] which will be explained in paragraphs 2.3.3 and 2.3.4, respectively.

Most of the antioxidants used in the rubber industry readily react with radical species, in order to avoid polymer degradation. Because of this, antioxidants often also work as scorch retarders. These chemicals contain readily abstractable hydrogen atoms. Normally, they release a hydrogen atom to the radical species and the radical is in this way transferred to the antioxidant molecule. When antioxidants act as scorch

retarders, they scavenge the first radicals formed by peroxide decomposition, until the antioxidant is consumed. At that point the normal vulcanisation mechanism takes over and crosslinking takes place. Since some radicals are consumed, by reacting with the antioxidant, the crosslink efficiency is lowered. This means that larger amounts of peroxide or co-agent need to be added to the formulation in order to maintain a proper cure state. On the other hand, when antioxidants act as scorch retarders they also loose their long term antioxidant activity, since they are consumed during the first stages of vulcanisation. Some examples of these chemicals are phenolic and amine antioxidants.[74, 81, 82]

Hindered phenolic compounds are commonly used as antioxidants but can also act as scorch retarders. They inhibit the vulcanisation process by donating an unpaired hydrogen atom to the radicals. B. Gustafsson et al.[74] studied the use of these compounds in peroxide cure using DCP. They found that the amount of substitution of the phenolic ring influences the scorch retarding characteristics. Unhindered phenols provide higher scorch times than hindered phenols. Consequently, unhindered phenols led to lower cure state than more hindered phenols. This influence of structure was larger for PE than for EPM, and that again larger than for EPDM.[83]

2.3.3 2,6-Di-tert-butyl-4-methylphenol (BHT)

BHT is a scorch retarder often used in peroxide cure of rubber. Other uses of BHT are as non-staining antidegradant.[84] The mechanism of retardation of BHT in DCP vulcanisation of EPDM was extensively studied by Dikland et al.[24, 75] The influence of BHT and peroxide concentration on the scorch time were examined at different temperatures. The largest effect of BHT concentration on the scorch time was found at 160ºC. At higher temperatures the influence of the BHT concentration becomes less significant. The influence of BHT concentration on the maximum torque level achieved is as follows: with increasing BHT concentration the maximum torque decreases. At 2 phr (parts per hundred rubber) of BHT the torque is reduced by a factor of 2 to 3, compared to the torque value in the absence of BHT. To achieve good torque levels when using BHT, more peroxide had to be added.

The suggested mechanism to explain the achievement of scorch delay is shown in Figures 2.16 to 2.18. First, hydrogen transfer from the phenolic group or the methyl group of BHT to the polymer radical or initiator radical takes place. As a result a radical is formed in the BHT molecule. Both BHT radicals formed, phenolic and benzylic, are mesomeric structures and are stabilised by resonance.

The benzylic radicals can dimerise, as shown in Figure 2.17 a, recombine with polymer radicals, Figure 2.17 b, or lead to disproportionation reactions, as shown in Figure 2.18. The phenolic radicals do not dimerise or recombine with polymer radicals but, most probably, do give rise to disproportionation, as shown in Figure 2.18.

In all cases a lower peroxide efficiency is obtained. In case of recombination, the fact that the BHT molecule stays pending in the main chain also causes steric hindrance. In case of disproportionation, an unsaturated moiety in the polymer main chain is obtained and the BHT molecule is regenerated and can react further. This means that when disproportionation takes place, one equivalent of BHT is able to inhibit more equivalents of initiator.
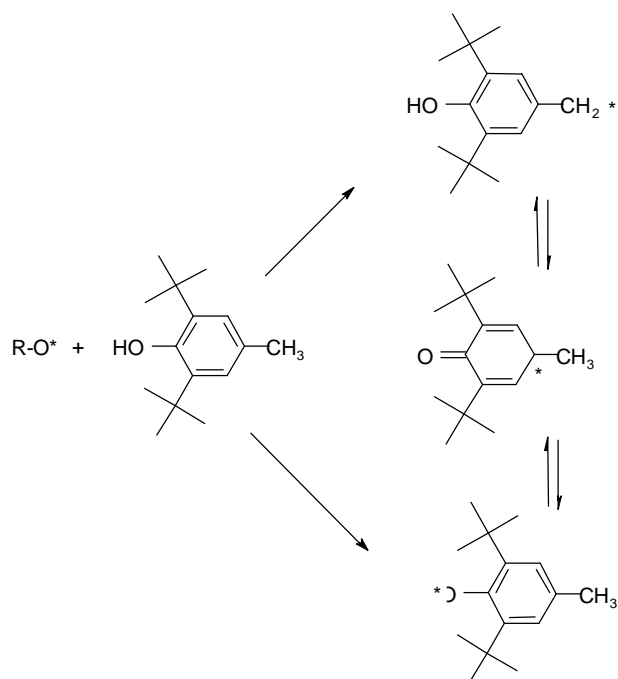
Figure 2.16 – Formation of BHT radical by hydrogen transfer.

The authors found, by Fourier-Transform Infrared spectroscopy (FT-IR) measurements that 60% of the initial BHT added to the peroxide cure formulation of EPDM still remained unreacted after vulcanisation. 25% of the BHT was found pending from the polymer chain, 5% formed dimers and 10% was unaccounted for. About 0.55 macroradicals would be scavenged per BHT molecule present. However, it was concluded that this number was most probably underestimated.
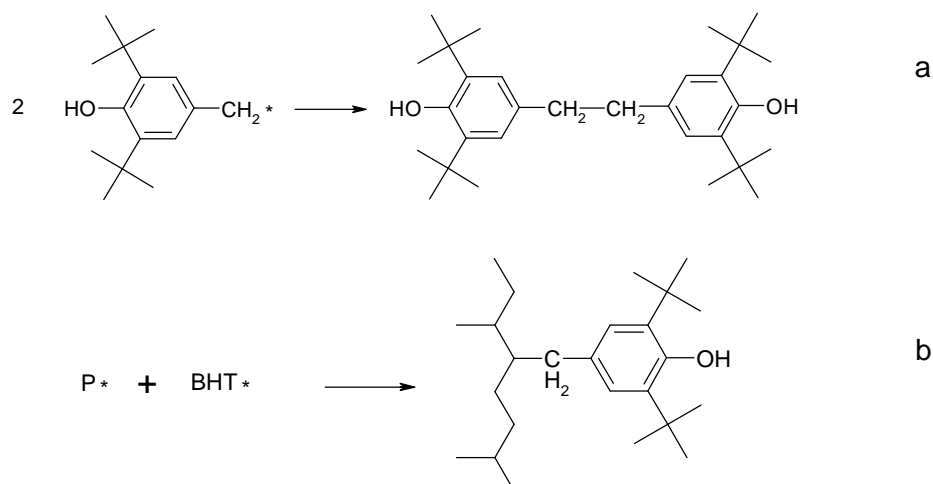

Figure 2.17 – Scavenging mechanism of BHT: dimerisation (a) and recombination with polymer radical (b).

Figure 2.18 – Scavenging mechanism of BHT: disproportionation.

Other authors [85, 86] have also reported the formation of dimers from the phenolic radical, as a result of reaction of BHT with an alkyloxy (RO*) or alkylperoxy (ROO*) radical, as well as other possible reaction products, as shown in Figure 2.19.
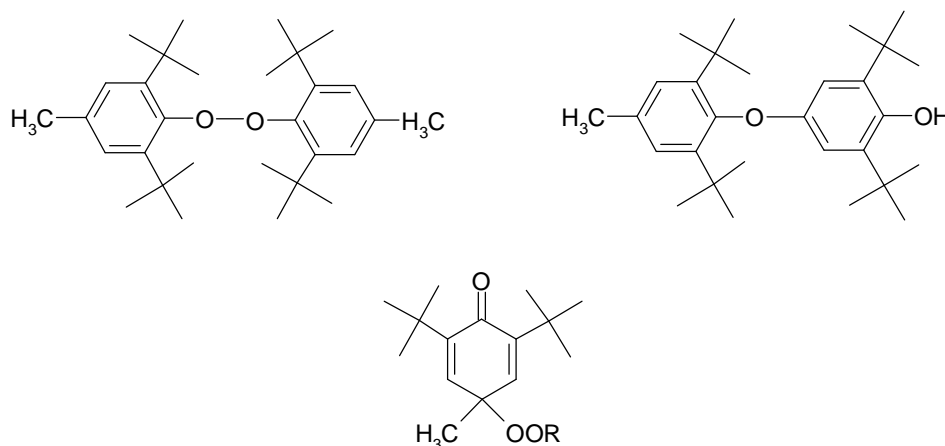
Figure 2.19 – Other possible reaction products obtained by radical reaction of BHT.[85, 86]

To summarise, the scorch retarder BHT can provide scorch safety when added to a formulation, since it reacts with the first radicals formed in the vulcanisation reaction. However, the torque level achieved is lowered because of the consumption of radicals in reactions by BHT, therefore peroxide efficiency is lowered. To maintain the torque level, more peroxide needs to be added to the formulation to compensate for the above mentioned loss of radicals.

2.3.4 α-Methylstyrene dimer (MSD)

2,4-diphenyl-4-methyl-1-pentene, also called alpha-methylstyrene dimer (MSD), was studied by S. Suyama and Y. Watanabe et al.[78-80] as scorch retarder in peroxide vulcanisation of several polyolefins, initiated by dicumyl peroxide (DCP). MSD is known as a chain transfer agent in styrene polymerisation[87] through a free radical addition fragmentation reaction.[87, 88] This addition fragmentation reaction occurs during polymer crosslinking, providing scorch retardation. MSD has excellent effects on the crosslinking of low-density polyethylene (LDPE), high-density polyethylene (HDPE) and ethylene propylene polymethylene rubber (EPM).

The influence of MSD on peroxide crosslinking depends strongly on temperature. At low temperatures, around 140ºC, a scorch delay is observed while at higher temperatures, 180ºC, it acts as an activator. The concentration of MSD was also found to be important: around 1phr provided the best performance.

As mentioned before, MSD is well known as a chain transfer agent in styrene polymerisation, by undergoing addition fragmentation. That means that propagating radicals add to the double bond of MSD to give intermediate adduct radicals, Figure 2.20 a. These adduct radicals fragment to expel cumyl radicals as shown in Figure 2.20 b. Fragmentation is very facile, because of the weak C-C bond in β-position to the adduct radical. In a normal chain transfer reaction, the cumyl radicals can then initiate a new propagation reaction.
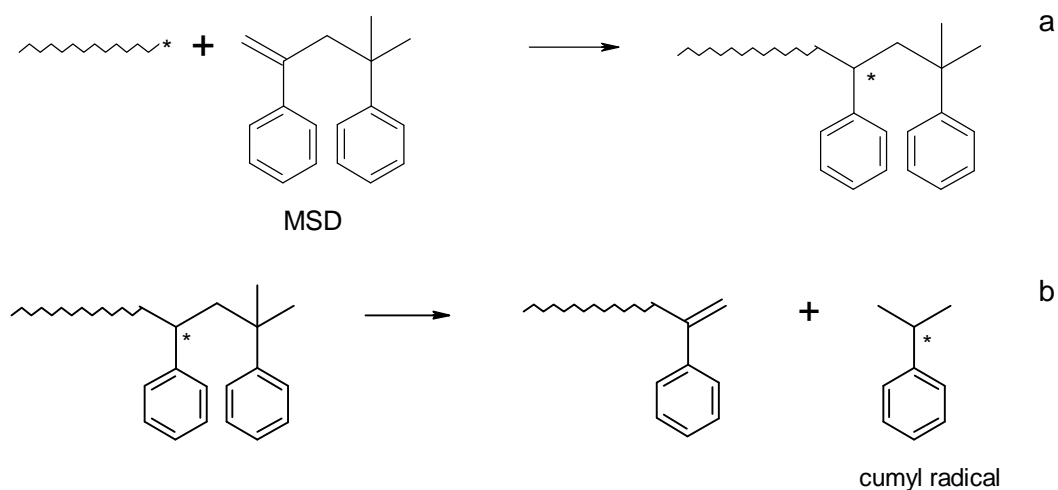
Figure 2.20 – MSD chain transfer reaction.

This reaction will also take place during vulcanisation, since the polymer radical can easily add to the styrenic double bond, as shown in Figure 2.21 a. S. Suyama et al.[79] studied the reaction between n-undecane and di-tert-butyl peroxide (DTBP). They observed that the addition of the polymer radical to the styrenic double bond of MSD takes place faster than the recombination of two polymer radicals. After the polymer radical adds to MSD subsequent fragmentation reactions take place, as shown in Figure 2.21 b.

The cumyl radical that results after fragmentation can create new polymer radicals, as shown in Figure 2.22 a; combine with itself to give biscumyl, Figure 2.22 b; disproportionate to give cumene and α-methylstyrene, Figure 2.22 c; or combine with polymer radicals, Figure 2.22 d.
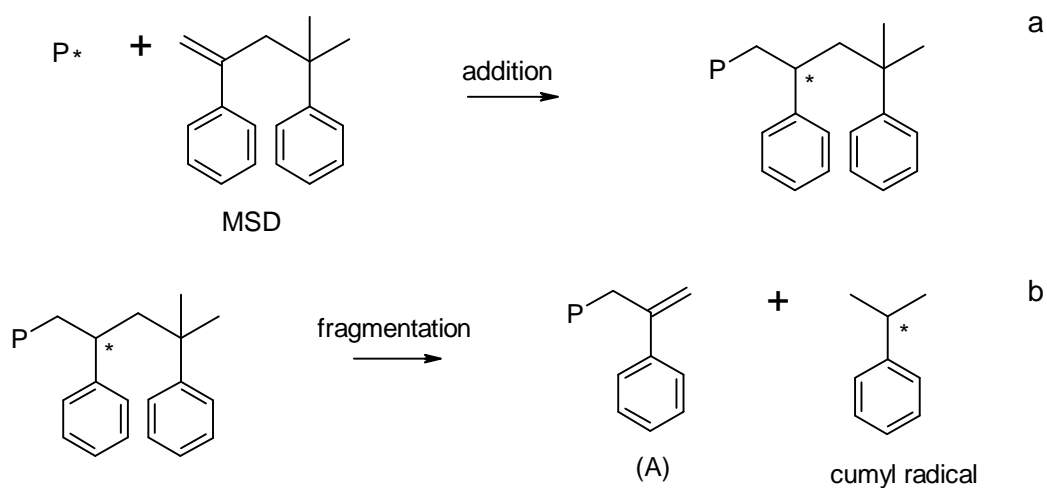
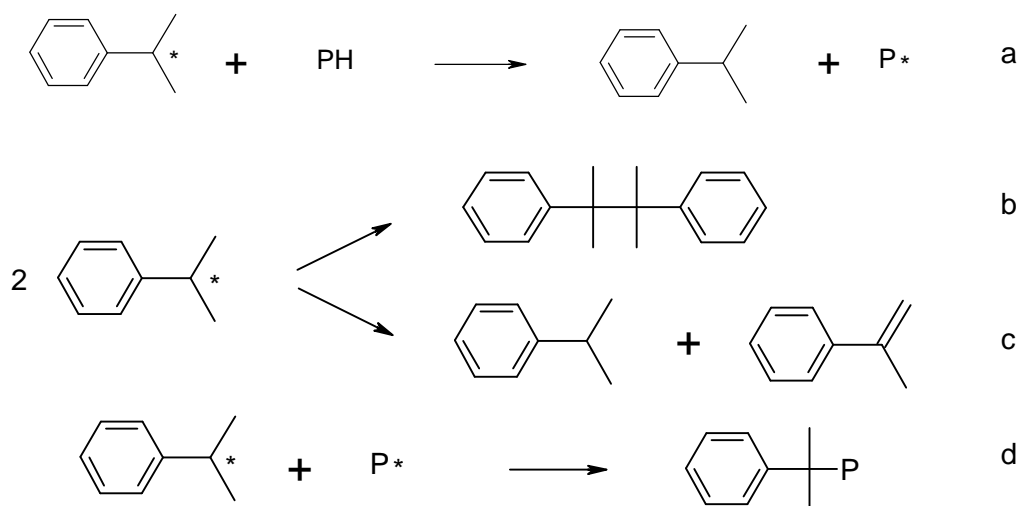Figure 2.21 – Addition of polymer radical to MSD (a) and subsequent fragmentation (b).

Figure 2.22 – Further reaction of de cumyl radical.

After the fragmentation has taken place, the remaining fragment of MSD attached to the polymer, marked as (A) in Figure 2.21 b, can undergo addition of a polymer radical to the double bond, as shown in Figure 2.23. The radical formed in this way, (B) in Figure 2.23, can lead to disproportionation, as shown in Figure 2.24 a, or can react with a polymer radical, as depicted in Figures 2.24 b and c.
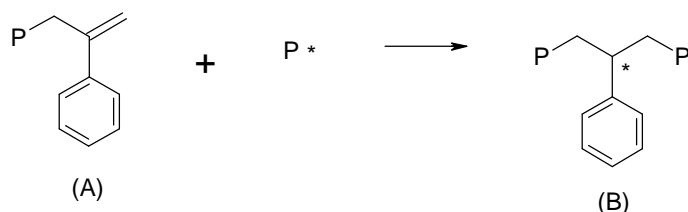

Figure 2.23 – Addition of a polymer radical to the polymer-MSD.
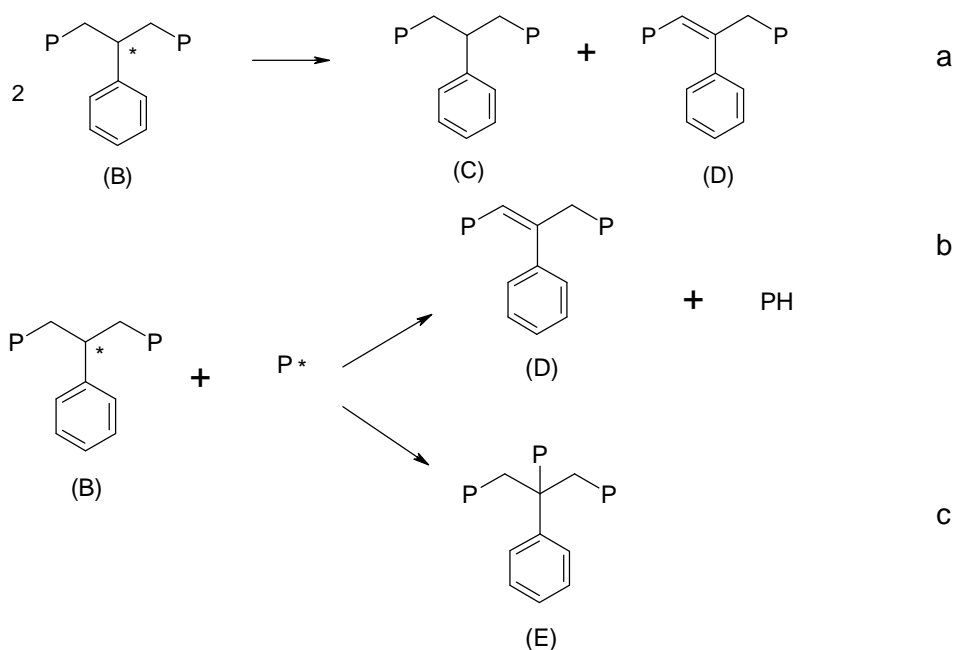
Figure 2.24 – Disproportionation (a) and reactions with a polymer radical (b and c).

The authors confirmed the presence of the several reaction intermediates and came to the conclusion that the mechanism by which MSD acts as scorch retarder or as crosslink promotor is explained by the formation of reactive olefinic intermediates, which further react with polymer radicals. Temperature is of crucial importance on these reactions, being able to shift them from a delay effect to a promoting effect on the vulcanisation reaction.

2.4   SULPHUR-LIKE PROPERTIES IN PEROXIDE VULCANISATES

2.4.1 Introduction

Despite the improvement in peroxide cure properties achieved by the use of co-agents, dynamic and some mechanical properties of peroxide vulcanisates are still inferior to those of typical sulphur vulcanisates. For this reason, there is a limitation in the use of peroxide cured rubber products, since an important part of rubber articles are used in dynamic applications. However, if the above mentioned properties of peroxide cured rubber can be improved, the range of applications can be significantly widened. To achieve that aim some properties, like tensile strength for instance, should be more similar to those typically obtained with sulphur cure.

2.4.2 Peroxide-like properties in sulphur vulcanisates

In literature some interesting investigations can be found about studies with sulphur vulcanisation, to obtain crosslinks different from the conventional sulphur bridges; viz. to obtain some C-C bonds in order to obtain peroxide-like properties. Farid[89] studied the influence of hexamethylene-1,6-bisthiosulphate disodium salt dihydrate (HTS), Figure 2.25, as a post-vulcanisation stabiliser for sulphur vulcanisation of NR, with the aim of obtaining a system without reversion. It was found that during vulcanisation HTS breaks down and inserts one or more hexamethylene-1,6-dithyl groups within sulphidic crosslinks, as shown in Figure 2.26. This kind of new crosslink formed is called a hybrid crosslink.
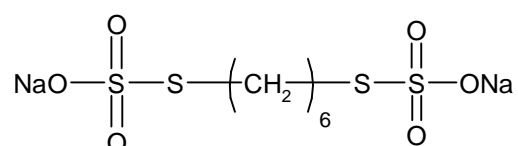

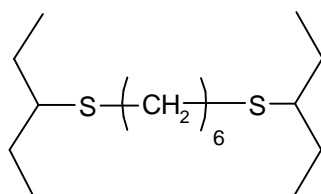**Figure 2.25** – Hexamethylene-1,6-bisthiosulphate disodium salt dihydrate (HTS).

Figure 2.26 –Hybrid crosslink formed by sulphur vulcanisation in the presence of HTS.

Normal sulphur vulcanisates, under certain conditions, can suffer from loss of crosslinks: the polysulphidic groups that constitute the crosslinks may break to form cyclic and pendant groups, which lead to reversion. Under the same conditions, the hybrid crosslinks convert to a crosslink formed by a monosulphidic link on each side of the hexamethylene group. This kind of crosslinks requires more energy to be broken

and, on the other hand, retains flexibility on account of the hexamethylene group, which causes the elimination of reversion.

2.4.3 Sulphur as co-agent

When sulphur-like properties are wanted in peroxide vulcanisates, the idea of the hybrid crosslinks can be considered. But in this case, instead of C-C crosslinks in sulphur cure, sulphur bridges are aimed for, in order to obtain sulphur-like properties in the peroxide cured articles.

The first approach to achieve sulphur bridges in peroxide cure would be the use of sulphur as co-agent.[18, 34] The effect of sulphur as an additive in peroxide vulcanisation was tested by Scheele and Hummel,[38, 90-92] who found that sulphur reduces the crosslinking efficiency of the peroxide while it does not affect its decomposition rate.[90] Accordingly, it belongs to the Type II co-agents. They suggested that sulphur may interfere with the free radical crosslinking reaction in a way that one sulphur atom prevents the formation of about one crosslink.

Manik and Banerjee[35-37] studied the influence of sulphur in peroxide vulcanisation of Natural Rubber using dicumylperoxide. They studied the influence of accelerators and other components of the formulation in order to gain information regarding the mechanism of the accelerator-sulphur curing system. Sulphur was found to reduce the crosslink density of the vulcanisate, like observed by Hummel.[90] Regarding the physical properties, the presence of sulphur lead to a vulcanisate with higher tensile strength and modulus, but worse ageing properties.

Das and Banerjee[39] carried out similar studies, in this case for the peroxide vulcanisation of SBR. They studied the influence of sulphur on dicumylperoxide vulcanisation of SBR. It was also concluded that the tensile strength of the vulcanisate was higher when using sulphur in DCP vulcanisation than when using DCP alone. On the other hand, the use of sulphur reduced the crosslink density, as well as the resilience.

Fujio et al.[34] studied the effect of sulphur on the peroxide cure of EPDM and Divinylbenzene (DVB) compounds, leading to the conclusion that small amounts of sulphur improved modulus and rupture energy, as well as cure state. When the amount of sulphur was too high in relation to the amount of peroxide, more than 0.20 phr in this case, the modulus was reduced. Their mechanism suggested for the peroxide decomposition in the presence of sulphur is shown in Figure 2.27.
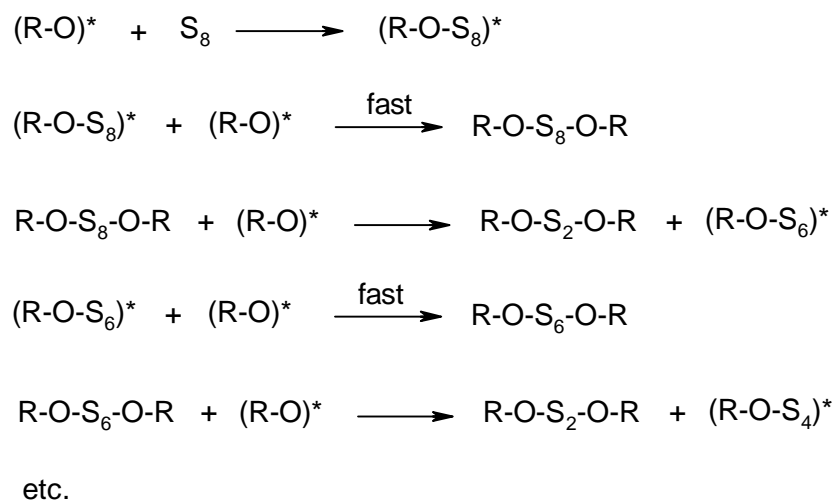
$$(R\text{-}O)^* \ + \ S_8 \ \longrightarrow \ (R\text{-}O\text{-}S_8)^*$$

$$(R\text{-}O\text{-}S_8)^* \ + \ (R\text{-}O)^* \ \xrightarrow{\text{fast}} \ R\text{-}O\text{-}S_8\text{-}O\text{-}R$$

$$R\text{-}O\text{-}S_8\text{-}O\text{-}R \ + \ (R\text{-}O)^* \ \longrightarrow \ R\text{-}O\text{-}S_2\text{-}O\text{-}R \ + \ (R\text{-}O\text{-}S_6)^*$$

$$(R\text{-}O\text{-}S_6)^* \ + \ (R\text{-}O)^* \ \xrightarrow{\text{fast}} \ R\text{-}O\text{-}S_6\text{-}O\text{-}R$$

$$R\text{-}O\text{-}S_6\text{-}O\text{-}R \ + \ (R\text{-}O)^* \ \longrightarrow \ R\text{-}O\text{-}S_2\text{-}O\text{-}R \ + \ (R\text{-}O\text{-}S_4)^*$$

etc.

Figure 2.27 – Reaction of sulphur and peroxide radicals suggested by Fujio et al.[34]

Later, it was proven by Das[93] that, when small amounts of sulphur are added as co-agent in the peroxide vulcanisation of an NBR/EPDM blend using DCP, it is possible to obtain co-agent bridges, which lead to an improvement of certain dynamic and mechanical properties of the vulcanisates. The mechanism suggested by this author is shown in Figure 2.28. According to this study, the addition of sulphur decreases the crosslink efficiency of DCP in all cases, and improves properties like tensile strength depending on the sulphur concentration, due to the formation of sulphur containing crosslinks. According to the same author the low sulphur containing radicals (R-O-Sx*), formed as shown in Figure 2.27, are the most reactive towards polymer radicals, as it was already suggested by Fujio.[34] In summary, this author concluded that sulphur can act as a free radical scavenger in the peroxide vulcanisation of NBR/EPDM blends and stabilizes the tertiary radicals formed from the proplylene units, thus restricting the main chain scission and improving the physical properties.

Considering the studies described above, it can be summarised that the effect of sulphur as co-agent in peroxide vulcanisation might lead to improvement of some properties, i.e: tensile strength, while worsening some other properties, i.e: ageing, but the decisive factor is the sulphur concentration. If only small amounts of sulphur are added, some improvements can be observed in the cured compound without significantly deteriorating other properties. Nevertheless, the improvement of properties achieved is still far away from leading to products with a similar level of dynamic properties as sulphur vulcanisates.
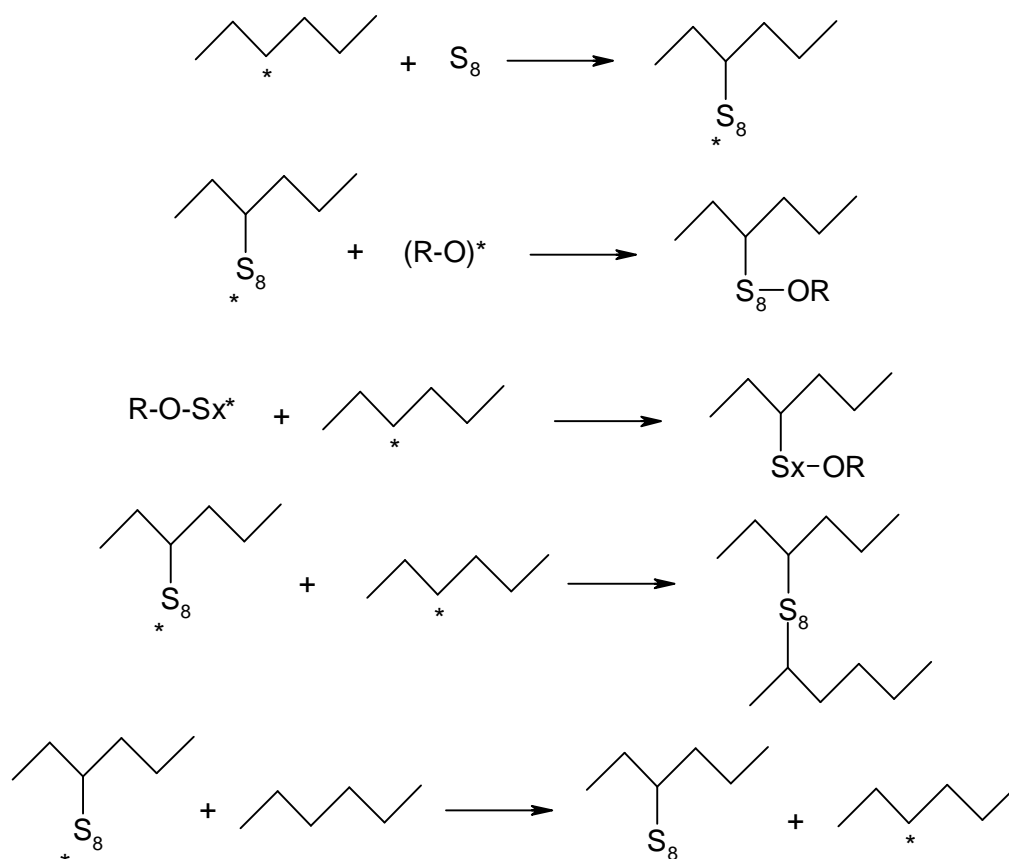

Figure 2.28 – Mechanism of peroxide vulcanisation in the presence of sulphur suggested by Das.[93]

2.4.4 Mixed vulcanisation

Another attempt to obtain sulphur-like properties in peroxide cured rubber was the use of mixed vulcanisation. As mentioned previously in this chapter, the cure behaviour of peroxide vulcanisation and sulphur vulcanisation is different and leads to different properties of the cured compounds. Sulphur vulcanisation leads to cured rubber with excellent tensile strength because of the nature of the network formed, consisting of sulphur bridges. On the other hand, the superior temperature stability of peroxide vulcanisates is due to the strength of the network, formed by C-C bonds between polymer chains. Therefore, if it were possible to obtain a cured polymer with both sulphur bridges and C-C bonds, it might be possible to achieve the good property characteristics from sulphur vulcanisates and also the good ones of peroxide vulcanisates, by means of combination of both vulcanisation systems. Such a rubber is called a mixed vulcanisate.[23] To achieve that, a few authors[7, 23, 94] have tried to combine the two vulcanisation systems: sulphur and peroxide, in order to obtain a cure system with the advantages of both and eliminate, as far as possible, their disadvantages.

If mixed vulcanisation is just defined as vulcanisation which leads to both sulphidic and C-C crosslinks, then the use of sulphur as co-agent in peroxide vulcanisation, as described in paragraph 2.4.3, can be considered as mixed vulcanisation. However, some authors[23] have defined mixed vulcanisation as a combination of two different vulcanisation systems in separate vulcanisation steps. In that case a peroxide cure system which uses sulphur as co-agent would not fulfil the definition of mixed vulcanisation.

Brodsky[7] combined sulphur/accelerator and peroxide cure for a blend of EPDM/BR/NR. He used a variety of mixed peroxide-sulphur curing systems and tested them to study the mechanical properties of the vulcanisates. Regarding the curing behaviour the results show that the mixed curing system leads to compounds with low scorch safety and low cure rate when compared to the usual sulphur/accelerator system. On the other hand, the mixed vulcanisates show a reduced reversion, proportional to the amount of peroxide used. Regarding physical properties, it was observed that mixed vulcanisates have improved tensile strength and similar tear resistance. Ageing resistance, compression set and fatigue life of mixed vulcanisates was also found to be improved, when compared with sulphur/accelerator cured rubber.

The mixed vulcanisation of EPDM with sulphur and peroxide in two vulcanisation steps was studied by van der Burg.[94] The vulcanisates were found to have lower crosslink density and intermediate tear strength and compression set.

Bevervoorde[23] studied the combination of electron beam irradiation curing, which leads to C-C bonds between polymer chains, and sulphur curing of EPDM, as a mixed vulcanisation system, viz. in two curing steps. Vulcanisates obtained without filler in the formulation show similar, or slightly higher strength properties and lower compression set when compared to sulphur vulcanisates. When carbon black was added to the formulation, tensile and tear strength increased substantially while the compression set was similar to the mixed vulcanisates without filler.

In view of the above mentioned studies, it can be summarised that by mixed vulcanisation it is possible to improve properties of rubber compounds to a certain extent, but on the other hand some important disadvantages are found, i.e. low scorch safety and low cure rate,[7] which makes this concept not very attractive from an industrial point of view.

2.5 SUMMARY AND CONCLUSIONS

Peroxide vulcanisation is a radical crosslinking method which offers the possibility of crosslinking saturated and unsaturated rubbers, as well as blends of these. It leads to a network structure with covalent C-C crosslinks, which provides excellent heat ageing and high temperature properties, in general. On the other hand, some mechanical properties of peroxide vulcanisates are inferior to those typically achieved by sulphur cure, i.e. tensile strength and dynamic behaviour.

Several co-agents are commercially available for peroxide cure. These have been studied and are reported in literature according to their chemical nature and ergo their classification. It has been reported that co-agents may react during vulcanisation and get incorporated in the polymer network as extra crosslinks. Co-agents also help to minimise side reactions, like chain scission. The use of co-agents in peroxide cure improves peroxide efficiency and therefore also improves cure state, which is reflected in an improvement in properties. Despite these improvements, some mechanical and dynamical properties should be further increased to reach the level of sulphur cured articles.

Another important concern in peroxide vulcanisation, especially when using co-agents, is scorch safety. Normally, scorch takes place rather fast, which makes processing of the still uncured rubber material difficult. In order to improve scorch safety, scorch retarders can be added to the formulation. A scorch retarder delays the occurrence of scorch by scavenging the first radicals formed. As a consequence, the crosslink efficiency is reduced. Therefore, higher dosages of peroxide and/or co-agent are necessary to maintain a proper cure rate and level when using scorch retarders.

The use of sulphur as co-agent in order to improve peroxide cure has been widely studied. In general, small amounts of sulphur added to a peroxide formulation improve mechanical properties very modestly. High dosages of sulphur result in worse overall mechanical properties. Mixed vulcanisation systems also slightly improve mechanical properties, but at the expense of scorch safety and cure state. Therefore, other solutions should be investigated to obtain sulphur-like properties in peroxide cure.

It can be concluded that peroxide vulcanisation is a widely used cure system and offers many possibilities for use, mainly due to the availability of co-agents and scorch retarders. However, the range of applications of peroxide cure could significantly be widened if certain mechanical properties could be improved, to reach the level of sulphur cured articles, yet maintaining the good high temperature properties typical of peroxide vulcanisates and providing a system with proper scorch safety.

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Chapter 3

Co-agents in Peroxide Vulcanisation
of EPM Rubber

"The beginning is the half of the whole."

Pythagoras (570-500 BC)

Peroxide cure is nowadays a widely used cure system for rubber goods. The use of co-agents is needed in order to improve peroxide efficiency and to reach improved mechanical properties such as tensile strength. Several co-agents are available in the market to perform this task. In this chapter four different, commercially available and widely used co-agents are investigated and compared to the peroxide cure in the absence of co-agent. The effect of N,N'-m-phenylenedimaleimide (BMI-MP), N,N'-p-phenylenedimaleimide (BMI-PP), triallylcyanurate (TAC) and ethylenedimethacrylate (EDMA) as co-agents in the peroxide cure of ethylene propylene polymethylene rubber (EPM) are studied. The results show that all co-agents improve cure characteristics as well as mechanical properties of the cured rubber. Amongst all co-agents, bismaleimides give the best overall performance, particularly BMI-PP gives most optimal properties for the same co-agent loadings, as calculated on basis of equivalent unsaturation levels.

3.1 INTRODUCTION

Peroxide cure in the absence of co-agents leads to a material with rather poor mechanical properties, in general. As mentioned in Chapter 2, the use of co-agents is necessary in peroxide vulcanisation in order to boost the peroxide efficiency.[1-5] This amelioration achieved by the use of co-agents is due to a combination of two factors: suppression of inefficient side reactions, which consume radicals, and formation of extra crosslinks via the co-agent molecules.[4, 6-17] This reflects in improved mechanical properties of the cured material, such as compression set, modulus, tensile strength, etc.[1, 18]

In literature many studies of peroxide/co-agent cure systems are reported, as already explained in Chapter 2. There is a wide range of co-agents commercially available for use in peroxide cure. However, no guidelines are reported in literature regarding the criteria for the co-agent selection for a specific system: type of rubber

and peroxide, and final properties which the material should meet. Therefore this matter is still treated in a rather empirical manner.

The present chapter describes the effect of several commercially available co-agents in the peroxide cure of ethylene propylene polymethylene rubber (EPM). The system is also studied in the absence of co-agents, in order to properly quantify the effect of the co-agents. Further, three different commercially available co-agents are tested and their results compared to those obtained in the absence of co-agent. In this manner the extent of improvement of every co-agent tested is evaluated.

3.2 EXPERIMENTAL

Materials - A masterbatch was prepared at DSM Elastomers B.V., the Netherlands, consisting of ethylene propylene polymethylene rubber from DSM (EPM Keltan 13, Mooney viscosiy ML(1+4)100°C of 46, containing 56% ethylene and 44% propylene), carbon black N-550 obtained from Cabot Corp., stearic acid obtained from Aldrich and paraffinic oil Sunpar 150 obtained from Sun Oil Cie.

Dicumyl peroxide (DCP, Perkadox BC-40 Bpd, 40% pure) was obtained from Akzo Nobel. The co-agents N,N'-m-phenylenedimaleimide (BMI-MP), N,N'-p-phenylenedimaleimide (BMI-PP), triallylcyanurate (TAC) and ethylene dimethacrylate (EDMA) were purchased from Acros. The structures of these compounds are shown in Table 3.1.

Table 3.1 Chemical names and structures of the different materials.

Chemical name	Abbreviation	Chemical structure
Ethylene propylene polymethylene rubber	EPM	
Dicumyl peroxide	DCP	
N,N'-m-phenylenedimaleimide	BMI-MP	
N,N'-p-phenylenedimaleimide	BMI-PP	
Triallylcyanurate	TAC	
Ethylene dimethacrylate	EDMA	

Mixing - The composition of the masterbatch is shown in Table 3.2. The compounds were mixed in a Banbury tangential mixer of 70 liters, with a fill factor of 74%. The mixing procedure is described in Table 3.3.

Table 3.2 Masterbatch formulation.

Material	Concentration (phr)
EPM	100
Carbon Black	60
Stearic Acid	1
Paraffinic Oil	45

Table 3.3 Masterbatch preparation.

Time (min)	Step
1.00	Crumbling polymer
1.00-2.30	Adding filler, processing oil, etc.
2.30	Ram down
2.50-4.50	Mixing
4.50	Ram up, sweeping
5.00	Ram down
5.00-6.30	Mixing
6.50	Dump batch
6.50-9.50	Cool batch down on open mill

Co-agent and peroxide were added to 206 phr of masterbatch on a Schwabenthan two roll mill (friction 1:1.22, temperature 40°C, mixing time 10 minutes).

Characterisation and Vulcanisation - The cure characteristics of the compounds were measured at 160°C using a torsional dynamic rheometer, RPA 2000 from Alpha Technologies. Delta torque or extent of crosslinking is the maximum torque (MH) minus the minimum torque (ML). Scorch time (t_{s2}) is taken as the time to reach 2% of the delta torque above minimum. This is not exactly in agreement with the definition of scorch time as mentioned in ISO 6502: "Rubber Measurement of vulcanisation characteristics with rotorless curemeters", but was implemented in the present form in the software of the RPA 2000. Optimum cure time (t_{90}) is the time to reach 90% of the delta torque above minimum.

The compounds were vulcanised by compression moulding in a Wickert laboratory press WLP 1600/5*4/3 at 100 bar and 160°C, for 2 times t_{90}.

Determination of Mechanical Properties – Mechanical properties of the vulcanisates were measured on a Zwick tensile tester, according to the conditions described in ISO 37, on dumb-bell shaped specimens of Type 2, with a nominal rate of the traverse of the moving grip of 500 mm/min.

3.3 RESULTS AND DISCUSSION

3.3.1 Peroxide cure of EPM rubber in the absence of co-agents

In order to understand the effect of co-agents in peroxide cure it is necessary to previously perform the cure in the absence of co-agents, in order to have a reference later for the extent of the co-agent effect. Therefore tests were carried out with only masterbatch and peroxide in the formulation.

A study on the influence of peroxide concentration on the cure characteristics was performed in order to select a concentration which reaches a good compromise between performance and peroxide concentration. For this reason, several formulations were tested, containing: no co-agent, the same amount of masterbatch (206 phr) and different amounts of dicumyl peroxide, as shown in Table 3.4. The delta torque values achieved by these formulations are listed in Table 3.4 and are depicted in Figure 3.1.

In all cases the delta torque achieved is quite low. However, there is a clear linear tendency for the delta torque to increase with increasing peroxide concentration: the more peroxide is added, the more radicals will be formed and thus the higher the crosslink efficiency will be, as reflected in the delta torque values. Nevertheless, the use of large amounts of peroxide in order to improve properties is not an attractive solution, because this leads to a high cost of the final product. In addition, an increase

in polymer degradation takes place, which also affects the physical and mechanical properties.

Table 3.4 Formulations with different peroxide content. They are all based on 206 phr of masterbatch compound.

Formulation	Peroxide Content (meq)	Peroxide Content (phr)	Delta torque (dNm)
PO1	1.48	1	0.14
PO2	2.96	2	0.23
PO3	5.93	4	0.41
PO4	8.89	6	0.58
PO5	11.85	8	0.78
PO6	14.81	10	0.96
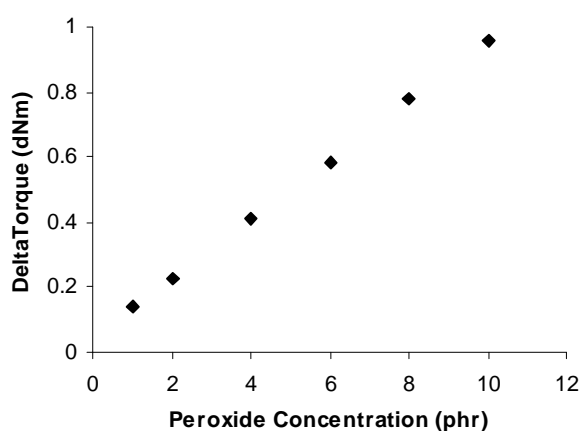
Figure 3.1 – Delta torque achieved with different concentrations of peroxide DCP 40% pure.

Based on these results, 6 phr of peroxide has been taken as the peroxide concentration to be used as control in further investigations, since this concentration already provides a good delta torque level. Higher peroxide concentrations would result in the disadvantages reported above. It should be mentioned that 6 phr is the total amount of peroxide added to the formulation. The content of peroxide in the commercial masterbatch is 40%, which means that there are effective 2.4 phr of peroxide in this formulation. Further tests have been performed using this control formulation in order to have a reference to compare with for the co-agent containing formulations. Table 3.5 shows the results achieved for the tensile properties.

Table 3.5 Tensile test results for sample PO4, containing 6 phr of peroxide 40% pure.

Property	Value
Tensile Strength (MPa)	0.5
Elongation at Break (%)	607
Modulus 100 (MPa)	0.5
Modulus 200 (MPa)	0.5

As can be observed, the values of tensile strength and moduli are very low, which indicates that the material properties leave a huge room for improvement.

3.3.2 Peroxide cure of EPM rubber in the presence of co-agents

Several commercially available co-agents were tested in the peroxide cure of EPM rubber in order to evaluate their influence on the vulcanisation reaction, as well as on the final properties of the material. Since different co-agents not only differ in molecular weight but, they also have other amounts of reactive functionalities in their molecular structures, comparisons were done in terms of equivalents of unsaturation. In this way a fair comparison, independent of molecular weight and number of functionalities, can be carried out amongst the different co-agents.

3.3.2.1 Peroxide cure of EPM rubber in the presence of EDMA

Ethylene dimethacrylate (EDMA) is a commonly used co-agent of the methacrylate type. Its effect on the peroxide cure of EPM was studied. Formulations according to Table 3.6 were tested. All formulations contained the same amount of masterbatch: 206 phr, and the same peroxide concentration: 6 phr.

Table 3.6 Formulations of the samples containing EDMA. They are all based on 206 phr of masterbatch and 6 phr of peroxide.

Sample	Concentration EDMA (meq of unsaturation)	Concentration EDMA (mmol)	Concentration EDMA (phr)
PO4	0	0	0
Ec1	10	5	0.99
Ec2	20	10	1.98
Ec3	30	15	2.97
Ec4	40	20	3.96
Ec5	50	25	4.95

As can be seen in Figure 3.2, the concentration of EDMA added to the formulation has a big influence on the final torque level achieved, while the rate of the vulcanisation reaction is not changed. The tendency is an increase in delta torque with increasing EDMA concentration.
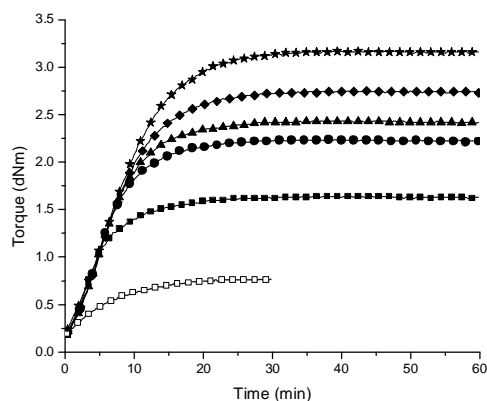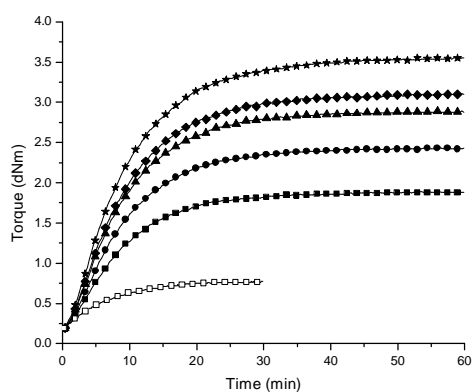

Figure 3.2 a – Rheogram of samples containing different EDMA concentrations: (□): 0 meq.; (■):10 meq; (●): 20 meq; (▲): 30 meq; (♦): 40 meq; (★): 50 meq.
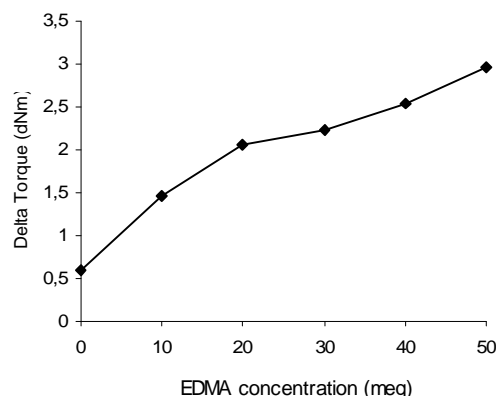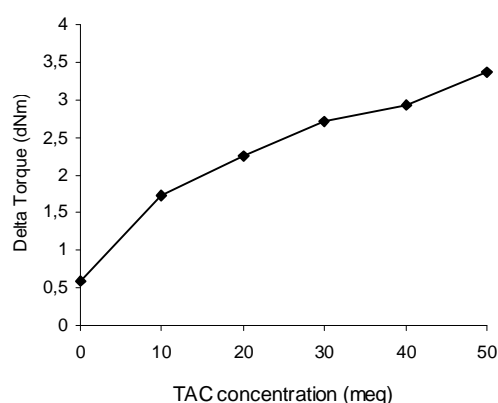
Figure 3.2 b – Delta Torque vs. EDMA concentration.

In all cases the delta torque is higher than that obtained in the absence of co-agent, which is 0.6 dNm for 6 phr of peroxide. EDMA is indeed improving the

crosslinking efficiency of dicumyl peroxide in the present system. The mechanical properties achieved with the use of different EDMA concentrations are plotted in Figures 3.3 to 3.6.
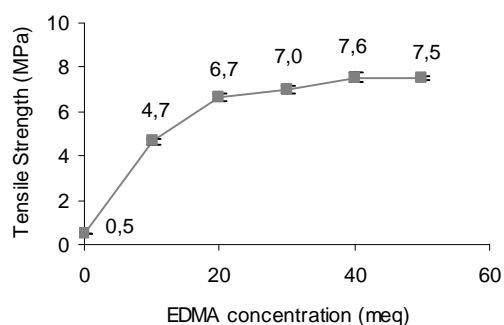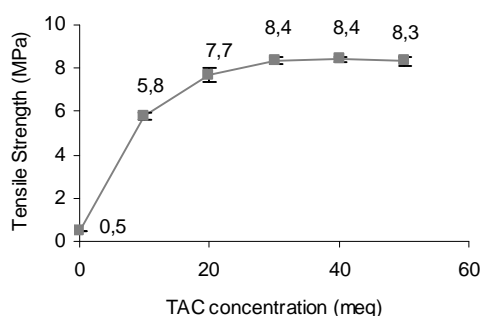

Figure 3.3 – Tensile Strength for samples containing different EDMA concentrations.
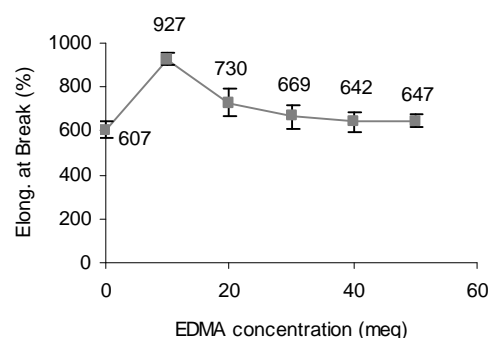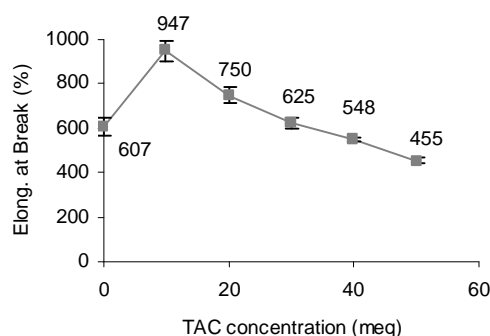

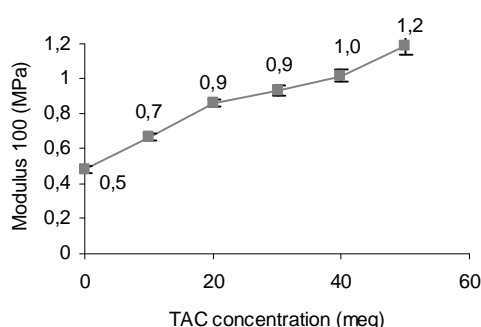**Figure 3.4** –Elongation at Break for samples containing different EDMA concentrations.
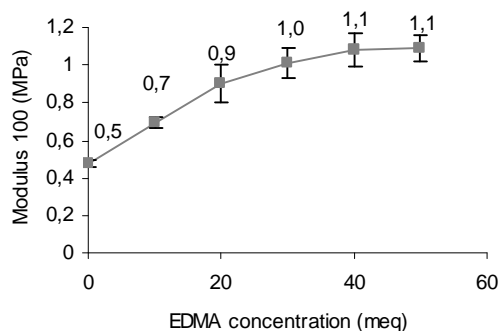
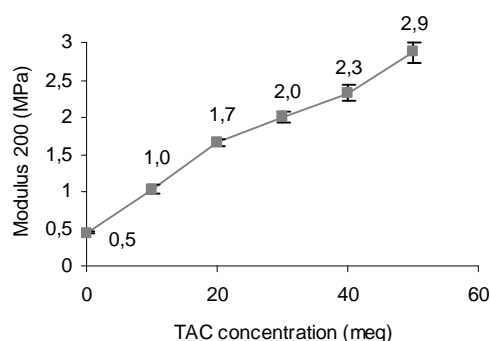**Figure 3.5** – Modulus at 100% elongation for samples containing different EDMA concentrations.
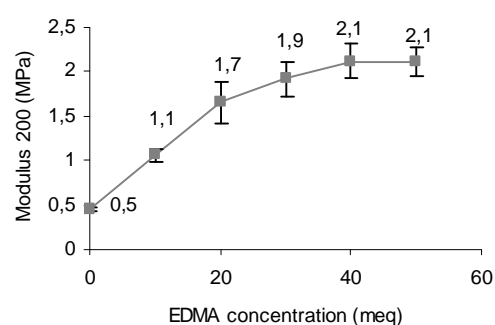
Figure 3.6 –Modulus at 200% elongation for samples containing different EDMA concentrations.

Mechanical properties also show an improvement with increasing EDMA concentration. This improvement is especially remarkable from 10 to 30 meq. However between 30 and 50 meq the changes in the overall properties are not large and seem to level off. It can be concluded that the optimal properties for this co-agent in this system are reached at a level of 30 to 40 meq of EDMA.

3.3.2.2 Peroxide cure of EPM rubber in the presence of TAC

The effect of triallylcyanurate (TAC), an allylic type of co-agent which is commonly used in the industry, was also studied. Formulations according to Table 3.7 were tested. All formulations contained the same amount of masterbatch: 206 phr and the same amount of peroxide: 6 phr, at different TAC concentrations.

Table 3.7 Formulations of the samples containing TAC. They are all based on 206 phr of masterbatch and 6 phr of peroxide.

Sample	Concentration TAC (meq of unsaturation)	Concentration TAC (mmol)	Concentration TAC (phr)
PO4	0	0	0
Tc1	10	3.3	0.82
Tc2	20	6.7	1.64
Tc3	30	10.0	2.46
Tc4	40	13.3	3.28
Tc5	50	16.7	4.10

In Figure 3.7 the rheograms obtained with these formulations are plotted. The delta torque increases with increasing TAC concentration. Also the cure rate is higher at higher concentrations of TAC.
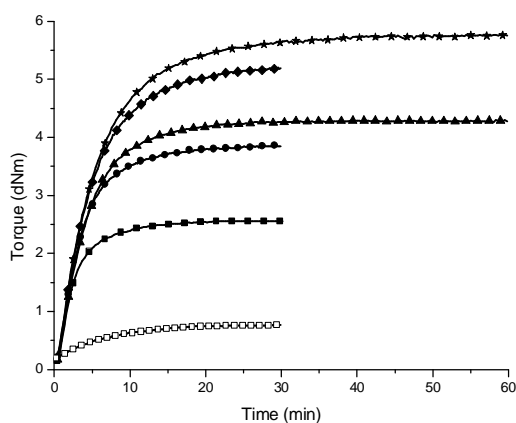

Figure 3.7 a – Rheogram of samples containing different TAC concentrations: (□): 0 meq.; (■):10 meq; (●): 20 meq; (▲): 30 meq; (♦): 40 meq; (★): 50 meq.

Figure 3.7 b – Delta Torque vs. TAC concentration.

The mechanical properties achieved with this co-agent are plotted in Figures 3.8 to 3.11. Tensile strength and moduli are improved with the addition of TAC to the peroxide system. From 20 meq onwards the tensile strength seems to level off while moduli keep increasing with increasing TAC concentration. In view of these results, it can be concluded that the optimal concentration of TAC to use in this system is a level of 30 mequivalents.

Figure 3.8 – Tensile Strength for samples containing different TAC concentrations.

Figure 3.9 –Elongation at Break for samples containing different TAC concentrations.

Figure 3.10 – Modulus at 100% elongation for samples containing different TAC concentrations.

Figure 3.11 –Modulus at 200% elongation for samples containing different TAC concentrations.

3.3.2.3 Peroxide cure of EPM rubber in the presence of BMI-MP and BMI-PP

Two co-agents of the bismaleimide family were tested: N,N'-m-phenylenedimaleimide (BMI-MP) and N,N'-p-phenylenedimaleimide (BMI-PP). The first bismaleimide is a widely used co-agent for peroxide cure, mentioned in literature for peroxide cure of several types of rubber.[5, 19] The latter is an existing chemical, which is however not commonly used in peroxide cure of rubber, but for completely different applications in industry, i.e. in biochemistry as crosslinker.[20, 21] This is not the only difference between these two bismaleimide compounds, another very important distinction is their toxicity: BMI-MP is a highly toxic compound, while BMI-PP is not. The reason why BMI-PP was taken as co-agent in this thesis is that, because of the lower steric hindrance compared to BMI-MP, better accessibility to the polymer chains might be expected. Figures 3.12 and 3.13 show the structures of these two co-agents obtained with Hyperchem where the charge density is displayed around the stuctures.

Figure 3.12 – Molecular structure of BMI-MP.

Figure 3.13 – Molecular structure of BMI-PP.

From these figures it can be deduced that once the co-agent has reacted with a polymer chain by one maleimide group, at one side of the molecule, the second maleimide group will be more available to react with another polymer chain in the case of BMI-PP than in the case of BMI-MP, since in BMI-MP the second maleimide site is more sterically hindered. According to this, more incorporation of BMI-PP, compared to BMI-MP, into the polymer network may be expected. This means that a higher crosslink density is expected for BMI-PP, thus higher delta torque and moduli values, for the same amounts of addition.

Table 3.8 shows the composition of the samples tested. Figures 3.14 and 3.15 show the rheograms achieved with these compounds.

Table 3.8 Formulations of the samples containing BMI-MP and BMI-PP. They are all based on 206 phr of masterbatch and 6 phr of peroxide.

Co-agent	Sample	Concentration (meq of unsaturation)	Concentration (mmol)	Concentration (phr)
none	PO4	0	0	0
BMI-MP	Mc1	10	5	1.34
	Mc2	20	10	2.68
	Mc3	30	15	4.02
	Mc4	40	20	5.36
	Mc5	50	25	6.70
BMI-PP	Pc1	10	5	1.34
	Pc2	20	10	2.68
	Pc3	30	15	4.02
	Pc4	40	20	5.36
	Pc5	50	25	6.70

Figure 3.14 a – Rheogram of samples containing different BMI-PP concentrations: (□): 0 meq.; (■):10 meq; (●): 20 meq; (▲): 30 meq; (♦): 40 meq; (★): 50 meq.
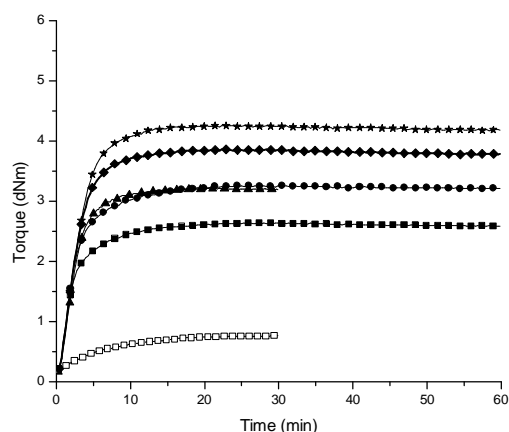
Figure 3.15 a – Rheogram of samples containing different BMI-MP concentrations: (□): 0 meq.; (■):10 meq; (●): 20 meq; (▲): 30 meq; (♦): 40 meq; (★): 50 meq.
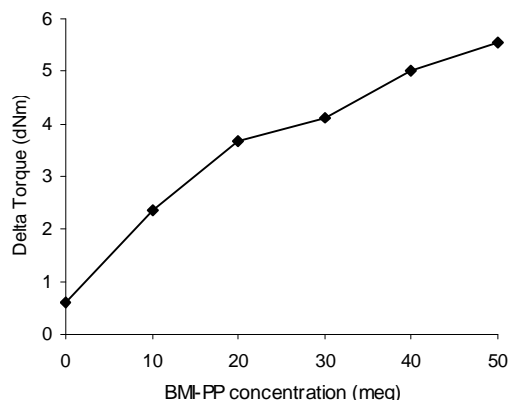
Figure 3.14 b – Delta Torque vs. BMI-PP concentration.
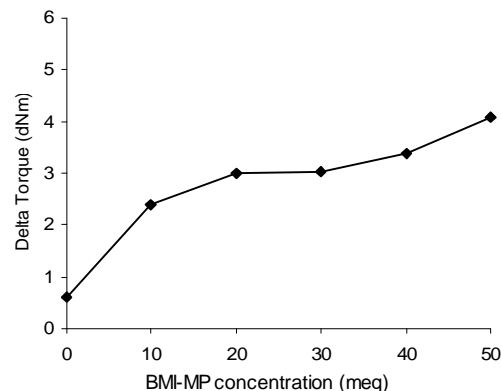
Figure 3.15 b – Delta Torque vs. BMI-MP concentration.

As can be observed in the figures above, there is an intrinsic difference between the performance of the two bismaleimide co-agents. At the same concentration, BMI-PP provides a higher delta torque than BMI-MP. This difference is larger with increasing co-agent concentration. The reason, as already mentioned, is most likely the better accessibility of the bismaleimide functionality of the BMI-PP compared to BMI-MP, due to larger sterical hindrance of the latter co-agent. On the other hand, the influence of co-agent concentration on the delta torque is an increase in torque level with increasing co-agent concentration for both bismaleimide co-agents.

The mechanical properties measured for BMI-PP at the different concentration levels are plotted in Figures 3.16 to 3.19. As can be noticed, the tensile strength levels off above an addition of 20 meq of co-agent, while moduli keep growing with increasing co-agent concentration.
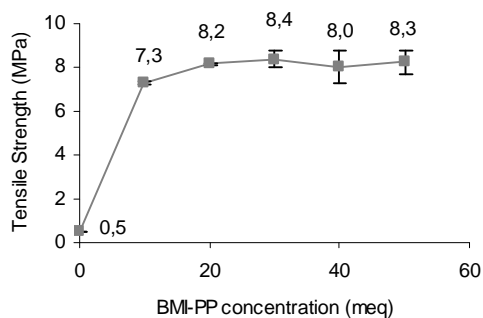
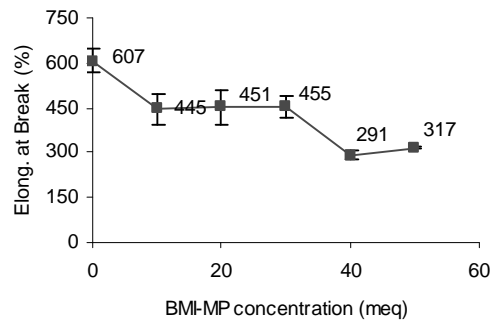**Figure 3.16** – Tensile Strength for samples containing different BMI-PP concentrations.
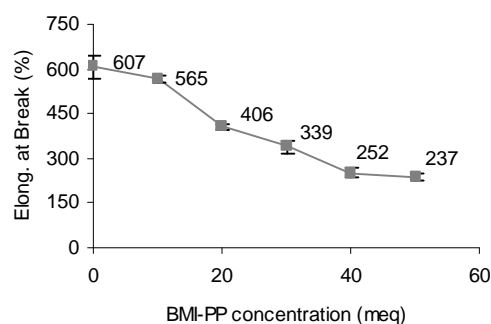
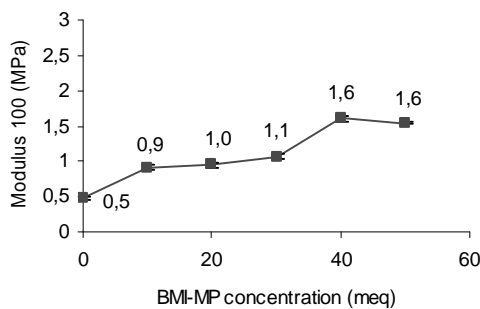**Figure 3.17** –Elongation at Break for samples containing different BMI-PP concentrations.
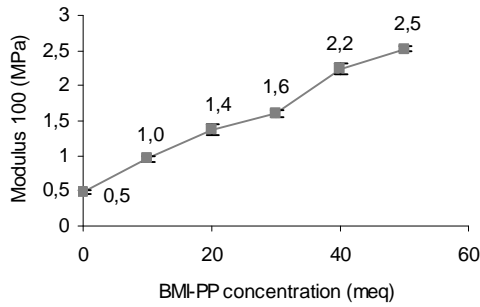
Figure 3.18 – Modulus at 100% elongation for samples containing different BMI-PP concentrations.
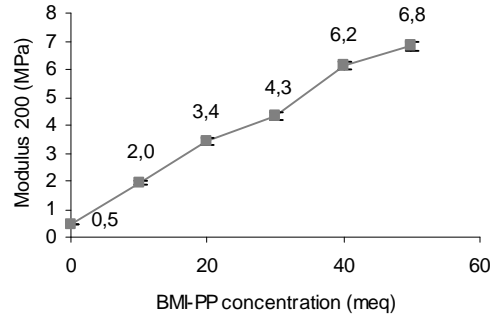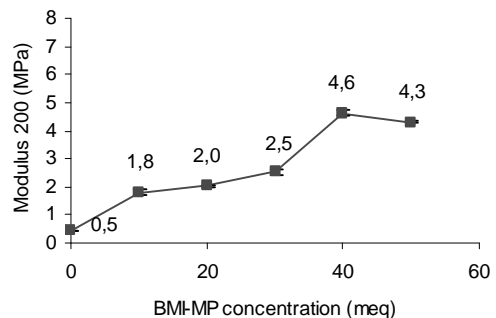

Figure 3.19 –Modulus at 200% elongation for samples containing different BMI-PP concentrations.

A similar tendency in properties can be observed for the samples containing BMI-MP, as shown in Figures 3.20 to 3.23. Tensile strength levels off above a co-agent concentration of approximately 30 meq. While the moduli increases with co-agent concentration.
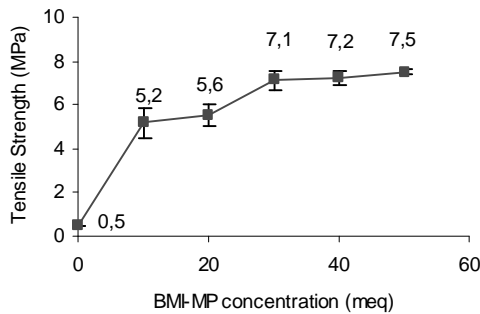
Figure 3.20 – Tensile Strength for samples containing different BMI-MP concentrations.

Figure 3.21 –Elongation at Break for samples containing different BMI-MP concentrations.

Figure 3.22 – Modulus at 100% elongation for samples containing different BMI-MP concentrations.

Figure 3.23 –Modulus at 200% elongation for samples containing different BMI-MP concentrations.

When the performance of BMI-PP and BMI-MP is compared, it can clearly be seen that both co-agents improve the material properties, when compared to the sample without co-agent. BMI-PP leads not only to higher torque levels, thus higher

crosslink density, but also to higher values of tensile strength and moduli. These results are in agreement with the prediction made on basis of the molecular structures of these co-agents: because of the lowest steric hindrance BMI-PP was predicted to lead to higher torque levels and better mechanical properties. This is indeed observed experimentally. Based on these data it can be concluded that BMI-PP performs better as co-agent in peroxide cure than BMI-MP for EPM rubber.

3.3.3 Comparison between different co-agents

Four commercially available co-agents of different type have been tested, three of them already in use in the industry: EDMA, TAC and BMI-MP, and another one used for a different kind of application, BMI-PP. In all cases the torque level as well as the final mechanical properties are significantly improved compared to the same system in the absence of co-agents. This is due to the improved peroxide efficiency in the presence of these co-agents.

For each co-agent, concentration plays an important role. However, in view of the results shown in the previous paragraphs and due to the fact that a co-agent is an expensive component of the formulation, it is not common to use excessive amounts of co-agents in order to reach an improvement in the system: for most of the applications, 30 milliequivalents of co-agent is satisfactory.

When the different co-agents are compared on the same milliequivalent basis, it can be seen that BMI-PP is the co-agent giving the best overall performance, followed by BMI-MP, TAC and EDMA. For instance, when comparing the properties at 30 meq of co-agents, as shown in Figures 3.24 to 3.28, BMI-PP provides the highest torque level, highest tensile strength and highest moduli. BMI-MP provides a slightly lower tensile strength than TAC, however both modulus at 100% and modulus at 200% elongation are higher for BMI-MP than for TAC. Finally, TAC gives a higher tensile strength and higher moduli than EDMA. A disadvantage for TAC is its marching cure behaviour, as can be observed in the rheogram in Figure 3.24.
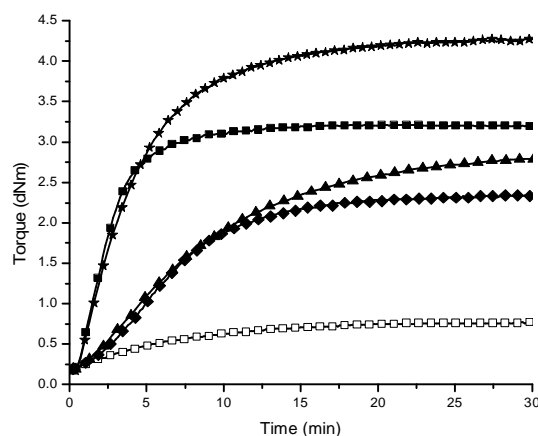

Figure 3.24 – Rheogram at 30 meq level with different co-agent:
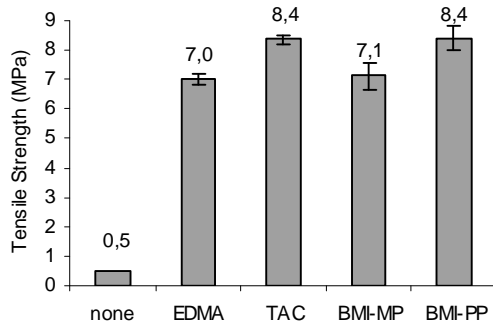(□): no co-agent; (★): BMI-PP; (■):BMI-MP; (▲):TAC; (♦): EDMA.

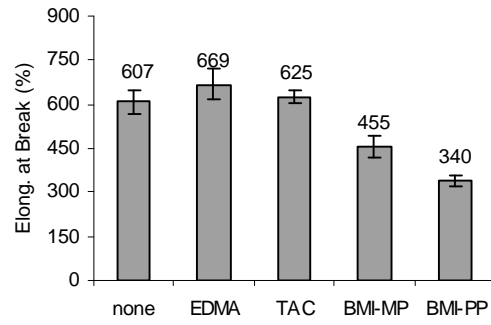**Figure 3.25** – Tensile Strength vs. Co-agent type for 30 meq of co-agents.

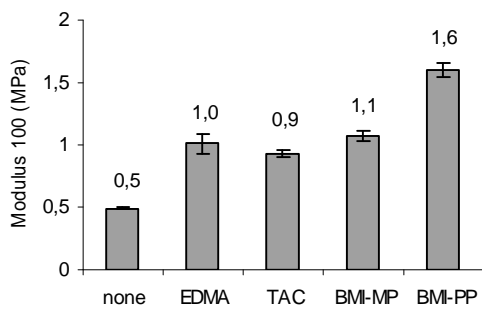**Figure 3.26** – Elongation at Break vs. Co-agent type for 30 meq of co-agents.

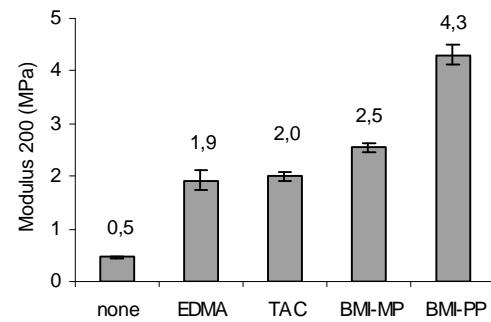**Figure 3.27** – Modulus at 100% elongation vs. Co-agent type for 30 meq of co-agents.

Figure 3.28 – Modulus at 200% elongation vs. Co-agent type for 30 meq of co-agents.

3.4 CONCLUSIONS

Peroxide cure of EPM in the absence of co-agents leads to a material with a low cure state and poor mechanical properties. The presence of co-agents in a peroxide cure system boosts the cure by increasing peroxide efficiency. The concentration of co-agent present in the formulation has a significant influence on the cure state and thus on the final mechanical properties that can be achieved: the higher the co-agent concentration, the better the mechanical properties. However, at concentrations above 30 milliequivalents of unsaturation of co-agent, the tensile strength levels off for all the co-agents tested. Besides, high concentrations of co-agent would also result in a more expensive product. In view of this, a concentration around 30 meq of unsaturation of the co-agents would be satisfactory for most applications to achieve a good improvement in properties. Amongst the different types of co-agents tested, BMI-PP provides the best improvement in properties, followed by BMI-MP, TAC and EDMA.

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Chapter 4

Sulphur Containing Co-agents
in Peroxide Vulcanisation[#]

"Aut viam inveniam aut faciam."

(I'll either find a way or make one).

The use of co-agents in peroxide vulcanisation boosts peroxide efficiency and results in improved mechanical properties, such as tensile strength and moduli. Despite these improvements, the level of some mechanical properties is still inferior to that typically achieved with sulphur cure. In order to bring sulphur-like properties into peroxide cured articles, a series of new co-agents has been developed as described in this chapter. These novel co-agents are analogous to already existing commercially available co-agents, but contain sulphur atoms in their molecular structure. Bismethacrylamide, bisacrylamide, biscitraconimide and bismaleimide co-agents have been synthesised and tested. During the peroxide vulcanisation process the co-agent will incorporate into the polymer network and in that way the sulphur contained in the co-agent becomes part of the network. The bismethacrylamide and the biscitraconimide containing a monosulphide in the bridging chain and the bismaleimide with a disulphide in the bridging chain give remarkably improved properties. Typical good properties of sulphur cured articles combined with the good properties of peroxide cured articles are obtained. Therefore, they provide an excellent overall performance when compared with commercially available co-agents.

[#]The work described in this chapter has been filed for a patent[1]

4.1 INTRODUCTION

As explained in Chapter 2, the crosslink structure of a rubber vulcanisate determines to a large extent its ultimate mechanical and dynamical properties.[2, 3] For instance, the excellent high temperature properties and relatively poor dynamic properties of peroxide vulcanisates are inherent to the crosslink structure formed: rigid covalent C-C bonds. In sulphur vulcanisation, the crosslinks consist of sulphur bridges of various lengths. Because of this fact, the thermal stability of sulphur vulcanisates is relatively poor, especially when large amounts of polysulphidic crosslinks are present. However, the nature of the sulphidic crosslinks is also the reason for the excellent dynamic and high tensile properties.

In Chapter 3 it was reported how the use of co-agents in peroxide vulcanisation significantly boosts the peroxide efficiency and improves the mechanical properties of the vulcanisates.[2, 4-11] This is mainly due to suppression of inefficient side reactions and incorporation of the co-agents into the polymer network, which has been proven, as explained in Chapter 2.[3, 4, 12]

Another way to improve the dynamic and mechanical properties of peroxide vulcanisates is to add some elemental sulphur to the formulation, as also explained in Chapter 2.[13-15] It was reported that the addition of small amounts of sulphur as co-agent in peroxide cure gives rise to the formation of sulphur bridges, which indeed results in a slight improvement of the dynamic and mechanical properties of the vulcanisates.[16, 17] However, next to a repulsive odor and staining of the vulcanisates, high temperature properties were worsened.[14] Therefore, a different solution should be sought in order to improve the properties of peroxide vulcanisates without compromising the properties which are already good in peroxide cured articles.

A synergistic combination between peroxide and sulphur cure might be achieved if it is possible to obtain a network which contains C-C crosslinks, to provide the thermal stability, and at the same time mono- or disulphidic crosslinks, to provide the good tensile strength, elongation at break and moduli. A possible way to modify a peroxide network in order to achieve such a synergism is via the co-agent. Since it is known that the co-agent incorporates into the polymer network during vulcanisation, it is possible to modify the network by tailoring the co-agent structure.

In the present chapter a series of new co-agents are synthesised and tested in peroxide cure of ethylene propylene polymethylene (EPM) rubber. These novel co-agents are analogous to commercially available co-agents, yet they have mono- or disulphidic moieties incorporated in their structure. The objective of the use of such co-agents is to achieve a network, in which the co-agent covalently bonds to the polymer chains during vulcanisation and in this way generates crosslinks which contain one or two sulphur atoms. Those sulphur containing crosslinks will help to improve certain mechanical properties, to raise them to the level of sulphur cured articles. Besides those sulphur containing crosslinks via the co-agent, C-C crosslinks are also formed, which will provide good high temperature performance. The ultimate aim is therefore to achieve a synergistic combination of peroxide and sulphur cure.

4.2 EXPERIMENTAL

Materials - A masterbatch was prepared at DSM Elastomers B.V., the Netherlands, consisting of ethylene propylene polymethylene rubber from DSM (EPM Keltan 13, Mooney viscosiy ML(1+4)100°C of 46, containing 56% ethylene and 44% propylene), carbon black N-550 obtained from Cabot Corp., stearic acid obtained from Aldrich and paraffinic oil Sunpar 150 obtained from Sun Oil Cie.

Dicumyl peroxide (DCP, Perkadox BC-40 Bpd, 40% pure) was obtained from Akzo Nobel. The co-agents N,N'-m-phenylenedimaleimide (BMI-MP), N,N'-p-phenylenedimaleimide (BMI-PP), triallylcyanurate (TAC) and ethylene dimethacrylate (EDMA) were purchased from Acros.

Dichloromethane, toluene, dioxane and triethylamine were purchased from Biosolve B.V. Methacryloyl chloride (97% pure), acryloyl chloride (96% pure), bis(4-aminophenyl) disulphide (99% pure), 4,4'-thiodianiline (99% pure) and sodium chloride (98% pure) were purchased from Aldrich. Acetic acid (glacial), hydrochloric acid (37%), sodium chloride, magnesium sulphate and acetic anhydride were purchased from Merk. Maleic anhydride was purchased from J.T. Baker. Aniline, sodium acetate and deuterated chloroform were purchased from Acros. Citraconic anhydride was kindly provided by Flexsys B.V.

Characterisation of synthesised co-agents – Melting points were measured on a Stuart Melting point Apparatus, SMP3.
^{1}H-NMR spectra were recorded on a Varian Unity 300 MHz system at 25°C. The purity of the synthesised co-agents was calculated from the integration in the ^{1}H-NMR spectra, according to Equation 4.1.

$$\frac{In^{product} \times Mw^{product}}{In^{product} \times Mw^{product} + \sum (In^{impurity} \times Mw^{impurity})} \times 100\% \qquad (4.1)$$

where:
In = Integration of a proton;
Mw = Molecular weight of a species.

Mixing - The composition of the masterbatch is given in Table 4.1. The compounds were mixed in a Banbury tangential mixer of 70 liters, with a fill factor of 74%. The mixing procedure is described in Chapter 3.

Table 4.1 Masterbatch formulation.

Material	Concentration (phr)
EPM	100
Carbon Black	60
Stearic Acid	1
Paraffinic Oil	45

Co-agent and peroxide were added to 206 phr of masterbatch on a Schwabenthan two roll mill (friction 1:1.22, temperature 40°C, mixing time 10 minutes).

Characterisation and Vulcanisation - The cure characteristics of the compounds were measured at 160°C using a torsional dynamic rheometer, RPA 2000 from Alpha Technologies. Delta torque, extent of crosslinking or cure state is the maximum torque (MH) minus the minimum torque (ML). Scorch time (t_{s2}) is taken as the time to reach 2% of the delta torque above minimum. This is not exactly in

agreement with the definition of scorch time as mentioned in ISO 6502: "Rubber measurement of vulcanisation characteristics with rotorless curemeters", but was implemented in the present form in the software of the RPA 2000. Optimum cure time (t_{90}) is the time to reach 90% of the delta torque above minimum. Cure rate is taken as the slope of the cure curve in the rheogram between t_{s2} and t_{90}.

The compounds were vulcanised by compression moulding in a Wickert laboratory press WLP 1600/5*4/3 at 100 bar and 160°C, for 2 times t_{90}.

Determination of Mechanical Properties – Mechanical properties of the vulcanisates were measured on a Zwick tensile tester, according to the conditions defined in ISO 37, on dumb-bell shaped specimens of Type 2, with a nominal rate of the traverse of the moving grip of 500 mm/min. For the tensile measurements of aged samples, the dumb-bells were aged in an air circulated oven at 150°C for different times.

Hardness of the vulcanised materials was measured using the Shore A scale with vulcanised samples of 5.8 mm thickness.

Compression set was measured using compression moulded samples in the form of circular cylinders with a height of 5.8 mm and a diameter of 10 mm. Six specimens were tested for each different sample. The exact height of the samples was always measured before testing. The samples were placed between two parallel plates and then compressed 25 percent of their initial height. Samples were kept compressed for 24 hours at two different temperatures: 23 and 70°C, after which the pressure was released. The samples were given 30 minutes time to relax and after that the height was measured again. The compression set was calculated using Equation 4.2.

$$\text{Compression Set} = \frac{h_0 - h_2}{h_0 - h_1} * 100\% \qquad (4.2)$$

where:
h_0 = initial height of the sample;
h_1 = the height of the sample during compression;
h_2 = the height of the sample after unloading and relaxation for a specific time.

A compression set of 0% means an ideal rubber that totally recovers to its original shape. If the compression set is 100% it indicates the absence of any elasticity at all.

4.3 SYNTHESIS OF NOVEL SULPHUR-CONTAINING CO-AGENTS

4.3.1 4,4'-(bismethacrylamide) diphenyl disulphide (BMA-PPS2)

BMA-PPS2 was synthesised through reaction of methacryloyl chloride and bis(4-aminophenyl) disulphide, as shown in Figure 4.1. Triethylamine was used to remove hydrochloric acid from the reaction solution by salt formation. Dichloromethane was used as solvent.[18]
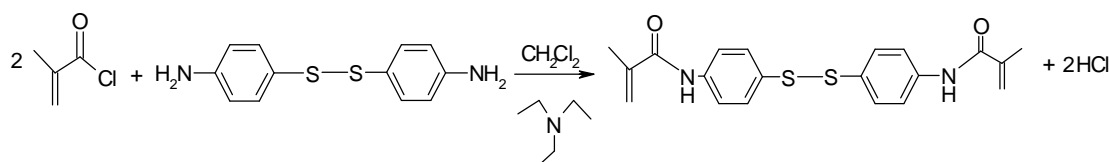

Figure 4.1 – Synthesis of 4,4'-(bismethacrylamide) diphenyl disulphide.

A solution of methacryloyl chloride in dichloromethane was slowly added, through a dropping funnel, to a three-necked flask containing triethylamine and dichloromethane. Simultaneously, through a different dropping funnel, a solution of bis(4-aminophenyl) disulphide in dichloromethane was added to the three-necked flask. The temperature was kept below 5°C during the addition, by means of an ice-salt bath. After the reactants had been added, the ice-salt bath was removed and the reaction was allowed to proceed for 16 hours at room temperature.

To separate the product from the reaction media two extractions were necessary. The first extraction was performed with a hydrochloric acid solution (pH=5) and the second with a sodium chloride solution (5%). As a result of these extractions a hydrochloride salt of the remaining triethylamine was formed and transfered to the water phase. After the extractions, the organic phase, containing the product, was dried with magnesium sulphate and filtered to eliminate insoluble impurities. The product was obtained after evaporation of the solvent on a rotatory evaporator and by recrystallisation from toluene.

The product obtained before recrystallisation was a yellow powder. After recrystallisation a light yellow coloured amorphous powder was obtained. The purity of the final product, calculated according to Equation 4.1, was 96%. The melting point of BMA-PPS2 was in a range from 163°C to 164.7°C. ^{1}H-NMR (CDCl$_3$): δ2.05 (s, 6H), δ5.45 (d, 2H), δ5.80 (d, 2H), δ7.45-7.65 (m, 8H).

4.3.2 4,4'-(bismethacrylamide) diphenyl monosulphide (BMA-PPS1)

BMA-PPS was synthesised through reaction of methacryloyl chloride and 4,4'-thiodianiline, as shown in Figure 4.2. This reaction, and work up of the product, were performed according to the same procedure as that of BMA-PPS2, described in paragraph 4.3.1.[18]
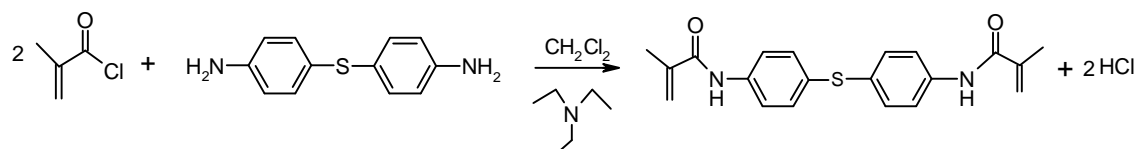
Figure 4.2 – Synthesis of 4,4'-(bismethacrylamide) diphenyl monosulphide.

The product obtained was a grey powder with a purity of 98%, calculated according to Equation 4.1. The melting point range measured was from 195.3°C to 197.8°C. ^{1}H-NMR (CDCl$_3$) δ2.00 (s, 6H), δ5.40 (d, 2H), δ5.70 (d, 2H), δ7.25-7.45 (m, 8H).

4.3.3 4,4'-(bisacrylamide) diphenyl disulphide (BA-PPS2)

BA-PPS2 was synthesised through reaction of acryloyl chloride and bis(4-aminophenyl) disulphide, as shown in Figure 4.3. Triethylamine was used to remove hydrochloric acid from the reaction solution by formation of a soluble salt. Dichloromethane was used as solvent.[18]
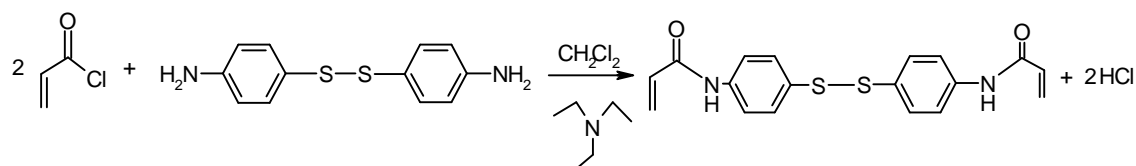

Figure 4.3 – Synthesis of 4,4'-(bisacrylamide) diphenyl disulphide.

The procedure carried out for this reaction was equivalent to that explained in paragraph 4.3.1 for BMA-PPS2. However, in this case the product precipitated from the reaction media due to its poor solubility and stayed in suspension in the water phase. A yellow coloured powder was obtained, after the water was removed by filtration. The purity of the product calculated according to Equation 4.1 gave a value of 92%. The melting point of the product was 189.5°C. ^{1}H-NMR (DMSO): δ5.80 (d, 2H), δ6.30 (d, 2H), δ6.55 (t, 2H), δ7.45-7.85 (m, 8H).

4.3.4 4,4'-(bisacrylamide) diphenyl monosulphide (BA-PPS1)

BA-PPS1 was synthesised through reaction of acryloylchloride and 4,4'-thiodianiline, as shown in Figure 4.4. Triethylamine was again used to remove hydrochloric acid from the reaction solution and dichloromethane was used as a solvent. The procedure of this reaction was analogous to that of BA-PPS2 described in paragraph 4.3.1.[18]

The product obtained was a yellow powder with a melting point of 203.9°C. The purity of the product was calculated according to Equation 4.1 and gave a value of 96%. ^{1}H-NMR (DMSO): δ5.75 (d, 2H), δ6.25 (d, 2H), δ6.42 (t, 2H), δ7.45-7.85 (m, 8H).
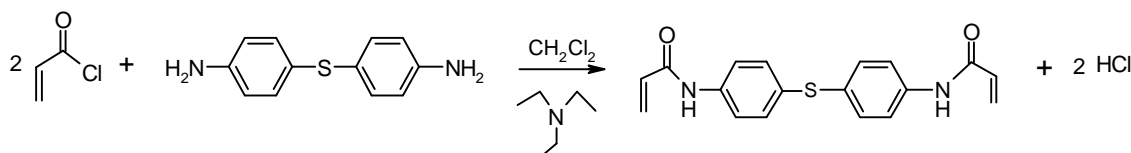
Figure 4.4 – Synthesis of 4,4'-(bisacrylamide) diphenyl monosulphide.

4.3.5 4,4'-(biscitraconimide) diphenyl disulphide (BCI-PPS2)

BCI-PPS2 was synthesised from citraconic anhydride and bis(4-aminophenyl) disulphide, as shown in Figure 4.5, according to the procedure described in literature.[19] Acetic acid was used as solvent in this reaction.
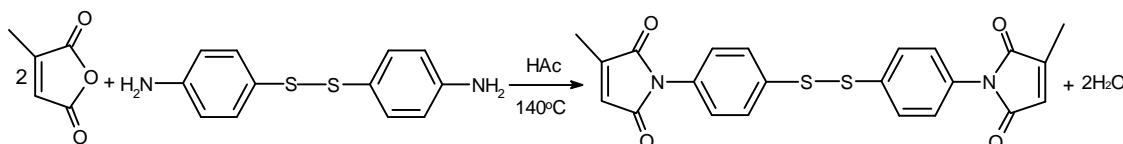
Figure 4.5 – Synthesis of 4,4'-(biscitraconimide) diphenyl disulphide.

Citraconic anhydride was dissolved in acetic acid in a three-necked flask at room temperature. The temperature was then increased to 80°C, while stirring under nitrogen atmosphere. Bis(4-aminophenyl) disulphide was slowly added by means of an addition funnel at 80°C. After the addition, the temperature was increased to 110°C and the reaction was allowed to proceed at this temperature for at least 3 hours. A dean-stark trap with a condenser was used to remove the azeotrope formed of water and acetic acid from the reaction system. After evaporation of the solvent on a rotatory evaporator a light yellow product was obtained. Purity was calculated according to Equation 4.1, as 95 %. The melting range of the product was from 149.7°C to 153.9°C. ^{1}H-NMR (CDCl$_3$) δ2.20 (s, 6H), δ6.45 (s, 2H), δ7.30-7.45 (m, 8H).

4.3.6 4,4'-(biscitraconimide) diphenyl monosulphide (BCI-PPS1)

BCI-PPS1 was synthesised through reaction of citraconic anhydride and 4,4'-thiodianiline, as shown in Figure 4.6. Acetic acid was used as solvent. The procedure of this reaction was analogous to that of BCI-PPS2 described in paragraph 4.3.5. The product was obtained, after evaporation of the solvent on a rotatory evaporator, as a green powder.
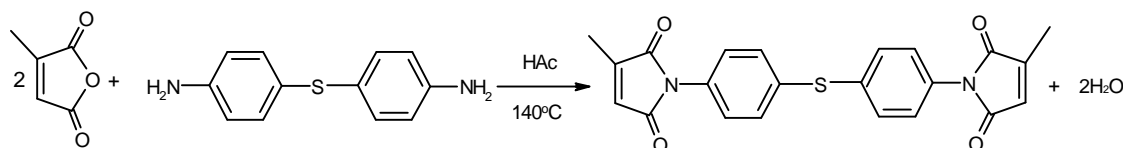

Figure 4.6 – Synthesis of 4,4'-(biscitraconimide) diphenyl monosulphide.

The NMR spectrum showed that the product was clean and that there was no residual solvent left. Little impurities contained in the product came from the residual reactant: 4,4'-thiodianiline. The purity was calculated according to Equation 4.1 as 91%. The melting range of the product was from 139.7°C to 146.8°C. ^{1}H-NMR (CDCl$_3$) δ2.10 (s, 6H), δ6.40 (s, 2H), δ7.25-7.50 (m, 8H).

4.3.7 4,4'-(bismaleimide) diphenyl disulphide (BMI-PPS2)

BMI-PPS2 was synthesised through reaction between bis(4-aminophenyl) disulphide and maleic anhydride in a two-step synthesis, as shown in Figure 4.7. First the reactants gave the maleamic acid and after ringclosure the bismaleimide product was obtained.[20]

In the first step dioxane was used as solvent. A solution of bis(4-amiophenyl) disulphide in dioxane was slowly added at room temperature to a solution of maleic anhydride in dioxane. After the addition, the mixture was stirred for one hour at room temperature. During that time a yellow precipitate appeared. The bismaleamic acid was obtained after dioxane was evaporated on a rotatory evaporator.

In the second step, sodium acetate and acetic anhydride were added to the bismaleamic acid and the mixture was refluxed during 3 hours. Afterwards, the warm reaction mixture was poured into water. The BMI-PPS2 precipitated and was separated from the water by filtration. The product was then dried in a vacuum oven at 80°C. The final product was a yellow powder with a melting point range from 179 to 182°C. Due to the absence of an NMR signal from impurities in the product, its purity was taken as 100% by NMR. ^{1}H-NMR (CDCl$_3$) δ6.85 (s, 4H), δ7.35-7.60 (m, 8H).
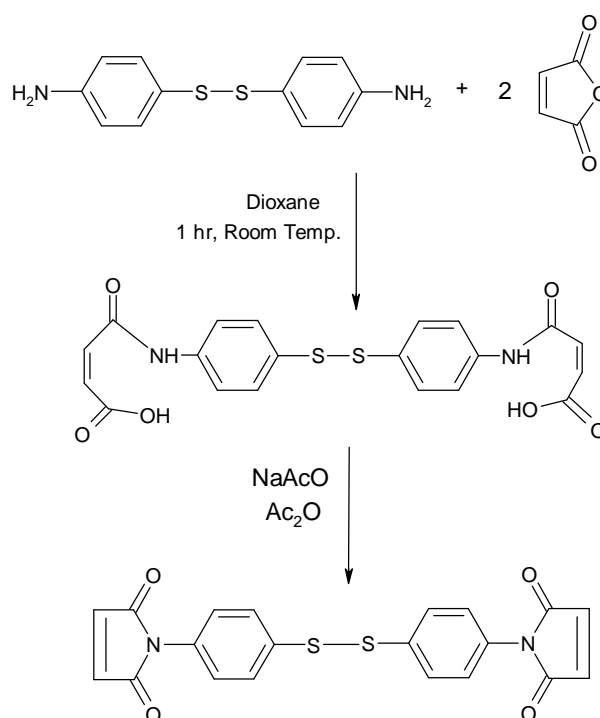
Figure 4.7 – Synthesis of 4,4'-(bismaleimide) diphenyl disulphide.

4.3.8 4,4'-(bismaleimide) diphenyl monosulphide (BMI-PPS1)

BMI-PPS1 was synthesised in the same manner as BMI-PPS2, as explained in the previous paragraph, by a two-step synthesis with bismaleamic acid as intermediate. In case of BMI-PPS1, 4,4'-thiodianiline was used instead of bis(4-aminophenyl) disulphide, as shown in Figure 4.8. Due to the absence of an NMR signal from identified impurities in the product, its purity could not be calculated using Equation 4.1. The final product was a yellow powder with a melting range from 155 to 165°C. The purity of the product was taken as 100% based on the NMR spectrum. ^{1}H-NMR (CDCl$_3$) δ7.20 (s, 4H), δ7.35-7.45 (m, 8H).
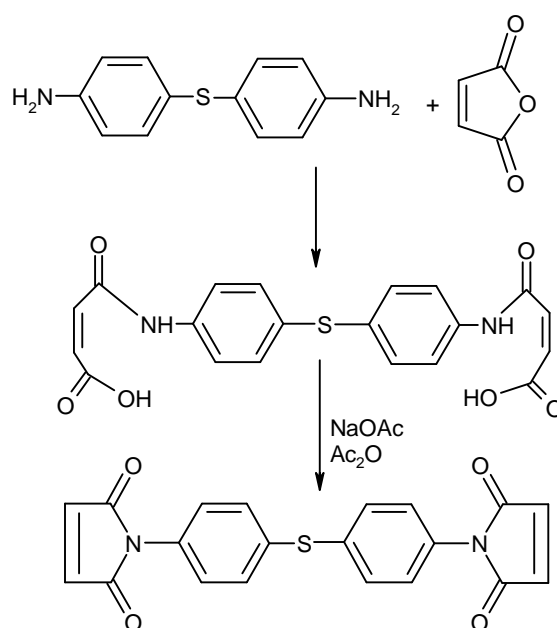
Figure 4.8 – Synthesis of 4,4'-(bismaleimide) diphenyl monosulphide.

4.4 RESULTS AND DISCUSSION

The newly synthesised co-agents were used in a peroxide cure formulation of EPM rubber, in order to evaluate their influence on the vulcanisation reaction as well as on the final properties of the material. Their performance was compared with that of their commercial counterparts, which were extensively studied in Chapter 3 of this thesis.

4.4.1 Sulphur-containing co-agents analogous to methacrylate and acrylate type co-agents

Formulations according to Table 4.2 were tested. The new sulphur-containing co-agents were compared to the commercially available ethylene dimethacrylate (EDMA). Since the different co-agents have different molecular weights, in order to compare them in terms of functionality, the same molar equivalent amount was used in all cases. In this way a fair comparison, independent of molecular weight, can be carried out amongst the different co-agents. The amount in phr of co-agents used in the formulation was calculated in order to have in every case 30 mequivalents of co-agent functionality, viz. methacrylate, methacrylamide or acrylamide groups. The curemeter rheograms obtained for the different samples are plotted in Figure 4.9.

Table 4.2 Formulations tested for methacrylamide and acrylamide sulphur-containing co-agents and EDMA. Amounts in phr.

Component	A	B	C	D	E
Masterbatch	206	206	206	206	206
DCP	6	6	6	6	6
EDMA	3	0	0	0	0
BMA-PPS2	0	5.8	0	0	0
BMA-PPS1	0	0	5.3	0	0
BA-PPS2	0	0	0	5.3	0
BA-PPS1	0	0	0	0	4.9
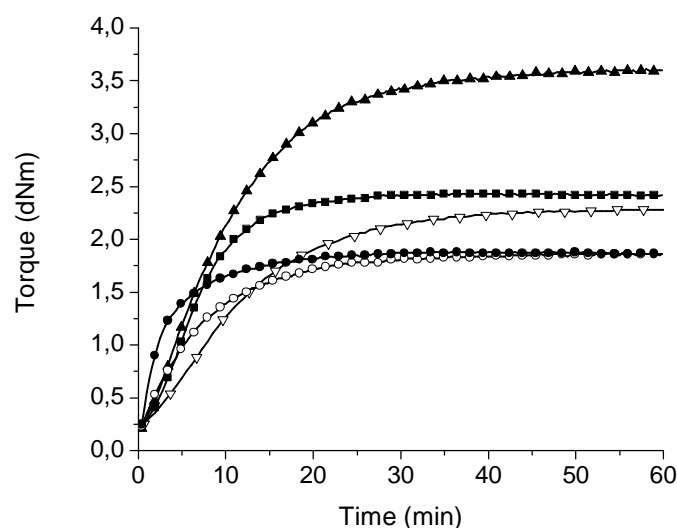
Figure 4.9 – Rheograms of samples with sulphur-containing methacrylamide and acrylamide co-agents and EDMA. (■): EDMA; (∇): BMA-PPS2; (▲): BMA-PPS1; (o): BA-PPS2; (●): BA-PPS1.

The rheograms clearly show that the only sulphur-containing co-agent that improves the cure state is BMA-PPS1, which provides a torque level significantly higher than EDMA. BMA-PPS2 leads to a torque level almost equal to that of EDMA, yet with a slower cure rate. Both acrylamide co-agents: BA-PPS2 and BA-PPS1, result in torque levels lower than that of EDMA.
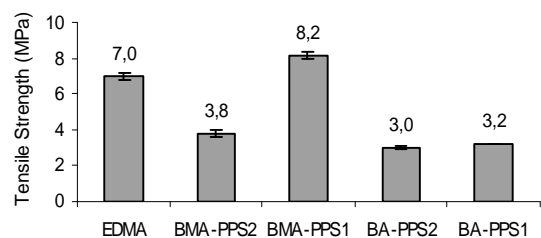

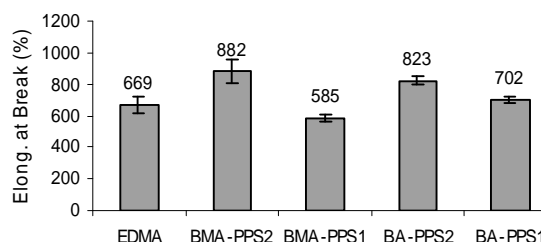**Figure 4.10** – Tensile strength obtained with sulphur-containing methacrylamide and acrylamide co-agents compared to the commercial co-agent EDMA.

Figure 4.11 – Elongation at break obtained with sulphur-containing methacrylamide and acrylamide co-agents compared to the commercial co-agent EDMA.
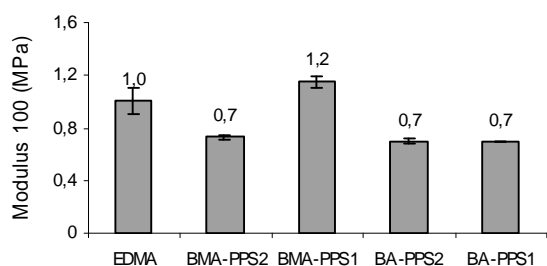
Figure 4.12 – Modulus at 100% elongation obtained with sulphur-containing methacrylamide and acrylamide co-agents compared to the commercial co-agent EDMA.
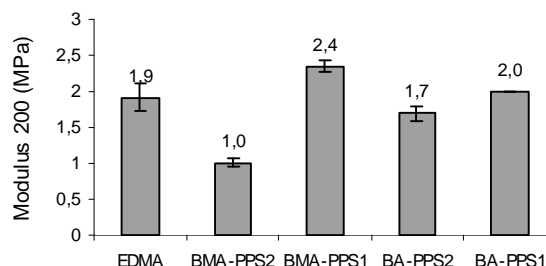
Figure 4.13 – Modulus at 200% elongation obtained with sulphur-containing methacrylamide and acrylamide co-agents compared to the commercial co-agent EDMA.

The tensile properties measured for the different samples are shown in Figures 4.10 to 4.13. It is very clear from the tensile properties that BMA-PPS1 offers the best performance of all co-agents tested. It leads to a higher tensile strength and higher moduli than the commercial EDMA, and only to a slightly lower elongation at break. The two acrylamide sulphur-containing co-agents perform rather similar; however, the monosulphide is slightly better. They lead to a much lower tensile strength than EDMA, yet the moduli obtained with these co-agents are only slightly reduced when compared to EDMA.

The hardness of the samples was measured using the Shore A scale. The results obtained are shown in Figure 4.14. The highest hardness value was found for the sample containing BMA-PPS1, followed by EDMA. The rest of co-agents lead to lower values of hardness.
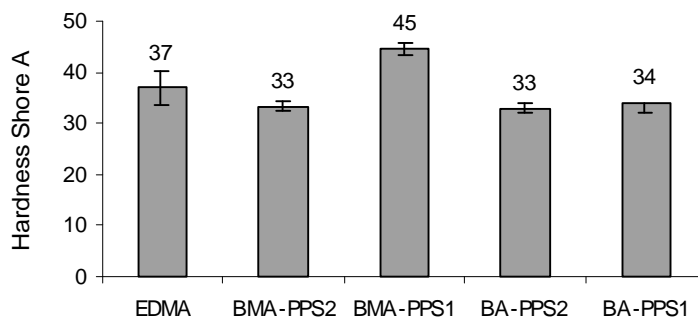
Figure 4.14 – Hardness of samples with sulphur-containing methacrylate and acrylate co-agents compared to the commercial co-agent EDMA

Compression sets of the samples containing the new co-agents and EDMA were measured at 23 and at 70°C. In Figure 4.15 the compression set at room temperature is plotted. The best compression set is found for BMA-PPS1, which is even lower than that of the commercial EDMA. The rest of sulphur containing co-agents gives rise to higher compression set values. At 70°C the results show the same tendency as found at 23°C: BMA-PPS1 provides the best compression set, followed by EDMA, BMA-PPS2, BA-PPS1 and BA-PPS2, as can be seen in Figure 4.16.
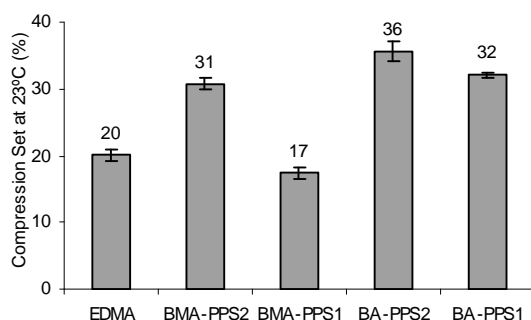
Figure 4.15 – Compression set at 23°C of samples with sulphur-containing methacrylate and acrylate co-agents and EDMA.
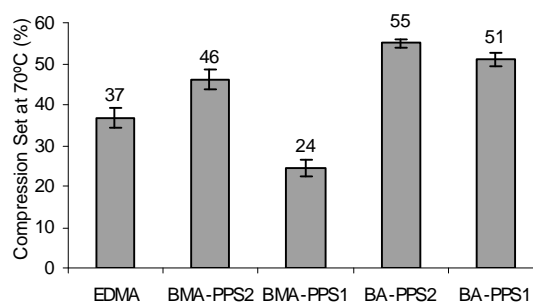
Figure 4.16 – Compression set at 70°C of samples with sulphur-containing methacrylate and acrylate co-agents and EDMA.

In view of such a remarkable improvement in the properties obtained by using BMA-PPS1 as co-agent, especially the improvement in compression sets, the high temperature properties, viz. ageing, of this sample were also measured. Also the ageing performance of the sample containing EDMA was measured, in order to compare it with the new co-agent. Figure 4.17 shows the stress-strain curves measured for EDMA, after several days of ageing at 150°C. As can be observed, the tensile properties deteriorate quite linearly with ageing time. On the other hand, the sample which contains the new co-agent, BMA-PPS1, retains the tensile properties significantly better with ageing time, as can be seen in Figure 4.18. From 1 to 3 days of ageing, the stress-strain curves overlap; only a small decrease in tensile strength and elongation at break is observed. Between 4 and 7 days the stress-strain curve is also maintained. Only after 10 days a larger decrease in tensile strength is observed, yet much less than that obtained for the sample containing EDMA after 10 days of ageing.
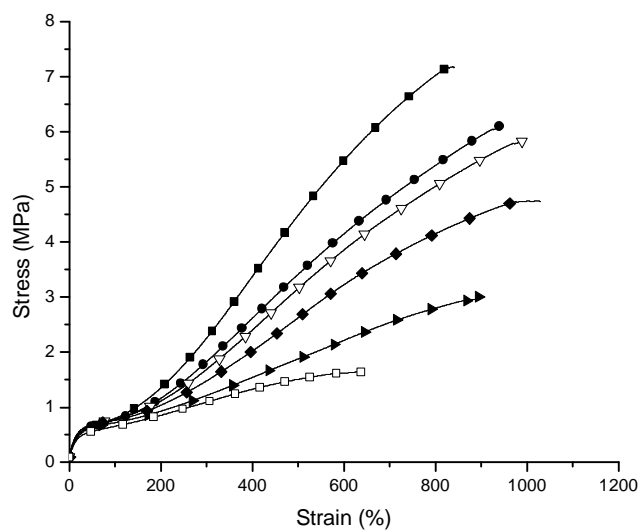
Figure 4.17 – Stress-strain curves measured for the sample containing EDMA after ageing several days at 150°C. (■): 0 days; (●): 1 day; (∇): 3 days; (♦): 4 days; (►): 7 days; (□): 10 days.
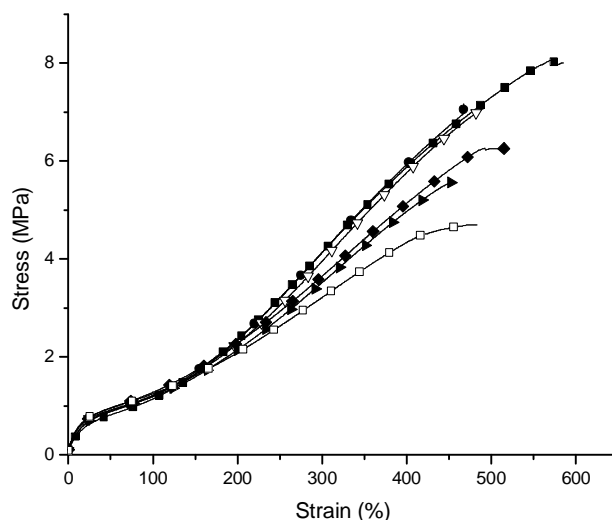

Figure 4.18 – Stress-strain curves measured for the sample containing BMA-PPS1 after ageing several days at 150°C. (■): 0 days; (●): 1 day; (∇): 3 days; (♦): 4 days; (►): 7 days; (□): 10 days.

It can be concluded that of the novel sulphur-containing co-agents of the methacrylamide and acrylamide types, the monosulphides perform better than the disulphides, as can be noticed when comparing the performance of BMA-PPS2 vs. BMA-PPS1 and BA-PPS2 vs. BA-PPS1.

For the methacrylamide co-agents the cure state reached in the rheometer is at the same level or even higher than that for EDMA, while for acrylamide co-agents it is lower in both cases. The mechanical properties measured, i.e. tensile strength, compression set, are also better for the methacrylamide than for the acrylamide co-

agents. The best overall performance is achieved with BMA-PPS1, which leads to a higher torque level and mechanical properties than any of the other co-agents tested. This effect is quite remarkable, since it is well known from literature that, when tensile properties are improved for peroxide cure by incorporation of sulphur, compression set and high temperature properties are dramatically worsened; see Chapter 2.[13, 14, 17, 21-24] In the case of BMI-PPS1 sulphur is incorporated via the co-agent, therefore in a more efficient manner, which could explain why the high temperature properties are maintained, and even improved, while at the same time the tensile properties improve.

It is evident that BMA-PPS1 provides a synergistic combination of peroxide and sulphur cure. It improves mechanical properties such as tensile strength, typically superior for sulphur cured articles, while at the same time typically good properties for peroxide cure, such as compression set at high temperature and ageing, are not only maintained but even improved.

However, the effect achieved by use of BMA-PPS1 is not reached with the disulphide version of this co-agent, BMA-PPS2, or by the acrylamide type co-agent BA-PPS1. A possible reason why the acrylamide co-agents lead to a lower cure state and inferior mechanical properties than the methacrylamides could be a strong tendency of acrylamides to homopolymerise during vulcanisation. If homopolymerisation takes place to a large extent, co-agent domains will be formed and the sulphur linkages will be concentrated in the co-agent domains. Depending on the mixing procedure and the different reasons explained in Chapter 2, an interpenetrating network of homopolymerised co-agent and rubber could also be obtained. Either in the case of co-agent domains or of an interpenetrating network, the influence of the sulphur linkages on the mechanical properties will be limited, since the sulphur is only built into the co-agent network. In the case of methacrylamide co-agents, because of a lower tendency to homopolymerise, the co-agent molecules will be more homogeneously distributed within the rubber network, grafted between polymer chains, forming short sulphur-containing crosslinks, which have a positive influence on the mechanical properties.

4.4.2 Sulphur-containing co-agents analogous to a maleimide type co-agent
Formulations according to Table 4.3 were tested. The new sulphur-containing co-agents were compared to the commercially available N,N'-m-phenylenedimaleimide (BMI-MP). Since the different co-agents have a different molecular weight the same molar equivalent amount of functionality was used in all cases. The amount in phr of co-agents used in the formulation was calculated to correspond in each case with 30 mequivalents of co-agent functionality, viz. maleimide or citraconimide groups. The rheograms obtained for the different samples are plotted in Figure 4.19.

Table 4.3 Formulations tested for bismaleimide and biscitraconimide sulphur-containing co-agents and BMI-MP. Amounts in phr.

Component	1	2	3	4	5
Masterbatch	206	206	206	206	206
DCP	6	6	6	6	6
BMI-MP	4	0	0	0	0
BMI-PPS2	0	6.1	0	0	0
BMI-PPS1	0	0	5.6	0	0
BCI-PPS2	0	0	0	6.5	0
BCI-PPS1	0	0	0	0	6.1
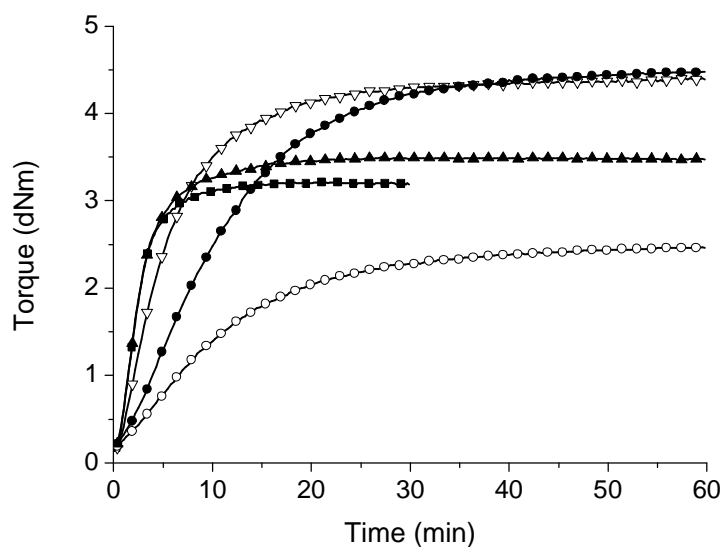
Figure 4.19 – Rheograms of samples with sulphur-containing bismaleimide and biscitraconimide co-agents and BMI-MP. (■): BMI-MP; (∇): BMI-PPS2; (▲): BMI-PPS1; (o): BCI-PPS2; (●): BCI-PPS1.

From the rheograms it can clearly be seen that all new co-agents, except BCI-PPS2 improve the torque level as indicative for crosslink density compared to that obtained with the commercial co-agent BMI-MP. BMI-PPS1 leads to a slight improvement, while BMI-PPS2 and BCI-PPS1 lead to torque levels remarkably higher compared to BMI-MP.
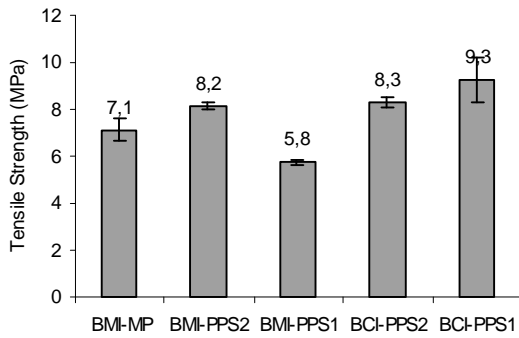
Figure 4.20 – Tensile strength obtained with sulphur-containing maleimide and citraconimide co-agents compared to the commercial co-agent BMI-MP.
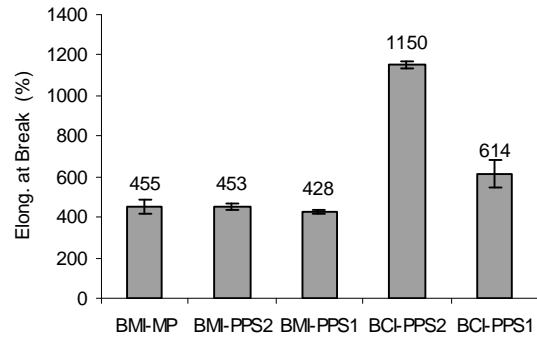
Figure 4.21 – Elongation at break obtained with sulphur-containing maleimide and citraconimide co-agents compared to the commercial co-agent BMI-MP.
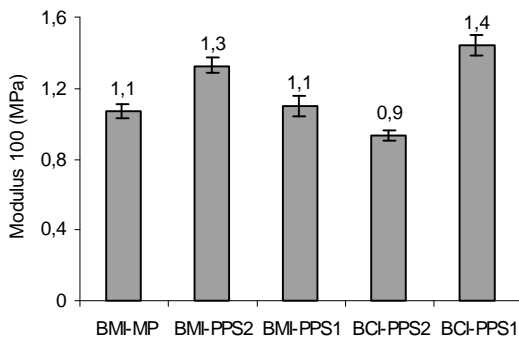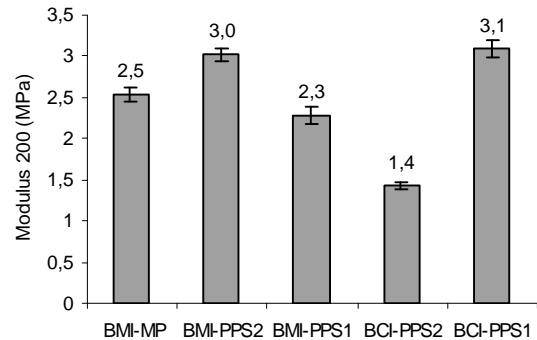

Figure 4.22 – Modulus at 100% elongation obtained with sulphur-containing maleimide and citraconimide co-agents compared to the commercial co-agent BMI-MP.

Figure 4.23 – Modulus at 200% elongation obtained with sulphur-containing maleimide and citraconimide co-agents compared to the commercial co-agent BMI-MP.

The tensile properties achieved for the samples containing these new co-agents are plotted in Figures 4.20 to 4.23. As could be expected already from the rheogram, the worst performance is obtained when BCI-PPS2 is used as co-agent: the moduli values are remarkably lower than for the rest of the co-agents. Neither a large improvement nor a dramatic deterioration in properties can be observed when using BMI-PPS1: tensile strength and moduli are decreased compared to BMI-MP. The best properties are achieved when using BMI-PPS2 and BCI-PPS1: these two co-agents give higher tensile strength, similar elongation at break and better moduli than BMI-MP.

Because of their good performance, these two co-agents were further tested in comparison with BMI-MP. In Figure 4.24 the hardness measured for the samples containing the new co-agents BMI-PPS2, BCI-PPS1 vs. BMI-MP is plotted. It is very clear, that the new co-agents give rise to harder vulcanised materials than BMI-MP, indicative of a higher crosslink density as well, next to the higher torque level obtained with the rheometer.
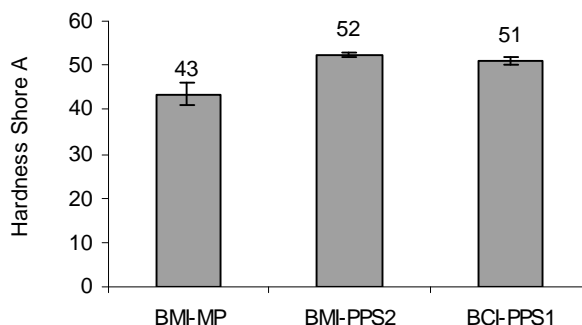
Figure 4.24 – Hardness of samples with the new sulphur-containing BMI-PPS2 and BCI-PPS1 co-agents compared to the commercial co-agent BMI-MP.

The compression sets for the samples containing these co-agents were tested at room temperature and at 70°C. Figure 4.25 shows the results obtained at room temperature. Both sulphur-containing co-agents improve compression set at room temperature compared to the commercial co-agent BMI-MP. The best performance is obtained for BMI-PPS2. At 70°C the best compression set is achieved with BCI-PPS1, as shown in Figure 4.26, but still both co-agents perform better than the commercial BMI-MP.

As was also observed for the methacrylamides in the previous paragraph, these results are again rather remarkable, since tensile properties and compression set are improved at the same time by incorporation of sulphur moieties into the co-agent structure. As already explained in Chapter 2, several attempts found in literature to incorporate sulphur into a peroxide crosslink network resulted in improved tensile properties, but at the expense of compression set and ageing performance. The ageing properties of the sample containing BMI-PPS2 were also tested in order to find out whether the sulphur, contained in the co-agent, would have an influence on ageing. In any case, the influence of sulphur on the ageing of BMI-PPS2 can be expected to be more outspoken than for BCI-PPS1, since monosulphide links are more thermally stable than a disulphide. Therefore, if an effect from the sulphur moieties within the co-agents can be found, it would be expected to be more negative for BMI-PPS2 than for BCI-PPS1.
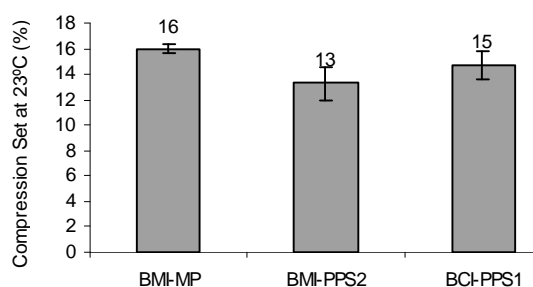

Figure 4.25 – Compression set at 23°C obtained with BMI-MP, BMI-PPS2 and BCI-PPS1
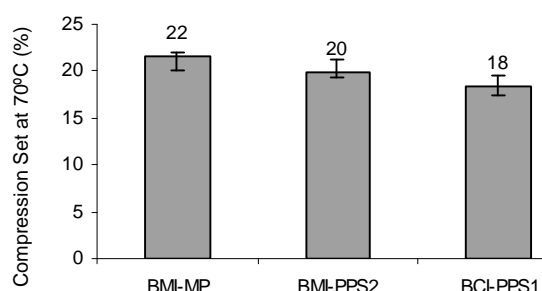

Figure 4.26 – Compression set at 70°C obtained with BMI-MP, BMI-PPS2 and BCI-PPS1

In Figure 4.27 the stress-strain curves of the BMI-MP containing sample aged during several days at 150°C are plotted. A clear decrease in tensile strength with

ageing time can be observed. From 5 to 10 days the lines are rather overlapping, but the tensile strength and elongation at break further decrease with time.
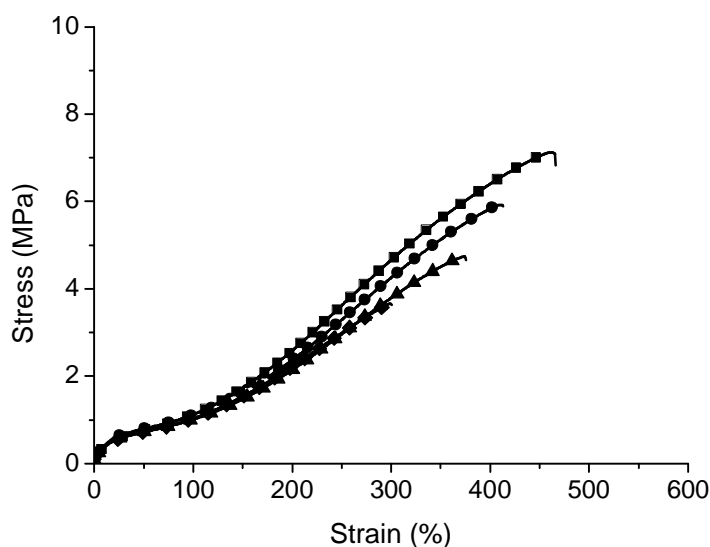

Figure 4.27 – Stress-strain curves obtained for the sample with BMI-MP as co-agent at 150°C for several days. (■): 0 days; (●): 3 days; (▲): 5 days; (♦): 7 days; (★): 10 days.

In Figure 4.28 the ageing behaviour of the sample containing BMI-PPS2 is plotted. From 0 to 3 days no major effect is found. However, from 3 to 5 days there is a notable decrease in tensile strength, while elongation at break also decreases. From 5 to 7 days the properties are maintained. From 7 to 10 days of ageing the tensile strength is well maintained, yet the elongation at break reduced.
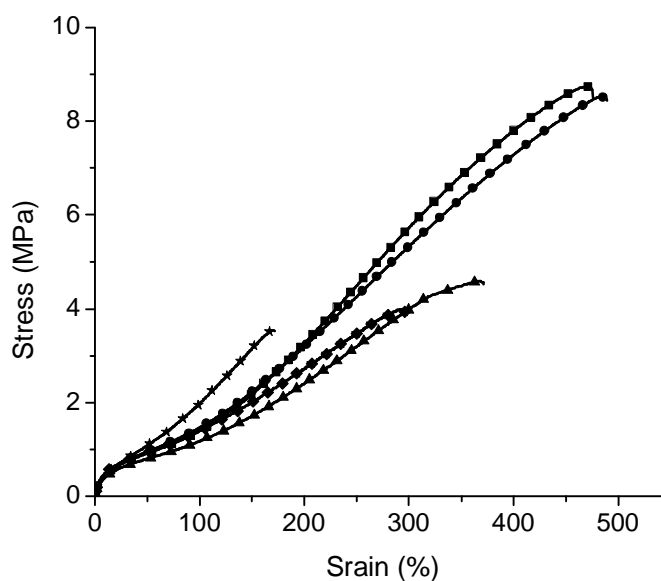

Figure 4.28 – Stress-strain curves obtained for the sample with BMI-PPS2 as co-agent at 150°C for several days. (■): 0 days; (●): 3 days; (▲): 5 days; (♦): 7 days; (★): 10 days.

In view of these results it may be concluded that both co-agent systems, BMI-MP and BMI-PPS2, lead to similarly decreased tensile properties after being aged at elevated temperature. Whether those changes are just typical for a normal peroxide ageing process, or whether sulphur has an extra influence for BMI-PPS2 is not very clear from the data. If sulphur has a negative influence, it is rather modest. In the previous paragraph, the ageing characteristics of the sulphur-containing methacrylamide co-agent clearly showed a positive influence of sulphur, but in the present case of BMI-PPS2 it does not lead to such conclusive data.

Overall, the effect of sulphur-containing bismaleimides and biscitraconimides has been found to be positive for BMI-PPS2 and BCI-PPS1, which lead to a higher cure state, tensile properties, hardness and lower, so better compression sets. BMI-PPS1 and BCI-PPS2 did not give significant improvements in material properties.

The reason why the monosulphide of the bismaleimide type co-agents does not improve properties while the disulphide does, could be attributed to a major effect of elemental sulphur released from the disulphide co-agent into the compound during vulcanisation. However, this argument contradicts the observation that the monosulphide citraconimide co-agent performs better than de disulphide of the same type. A clear explanation for these phenomena has not been found yet. The experiments were repeated several times and confirmed the observations. Therefore, further investigations are necessary in order to understand the influence of these new co-agents on the vulcanisation process, as well as on the final networks obtained.

4.5   CONCLUSIONS

A series of new sulphur-containing co-agents has been synthesised and tested in an EPM rubber formulation. These new co-agents consist of structures similar to already existing, and commercially available co-agents, but contain either one or two sulphur atoms in their bridging structure. Bismethacrylamides, bisacrylamides, biscitraconimides and bismaleimides have been synthesised.

Bismethacrylamides lead to better mechanical properties than acrylamides, when compared to EDMA. Within these co-agent types, the monosulphides provide better properties than the disulphides. Especially remarkable is the performance of BMA-PPS1, which leads to greatly improved cure state, tensile strength, moduli, hardness, compression set and ageing, compared to EDMA.

The disulphide bismaleimide co-agent BMI-PPS2 and the monosulphide biscitraconimide BCI-PPS1 have a large positive effect on the mechanical properties as well. BMI-PPS1 and BCI-PPS2 do not lead to a clear improvement. With BMI-PPS2 and BCI-PPS1 better cure state, tensile strength, moduli, hardness and compression set are obtained, compared to commercial BMI-MP.

Further studies are needed in order to fully understand the mechanistic differences in the performance of these co-agents. If these reasons could be found, more tailor-made co-agents with optimal characteristics might be synthesised to achieve ultimately even better properties.

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Chapter 5

Scorch Delay and Property Improvement in a
Peroxide/Co-agent System [#][*]

"It is not because things are difficult that we do not dare; it is because we do not dare that they are difficult."

Lucius Annaeus Seneca (ca. 4 BC–AD 65)

Traditionally used scorch retarders have been tested in the peroxide cure of EPM in the presence of several co-agents. BHT does not provide scorch delay in any case. Thiuram disulphides provide scorch delay when a bismaleimide co-agent is used. The addition of elemental sulphur to a peroxide/bismaleimide cure formulation was found to provide a slight increase in mechanical properties without affecting scorch delay. To achieve scorch delay and property improvement at the same time, a sulphur spender, DPTT, was added to the formulations of several peroxide/co-agent EPM cure systems. In case of TAC and EDMA co-agents no positive influence from the addition of DPTT to the formulation was observed. In case of the bismaleimide co-agents, BMI-MP and BMI-PP, the addition of DPTT to the formulation provides both scorch delay and property improvement.

5.1 INTRODUCTION

Scorch safety is an important issue in peroxide vulcanisation of rubber. Several attempts have been made to delay scorch of the crosslinking reaction, in order to improve scorch safety and thus improve processability. The usual solution to the peroxide scorch problem consists of the addition of a scorch retarder to the formulation. A scorch retarder is a chemical which consumes peroxy radicals in the first stages of the vulcanisation. The peroxy radicals are more prone to react with the scorch retarder than towards the polymer chain, this means that the first radicals formed are consumed until the scorch retarder is totally consumed. Due to this fact, the amount of scorch retarder is of crucial importance and is normally adjusted according to the extent of delay that is desired. Usually, very small amounts of these compounds are enough to delay the crosslinking reaction suitably. On the other hand, because of the consumption of radicals on the part of the scorch retarder, the efficiency of the crosslinking reaction is reduced. This results in a lower cure state of the product which is subsequently reflected in the final properties of the material. The ultimate properties of the vulcanisates are inferior to those obtained without the scorch retarder. To overcome this disadvantage, normally additional amounts of peroxide are added to the system to compensate for the loss of radicals during the first stages of the reaction. This obviously results in a more expensive final product. Another approach to the problem would be an increase in amount of co-agent. It has been reported that co-agents have a booster effect in peroxide vulcanisation by improving peroxide efficiency and thus final properties, i.e. by suppressing unwanted side reactions and/or leading to extra crosslink formation by co-agent bridges and co-agent domains.[2-8] Nevertheless, this would also result in a more expensive product, since the co-agent is one of the most expensive additives in the formulation.

2,6-Di-tert-butyl-4-methylphenol (BHT) has been used successfully as scorch retarder in ethylene propylene diene polymethylene rubber (EPDM) compounds[9,10] as well as in low density polyethylene (LDPE).[11] Tetramethylthiuram disulphide (TMTD) has also been found to provide scorch safety in an EPDM/tryallylcyanurate (TAC) system,[12] leading to a reasonably good cure state.

Since the use of conventional scorch retarders often results in a lower cure state and in inferior mechanical properties, research has been done to overcome this issue. A typical additive used in peroxide vulcanisation in order to improve cure state, and therefore the final properties, is elemental sulphur. Already in the early sixties Loan[13] found the addition of elemental sulphur to a peroxide system to increase tensile strength and moduli, apparently by introducing crosslinks more labile than the carbon-carbon crosslinks to ethylene-propylene rubber, thus probably sulphur crosslinks.

In an EPDM system with divinylbenzene as co-agent, sulphur was found to be an effective co-agent for peroxide cure only when used in small amounts, i.e. less than 0.2 phr. With addition of 0.15 phr of elemental sulphur to the system, Young's modulus and the rupture energy were increased remarkably, as well as the crosslink density.[14]

Manik and Banerjee studied not only the influence of sulphur in peroxide vulcanisation of Natural Rubber (NR), but they also studied the influence of conventional accelerators and zinc oxide/stearic acid in order to get some insight into the mechanism of the peroxide-accelerator-sulphur curing system.[15-17] They concluded that sulphur, zinc oxide and stearic acid do not affect the decomposition rate of dicumyl peroxide (DCP), while in the presence of accelerators this decomposition is faster. In all cases the kinetics of the decomposition of dicumyl peroxide was identified as first order. Accelerators like 2-mercaptobenzothiazole (MBT), N-cyclohexyl-2-benzothiazylsulphenamide (CBS) or TMTD and sulphur, reduced the crosslink density of the vulcanisate, compared to curing without these substances, as observed by Hummel.[18] Regarding the physical properties, it was observed that the presence of sulphur and/or free MBT in DCP curing leads to a vulcanisate with higher tensile strength and modulus, but worse ageing properties.

Later it was reported that sulphur can act as a free radical scavenger in the peroxide vulcanisation of Nitrile-Butadiene rubber (NBR)/EPDM blends.[18] About 1 mole of peroxide is destroyed by every mole of elemental sulphur consumed. Sulphur stabilises the tertiary radicals formed from the propylene units, thus restricting main chain scission and improving the physical properties.[19,20]

To summarise, the addition of a scorch retarder to a peroxide cure formulation provides the scorch safety necessary for most of its applications but at the expense of final cure state, which can only be surmounted by increasing peroxide and/or co-agent levels. Addition of small amounts of elemental sulphur improves the mechanical properties to a certain extent, but without improvement in scorch time. Therefore there is still a need for a new additive that provides scorch safety and at the same time maintains the state of cure, thus the final properties. Such a chemical would facilitate the production of peroxide cured goods. This new additive should take part in the crosslinking reaction in a positive way, preferably by increasing the final cure state. It should also provide the desired scorch delay. In order to achieve this, chemicals which do not have a strong radical scavenging effect are needed.

5.2 EXPERIMENTAL

Materials - A masterbatch was prepared at DSM Elastomers B.V., the Netherlands, consisting of ethylene propylene polymethylene rubber from DSM (EPM Keltan 13, Mooney viscosity ML(1+4)100°C of 46, containing 56% ethylene and 44% propylene), carbon black N-550 obtained from Cabot Corp., stearic acid obtained from Aldrich and paraffinic oil Sunpar 150 obtained from Sun Oil Cie. For details on the masterbatch preparation see Chapter 3.
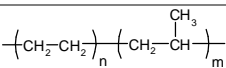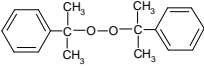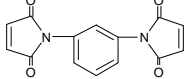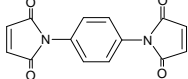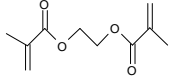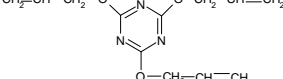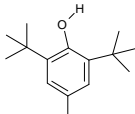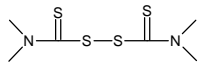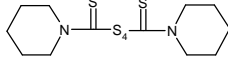
Dicumyl peroxide (DCP), (Perkadox BC-40 Bpd) was obtained from Akzo Nobel. The co-agents N,N'-m-phenylenedimaleimide (BMI-MP), N,N'-p-phenylenedimaleimide (BMI-PP), triallylcyanurate (TAC) and ethylene dimethacrylate (EDMA) were purchased from Acros. 2,6-Di-tert-butyl-4-methylphenol (BHT) and sulphur (S_8) were purchased from Merck. Tetramethylthiuram disulphide (TMTD) and dipentamethylenethiuram tetrasulphide (DPTT) were kindly provided by Flexsys B.V. The structures of all these compounds are shown in Table 5.1.

Mixing - The masterbatch consisted of 100 phr EPM, 60 phr carbon black, 1 phr stearic acid and 45 phr paraffinic oil. Peroxide and co-agent were added to 206 phr of masterbatch on a Schwabenthan two roll mill (friction ratio 1:1.22, temperature 40°C, mixing time 10 minutes).

Characterisation and Vulcanisation - The cure characteristics of the compounds were measured at 160°C using a torsional dynamic rheometer, RPA 2000 from Alpha Technologies. Delta torque, extent of crosslinking or cure state is the maximum torque (MH) minus the minimum torque (ML). Scorch time (t_{s2}) is taken as the time to reach 2% of the delta torque above minimum. This is not exactly in agreement with the definition of scorch time as mentioned in ISO 6502: "Rubber measurement of vulcanisation characteristics with rotorless curemeters", but was implemented in the present form in the software of the RPA 2000. Optimum cure time (t_{90}) is the time to reach 90% of the delta torque above minimum. Cure rate is taken as the slope of the cure curve in the rheogram between t_{s2} and t_{90}.

The compounds were vulcanised by compression moulding in a Wickert laboratory press WLP 1600/5*4/3 at 100 bar and 160°C, for 2 times t_{90}.

Table 5.1 Chemical name and structure of the different materials used in the present study.

Chemical name	Abbreviation	Chemical structure
Ethylene propylene polymehtylene rubber	EPM	
Dicumyl peroxide	DCP	
N,N'-m-phenylenedimaleimide	BMI-MP	
N,N'-p-phenylenedimaleimide	BMI-PP	
Ethylene dimethacrylate	EDMA	
Triallylcyanurate	TAC	
2,6-Di-tert-butyl-4-methylphenol	BHT	
Tetramethylthiuram disulphide	TMTD	
Dipentamethylenethiuram tetrasulphide	DPTT	

Determination of Mechanical Properties – Mechanical properties of vulcanisates were measured on a Zwick tensile tester, according to the conditions defined in ISO 37, on dumb-bell shaped specimens of Type 2, with a nominal rate of the traverse of the moving grip of 500 mm/min.

5.3   RESULTS AND DISCUSSION

5.3.1 Effect of commonly used scorch retarders

The effect of two commonly used scorch retarders, BHT and TMTD, on the peroxide cure of EPM rubber in the presence of different co-agents was studied. The formulations tested are shown in Table 5.2. The concentrations of co-agent shown in the table correspond to 30 meq of co-agent in every case. The concentration of BHT and TMTD were chosen based on the amounts described in literature.[12]

The different formulations were mixed and tested as described in the experimental section. The rheograms obtained for the different samples are shown in Figures 5.1 to 5.4. As mentioned in the introduction, BHT has been used as scorch retarder in EPDM compounds, leading to an increased scorch time as well as a good cure rate. The effect of BHT in the peroxide cure of EPM is far from achieving an increase in scorch safety, as can be seen from the first stages of the cure curves of the compounds containing BHT in Figures 5.1 to 5.4. The delta torque achieved with BHT is even slightly increased, in the case of BMI-MP and EDMA, which indicates the lack of a radical scavenging effect. In the case of BMI-PP the torque level is lower when using BHT. In the case of TAC it is at the same level as without BHT. No scorch improvement was observed in any of the cases.

Table 5.2 Formulations tested for common scorch retarders BHT and TMTD. Amounts in phr.

Component	M0	M1	M2	P0	P1	P2	E0	E1	E2	T0	T1	T2
Masterbatch	206	206	206	206	206	206	206	206	206	206	206	206
DCP	6	6	6	6	6	6	6	6	6	6	6	6
BMI-MP	4	4	4	0	0	0	0	0	0	0	0	0
BMI-PP	0	0	0	4	4	4	0	0	0	0	0	0
EDMA	0	0	0	0	0	0	3	3	3	0	0	0
TAC	0	0	0	0	0	0	0	0	0	2.5	2.5	2.5
BHT	0	0.09	0	0	0.09	0	0	0.09	0	0	0.09	0
TMTD	0	0	1.8	0	0	1.8	0	0	1.8	0	0	1.8
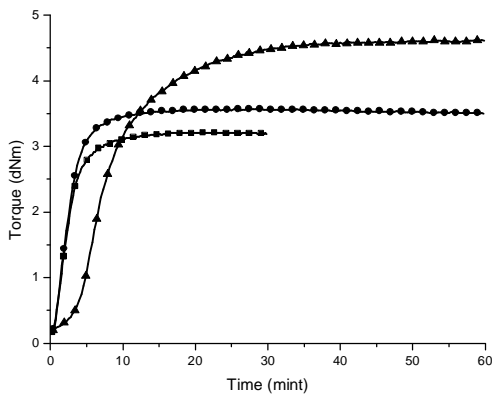
Figure 5.1 – Rheograms of samples containing BMI-MP and scorch retarder. (■): M0, no retarder; (●): M1, BHT; (▲): M2, TMTD.
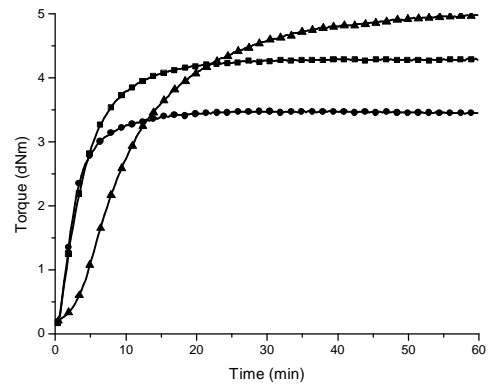

Figure 5.2 – Rheograms of samples containing BMI-PP and scorch retarder. (■): P0, no retarder; (●): P1, BHT; (▲): P2, TMTD.
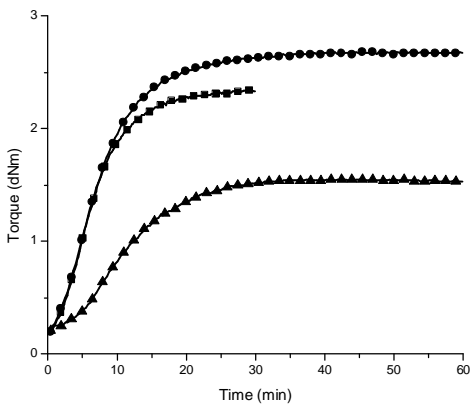

Figure 5.3 – Rheograms of samples containing EDMA and scorch retarder. (■): E0, no retarder; (●): E1, BHT; (▲): E2, TMTD.
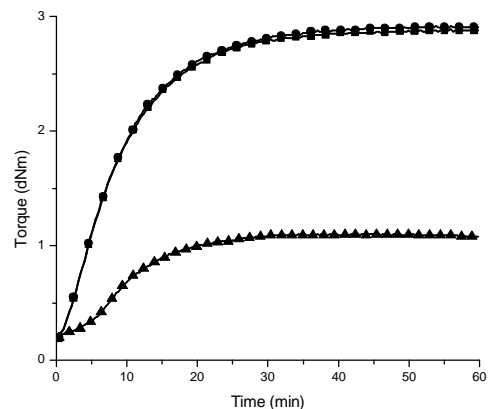

Figure 5.4 – Rheograms of samples containing TAC and scorch retarder. (■): T0, no retarder; (●): T1, BHT; (▲): T2, TMTD.

When TMTD is added to the formulations a certain scorch delay can be observed. This can be seen in the first minutes of the rheograms plotted in Figures 5.1 to 5.4. In the case of TAC and EDMA this delay goes at the expense of torque level,

which is significantly lowered when TMTD is present. Probably because of the radical scavenging effect from TMTD, in the first stages of vulcanisation, scorch delay is achieved. But the overall radical efficiency is diminished because of the consumption of radicals by TMTD, which explains the lower torque level achieved. Especially interesting is the case of BMI-MP and BMI-PP, where both scorch time and delta torque increase by addition of TMTD to the system. Thus TMTD is not scavenging radicals at the expense of torque level in the case of bismaleimide co-agents.

The mechanical properties of all these compounds are depicted in Figures 5.5 to 5.8.
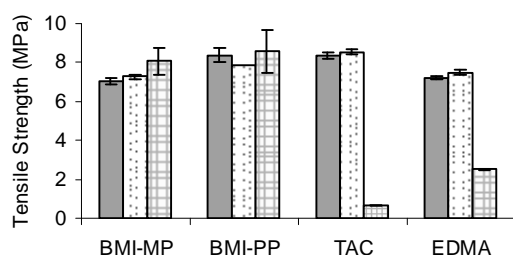

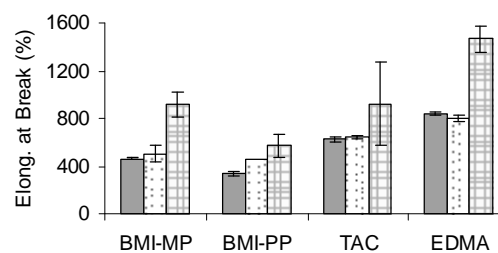**Figure 5.5** – Tensile strength of samples containing no retarder (smooth), BHT (dotted) and TMTD (squares).

Figure 5.6 – Elongation at break of samples containing no retarder (smooth), BHT (dotted) and TMTD (squares).
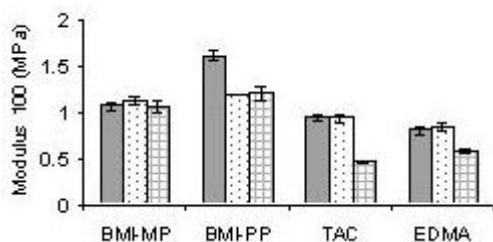

Figure 5.7 – Modulus at 100% elongation of samples containing no retarder (smooth), BHT (dotted) and TMTD (squares).
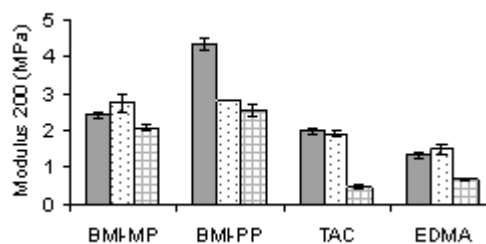

Figure 5.8 – Modulus at 200% elongation of samples containing no retarder (smooth), BHT (dotted) and TMTD (squares).

As could already be expected from the rheological data, the addition of BHT to the formulation does not lead to a significant change in properties for any of the co-agents tested. TMTD worsens drastically the mechanical properties achieved by TAC and EDMA, but slightly improves the tensile properties of the BMI-MP formulation. This is quite remarkable, especially because it also led to an improved scorch delay.

The effect of TMTD is much larger in BMI-MP than in BMI-PP. In both cases a good scorch delay is obtained. Moreover, the final delta torque achieved by addition of TMTD is at the same level for both co-agent systems.

Overall it can be concluded that in the peroxide/co-agent cure of EPM, BHT does not provide any scorch delay at the concentration used, while TMTD provides scorch safety for all the co-agents tested, but only maintains a good torque and property level in the case of BMI-MP and BMI-PP as co-agents.

5.3.2 Effect of elemental sulphur in peroxide cure

Due to the interesting improvement in properties achieved by the addition of a little sulphur to a peroxide system reported in literature,[13, 14] elemental sulphur was tested in combination with bismaleimide co-agents in order to evaluate its effect on peroxide cure rate and cure state of EPM rubber. In Table 5.3 the different formulations are

listed. Three different sulphur dosages were tested to find out the influence of sulphur concentration on the properties.

Table 5.3 Formulations tested for influence of elemental sulphur. Amounts in phr.

Component	M0	MS1	MS2	MS3	P0	PS1	PS2	PS3
Masterbatch	206	206	206	206	206	206	206	206
DCP	6	6	6	6	6	6	6	6
BMI-MP	4	4	4	4	0	0	0	0
BMI-PP	0	0	0	0	4	4	4	4
Sulphur	0	0.1	0.63	0.96	0	0.1	0.63	0.96

As can be seen in the cure curves in Figures 5.9 and 5.10, the effect of the addition of a small amount of elemental sulphur, 0.1 phr, to the formulation is positive in terms of cure state. The cure rate is not changed by addition of 0.1 phr of sulphur, neither is the scorch safety. The use of larger quantities of sulphur, 0.63 phr, leads to a slower cure rate and higher torque level, especially in the case of BMI-MP. When even larger amounts of sulphur are used, 0.96 phr, both cure rate and cure state are worse to those obtained with 0.63 phr of elemental sulphur. For BMI-PP the effect of higher sulphur concentrations is even more negative than for BMI-MP: with 0.96 phr the final torque is lower than that in the absence of sulphur, and cure rate is very slow.
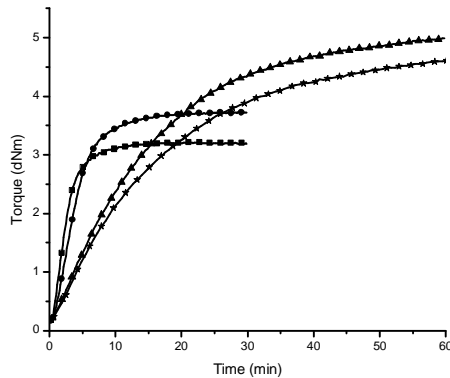

Figure 5.9 – Rheograms of samples containing BMI-MP and elemental sulphur. (■): M0, no S_8; (●): MS1, 0.1phr S_8; (▲): MS2, 0.63phr S_8; (★): MS3, 0.96phr S_8.
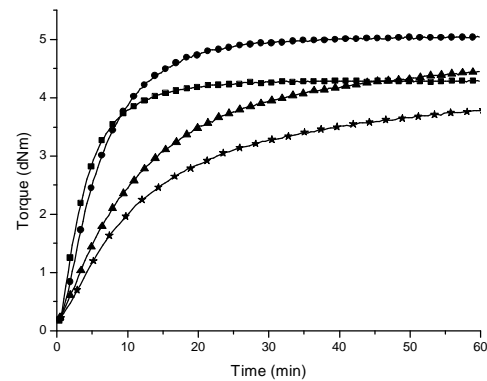
Figure 5.10 – Rheograms of samples containing BMI-PP and elemental sulphur. (■): P0, no S_8; (●): PS1, 0.1phr S_8; (▲): PS2, 0.63phr S_8; (★): PS3, 0.96phr S_8.

The mechanical properties of these compounds are shown in Figures 5.11 to 5.14. As can be expected from the cure curves, the effect of the addition of 0.1 phr of elemental sulphur is positive in terms of mechanical properties such as tensile strength and moduli for both co-agents, which are slightly improved when compared to the formulations without sulphur. The use of larger amounts of sulphur, 0.63 phr, leads to superior mechanical properties like tensile strength and moduli for BMI-MP while for BMI-PP these properties start to decrease. Further increase in sulphur concentration, 0.96 phr, leads to inferior properties compared to the formulations with lower sulphur content.
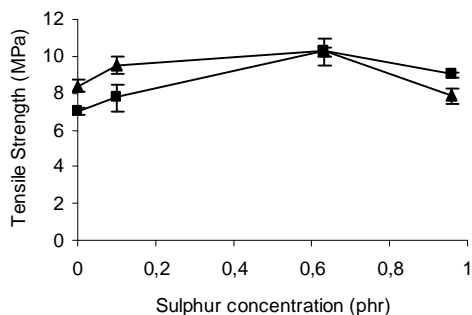
Figure 5.11 – Tensile Strength for samples containing BMI-MP (■), BMI-PP (▲) and different sulphur concentrations.
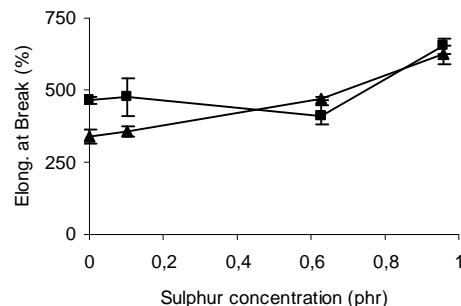

Figure 5.12 –Elongation at Break for samples containing BMI-MP (■), BMI-PP (▲) and different sulphur concentrations.
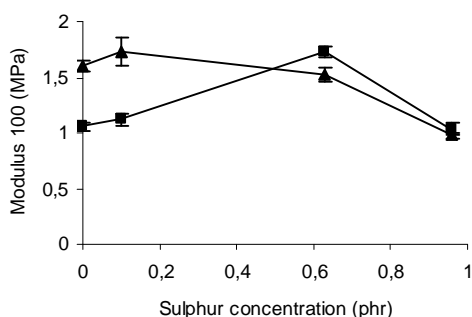

Figure 5.13 – Modulus at 100% elongation for samples containing BMI-MP (■), BMI-PP (▲) and different sulphur concentrations.
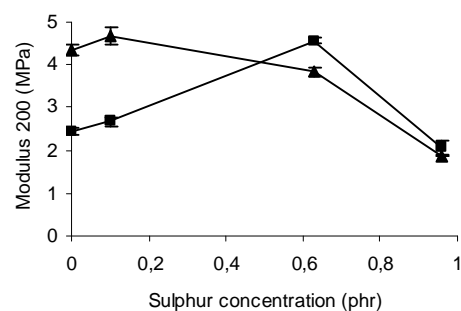

Figure 5.14 – Modulus at 200% elongation for samples containing BMI-MP (■), BMI-PP (▲) and different sulphur concentrations.

It is clear from these results that there is a limitation in the amount of sulphur which can be added to a peroxide formulation in order to improve mechanical properties. In this EPM formulation an improvement in torque level and mechanical properties is observed between 0.1 and 0.63 phr of sulphur added. For BMI-PP the optimum of sulphur to be added is lower than for BMI-MP. With concentrations higher than 0.63 phr delta torque decreases, which indicates that amongst the concentrations tested 0.63 phr is the optimum sulphur amount which can be added to BMI-MP and 0.1 phr is the best concentration found for BMI-PP. Addition of higher amounts of sulphur would only result in a worse cure rate, inferior delta torque and mechanical properties. These data indicate that elemental sulphur can help to improve cure state. It plays a role in the radical reaction, probably giving rise to a different network structure, but it is indeed consuming radicals during the crosslinking reaction; i.e. from a certain amount of sulphur onwards, the more sulphur that is added the lower the cure state achieved. Accordingly, elemental sulphur can be used to improve mechanical properties in the EPM/peroxide/bismaleimide system as long as the amounts used are very low. In that case there is no significant influence on scorch time and the properties are modestly improved.

5.3.3 Addition of DPTT to a peroxide/co-agent system

Since it was observed that TMTD improves scorch safety and that the addition of small amounts of elemental sulphur can improve the cure state of the EPM/peroxide/bismaleimide formulation, interest in the influence of sulphur containing

compounds was raised. In an attempt to achieve similar properties as with elemental sulphur, yet providing the desired scorch safety as that obtained with TMTD.

A sulphur spender, DPTT (see Table 5.1) was added to the formulations of the two different bismaleimide co-agents, as well as to the bismethacrylate and triallylcyanurate co-agents. The formulations tested are listed in Table 5.4. The concentrations of co-agent shown in the table correspond to 30 meq of co-agent in each case. The concentration of DPTT corresponds to 5 mmol of DPTT, and this corresponds with 0.63 phr of effective sulphur into its molecular structure. This amount was chosen on basis of the results of paragraph 5.3.2.

Table 5.4 Formulations tested for the effect of sulphur spender DPTT in combination with co-agents. Amounts in phr.

Component	M0	M3	P0	P3	E0	E3	T0	T3
Masterbatch	206	206	206	206	206	206	206	206
DCP	6	6	6	6	6	6	6	6
BMI-MP	4	4	0	0	0	0	0	0
BMI-PP	0	0	4	4	0	0	0	0
EDMA	0	0	0	0	3	3	0	0
TAC	0	0	0	0	0	0	2.5	2.5
DPTT	0	1.9	0	1.9	0	1.9	0	1.9

In Figures 5.15 to 5.18 the cure behaviour of the rubber compounds containing DPTT is plotted. The cure curves clearly show that in the case of EDMA and TAC, Figures 5.17 and 5.18, the addition of DPTT leads to a lower torque level, especially in the case of TAC. On the other hand, the addition of DPTT to the bismaleimide co-agent BMI-MP improves delta torque from 3.24 to 5.20 dNm and at the same time increases scorch time from 0.50 to 1.38 minutes, as can be seen in Table 5.5. For BMI-PP the increase in torque level by addition of DPTT is from 4.30 to 5.14 dNm and scorch time increases from 0.53 to 1.47 minutes. The addition of the sulphur spender DPTT to the formulations has a negative influence on the torque level in the case of TAC and EDMA as co-agents, contrary to both bismaleimide co-agents where it has a positive effect in terms of scorch safety and torque level. These results are surprising, because according to our knowledge this is the first occasion where at the same time scorch safety and torque level are improved in a peroxide cure system.
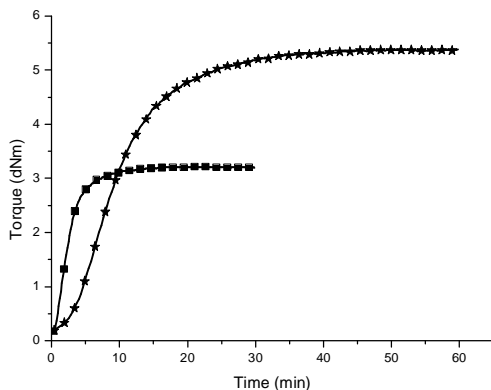

Figure 5.15 – Rheogram of sample containing BMI-MP and DPTT.
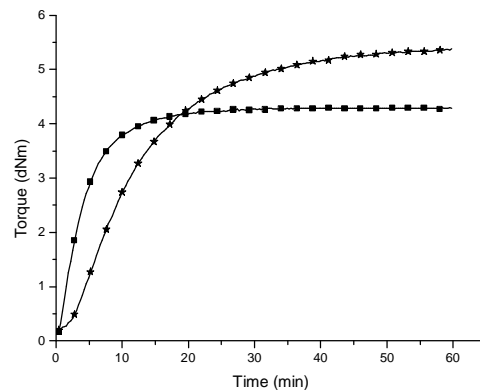(■): M0, 0phr DPTT; (★): M3, 1.9phr DPTT.

Figure 5.16 – Rheogram of sample containing BMI-PP and DPTT.
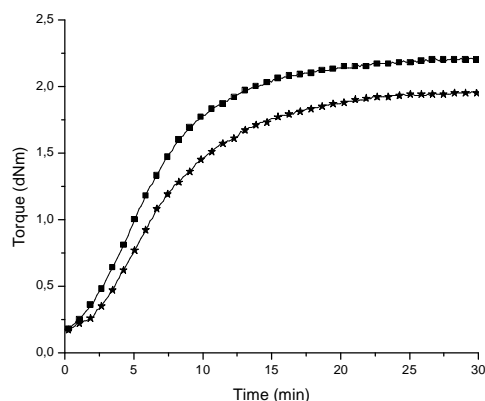(■): P0, 0phr DPTT; (★): P3, 1.9phr DPTT.

Figure 5.17 – Rheogram of sample containing EDMA and DPTT.
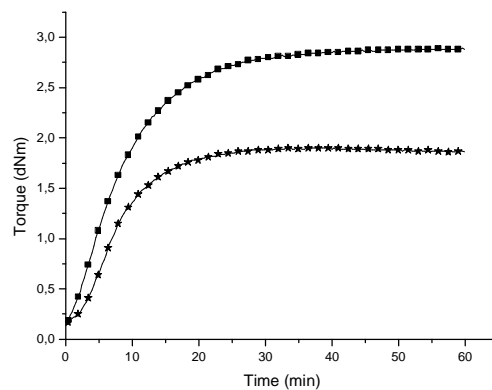(■): E0, 0phr DPTT; (★): E3, 1.9phr DPTT.

Figure 5.18 – Rheogram of sample containing TAC and DPTT.
(■): T0, 0phr DPTT; (★): T3, 1.9phr DPTT.

Table 5.5 Rheological data of the effect of DPTT in combination with co-agents.

	M0	M3	P0	P3	E0	E3	T0	T3
Delta Torque (dNm)	3.24	5.20	4.30	5.14	2.03	1.77	2.72	1.73
ts_2 (min)	0.50	1.38	0.53	1.47	0.69	0.69	0.57	0.79
t_{90} (min)	7.2	21.5	10.8	25.1	13.8	15.2	21.1	17.5

A small decrease in cure rate is found when using bismaleimide co-agents in combination with DPTT. This could be improved by raising the cure temperature, as shown in Table 5.6 and in Figure 5.19. As can be seen from these data, an increase in cure temperature by 10°C provides a faster cure rate in the presence of DPTT, i.e. similar to BMI-MP at 160°C, while maintaining scorch delay.

Table 5.6 Influence of temperature on ts_2 and t_{90} of compound M3 vs M0.

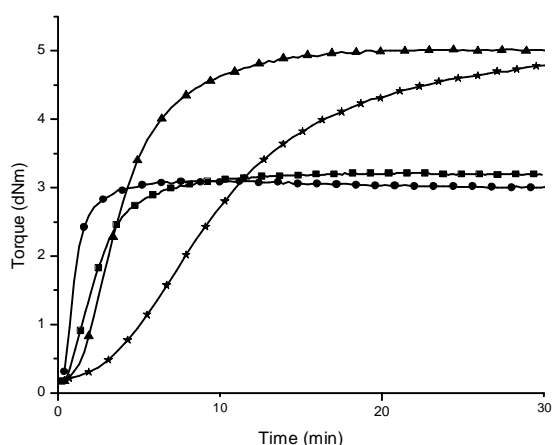| Cure temperature	Compound	ts_2 (min)	t_{90} (min)
160°C	M0	0.5	7.2
	M3	1.4	21.5
170°C	M0	0.3	2.6
	M3	0.9	12.1

Figure 5.19 – Rheogram of sample containing BMI-MP and DPTT at different temperatures. (■): BMI-MP at 160°C; (●): BMI-MP at 170°C; (★): BMI-MP + DPTT at 160°C; (▲): BMI-MP + DPTT at 170°C.

The mechanical properties obtained with the different formulations are shown in Figures 5.20 to 5.23. For both allylic and methacrylate co-agents TAC and EDMA, mechanical properties such as tensile strength and moduli decrease with the addition of DPTT to the system. This reveals the negative influence of the sulphur spender in these two co-agent systems, as could already be expected from the decrease in torque level observed in the cure curves. On the other hand, the addition of sulphur spender to the bismaleimide co-agents BMI-MP and BMI-PP provides a higher tensile strength and a higher elongation at break at the same time, however the moduli are lower when DPTT is added, especially in the case of BMI-PP.
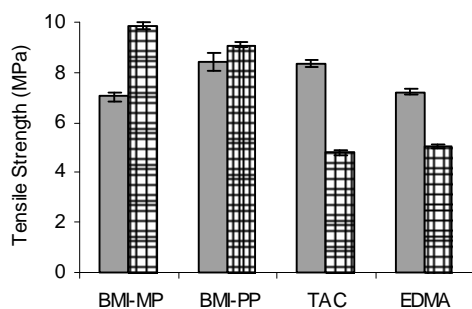

Figure 5.20 – Tensile strength of samples containing co-agent (smooth) and co-agent + DPTT (squares).
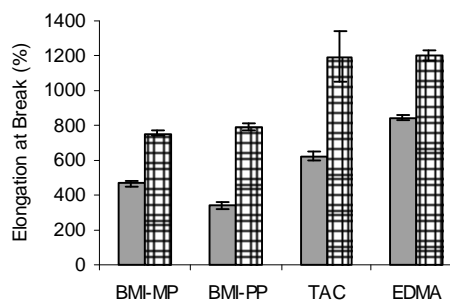
Figure 5.21 – Elongation at break of samples containing co-agent (smooth) and co-agent + DPTT (squares).
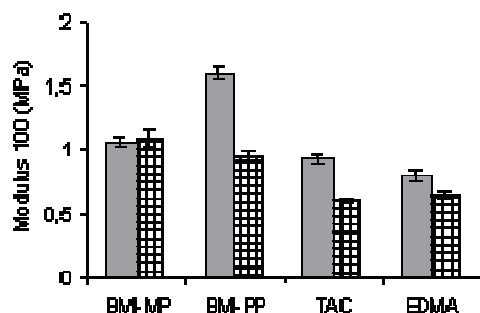
Figure 5.22 – Modulus at 100% elongation of samples containing co-agent (smooth) and co-agent + DPTT (squares).
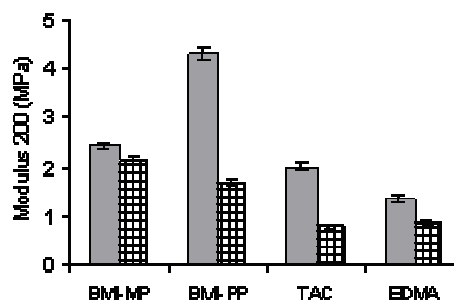
Figure 5.23 – Modulus at 200% elongation of samples containing co-agent (smooth) and co-agent + DPTT (squares).

These results indicate that the effect of DPTT in the EPM/peroxide/co-agent vulcanisation reaction is such that only in case of bismaleimide type co-agents it shows a positive influence on scorch safety and final properties of the product. These results shed some light onto the mechanistics of the reaction between the sulphur containing compound and the co-agent. The presence of maleimide groups is necessary for DPTT to perform its positive action, which does not take place with methacrylates or allylic groups. The DPTT/co-agent reaction after the generation of the first radicals, from the peroxide decomposition, involves the maleimide function of the co-agent. Probably, the sulphur donor effect of DPTT is playing an important role in the vulcanisation reaction. In the first minutes, crosslinking does not take place, which indicates that DPTT is reacting with the first radicals formed, thus preventing vulcanisation to take place and providing the desired scorch safety. Once vulcanisation starts, the cure rate is high enough and the final state of cure is higher than that obtained without DPTT, from which can be derived that the efficiency of the peroxide radical reaction is not sacrificed by the addition of DPTT, but even improved. Most likely, the presence of DPTT is giving rise to a different network structure than that obtained with the co-agent only. Some of the sulphur from the spender gets incorporated into the network, maybe even via a reaction with the co-agent. Thereby it generates extra crosslinks, and even more important, crosslinks of a different nature than the typical C-C crosslinks formed in a normal peroxide vulcanisation. This results in a drastic influence on the final properties of the product, which are improved. A more fundamental investigation to elucidate the exact mechanism that takes place is described in Chapter 7 of this thesis.

5.4 CONCLUSIONS

The scorch retarder BHT, which is being used in EPDM rubber, does not provide scorch delay in the peroxide/co-agent cure of EPM at the concentration used.

TMTD, also used as scorch retarder for EPDM, strongly deteriorates the properties of the vulcanisate when TAC and EDMA are used as co-agents. On the other hand, TMTD provides scorch delay and a slight improvement in tensile strength in case a bismaleimide type co-agent is used.

The addition of elemental sulphur in the peroxide/bismaleimide cure of EPM provides a small improvement in properties, depending on the concentration of elemental sulphur added to the formulation. Low concentrations, around 0.1 phr, of sulphur lead to a slight improvement in mechanical properties without affecting the scorch time of the vulcanisation process.

The peroxide/bismaleimide co-agent cure formulation for EPM rubber can be improved by addition of a sulphur spending compound like DPTT. An improvement in scorch time is obtained to provide scorch safety. Also the mechanical properties such as tensile strength are significantly improved. This effect achieved by addition of a sulphur containing compound to the peroxide formulation is positive for bismaleimide type co-agents such as BMI-MP and BMI-PP, whereas other type co-agents like TAC and EDMA are negatively influenced by DPTT.

The co-agents BMI-MP and BMI-PP show a somewhat different reactivity during peroxide curing, which leads to a higher crosslink density and therefore better mechanical properties of the final vulcanisate in the case of BMI-PP. However, the addition of DPTT to the bismaleimide co-agents leads to a relative larger improvement in the case of BMI-MP.

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Chapter 6

A Synergistic Concept of Co-agents for Scorch Delay and Property Improvement in a Peroxide/Bismaleimide Cure System[#]

"Concentrate all your thoughts upon the work at hand. The sun's rays do not burn until brought to a focus."

Alexander Graham Bell *(1847-1922)*

In the previous chapter a new concept of co-agents for peroxide vulcanisation has been introduced which provides both scorch delay and property improvement. This concept consists of the combination of a bismaleimide type co-agent and DPTT in a peroxide cure formulation of EPM rubber. In the present chapter this new system is studied in more detail. The effect of sulphur spenders other than DPTT and other peroxides than DCP are tested. Further, the influence of both co-agent and DPTT concentration are studied. Several properties, like compression set, ageing and hardness are tested for this new system. Overall, it has been found that, under optimal conditions, this new concept of co-agents behaves as a synergistic combination between peroxide and sulphur cure. It leads to improved scorch safety, improved mechanical properties and improved high temperature properties at the same time. In order to achieve this synergism between the two vulcanisation systems the concentration of co-agent and DPTT needs to be tuned to meet optimal properties. Finally, this new concept of co-agents has been found to be applicable to EPDM rubber as well.

6.1 INTRODUCTION

A new concept of co-agents has been described in the previous chapter. This new concept consists of the combination of a bismaleimide type co-agent and a sulphur spender compound, dipentamethylenethiuram tetrasulphide (DPTT), in a peroxide cure formulation. The remarkable characteristic from this new concept is that scorch safety and mechanical properties are improved at the same time.[1] This new concept works for bismaleimide type co-agents like N,N'-m-phenylenedimaleimide (BMI-MP) and N,N'-p-phenylenedimaleimide (BMI-PP), however it does not work for other co-agent types like triallylcyanurate (TAC) and ethylenedimethacrylate (EDMA).

In order to study in more detail this new concept of co-agents, further experiments have been performed and are described in this chapter. The influence of co-agent and sulphur spender concentration has been studied as well as the effect of other sulphur spender compounds, another peroxide and another polymer. Further the mechanical properties of the cured compounds are studied in more detail, with special emphasis on high temperature properties.

6.2 EXPERIMENTAL

Materials - A masterbatch was prepared at DSM Elastomers B.V., the Netherlands, consisting of ethylene propylene polymethylene rubber from DMS (EPM Keltan 13, Mooney viscosity ML(1+4)100°C of 46, containing 56% ethylene and 44% propylene), carbon black N-550 obtained from Cabot Corp., stearic acid obtained from Aldrich and paraffinic oil Sunpar 150 obtained from Sun Oil Cie. For details on the masterbatch preparation see Chapter 3. A second masterbatch was prepared in the exact same manner as the previous one but using ethylene propylene diene polymethylene rubber (EPDM Keltan 2340A, 53% ethylene content, 41% propylene content, 6% ethylidene norbornene, (ENB)) instead of EPM.

Dicumyl peroxide (DCP, Perkadox BC-40 Bpd, 40% pure) and di(t-butyl)peroxy-isopropyl benzene (DTBPIB, Perkadox 14 BC-40-gr, 40% pure) were obtained from Akzo Nobel. The co-agents BMI-MP and BMI-PP were purchased from Acros. Tetramethylthiuram disulphide (TMTD), tetrabenzylthiuram disulphide (TBzTD), DPTT and dipentamethylenethiuram hexasulphide (DPTH) were kindly provided by Flexsys B.V. Bis-triethoxysilylpropyl tetrasulphide (TESPT) was obtained from Degussa. The structures of all these compounds are shown in Table 6.1.

Mixing - The masterbatch consisted of 100 phr EPM or EPDM, 60 phr carbon black, 1 phr stearic acid and 45 phr paraffinic oil. Peroxide and co-agent were added to 206 phr of masterbatch on a Schwabenthan two roll mill (friction ratio 1:1.22, temperature 40°C, mixing time 10 minutes).

Table 6.1 Chemical names and structures of the different materials.

Chemical name	Abbreviation	Chemical structure
Ethylene propylene polymethylene rubber	EPM	
Ethylene propylene diene polymethylene rubber	EPDM	
Dicumyl peroxide	DCP	
Di(t-butyl)peroxy-isopropyl benzene	DTBPIB	
N,N'-m-phenylenedimaleimide	BMI-MP	
N,N'-p-phenylenedimaleimide	BMI-PP	
Tertramethylthiuram disulphide	TMTD	
Tetrabenzylthiuram disulphide	TBzTD	
Dipentamethylenethiuram tetrasulphide	DPTT	
Dipentamethylenethiuram hexasulphide	DPTH	
Bis-triethoxysilylpropyl tetrasulphide	TESPT	

Characterisation and Vulcanisation - The cure characteristics of the compounds were measured at 160°C using a torsional dynamic rheometer, RPA 2000 from Alpha Technologies. Delta torque, extent of crosslinking or cure state is the maximum torque (MH) minus the minimum torque (ML). Scorch safety (t_{s2}) is taken as the time to reach 2% of the delta torque above minimum. This is not exactly in agreement with the definition of scorch time as mentioned in ISO 6502: "Rubber measurement of vulcanisation characteristics with rotorless curemeters", but was implemented in the present form in the software of the RPA 2000. Optimum cure time (t_{90}) is the time to reach 90% of the delta torque above minimum. Cure rate is taken as the slope of the cure curve between t_{s2} and t_{90}.

The compounds were vulcanised by compression moulding in a Wickert laboratory press WLP 1600/5*4/3 at 100 bar and 160°C, for 2 times t_{90}.

Determination of Mechanical Properties – Tensile properties of vulcanisates were measured on a Zwick tensile tester, according to the conditions described in ISO 37, on dumb-bell shaped specimens of Type 2, with a nominal rate of the traverse of the moving grip of 500 mm/min. For the tensile measurement of aged samples, the dumb-bells were aged in an air circulated oven at 150°C for different times.

Hardness of the vulcanised materials was measured using the Shore A scale with vulcanised samples of 5.8 mm thickness.

Compression set was measured using compression moulded samples in form of circular cylinders with a height of 5.8 mm and a diameter of 10 mm. Six specimens

were tested for each different sample. The exact height of the samples was always measured before testing. The samples were placed between two parallel plates and then compressed 25 percent of their initial height. Samples were kept under pressure for 24 hours at three different temperatures (23, 70 and 150°C) after which the pressure was released. The samples were given 30 minutes time to relax and after that the height was measured again. The compression set was calculated using Equation 6.1.

$$\text{Compression Set} = \frac{h_0 - h_2}{h_0 - h_1} * 100\%$$ (6.1)

where:
h_0 = initial height of the sample;
h_1 = the height of the sample during load;
h_2 = the height of the sample after unloading and relaxation for a specific time.

A compression set of 0% means an ideal rubber that totally recovers to its original shape. If the compression set is 100% it indicates the absence of any elasticity at all.

Crosslink density – Crosslink density was measured using 2 grams of vulcanised rubber sample, cut into small pieces. The crosslinked rubber contains polar and non-polar molecular rest products; therefore extraction is needed prior to the crosslink density measurement. The first step was extraction with acetone for 24 hours to remove polar molecules. The samples were wrapped in filter paper during extraction, and then dried in a vacuum oven overnight. Sample weights were measured. The second step was extraction with THF for 48 hours to remove all non-polar rest molecules. For this extraction, fat-free paper was used to wrap the rubber. The samples were again dried overnight, and their weight was measured. Finally, 0.2 grams of the extracted sample were taken and swollen in decalin for 72 hours. After swelling, the samples were lightly wiped off with filter paper and their weight was again measured. The overall crosslink density was calculated using equations 6.2a, 6.2b[2, 3] and Table 6.2.

$$m_e = \frac{\ln(1 - v_r) + v_r + cv_r^2}{v_0(\frac{1}{2}v_r - v_r^{\frac{1}{3}})}$$ (6.2a)

where:
m_e = overall crosslink density;
v_0 = molar volume of the solvent;
v_r = polymer volume fraction of the swollen sample;
χ = Flory-Huggins interaction parameter.

$$v_r = \frac{m_r}{m_r + m_s \frac{r_r}{r_s}}$$ (6.2b)

where:
r_r = density of rubber;
r_s = density of solvent;
m_r = weight of rubber network;
m_s = weight of solvent in sample at equilibrium swelling.

Table 6.2 Data used for calculation of crosslink density.

For decalin:	For EPDM / decalin systems:
v_0 = 0.154 l/mol	$\chi = 0.121 + 0.278v_r$ [4]
r_s = 0.896 g/cm^3	r_r = 0.86 g/cm^3

For sulphur vulcanisates χ changes with the type and concentration of sulphur and sulphur accelerators used. Chemical modification of the network occurs, resulting in a change of polymer/swelling agent interactions.[5] For peroxide vulcanisates this is not the case,[6] which makes equilibrium swelling a very valuable method for quantitative determination of crosslink density.

6.3 RESULTS AND DISCUSSION

6.3.1 Effect of various sulphur spenders

In order to investigate whether the scorch delay and property improvement phenomenon described in Chapter 5 is specific for DPTT or also applicable to other sulphur spenders, several sulphur containing compounds were tested in a peroxide cure formulation with EPM and a bismaleimide co-agent, as shown in Table 6.3. The different sulphur spenders tested differ from DPTT in the amount of effective sulphur atoms contained in their molecular structure, i.e.: DPTH has six, TBzTD has two. Further, a special type of sulphur spender was also tested, a molecule commonly used as a coupling agent for silica-reinforcement of tyre rubber: TESPT.[7-10] The dosage of each sulphur spender was calculated so that the same sulphur amount was added, based on molecular structure, to each formulation. The rheograms obtained for the different samples are shown in Figures 6.1, for BMI-MP, and 6.2, for BMI-PP.

Table 6.3 Formulations tested with different sulphur containing compounds. Amounts in phr.

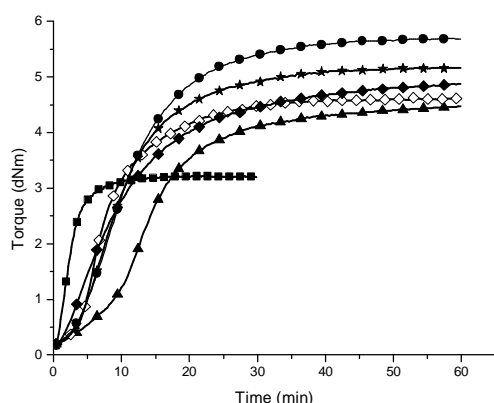| Component	M1	M2	M3	M4	M5	M6	P1	P2	P3	P4	P5	P6
EPM Masterbatch	206	206	206	206	206	206	206	206	206	206	206	206
DCP	6	6	6	6	6	6	6	6	6	6	6	6
BMI-MP	4	4	4	4	4	4	0	0	0	0	0	0
BMI-PP	0	0	0	0	0	0	4	4	4	4	4	4
TMTD	0	1.8	0	0	0	0	0	1.8	0	0	0	0
DPTT	0	0	1.9	0	0	0	0	0	1.9	0	0	0
TBzTD	0	0	0	4.1	0	0	0	0	0	4.1	0	0
DPTH	0	0	0	0	1.7	0	0	0	0	0	1.7	0
TESPT	0	0	0	0	0	4	0	0	0	0	0	4

Figure 6.1 – Rheograms of samples containing BMI-MP and several sulphur containing compounds. (■): M1, none; (◊): M2, TMTD; (★): M3, DPTT; (▲): M4, TBzTD; (●): M5, DPTH; (♦): M6, TESPT.
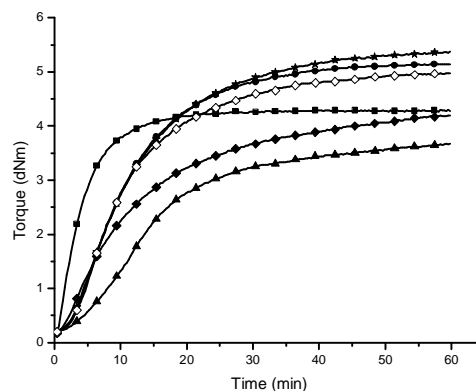
Figure 6.2 – Rheograms of samples containing BMI-PP and several sulphur containing compounds. (■): P1, none; (◊): P2, TMTD; (★): P3, DPTT; (▲): P4, TBzTD; (●): P5, DPTH; (♦): P6, TESPT.

As can be observed in the rheograms, all the different sulphur containing compounds tested provide scorch delay for both co-agents. The positive effect in torque level is larger in the case of BMI-MP, since this co-agent has a delta torque lower than BMI-PP in the absence of sulphur spender.

In an ideal situation, a good scorch retarder should provide scorch time and at the same time maintain or, if possible, increase the torque level, while maintaining the cure rate. In Figure 6.3 a general graph is shown in which the arrow points to the best performance achievable. Scorch retarders that would lead to a relation delta torque-scorch time in the upper right corner of the graph would be ideal, since they increase both scorch safety and cure state. The relation delta torque-scorch time achieved for BMI-MP and BMI-PP by using these sulphur containing compounds is shown in Figures 6.4 and 6.5.
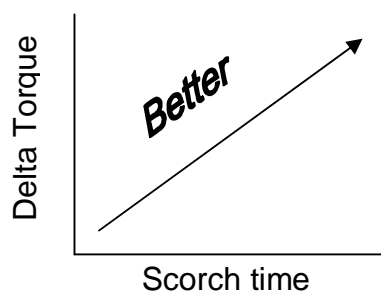

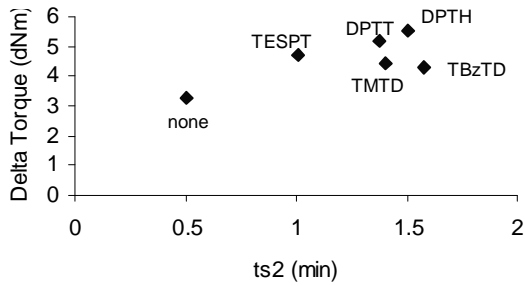**Figure 6.3** – Ideal combination of delta torque and scorch time.

Figure 6.4 – Relation delta torque/scorch time achieved for BMI-MP in combination with various sulphur containing compounds.
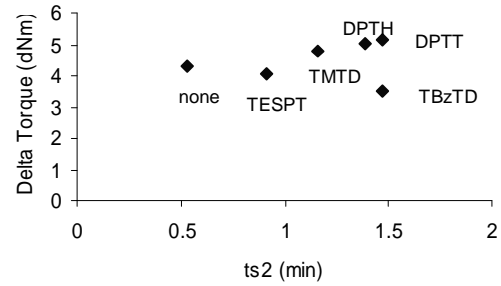
Figure 6.5 – Relation delta torque/scorch time achieved for BMI-PP in combination with various sulphur containing compounds.

As can be observed, all the sulphur spenders improve scorch time for both co-agents, since they are all located in the graph on the right side of the reference point without sulphur spender. In the case of BMI-MP all sulphur spenders improve delta torque. DPTH offers the best relation torque/scorch time, followed by DPTT, TMTD, TBzTD and TESPT. In the case of BMI-PP the delta torque is slightly lower when TBzTD is used. For TESPT it is maintained while for the rest of sulphur spenders it is improved. The best torque/scorch time relation is provided by DPTT, followed by DPTH, TMTD, TESPT and TBzTD.

The mechanical properties achieved with these compounds are plotted in Figures 6.6 to 6.9. As can be observed, the tensile strength is increased by addition of the sulphur spender species into the formulation, especially in the case of BMI-MP. At the same time elongation at break also increases for both co-agent systems.
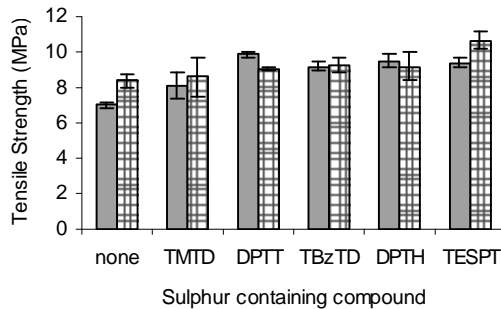

Figure 6.6 – Tensile Strength.
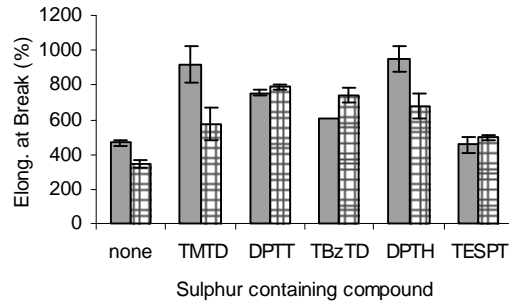Smooth: BMI-MP; Squares: BMI-PP.

Figure 6.7 – Elongation at Break.
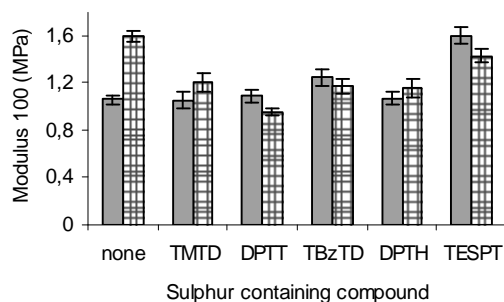Smooth: BMI-MP; Squares: BMI-PP.

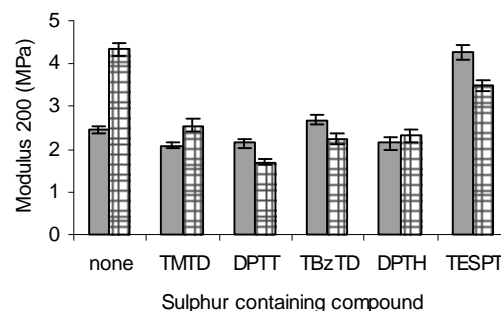**Figure 6.8** – Modulus at 100% elongation. Smooth: BMI-MP; Squares: BMI-PP.

Figure 6.9 – Modulus at 200% elongation. Smooth: BMI-MP; Squares: BMI-PP.

Modulus at 100% elongation is maintained or very slightly improved by addition of the sulphur spenders to the BMI-MP formulation, but in the case of BMI-PP the modulus 100% worsens when the sulphur spenders are added.

Modulus at 200% elongation is maintained at the same level or slightly improved with TBzTD and TESPT, for BMI-MP. For BMI-PP the modulus 200% decreases in all cases.

Overall, it can be concluded that by using other sulphur spenders than DPTT in the EPM/bismaleimide formulation of this study the same effect can be obtained of scorch delay and property improvement as obtained with DPTT. The values of the moduli however are not improved. Later on in this chapter, the influence of the sulphur spender concentration on mechanical properties will be further studied and better moduli will be achieved by lowering the sulphur spender concentration.

6.3.2 Effect of DPTT on another peroxide type

In order to study the influence of the type of peroxide with respect to the effect of DPTT on the peroxide/BMI-PP formulation, a different peroxide was tested. Di(t-butyl)peroxy-isopropyl benzene (DTBPIB) is a difunctional peroxide, as shown in Table 6.1. The amount of this difunctional peroxide used in the formulation was calculated in order to have the same amount of peroxide equivalents as that in 6 phr of 40% pure DCP. In Table 6.4 the formulations of the samples tested are given. In Figure 6.10 the cure curves of the samples are depicted.

Table 6.4 Formulations tested with two different peroxides. Amounts in phr.

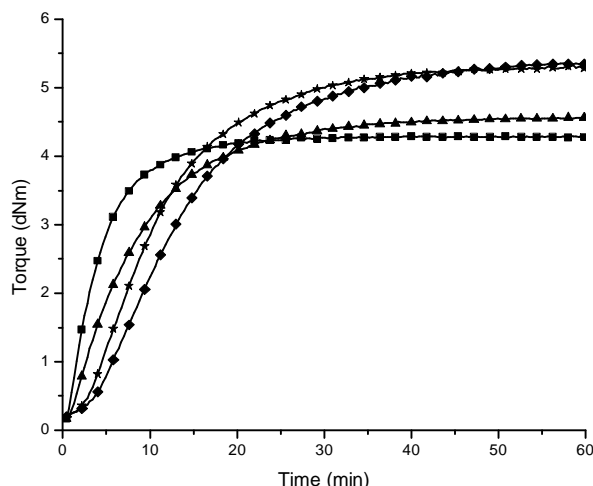| Component	P1	P3	X1	X2
EPM Masterbatch	206	206	206	206
DCP	6	6	0	0
DTBPIB	0	0	3.75	3.75
BMI-PP	4	4	4	4
DPTT	0	1.9	0	1.9

Figure 6.10 – Rheograms of samples containing DCP and DTBPIB with and without DPTT. (■): P1, DCP without DPTT; (★): P3, DCP with DPTT; (▲): X1, DTBPIB without DPTT; (♦): X2, DTBPIB with DPTT.

As can be deduced from the cure curves, the effect of DPTT is exactly the same for both peroxide types. In both cases the scorch time is prolonged and delta torque improved with addition of DPTT. In Figures 6.11 to 6.14 the mechanical properties are plotted, as achieved with the different formulations. In general, the effect of DPTT on mechanical properties is practically the same for both types of peroxide.
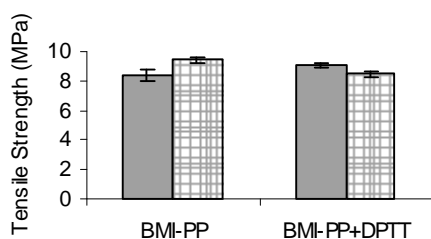

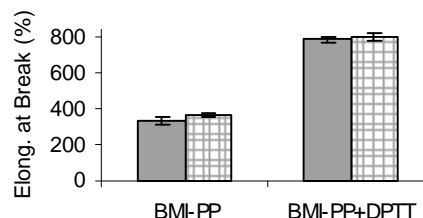**Figure 6.11** – Tensile strength.
Smooth: DCP; Squares: DTBPIB.

Figure 6.12 – Elongation at Break.
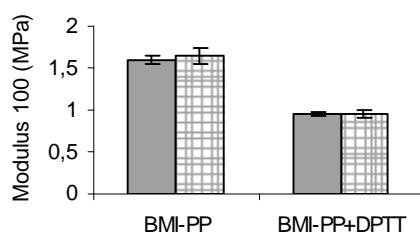Smooth: DCP; Squares: DTBPIB.

Figure 6.13 – Modulus at 100% elongation.
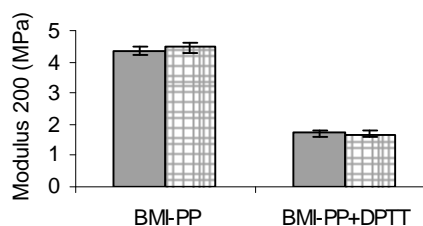Smooth: DCP; Squares: DTBPIB.

Figure 6.14 – Modulus at 200% elongation.
Smooth: DCP; Squares: DTBPIB.

For both peroxides tested the effect of addition of DPTT is the same in terms of scorch time and delta torque: a remarkable improvement. The change in mechanical properties measured for both peroxide types when adding DPTT to the system is also

very similar. It can be concluded that the overall effect of DPTT is the same, independent of the type of peroxide used.

6.3.3 Influence of co-agent concentration

The influence of the co-agent BMI-MP concentration with variation in DPTT content was studied in order to quantify the contribution of this factor to the material properties. The formulations according to Table 6.5 were tested. In Figure 6.15 the cure curves of the samples with different co-agent and DPTT concentrations are plotted.

When compounds M1 and H1, without sulphur spender, are compared, it can be noticed that the decrease in co-agent concentration has a negative influence on the torque level, while scorch time (t_{s2}) and t_{90} are not significantly changed. When the rheograms of the compounds which contain 4 phr of co-agent are compared to those with 2 phr of co-agent, in the presence of DPTT, the same effect of the DPTT concentration can be seen: an increase in delta torque level from 0 to 0.96 phr DPTT and a slight decrease from 0.96 to 1.9 phr. This indicates that the effect of the DPTT concentration on the delta torque level is similar for both co-agent concentrations. Also an improvement in scorch time is observed for both co-agent concentrations by addition of DPTT, as can be seen from t_{s2} in Table 6.5.

Table 6.5 Formulations tested with two different co-agent concentrations. Amounts in phr.

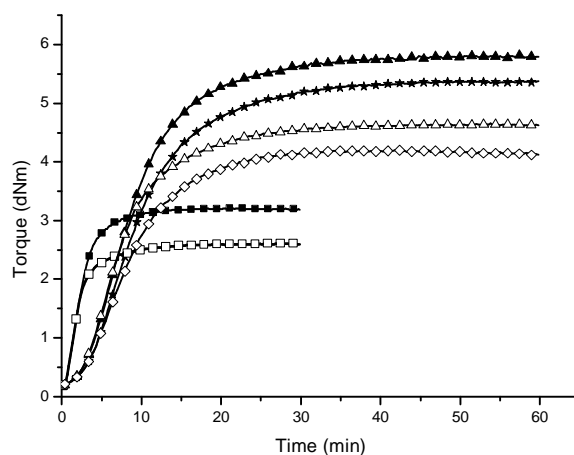| Component	M1	M7	M3	H1	H2	H3
EPM Masterbatch	206	206	206	206	206	206
DCP	6	6	6	6	6	6
BMI-MP	4	4	4	2	2	2
DPTT	0	0.96	1.9	0	0.96	1.9
t_{s2} (min)	0.50	1.45	1.38	0.47	1.32	1.20
t_{90} (min)	7.2	19.7	21.5	6.1	17.9	18.2

Figure 6.15 – Cure curves of samples with different co-agent and DPTT concentration. (■): M1; (▲): M7; (★): M3; (□): H1; (Δ): H2; (◊): H3.

In Figures 6.16 to 6.19 the mechanical properties of the samples are plotted. When compounds without sulphur spender are compared, M1 and H1, it can be noticed that the decrease in co-agent concentration has a negative influence on the mechanical properties: lower tensile strength and moduli are obtained. In the presence of DPTT, the material properties also worsen with decreasing co-agent concentration, as observed when comparing, for instance, the moduli of compounds with 4 phr of co-agent to the moduli of compounds with 2 phr, which are lower. In addition, the scorch safety, achieved by addition of DPTT to the system, is slightly worsened by lowering co-agent concentration from 4 to 2 phr, as shown in Table 6.5.
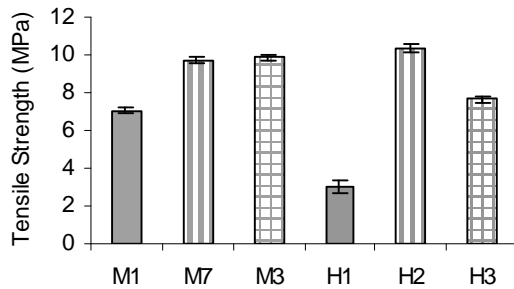

Figure 6.16 – Tensile strength for different co-agent and DPTT concentrations.
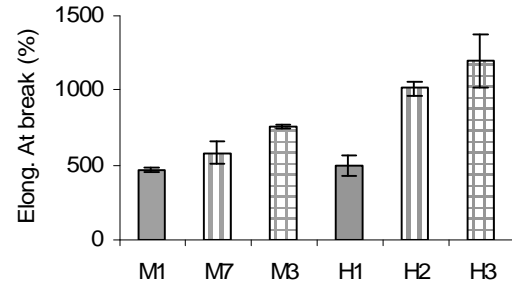

Figure 6.17 – Elongation at break for different co-agent and DPTT concentrations.
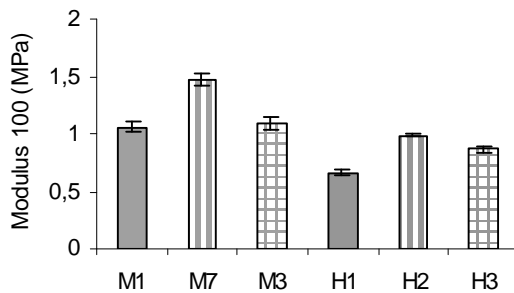

Figure 6.18– Modulus at 100% elongation for different co-agent and DPTT concentrations.
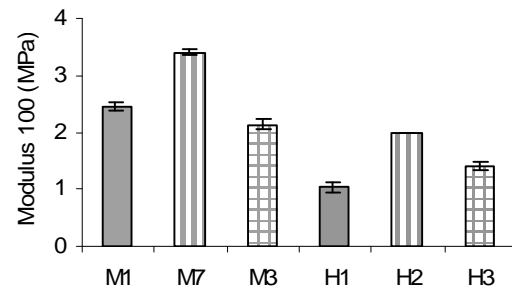

Figure 6.19 – Modulus at 200% elongation for different co-agent and DPTT concentrations.

It can be concluded from these data that the co-agent concentration is of importance in the present EPM/peroxide/co-agent system. In order to achieve the best scorch safety as well as better mechanical properties by addition of a sulphur spender, 4 phr of co-agent is preferred over 2 phr. It indicates that the mechanism that takes place during peroxide vulcanisation in the presence of the co-agent and the sulphur spender directly involves the co-agent, as was already noticed in Chapter 5. Otherwise there would be no difference in t_{s2} by changing the co-agent concentration. For this reason, a minimum concentration of co-agent is required. Lowering this concentration involves a decrease in scorch time, as well as a decrease in mechanical properties. The results also show that the DPTT concentration is of major importance: 0.96 phr of DPTT provides better scorch time, cure state and mechanical properties than 1.9 phr.

6.3.4 Influence of DPTT concentration

In the previous paragraph it was observed that the concentration of DPTT added to the peroxide/bismaleimide formulation was of importance in terms of scorch safety, cure state and mechanical properties obtained. 0.96 phr of DPTT provided better mechanical properties than 1.9 phr. In order to study in detail what the exact influence of the DPTT concentration is, several formulations were tested with different DPTT concentrations, as shown in Table 6.6. The aim was to find the concentration of DPTT that provides optimal properties.

Table 6.6 Formulations tested with different DPTT concentrations. Amounts in phr.

Component	M1	M8	M9	M10	M7	M3
EPM Masterbatch	206	206	206	206	206	206
DCP	6	6	6	6	6	6
BMI-MP	4	4	4	4	4	4
DPTT	0	0.1	0.5	0.7	0.96	1.9
t_{s2} (min)	0.50	0.61	1.21	1.38	1.45	1.38
t_{90} (min)	7.2	7.9	15.3	17.4	19.7	21.5

The cure curves obtained with different DPTT concentrations are plotted in Figure 6.20 and the scorch time and t_{90} values are shown in Table 6.6. The addition of 0.1 phr of DPTT, does not vary the scorch time or cure rate but leads to a higher delta torque. The addition of higher DPTT concentrations provides a large increase in scorch time and at the same time improves the torque level.
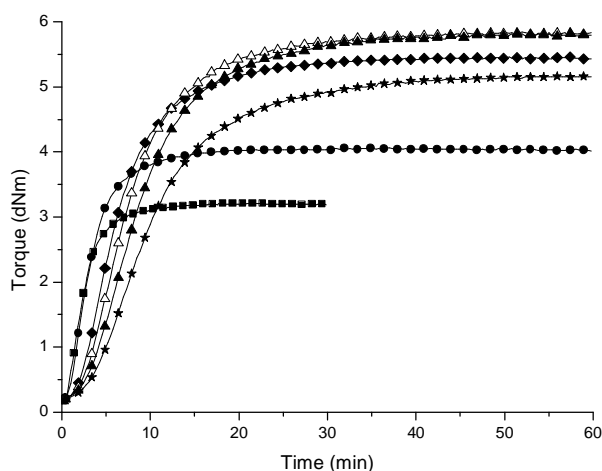

Figure 6.20– Rheograms of samples containing BMI-MP and DPTT.
(■): 0phr DPTT; (●): 0.1phr DPTT; (♦): 0.5 phr DPTT; (△): 0.7phr DPTT; (▲): 0.96phr DPTT;
(★): 1.9phr DPTT.

In order to more clearly compare the performance of the samples with different DPTT concentrations, in Figure 6.21 the delta torque and scorch time are plotted against concentration of DPTT. A clear trend can be seen of increasing delta torque and scorch time at the same time with increasing DPTT concentration, up to 0.96 phr, and from there on both delta torque and scorch time level off.
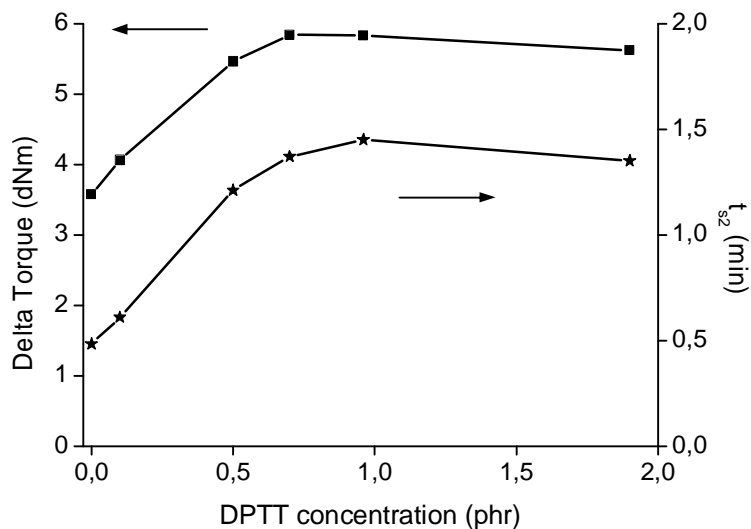
Figure 6.21– Delta torque (■) and scorch time, t_{s2} (★) vs. DPTT concentration.

In Figure 6.22 the tensile strength and elongation at break achieved with different DPTT concentrations are plotted. It can be seen, that tensile strength is significantly improved by the addition of DPTT, especially for 0.7 and 0.96 phr. At the same time elongation at break is similar or slightly higher than that of the compounds without DPTT, which is unusual because the normal tendency would be for the elongation at break to decrease with increasing tensile strength.
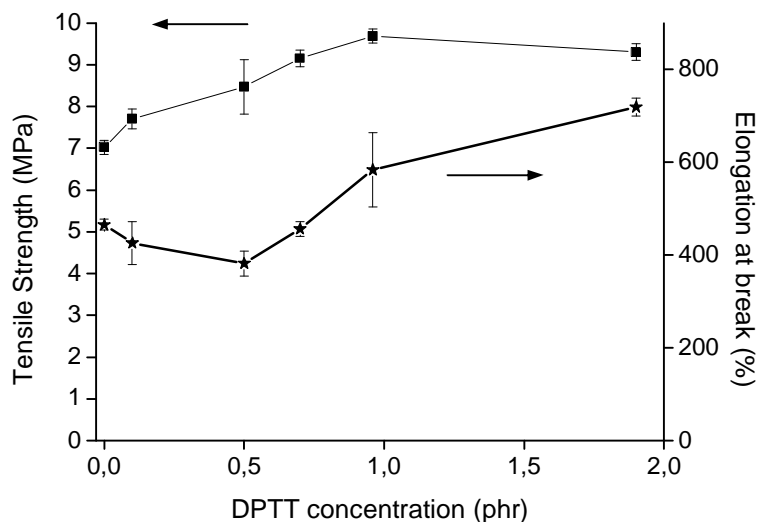

Figure 6.22– Tensile strength (■) and elongation at break (★) vs. DPTT concentration.
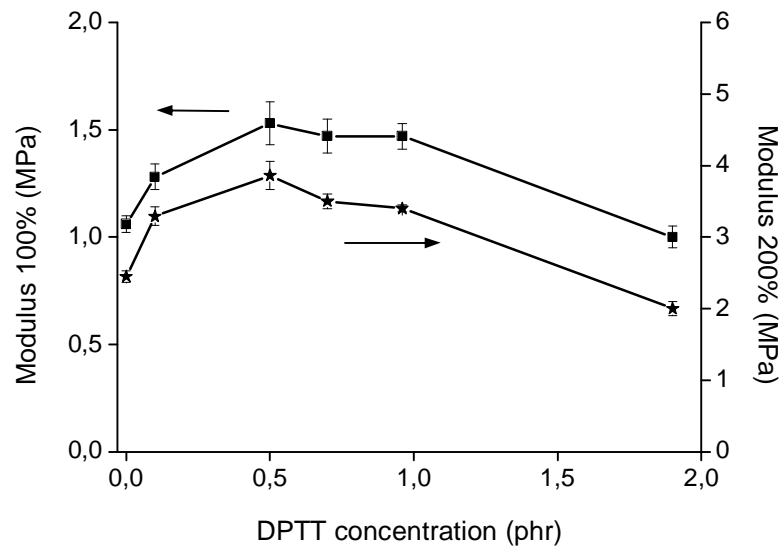
Figure 6.23– Modulus at 100% (■) and 200% (★) elongation vs. DPTT concentration.

Figure 6.23 shows the moduli achieved with the different DPTT concentrations. The moduli at 100 and 200% elongation follow the exact same trend. Up to 0.5 phr of DPTT the moduli are improved, while from 0.5 to 0.96 they are slightly decreased, yet maintained at the same level. From 0.96 to 1.9 phr of DPTT there is a clear decrease in moduli.

It was also found that DPTT concentration has a significant influence on the hardness of the material, as shown in Figure 6.24. The effect of DPTT concentration on the hardness of the material follows the same trend as observed for the moduli: up to 0.5-0.96 phr of DPTT the hardness increases and from 0.96 phr onwards it decreases again.
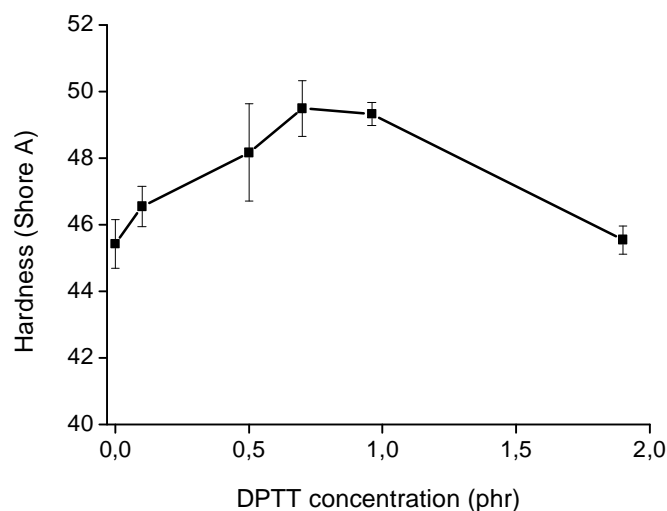

Figure 6.24– Hardness Shore A vs. DPTT concentration.

It should be mentioned that the method for determination of hardness is not optimal for this material, since the differences in hardness are very small, as shown in

Table 6.7. Nevertheless, it gives a good indication of the effect of DPTT on the hardness of the material. There is a clear tendency for the hardness of the material to increase with increasing DPTT concentration, up to 0.96 phr of DPTT.

Table 6.7 Hardness Shore A of BMI-MP samples.

Sample	Hardness Shore-A
M1: no DPTT	45.4
M8: 0.10 phr DPTT	46.6
M9: 0.50 phr DPTT	48.2
M10: 0.70 phr DPTT	49.5
M7: 0.96 phr DPTT	49.3
M3: 1.90 phr DPTT	45.6

Overall, it can be concluded that the effect of DPTT concentration is as follows: at the level of 0.1 phr or lower, DPTT slightly improves mechanical properties without an effect on scorch time, while higher concentrations not only result in improved properties but also provide scorch safety. There is an optimum for the DPTT concentration, around 0.5 to 0.96 phr, where the best scorch safety, highest delta torque, tensile strength, moduli and hardness values are obtained.

6.3.5 High temperature properties

One of the advantages of using peroxide cure over sulphur cure is the excellent high temperature properties of peroxide cured articles.[11-14] In order to achieve a synergistic combination of sulphur and peroxide cure, it is necessary not only to improve the cure state, as reflected for example in tensile strength at room temperature, to make the system behave more sulphur-like, but also to keep the good high temperature properties typical for peroxide curing.

Ageing tests were performed for samples with the formulations shown in Table 6.6. Samples were aged in an air circulated oven at 150°C for different times and their tensile strength properties were measured after ageing. In the appendix of this chapter all the stress-strain plots for the various samples after different ageing times are shown. Figure 6.25 shows the tensile strength as a function of the ageing time for the samples with different DPTT concentrations. It can be seen that after 7 days of ageing the sample with 0.7 phr of DPTT shows the least decrease in tensile strength. After 10 days of ageing all the samples show a lower tensile strength than at time 0, however the difference is smallest for the samples containing 0.5 and 0.7 phr of DPTT. Therefore, they provide the best ageing resistance.

Elongation at break along ageing time shows the same tendency as tensile strength, as shown in Figure 6.26: a decrease with ageing time. The smallest change is obtained when using 0.5 and 0.7 phr of DPTT, especially after seven days of ageing, where these two samples still have a very similar elongation at break compared to the sample at time 0.
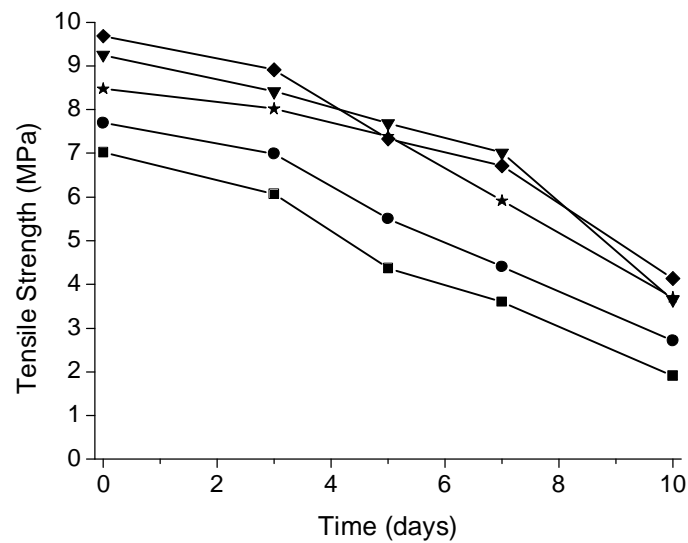
Figure 6.25– Tensile strength versus ageing time for different DPTT concentrations.
(■): 0phr DPTT; (●): 0.1phr DPTT; (★): 0.5 phr DPTT; (▼): 0.7phr DPTT; (♦): 0.96phr DPTT.
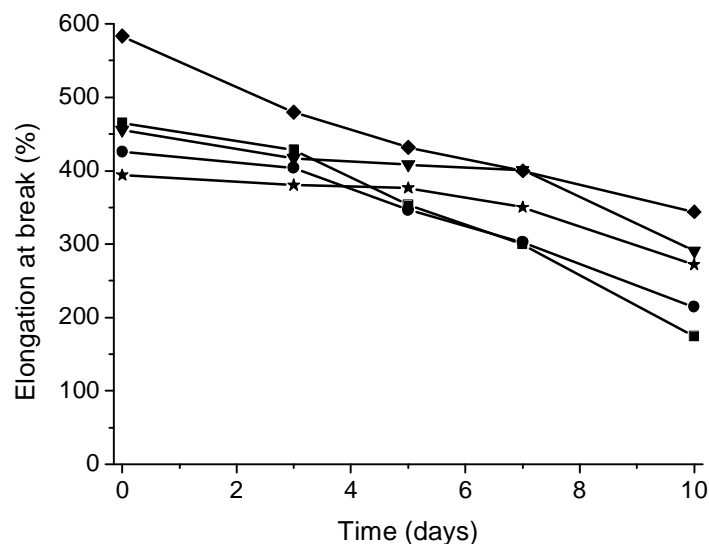

Figure 6.26– Elongation at break versus ageing time for different DPTT concentrations.
(■): 0phr DPTT; (●): 0.1phr DPTT; (★): 0.5 phr DPTT; (▼): 0.7phr DPTT; (♦): 0.96phr DPTT.

It is clear from these results, that with 0.5-0.7 phr of DPTT in the formulation the best ageing properties are obtained, significantly better than the ageing properties in the absence of DPTT. This can be more clearly seen by comparing the stress-strain curves of the sample with 0 phr DPTT and the sample with 0.7 phr, Figures 6.27 and 6.28, respectively. The sample with 0.7 phr of DPTT reaches a higher tensile strength at time 0 than the sample without DPTT. With ageing time, the sample with 0.7 phr maintains tensile strength and elongation at break very close to the values before ageing, and only after 10 days of ageing a clear deterioration in tensile and elongation at break can be observed.
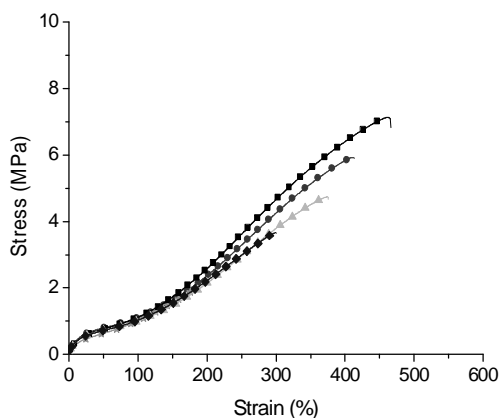
Figure 6.27– Stress strain curve for sample M1, without DPTT, after ageing at 150°C for different times. (■): 0 days; (●): 3 days; (▲): 5 days; (♦): 7days; (★): 10 days.
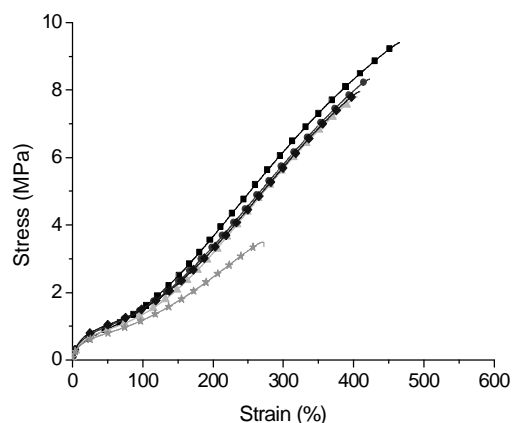
Figure 6.28– Stress strain curve for sample M10, with 0.7 phr of DPTT, after ageing at 150°C for different times. (■): 0 days; (●): 3 days; (▲): 5 days; (♦): 7days; (★): 10 days.

From these experiments it can be concluded that there is a certain DPTT concentration that provides optimal ageing properties, even better than those obtained in the absence of DPTT. This optimal DPTT concentration ranges from 0.5 to 0.7 phr: higher or lower concentrations lead to worse heat ageing properties.

Compression set was also measured for the samples containing different DPTT concentrations in order to obtain more information regarding the type of network formed in the presence of DPTT. Typically, at high temperature sulphur cured articles have a worse compression set than peroxide cured. Figure 6.29 shows the compression sets measured for the samples with different DPTT concentrations at three different temperatures: 23, 70 and 150°C.

Low concentrations, up to 0.96 phr, of DPTT improve the compression set properties of the rubber at 23 and 70°C if compared to the reference sample without DPTT. The opposite result is obtained for the sample with 1.9 phr of DPTT. For both high and low temperatures this sample leads to a higher compression set. Overall, the sample containing 0.5 phr of DPTT shows the lowest compression set at all three temperatures, which means that it has the best ability to regain its initial shape after being compressed by 25% of its initial height for 24 hours.
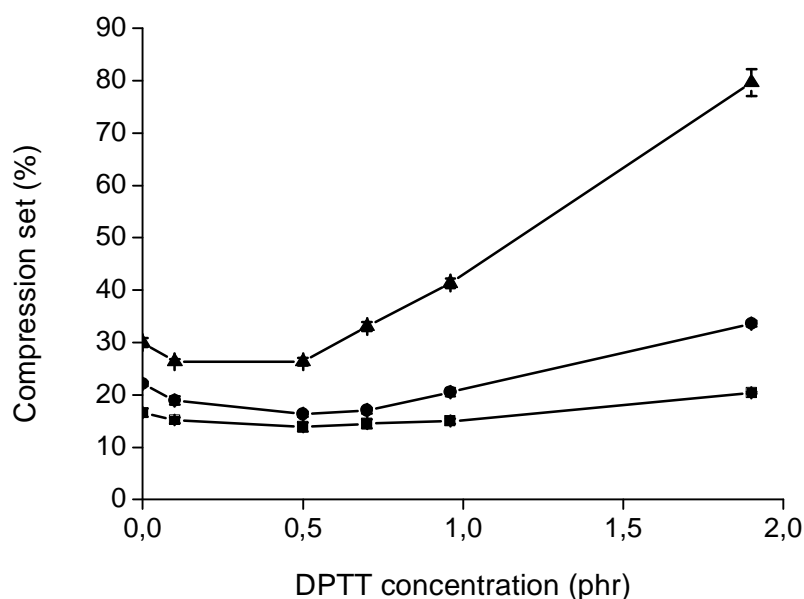
Figure 6.29– Compression set vs. DPTT concentration at different temperatures.
(■): 23°C; (●): 70°C; (▲): 150°C.

A higher value of the compression set with increasing temperature can be observed for all samples, as commonly found. At higher temperature the mobility of the rubber is higher and the polymer chains have a better chance to reorient themselves in a more energetically favourable configuration. Therefore, part of the driving force to retain the original shape has been lost, due to reorientation of the polymer chains. This leads to higher compression set.

Compression set measurements are normally carried out at 23 and 70°C. Temperatures around 150°C are more typical for ageing experiments. The compression set measurement at high temperature can be very useful to obtain valuable information about the type of rubber network formed. If the crosslinked network contains polysulphidic linkages, it is likely that those will break and recombine, to shorter and more stable linkages, easier at higher temperatures than at low temperatures, leading to worse compression set values at high temperature. C-S-C and especially C-C crosslinks remain stable at high and low temperatures, therefore compression set will not change largely. Information about the sulphur content in the network can be thus obtained from the compression set values achieved at high temperature. In Figure 6.29 it can clearly be seen that at 150°C, from a concentration of 0.5 phr DPTT onwards, the compression set increases drastically with DPTT concentration. This may be taken as an indication that at high DPTT concentrations there are indeed polysulphidic linkages built into the network. The fact that at lower DPTT concentrations, 0.1 to 0.5 phr, the compression set is maintained does on the other hand not necessarily mean that there are no sulphur linkages in the network: most probably they are built in in an efficient manner, as mono- or disulphide linkages, which cannot easily break and recombine.

6.3.6 Crosslink density

Crosslink density tests were carried out with samples with different DPTT concentrations, as shown in Table 6.6, that had been extracted in acetone during 24h, in THF during 48h and finally swollen in decalin during 72h. The same swelling test was also performed on the same samples without any extraction. The purpose of these experiments was not to obtain an exact value of the crosslink density, but to see if there was an influence of DPTT concentration on the crosslink density. Figure 6.30 shows the plot of crosslink density measured for samples with different DPTT concentrations.

The results obtained with and without extraction show the same trend. The highest crosslink density was achieved with concentrations around 0.5 to 0.7 phr DPTT. Higher or lower DPTT concentrations lead to lower crosslink density values.
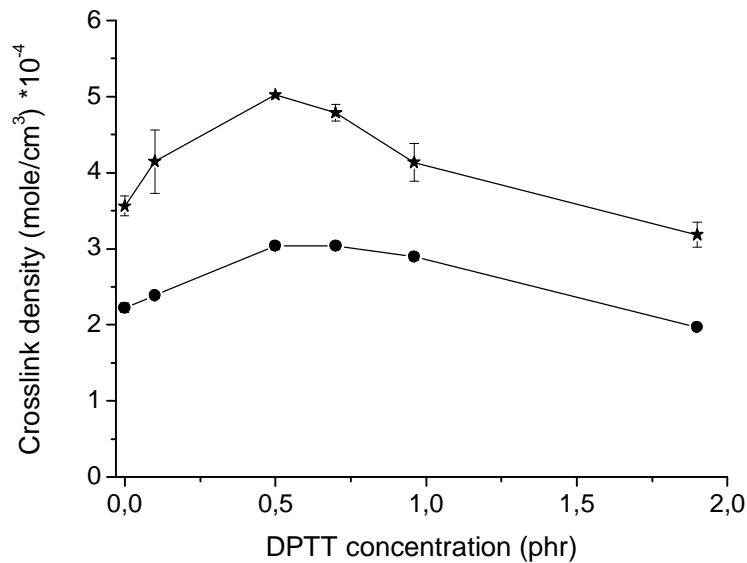

Figure 6.30– Crosslink density vs. DPTT concentration.
(●): extracted samples ; (★): not extracted samples.

Especially interesting is the fact that the crosslink density measured for the sample with 1.9 phr of DPTT gives a lower value than the reference sample, without DPTT, while the torque level of the sample with 1.9 phr of DPTT was higher than that of the sample without DPTT. Most likely, a different type of network is formed in the presence of DPTT. From compression set experiments at high temperature it is obvious that some sulphur was built into the rubber network when using DPTT. If the network formed is more sulphur-like, another χ parameter should be used for the samples with high concentration of DPTT when the crosslink density is calculated using Equation 6.2a. This could explain why the calculations of crosslink density for the samples with high concentration of DPTT are not precise, and do not necessarily correlate with the others. Since the exact sulphur content of the networks is unknown, it is impossible to know what χ parameter should be used.

6.3.7 Effect of DPTT for EPDM instead of EPM

Up to this point, the effect of DPTT in the peroxide/co-agent cure formulation has been studied using EPM rubber as polymer. It is also interesting to study whether the positive effect achieved with this new cure concept could also be obtained with other types of rubber. The effect of DPTT in a peroxide/bismaleimide cure formulation was studied using EPDM rubber. For this purpose, a new masterbatch was prepared, as described in the experimental section, with the exact same formulation as the EPM masterbatch previously tested, but with EPDM instead of EPM. The formulations tested are shown in Table 6.8. Two different DPTT concentrations were tested.

Table 6.8 Formulations tested with EPDM rubber. Amounts in phr.

Component	EO	E1	E2	E3
EPDM Masterbatch	206	206	206	206
DCP	6	6	6	6
BMI-PP	0	4	4	4
DPTT	0	0	0.96	1.9

In Figure 6.31 the cure curves of the formulations containing EPDM with and without DPTT are plotted. The torque level achieved in the absence of co-agent or DPTT, sample EO, is higher than it was for EPM, where the delta torque achieved in the absence of co-agent was 0.6 dNm, as shown in Chapter 3. This fact already reflects the difference in cure behaviour for both rubbers, due to the unsaturation present in EPDM. When BMI-PP is added as co-agent to the EPDM formulation, sample E1, the cure rate and cure state are largely increased, but the scorch time becomes very short: t_{s2} is only 0.55 min. The addition of DPTT to the formulation provides an improvement in scorch time, formulations E2 and E3: a t_{s2} of 1.55 and 1.43 min, respectively. The cure state is not further improved with DPTT, as it was in the case of EPM, yet maintained at the same level.
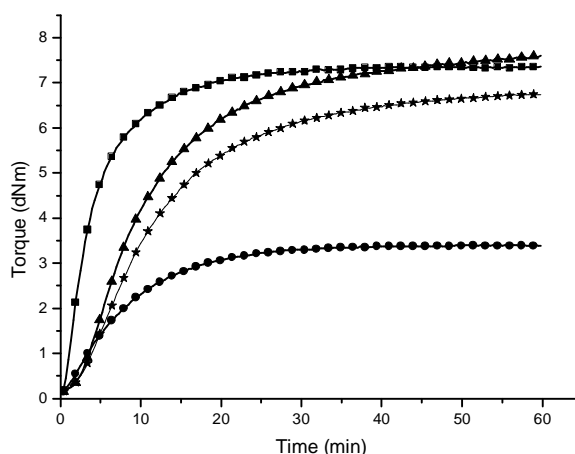

Figure 6.31 – Cure curves of samples with EPDM rubber.
(●): E0, no co-agent and no DPTT; (■): E1, BMI-PP and no DPTT;
(▲): E2, BMI-PP+ 0.96 phr DPTT; (★): E3, BMI-PP+1.9 phr DPTT.

The mechanical properties tested for these EPDM samples are plotted in Figures 6.32 to 6.35. The addition of DPTT to the formulation provides an improvement on tensile strength, as can be seen by comparing samples E2 and E3 with sample E1 in Figure 6.32. The effect of DPTT on elongation at break, Figure 6.33, is the same as was observed for the EPM formulation: an increase in elongation at break by addition of DPTT. Further, the effect of DPTT on the moduli depends on the concentration used: the sample with 0.96 phr of DPTT, E2, has higher moduli than E1, while the sample with 1.9 phr of DPTT, E3, provides lower moduli than sample E1, as shown in Figures 6.34 and 6.35.
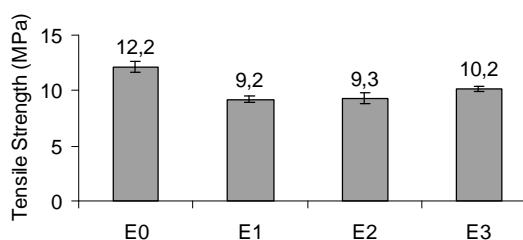

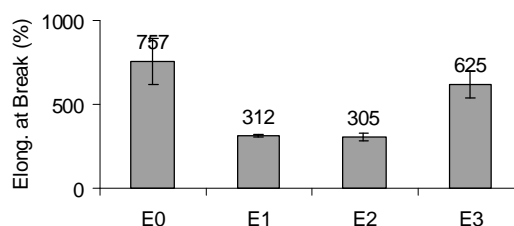**Figure 6.32** – Tensile strength of the EPDM samples with and without DPTT.

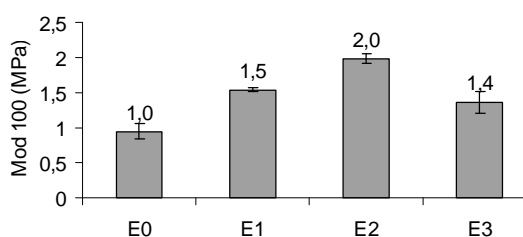**Figure 6.33** – Elongation at break of the EPDM samples with and without DPTT.

Figure 6.34 – Modulus at 100% elongation of the EPDM samples with and without DPTT.
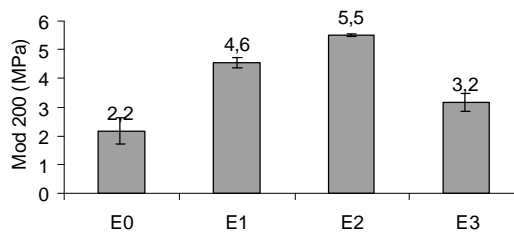
Figure 6.35 – Modulus at 200% elongation of the EPDM samples with and without DPTT.

From these results it can be concluded that the overall effect achieved by addition of DPTT to the peroxide/BMI-PP cure formulation of EPDM is analogous to that observed for EPM. In both cases scorch time is significantly improved, tensile strength is improved and moduli are increased, with 0.96 phr of DPTT. Or slightly decreased with 1.9 phr. The only difference between the two rubbers is that in the case of EPM the delta torque level was increased, while for EPDM it remained at the same level.

For both rubbers the DPTT concentration used in the formulation has a significant influence on the cure state and therefore also on the mechanical properties achieved. A concentration of 0.96 phr of DPTT provides a better scorch time, cure state and mechanical properties than 1.9 phr.

6.4   CONCLUSIONS

The effects achieved by addition of DPTT to a peroxide/bismaleimide cure formulation, as reported in Chapter 5, also take place when other sulphur spenders are used, like DPTH for instance. This new concept of peroxide/bismaleimide cure in the presence of a sulphur spender works also for several types of peroxide.

The co-agent concentration is of importance in order to obtain optimal properties and the best scorch safety when using DPTT in the peroxide/cure formulation. 4 phr of bismaleimide co-agent performs better than 2 phr, for the same DPTT concentration.

The concentration of the sulphur spender, DPTT, has also been found to be of importance in order to meet optimal properties. Concentrations of 0.5 to 0.7 phr of DPTT in the peroxide/bismaleimide cure system improve at the same time: scorch safety, cure state, tensile strength, moduli, hardness, ageing properties and compression set at room and at high temperatures. It means that this system achieves a synergistic combination between sulphur cure and peroxide cure.

Finally, this new concept of cure has been proven to work not only for EPM rubber but also for EPDM rubber; therefore, this principle can be widely applied.

6.5 REFERENCES

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APPENDIX

Figure A1– Stress strain curves for sample M1 containing BMI-MP and no DPTT, at 150°C for 0, 3, 5, 7, and 10 days.

Figure A2– Stress strain curves for sample M8 containing BMI-MP and 0.1phr of DPTT, at 150°C for 0, 3, 5, 7, and 10 days.
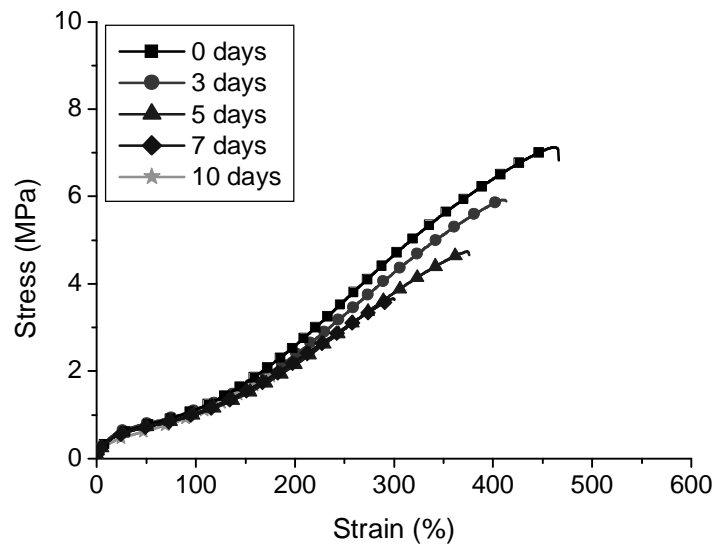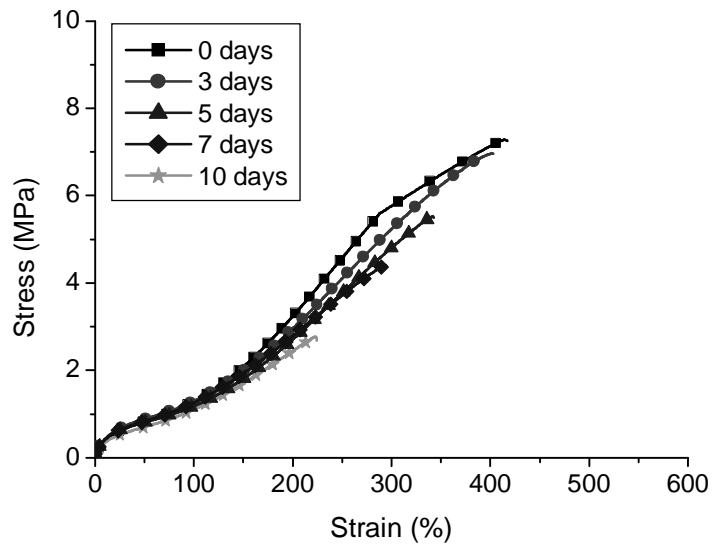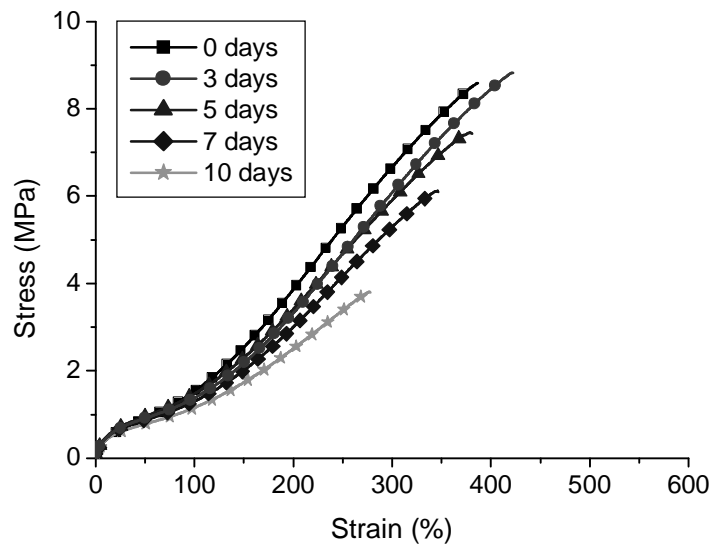
Figure A3– Stress strain curves for sample M9 containing BMI-MP and 0.5 phr of DPTT, at 150°C for 0, 3, 5, 7, and 10 days.
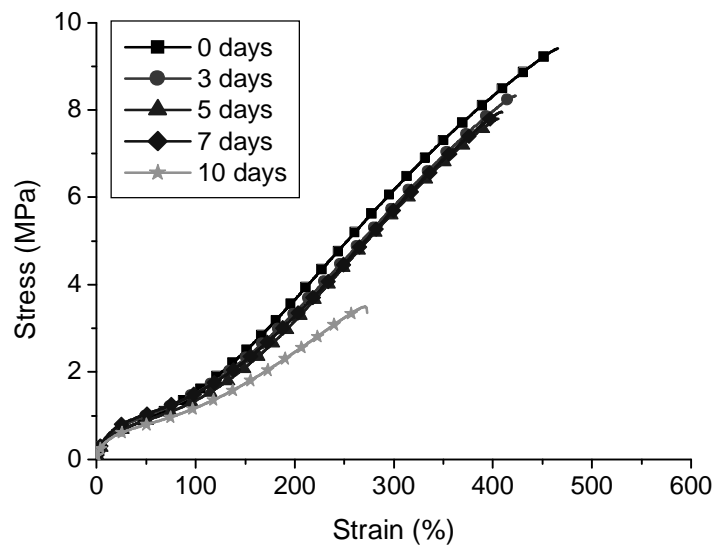

Figure A4– Stress strain curves for sample M10 containing BMI-MP and 0.7 phr of DPTT, at 150°C for 0, 3, 5, 7, and 10 days.
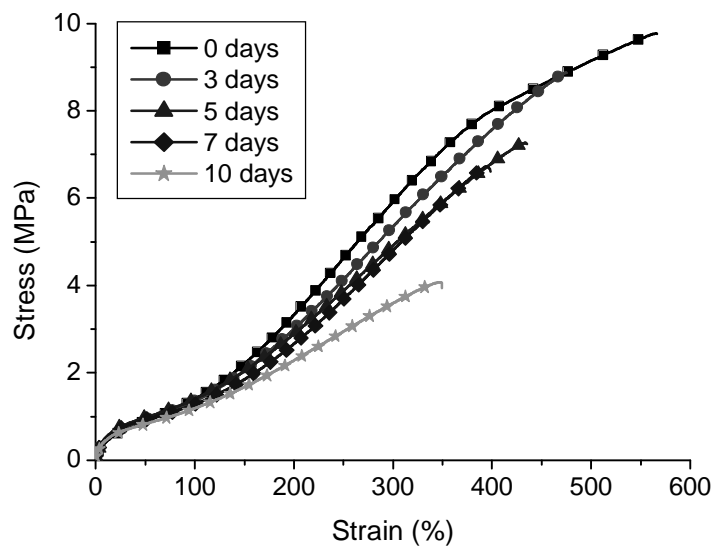
Figure A5– Stress strain curves for sample M7 containing BMI-MP and 0.96 phr of DPTT, at 150°C for 0, 3, 5, 7, and 10 days.

Chapter 7

Mechanistic Studies on the
Peroxide/Co-agent Cure System[#]

"…it is not possible to untie a knot of which one does not know."

Aristóteles *(384 AC-322 AC)*

In Chapter 5 of this thesis a new concept of a peroxide cure system for rubber has been introduced where scorch safety and mechanical properties are improved at the same time. This new system consist of the use a combination of a peroxide, a bismaleimide type co-agent and a sulphur spender for the cure of saturated or low-unsaturated rubber. Several mechanical properties have been found to be improved by using this new system, as extensively investigated in Chapter 6. The present chapter deals with the understanding of the reported phenomena from a fundamental point of view. Mechanistic studies are carried out in order to understand the chemistry that takes place between polymer, peroxide and a maleimide type co-agent during the vulcanisation reaction. Further, the chemistry of the peroxide vulcanisation reaction in the presence of a bismaleimide co-agent and a sulphur spender like dipentamethylenethiuram tetrasulphide, DPTT, is also studied in order to understand the phenomena of scorch delay and property improvement described in Chapters 5 and 6.

From Nuclear Magnetic Resonance and Infrared analysis the loss of the maleimide unsaturation from the co-agent is observed, due to reaction with the sulphur spender. This reaction already takes place at room temperature, thus previous to peroxide decomposition.

Further, Model Compound Vulcanisation studies are performed using 3-methylpentane as representative model for the saturated rubber backbone. The reaction products of the peroxide vulcanisation of 3-methylpentane in the presence of a maleimide type co-agent and a sulphur spender have been analysed by means of Liquid Chromatography-Mass Spectrometry. Several reaction products have been identified and a reaction mechanism that explains the scorch delay and the property improvement by the new cure system is proposed.

7.1 INTRODUCTION

The addition of a sulphur spender to a peroxide/bismaleimide cure system provides an improvement in mechanical properties as well as in scorch safety as reported in Chapters 5 and 6 of this thesis. The exact reaction mechanism that takes place is, however, not yet fully understood. The effect of a bismaleimide co-agent in peroxide cure has been studied by several authors,[1-4] as explained in Chapter 2 of this thesis. The influence of sulphur and other sulphur species in peroxide cure has also been reported in literature[5-13] and it is also summarised in Chapter 2. However, the effect of the combination of both chemicals: bismaleimide co-agent and sulphur spender, has not been studied from a fundamental point of view. Therefore, in the present chapter mechanistic studies are presented on model compounds in order to understand the effect that the combination of a sulphur spender and a bismaleimide type co-agent has on the cure characteristics and the mechanical properties of peroxide cure articles.

7.1.1 Definition of Model Compound Vulcanisation

Model Compound Vulcanisation (MCV) is defined as the vulcanisation of a low-molecular-weight model olefin as a substitute for the reactive unit of polymeric rubber.[14] MCV is a very useful technique to investigate the chemistry of vulcanisation, because rubber, vulcanised or unvulcanised, is difficult to analyse using standard analytical and spectroscopic techniques. This is mainly due to the poor solubility of real rubber, which is even more difficult after vulcanisation. The model olefins used in MCV remain in the liquid state even after vulcanisation; therefore they can be readily analysed by standard analytical techniques.

The main objectives of MCV are:
1. To obtain information regarding the chemistry of the repeating rubber unit.
2. To elucidate the structure of the crosslinked products that are formed during vulcanisation.
3. To study the reactions of curatives in a rubber-like environment, and then obtain information about the mechanism of the vulcanisation reactions.

The model used in MCV should be as much as possible a representative for the reactive unit of the polymer. This is to make sure that its chemical behaviour during vulcanisation is similar to the behaviour of the reactive unit of the rubber itself. First, the model compound should be carefully selected with respect to its molecular structure, its physical and chemical properties, and the ease of analysis. Second, the experimental conditions should be evaluated, in particular the influence of solubility and volatility.

There are three conditions that are obligatory in order to design a successful MCV study. These are the following:
- To choose a suitable model compound.
- To apply well-defined experimental conditions.
- To apply a suitable method of analysis to obtain and evaluate the results.

An elementary disadvantage of low-molecular-weight model compounds is the high concentration of end-groups, which makes it differ from the real rubber system. This disadvantage can be overcome by using larger models, but then the amount of isomers of reaction products formed increases and that makes the analysis more complicated.

Although most MCV studies have dealt with sulphur vulcanisation and have employed models for rubbers that contain unsaturations,[14-23] MCV has also been used to investigate peroxide vulcanisation. Already in the early seventies Cornell et al.[24] used decane as a model olefin to study the vulcanisation reaction of polyethylene with dicumyl peroxide and a methacrylate co-agent. Fujio et al.[5] suggested a mixture of

squalane with divinylbenzene (DVB) and dicumyl peroxide (DCP) to model the peroxide cure of ethylene propylene polymethylene rubber (EPM) and ethylene propylene diene polymethylene rubber (EPDM) with DVB as co-agent, in order to study the effect of sulphur in peroxide cure. They found that DVB was homopolymerising and sulphur could act as a retarder but not as an inhibitor. Dikland et al.[25] used n-pentadecane as a model for EP(D)M in peroxide vulcanisation using triallylcyanurate (TAC) as co-agent and analysed the results by means of Infrared spectroscopy (IR).

Liquid and gas chromatography (LC and GC respectively) are the most commonly used analytical techniques for MCV, used to separate the reactants and resulting reaction products. IR is a very powerful analytical technique in mechanistic studies as well, since it allows the analysis of unfilled rubber, of which the behaviour is more similar to the actual rubber than that of the model compound. Dikland et al.[26, 27] explored this analytical tool very extensively. By means of IR, equilibrium swelling and atomic force scanning microscopy the mechanism of peroxide vulcanisation in the presence of various bis(allyl)esters as co-agents was elucidated. Further, other analytical techniques, like Nuclear Magnetic Resonance Spectroscopy (NMR), are also valuable tools for model compound vulcanisation studies.

7.1.2 Liquid Chromatography-Mass Spectrometry (LC-MS)

A short introduction to the LC-MS technique is here presented, in order to understand better the discussion at the end of this chapter, where some important details about the technique partake in the discussion.

The LC-MS analytical technique requires two instruments: a liquid chromatograph and a mass spectrometer, with an intermediate step (interface) between them. The knowledge of the theory behind the equipment is crucial in order to obtain good and repeatable results and to interpret them in a proper way. Figure 7.1 shows a schematic set-up of an LC-MS.[28]
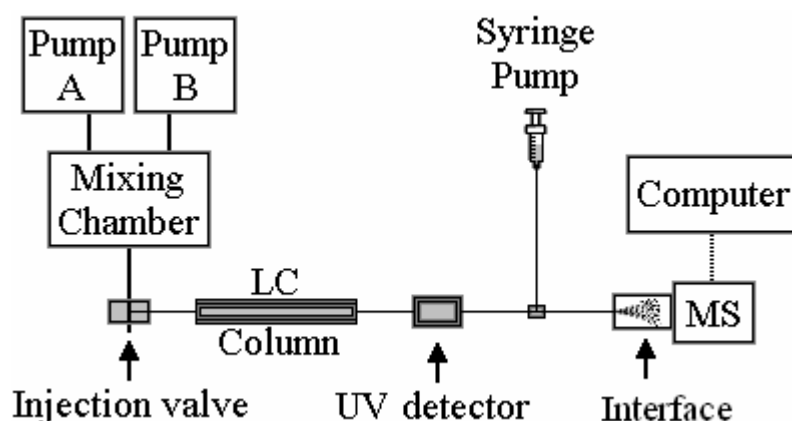
Figure 7.1: Experimental set-up used for LC/MS.

In the first part of the system, left on Figure 7.1, a fraction of the liquid sample (in the order of μL) is injected in the liquid chromatographic system by the injection valve. Then the sample is dragged from the injection loop by a flow of eluent (or mixture of eluents), which are pumped and mixed (in case of a mixture) before arriving to the injection loop. The sample is dragged by that eluent flow to the column, where it will separate according to the polarity of the components that form the sample. After the chromatographic column, an ultraviolet (UV) detector registers UV sensitive compounds which come out of the column along time.

After the chromatographic separation and UV detection the liquid flow from the LC should be adapted in order to enter the MS system, which works at high vacuum condition, and to enable the components of the sample to be detected by the MS. Therefore the sample needs to pass through an interface, situated between the LC and the MS, where it is transformed from a liquid flow into an ionised gas flow.

On the MS system, right part of Figure 7.1, the different components of the sample arrive already separated in time (by the previous LC step) and ionised (which is done in the interface). Then according to the mass/charge ratio of the compounds they will be detected and registered in the MS.

It is also possible to inject a compound in liquid state directly into the MS system without previous LC step, which can safe some time for instance in the case of pure compounds, where no previous separation is necessary since they are already pure. In this case the sample can be directly injected to the interface by a syringe pump.

Liquid chromatography, LC

The most important part of the Liquid Chromatograph (LC) is the column where the separation of the different components of the liquid sample takes place. Some columns are used in normal phase mode and some are used in reverse phase mode. The normal phase mode of chromatography is carried out with a polar adsorbent surface (silica gel) in the inner side of the column and a nonpolar mobile phase. The reverse phase mode consists of a nonpolar adsorbent surface i.e.: C_{18} chains, covering the silica gel of the inner side of the column, and a polar mobile phase, where the eluent usually is a mixture of water and some polar organic solvent like acetonitrile. A nonpolar compound will stay in the reverse phase column longer than a polar compound. When working with MCV, the model used as well as the reaction products are normally nonpolar, thus a good separation can be obtained by using a reverse phase column rather than a normal phase column.

The time that it takes for the compounds that form the sample to pass through the column, called the retention time or elution time, can be adjusted with the polar mobile phase. The polarity of the mobile phase can be adjusted depending on the ratio water/acetonitrile. Water is more polar than acetonitrile, therefore the higher the water ratio in the mobile phase the faster the polar molecules will pass through the column and viceversa. After separation, the eluent containing the sample passes through a UV detector, where every compound that absorbs UV light is detected with a certain intensity depending on its response factor and on its concentration. Normal UV lamp detectors allow measuring at one or two UV wavelengths, diode arrange UV detectors (DAD) also allow to set a range of wavelengths, which makes it more sensitive. As a result of the LC step a UV chromatogram is obtained where intensity of the absorbing compounds vs. retention time is depicted.

Interface

As already mentioned, the interface is located between the LC and the MS and its function is to transform the liquid flow coming from the LC into an ionised gas flow going to the high vacuum condition of the MS.

There are several types of interfaces which differ in the ionisation technique. The most important are:
- ESI: Electrospray Ionisation.
- APCI: Atmospheric Pressure Chemical Ionisation
- APPI: Atmospheric Pressure Photo Ionisation

The choice for the interface depends on the polarity of the compounds that need to be analysed, i.e.: ESI works the best for polar compounds. In this thesis the three interfaces mentioned above have been used and APCI has been found to give the

best ionisation thus the most significant and repeatable results. Therefore the explanation and results refer to this type of interface.

Atmospheric Pressure Chemical Ionisation (APCI) uses a reagent ion to react with the target molecules and form ions by a proton transfer mechanism. The reagent ions are produced by introducing a large excess of methane into an electron impact ion source. Electron collisions produce CH_4^+ and CH_3^+, which further react with methane to form CH_5^+ and $C_2H_5^+$. In the reaction below M represents the target molecule, with a molar mass of M:

$$M + CH_5^+ \text{ à } [M+H]^+ + CH_4$$
$$M + C_2H_5^+ \text{ à } [M+H]^+ + C_2H_4$$
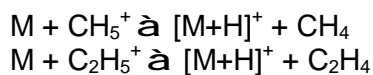
As the reaction indicates, the peak from the target molecule M in the mass spectra can be found with the molar mass M+1 since the $[M+H]^+$ ion is formed.

All molecules can be broken down in the interface, depending on their stability, and they will form distinctive fragmentation patterns according to their structure. This information can be used to trace back the initial structural component and therefore identify compounds.

Once the ions are formed they are introduced into the MS block by applying a potential difference, that sucks the ions into the MS.

Mass spectrometry, MS

A mass spectrometer is an instrument that measures the masses of individual molecules that have been converted into ions. The molecular mass is not directly measured, but rather the mass-to-charge ratio (m/z). However, in many cases the molecules encountered in the spectrometer have only one charge (z=1), which means that the numerical value of the molar mass corresponds to the m/z ratio. Mass spectrometers use the difference in mass-to-charge ratio of ionised molecules and atoms to separate them from each other.

Mass spectrometry is useful to determine chemical and structural information of molecules, thus to identify, and also for quantitative analysis of molecules and atoms. Mass spectrometry is used for many purposes like determine the composition of molecules in an unknown sample, locate oil deposits in rock by measurement of petroleum precursors and detect dioxins in contaminated fish. In this thesis it was used to study the chemistry of peroxide vulcanisation of a model olefin.

A mass spectrometer has mainly three tasks:

*   Creation of gas-phase ions (in the interface).
*   Separation of the ions based on their mass-to-charge ratio.
*   Measurement of the quantity of each mass-to-charge ratio ion.

There are several options for the separation of the ions, for instance: quadrupole mass filters and ion traps are used in this purpose. In the present thesis, the experiments have been performed with an MS system that uses an ion trap to separate the ions. The ion trap mass spectrometer uses three electrodes to trap or collect a certain amount of ions in a small volume called trap. These ions are then selectively (according to their m/z) ejected from the trap by changing the electrode voltages. The ions are subsequently counted by converting the ion flux into a proportional electronic current. A data system is used to record the magnitude of these electric signals as a function of m/z and convert this information into a mass spectrum. The mass spectrum shows a graph of ion intensity as a function of m/z ratio. Not only will the ionised target molecule be found in the spectra but also the fragments of the target molecule.

The recorded data consists of a series of mass spectra that are acquired sequentially in time. To generate this information, the mass spectrometer scans a

mass range (e.g., m/z 30-500) repetitively during the chromatographic run. If a scan is taken every second and the run is 30 minutes long, 1800 spectra are recorded. This information may be displayed as the sum of intensities of all the ions in each spectrum and this sum plotted as a function of chromatographic retention time to give a total ion chromatogram (TIC). Each peak in the TIC represents an eluding compound that can be identified by interpretation of the mass spectra recorded for the peak. Also a scan along the whole retention time can be done for a selected ion with a certain m/z, as a result a plot of intensity of that ion vs. retention time will be obtained, which is called Extracted Ion Chromatogram (EIC).
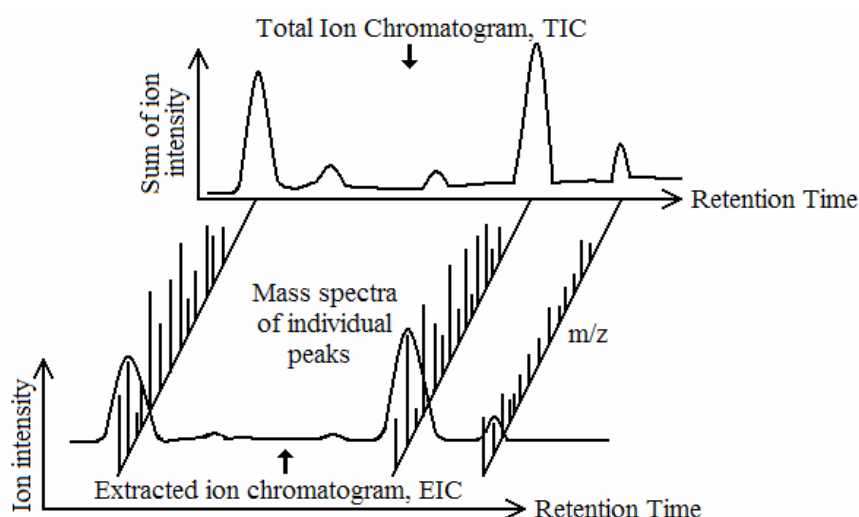

Figure 7.2 Data display of a TIC and an EIC.

7.2 EXPERIMENTAL

7.2.1 Materials

Table 7.1 Chemical name and structure of the different materials.

Chemical name	Abbreviation	Chemical structure
Ethylene propylene polymethylene rubber	EPM	
Dicumyl peroxide	DCP	
N-phenylmaleimide	MI	
N,N'-m-phenylenedimaleimide	BMI-MP	
3-methylpentane	-	
n-hexane	-	C_6H_{14}
Deuterated dimethylsulphoxide	DMSO	
Acetonitrile	AcN	CH_3CN
Dipentamethylenethiuram tetrasulphide	DPTT	

Ethylene propylene polymethylene rubber (EPM Keltan 13, Mooney viscosity ML(1+4)100°C of 46, containing 56% ethylene and 44% propylene) was provided by DSM Elastomers B.V. Dicumyl peroxide (DCP, 99% pure) was provided by Akzo Nobel. The co-agents N-phenylmaleimide (MI) and N,N'-m-phenylenedimaleimide (BMI-MP), 3-methylpentane, n-hexane, deuterated dimethylsulphoxide and acetonitrile were purchased from Acros. Dipentamethylenethiuram tetrasulphide (DPTT) was provided by Flexsys B.V. The structures of all these compounds are shown in Table 7.1.

7.2.2 Nuclear Magnetic Resonance (NMR)

To investigate direct chemical reactions between the peroxide DCP, the maleimide co-agent and the sulphur spender DPTT in absence of rubber, various combinations were separately reacted and tested with NMR. Table 7.2 shows the different samples tested. All the experiments were carried out using DMSO as solvent. Initially the pure compounds were tested and then combinations of them, first at room temperature and then after reaction at 150°C during one hour in a preheated thermostatic oil bath.

Table 7.2 List of experiments analysed by NMR.

Sample	Temperature	Colour Observations
DMSO	Room Temp.	Colourless
DCP	Room Temp.	Colourless
MI	Room Temp.	Bright pink
DPTT	Room Temp.	Colourless
MI + DPTT	Room Temp.	Bright orange
MI + DPTT	1hour at 150°C	Dark orange
DCP + MI	Room Temp.	Bright pink
DCP + MI	1hour at 150°C	Dark pink
DCP + MI + DPTT	Room Temp.	Bright orange
DCP + MI + DPTT	1hour at 150°C	Dark orange

All chemicals, except for the solvent, were added on molar basis compared to each other, according to the ratios used in the real rubber formulations and expressed there in phr, for which the mechanical properties have previously been tested in Chapters 5 and 6. The exact amounts of chemicals used in every sample are listed in Table 7.3. 2.5 ml of DMSO were added as solvent to each sample mixture. The ^{1}H-NMR spectra were recorded for all the samples in a Varian Unity 300 MHz system at 25°C.

Table 7.3 Amount of ingredients used in NMR samples.

Chemical	Concentration (phr)	Amount (mmol)	Amount (mg)
DCP	2.4	8.89	5.76
DPTT	0.7	1.82	1.60
MI	5.2	30.0	12.2

7.2.3 Fourier-Transform InfraRed Attenuated Total Reflection Spectroscopy (FT-IR ATR)

IR experiments were carried out with the pure EPM rubber. Samples with compositions according to Table 7.4 were prepared as follows. First all the chemicals except the rubber were dissolved in n-hexane in a 25 ml beaker with stirring. Then the EPM rubber, cut into small pieces, was added. The BMI-MP and the DPTT did not completely dissolve in n-hexane, but when the EPM rubber was added and the liquid

became highly viscous, the BMI-MP and DPTT were equally distributed in the sample. Aluminium foil was placed over the beaker during mixing to prevent the n-hexane as much as possible from evaporating. The components were mixed until a highly viscous liquid was obtained, without visible pieces of EPM rubber remaining, that took about 1 hour. The mixture was then poured into a steel mould (1x6x0.3 cm) placed on aluminium foil. The solvent was allowed to evaporate. Evaporation of the solvent took about 1 hour and was carried out in the fumehood at room temperature. Subsequently, the samples were removed from the mould and dried for an hour at room temperature.

The samples were first measured in the FT-IR-ATR and then vulcanised for 30 minutes at 160°C in a compression moulding press at 10 MPa. The resulting sample was measured again in the FT-IR-ATR.

FT-IR-ATR spectra of the samples were recorded on a BIORAD FTS-60 spectrometer (resolution = 4.0 cm^{-1}, 512 scans, scan range 750 – 4000 cm^{-1}).

Table 7.4 Composition of samples analysed with IR.

Compound	A	B	C	D
EPM (g)	1	1	1	1
BMI-MP (g)	0.04	-	0.04	0.24
DCP (g)	-	0.024	0.024	0.144
DPTT (g)	-	-	-	0.042

7.2.4 Model compound vulcanisation analysed with LC-MS

For the MCV studies 3-methylpentane was selected as model olefin to represent EPM rubber for reason of its molecular similarity, as can be observed by comparing Figure 7.3 to Figure 7.4.
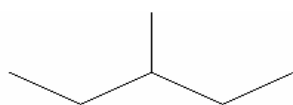

Figure 7.3 3-methylpentane.   **Figure 7.4** EPM rubber.

Samples according to Table 7.5 were prepared. The proportion of reactants was again taken in the same ratio as in the real rubber formulation tested in Chapters 5 and 6 of this thesis. The DPTT amount used, 8,89 mmol, corresponds to 0,7 phr of DPTT, which was found in Chapter 6 as an optimum concentration in terms of mechanical properties.

Table 7.5 List of experiments for MCV analysed by LC-MS.

Sample	3-methyl-pentane (ml)	MI (mmol)	BMI-MP (mmol)	DCP (mmol)	DPTT (mmol)	React. time (min)
1	-	-	-	-	1.82	0
2	15	-	15	8.89	-	0, 15, 30, 60
3	15	-	15	8.89	1.82	0, 15, 30, 60
4	15	30	-	8.89	-	0, 15, 30, 60
5	15	30	-	8.89	1.82	0, 15, 30, 60

Special glass ampoules like the one shown in Figure 7.5 were prepared by melting a glass tube to obtain an ampoule with a thin neck. The inner volume of the ampoule can be calculated to about 2 ml. Every ampoule contained a small magnetic stirrer inside. The chemicals were introduced into the glass ampoule by using a long needle, flushed with N_2 and sealed by melting the glass ampoule neck. Subsequently,

they were introduced in a thermostatic oil bath at 140°C with magnetic stirring, for different reaction times. After the reaction, the samples were cooled down in an ice/salt/water bath in order to quench the reaction. Once the samples had cooled down, they were opened by breaking the glass ampoule and the contents were transferred into a small beaker.
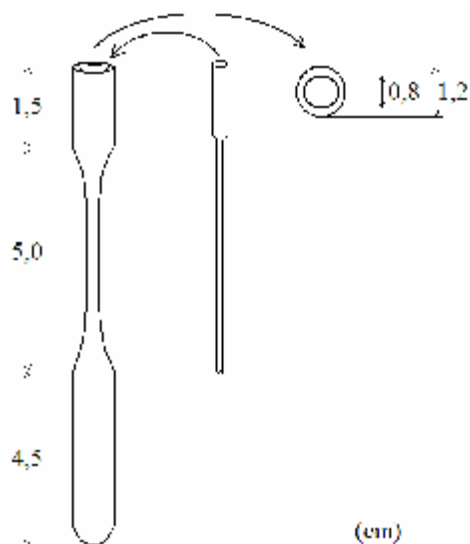

Figure 7.5 Glass ampoule used for the model compound study.

From each reacted sample 0.03 g was taken for further analysis. The 3-methylpentane was vaporised and the remaining sample was diluted with 2.5 ml of acetonitrile, filtered through a 45 µm porous filter and finally transferred to a LC-MS vial. The samples were analysed by LC-MS, according to the chromatographic conditions shown in Table 7.6 and Figure 7.6, in a Bruker Daltonics LC-MS equipment. An Atmospheric Pressure Chemical Ionization (APCI) interface was used to couple the LC with the MS and to ionise the sample. The conditions used for the ionisation are shown in Table 7.7.

Table 7.6 Chromatographic conditions.

Column	Nucleosil 100-5 C18 HD (reverse phase)
Length of column	250 mm
Internal diameter of column	4.6 mm
Mobile Phase	Acetonitrile:Water. Gradient in Figure 7.6
Flow rate	0.3 ml/min
Temperature	23°C
Detector	UV (DAD)
Wavelength	254 nm (200 to 700nm)
Injected volume	5 µl
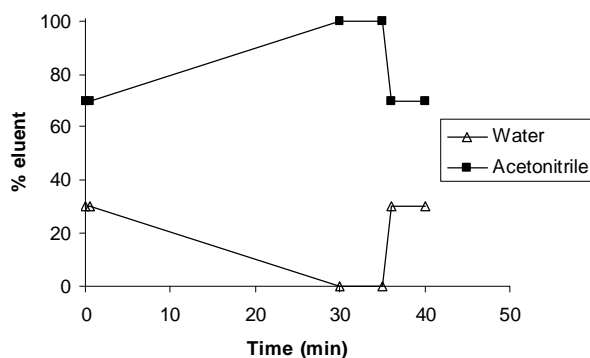
Figure 7.6 Gradient of mobile phase for LC measurements.

Table 7.7 Ionisation conditions in the APCI interface.

Flow rate	20 µL/min
Nebuliser Gas Pressure	25 psi
Dry Gas Flow	3 L/min
Dry Gas Temperature	325°C
Vaporis. Temperature	425°C

7.3 RESULTS AND DISCUSSION

7.3.1 Direct reaction between curatives and rubber analised with NMR

NMR experiments were performed in the absence of rubber and model compound, in order to understand the chemistry that takes place between the pure co-agent, the peroxide and the sulphur spender DPTT. In order to simplify the analysis of the spectra a monofunctional maleimide co-agent, N-phenylmaleimide (MI), was used instead of the difunctional molecule N,N'-m-phenylenedimaleimide (BMI-MP), which would give several different isomers after reaction. The maleimide functionality from the MI behaves chemically in the same manner as those from BMI-MP, but the number and structure of reaction products will be easier to analyse in the case of MI. All the spectra obtained are plotted in the Appendix.

From the spectra of the pure compounds the characteristic peaks of each chemical were identified. Figure 7.7 shows the spectrum of MI. The most remarkable peaks are from the two protons of the maleimide unsaturation at 7.15 ppm, marked as 1 in Figure 7.7. On Figure 7.8 the spectrum of DPTT is displayed. As can be observed, the characteristic peaks from DPTT are found in the region under 4.5 ppm.
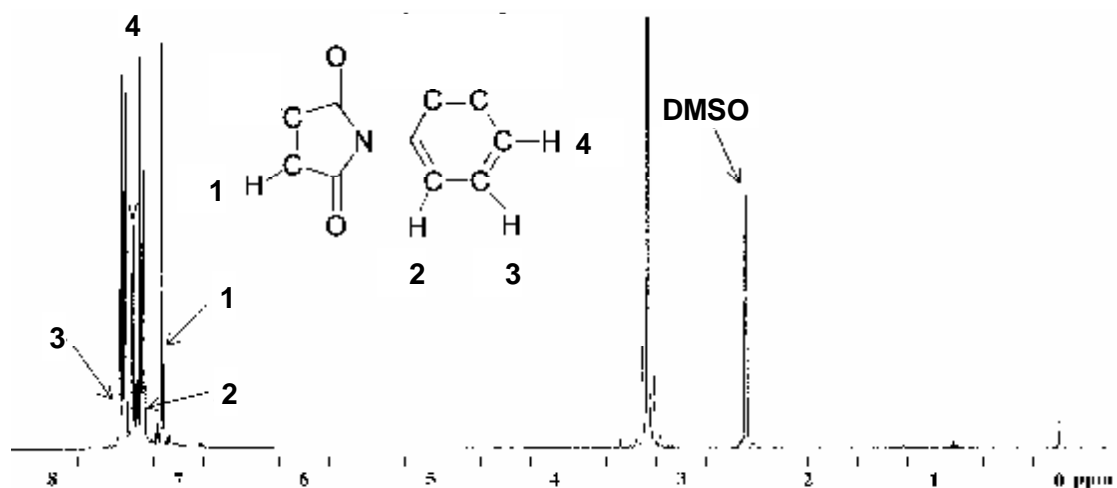
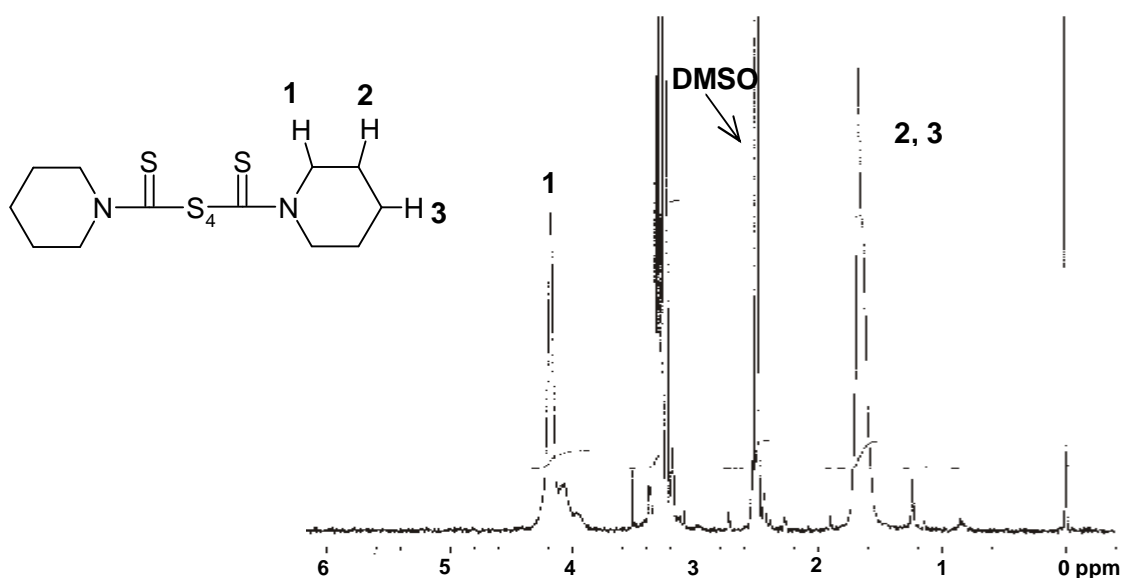**Figure 7.7** ^{1}H-NMR spectrum of MI in DMSO at 25°C.

Figure 7.8 ^{1}H-NMR spectrum of DPTT in DMSO at 25°C.

The spectrum obtained for the sample containing a mixture of MI and DPTT at room temperature already differs from the sum of the two individual spectra, as can be seen comparing Figure 7.9A with Figures 7.7 and 7.8. Not only the peak from the maleimide functionality, at 7.15 ppm, is relatively decreasing but there are also new peaks visible in the region between 4.4 and 5.4 ppm. This means that at room temperature, and in the absence of peroxide, these two chemicals are already reacting. When the same sample is heated for one hour at 150°C, the reaction peaks increase and the malemide peak decreases further, as shown in Figure 7.9B.
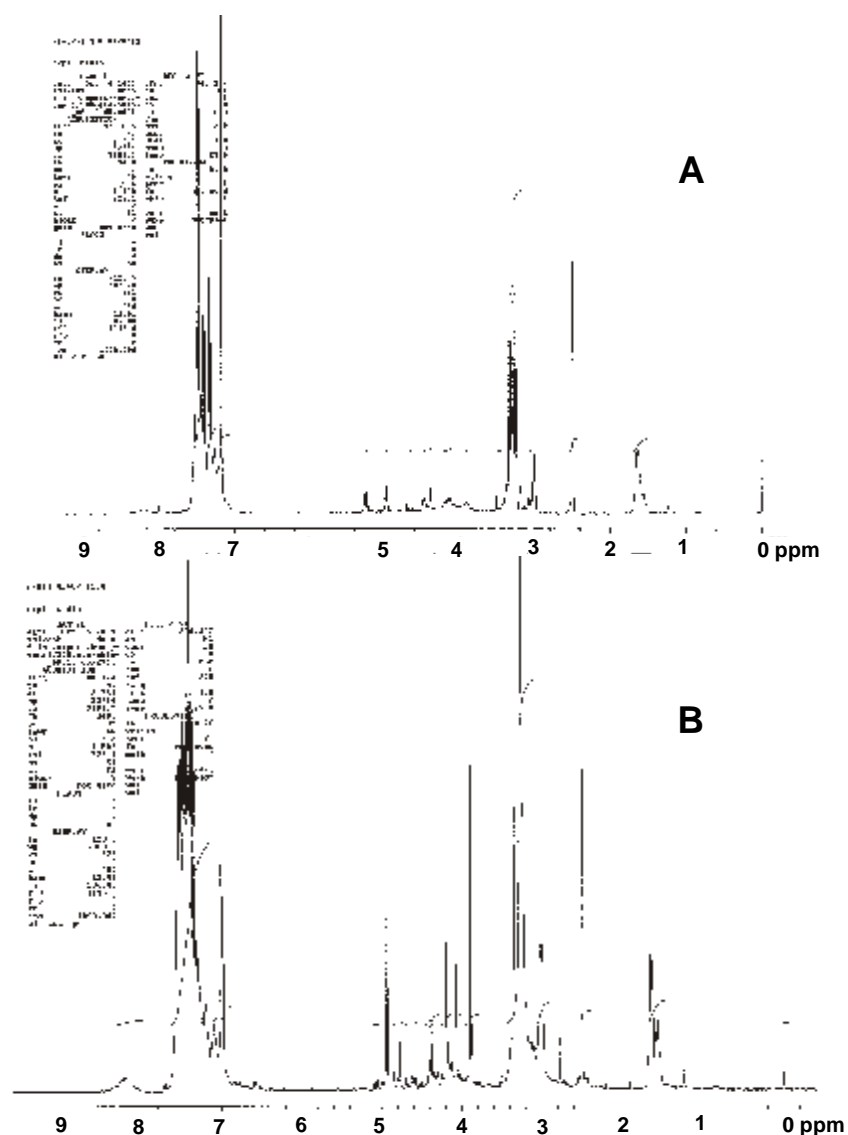
Figure 7.9 ^{1}H-NMR spectra of MI + DPTT in DMSO at 25°C: A

and after 1 hour of reaction at 150°C: B.

A possible reaction that can take place between MI and DPTT is suggested in Figure 7.10, where MI and DPTT could react to yield an adduct and release some active sulphur. The theoretical spectrum for this adduct molecule was calculated and it gave signals at around 4 ppm with the same pattern as that obtained experimentally for the reaction product between MI and DPTT shown in Figure 7.9.
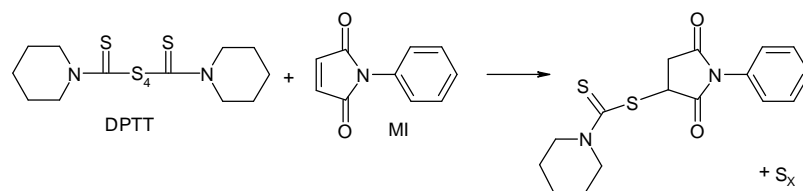

Figure 7.10 Possible reaction between the sulphur spender (DPTT) and the maleimide co-agent (MI).

The reaction between the maleimide co-agent and the peroxide, in the absence of DPTT, leads to a decrease of the maleimide peak at 7.15 ppm as well as a decrease from the signal of the methylic hydrogens from DCP at 1.45 ppm. Several products appear in the region between 2 and 5 ppm, as shown in Figure 7.11. A possible explanation for these would be the homopolymerisation of the maleimide co-agent as well as decomposition products from the peroxide, which are also responsible for the changes observed in the aromatic region. Probably acetophenone is being formed as decomposition product of dicumyl peroxide. The theoretical shifts from acetophenone are 2.55 ppm for the methylic hydrogens and 7.88, 7.40 and 7.47 for the aromatic hydrogens. These shifts can indeed be observed in Figure 7.11 B from the reaction between MI and DCP.
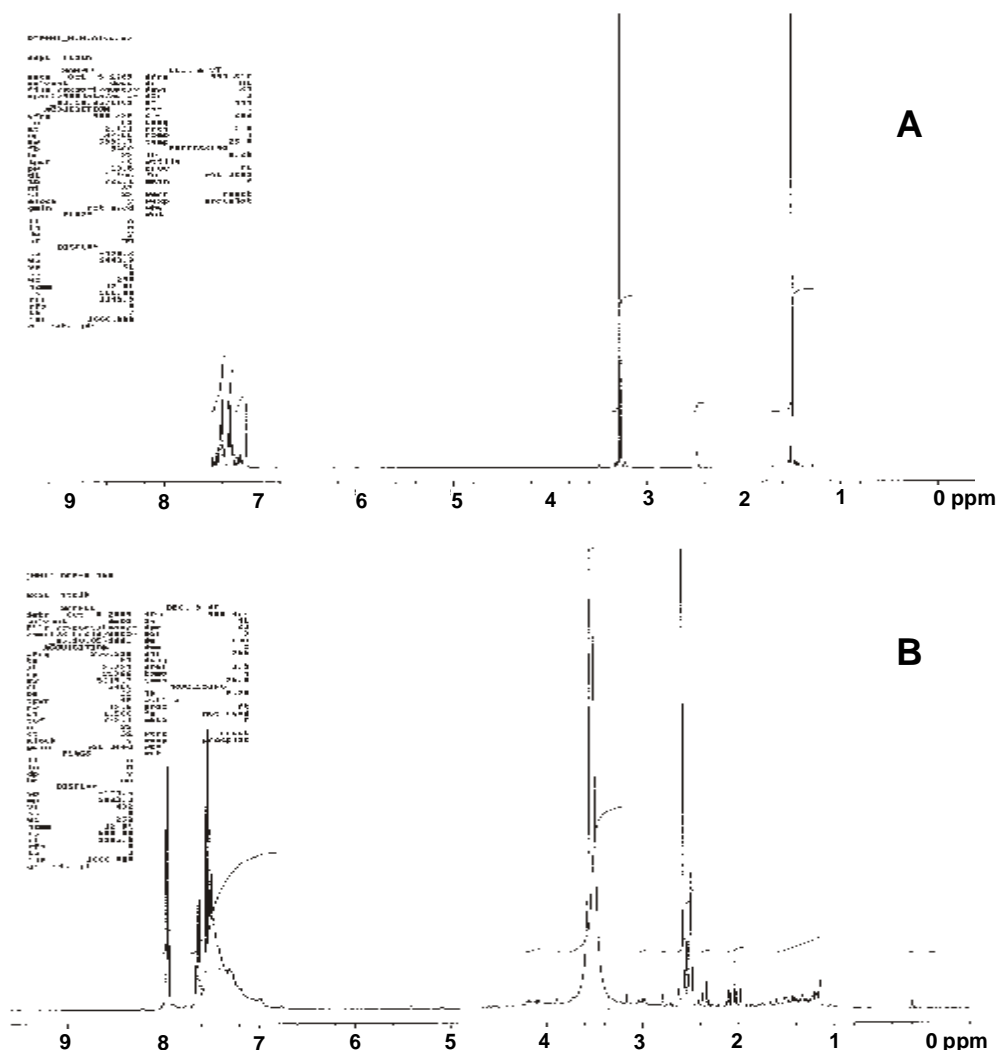

Figure 7.11 ^{1}H-NMR spectra of DCP + MI in DMSO at 25°C: A

and after one hour of reaction at 150°C : B.

Finally, the mixture of the maleimide, the peroxide and the DPTT shows the loss of the maleimide unsaturation, already at room temperature, as was also observed in the absence of peroxide. Further, reaction products appear in the region 2 to 5 ppm and changes in the aromatic region take place, as can be observed in Figure 7.12. The peaks that appear from 4 ppm to 5 ppm were not observed in the absence of

DPTT but they were observed in the reaction between MI and DPTT, so they are probably originated from the formation of the adduct shown in Figure 7.10.
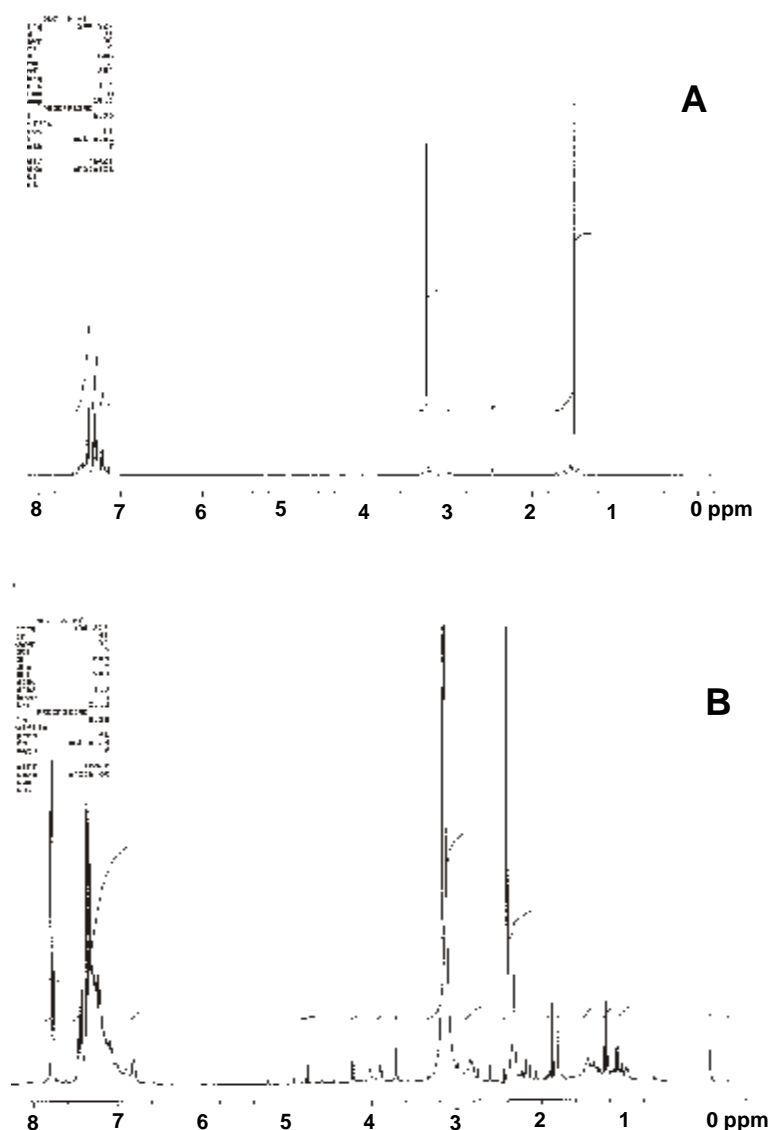

Figure 7.12 ^{1}H-NMR spectra of DCP + MI + DPTT in DMSO at 25°C: A

and after one hour of reaction at 150°C : B.

From these NMR experiments it can be concluded that the sulphur spender, DPTT reacts very fast with the maleimide co-agent, MI in the absence of peroxide, already at room temperature. In the presence of peroxide this reaction also takes place at room temperature. At elevated temperatures the reaction between these two chemicals proceeds further. However, in the presence of peroxide it is most likely competing with other reactions engendered by the formation of radical species formed by the decomposition of the peroxide. Generally, the structure shown in Figure 7.10 is formed as a result of the reaction between MI and DPTT.

7.3.2 Reactions of EPM with curatives analysed with FT-IR-ATR

The IR spectrum of the pure EPM rubber showed the presence of three overlapping peaks in the region between 2850-3000 cm^{-1} due to C-H stretching, as shown in Figure 7.13. The strongest peak at 2921 cm^{-1} was used as reference peak to normalise the graphs, in order to be able to compare them.

The BMI-MP showed absorbance peaks at 824 cm^{-1} and 1721 cm^{-1}, Figure 7.14. The peak at 824 cm^{-1} is due to C=C-C=O vibrations from the maleimide functionality in BMI-MP. This peak was used to follow the reaction of the BMI-MP co-agent, by studying it before and after vulcanisation. The other peak at 1721 cm^{-1} corresponds to C=O stretching vibrations, which are present in BMI-MP. This peak cannot be used to follow the reaction of the co-agent when dicumyl peroxide is used, because several decomposition products from the peroxide will give rise to absorbance at the same wavelength.
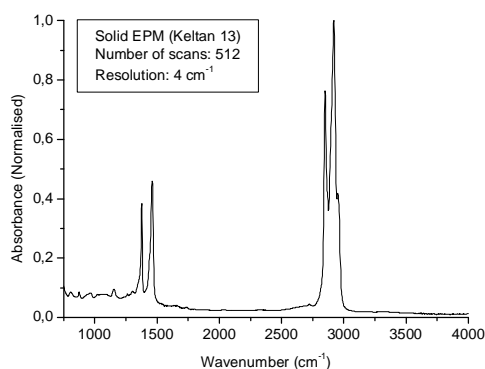

Figure 7.13 – FT-IR ATR spectrum of pure EPM rubber.
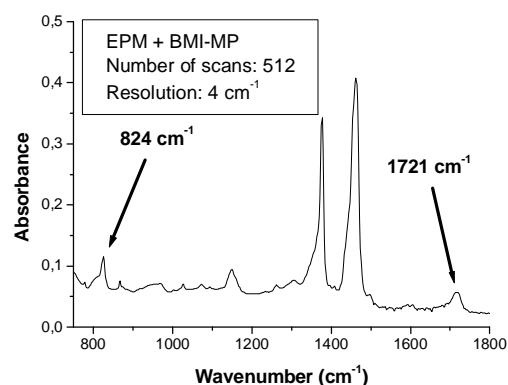

Figure 7.14 – FT-IR ATR spectrum of EPM + BMI-MP

When the EPM + BMI-MP sample was heated up in the press (160°C, 30 min), the resulting spectrum appeared to be the same as the original one (Figure 7.14). This indicates that BMI-MP is stable at 160°C if no other ingredients are added, and no vulcanisation takes place without the peroxide.
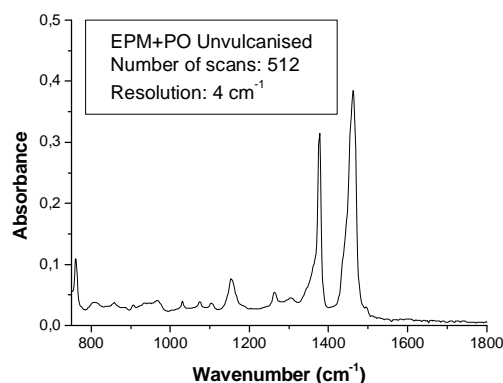

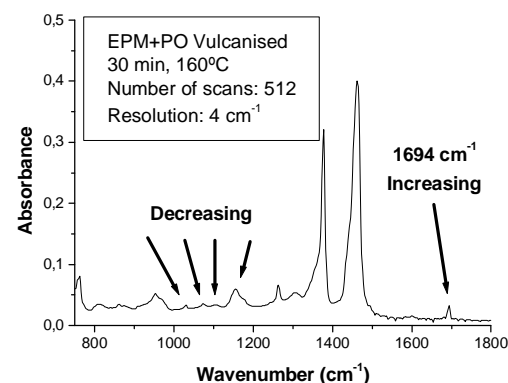**Figure 7.15** – FT-IR ATR spectrum of pure EPM + peroxide, unvulcanised.

Figure 7.16 – FT-IR ATR spectrum of EPM + peroxide, vulcanised.

The spectra from the samples containing EPM and peroxide before and after vulcanisation are shown in Figures 7.15 and 7.16, respectively. A small peak arises

after vulcanisation at 1694 cm^{-1}. This is due to acetophenone formation, a decomposition product of dicumyl peroxide. The C=O bond from acetophenone gives rise to this peak.

Figures 7.17 and 7.18 show the spectra from the rubber formulation containing EPM, DCP and BMI-MP, before and after vulcanisation respectively. The peak at 824 cm^{-1} from the BMI-MP shows a remarkable decrease as a result of vulcanisation, which indicates that the maleimide functionality of the co-agent has taken part in the vulcanisation reaction and therefore the double bond has been lost. Whether the co-agent is homopolymerising, creating crosslinks in the rubber network or a combination of these two options, cannot be concluded from these IR measurements, but it is clear that the maleimide unsaturation has reacted.

The large peak that appears at 1721 cm^{-1} (Figure 7.18) after vulcanisation is probably due to by-products from the cure. In order to check that, the sample was extracted in acetone for 72 hours and dried in a vacuum oven for three hours to see if the peak would decrease or disappear. The resulting IR spectra taken after the extraction showed the exact same peaks as before extraction, Figure 7.18, which indicates that the peak at 1721 cm^{-1} belongs to some functionality incorporated in the rubber network. Other solvents like toluene or hexane were not tried for extraction, because they had showed tendency to dissolve the EPM rubber.
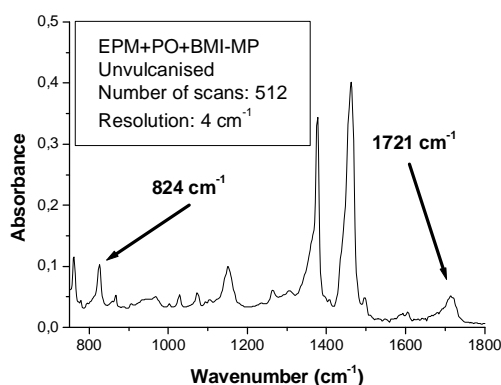

Figure 7.17 – FT-IR ATR spectrum of pure EPM + peroxide + BMI-MP, unvulcanised.
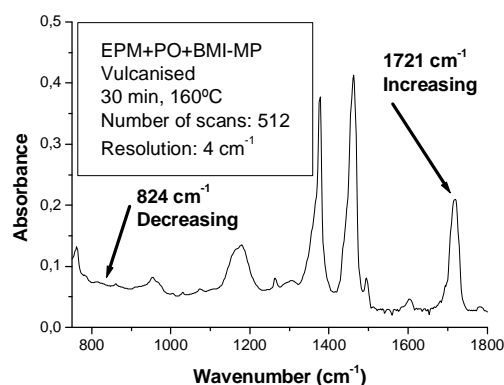
Figure 7.18 – FT-IR ATR spectrum of EPM + peroxide + BMI-MP, vulcanised.

Finally, the sample containing EPM, DCP, BMI-MP and DPTT was tested. At first a DPTT concentration of 0.7 phr was used, since this was found to be the optimal concentration of sulphur spender in terms of mechanical properties, as described in Chapter 6. However this concentration turned out to be too low to be detected. Therefore samples with a higher concentration of DPTT (4.2 phr) were prepared and analysed. The other ingredients were proportionally increased in order to maintain the relative ratio between them. The peaks from the DPTT at 1100 cm^{-1} became then detectable (Figures 7.19 and 7.20). Probably because of the high DPTT concentration, during the heating in the press the sample turned brown, along with a very bad smell. The resulting spectrum after vulcanisation can be seen in Figure 7.21, where peaks are broadened and the intensity is higher. No new peaks were found that could give relevant information about the vulcanisation reaction in the presence of DPTT.
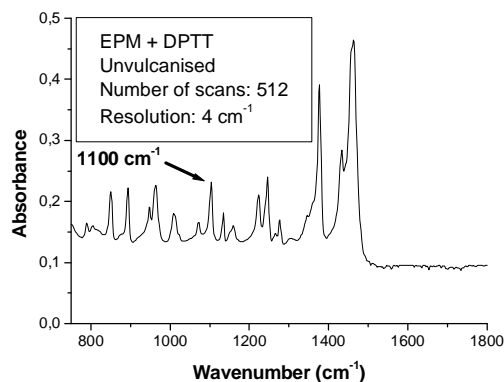
Figure 7.19 – FT-IR ATR spectrum of EPM + DPTT, before reaction. The peak from C=S vibrations in DPTT are marked with an arrow.
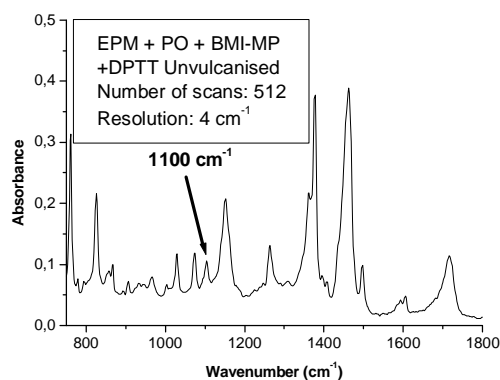

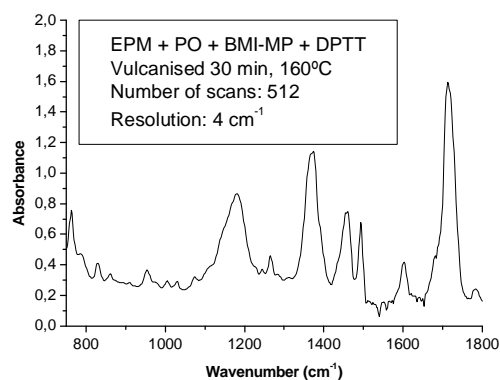**Figure 7.20** – FT-IR ATR spectrum of EPM + peroxide + BMI-MP + DPTT, unvulcanised.

Figure 7.21 – FT-IR ATR spectrum of EPM + peroxide + BMI-MP + DPTT, vulcanised.

From the IR experiments it can be concluded that the double bond from the maleimide functionality of the co-agent is lost after vulcanisation as a result of the reaction between the co-agent and the EPM rubber. The fact that this reaction only takes place in the presence of peroxide means that it originates from active radical species. The interaction with DPTT in the vulcanisation reaction could not be studied successfully with IR.

7.3.3 Model compound vulcanisation analysed with LC-MS
Although some insight has already been gained about the chemical reactions taking place between the various components, MCV was invoked to further clarify the mechanism.

Sample 1: DPTT
First of all, sample 1 of Table 7.5: DPTT dissolved in acetonitrile, was analysed individually, with a different chromatographic method, in order to find out its compositional pattern. The concentration of DPTT shown in Table 7.5 turned out to be too low; therefore a more concentrated DPTT solution was prepared. In Figure 7.22 top, the UV chromatogram of DPTT is displayed. The average number of sulphur atoms into the middle part of the DPTT molecular structure is 4, but there is a sulphur rank distribution, from approximately 2 to 6 sulphur atoms. Because of this distribution

several peaks appear in the UV chromatogram, corresponding to the different DPTT sulphur rank species, since they are separated in the LC-column. This type of pattern for sulphur containing species is well known from literature.[28]
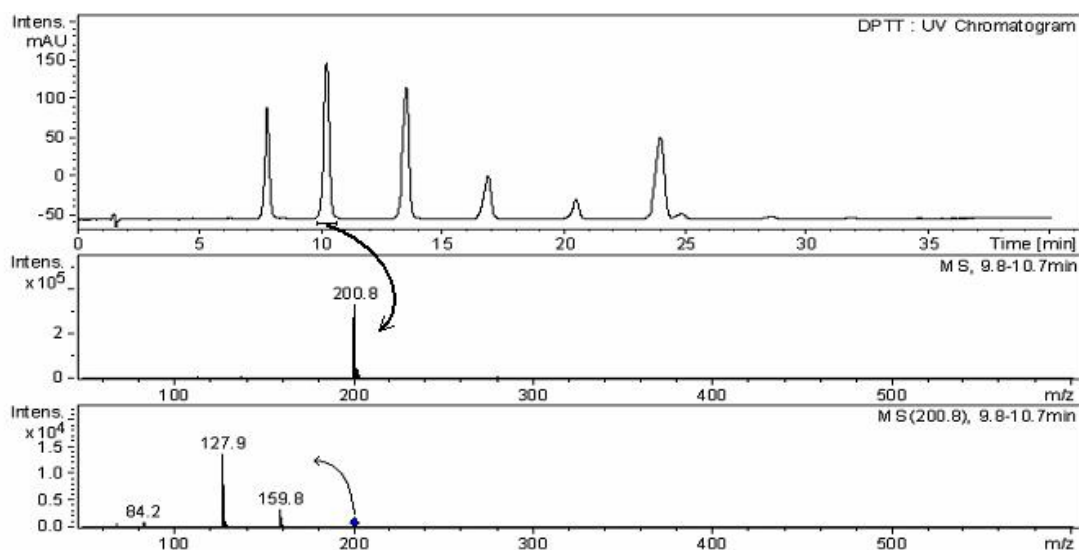

Figure 7.22 – LC-MS analysis of DPTT. Top: UV chromatogram; Middle: MS spectrum of the compound under the UV peak; Bottom: Fragmentation pattern of fragment with 200.8 m/z.

All the compounds under the UV peaks with different sulphur ranks led to exactly the same mass spectra, like the one shown in Figure 7.22 middle. This means that the DPTT molecule is stable during the liquid chromatographic process; it allows chromatographic separation along time of the different sulphur ranked species. Nevertheless, there was no mass detected corresponding to the whole DPTT molecule. This means that the DPTT molecules are unstable under Atmospheric Pressure Chemical Ionisation (APCI) conditions and as a consequence they are all broken down into fragments during ionisation in the interface, between the LC and the MS. All different sulphur rank species lead to exactly the same fragment: 200.8 m/z.

To make sure that the fragment at 200.8 m/z corresponds to DPTT, this mass fraction was further fragmentised by a so called MS/MS analysis. This analysis selects the ion corresponding to 200.8 m/z and fragments it further down. These fragments can be seen in Figure 7.22 bottom. The same analysis was performed for all UV peaks of different sulphur ranked species, with the exact same results. The explanation of these fragments in terms of molecular structure is given in Figure 7.23. As can be seen, this is a clear identification. The peak of 200.8 m/z corresponds to the 160 m/z fragment shown in Figure 7.22 middle complexed with an acetonitrile molecule of 41 m/z.

In order to detect the unfragmentised DPTT molecule another technique was performed. From literature[28] it is know that by addition of certain specific ions to sulphur containing compounds a complex can be formed, which is stable under some ionisation conditions and therefore allows the MS detection of the sulphur containing compound in its complex form.

A solution of $AgNO_3$ was prepared since silver ions are known to form a stable complex with some sulphur containing compounds, i.e. bis-triethoxisilylpropyltetrasulphide, (TESPT).[28] This silver solution was injected to the flow of sample after LC separation and UV detection. Unfortunately, the method did not show any improvement in the mass detection of DPTT.
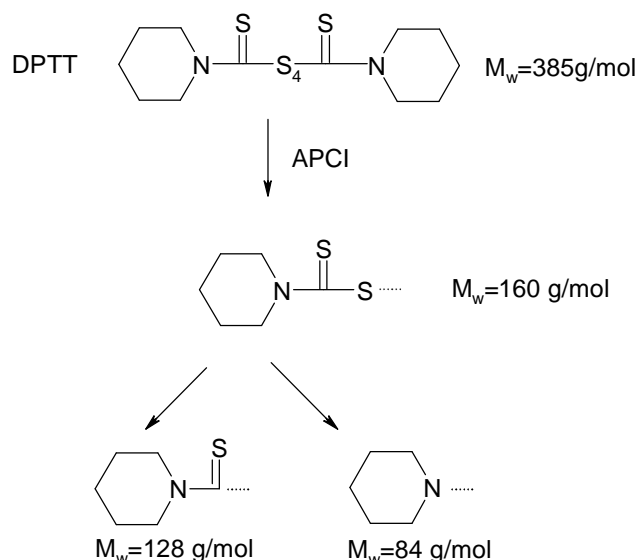
Figure 7.23 Possible fragments of DPTT.

Samples 2 and 3: model + DCP + BMI-MP with/without DPTT

The analysis of samples 2 and 3 in Table 7.5, corresponding to model compound vulcanisation with BMI-MP as co-agent, did not show any change between the UV chromatograms before and after vulcanisation nor between the mass spectra. The reason is most probably the poor solubility of BMI-MP in the model mixture. Because of this reason only the samples containing MI as co-agent are discussed: 4 and 5 in Table 7.5. The reactivity of the maleimide functionalities in MI and BMI-MP is chemically the same, and therefore the results obtained with MI can reasonably be considered to be representative for BMI-MP.

Sample 4: model + DCP + MI

In Figure 7.24 top, the UV chromatogram of sample 4: the mixture of MI, peroxide and 3-methylpentane, before reaction is shown. In order to identify which peak belongs to which compound the pure components of the sample were also injected separately into the LC-MS under the same test conditions. The retention time of every pure compound was in this manner obtained. MI elutes at around 2.75 minutes and DCP at around 14 minutes.

The mass spectra from the MI and the DCP are displayed in the middle and bottom of Figure 7.24, respectively. The spectrum of MI shows a clear base peak at 172.9 m/z, which corresponds with the molar mass of MI. The spectrum of DCP shows fragments corresponding to decomposition products of the peroxide, depicted in Figure 7.25, since the peroxide molecule breaks down in the interface under the APCI ionisation conditions. The ion of 119 m/z, which corresponds to α-methylstyrene (M_w = 118 g/mol), is detected with a high intensity.
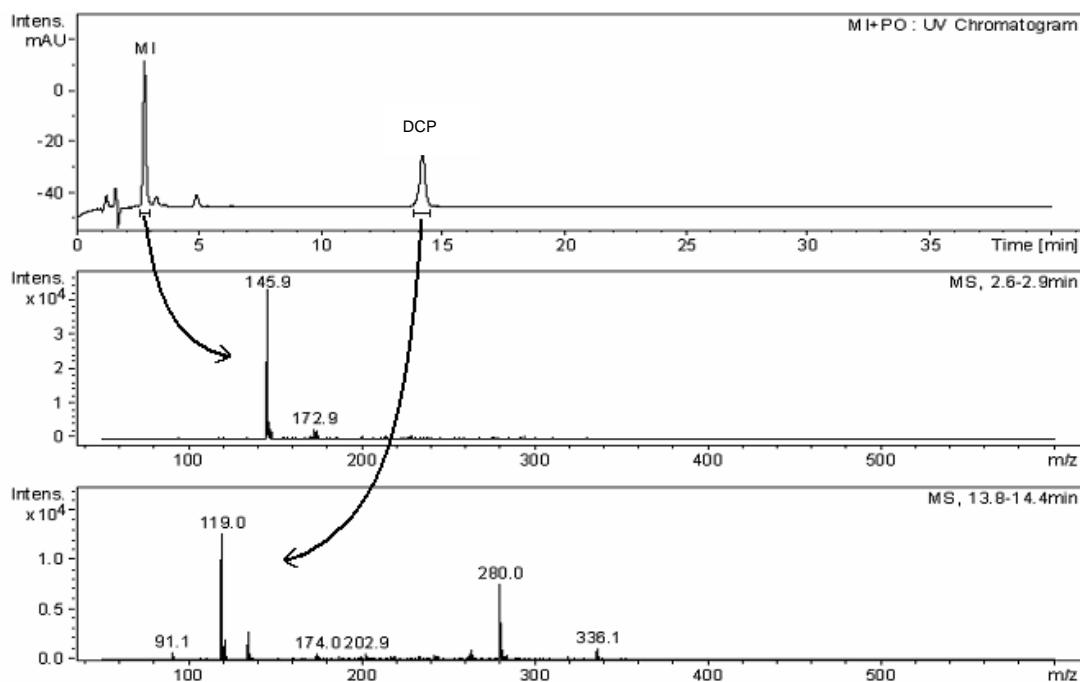
Figure 7.24 – UV chromatogram of MI + peroxide (top), mass spectrum of MI (middle) and mass spectrum of DCP (bottom).
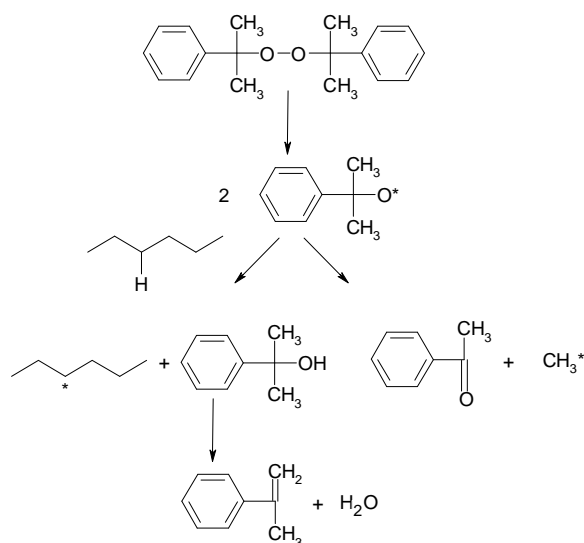
Figure 7.25 Decomposition of dicumyl peroxide in the presence of polymer.

In Figure 7.26 the UV chromatograms from the analysis of sample 4 along various vulcanisation reaction times is displayed. Times 0 (before reaction) 30 and 60 minutes are shown. It can clearly be observed that the peaks corresponding to the co-agent and the peroxide decrease with reaction time, being almost completely consumed after 60 minutes. The peaks marked as A, B, C and D increase with vulcanisation time; therefore they belong to reaction products. The peak marked as B is already present at t=0, however after 30 and 60 minutes of reaction it has significantly grown, which indicates that this corresponds to a reaction product. The peaks A, C and D, show up after 30 minutes of reaction and grow further with time.

Figure 7.26 – UV chromatograms of MI + PO + Model + at time 0, 30 and 60 minutes after reaction at 140°C.

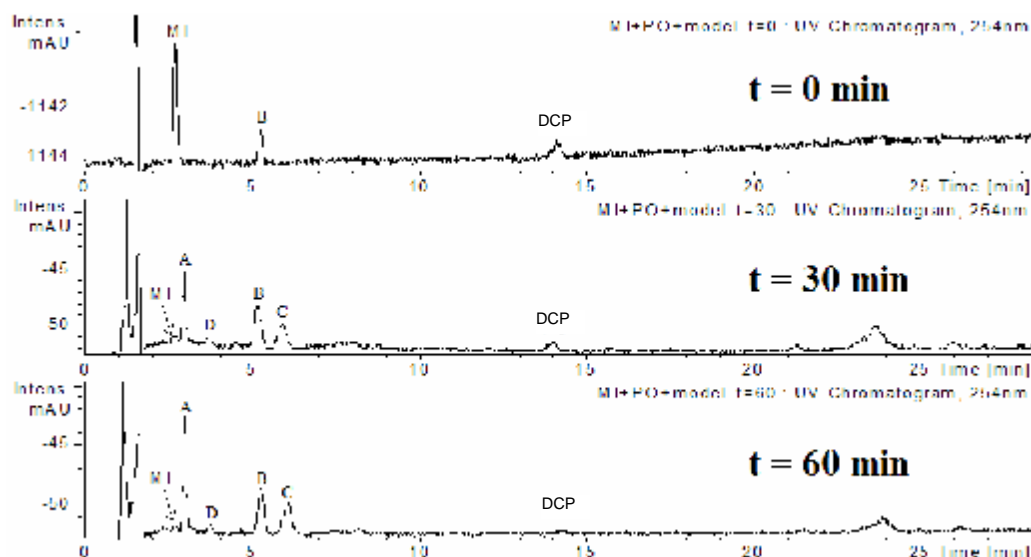In order to identify the reaction products, the samples were selectively scanned along the whole chromatographic run time for masses corresponding to possible reaction products. That kind of analysis gives as result an Extracted Ion Chromatogram (EIC): a plot of intensity detected for a specific ion vs. run time. In this way even compounds that do not show a UV absorption at 254 nm can be detected. For instance, the ion 119 m/z was scanned in the sample of reaction time 60 minutes, this means that the software scans the whole mass spectra recorded for this sample and counts the intensity of the ion with 119 m/z along the analysis time. In Figure 7.27, the EIC for 119 m/z is displayed. This m/z corresponds with the mass of α-methylstyrene, 118 g/mol, a decomposition product of DCP. It can clearly be seen that the intensity of that ion is very high at 3 minutes, the same retention time of product A in the UV chromatogram in Figure 7.26. This indicates that the reaction product marked as A is most probably α-methylstyrene.
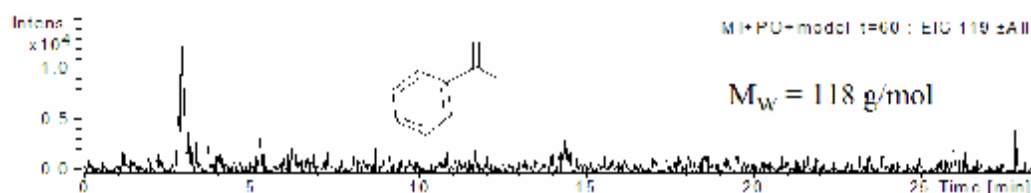
Figure 7.27 – Extracted ion chromatogram for 119 m/z of the sample MI + PO + model, after 60 minutes of reaction.

Further, ions corresponding to the masses of 259 and 432 g/mol, corresponding to the model compound linked to one and two molecules of MI, respectively, were also scanned. The resulting EIC spectra are shown in Figures 7.28 and 7.29. The intensity of the ion 260 m/z was found to be very high at the same retention time as peak B, after 30 and 60 minutes of reaction, but was not found at t=0. This indicates that the compound under peak B at t=0 is something else than the MI molecule attached to a 3-methylpentane molecule. The ion 433 m/z was found with high intensity at the same retention time as peak C.

Figure 7.28 – Extracted ion chromatogram at 260 m/z of MI + PO + model after 60 minutes of reaction. The same product is also present after 30 minutes but, not at t=0.
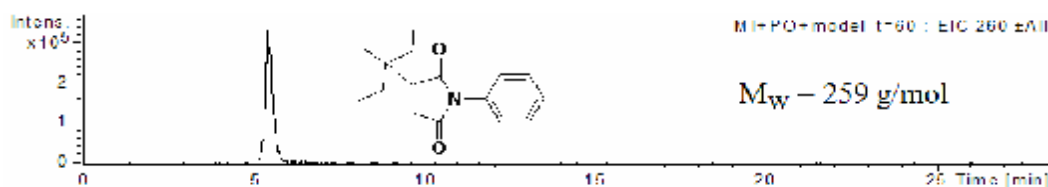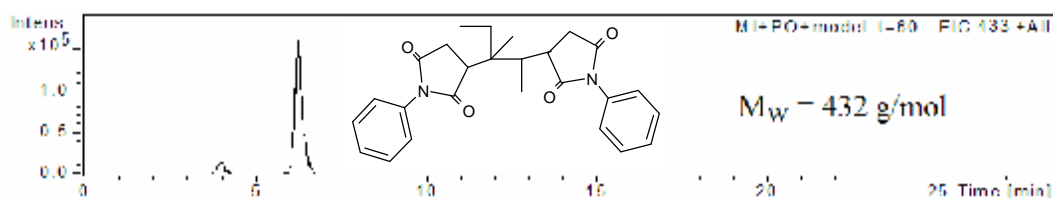

Figure 7.29 – Extracted ion chromatogram at 433 m/z of MI + PO + model after 60 minutes of reaction. The same product is also present after 30 minutes.

Herewith the reaction products A, B and C are identified. A is probably α-methylstyrene from peroxide decomposition. B could be a model molecule attached to a MI molecule, as shown in Figure 7.28. And C could be a model molecule linked to two MI molecules, like the structure shown in Figure 7.29, or some isomer of this structure.

Sample 5: model + DCP + MI + DPTT

In Figure 7.30 the UV chromatogram of sample 5 of Table 7.5, containing 3-methylpentane, MI, DCP and DPTT, at different vulcanisation reaction times is displayed. Like observed for sample 4, the MI and PO peaks decrease with reaction time, being almost completely consumed after 60 minutes of vulcanisation. Under these chromatographic conditions (shown in Table 7.6) the different sulphur ranked species of DPTT are not separated in the column but they elute together under the peak marked as DPTT in Figure 7.30. The previously obtained mass spectrum of DPTT, with a base ion of 200.8 m/z, was used to confirm the identification of the DPTT peak. DPTT, is only present at time 0, which means that it has completely reacted already after 15 minutes.

Reaction products elute at 3, 5.3 and 6 minutes of analysis, marked as A, B and C in the chromatograms. The peak marked as D for sample 4 was not detected in the presence of DPTT. The peak marked as B is present at all reaction times but its intensity increases after 30 minutes. Peak C on the other hand increases from 0 to 30 minutes and slightly decreases from 30 to 60 minutes. Several EIC's were performed in order to identify the reaction products.

In contrast to what was found for sample 4, peak A does not correspond to α-methylstyrene. In fact, no logical matching mass has been found for this reaction product. It can be concluded therefore, that in the presence of DPTT the decomposition of dicumyl peroxide follows a different pattern, otherwise α-methylstyrene would also have been found for sample 5.
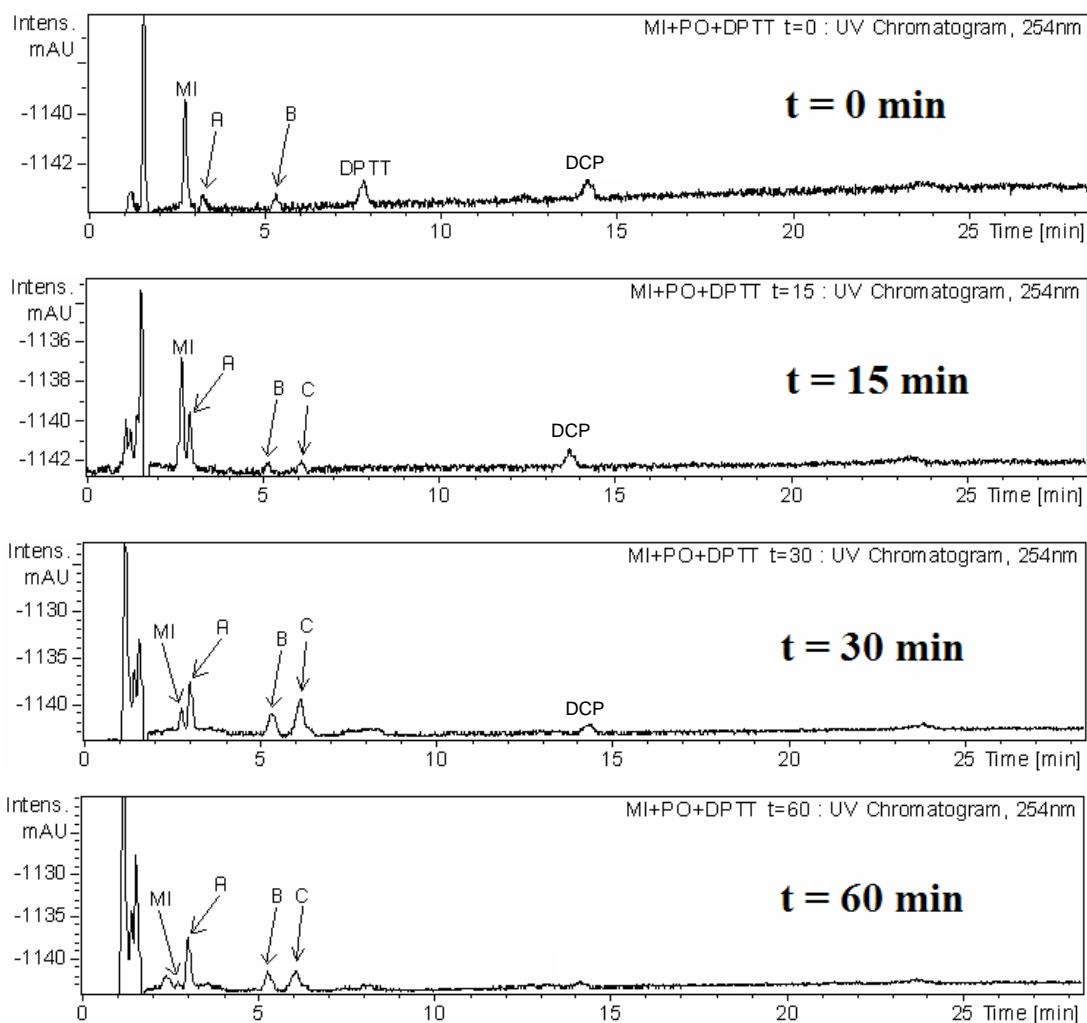
Figure 7.30 - UV chromatograms of MI + PO + Model + DPTT after reaction at 140°C for 0, 15, 30 and 60 minutes.

The ion of 260 m/z, corresponding to the molecular mass of a model molecule attached to a co-agent molecule, was not found at time zero and 15 minutes, but after 30 and 60 minutes the mass was found in the spectra with a high intensity. Figure 7.31 shows the Extracted Ion Chromatogram of 260 m/z from the sample after 60 minutes of vulcanisation. The highest intensity of this ion matches the retention time of reaction product B, just like observed in sample 4.
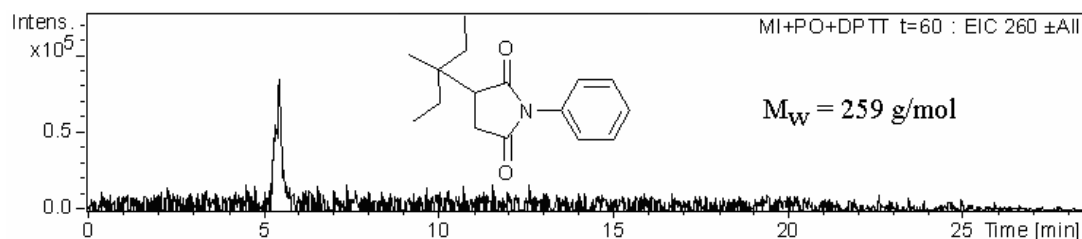
Figure 7.31 - Extracted ion chromatogram at 260 m/z of MI + PO + DPTT + model after 60 minutes of reaction. The same product also appears after 30 minutes, but not at t=0.

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The ion of 433 m/z, corresponding to the molecular mass of a model molecule attached to two co-agent molecules or an isomer of this, was found with a high intensity coinciding with the retention time of peak C in Figure 7.30, as shown in Figure 7.32. The same was observed for sample 4.
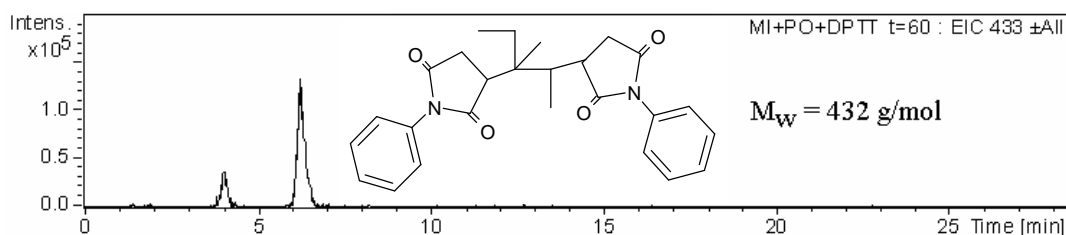
Figure 7.32 - Extracted ion chromatogram at 433 m/z of MI + PO + DPTT + model after 60 minutes of reaction. The same product also appears after 30 minutes.

In order to confirm that the structures of 260 m/z and 433 m/z belong to the molecules shown in Figures 7.31 and 7.32 respectively, an MS/MS method was used to fragmentise the masses 260 m/z and 433 m/z of the sample after 60 minutes of vulcanisation reaction. The fragments obtained matched the molecules suggested, as shown in Figures 7.33 and 7.34.
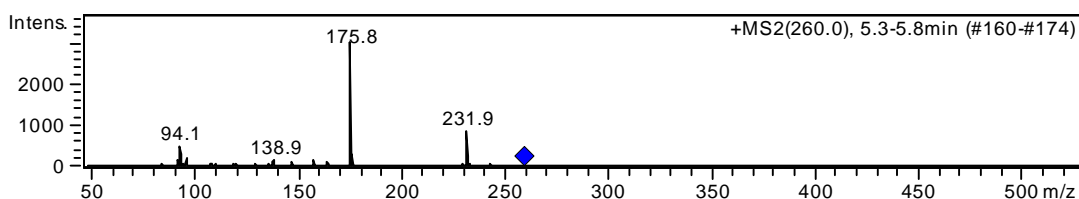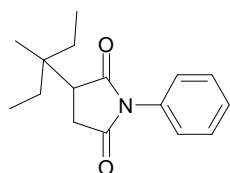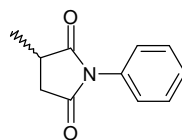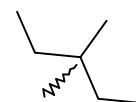
Figure 7.33 – MS/MS spectrum of ion 260 m/z and structures with their corresponding masses.

In Figure 7.33 top the MS/MS spectrum of the ion with 260 m/z is shown. The largest ion formed as a result of this fragmentation is 175.8 m/z, which corresponds to a mass of 174.8 g/mol, this is most probably a molecule of MI, as shown at the bottom of Figure 7.33.

In Figure 7.34 top, the MS/MS spectrum of the ion with mass 433 m/z is shown. As can be observed the largest ion after its fragmentation is 348.9 m/z. This means that there is a difference of 84 m/z (=433-349 m/z) and that corresponds to a model molecule. The resulting fragment of charge 349 m/z belongs to a molecular mass of 348 g/mol, therefore it is probably composed by two co-agent molecules of 174 g/mol.
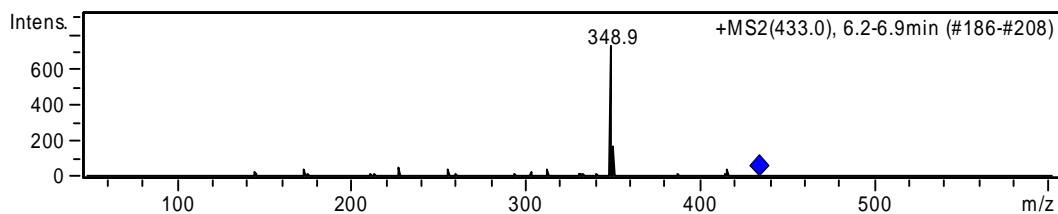
Mw= 174*2+ 84 = 432 g/mol
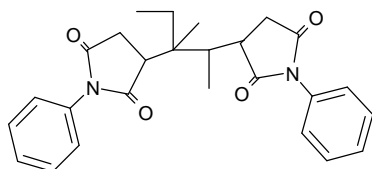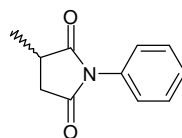
Mw= 174 g/mol   Mw= 84 g/mol
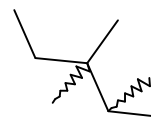
Figure 7.34 – MS/MS spectrum of ion 433 m/z and structures with their

corresponding masses.

Further, several EIC's for supposed ions corresponding to DPTT fragments or sulphur containing structures were studied. No clear evidence of sulphur containing species was found. However, it is very clear from the UV spectra that the DPTT peak does disappear, thus it does react. It was previously observed by NMR experiments that, even prior to peroxide decomposition, DPTT reacts with MI at room temperature, probably giving rise to the adduct shown in Figure 7.10. The mass of the adduct was selectively scanned in an EIC and it was indeed found at reaction time 0, as shown in Figure 7.35, but not anymore for longer reaction times. This confirms the formation of the adduct and the fact that in the presence of peroxide radicals it reacts further.

Mw = 334 g/mol
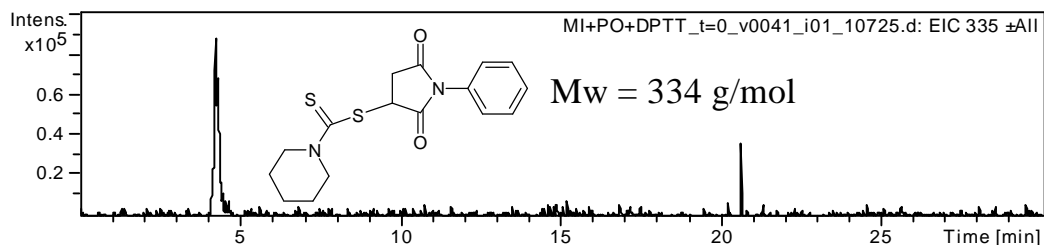
Figure 7.35- Extracted ion chromatogram of ion 335 m/z from the sample containing

MI + PO + DPTT + model at reaction time 0 minutes.

7.3.4 Proposed mechanism for peroxide vulcanisation in the presence of a maleimide type co-agent and a sulphur spender

Considering all the NMR, IR and LC-MS data, the mechanism shown in Figures 7.10 and 7.36 is proposed in order to explain the improvement in mechanical properties as well as in scorch safety, achieved by addition of a sulphur spender like DPTT to a bismaleimide/peroxide cure system, as reported in Chapters 5 and 6.

By NMR and IR analysis of mixtures of additives, the loss of the maleimide unsaturation from the co-agent has been confirmed. It was clearly observed that DPTT reacts by itself with the co-agent at room temperature. This means that in a real rubber system, this reaction already takes place during mixing. The formation of the adduct shown in Figure 7.10 is observed by NMR and confirmed by LC-MS. This molecule is not detected in the presence of peroxide after reaction at elevated temperature, which means that it reacts further with the radical species formed by the peroxide decomposition.

The fact that active sulphur is released from the reaction between the co-agent and DPTT, as shown in Figure 7.10, would explain the improvement in mechanical properties like tensile strength, observed when a sulphur spender is added to a maleimide/peroxide cure system. Probably the presence of sulphur is leading to additional sulphur containing crosslinks, more flexible than the C-C crosslinks from peroxide cure. This reflects in the mechanical properties as an improvement. The fact that compression set and ageing were improved in the presence of 0,5 to 0,7 phr of DPTT means that the sulphur is build-in in the network in an efficient way, therefore by mono- or di-sulphidic linkages. If polysulphidic crosslinks would be formed the compression set at high temperature and the ageing properties would be worsened, and that was not observed in Chapter 6 for optimal DPTT concentrations. Further confirmation of the sulphur influence would be the fact that there exists an optimal DPTT concentration to obtain the best mechanical properties, which is also the case when elemental sulphur is added as co-agent in peroxide vulcanisation. [2-10]

According to the mechanism proposed, the first radicals formed from peroxide decomposition, depicted as methyl radicals in Figure 7.36 I, would react with the MI-DPTT adduct immediately after their formation. Therefore these radicals are held-up by reacting with the adduct, providing scorch delay. This delay is not at the expense of crosslinking efficiency, since a radical in the co-agent molecule is released when the adduct reacts further, and therefore the radical is not lost: Figure 7.36 II. Also a methyl radical is given back to the reaction mixture as shown in Figure 7.36 III, which also contributes to improve the efficiency. This radical can now react again with a new MI-DPTT adduct molecule and this process can go further until all the adduct is consumed. At that moment, normal peroxide vulcanisation mechanism will take over.

The fact that the radicals are held-up immediately after their formation could also help to minimise chain scission reactions of the EPM polymer molecules, which would explain the higher delta torque and crosslink density obtained in the presence of DPTT.
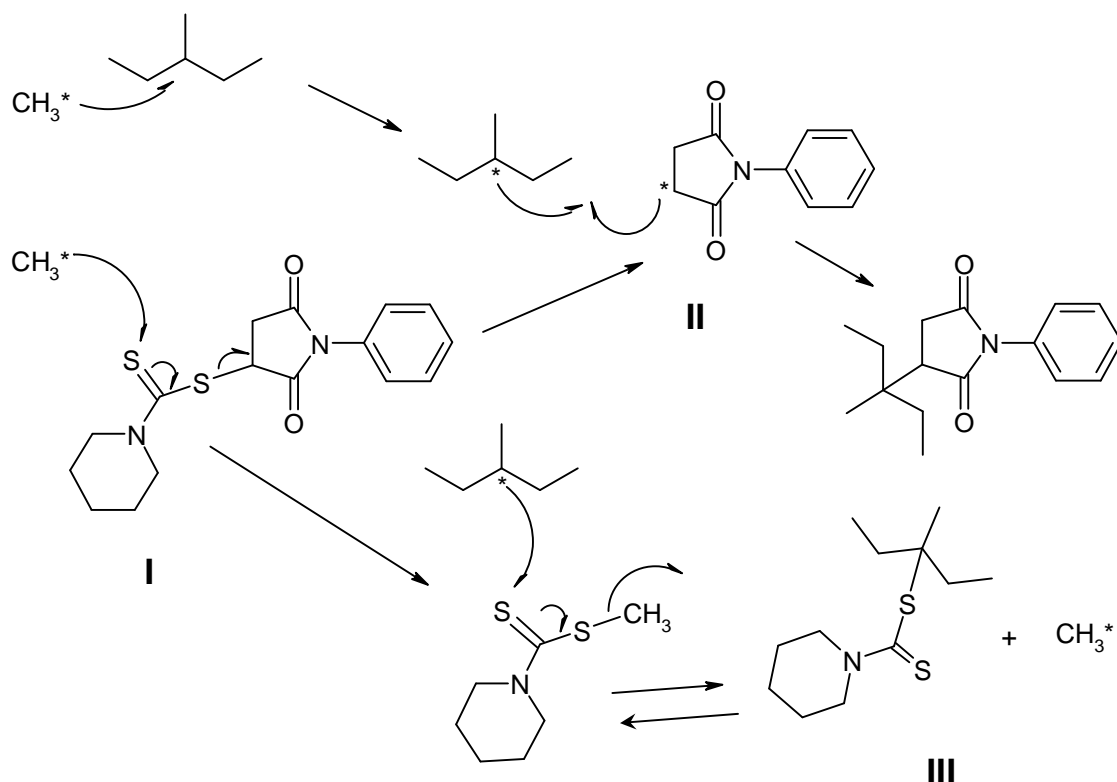
Figure 7.36 The reaction product between MI and DPTT (I) traps the methyl radical, from the decomposition of the peroxide, to give better scorch safety. The radical MI is free again and can form extra crosslinks (II) to give improved mechanical properties. In a final step the methyl radical is set free (III) and can react in a new cycle until there is no MI-DPTT adduct left.

7.4   CONCLUSIONS

From Nuclear Magnetic Resonance and Infrared analysis of the reaction mixtures the loss of the maleimide unsaturation from the co-agent, as a result of vulcanisation was found.

The maleimide type co-agent reacts with the sulphur spender prior to peroxide decomposition, even at room temperature, giving rise to an adduct and active sulphur. The formation of the adduct was confirmed by NMR and LC-MS. The release of active sulphur species was not detectable with the analysis techniques employed, but could be held responsible for the improvement of macroscopic mechanical properties like tensile strength and moduli, observed when a sulphur spender is added to a bismaleimide/peroxide cure system, reported in Chapters 5 and 6 of this thesis.

Several reaction products of the peroxide vulcanisation of 3-methylpentane in the presence of a maleimide type co-agent have been identified by LC-MS. Most of these have also been found in the presence of DPTT.

The reaction mechanism that could explain the scorch delay and the property improvement achieved by addition of a sulphur spender to a bismaleimide/peroxide cure system has been elucidated.

7.5 REFERENCES

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APPENDIX
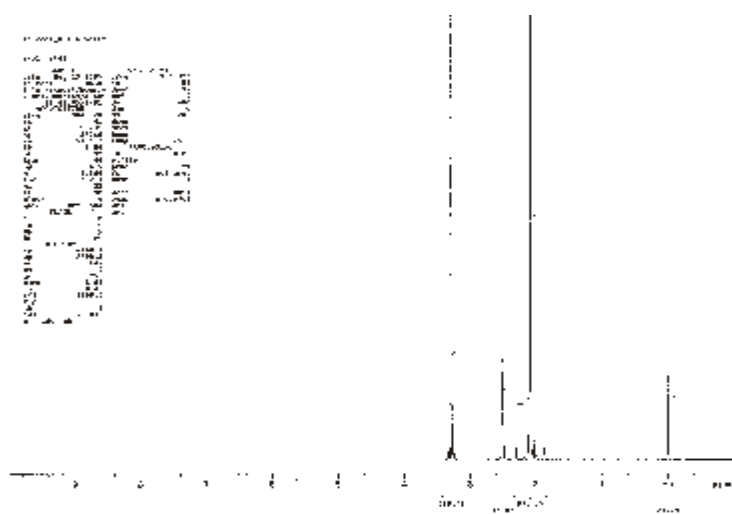
Figure A.1 NMR spectrum of DMSO at 25°C.
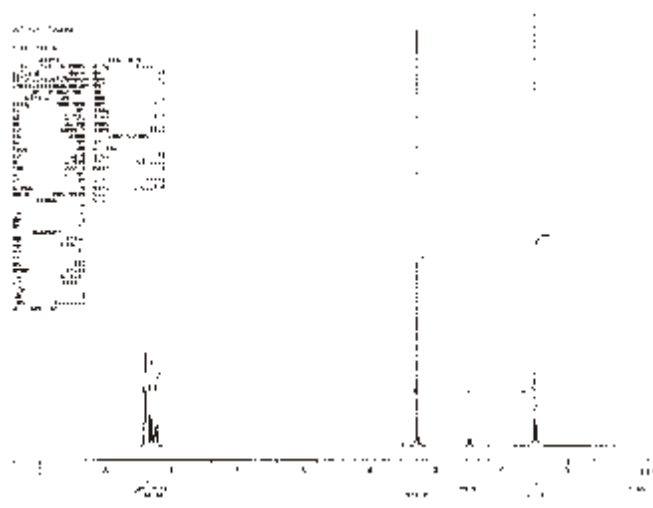
Figure A.2 NMR spectrum of DCP in DMSO at 25°C.
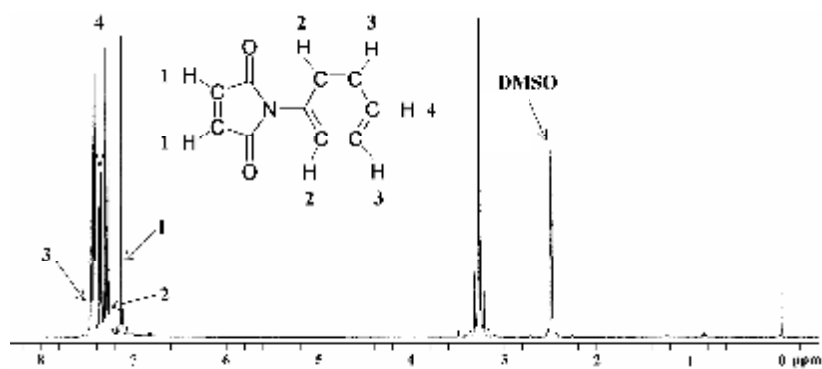
Figure A.3 NMR spectrum of MI in DMSO at 25°C.
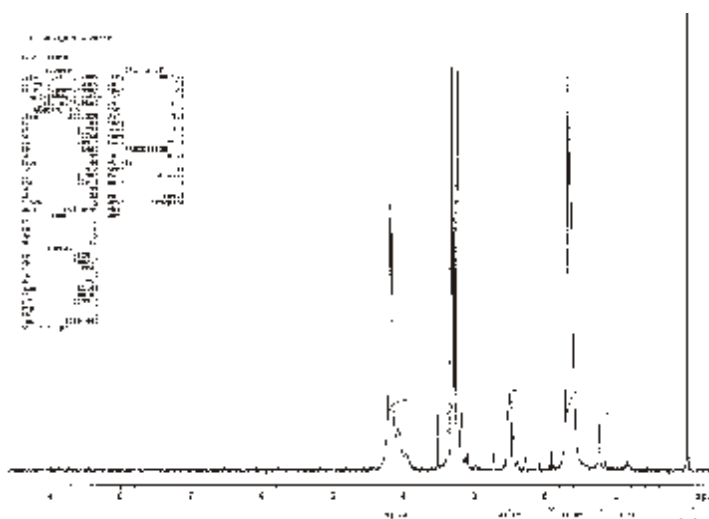
Figure A.4 NMR spectrum of DPTT in DMSO at 25°C.
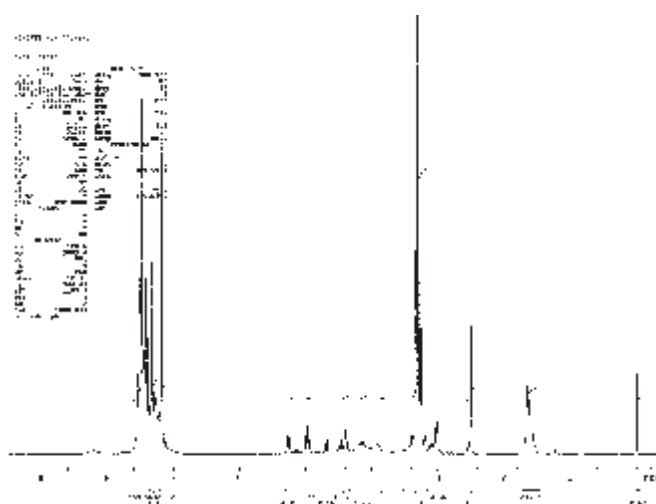
Figure A.5 NMR spectrum of MI + DPTT in DMSO at 25°C.
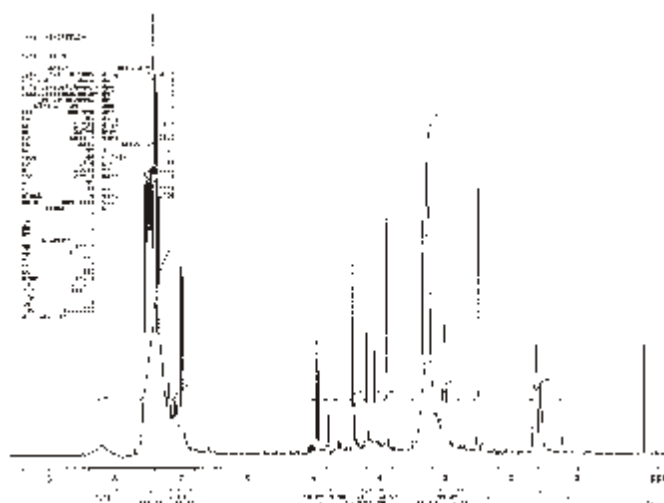
Figure A.6 NMR spectrum of MI + DPTT in DMSO at 150°C.
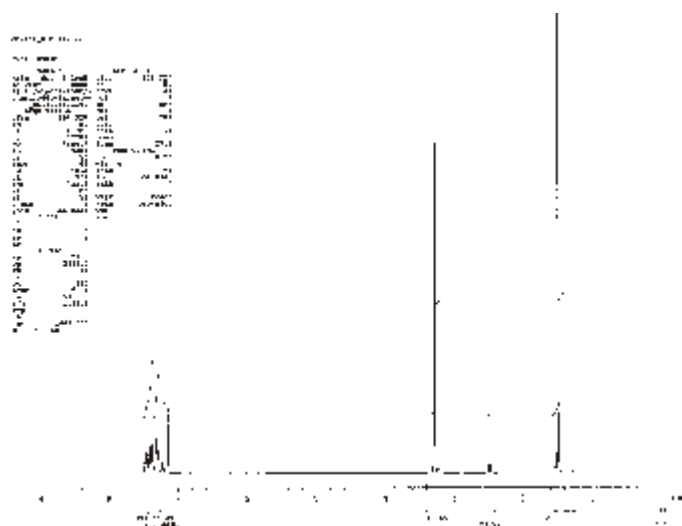
Figure A.7 NMR spectrum of DCP + MI in DMSO at 25°C.
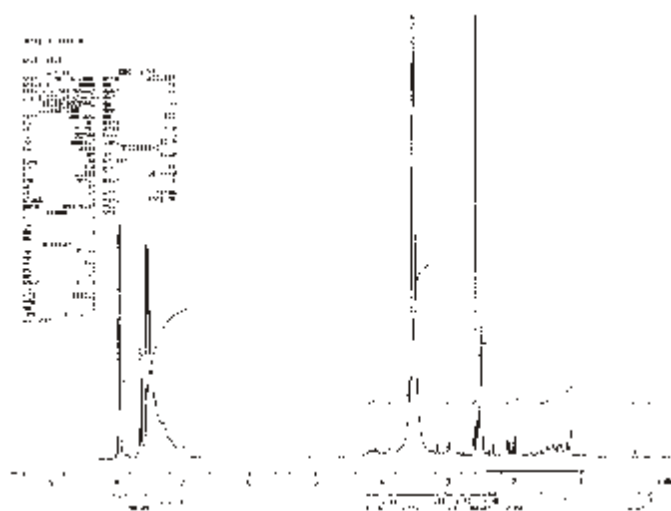
Figure A.8 NMR spectrum of DCP + MI in DMSO at 150°C.
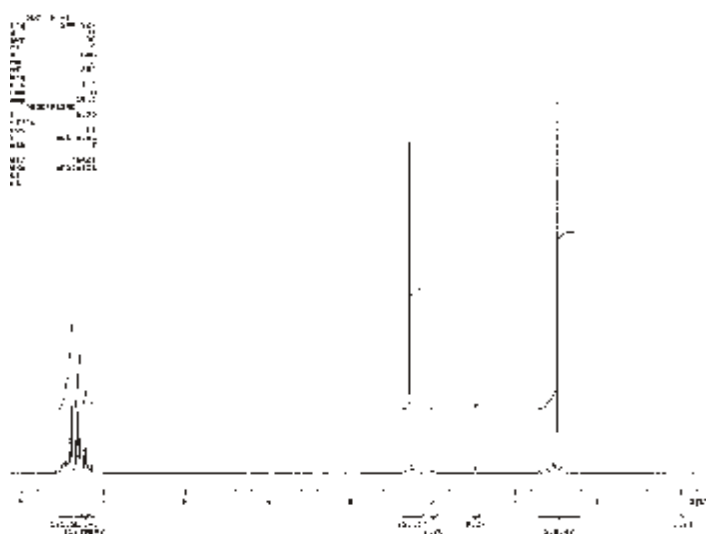
Figure A.9 NMR spectrum of DCP + MI + DPTT in DMSO at 25°C.
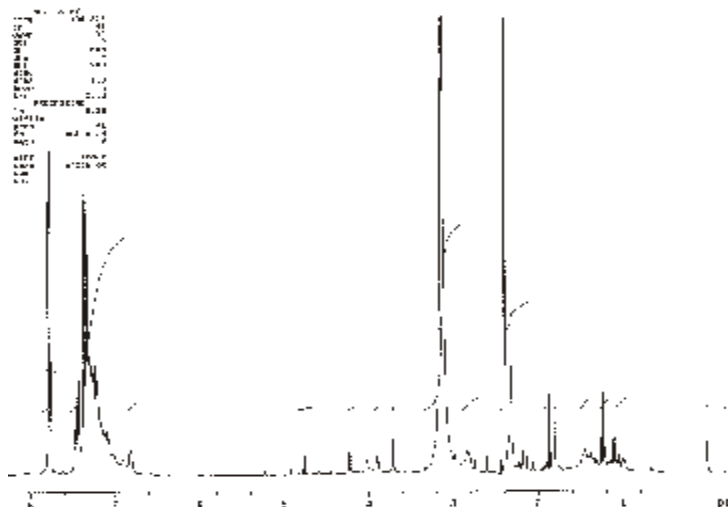
Figure A.10 NMR spectrum of DCP + MI + DPTT in DMSO at 150°C.
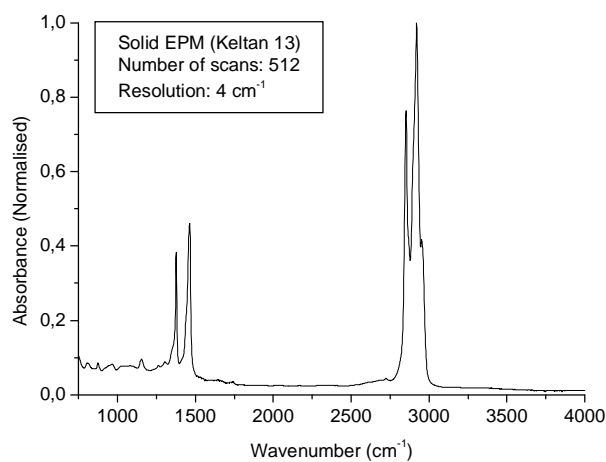
Figure A.11 FT-IR ATR spectrum of pure EPM.
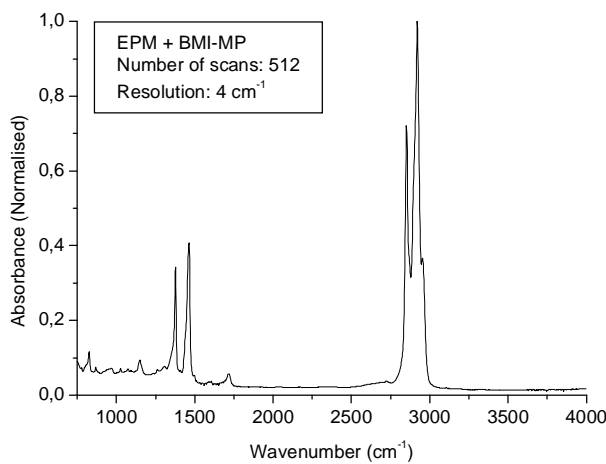
Figure A.12 FT-IR ATR spectrum of EPM + BMI-MP.
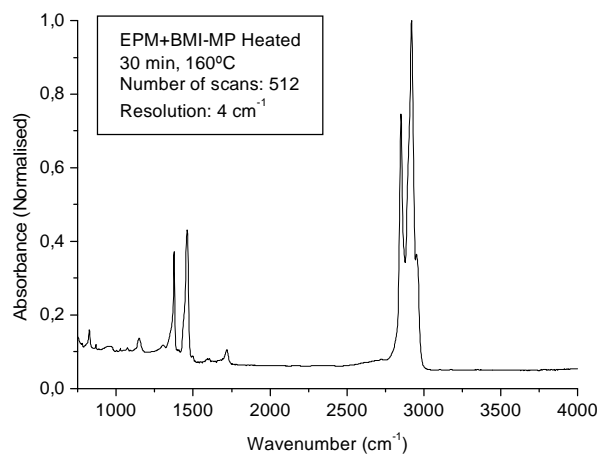
Figure A.13 FT-IR ATR spectrum of EPM + BMI-MP, heated for 30 min, 160°C.
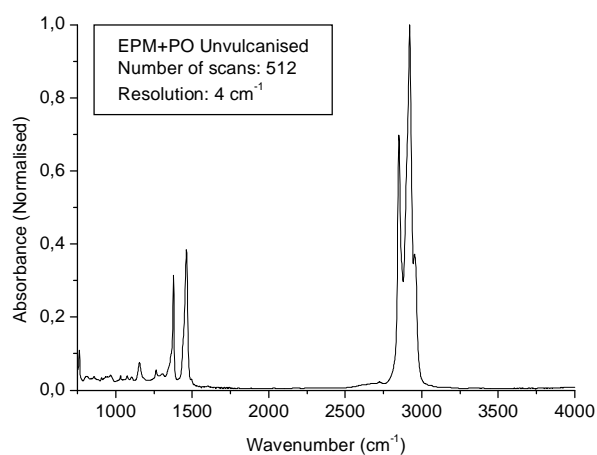
Figure A.14 FT-IR ATR spectrum of EPM + DCP, unvulcanised.
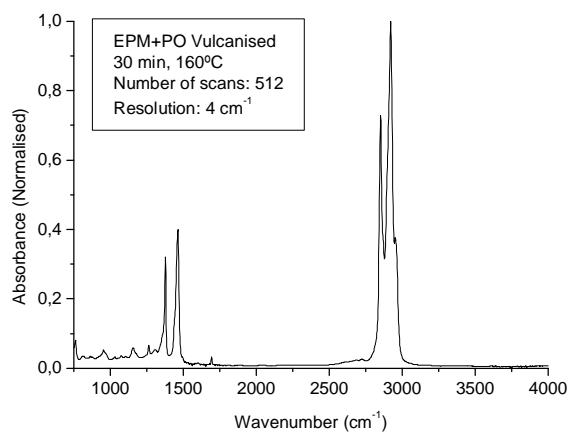
Figure A.15 FT-IR ATR spectrum of EPM + DCP, vulcanised 30 min, 160°C.
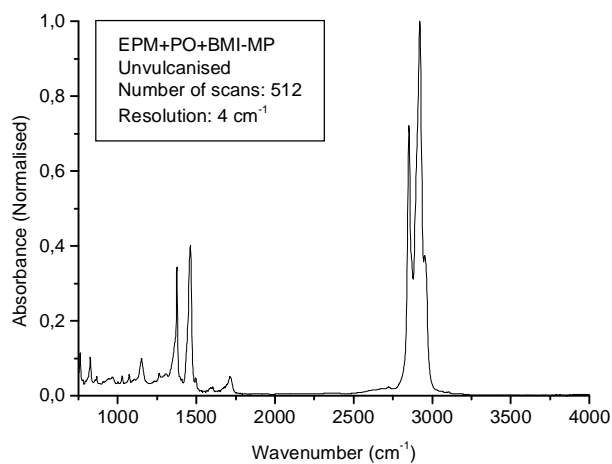
Figure A.16 FT-IR ATR spectrum of EPM + DCP + BMI-MP, unvulcanised.
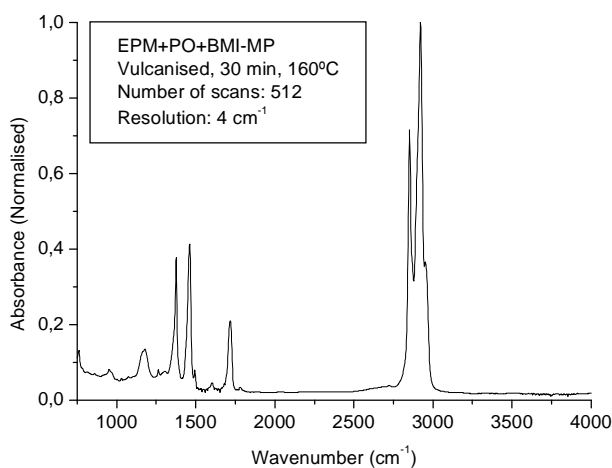
Figure A.17 FT-IR ATR spectrum of EPM + DCP + BMI-MP, vulcanised 30 min, 160°C.
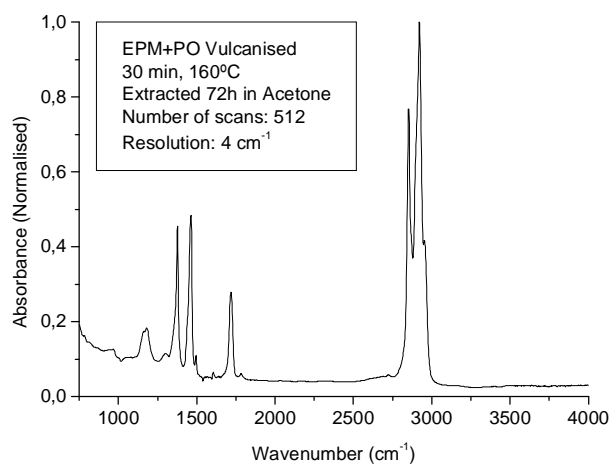
Figure A.18 FT-IR ATR spectrum of EPM + DCP + BMI-MP, vulcanised 30 min, 160°C,

extracted 72h in acetone.
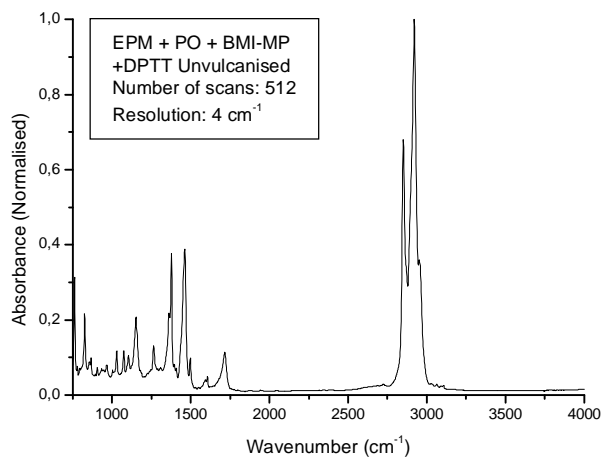
Figure A.19 FT-IR ATR spectrum of EPM + DCP + BMI-MP + DPTT, unvulcanised.
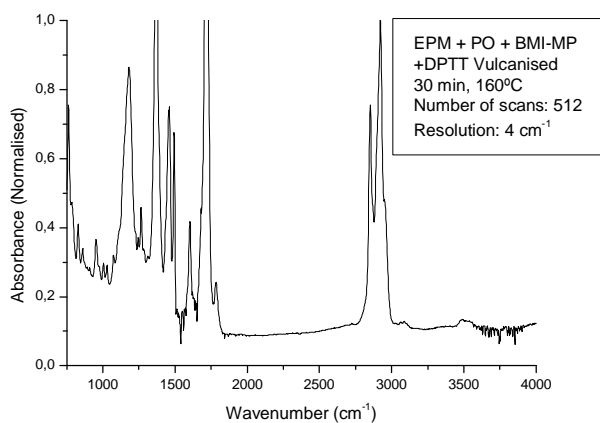
Figure A.20 FT-IR ATR spectrum of EPM + DCP + BMI-MP + DPTT, vulcanised.

Chapter 8

Summary and Final Remarks

"Lo bueno, si breve, dos veces bueno."

"That which is brief, if it be good, is good twice over."

Baltasar Gracián (1601-1658)

This last chapter provides a summary of the work described in this thesis. A general evaluation of the results obtained is given, together with some remarks. Finally some suggestions for further research are given.

8.1   MOTIVATION

Peroxide vulcanisation is a widely used cure system for elastomers and offers many possibilities for use, mainly because of the availability of co-agents and scorch retarders. The range of applications of peroxide cure could significantly be widened, if certain mechanical properties could be improved, to reach the level attained with sulphur curing, yet maintaining the good high temperature properties typical of peroxide vulcanisates and providing a system with proper scorch safety.

In order to achieve this synergistic combination of sulphur and peroxide properties in a peroxide cure system, co-agents play a key role in the compound formulation. The use of commercially available co-agents in peroxide vulcanisation boosts the cure efficiency and provides an improvement in mechanical properties. However, a step forward is still needed in order to bring several mechanical properties, such as tensile strength, to the level achieved with sulphur curing.

The development of new co-agents which are able to improve the mechanical properties of peroxide vulcanisates to reach the level of sulphur vucanisates, yet maintaining the excellent high temperature properties typical for peroxide cured articles, can be the way of achieving the synergistic system aimed for. These new co-agents should, at the same time, provide scorch safety.

The work described in this thesis is dedicated to seek this synergistic combination of sulphur and peroxide cure by using new co-agents. Further, the understanding of the co-agent reaction mechanism during vulcanisation is also addressed, in order to comprehend the chemistry that takes place and therefore to be able to tune the co-agent system to obtain optimal properties.

8.2 GENERAL SUMMARY

In the first chapter of this thesis an introduction into rubber technology is given. The aim of the thesis is described as well as its structure.

In Chapter 2 an overview of the literature regarding the peroxide cure process is given, with special emphasis on the use of co-agents. Relevant background information about this topic is reported. The importance of using co-agents in peroxide cure, in terms of peroxide efficiency, and their positive effect on the final material properties are reported, as found in literature. The chapter also focuses on the importance of scorch safety in peroxide cure and the use of scorch retarders to achieve this. Further, several attempts found in literature in order to achieve sulphur-like properties in peroxide vulcanisates are reported in this chapter.

Chapter 3 describes the use of a variety of commercially available co-agents in the peroxide cure of Ethylene Propylene polymethylene rubber (EPM). The results obtained in this chapter show the importance of using a co-agent in a peroxide cure formulation. Peroxide cure of EPM in the absence of co-agents leads to a material with a low cure state and poor mechanical properties. Therefore, co-agents are needed in order to boost peroxide efficiency and improve the mechanical properties. Three different commercially available co-agents are tested and they all show a big influence of co-agent concentration on the cure state and final properties achieved. The tendency is to achieve better cure characteristics with higher co-agent concentrations. However, at concentrations above 30 milliequivalents of unsaturation of co-agent, the tensile strength levels off for all the co-agents tested. Next to that, high concentrations of co-agent would result in an expensive product. Amongst the different co-agents tested, N,N'-p-phenylenedimaleimide (BMI-PP) provides the best improvement in properties, followed by N,N'-m-phenylenedimaleimide (BMI-MP), triallylcyanurate (TAC) and last, ethylene dimethacrylate (EDMA).

In Chapter 4 a series of new co-agents is introduced. These co-agents have as main characteristic the presence of one or two sulphur atoms in their bridging structure. Further, their structures are very similar to commercially available co-agents. The synthesis of these co-agents is reported as well as their performance in peroxide cure of EPM rubber. Bismethacrylamides, bisacrylamides, biscitraconimides and bismaleimides are synthesised and tested. Sulphur containing bismethacrylamides lead to better mechanical properties than the sulphur containing acrylamide co-agents. Within the series of acrylamide and methacrylamide co-agent types, the monosulphides provide better properties than the disulphides. Especially remarkable is the performance of the monosulphide bismethacrylamide BMA-PPS1, which leads to an improved cure state, higher tensile strength, moduli and hardness; and at the same time leads to better compression set and ageing, compared to the commercial co-agent EDMA. The disulphide bismaleimide, BMI-PPS2, and the monosulphide biscitraconimide, BCI-PPS1, provide a large improvement in the mechanical properties of the vulcanisates. They lead to better cure state, tensile strength, moduli, hardness and compression set, compared to their commercial counterpart, BMI-MP. On the other hand, the monosulphide bismaleimide, BMI-PPS1, and the disulphide biscitraconimide, BCI-PPS2, do not lead to any improvement. So far, no explanation could be found to understand the behaviour of these new co-agents. Therefore, further studies are needed to understand the differences in the performance of the sulphur containing co-agents. If an explanation for their performance can be found, new tailor-made co-agents to reach optimal characteristics might be synthesised and tested to achieve ultimately better properties.

In Chapter 5, the effect of two scorch retarders on the peroxide cure of EPM rubber is reported, for four co-agent systems: EDMA, TAC, BMI-MP and BMI-PP. 2,6-Di-tert-butyl-4-methylphenol (BHT) does not provide scorch safety in any case. Tetramethylthiuram disulphide (TMTD) provides an improvement in scorch time when

used in a bismaleimide/peroxide cure system. In this chapter the effect of elemental sulphur in the peroxide/bismaleimide cure of EPM rubber is also reported. The results show that the addition of elemental sulphur provides a slight improvement in properties, depending on the concentration used. Concentrations around 0.1 phr are able to slightly improve the mechanical properties without affecting the scorch time of the vulcanisation process. The most remarkable results of this chapter are those that describe the improvement in scorch time and mechanical properties achieved by addition of a sulphur spending compound, like dipentamethylenethiuram tetrasulphide (DPTT), to the formulation. An improvement in scorch time is obtained to provide scorch safety. Also the mechanical properties such as tensile strength are significantly improved. This positive effect achieved by addition of a sulphur containing compound to the peroxide formulation takes place for bismaleimide type co-agents such as BMI-MP and BMI-PP, while with other co-agent systems, like TAC and EDMA, DPTT has a large negative effect on cure state and mechanical properties. Further, the results presented in this chapter evidence that the co-agents BMI-MP and BMI-PP have different reactivities during peroxide curing, which leads to a higher crosslink density and therefore better mechanical properties in the case of BMI-PP.

Chapter 6 explores the effect of sulphur spending compounds on the bismaleimide/peroxide cure of EPM rubber. The remarkable improvement in scorch safety as well as in mechanical properties achieved with DPTT also takes place when other sulphur spending compounds are used, like dipentamethylenethiuram hexasulphide (DPTH), for instance. It is also proven in this chapter that this phenomenon is independent of the type of peroxide used. The results of this chapter show that the co-agent concentration is important to obtain optimal properties. The best scorch safety and mechanical properties obtained in a DPTT/bismaleimide/peroxide cure formulation are achieved when using 4 phr of bismaleimide co-agent. Special emphasis is put in this chapter to study the influence of sulphur spender concentration in the cure characteristics. The concentration of the sulphur spender, DPTT, is of significant importance in order to achieve optimal scorch time and mechanical properties. The results show that concentrations of 0.5 to 0.7 phr of DPTT improve at the same time: scorch safety, cure state, tensile strength, moduli, hardness, ageing properties and compression set at room and at high temperatures. It means that this system achieves a synergistic combination between sulphur cure and peroxide cure. Finally, this improvement achieved by using a sulphur spender in peroxide cure is also proven to work for EPDM rubber, which widens the possibilities of applying this new synergistic concept of co-agents.

In Chapter 7 mechanistic studies are reported which have been performed in order to understand the chemistry that takes place during peroxide vulcanisation in the presence of a bismaleimide co-agent and DPTT. The results from Nuclear Magnetic Resonance (NMR) and Infrared analysis (IR) clearly show the loss of maleimide unsaturation from the co-agent, as a result of vulcanisation. It is also observed that prior to peroxide decomposition, even at room temperature, the maleimide functionality of the co-agent already reacts with the sulphur spender, giving rise to an adduct and active sulphur. The formation of the adduct is confirmed by NMR and LC-MS. The release of active sulphur species was not detectable with the analysis techniques employed, but is most probably responsible for the improvement of the mechanical properties. From Model Compound Vulcanisation (MCV) analysed by Liquid-Chromatography Mass-Spectrometry (LC-MS) several reaction products of the peroxide vulcanisation of a model olefin in the presence of a maleimide co-agent are identified. Most of these have also been found in the presence of DPTT. In this chapter a reaction mechanism, based on the results of the mechanistic studies, is given. This mechanism explains how the addition of a sulphur spender improves scorch time and mechanical properties at the same time. The mechanism is based on the formation of the maleimide/sulphur spender adduct generated prior to vulcanisation. Once the peroxide decomposition takes place and the first radicals are formed, they react with

the adduct providing scorch safety. The improvement in mechanical properties can be attributed to the liberation of active sulphur from the sulphur spender, as a result of reaction with the co-agent, but also to the limitation of inefficient side reactions which consume radicals.

8.3 SUGGESTIONS FOR FURTHER RESEARCH

In Chapter 4 of this thesis a series of new co-agents for peroxide cure is described, which provide a synergistic combination between peroxide and sulphur cure. The common feature of these new co-agents is the presence of sulphur atoms in their molecular structure. Some of these co-agents have been found to provide the synergistic effect, and others not. However, no explanation has been found to understand their performance. Therefore, it would be very interesting to further study this series of new co-agents. Mechanistic studies could provide relevant information to understand the effect of these co-agents. MCV studies using LC-MS as analytical tool could provide information about the reaction products formed in the presence of the sulphur-containing co-agents. In this manner, the reaction between the co-agent and the model olefin can probably be studied in detail. Further, if the mechanistic studies provide understanding of the sulphur containing co-agent performance, new co-agents can be tailored and designed to meet optimal properties. These co-agents should then be synthesised, tested and compared to the previous co-agents in the same series as already tested.

In Chapters 5, 6 and 7 a different, yet also new, concept of co-agents for peroxide cure is presented, which also meets a synergistic combination of sulphur and peroxide cure. This concept consists of the addition of a sulphur spender into a bismaleimide/peroxide cure formulation, to achieve better scorch safety and mechanical properties. Although this new concept has been studied in detail in chapters 6 and 7, it has not been possible to evidence the incorporation of sulphur into the network formed during vulcanisation. Therefore, it would be necessary to analyse the system further, in order to prove that sulphur is indeed incorporated into the rubber network.

Samenvatting en afsluitende opmerkingen

In dit laatste hoofdstuk wordt het werk in dit proefschrift samengevat. De resultaten worden geëvalueerd en voorzien van enkele opmerkingen. Tot slot worden enkele suggesties gedaan voor vervolgonderzoek.

8.1 MOTIVATIE

Peroxide vulkanisatie wordt veelvuldig gebruikt voor elastomeren en biedt vele toepassingsmogelijkheden, met name door de beschikbaarheid van co-agentia en vertragers van de aanvulkanisatie: scorch. De toepasbaarheid van peroxide vulkanisatie zou nog aanzienlijk vergroot kunnen worden, als diverse mechanische eigenschappen van de gevulkaniseerde rubber verbeterd zouden kunnen worden tot een niveau vergelijkbaar met zwavel-vulkanisaten, maar met behoud van de hoge temperatuur eigenschappen gebruikelijk voor peroxide vulkanisaten. Voorwaarde is wel een voldoend lange scorch-tijd, hierna aangeduid met scorch-veiligheid.

Co-agentia spelen een belangrijke rol bij het bereiken van deze combinatie van zwavel en peroxide vulkanisaat-eigenschappen. Door commerciëel verkrijgbare co-agentia te gebruiken bij peroxide-vulkanisatie, kan al een enorme verbetering bereikt worden in de vulkanisatie-efficiëntie en de resulterende mechanische eigenschappen. Toch halen hiermee enkele mechanische eigenschappen, zoals de treksterkte, niet het niveau van zwavel vulkanisatie, en is er een stap voorwaarts vereist om het verschil tussen peroxide- en zwavel-vulkanisatie te overbruggen.

De ontwikkeling van nieuwe co-agentia, die het mogelijk maken om de mechanische eigenschappen van peroxide-gevulkaniseerde rubber te verbeteren naar het niveau van zwavel-gevulkaniseerd, met behoud van de goede hoge temperatuur eigenschappen behorende bij peroxide-vulkanisaten, kan een manier zijn om dit doel te bereiken. Deze nieuwe co-agentia moeten tevens scorch-veiligheid bewerkstelligen.

Het doel van het werk beschreven in dit proefschrift is het vinden van een combinatie van zwavel- en peroxide-vulkanisatie door middel van nieuwe co-agentia. Daarnaast wordt er aandacht besteed aan het reactiemechanisme van co-agentia tijdens vulkanisatie, zodat de chemie die plaatsvindt kan worden begrepen en het co-agent systeem zodanig aangepast, dat optimale eigenschappen worden verkregen.

8.2 ALGEMENE SAMENVATTING

Het eerste hoofdstuk van dit proefschrift bevat een inleiding in de rubber-technologie. Tevens worden het doel en de structuur van dit proefschrift beschreven.

In Hoofdstuk 2 wordt een literatuuroverzicht van peroxide vulkanisatie gegeven, met de nadruk op het gebruik van co-agentia. Alleen de relevante achtergrondinformatie over dit onderwerp wordt gegeven. Het belang van het gebruik van co-agentia bij peroxide-vulkanisatie wordt beschreven, zoals gevonden in de literatuur, betrokken op peroxide-efficiëntie en het positieve effect op de daarmee verkregen mechanische eigenschappen van de vulkanisaten. Dit hoofdstuk benadrukt ook het belang van scorch-veiligheid in peroxide-vulkanisatie en het gebruik van scorch-vertragers om dit te bereiken. Daarnaast worden enkele pogingen om zwavel-achtige eigenschappen te bereiken beschreven in dit hoofdstuk, zoals gevonden in de literatuur.

In Hoofdstuk 3 wordt het gebruik van een verscheidenheid aan co-agentia bij de peroxide-vulkanisatie van Etheen-Propeen-PolyMethyleen-rubber (EPM) onderzocht. De resultaten in dit hoofdstuk onderschrijven het belang van het gebruik van co-agentia in een peroxide-formulering. Peroxide-vulkanisatie in afwezigheid van co-agentia resulteert in een materiaal met lage vulkanisatiegraad en slechte mechanische eigenschappen. Co-agentia zijn vereist om de peroxide-efficiëntie sterk te verhogen en de mechanische eigenschappen te verbeteren. Drie verschillende commercieel verkrijgbare co-agentia zijn getest. Zij vertonen allemaal een grote afhankelijkheid van vulkanisatiegraad en de verkregen mechanische eigenschappen van de concentratie co-agent. Betere vulkanisatie-karakteristieken worden verkregen met een toenemende concentratie co-agent. Echter, bij concentraties hoger dan 30 milli-equivalenten onverzadiging in de co-agent neemt de treksterkte niet verder meer toe. Dit geldt voor alle co-agentia. Bovendien zouden hogere concentraties co-agent slechts resulteren in een kostbaar eindproduct. Van de onderzochte co-agentia verbetert N,N'-p-fenyleen-dimaleimide (BMI-PP) de eigenschappen het meest, gevolgd door N,N'-m-fenyleen-dimaleimide (BMI-MP), triallylcyanuraat (TAC) en als minste: ethyleen-dimethacrylaat (EDMA).

In Hoofdstuk 4 wordt een serie nieuwe co-agentia geïntroduceerd. Alle hebben een brug in hun chemische structuur bestaande uit één of twee zwavelatomen. Verder zijn deze co-agentia vergelijkbaar met commercieel verkrijgbare co-agentia. De synthese van deze co-agentia en hun prestaties in peroxide-vulkanisatie van EPM rubber worden beschreven. Bis-methacrylamides, bis-acrylamides, bis-citraconimides en bis-maleimides zijn gesynthetiseerd en getest. Bis-methacrylamides die zwavel bevatten, leiden tot betere mechanische eigenschappen dan acrylamide co-agentia met zwavel. Binnen de reeksen van acrylamide en methacrylamide co-agentia presteren monosulfiden beter dan disulfiden. Uitgesproken goed presteert het monosulfide bis-methacrylamide BMA-PPS1. Het gebruik van deze co-agent leidt tot een betere vulkanisatiegraad en hogere treksterkte, modulus en hardheid, met daarnaast betere compressie set en veroudering, vergeleken met het commercieel verkrijgbare co-agent EDMA. De disulfide bis-maleimide, BMI-PPS2, en monosulfide bis-citraconimide, BCI-PPS1, verbeteren de mechanische eigenschappen van de vulkanisaten. Zij leiden tot een hogere vulkanisatiegraad, treksterkte, modulus en betere compressie set vergeleken met hun commerciële tegenhanger: BMI-MP. Daarentegen leiden de monosulfide bis-maleimide, BMI-PPS1, en disulfide bis-citraconimide, BCI-PPS2, niet tot verbeteringen. Tot dusverre is er nog geen verklaring gevonden voor het gedrag van deze nieuwe co-agentia. Er zijn verdere studies vereist, om het verschil in prestaties tussen de nieuwe zwavel-houdende co-agentia te begrijpen. Wanneer verklaringen gevonden worden, kunnen nieuwe co-agentia op maat gesynthetiseerd en getest worden om nog optimalere eigenschappen te bereiken.

In Hoofdstuk 5 wordt het effect van twee scorch-vertragers op de peroxide vulkanisatie van EPM beschreven, voor vier co-agent systemen: EDMA, TAC, BMI-MP en BMI-PP. 2,6-Di-tert-butyl-4-methylfenol (BHT) geeft in geen geval scorch-veiligheid. Tetramethylthiuram-disulphide (TMTD) geeft alleen scorch-veiligheid wanneer het gebruikt wordt in een bis-maleimide/peroxide vulkanisatiesysteem. In dit hoofdstuk wordt ook het effect beschreven van elementaire zwavel als toevoeging bij de bis-maleimide/peroxide vulkanisatie van EPM rubber. De resultaten wijzen erop, dat het toevoegen van elementaire zwavel een lichte verbetering van eigenschappen geeft, afhankelijk van de concentratie die gebruikt wordt. Concentraties rond 0.1 phr (parts per hundred rubber) kunnen de mechanische eigenschappen licht verbeteren zonder de scorch-tijd van het vulkanisatieproces te beïnvloeden. De meest opmerkelijke resultaten in dit hoofdstuk zijn verbeteringen in scorch-tijd en mechanische eigenschappen, verkregen door toevoeging van een zwaveldonerende verbinding, zoals dipentamethyleenthiuram tetrasulfide (DPTT) aan de formulering. Een verlenging in scorch-tijd wordt waargenomen, resulterend in scorch-veiligheid. Ook de mechanische eigenschappen, zoals treksterkte, zijn beduidend beter. Dit positieve effect, bereikt door het toevoegen van een zwavelhoudende verbinding aan de peroxide formulering, wordt waargenomen voor bis-maleimide-type co-agentia als BMI-MP en BMI-PP. Voor andere co-agent systemen, zoals TAC en EDMA, heeft DPTT een sterk negatief effect op de vulkanisatiegraad en mechanische eigenschappen. Verder worden in dit hoofdstuk resultaten getoond, die bewijzen dat de co-agentia BMI-MP en BMI-PP een verschillende reactiviteit hebben gedurende de peroxide vulkanisatie, hetgeen leidt tot een hogere crosslinkdichtheid en daardoor betere mechanische eigenschappen in het geval van BMI-PP.

Hoofdstuk 6 verkent het effect van verschillende zwavel-donerende verbindingen op de bis-maleimide/peroxide vulkanisatie van EPM rubber. De opmerkelijke verbetering in scorch-veiligheid alsmede de mechanische eigenschappen, zoals bereikt met DPTT in Hoofdstuk 5, wordt ook gevonden wanneer andere zwavel-donerende verbindingen worden gebruikt, zoals dipentamethyleen-thiuram hexasulfide (DPTH). In Hoofdstuk 6 wordt tevens aangetoond, dat de positieve werking van de zwavel-donerende verbinding onafhankelijk is van het type peroxide, dat gebruikt wordt. Wel is de concentratie co-agent belangrijk om optimale eigenschappen te bereiken. De beste scorch-veiligheid en mechanische eigenschappen in een DPTT/bis-maleimide/peroxide vulkanisatie formulering worden bereikt, wanneer 4 phr bis-maleimide co-agent wordt gebruikt. De nadruk in dit hoofdstuk ligt op de invloed van de concentratie zwaveldonerende verbinding op de vulkanisatie karakteristieken. De concentratie van de zwaveldonor, DPTT, is van belang om een optimale scorch-tijd en de beste mechanische eigenschappen te behalen. DPTT-concentraties tussen 0,5 en 0,7 phr verbeteren scorch-veiligheid, vulkanisatiegraad, treksterkte, modulus, hardheid en compressie set, zowel bij hoge als bij lage temperatuur gemeten. Dit betekent, dat met dit systeem daadwerkelijk een combinatie van zwavel- en peroxide-vulkanisatie wordt bereikt. Uiteindelijk is deze verbetering, bereikt door het gebruik van een zwavel donor, ook aangetoond voor Etheen-Propeen-Diëen-polyMethyleen (EPDM) rubber. Dit verbreedt de toepassings-mogelijkheden van dit nieuwe concept van co-agentia.

In Hoofdstuk 7 worden mechanistische studies beschreven, uitgevoerd om de chemie tijdens peroxide vulkanisatie in aanwezigheid van een bis-maleimide co-agent en DPTT in kaart te brengen. De resultaten verkregen met Nuclear Magnetic Resonance (NMR) en Infrarood (IR) analyse laten duidelijk het verdwijnen van de maleimide-onverzadiging van de co-agent zien ten gevolge van de vulkanisatie. Een reactie tussen de maleimide- functionaliteit van de co-agent en de zwaveldonor wordt waargenomen, hetgeen resulteert in een samengesteld molecuul en vrije zwavel in het mengsel. Dit gebeurt vóór de ontleding van het peroxide en zelfs al bij kamertemperatuur. De vorming van dit samengestelde molecuul wordt bevestigd met NMR en IR. Het vrijkomen van actieve zwavel kon niet vastgesteld worden met de

gebruikte analyse technieken, maar is waarschijnlijk verantwoordelijk voor de verbetering van de mechanische eigenschappen. Door middel van Model Compound Vulcanisatie (MCV), geanalyseerd met Liquid-Chromatography Mass-Spectrometry (LC-MS) konden enkele reactieproducten van de peroxide-vulkanisatie van een model-olefine in aanwezigheid van een maleimide co-agent worden geïdentificeerd. De meeste verbindingen werden ook gevonden in aanwezigheid van DPTT. Een reactiemechanisme wordt gepostuleerd op basis van de resultaten verkregen met de mechanistische studies. Dit mechanisme verklaart hoe, door toevoeging van een zwaveldonor, zowel de scorch-tijd als ook de mechanische eigenschappen verbeterd worden. Dit mechanisme is gebaseerd op de vorming van het maleimide/zwaveldonor samengestelde molecuul vóór de feitelijke vulkanisatie. Zodra het peroxide ontleedt en radicalen worden gevormd, reageren de radicalen met het samengestelde molecuul, resulterend in scorch-veiligheid. De verbetering in mechanische eigenschappen kan toegeschreven worden aan het vrijkomen van actieve zwavel uit de zwaveldonor, ten gevolge van reactie met de co-agent, maar beperkt door inefficiënte nevenreacties, die radicalen verbruiken.

8.3   SUGGESTIES VOOR VERDER ONDERZOEK

In Hoofdstuk 4 van dit proefschrift wordt een reeks nieuwe co-agentia beschreven, die een combinatie leveren van peroxide- en zwavel-vulkanisatie. Deze nieuwe co-agentia hebben allemaal zwavel-atomen in hun chemische structuur. Sommige van deze co-agentia bleken de gewenste combinatie van zwavel- en peroxide-vulkanisatie op te leveren, andere niet. Er is echter geen verklaring gevonden waarmee de prestaties van deze nieuwe co-agentia begrepen kunnen worden. Daarom is het de moeite waard om deze nieuwe co-agentia nader te bestuderen. Mechanistische studies kunnen belangrijke informatie verschaffen, waardoor het effect van deze co-agentia begrepen kan worden. MCV studies met LC-MS als analyse-techniek kunnen verdere inzichten verschaffen in de reactieproducten, die gevormd worden in aanwezigheid van de zwavelhoudende co-agentia. Waarschijnlijk kan op deze manier de reactie tussen co-agent en model-olefine in detail bestudeerd worden. Als de mechanistische studies voldoende begrip over de zwavelhoudende co-agentia opgeleverd hebben, kunnen nieuwe co-agentia op maat worden ontworpen en gemaakt, om zo optimale eigenschappen te bereiken. Deze co-agentia moeten dan gesynthetiseerd, getest en vergeleken worden met de voorgaande co-agentia in dezelfde serie, zoals al getest.

In Hoofdstukken 5, 6 en 7 wordt een ander, en tevens nieuw, concept voor co-agentia beschreven, dat ook een combinatie oplevert van zwavel- en peroxide-vulkanisatie. Dit concept bestaat uit het toevoegen van een zwaveldonor aan een bis-maleimide/peroxide vulkanisatie formulering, om zo een verbeterde scorch-veiligheid en mechanische eigenschappen te krijgen. Ook al is dit nieuwe concept uitgebreid onderzocht in hoofdstukken 6 en 7, er is nog niet aangetoond, dat zwavel zich in het netwerk nestelt tijdens de vulkanisatie. Daarom is het noodzakelijk om dit systeem verder te onderzoeken teneinde dit daadwerkelijk te bewijzen.

Symbols and Abbreviations

1,2-BR	1,2-Polybutadiene
ABS	Acrylonitrile butadiene styrene copolymer
AcN	Acetonitrile
Ac_2O	Acetic anhydride
ACM	Polyacrylate rubber
AE/EU	Polyurethane rubber
$AgNO_3$	Sodium nitrate
APCI	Atmospheric pressure chemical ionisation
APPI	Atmospheric pressure photo ionisation
BHT	2,6-Di-tert-butyl-4-methylphenol
BA-PPS1	4,4'-(bisacrylamide) diphenyl monosulphide
BA-PPS2	4,4'-(bisacrylamide) diphenyl disulphide
BCI-PPS1	4,4'-(biscitraconimide) diphenyl monosulphide
BCI-PPS2	4,4'-(biscitraconimide) diphenyl disulphide
BMA-PPS1	4,4'-(bismethacrylamide) diphenyl monosulphide
BMA-PPS2	4,4'-(bismethacrylamide) diphenyl disulphide
BMI-MP	N,N'-m-phenylenedimaleimide
BMI-PP	N,N'-p-phenylenedimaleimide
BMI-PPS1	4,4'-(bismaleimide) diphenyl monosulphide
BMI-PPS2	4,4'-(bismaleimide) diphenyl disulphide
BR	Polybutadiene rubber
CBS	N-cyclohexyl-2-benzothiazylsulphenamide
$CDCl_3$	Deuterated chloroform
CIIR	Chlorobutyl rubber
CM	Chlorinated polyethylene
CO	Epichlorohydrin rubber
CR	Polychloroprene rubber
CSM	Chlorosulphonated polyethylene
DAD	Diode array detector
DATP	Diallylterephthalate
DCP	Dicumyl peroxide
DMSO	Deuterated dimethylsulphoxide
DPTT	Dipentamethylenethiuram tetrasulphide
DPTH	Dipentamethylenethiuram hexasulphide
DTBP	Di-tert-butyl peroxide
DTBPH	2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane
DTBPIB	Di(tert-butylperoxyisopropyl)benzene
DVB	Divinylbenzene
EBA	Ethylene butylacrylate copolymer
ECO	Epichlorohydrin copolymer
EDMA	Ethylene dimethacrylate
EIC	Extracted ion chromatogram
ENB	Ethylidene norbornene

EPM	Ethylene propylene polymethylene rubber	
EPDM	Ethylene propylene diene polymethylene rubber	
eq	equivalents	
ESI	Electrospray ionisation	
EVA	Ethylene vinylacetate copolymer	
FKM	Fluoro elastomers	
FPM	Fluor rubber	
FT-IR	Fourier-transform infrared spectroscopy	
FT-IR-ATR	Fourier-transform infrared attenuated total reflection spectroscopy	
GC	Gas chromatography	
HDPE	High-density polyethylene	
HNBR	Hydrogenated butadiene acrylonitrile rubber	
^{1}H-NMR	Proton nuclear magnetic resonance	
HTS	Hexamethylene-1,6-bisthiosulphate disodium salt dihydrate	
IIR	Butyl rubber	
ISO	International Organization for Standardization	
IR	Polyisoprene rubber	
IR	Infrared spectroscopy	
LC	Liquid chromatography	
LC-MS	Liquid-chromatography mass-spectrometry	
LDPE	Low-density polyethylene	
MBT	2-Mercaptobenzothiazole	
MCV	Model compound vulcanisation	
MH	Maximum torque	[dNm]
MI	N-phenylmaleimide	
ML	Minimum torque	[dNm]
ML(1+4)	Mooney viscosity	
MS	Mass spectrometry	
MSD	α-methylstyrene dimer	
Mw	Molecular weigth	[g/mol]
N_2	Nitrogen	
NaAcO	Sodium acetate	
NBR	Butadiene acrylonitrile rubber	
NR	Natural rubber	
PB	Polybutene-1	
PE	Polyethylene rubber	
phr	Parts per hundred rubber	
PIB	Polyisobutene	
PP	Polypropylene	
ppm	Parts per milion	
PVC	Polyvinylchloride	
Q	Silicone rubber	
RPA	Rubber Process Analyser	
S_8	Sulphur	
SBR	Styrene butadiene rubber	
SMP3	Stuart melting point apparatus	
SR	Synthetic rubber	
t_{s2}	Scorch time	[min]
t_{90}	Optimum cure time	[min]
T	Polysulphide rubber	
TAC	Triallylcyanurate	
TAIC	Triallylisocyanurate	
TAP	Triallylphosphate	

TBzTD	Tetrabenzylthiuram disulphide	
TESPT	Bis-triethoxysilylpropyl tetrasulphide	
THF	Tetrahydrofurane	
TIC	Total ion chromatogram	
TMPTM	Trimethylolpropane trimethacrylate	
TMTD	Tetramethylthiuram disulphide	
UV	Ultraviolet	
WLP	Wickert laboratory press	
χ	Flory-Huggins interaction parameter	[-]
m_e	Overall crosslink density	[mol/cm^3]
v_0	Molar volume of the solvent	[l/mol]
v_r	Polymer volume fraction of the swollen sample	[l/mol]
r_r	Density of rubber	g/cm^3
r_s	Density of solvent	g/cm^3
m_r	weight of rubber network;	[g]
m_s	weight of solvent in sample at equilibrium swelling	[g]

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EXTERNAL PRESENTATIONS

- M.M. Alvarez Grima, International Rubber Conference, June 2004, Moscow, Russia.

- M.M. Alvarez Grima, 168th Technical meeting – Rubber Division, ACS, November 2005, Pittsburgh (PA), USA.

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PATENT APPLICATIONS

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Curriculum Vitae

"Live as if you were to die tomorrow. Learn as if you were to live forever."

Mahatma Gandhi (1869-1948)

Maria Montserrat Alvarez Grima was born in Barcelona (Spain) on the 6th of April, 1978. From 1996 to 2001 she studied chemistry at Institut Químic de Sarrià (IQS) from the Universitat Ramon Llull, in Barcelona. She did her Master's Thesis at Institut Químic de Sarrià, under the supervision of prof. dr. Borros, in cooperation with the University of Twente, in the Rubber Technology group from prof. dr. ir. Noordermeer. During her Master's Thesis she studied the reactivity of the sulphur chain of the coupling agent TESPT during vulcanisation. She graduated in September 2002.

From October 2002 to September 2006 the author worked as a PhD student under the supervision of prof. dr. ir. J.W.M. Noordermeer at the University of Twente, (Faculty of Science and Technology) in a project which is part of the Research Programme of the Dutch Polymer Institute (DPI), project #357. The results of this work are described in this thesis.

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"Let us be grateful to people who make us happy; they are the charming gardeners who make our souls blossom."

Marcel Proust (1871-1922)

"Not what we give,
But what we share,
For the gift
without the giver
Is bare."

James Russell Lowell (1819-1891)

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"… The important thing is not to be bitter over life's disappointments. Learn to let go of the past. And recognize that every day won't be sunny, and when you find yourself lost in the darkness and despair remember it's only in the black of night you see the stars. And those stars will lead you back home.

So don't be afraid to make mistakes, or stumble and fall, cause most of the time the greatest rewards come from doing the things that scare you the most. Maybe you'll get everything you wish for. Maybe you'll get more than you ever could have imagined. Who knows where life will take you. The road is long and in the end, the journey is the destination."

- Whitey, One Tree Hill.