INVESTIGATION OF PEROXIDE CROSSLINKING OF EPDM RUBBER BY SOLID-STATE NMR

PROEFSCHRIFT

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INVESTIGATION OF PEROXIDE CROSSLINKING OF EPDM RUBBER BY SOLID-STATE NMR by Ramona Orza

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To my family
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1.1 Elastomers

Elastomers, colloquially called rubbers, are an important class of materials with a large number of applications. Elastomers possess several significant defining characteristics:

1. They have a low glass transition temperature, $T_g$

2. They possess the property of elasticity. Invoking the theory of rubber elasticity, one considers a polymer chain in a crosslinked network as an entropic spring. When the chain is stretched, the entropy is reduced by a large margin because there are fewer conformations available. Therefore, there is a restoring force, which causes the polymer chain to return to its equilibrium or unstretched state, such as a high entropy random coil configuration, once the external force is removed. This is the reason why rubber bands return to their original state.

3. The polymer is preferably free of crystallinity

4. The polymer is lightly crosslinked. Some type of permanent structure is necessary to form a coherent solid and prevent liquidlike flow of elastomer molecules. This requirement is usually met by incorporating a number of intermolecular chemical bonds (crosslinks) to make a loose three-dimensional molecular network.

One of the first materials found to exhibit a sizeable elastic region was a natural substance obtained from the tree *Hevea brasiliensis*. It was first used by indigenous South Americans and was called *caoutchouc*, but later, simply *rubber*, when it was discovered by Priestley that the material rubbed out pencil marks. A large number of polymers with rubber-like characteristics at ambient temperatures are now available, and it is preferable to call this general group of polymers *elastomers*. 
From the early 20th century, chemists have been attempting to synthesize materials whose properties duplicate or at least simulate those of natural rubber, and this has led to the production of a wide variety of synthetic elastomers. Some of these have become technologically important and are listed in Table 1.1, together with their general uses. EPDM (Ethylene-Propylene-Diene polyMethylene) was developed and commercialized in the late 1950s. With an annual production capacity of more than 1,000 kt in 1998, EPDM is currently the fourth elastomer by volume and has become more or less a commodity rubber. Actually, EPDM is the largest non-tire rubber. The annual growth rate is about 4%. Exxon mobil, Dow and DSM and are market leaders.

Table 1.1 Different polymers and their applications

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Formula</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>([-\text{CH}_2-\text{C(CH}_3\text{)=CH-CH}_2\text{-}]_n)</td>
<td>General purposes</td>
</tr>
<tr>
<td>Polybutadiene</td>
<td>([-\text{CH}_2-\text{C}=\text{CH-CH}_2\text{-}]_n)</td>
<td>Tire treads</td>
</tr>
<tr>
<td>IIR</td>
<td>([-\text{CH}_2-\text{C(CH}_3\text{)}_2\text{-][CH}_2-\text{C(CH}_3\text{)=CH-CH}_2\text{-}]_n)</td>
<td>Inner tubes, cable sheeting, roofing, tank liners</td>
</tr>
<tr>
<td>SBR</td>
<td>([-\text{CH}_2-\text{C}=\text{CH-CH}_2\text{-][CH(C}_6\text{H}_6\text{-CH}_2\text{-}]_n)</td>
<td>Tires, general purposes</td>
</tr>
<tr>
<td>CR</td>
<td>([-\text{CH}_2-\text{CCl}=\text{CH-CH}_2\text{-}]_n)</td>
<td>Used when oil resistance, good weathering, and inflammability characteristics are needed</td>
</tr>
<tr>
<td>Silicones</td>
<td>([-\text{Si(CH}_3\text{)}_2-\text{O-}]_n)</td>
<td>Gaskets, door seals, medical application, flexible molds</td>
</tr>
<tr>
<td>Polyurethanes</td>
<td>([-\text{R-O-CO-NH-R-NH-CO-O-}]_n)</td>
<td>Printing rollers, sealing and jointing</td>
</tr>
<tr>
<td>EPM</td>
<td>([\text{CH}_2-\text{CH}_2\text{-][CH(CH}_3\text{)-CH}_2\text{-}]_n)</td>
<td>Window strips, channeling, pipes, tubes, hoses, seals</td>
</tr>
</tbody>
</table>

The outstanding property of the ethylene-propylene copolymer and the ethylene-propylene-diene terpolymer are their good weather-resistance compared with polybutadiene (BR), polyisoprene (IR), and styrene/butadiene copolymer (SBR), since EP(D)M rubbers have no double bonds in the backbone of the polymer chains and, thus, are less sensitive to oxygen and ozone and have high UV-resistance. Other excellent properties of these rubbers are high resistance to acid and alkali, insulation properties, and high and low temperature performance. The copolymer and terpolymer are used in the automotive industry for windows, hoses, gaskets, wipers, bumpers,
belts, door seals, etc. Furthermore, they are used for cable insulation and for roofing. Additional uses are in white sidewall compounds of tires.

A large number of commercial EP(D)M grades are produced. The main structural characteristics are the following:\textsuperscript{2,3,4,5,6}

- Concentration ratio of ethylene and propylene chain units (amorphous or crystalline grades)
- Co- or terpolymerization of ethylene, propylene and diene monomers (EPM or EPDM)
- The type and amount of termonomer (chain branching, the type of crosslinking, mechanical properties)
- Molecular weight and molecular weight distribution
- Chain branching (differences in viscosity and processability)
- Processability and price

Copolymers which contain below 55 wt. % ethylene are completely amorphous and are not self-reinforcing. At higher ethylene contents of the order of 60 to 70 wt.%, the polymers contain long ethylene sequences, which form crystalline domains. These polymers are referred to as “sequential” grades and their processing behavior differs considerably from that of the normal amorphous grades. The partially crystalline domains form thermally reversible physical crosslinks, which, as in thermoplastic elastomers, provides the elastomers with a higher mechanical strength without chemical crosslinks\textsuperscript{7}, but can worsen tensile properties in vulcanisates. Most applications require crosslinking (see next chapter). Traditionally, sulfur vulcanization requires unsaturation and therefore fully saturated EPM can not be crosslinked with sulfur. Non-conjugated diene monomers have been introduced in EPM, yielding EPDM for sulfur vulcanization. For peroxide crosslinking the presence of the diene increases the crosslinking efficiency.

Figure 1.1.1 Chemical structure of diene third monomers: (a) VNB, (b) DCPD and (c) ENB, as built into the polymer chain.
From a practical point of view, ENB and DCPD are the most important diene termonomers because of high amounts of diene that can be easily incorporated in commercial EPDMs.\textsuperscript{8,9,10} Increasing the amount of diene results in increased crosslink densities and, thus, in corresponding changes in mechanical and elastic properties. The preferred third monomer for peroxide cure is VNB.\textsuperscript{8}

### 1.2 Crosslinking methods

The term *vulcanization* or *crosslinking* is generally applied to rubbery or elastomeric materials. The crosslinked materials forcibly retract to their approximately original shape after a rather large mechanically imposed deformation. Viscoelastic properties of vulcanisates are largely influenced by the density of crosslinks.

According to the theory of rubber elasticity, the retractive force resisting to a deformation is proportional to the number of force bearing network chains per unit volume of elastomer.\textsuperscript{11} An increase in the number of junctions or crosslinks gives an increase in the number of network chains. In a non-crosslinked linear high molar mass polymer (above its melting point) only chain entanglements cause viscoelasticity.

Crosslinking is a process of chemically producing network junctions by the insertion of crosslinks between the polymer chains. The crosslink may be a group of sulfur atoms in a short

![Diagram](image)

**Figure 1.2.1** Properties as a function of the extent of crosslinking.
chain, a single sulfur atom, carbon-to-carbon bond, a polyvalent organic radical, an ionic cluster, or a polyvalent metal ion. The process is usually carried out by heating the rubber (mixed with the crosslinker) in a mold under pressure.

Major effects of crosslinking on use-related properties are schematically shown in Fig. 1.2.1. It should be noted that the static modulus increases with crosslinking to a greater extent than does the dynamic modulus. The dynamic modulus is a composite of viscous and elastic behavior, whereas the static modulus is a measure of only the elastic component of rheological behavior. Hysteresis is the ratio of the rate-dependent or viscous component to the elastic component of the complex modulus. It is a measure of the deformation energy which is not stored but which is converted to heat. Hysteresis is reduced with increasing crosslink formation. Tear strength, fatigue life, and toughness are related to the breaking energy. Values of these properties increase with small amounts of crosslinking but they are reduced by further crosslink formation. Properties related to the energy-to-break increase with increasing both the number of network chains and hysteresis. Since hysteresis decreases as more network chains are formed, the energy-to-break related properties reach a maximum at some intermediate crosslink density. It should be noted that the properties given in Fig. 1.2.1 are not only functions of crosslink density. They are also affected by the type of crosslinks, the type of polymer, and type and amount of filler.

The first and by far the most important crosslinking agent is sulfur, which is relatively inexpensive and yet vital to the rubber industry. For a number of elastomers, there are unsaturated double bonds on the polymer chain. Elastomers such as NR and SBR need only a

![Figure 1.2.2](image_url)  
(a) Single sulfur atom linking two polymer chains; (b) multiple sulfur link
small percentage of these double bonds to be utilized in order to produce a useful product; however this leaves a larger percentage of unreacted double bonds that are vulnerable to attack by oxygen, ozone and heat, deteriorating properties.

At one extreme, a single sulfur atom connects the carbon atom of one chain to that of another\textsuperscript{13}. In practice the di- or tri-sulfidic links are predominant, see Fig. 1.2.2 a)

\textbf{Figure 1.2.3} Products and reaction mechanism of accelerated sulphur vulcanization of EPDM (X=accelerator residue)\textsuperscript{14}

Efficient vulcanization can be achieved by adding to the rubber formulation a particular type of accelerator, which has available sulfur atoms in its molecule, and avoids using elemental sulfur altogether. In this case the accelerator, now more appropriately called a crosslinking agent becomes a sulfur donor. Efficient vulcanization can also be achieved by using a small amount of elemental sulfur, about 0.3 to 0.8 phr (parts per hundred rubber), together with larger amounts of accelerator (2-5 phr).

At the other extreme, the conventional crosslinking system comprises 2-3 phr elemental sulfur and smaller quantities of accelerator (0.5-1 phr). This produces predominantly multiple sulfur
atoms in the crosslink, known as polysulfidic crosslinks, see Fig. 1.2.2 b). In between these two extremes lies the semi efficient vulcanization system using about 1.5 phr elemental sulfur and a correspondingly adjusted accelerator level. The symbol $S_x$ in Fig. 1.2.2 b) represents the multiple sulfur link.

Accelerated sulphur vulcanization results in the substitution of the labile allylic H-atoms by sulphur bridges, yielding alkenyl sulphides. The unsaturation of the third monomer is not consumed, but activates the allylic positions. Initially, accelerator residues are attached to the allylic positions via a sulphur bridge, yielding crosslink precursors (Fig. 1.2.3). Subsequently, the actual sulphur crosslinks are formed. Sulphur substitution of ENB occurs at C3-exo, C3-endo and C9 (see Fig. 1.2.4.).

![Figure 1.2.4 Example of C3-exo and C3-endo positions and the E and Z isomers of the ENB.](image)

In combination with the $E/Z$ isomerism of the ENB ethylidene unit and the formation of sulphidic species with 1 up to 5 S-atoms a large number of crosslink structures is finally produced. A crosslink consisting of many sulfur atoms would be more flexible than a crosslink consisting of a single sulfur atom. In terms of properties, this means that vulcanizates with a conventional cure system are generally better at relieving stress when flexed. Thus they have a better fatigue life in a repetitious (cyclic) deformation environment. A disadvantage is that sulfur to sulfur bonds are weaker (less thermally stable) than sulfur to carbon links and the conventionally cured system is therefore less heat resistant than a system from a semi-efficient or efficient vulcanization.

Although sulfur is the best known and most used vulcanizing agent, there is another class of crosslinking agents known as peroxides. They don’t necessarily need the reactivity of a double bond to cure, nor do they need accelerators, although chemicals known as coagents are often used to improve overall vulcanization.
Crosslinking with peroxides has been known for a long time, but gained importance with the development of the saturated synthetic rubbers. Based on the heat stability that can be obtained by peroxide vulcanization of diene rubbers, especially of EPDM, this type of vulcanization has achieved a great importance.

The temperature of decomposition (half-life) of the peroxide is the main determinant for the so-called scorch temperature (which gives an indication when crosslinking starts to take place) and cure rate. The chemical structure of the peroxide determines its usefulness as a vulcanizing agent.

The chemical structure of all peroxides can be derived from hydrogen peroxide; the single substituted products are the hydroperoxides; the double substituted products are the peroxides:

- H-O-O-H hydrogen peroxides
- R-O-O-H hydroperoxides
- R-O-O-R peroxides

Hydroperoxides do not lead to the formation of crosslinks, but can interfere with the crosslinking capacity of other peroxides, respectively can degrade polymer molecules. They are therefore not important in the crosslinking of rubber. They are important in the radical initiation during polymerization and frequently initiate aging reactions.

For the crosslinking of rubber, only peroxides can practically be used, which are stable and not dangerous during the usual handling, and which, on the other hand, decompose sufficiently fast at customary curing temperatures. Peroxides with tertiary carbon atoms are less stable. One can distinguish two groups of organic peroxides that are stable enough for rubber processing. Almost all peroxides that are of interest in curing of rubbers can be derived from these basic types.
Peroxides typically react with the elastomer chains by removing hydrogen atoms from the carbon backbone of the polymer, thus creating highly active radicals on the chain, which attach to a similar site on another chain. This creates a carbon to carbon crosslink, which is stronger than a sulfur to carbon link and more thermally stable, see Fig. 1.2.5.

The mechanism of peroxide crosslinking is much less intricate than that of sulfur vulcanization. Crosslinking is initiated by the thermal decomposition of the peroxide. Next, the active radicals thus formed abstract hydrogen from elastomer chains to form macro-radicals. Finally, crosslinking results either from the combination of two macro-radicals or from the addition of a macro-radical to an unsaturated moiety of another primary elastomer chain. (Fig. 1.2.7)

Peroxide crosslinking confers a higher heat aging resistance due to higher stability of C–C bonds as compared to C–S and S–S bonds. Peroxide crosslinking gives better compression set than sulfur cured crosslinking, at the expense of fatigue life and some tensile strength at high temperature. Peroxide curing can vulcanize some elastomers which cannot be cured with sulfur, because of a total lack of double bonds, for example the copolymer of ethylene and propylene rubber (EPM).
1.3 Network heterogeneity

An elastomeric non-crosslinked network can be pictured as an ensemble of long-chain molecules. Entanglements develop from the interpenetration of random-coil chains and are important in determining rheological, dynamic and fracture properties\(^\text{15}\). By the introduction of a certain number of crosslinks or junctions between the chains at a very few points along their length it is possible to produce a network in which all the molecules are linked together and hence can no longer move independently. The structure of the network depends on the kind and extent of the chemical crosslinking reaction.

Mechanical properties of crosslinked elastomers are influenced not only by the volume average crosslink density but also by network heterogeneity. The influence of structural defects (such as residual sol, dangling chains, chain loops and the heterogeneity of the junction distribution) on the visco-elastic properties and the equilibrium swelling data is still under discussion. Local methods which probe molecular properties are very suitable for the determination of the degree of network heterogeneity.\(^\text{16}\)
Several types of heterogeneity may occur in rubbery materials:

1) molecular-scale heterogeneity, which is caused by the chemical heterogeneity of uncured elastomers, network defects and heterogeneous distribution of network junctions on a molecular level (see Fig. 1.3.1);

2) morphological heterogeneity of rubber compounds and other components due to spatially heterogeneous distribution in the rubber of coagents and fillers;

3) spatial heterogeneity due to differences in curing conditions such as temperature and concentration of crosslinking agents throughout the sample volume.\textsuperscript{17}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{schematic_diagram.png}
\caption{Schematic drawing of an ensemble of linear polymer chains being crosslinked into an infinite network}
\end{figure}

Besides chemical crosslinks the following types of physical network junctions may occur in elastomeric materials: (1) temporary and trapped chain entanglements, (2) junctions that are formed due to chain adsorption at the surface of active fillers, (3) junctions that are formed by crystallites, (4) junctions deriving from strong hydrogen and ionic bonds, and (5) junctions that are formed at the interface in polymer blends and in materials that reveal nano-scale phase separation.\textsuperscript{17} Knowledge about all types of junctions in the rubbery materials is important because the mechanical properties are influenced not only by the chemical crosslink density but also by the physical network junctions and network heterogeneity.

In the case of peroxide-cured EPDM, the network has a complex structure with various types of chemical crosslinks, as well as both temporary and trapped entanglements. Usually, additional components such as residual sol, dangling chains, chain loops and differences in the distribution of the crosslinks may be present. Different types of network junctions are shown in Fig. 1.3.2. The first picture in Fig. 1.3.2 shows an example of a perfect network, without entanglements and defects. The second and third pictures consist of the physical entanglements (temporary or
trapped) between chains, by restricting the number of available configurations. The effect is comparable to that of a chemical crosslink and will tend to increase the modulus.

![Types of junctions compared to an ideal network](image)

The fourth type of junctions occurs as a result of the linkage of two points on a single chain, giving rise to a closed loop which makes no contribution to the network elasticity. The fifth type consists of chains which are connected to the network at one end only; such terminal chains or loose ends make no contribution to the network elasticity.

In the case of filled rubbers or in the presence of coagents, the network structure is additionally complicated by physical and chemical interactions of the chains. The use of co-agents together with the peroxides can result in improved crosslink density. By use of the appropriate co-agent with the peroxide, properties such as dynamic flexibility, tear resistance and tensile strength can be improved to a level comparable or superior to the sulfur-cured systems, but with much better heat stability. There are various possible mechanisms for coagents to react. Since all common coagents contain terminal unsaturations, addition and polymerization may be expected as the principal mechanism by which coagents react in a rubber compound. It is well known that coagents can homopolymerize in domains, leading to the co-vulcanization of these domains with the polymer.\(^{18,19}\)

These are the variables in the network structure that can be utilized to modify the properties of cured materials. However, they also cause difficulties in the analysis of network structures and complicate efforts to determine structure-property relationships.
1.4 Characterization of rubbery networks

The extensive and still increasing usage of polymeric materials stems from their unique physical and mechanical properties. Combined with economic advantages in terms of price and market availability polymeric materials became a logical choice for a wide range of applications. The characterization of crosslinked elastomers is of great scientific and technological interest. It enables the understanding of the network formation in terms of rubber molecular structure, cure recipe and conditions, and it allows the correlation of macroscopic properties with network structure to be established. The crosslink density is one of the main characteristics of a crosslinked rubber with network heterogeneity as a second feature.

To be able to relate mechanical properties to the composition of rubbery compounds and curing chemistry it is essential to understand the network topology of the resultant cured materials. The methods that are used to analyze network structures can be generally subdivided into three categories on the basis of their methodology:

a) characterization of physical properties
b) analysis of chemical conversion and cure chemistry
c) analysis of molecular mobility of polymer chains

The most common methods for determining the volume-average network density are equilibrium swelling and mechanical measurements. Besides information on the network structure, the mechanical methods provide information that is useful for practical applications, such as information on the modulus of elasticity, ultimate tensile properties and glass transition temperature ($T_g$). Rubber elasticity theory and phenomenological theories are used to relate a measured quantity to the density of chemical and physical crosslinks. Several molecular models have been developed for “ideal” defect-free networks. The validity and applicability of these models is however a heavily debated topic and several discrepancies between theory and experiments still remain, e.g., on the role of chain entanglements, network defects and network heterogeneity. It is generally acknowledged that traditional methods are not capable of providing fully reliable information on network topology.

For the analysis of chemical conversion and chemistry of crosslinking, several techniques are used: optical spectroscopy, high-resolution NMR, titration of non-reacted functional groups. The spectroscopic methods can be used for quantitative analysis of crosslinks. Chemical conversion is usually closely related to the network density. However, no exact quantitative
information on the network structure can be obtained because reacted groups can form not only chemical crosslinks but also visco-elastically ineffective chains, such as chain branches and chain loops. Furthermore, side-reactions, which may readily lead to the formation of additional crosslinks, complicate data interpretation due to the overlapping of signals from different types of chemical groups in complex mixtures. Moreover, physical network junctions are virtually not detected by spectroscopic methods.

Dynamic mechanical analysis (DMA) and dielectric spectroscopy provide information on the mobility of polymer chains, which is influenced by the network density. One of the most informative and sensitive methods of network analysis is solid-state NMR relaxometry. Furthermore, NMR imaging or optical microscopy is used to determine the spatial heterogeneity of rubbery materials on a scale of above 15-50 micrometers. Different types of NMR magnetization relaxation experiments are used to analyze local and long-range spatial mobility of polymer chains. Since chain motion is closely coupled to the length of network chains, chemical information on network structure and network defects can be obtained in this way. The mobility of polymer chain units of different chemical origins can be determined by means of selective NMR magnetization relaxation experiments using high-resolution solid-state NMR techniques. These techniques can be also used for the analysis of the network structure in rubbery blends. Relationships between NMR relaxation parameters, dielectric and mechanical properties have been established.

1.5 Outline of the thesis

The primary aim of this work is to study, mainly by NMR, the various aspects of peroxide cure of EPDM, namely crosslinking chemistry, the effect of the EPDM composition and the amount of peroxide on the total crosslink density, and the contribution of different types of chemical crosslinks and chain entanglements to the total network density, as well as network heterogeneity in the presence of coagents and carbon black.

Different methods are used for this purpose, i.e. $^1$H NMR $T_2$ relaxometry, $^{13}$C MAS (Magic Angle Spinning) NMR spectroscopy, 1D INADEQUATE (Incredible Natural Abundance Double QUantum Transition Experiment), $^1$H NMR spectroscopy, FT-IR spectroscopy and DQ (Double-Quantum) build-up and DQ filtered $T_2$ relaxation experiments. Applied to an array of
EPDM grades, this yields a consistent picture in terms of crosslinking chemistry and network density.

Chapter 1 provides the introduction in the field of elastomers. First, the chemical structures, the crosslinking process and the characterization of networks using different techniques, are discussed.

Chapter 2 describes the NMR techniques that have been used for the investigation of EPDM rubber as such and in the presence of coagents and carbon black. Several methods like transverse $^1\text{H}$ NMR relaxation, $^1\text{H}$ and $^{13}\text{C}$ NMR spectroscopy and multiple quantum experiments have been used to probe different aspects of the network structure and dynamics of the polymer chains at the molecular level.

In Chapter 3 the effect of the amount of peroxide, and the type and content of diene on the network density are studied. $^1\text{H} T_2$ relaxation experiments prove to be a useful method for quantitative characterization of polymer networks with respect to their crosslink density, as well as for assessing the contribution of trapped and temporary entanglements. Network heterogeneity is also studied by means of DQ filtered $T_2$ and $T_2$ relaxation experiments for swollen vulcanisates. A good correlation with mechanical properties is established.

Chapter 4 provides information about the reaction mechanism of peroxide cure based on the results obtained for EPDM with $^{13}\text{C}$ labeled ENB (5-ethylidene-2-norbornene) studied using $^{13}\text{C}$ NMR spectroscopy and 1D INADEQUATE. New structures with intact unsaturations as well as oxidation signals have been found and a more complex crosslinking mechanism is proposed.

In Chapter 5 the effect of different types of coagents on network density and network heterogeneity is investigated. The crosslink density and network heterogeneity are compared for different types of coagents and for different compositions for the peroxide-cured EPDM.

Chapter 6 deals with the effect of carbon black on EPDM sulfur vulcanisates. Results from $^1\text{H}$ NMR relaxation are presented and correlated with a dynamic flocculation model. The effects of chemical crosslinks, chain entanglement, carbon black-rubber interactions and other factors causing rubber reinforcement are discussed.

Chapter 7, as the last one of this thesis, summarizes the main results obtained in this project by use of both high- and low-field solid state NMR.
1.6 References

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Chapter 2

NMR methodology

2.1 Anisotropy of chain motion as probed by NMR

Polymer chain dynamics

The physics of rubber elasticity is characterized by a large variety of approaches, models and concepts, which have been extensively reviewed.\textsuperscript{1,2,3,4,5,6,7} Based on the Gaussian chain model, different routes to the description of the real stress-strain behavior of amorphous polymer networks have been explored. The basic theories and models of dynamics of linear polymer chains have been tested using the potential of NMR techniques for probing the characteristics of molecular motions in such systems.\textsuperscript{8}

With regard to the molecular weight $M_w$, there are two important cases of chain dynamics for polymer solution and melts.\textsuperscript{9}

First, in non-entangled chains, $M_w < M_c$, where $M_c$ is the critical molecular weight when entanglements start. Topological interactions between chains are unimportant because the chains do not sufficiently overlap. In order to see the effect of entanglements, chains must typically be hundred monomer units long. The non-entangled dynamics regime is divided into two sub-cases depending on whether or not non-chemical van der Waals interactions are important for the drag on the chains. The case where there is only local dissipation due to frictional forces as the chains slide past one another has been considered by Rouse.\textsuperscript{10} He constructed a model for non-crosslinked polymers which finds its realization in low molecular weight melts. In solutions, the more complicated situation with hydrodynamic interactions is dominating and the relevant model has been devised by Zimm\textsuperscript{11}.

Second, for entangled chains, $M_w > M_c$, chain movements are restricted by topological constraints from the surrounding chains. The mathematical formulation of the local drag needs to
be modified by a model introducing the topological restrictions on chain dynamics. The effect of the topological restriction has been incorporated in the tube model introduced and developed by Doi and Edwards\textsuperscript{12} together with the reptation motion (a snake like Brownian motion) suggested by de Gennes.\textsuperscript{13}

![Figure 2.1.1 Illustration of a polymer chain confined in the tube of diameter $d$. The contour line of the tube is called the primitive path having a random-walk conformation with a step length $a = d$. The four characteristic types of dynamic processes (dotted arrow lines) and their time constants, $\tau_s =$ segment fluctuation time, $\tau_e =$ entanglement time, $\tau_R =$ Rouse relaxation time and $\tau_d =$ (tube) disengagement time, defined in the frame of the Doi/Edwards tube/reptation model are indicated.\textsuperscript{12}](image)

The tube model with the reptation motion considers the dynamics of the polymer chain in the presence of fixed obstacles. In contrast, Schweizer\textsuperscript{14} proposed the renormalized Rouse formalism without fixed obstacles, in which the entanglement effects were taken into a so-called memory function. In fact, this regime also divides into two classes depending on the chain topology, i.e. whether chains are linear or branched.

Thus, the Rouse model is used to describe the dynamics of polymer chains if $M_w < M_c$. For the case of $M_w > M_c$, the renormalized Rouse formalism and the tube model are combined. The difference between these two is that the renormalized Rouse formalism considers other chains surrounding the ‘entangled’ chain to be movable and also entangled in contrast to the tube model. In terms of polymer dynamics, the shortest chain fragment used to describe the motion is the so-called Kuhn segment (see Fig. 2.1.2). The Kuhn length is based on the theory of a polymer chain divided into $N$ Kuhn segments with the length $b$, so that all Kuhn segments can be thought of as if they are freely jointed with each other. The contour length satisfies $L = Nb$. The time $\tau_s$ is described as the reorientation time of the Kuhn segment.
The polymer dynamics, which can be probed with NMR relaxometry, can be divided into three components with different time scales, viz. components A, B and C, as shown in Fig. 2.1.3. Component A is the first and fastest component of the segmental motion and represents conformational transitions occurring within Kuhn segments, that is on a time-scale up to $t \approx \tau_s$. These motions can be supplemented or superimposed by side-group rotation.

Component B refers to the hydrodynamic chain-mode regime which is of particular interest in context with chain dynamics models. The time scale for this component is between $\tau_s$ and the terminal chain relaxation time $\tau_t$. It is caused by the reptational displacements along the tube whereby the segments are reoriented according to the tube conformation.

Component C corresponds to the terminal chain relaxation $\tau_t$ after which all memory of the initial conformation has been lost. From the NMR relaxometry point of view, elastomers and other viscoelastic polymers above their glass-transition temperature exhibit both solid and liquid-like features. Whereas the segmental motions lead to liquid-like behavior, the presence of permanent crosslinks and chain entanglements leads to residual dipolar or quadrupolar couplings that are responsible for the solid-like NMR properties. The important topics of anisotropy of chain dynamics and segmental order in polymer networks were already studied by Cohen-Addad, Spiess, Callaghan and Kimmich. For example, based on dynamical aspects of the molecular motions and their anisotropy, as determined by the transverse and longitudinal relaxation times, crosslink density and its heterogeneity, curing efficiency, the effect of filler particles and their distribution, crosslinking kinetics and aging of elastomers can be investigated.
Figure 2.1.3 Schematic representation of the temperature/frequency “window” accessible by the relaxometry in combination with high field spectrometers. 25

Dipole coupling and the averaging effect of chain motion

1H NMR spectroscopy and relaxometry are powerful tools to obtain information on the chain dynamics in polymers. The observed NMR lineshape or relaxation reflects the motion-induced fluctuations of the magnetic dipole couplings between the hydrogen nuclei. The dipole coupling represents the close-distance (< 5 Å) effect, which pairs of hydrogen nuclei have on each other’s local magnetic field. The local-field change can be positive or negative depending on the relative spin configuration (parallel/anti-parallel) and angle $\theta$ between the internuclear vector and $B_0$ (Fig. 2.1.4). For two parallel 1H spins at an interdistance $d_{HH}$, the NMR frequency change caused by the dipole interaction is:

$$\Delta v_D(\theta) = D_0 \ P_2(\cos \theta)$$

with the second-order Legendre polynomial

$$P_2(\cos \theta) = \frac{3\cos^2 \theta - 1}{2}$$

and dipole coupling constant in kHz,

$$D_0 = \frac{121}{d_{HH}^3}$$
inversely proportional to the cube distance $d_{HH}$ in Å between the hydrogen nuclei. A typical $D$ value for $^1\text{H}-^1\text{H}$ coupling within the CH$_2$ moieties in EPDM is 24 kHz. For rigid non-oriented polymers the orientation dependence of the dipolar $^1\text{H}-^1\text{H}$ coupling leads to broad $^1\text{H}$ NMR lineshapes. In multi-spin systems, such as hydrogen nuclei in polymers, this lineshape tends to be Gaussian. Rotational chain motions in a mobile polymer, however, make the $^1\text{H}-^1\text{H}$ vector orientations $\theta$ time dependent. Motions which are fast compared to the static dipole coupling constant $D_0$ ($10^4$ Hz), lead to partial averaging of $P(\cos \theta)$ and thus to a reduction of the dipole coupling. Since in a real mobile polymer the cumulative rotational effect of chain motions is not isotropic, a residual dipole coupling with reduced coupling constant $D$ remains. This is reflected in the NMR spectrum by a narrower lineshape. The less restricted the chain motion, the narrower the lineshape. An order parameter $S = D/D_0$ can be defined which reflects the cumulative anisotropy of chain motions at the sub-ms timescale.

**Figure 2.1.4** (left) Magnetic dipole field for two hydrogen nuclei also indicating the angle $\theta$ between the H-H vector and the magnetic field $B_0$; (right) schematic illustration of a broad and a narrow $^1\text{H}$ NMR resonance for a polymer with highly restricted and less restricted chain motions, respectively

**$^1\text{H}$ NMR $T_2$ relaxation**

Although in principle the linewidth $\Delta \nu$ in a $^1\text{H}$ NMR spectrum can be used as a source of information about chain mobility, it tends to be polluted by other linebroadening mechanisms, like chemical-shift heterogeneity and magnetic susceptibility. For mobile polymers with narrow $^1\text{H}$ NMR lines, such as weakly crosslinked elastomers above $T_g$, this inhomogeneous broadening can significantly spoil the interpretation. Therefore as an improved approach, $T_2$ relaxation (also called transversal or spin-spin relaxation), which is the time-domain equivalent of the homogeneous linewidth, is often investigated for characterization of polymer networks. By reflecting the overall anisotropy of sub-millisecond polymer motions, the $T_2$ relaxation time for
elastomer networks is sensitive to the conformational mean position of the network chains, which is affected by the presence of chemical and physical network junctions. Long network chains undergo less restricted motions, resulting in strongly averaged dipole couplings and thus long $T_2$ values. Short network chains have short $T_2$ relaxation times.

The theory of the transverse relaxation is based on a model of a network chain with both ends fixed in a laboratory system of coordinates regardless of the origin of the junctions.\textsuperscript{26} By assumption, the network chain consists of a number of statistical segments between the network junctions. The Kuhn and Grün model of freely jointed chains is used to calculate the conformational mean of the chain function in elastomers with low crosslink density (network chains obeying the Gaussian chain statistics).\textsuperscript{26, 27}

The weight average molar mass of network chains in crosslinked elastomers can be calculated from the transverse relaxation value at the high temperature plateau, $T_2^p$. The temperature independence of $T_2$ at temperatures well above $T_g$ (see Fig. 2.1.5) is attributed to constraints which limit the number of possible conformations of a network chain with respect to those of a free chain. In other words, due to high segmental mobility, the network chains take a mean conformational position, which depends on the number of statistical segments between network junctions. The correlation time for the local and semi-local (Rouse) chain motion is much shorter than $T_2^p$. Therefore, the $T_2^p$ value does not depend on the mechanism and the frequency of the chain motion and is determined by the residual strength of the nuclear dipole-dipole interactions.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.1.5.png}
\caption{Temperature dependence of the transverse relaxation}
\end{figure}
Double-Quantum $^1$H NMR

$^1$H NMR $T_2$ relaxation of polymer reflects the overall anisotropy of chain motions that are fast on the sub-millisecond timescale.\textsuperscript{28} It is also particularly sensitive to intermediate motions at the millisecond timescale. If intermediate motions are significantly present in the broad range of timescales governing polymer dynamics, the validity of standard theories relating network density via the anisotropy of sub-millisecond motions to $T_2$ relaxation can be questioned. As further improvement, Double-Quantum (DQ) NMR has therefore recently been advocated.\textsuperscript{28} The same residual dipolar couplings that underlie $T_2$ relaxation can also be used to generate double-quantum coherences in hydrogen spin pairs. The idea is that by a strategic combination of NMR signals (\textit{vide infra}), the DQ NMR technique is able to distinguish between a coherent build-up of double-quantum coherence, and incoherent loss of transversal magnetization. The DQ build-up rate measured in this way only reflects the residual dipole couplings averaged by the fast chain motions. The effect of intermediate motions ends up in the incoherent part and is not included in analysis in terms of network density. The advantage is that the technique zooms in on the anisotropy of fast motions, which is easier to analyze in terms of network density by use of the existing theories for rubber networks. A disadvantage is that the part of the NMR signal associated with intermediate motions is discarded together with the incoherent component, and that analysis therefore may not always give the complete, truly quantitative picture.

2.2 NMR methods for investigating network structure

In this study, various solid-state NMR experiments were used to characterize the EPDM rubber networks. $^1$H NMR transverse relaxometry based on the Hahn Echo experiment was used to determine the crosslink density in the crosslinked rubber.\textsuperscript{29} The experiments provide information about the total network density composed of chemical crosslinks, temporary and trapped chain entanglements. For determining the contribution of the temporary entanglements to the total network density, $T_2$ experiments are performed on swollen rubber samples at different solvent concentrations.

It is not always straightforward to assign different components of the $T_2$ relaxation decays to short and long network chains and network defects such as dangling chains and chain loops. The Double-Quantum technique is a recently developed versatile method which provides not only reliable information on local chain order, but also on the distribution of residual dipolar
couplings, and thus on semi-local dynamic heterogeneity in rubber compounds. Therefore, a new double-quantum NMR method has been developed. This technique allows separating the contribution to the $T_2$ relaxation decay from network fragments with different anisotropy of chain motions (large spatial scale chain dynamics). To get more insight in the heterogeneous nature of the networks, the overall Hahn-Echo decays have been separated into the underlying Hahn-decay components by use of a Double-Quantum filtered Hahn-Echo Pulse Sequence (DQHEPS).

To investigate the crosslinking reaction mechanism and chemical structures of crosslinks formed via addition and combination reactions (see Chapter 1), we have used solid-state $^1$H and $^{13}$C NMR spectroscopy with or without magic angle spinning (MAS). INADEQUATE spectra were employed to identify the chemical structure of the crosslinks in peroxide-cured EPDM. By monitoring the intensity of the olefinic $^{13}$C resonances of the ENB third monomer, we have followed the ENB conversion as a function of the curing time, and established correlations with the crosslink density as determined by the $T_2$ relaxation analysis. The $^{13}$C enrichment of the ENB EPDM at the C2 and C8 positions dramatically increases the NMR sensitivity and enables the identification of the structure of the crosslinks involving the third monomer.

The co-agents together with the peroxide usually result in increased crosslink density as compared with peroxide alone. The effect of coagents on the heterogeneity of the crosslinked EPDM network has been investigated by the use of $T_2$ experiments, combined with $^{13}$C NMR spectroscopy.

The incorporation of carbon black into a rubber is of significant importance, since carbon black not only enhances the mechanical properties of the final rubber products, but also decreases the total costs. The NMR relaxometry is used for studying the elastomer-filler interactions. The outcomes of these experiments are compared with the results obtained with the dynamic flocculation model of stress softening and filler induced hysteresis of elastomer materials developed recently by Klüppel. It combines well established concepts of rubber elasticity with filler effects using a micro-mechanical approach of dynamic filler flocculation in the cyclically strained rubber matrix.

The methods above have been addressed to the following topics: (i) volume average network density, (ii) network heterogeneity and defects, (iii) effect of coagents and (iv) effect of carbon
NMR Methodology

2.2.1 $^1$H NMR Hahn-echo experiments

NMR relaxation experiments provide information about the molecular dynamics of polymers, both in solution and in solid state, since the NMR relaxation times can be related to the molecular correlation times and anisotropy of molecular motions.

For elastomer networks above $T_g$ the crosslink density is related to the residual dipolar couplings. The presence of physical and chemical crosslinks leads to a non-zero average of the homonuclear and heteronuclear dipolar couplings, which results in the NMR relaxation behavior.

The main point is that any anisotropic spin interaction fixed to a chain segment has a non-zero motional average value as a result of the constraints imposed by interactions between chains in the bulk and by crosslink junctions. One has to distinguish between interactions between two nuclei located on the same segment and interactions between nuclei located on different segments. The former are largely averaged by chain motions; the latter are additionally averaged by translational chain diffusion, which further reduces the dipolar couplings. As a result, the short range couplings resulting from inter-chain interactions are much smaller than intra-chain ones. Crosslinks limit the translational diffusion and rotational motions of the chains, which result in residual dipole-dipole interactions affecting the $T_2$ relaxation rate. In the case of crosslinked chains, $T_2$ is significantly shorter than in the case of the corresponding non-crosslinked chains.

At temperatures above $T_g$ the chain motion is not isotropic. Additional restrictions of chain motions in elastomers are caused by chain entanglements, interaction/immobilization of chains by carbon black and other fillers. Chain entanglements also affect $T_2$ relaxation in polymer melts and concentrated solutions of high molar mass polymers.

The residual dipolar couplings originating from chemical crosslinks and entanglements are treated by statistical chain models and are reflected in different ways in various NMR parameters. Depending on the degree of motional restrictions, the residual dipolar interactions of rubbery networks are significantly lower compared to those in rigid solids, i.e. below a few percent. Transverse $^1$H NMR relaxometry based on Hahn echoes is a convenient and robust method to characterize the crosslink density of polymer networks. This pulse sequence
eliminates the magnetic field and chemical shift inhomogeneities and allows quantitative measurements.

All decays of the transverse magnetization were analyzed using a fitting program written at DSM which employs the Levenberg-Marquardt algorithm. The decays can be usually decomposed into two or three discrete relaxation components with different decay times characterized by $T_2$ values. Weibull and bi-exponential functions were used to describe the shape of the individual components. The most relevant fit of the overall decay for the rubber is obtained with:

\[ A(t) = A_0 \exp(-t / T_{2,A})^\beta + B_0 \exp(-t / T_{2,B}) + C_0 \exp(-t / T_{2,C}) \]  

(2.1)

where $\beta = 1.357$. In most cases, the $T_2$ values given are the weight averages of the values ($T_{2}^{av}$) that were calculated using the fitting program.

\[ (T_{2}^{av})^{-1} = \sum (f_i / T_i), \text{ where } f_i = \frac{A_i}{A_0 + B_0 + C_0} \]  

(2.2)

The shape of the $T_2$ decay for unimodal networks largely deviates from the exponential behavior due to the complex origin of chain dynamics\(^{16}\) and defects.\(^{38}\) Therefore, no reliable assignment to different fragments of heterogeneous networks can be made for samples as a whole. In a simplified picture, the total $T_2$ relaxation decay for a heterogeneous elastomer network is a weighted sum of decays from the different sub-molecules, which are defined as network chains between the chemical and physical junctions, the chain loops and the loose chain-ends.

The high-temperature limit value $T_2^{pl}$ is a measure for the crosslink density. The $T_2^{pl}$ value is related to the number of statistical segments between chemical and physical network junctions.\(^{26,39}\) The weight average molar mass $M_w$ of the chains between the network junctions with fixed positions at the $10^{-3}$ s time scale follows from $T_2^{pl}$ according to:

\[ M_w = \frac{T_2^{pl}}{a T_2^{rl}} C_\infty \frac{M_u}{n} \]  

(2.3)

where $M_u$ and $n$ are the average mass and number of backbone bonds per elementary chain unit respectively. $C_\infty$ and $a$ are model parameters. The first represents the number of rotating
backbone bonds in the statistical segment of an infinite polymer chain, and equals 6.62 at 363 K for an alternating EPM.\textsuperscript{40} The latter relates the proton-proton distances in the chain unit and the mechanism of local segment motion to the resulting NMR relaxation. More precisely, it depends on the angle between the polymer segment axis and the inter-nuclear vector for the nearest $^1\text{H}$ spins at the main chain. For polymers containing aliphatic $^1\text{H}$ atoms in the main chain, the coefficient $a \sim 6.2 \pm 0.7$.\textsuperscript{26,27} The rigid-limit value $T_2^{rl}$ at temperatures far below $T_g$ is related to the strength of the intra-chain $^1\text{H}-^1\text{H}$ interactions in the rigid lattice. For EPDM swollen in tetrachloroethane, the $T_2^{rl}$ value equals $10.4 \pm 0.2$ µs at 140 K.\textsuperscript{29} The total network density $D_{tot}$ is inversely proportional to $M_w$,

$$D_{tot} = \frac{2}{f \cdot M_w}$$

where $f$ is the functionality of the network junctions, e.g., equal to 4 for pair-wise-connected polymer chains ($X$ shaped crosslink).

### 2.2.2 Double Quantum build-up NMR

Double-Quantum NMR discriminates between coherent and incoherent processes arising from the dipole coupling between the hydrogen spins in the polymer, and provides information on the distribution of residual dipole couplings in rubbery networks.\textsuperscript{41,42} One of the aims of the project described in this thesis was to implement this novel technique in the solid-state NMR lab in Eindhoven. We therefore describe the technique in a more detailed manner than the other NMR techniques used in this research. The DQ NMR is based on the multi-pulse sequence depicted in Fig. 2.2.2.1. In the first half of the experiment the longitudinal equilibrium polarization of the hydrogen spins is converted into various multi-quantum coherences, which are reconverted to longitudinal magnetization in the second half and observed after the final $90^\circ$ pulse. By a proper pulse-phase scheme one can selectively observe the build-up of double-quantum coherence (along with other $4n+2$ quantum coherences), and a reference decay dominated by the longitudinal polarization (along with other $4n$ quantum coherences) as a function of time. The excitation and reconversion stages in the full DQ experiment depicted in Fig. 2.2.2.1 are usually chosen to be of equal duration $\tau_{DQ} = n_c t_c$, whereby $n_c$ denotes the number of repeated
cycles in the multi-pulse sequence and $t_c$ the duration of every cycle. The pulse sequence may either be applied using a fixed $t_c$ and incrementing the number of cycles $n_c$ or by choosing a fixed $n_c$ and incrementing $t_c$. Both variants differ drastically in the overall duty cycles. In our experiments with varying $n_c$ we have used a $t_c$ value of 200 µs (minimum of ca. 60 µs on Minispec), while in the experiments with varying $t_c$ we have used two cycles for excitation and reconversion, each.

![Scheme of a typical MQ experiment](image)

As indicated above, by use of a proper pulse-phase cycling the DQ NMR experiment yields two data sets as a function of the excitation and reconversion time $\tau_{DQ}$: an overall decay $S_{\text{ref}}$ reflecting the $4n$ quantum coherences dominated by the longitudinal magnetization decay, and an overall build-up $S_{DQ}$ of $4n+2$-quantum coherences dominated by DQ coherence. In the spin-pair limit, i.e. if multi-spin interactions can be neglected, the time dependence of $S_{\text{ref}}$ and $S_{DQ}$ is basically a multi-periodic exchange between the longitudinal magnetization and DQ coherence:

\[
S_{\text{ref}}(\tau_{ea}) = \left\langle \cos^2(\omega(D, \beta) \tau_{DQ}) \right\rangle_D, \tag{2.5}
\]

\[
S_{DQ}(\tau_{ea}) = \left\langle \sin^2(\omega(D, \beta) \tau_{DQ}) \right\rangle_D, \tag{2.6}
\]

with the dipolar frequency

\[
\omega(D, \beta) = 2\pi D P_2(\cos \beta) \tag{2.7}
\]
depending on the residual dipole coupling constant $D$ as averaged by chain motions and the angle $\beta$ between the major axis of the residual dipole tensor and the magnetic field. The ensemble average is taken over the orientation distribution supposed to be isotropic, $P_{\text{or}}(\beta) = \sin \beta$, and the distribution $P_{\text{dip}}(D)$ of residual dipole constants $D$, which reflects the different motional restrictions in a rubber network with varying chain lengths. Fig. 2.2.2.2 shows the orientation averages of $S_{\text{ref}}$ and $S_{\text{DQ}}$ for a non-oriented polymer with a single $D$ value.

As follows from Eq. 2.5 and the behavior illustrated in Fig. 2.2.2.2, (1) the sum $S_\Sigma$ of $S_{\text{ref}}$ and $S_{\text{DQ}}$ should be conserved, and (2) $S_{\text{ref}}$ and $S_{\text{DQ}}$ become approximately equal at sufficiently long time, irrespective of the shape of $P_{\text{dip}}(D)$. In reality, however, also incoherent $T_2$ relaxation associated with intermediate motions at the millisecond timescale takes place. This will lead to an overall decay of $S_\Sigma$, according to the “true” $T_2$ relaxation without the coherent dipolar dephasing which supposedly dominates the $^1$H NMR Hahn-echo decay for crosslinked rubbers.

In addition, $S_{\text{ref}}$ contains contributions from hydrogen atoms with small residual coupling $D$ compared to $T_2$ relaxation ($DT_2 < 1$), which do not effectively contribute to $S_{\text{DQ}}$. As a result, $S_{\text{ref}}$ tends to be larger than $S_{\text{DQ}}$ also in the long-time limit. If, on the overall DQ build-up timescale, $T_2$ differences between the “coherent” components ($DT_2 > 1$) can be neglected, and the contribution of incoherent components to $S_{\text{ref}}$ can be phenomenologically described by a bi-exponential decay, we can modify Eq. 2.5 to:

$$S_{\text{ref}}(\tau_{ex}) = e^{-\tau_{ex}/T_2} < \cos^2(\omega(D, \beta) \tau_{\text{DQ}}) > + a e^{-\tau_{ex}/T_{2a}} + b e^{-\tau_{ex}/T_{2b}}$$

(2.8)

$$S_{\text{DQ}}(\tau_{ex}) = e^{-\tau_{ex}/T_2} < \sin^2(\omega(D, \beta) \tau_{\text{DQ}}) >$$

(2.9)

where the ensemble average is taken over the coherent components ($DT_2 > 1$) only. The parameters $a$, $T_{2a}$, $b$, and $T_{2b}$ are obtained from a bi-exponential fit to the tail of the difference $S_\Delta = S_{\text{ref}} - S_{\text{DQ}}$, because the contribution of the coherent components to $S_\Delta$ vanishes at long $\tau_{\text{DQ}}$. ($D \tau_{\text{DQ}} > 1$ in Fig. 2.2.2.2) Strictly mathematically, in a multi-spin system like a polymer, the two-spin approach underlying Eqs. 2.5 and 2.7 is only valid in the initial parabolic part of the DQ...
build-up and reference decay. However, more elaborate spin-counting experiments in which the various multi-quantum coherences are resolved, indicate that in practice the higher-quantum coherences build up slowly compared to the dominant double-quantum build-up. As a result, Eq. 2.7 offers a good approximation for analyzing double-quantum build-up curves in multi-spin systems, even beyond the initial regime.

Eq. 2.7 allows removing incoherent components and normalized double-quantum build-up curves from experimentally measured $S_{\text{ref}}$ and $S_{\text{DQ}}$ data for real polymers:

$$S_{\text{DQ}}^{N}(\tau_{s}) = \frac{S_{\text{DQ}}(\tau_{s})}{S_{\text{ref}}(\tau_{s}) + S_{\text{DQ}}(\tau_{s}) - a \exp(-\tau_{s} / T_{2a}) + b \exp(-\tau_{s} / T_{2b})}$$ (2.10)

As Fig. 2.2.2.3 illustrates, the normalized DQ build-up curve for an isotropic orientation distribution and a single residual dipole coupling constant $D$ has an approximately Gaussian shape of the form:

$$S_{\text{DQ}}(\tau_{s}) \approx \frac{1}{2} \left[ 1 - \exp \left\{ -\frac{2}{5} D_{\text{DQ}}^{2} \tau_{s}^{2} \right\} \right]$$ (2.11)

(the factor 2/5 derived from the properties of $P_{2}(\cos \theta)$ up to ~50% of the plateau value.)
A distribution $P_{dp}(D)$ for a rubber network with varying network chain lengths should therefore result in an approximately multi-Gaussian shape. In fact, this is the basis on which $P_{dp}(D)$ is extracted from the initial DQ build up. In practice, an additional assumption about the qualitative shape of $P_{dp}(D)$ (e.g. Gaussian) is helpful to interpret the DQ build up curve.\(^{44}\)

2.2.3 \(^1\)H Double-Quantum filtered $T_2$ NMR experiments (DQHE)

To get insight into the heterogeneous nature of the Hahn-echo decays, we have made a combination of the above techniques.\(^{45}\) The contribution of short and long network chains and network defects to the Hahn-echo decay could be separated by use of a double-quantum (DQ) filtered Hahn-echo pulse sequence (HE). DQ coherence is generated faster in less mobile than in more mobile polymer chain fragments. Therefore, based on their different response to the DQ filter, local polymer regions with different chain mobility can be selected and their $T_2$ relaxation decay could be measured separately.\(^{30}\)

The pulse sequence is shown in Fig. 2.2.3.1. The subscripts EX, EV, RE and DE stand for excitation, evolution, reconversion and detection periods, respectively. The first three pulses $90^\circ - \tau_{EX}/2 - 180^\circ - \tau_{EX}/2 - 90^\circ$ separated by time delays $\tau_{EX}/2$ convert the longitudinal spin polarization to the DQ coherence. The $180^\circ$ refocusing pulse eliminates the effects of frequency offsets, resulting from chemical-shift heterogeneity and susceptibility effects.
Depending on the relative phase shift $\phi - \psi$, the second three pulses $90^\circ - \psi - \tau_{EX}/2 - 180^\circ - \psi - \tau_{EV}/2 - 90^\circ - \psi$ yield either a further loss of polarization, or reconvert the DQ coherence back to polarization. By means of a proper phase cycle only magnetization components produced by the excitation and the reconversion are selectively accumulated. With the appropriate values for the excitation and reconversion times, polymer regions with varying mobility can be selected. The time interval $\tau_{EV}$ was set to 5 $\mu$s. Between the DQ-filter and the actual Hahn-echo pulses a filter time $\tau_{DE}$ of 5 ms ($z$-filter) is applied to eliminate unwanted coherences arising from pulse imperfections, which could otherwise perturb the acquired NMR signal. Another role of this interval is to cause isotropic mixing of the $z$ magnetization, resulting from the DQ reconversion. By a proper choice of the excitation and reconversion times, i.e. $\tau_{EX} = \tau_{RE}$, the decay of the transverse magnetization of phases and chain fragments with different molecular mobility and consequently with different strengths of the dipole-dipole interactions, can be selected.\textsuperscript{46,47,48,49}

### 2.2.4 MAS $^{13}$C NMR Spectroscopy

Solid-state $^{13}$C NMR has been proven to be a very powerful technique for investigating network structures formed upon crosslinking of rubbers.\textsuperscript{50,51,52,53,54,55,56,57} The $^{13}$C NMR chemical shifts are sensitive to structural changes due to crosslinking and therefore, the different crosslink structures and the main chain modifications may be detected.

For static samples, the chemical shift anisotropy lineshapes contain valuable information about orientational order and dynamics in polymers, but the peaks tend to overlap in all but the simplest polymers. In order to observe a high-resolution spectrum, it is necessary to sacrifice this information and collapse the lineshape into a single sharp line. This can be accomplished by MAS (magic angle spinning) and high power proton decoupling.
The chemical shift is described by a tensor (a mathematical quantity having both orientation and magnitude) and is composed of three principal components $\sigma_{ij}$. The chemical shift depends on the orientation of the chemical shift anisotropy axis relative to the magnetic field. Anything that changes the molecular orientation, including molecular motion or rotating the sample, leads to a change in the chemical shift. For static experiments, the broadening of the NMR line reduces the chemical resolution in the spectrum. By rotating the sample about the magic angle with the magnetic field, this broadening is eliminated. The so-called magic angle equals 54.7 °, as a result of the $(3 \cos^2 \beta - 1)$ term becoming equal to zero. Thus, under the rapid MAS rotation, the chemical shift pattern collapses to the isotropic average, giving the high-resolution spectrum.

### 2.2.5 $^1$H MAS NMR Spectroscopy

In contrast to $^{13}$C NMR spectra, $^1$H NMR spectra of polymers tend to show more overlap as result of the smaller chemical shift range for typical compounds ($\approx 10$ ppm). The solid-state $^1$H NMR spectrum for static rubbery samples is broadened by homonuclear dipole-dipole interactions.

$^1$H atoms are common to almost all polymers and they can be detected with a high sensitivity. High-resolution $^1$H spectra can be acquired using either multiple-pulse NMR or ultrafast MAS to average the dipolar couplings.

### 2.2.6 1D-INADEQUATE NMR

The advantage of the so-called INADEQUATE (Incredible Natural Abundance Double QUAntum Transition Experiment) technique is that it selectively measures signals from coupled spin pairs such as neighboring $^{13}$C - $^{13}$C atoms in the polymer chains.\textsuperscript{58,59} The experiment relies on two ideas. The first is to note that the natural abundance of $^{13}$C is rather low, about 1%. This means that the probability of there being two $^{13}$C atoms in a molecule without $^{13}$C enrichment is $10^{-4}$. The second point is that the one-bond carbon-carbon coupling constant is quite large, and covers a modest range (40-60 Hz); this coupling is also much larger than that for two- or three-bond couplings. It is therefore possible to generate double-quantum coherence between two adjacent $^{13}$C atoms by setting a delay in the pulse sequence below (Fig. 2.2.6.1). The resulting spectrum will contain only responses from adjacent pairs of $^{13}$C.
The discrimination between the $^{13}$C signals is based on the homonuclear $^{13}$C–$^{13}$C $J$ coupling, creating the DQ coherence (only doubly $^{13}$C labeled molecules can have double quantum coherences) and then exploiting their unique phase property. INADEQUATE requires enriched or very concentrated samples and careful pulse calibration. The resulting spectra are simple to interpret since they exhibit a pair of doublets for every coupled $^{13}$C spin pair, the relative probability of a third $^{13}$C in the same molecule as the first two being one in a hundred at natural abundance.

2.3 NMR Equipment

Different solid-state NMR methods, namely $^1$H transverse relaxometry ($T_2$ relaxation), Double-Quantum $^1$H NMR and $^1$H and $^{13}$C MAS NMR spectroscopy were used to study the molecular mobility in the absence and presence of carbon black, the network heterogeneity and the chemical structures in peroxide-cured and sulphur vulcanized EPDM. The experiments were performed at low magnetic field using a Bruker Minispec MQ20 spectrometer operating at a $^1$H resonance frequency of 19.6 MHz, and at high magnetic field using a Bruker DMX-500 MHz spectrometer operating at a $^1$H resonance frequency of 500.45 MHz.

The data were collected at 90 °C, unless specified differently. The measurements were conducted after stabilization at 90 °C during 10 minutes.

The $^1$H transverse magnetization relaxation and the double-quantum buildups of crosslinked EPDM as such and after swelling in C$_2$D$_2$Cl$_4$, were measured on the Bruker Minispec. The decay of the transverse magnetization was measured with the Hahn-Echo (HE) pulse sequence: $90^\circ_x$ -
The echo signal is formed with a maximum at time $t = (2t_{HE} + \frac{t_{90}}{2} + t_{180})$ from the beginning of the first pulse, where $t_{90}$ and $t_{180}$ are the durations of the 90° and 180° pulses, respectively. By varying the pulse spacing in the sequence, the amplitude of the transverse magnetization is measured as a function of the echo time $2t_{HE}$. This spectrometer is equipped with a BVT-3000 variable temperature unit. For measurements in the swollen state a weighted amount of C$_2$D$_2$Cl$_4$ was added to the sample which was then allowed to equilibrate over night. C$_2$D$_2$Cl$_4$ was used because of its high boiling point (146 °C) that enables NMR experiments for swollen samples at 90 °C without solvent evaporation.

The $^{13}$C and $^1$H NMR spectra were recorded on a Bruker DMX-500 spectrometer using a standard triple resonance wide-bore 4-mm MAS probe-head. Samples were packed into a 4 mm rotor. Direct excitation $^{13}$C NMR spectra with $^1$H decoupling were recorded with a delay time of 5 s for the $^{13}$C-ENB labeled EPDM. The experiments were performed at room temperature and at 90 °C. Adamantane was used as a reference. The $^{13}$C 90° pulse length was 5 µs and the MAS speed was 4 or 8 kHz.

The 4-mm probe-head was used with a MAS rate of 12.5 kHz for the $^1$H NMR spectroscopy. The spectra were acquired by means of a single-pulse excitation with a 90° pulse of 5 µs and a recycling delay time of 5 s.

The 1D-INADEQUATE spectra were recorded on the Bruker DMX-500 spectrometer using the same standard triple resonance wide-bore 4 mm MAS probe. The experiments were performed at room temperature and at 90 °C for the non-crosslinked and crosslinked samples. The pulse delay in this type of experiments is set to $1/(4J)$. INADEQUATE spectra were  recorded with a delay time of 5 s for the $^{13}$C-ENB labeled EPDM. The experiments recorded for the noncrosslinked samples containing peroxide were performed at room temperature.

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Chapter 3

Solid-state $^1$H NMR study on chemical crosslinks, chain entanglements and network heterogeneity in peroxide-cured EPDM rubbers*

Abstract

Peroxide crosslinked ethylene-propylene-(diene) rubbers [EP(D)M] have complex network structures with various types of chemical crosslinks, as well as both temporary and trapped chain entanglements. To obtain a detailed picture of the respective contributions of these different types of crosslinks and entanglements to the total network density solid-state $^1$H NMR relaxometry and spectroscopy have been applied to a series of peroxide-cured EPDM, with systematic variation of the peroxide and diene contents. The effective Hahn-echo decay time $T_2$ reflects the volume average network density, which correlates well to mechanical properties, such as torque and modulus; these all linearly depend on the initial peroxide content for the compositions probed. The slope reflects the peroxide induced chemical crosslinks. The chain-entanglement density that is estimated from the intercept agrees with published neutron-scattering values. The observed differences in crosslink density between EPDM an EPM are consistent with the double-bond conversion estimated from magic-angle spinning $^1$H NMR and Raman spectra. By comparing $T_2$ relaxation times in solid and swollen EPDM we can distinguish between the contributions of temporary and trapped entanglements. The shapes of the Hahn-echo decays suggest strong network heterogeneity, which has been probed also by use of double-quantum filtered $T_2$ relaxometry.

3.1 Introduction

Ethylene-propylene copolymers (EPM) and ethylene-propylene-diene terpolymers (EPDM) are among the most versatile synthetic rubbers. The ethylene and propylene comonomers result in a saturated polymer backbone in which the non-conjugated diene monomers are randomly distributed. The properties of these elastomers can be modified by adjusting the copolymer structure, including the ethylene/propylene ratio and content of diene, the molecular weight (distribution) and the degree of branching. In commercial EPDM terpolymers, the diene is mainly ethylidene norbornene (ENB) or dicyclopentadiene (DCPD) (Fig. 3.1.1). Incorporation of the diene introduces unsaturation in EPDM and enables sulfur vulcanization and enhances peroxide crosslinking.

![Chemical structures of EPDM third monomers: ENB (a) and DCPD (b)](image)

The hydrocarbon character of EPDM in combination with the high molecular weight explains the ability to accommodate large quantities of fillers and oil without creating processing instabilities and unacceptable loss of physical properties. Because of the saturated main chain, EPDM provides excellent resistance to oxygen, ozone, heat and irradiation without the need of large quantities of stabilizers. As a result, EPDM is suitable for outdoor and high-temperature applications. EPDM has found widespread application, ranging from automotive sealing (windows, door and trunk) to building and construction profiles, roof sheeting, pipes, hoses and seals.

Elastomers are usually crosslinked to have the best performance, such as high elasticity, high tensile strength and good resistance to solvents. Traditionally, sulfur vulcanization is applied, which however suffers from S-S bond cleavage at elevated temperatures. Peroxide cure results in more thermally stable networks. The commonly accepted reaction scheme for peroxide cure is shown in Fig. 3.1.2.¹ At elevated temperatures the peroxide decomposes into radicals, which can
react with the polymer chains by abstraction of hydrogen atoms to produce macro-radicals. Combination of these macro-radicals leads to crosslinking between polymer chains.

![Mechanism of peroxide curing of EPDM](image)

**Figure 3.1.2** Mechanism of peroxide curing of EPDM.

Peroxide cure of EPM is relatively inefficient, but the incorporation of diene strongly enhances peroxide cure. In EPDM the radicals can react with the residual double bonds of dienes in two ways: abstraction of allylic hydrogen atoms or addition to the double bonds. This second route is favored when the double bond is terminal, while an internal double bond in converted more via H-abstraction. The radicals produced via the addition reaction undergo hydrogen transfer,
yielding new macro-radicals that can add to another terminal bond to produce another cross-link without radical destruction. In this case, the peroxide cross-linking efficiency is relatively high.\textsuperscript{2} The characterization of crosslinked elastomers is of great scientific and technological interest.\textsuperscript{3-5} It enables the understanding of the network formation in terms of rubber molecular structure, cure recipe and conditions, and it allows the correlation of macroscopic properties with network structure. The crosslink density is one of the main characteristics of a crosslinked rubber with network heterogeneity as a second feature.

Solid-state \textsuperscript{1}H NMR transverse magnetization relaxometry yields detailed insight in the network structure of crosslinked rubbers.\textsuperscript{6-11} For highly mobile polymer chains as in rubbers, the transverse relaxation is slow and the corresponding $T_2$ value is long. At temperatures far above the glass transition temperature $T_g$, the chain motion in crosslinked polymers is restricted by the network junctions, causing a high-temperature plateau in the temperature dependence of $T_2$. At this high-temperature limit, the $T_2$ value mainly depends on the anisotropy of the chain motions, which is controlled by the chain lengths between the network junctions. As a result, information on the network structure and defects can be obtained from \textsuperscript{1}H NMR relaxometry.\textsuperscript{12} The shorter the chain length between crosslinks, the higher is the anisotropy of chain motion, and the lower is the $T_2$ value at the plateau, $T_{2,pl}$.

The aim of this work is to study the various aspects of peroxide cure of EPDM, namely \textit{i)} crosslinking chemistry, \textit{ii)} the effect of the EPDM composition and the amount of peroxide on the total crosslink density, and the contribution of different types of chemical crosslinks and chain entanglements to the total network density, as well as \textit{iii)} network heterogeneity. Different methods are used for this purpose, viz. \textsuperscript{1}H NMR $T_2$ relaxation experiments, \textsuperscript{1}H NMR spectroscopy, FT-Raman spectroscopy and double quantum (DQ) edited $T_2$ relaxation experiments. Applied to an array of EPDM grades, this yields a consistent picture in terms of conversion and network density.
3.2. Experimental

3.2.1 Sample composition and preparation

The chemical composition of the studied EPM and EPDM grades is given in Table 3.2.1.1.

<table>
<thead>
<tr>
<th>Diene type</th>
<th>ENB</th>
<th>ENB</th>
<th>ENB</th>
<th>DCPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diene content (wt. %)</td>
<td>0</td>
<td>1.9</td>
<td>4.5</td>
<td>9.0</td>
</tr>
<tr>
<td>Ethylene content (wt. %)</td>
<td>49</td>
<td>54</td>
<td>52</td>
<td>48</td>
</tr>
</tbody>
</table>

The EPDM/peroxide mixtures have been selected to cover a wide range of both diene termonomer and peroxide content. Amorphous EPDMs (ethylene contents below 55%) with both ENB and DCPD as dienes were used. The samples have been cured with different amounts of di(tert.buty1 perox1 isopropyl)benzene (BPB). BPB was used as a 40% master-batch (Perkadox14-40 MB-GR, from Akzo Nobel). The peroxide levels are given in parts per hundred rubbers (phr), which is common practice in rubber technology. However, for a more scientific interpretation, phr BPB has been converted into mmol peroxide function per kg of EPDM, taking into account the purity (40% BPB on 60% of whiting silica and EPDM), the molecular weight (338.5 g/mol) and the functionality (two peroxide functionalities in one BPB molecule). Each type of EPDM was cured with different amounts of peroxide master-batch: 1.25, 2.5 and 5 phr, and for the EPM also 10 phr was used. The constituents were mixed in an open mill and vulcanized in a hot press at 175°C for 17 minutes. For some NMR experiments samples were swollen in C₂D₂Cl₄ from Merck.

3.2.2 ¹H NMR Hahn-echo experiments

The experimental conditions for ¹H NMR transverse magnetization relaxation and the relation of the latter to crosslink density are described in Chapter 2.2.1.
3.2.3 $^1$H Double-Quantum filtered $T_2$ experiments

The experimental conditions for the DQ filtered $^1$H transverse relaxation are described in Chapter 2.2.3.

3.2.4 $^1$H NMR Spectroscopy

Magic-angle spinning (MAS) $^1$H NMR spectra were recorded on a Bruker DMX500 spectrometer at a resonance frequency of 500 MHz. A 4-mm probe-head was used with a MAS rate of 12.5 kHz. The spectra were acquired by means of a single-pulse excitation with a 90° pulse of 5 $\mu$s and recycle delay time of 5 s. The experiments were performed at 90°C.

3.2.5 Raman Spectroscopy

In order to determine the conversion of the residual unsaturation of the EPDM diene, Raman spectroscopy was performed on 2 mm thick EPDM coupons using a Raman Station, Avalon Instruments (Belfast, Northern Ireland) equipped with a 785 nm laser and a dispersive detector. Spectra were taken with a spectral resolution of 2 cm$^{-1}$ and a typical measurement time of 10 minutes per sample. The ratio of the ENB unsaturation peak height at 1688 cm$^{-1}$ to a reference peak height (at 1438 cm$^{-1}$, caused by the $>\text{CH}_2$ scissoring) is calculated after subtraction of the baseline height in the areas of interest. Subsequently, the conversion is calculated from the change in the peak height ratio.

3.2.6 Mechanical measurements

The compounds were fully cured in an MDR 2000 E rheometer from Dynisco (formerly Alpha Technologies) at 175 °C to measure the increase in torque during curing, according to ISO 6502. The compounds were cured in a hot press at 175 °C at appropriate cure times as well, and characterized by hardness, tensile strength and compression set at 23 °C and 70 °C, measured according to DIN 53505, ISO 37 and ISP 815, respectively. For the modulus at 100% elongation, the tensile strength and the elongation at break, the median value of 5 experiments is presented.
3.3 Results and discussion

3.3.1 Network heterogeneity of peroxide-cured EPDM rubber

$^1$H NMR Hahn-echo decays of crosslinked elastomers can often be empirically described in terms of two or three exponentials. A quantitative analysis of the Hahn-echo decay for crosslinked elastomers is not always straightforward due to the structural heterogeneity of rubbery networks, and the fact that the transverse magnetization loss of the underlying “pure” components is not intrinsically mono-exponential. The structural heterogeneity is related to the different types of network junctions, i.e. chemical network junctions, temporary and trapped chain entanglements and the molar mass distribution of the network chains, and network defects, such as dangling chain-ends and chains loops. A complex network topology is expected for peroxide-cured rubbers, because there are several types of chemical reactions producing crosslinks; also radical-induced chain scission may occur, and there may be concentration gradients of peroxide in the rubbery matrix caused by the low peroxide solubility. $T_2$ relaxometry can provide information on the heterogeneous distribution of network junctions. The sensitivity of the $T_2$ experiments to the molecular scale heterogeneity is related to the local origin of the relaxation process, which is predominantly governed by the near-neighbor environment and intra-chain effects for $T_2$ relaxation at temperatures well above $T_g$. Therefore, the submolecules concept can be used to describe the relaxation behaviour. In a simplified picture, the total $T_2$ relaxation decay for a heterogeneous elastomer is the weighted sum of the decays from the different submolecules, which are defined as the network chains between the chemical and physical junctions, chain loops and chain-ends. These submolecules possess different relaxation behavior due to differences in the large spatial scale mobility. Indeed, non-exponential Hahn-echo decays have been observed for all crosslinked EPDM samples in this study as illustrated in Fig. 3.3.1.1. The underlying heterogeneity is demonstrated in DQ-filtered relaxation experiments (Fig. 3.3.1.2), a method which was recently developed.

By controlling the DQ-filter parameter, i.e. the DQ excitation and reconversion times, the Hahn-echo decays of chain segments with large or small motional anisotropy i.e. with either more restricted or less restricted chain mobility, respectively, can be selectively observed. For the solid (non-swollen) materials the DQ-filtered $T_2$ relaxation decays have been measured at three
excitation times $\tau_{EX}$: 80 $\mu$s, 500 $\mu$s and 1100 $\mu$s and are compared with the non-filtered overall decay (Fig. 3.3.1.1).

The least mobile segments are selected by the 80-$\mu$s filter, whereas the DQ-filter of 1100 $\mu$s selects the highly mobile segments, such as longer network chains and chain defects. As expected, the most restricted segments show faster Hahn-echo decays than the least restricted ones.

For non-crosslinked EPDM (Fig. 3.3.1.2 a,c) the various DQ-filtered decays are relatively close to together, indicating that the sample is rather homogeneous. The additional heterogeneity in chain mobility caused by peroxide crosslinking is evident from the broader range of relaxation time scales for crosslinked EPDM at various DQ-filter times.

Although powerful as a semi-quantitative method to probe the heterogeneity of chain motions, DQ-filtered $T_2$ relaxation measurements do not yield accurate quantitative information. We therefore fall back on the robust Hahn-echo decay method.

In spite of the possible flaws regarding the validity of its underlying polymer model and NMR theory, the Hahn-echo method has proven its validity in practice for a wide range of industrially relevant rubbers. Due to the complex nature of peroxide-crosslinked rubbers it will not be attempted to set up a detailed realistic model to analyze the observed relaxation curves. Instead, the $T_2$ relaxation decay is analyzed in terms of a phenomenological model with two or three
Solid-state NMR study on chemical crosslinks, chain entanglements and network heterogeneity in peroxide-cured EPDM rubber

The mean decay time, $T_2^{av}$, defined as $(\sum f_k^{} / T_2^{(k)})^{-1}$ is the inverse weighed average of the decay frequencies and is related to the volume-averaged crosslink density in the samples, where $f_k$ is the fraction of the respective components from the three-exponential fit. Although $T_2^{av}$ is determined from a fit of the curve as a whole, in the context of the multi-exponential model it is directly related to the initial slope.

$T_2$ relaxation decays measured with Hahn-echo and Double Quantum filtered Hahn-echo pulse sequences for EPDM with 9 % ENB and 5 phr peroxide, before and after crosslinking and swelling. The decay amplitude is normalized to its value at time zero. The slopes of the initial parts of the decays at short $\tau_{\text{EX}}$ are shown by the dotted lines.

The $T_2$ decay of non-crosslinked EPDM with the highest diene content and the crosslinked sample are compared in Fig. 3.3.1.1. Obviously, crosslinking causes a large decrease in the decay.
time, because chemical crosslinks impose severe restrictions on the chain mobility as compared to the entangled melt.

### 3.3.2 Total network density

The total network density $D_{\text{tot}}$ of the heterogeneous EPDM network after peroxide crosslinking follows from the mean molar mass $M_w$ of the chains between the network junctions (chemical crosslinks and chain entanglements), which is calculated from $1/ T_2^{av}$.

Fig. 3.3.2.1 shows the plot of $D_{\text{tot}}$ at varied peroxide content for the different EPDMs. For all EPDM compositions investigated the network density increases linearly with the peroxide content up to at least 5 phr peroxide. These results are consistent with a simple additivity model with a constant entanglement density $D_{\text{EN}}$ and a chemical crosslink density $D_{\text{CC}}$ proportional to the peroxide content $p$. Both the entanglement and chemical crosslink density further depend on the diene content $d$.

$$D_{\text{tot}}(d,p) = D_{\text{EN}}(d) + D_{\text{CC}}(d,p)$$  \hspace{1cm} (3.3)

<table>
<thead>
<tr>
<th>Sample composition and total crosslink density</th>
</tr>
</thead>
<tbody>
<tr>
<td>ENB (wt %)</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>1.9</td>
</tr>
<tr>
<td>1.9</td>
</tr>
<tr>
<td>1.9</td>
</tr>
<tr>
<td>4.5</td>
</tr>
<tr>
<td>4.5</td>
</tr>
<tr>
<td>4.5</td>
</tr>
<tr>
<td>9</td>
</tr>
<tr>
<td>9</td>
</tr>
<tr>
<td>9</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>0</td>
</tr>
</tbody>
</table>

Extrapolation of $D_{\text{tot}}$ to zero peroxide yields the entanglement density $D_{\text{EN}}$, which is quite similar for the various EPDMs as expected. The entanglement densities are in the range 200 - 240 mmol/kg, which agrees with previous NMR studies and is also consistent with the outcome of other studies, based on rheology, neutron scattering and mechanical properties.$^{30-32}$
Entanglements in EPDM contribute significantly to the total network density and consequently to related macroscopic properties.

The lowest value of $D_{EN}$ is found for EPM without diene because this polymer has the most flexible chain due to the absence of the rigid diene monomer. The small differences in $D_{EN}$ for the four EPDM grades with diene are caused by differences both in diene and ethylene contents, resulting in subtle differences in the conformational states of the rubber chains.

![Graph](image)

**Figure 3.3.2.1.** Total network crosslink density $D_{tot}$ in peroxide-cured EPDM as a function of peroxide content. The contribution of different types of network junctions to the total crosslink density is described in the text.

### 3.3.3 Combination versus addition

#### 3.3.3.1. $^1$H NMR transverse relaxometry

The difference between the total network density $D_{tot}$ at any given peroxide content and the intercept in Fig. 3.3.2.1, representing the entanglement density $D_{EN}$, gives the number $D_{CC}$ of the chemical crosslinks formed (Fig. 3.3.3.1.1). According to the generally accepted reaction scheme as presented in Fig. 3.1.2, two types of chemical crosslinks are formed in peroxide-cured EPDM,
viz. one type via combination of peroxide-induced EPDM macro-radicals, and the other one via addition of the macro-radicals to the residual double bonds of the termonomer.

Figure 3.3.3.1.1 Density of chemical crosslinks $D_{CC}$ in peroxide-cured EPDM as a function of peroxide content.

Since EPM does not contain any unsaturation, peroxide crosslinking occurs only via the combination route. The enhanced chemical crosslink density determined for EPDM relative to EPM (compare slopes in Fig. 3.3.3.1.1) indicates that both types of crosslinks are formed in EPDM. In principle, the two types of chemical crosslinks are additive since all addition reactions generate new radicals, which eventually are all terminated via combination reactions.

At low termonomer content the density of crosslinks via combination is probably independent of the termonomer content. Then the chemical crosslink density $D_{CC}(d, p)$ in Eq. 3.3 can be linearly decomposed into a term resulting from combination $D_{CC,comb}(p)$, depending on the peroxide content $p$ only, and an addition term $D_{CC,add}(d,p)$, which also depends on the termonomer content $d$:

$$D_{CC}(d, p) = D_{CC,comb}(p) + D_{CC,add}(d,p) \quad (3.4)$$
Note that both terms are linearly dependent on the peroxide content. According to Eq. 3.4 the amount of crosslinks formed via addition can be obtained by subtracting the density of chemical crosslinks formed for EPM via combination from that of the total chemical crosslink density of EPDM cured with the same amount of peroxide. Fig. 3.3.3.1.1 shows that increasing the ENB level results in increased contribution of addition to the total crosslink density.

Comparing the obtained chemical crosslink density with the initial peroxide content, one can calculate the peroxide crosslinking efficiency for EP(D)M, which is defined as the number of crosslinks formed per peroxide moiety (Table 3.3.3.1.1).

<table>
<thead>
<tr>
<th>Peroxide content (phr)</th>
<th>Diene type and content (phr)</th>
<th>Peroxide efficiency (%)</th>
<th>Diene conversion (%)</th>
<th>Number of addition cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25</td>
<td>0 % ENB</td>
<td>38</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.5</td>
<td></td>
<td>52</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>53</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>49</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.25</td>
<td></td>
<td>99</td>
<td>9</td>
<td>1.9</td>
</tr>
<tr>
<td>2.5</td>
<td>1.9 % ENB</td>
<td>127</td>
<td>29</td>
<td>1.2</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>113</td>
<td>47</td>
<td>1.5</td>
</tr>
<tr>
<td>1.25</td>
<td></td>
<td>157</td>
<td>8</td>
<td>0.9</td>
</tr>
<tr>
<td>2.5</td>
<td>4.5 % ENB</td>
<td>173</td>
<td>19</td>
<td>0.8</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>165</td>
<td>36</td>
<td>0.8</td>
</tr>
<tr>
<td>1.25</td>
<td></td>
<td>198</td>
<td>6</td>
<td>0.6</td>
</tr>
<tr>
<td>2.5</td>
<td>9 % ENB</td>
<td>207</td>
<td>12</td>
<td>0.6</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>203</td>
<td>24</td>
<td>0.6</td>
</tr>
<tr>
<td>1.25</td>
<td></td>
<td>181</td>
<td>11</td>
<td>0.7</td>
</tr>
<tr>
<td>2.5</td>
<td>4.5 % DCPD</td>
<td>192</td>
<td>25</td>
<td>0.7</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>186</td>
<td>47</td>
<td>0.7</td>
</tr>
</tbody>
</table>

All calculations are performed in mmol/kg compound, with the peroxide being bifunctional and being used as a 40 % pure masterbatch. The peroxide crosslinking efficiencies are more or less constant for a given type of EP(D)M. For EPM it amounts to 50 %, which is similar to values obtained via low-molecular-weight model experiments. It indicates that only 50 % of the original peroxide functions is effectively used for crosslinking; the other 50 % of the peroxide functions reacts towards non- elastically active products. Although the presence of a diene termonomer is not a prerequisite for peroxide crosslinking, it does provide a significant increase.
Clearly, increasing the ENB content of EPDM results in increased peroxide crosslinking efficiency, although at higher ENB contents the increase levels off.

**Figure 3.3.3.1.2** The conversion of ENB estimated from $T_2$ relaxation in peroxide-cured EPDM as a function of peroxide content as calculated from NMR relaxometry.

From the slopes in Fig. 3.3.3.1 it is concluded that 4.5 % DCPD-EPDM has similar reactivity as 9 % ENB-EPDM, which indicates that DCPD is almost twice as efficient in peroxide crosslinking than ENB. This is fair agreement with previous studies. The number of EPDM macro-radicals which are actually formed can be calculated using the amount of peroxide functionality in mmols per kg EPDM and the peroxide crosslinking efficiency of EPM. Combining this number with the number of crosslinks formed via addition allows the calculation of the number of addition cycles per EPDM macro-radical formed. The data given in Table 3.3.3.1.1 are rather low (<2) indicating that termination of the free-radical reaction sequence by combination is relatively fast compared to crosslink formation. From the data shown in this table the ratio of DCPD versus ENB conversion can be calculated. DCPD conversion is 1.3 times
higher than that of ENB in similar recipes, which is perfect agreement with the known ratio for crosslinking.\textsuperscript{34}

### 3.3.3.2 Chemical conversion of diene third monomer

Comparison of the crosslink density via addition with the initial termonomer content (Table 3.3.2.1) allows the calculation of the molar diene conversion (Table 3.3.3.1.1). Obviously, the higher the peroxide content, the higher the diene conversion. For 1.9 % ENB-EPDM, the ENB conversion is far from complete (<50 %), and at higher ENB content it is even lower (<40 %). In other words, a major part of the diene is not used during peroxide crosslinking of EPDM. The residual diene content after peroxide crosslinking is of practical importance, since it increases the sensitivity to hot air ageing.

The MAS $^1$H NMR spectra of the EPDM samples are dominated by the signals of the aliphatic protons of the EPM backbone around 1 ppm (Fig. 3.3.3.2.1).

\[ \text{Figure 3.3.3.2.1 MAS } ^1\text{H NMR spectra of peroxide-cured EPDM (9 \% ENB and 5 phr peroxide) before and after crosslinking.} \]

At large magnification of the spectra, the resonances of the vinyl protons of ENB, as well as the aromatic protons of the peroxide are seen in the spectral range of 4 – 6 ppm and 7 – 9 ppm, respectively.
Comparison of the spectra of the EPDM with 9 % ENB before and after crosslinking suggests that the peroxide has been largely converted; the remaining aromatic signals are related to the aromatic ketone and alcohols, which are formed upon decomposition. The intensity of the unsaturated ENB resonances decreases, as a result of the addition of the EPDM macro-radicals to the unsaturation, which allows the determination of the ENB conversion. Fig. 3.3.3.2.1 shows that for the EPDM sample of 9 % ENB and 5 phr peroxide, the ENB conversion estimated from the MAS $^1$H NMR spectrum equals approximately 30 %. This value may be compared with the ENB conversion determined from the $T_2$ relaxation experiments, as discussed above.

In addition, the diene conversion has also been determined via FT-Raman spectroscopy. The ENB conversion values, which are determined by these three methods for EPDM vulcanizates with the highest amount of ENB, are given in Table 3.3.3.2.1. The results of all the three methods are in good agreement. Thus, it can be concluded that the $T_2$ relaxation method is a reliable tool for quantifying a series of network characteristics of crosslinked rubber.

<table>
<thead>
<tr>
<th>Peroxide content (phr)</th>
<th>$^1$H NMR Relaxation (%)</th>
<th>$^1$H NMR Spectroscopy (%)</th>
<th>Raman Spectroscopy (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25</td>
<td>6</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>2.5</td>
<td>12</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>24</td>
<td>28</td>
<td>24</td>
</tr>
</tbody>
</table>

3.3.4. Enhanced distinction between network chains and defects in swollen crosslinked EPDM

The largest distinction in the mobility of network chains and defects is observed for swollen samples. Swelling has two opposite effects on the chain mobility. On the one hand, it enhances the mobility by diminishing the density of temporary chain entanglements. On the other hand, it stretches the network chains and, in this way, increases the anisotropy of the network chain motions.\(^{35}\) Under mild swelling conditions the first occurs, but at extensive swelling the stretching
prevails. Network defects, such as chain segments not connected to the network on both sides, do not take part in the stretching and become only more mobile upon swelling.

The contribution of the temporary chain entanglements to the total network density is usually evaluated by comparing the network density for samples in the swollen and solid (non-swollen) state. $T_2$ was investigated as a function of the solvent content for the non-crosslinked and the highly crosslinked EPDM (Fig. 3.3.4.1).

![Figure 3.3.4.1](image)

**Figure 3.3.4.1** $T_2$ values characterizing the relaxation components of the $T_2$ decay versus the amount of solvent in swollen peroxide-cured EPDM (9 % ENB and 5 phr peroxide). The components are tentatively assigned to short and long network chains, as discussed in the text.

For the non-crosslinked EPDM $T_2$ shows a monotonous increase versus the volume fraction of tetrachloroethane, reflecting the increasing mobility of the chains. The trend for the crosslinked EPDM is more complex. Analyzing the observed Hahn-echo decay in terms of three components, it was found that the shortest $T_2$ component, representing the shortest segments in the network, is hardly affected by the swelling. In contrast, the longest $T_2$ component, probably related to the network defects, shows a monotonous increase like the non-crosslinked EPDM. The intermediate $T_2$ component, associated with long network chains, initially increases up to a solvent content $V_s \approx 40$ vol %, where it reaches a maximum, and then decreases upon a further increase of the amount of swelling solvent. This reflects the changing balance between the above
mentioned disentangling versus stretching effects by swelling. At a volume fraction of the solvent of approximately 40%, the network density is mainly composed of chemical crosslinks and trapped chain entanglements. The density of temporary entanglements in the crosslinked samples can be estimated by subtracting the network density in partially swollen samples from that of non-swollen vulcanizates. The main contribution to the total network density for the 9% ENB EPDM crosslinked with 5 phr peroxide is that of the chemical crosslinks and the trapped chain entanglements. For low crosslink densities, the temporary chain entanglements provide the dominant contribution to the total network density. At the equilibrium swelling degree, the fraction (≈ 7%) of the long $T_2$ relaxation component can be used as a measure of the fraction of network defects.

To resolve the effect of swelling on the mobility of the short and long network chains as well as the network defects more clearly, DQ-filtered $T_2$ measurements have been performed on the swollen samples and the results have been compared with those on the non-swollen rubbers discussed above (Fig. 3.3.1.2).

### Table 3.3.4.1

<table>
<thead>
<tr>
<th>Excitation time</th>
<th>Volume of solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 %</td>
</tr>
<tr>
<td>$\tau_{\text{short}}$ (80 $\mu$s)</td>
<td>394 (4.1)</td>
</tr>
<tr>
<td>$\tau_{\text{max}}$ (500 $\mu$s)</td>
<td>683 (18.2)</td>
</tr>
<tr>
<td>$\tau_{\text{long}}$ (1100 $\mu$s)</td>
<td>954 (9.7)</td>
</tr>
</tbody>
</table>

Table 3.3.4.1 presents the effective relaxation times of the DQ-filtered $T_2$ decays measured at excitation times of 80 $\mu$s, 500 $\mu$s and 1100 $\mu$s, and solvent fractions of 0, 40 and 80 vol-%. The shape of the DQ-filtered decays of the crosslinked EPDM depends largely on the excitation time and differs from that of the overall Hahn-echo decay (Fig. 3.3.1.2). At long DQ-filter time $\tau_{\text{EX}}$, the Hahn-echo decay is slower, and at a short filter time the decay is faster than the non-filtered overall decay (Fig. 3.3.1.2; Table 3.3.4.1). The slow component at long excitation time is observed to become even slower upon swelling, whereas the initial decay rates at short excitation
time increase with increasing solvent amount. The latter is caused by an increase in the anisotropy of the chain motions as a result of chain stretching upon swelling, which is also reflected by an increase in the amplitude of the DQ signal. Swelling-induced changes in the decays are more pronounced for crosslinked EPDM compared to non-crosslinked EPDM. This suggests that the network structure of the crosslinked samples is far more heterogeneous than the structure of entangled EPDM chains in the virgin rubber. Thus, the results of the DQ-filtered HEPS experiments support the assignment of the short and long $T_2$ relaxation components to network chains and network defects, respectively, for swollen EPDM vulcanizates. DQ-filtered $T_2$ relaxometry is a powerful tool to resolve components with a different mobility in a heterogeneous rubber network. However, quantitative analysis of this experiment in the relation to network heterogeneity is hampered by a number of issues that have been recently discussed.28

3.3.5 Correlation of the network density with mechanical properties

In general, the physical properties of a crosslinked rubber depend not only on the crosslink density, but also on the details of the curing. One cause for the latter is the nature of the chemical bonds formed between the chains (for example sulphur bridges in sulphur-vulcanisates versus C-C bonds in peroxide cures) and the functionality of the crosslinks. Another is attributed to the differences in network heterogeneity i.e. the distribution of the crosslinks and defects in the network.38-40

The results of the present NMR study suggest significant network heterogeneity in peroxide-cured EPDMs. Therefore, the relationships between the average crosslink density, as determined by NMR, and the physical properties are not always straightforward; nevertheless, some correlations can be established.

Common rubber properties, such as hardness, torque, elongation at break, modulus at 100%, and compression sets at 23 and 70 °C have been measured for the complete set of peroxide-cured EPDM samples (Table 3.3.5.1). Even across the series with different diene and peroxide contents these mechanical properties correlate well with the total network density (Fig. 3.3.5.1) in a way consistent with existing network models. Apparently, the network density calculated from $T_2$
relaxometry has a real physical meaning and is relevant for the macroscopic properties of the crosslinked EPDM rubbers.

Table 3.3.5.1 Physical properties of peroxide-cured EP(D)M

<table>
<thead>
<tr>
<th>Diene type and content</th>
<th>Px14-40 content (%)</th>
<th>Torque (Nm)</th>
<th>Hardness (ShA)</th>
<th>Elongation at break (%)</th>
<th>Modulus 100% (MPa)</th>
<th>CS 23°C (%)</th>
<th>CS 70°C (%)</th>
<th>Tensile strength (MPa)</th>
<th>Tear strength (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25</td>
<td>0.23</td>
<td>29</td>
<td>-</td>
<td>0.6</td>
<td>40</td>
<td>68</td>
<td>-</td>
<td>8.4</td>
<td></td>
</tr>
<tr>
<td>0 ENB</td>
<td>2.5</td>
<td>0.48</td>
<td>36</td>
<td>1050</td>
<td>0.7</td>
<td>24</td>
<td>42</td>
<td>3.0</td>
<td>10.3</td>
</tr>
<tr>
<td>5</td>
<td>0.77</td>
<td>41</td>
<td>370</td>
<td>0.9</td>
<td>13</td>
<td>19</td>
<td>1.4</td>
<td>9.6</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.95</td>
<td>45</td>
<td>250</td>
<td>1.0</td>
<td>6</td>
<td>10</td>
<td>1.4</td>
<td>9.6</td>
<td></td>
</tr>
<tr>
<td>1.25</td>
<td>0.72</td>
<td>45</td>
<td>580</td>
<td>1.0</td>
<td>14</td>
<td>25</td>
<td>2.7</td>
<td>12.0</td>
<td></td>
</tr>
<tr>
<td>1.9 ENB</td>
<td>2.5</td>
<td>1.07</td>
<td>48</td>
<td>340</td>
<td>1.1</td>
<td>9</td>
<td>15</td>
<td>2.2</td>
<td>11.5</td>
</tr>
<tr>
<td>5</td>
<td>1.48</td>
<td>52</td>
<td>167</td>
<td>1.3</td>
<td>5</td>
<td>7</td>
<td>1.9</td>
<td>10.1</td>
<td></td>
</tr>
<tr>
<td>1.25</td>
<td>1.11</td>
<td>49</td>
<td>390</td>
<td>1.1</td>
<td>7</td>
<td>11</td>
<td>2.0</td>
<td>11.8</td>
<td></td>
</tr>
<tr>
<td>4.5 ENB</td>
<td>2.5</td>
<td>1.42</td>
<td>51</td>
<td>200</td>
<td>1.3</td>
<td>3</td>
<td>5</td>
<td>1.7</td>
<td>11.1</td>
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<tr>
<td>5</td>
<td>1.92</td>
<td>56</td>
<td>120</td>
<td>1.6</td>
<td>2</td>
<td>3</td>
<td>1.7</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td>1.25</td>
<td>0.94</td>
<td>46</td>
<td>440</td>
<td>1.0</td>
<td>7</td>
<td>11</td>
<td>2.9</td>
<td>11.2</td>
<td></td>
</tr>
<tr>
<td>9 ENB</td>
<td>2.5</td>
<td>1.37</td>
<td>50</td>
<td>230</td>
<td>1.4</td>
<td>3</td>
<td>4</td>
<td>2.5</td>
<td>11.0</td>
</tr>
<tr>
<td>5</td>
<td>2.02</td>
<td>57</td>
<td>90</td>
<td>1.8</td>
<td>1</td>
<td>2</td>
<td>1.6</td>
<td>9.3</td>
<td></td>
</tr>
<tr>
<td>1.25</td>
<td>0.83</td>
<td>46</td>
<td>420</td>
<td>1.1</td>
<td>10</td>
<td>15</td>
<td>4.1</td>
<td>13.2</td>
<td></td>
</tr>
<tr>
<td>4.5 DCPD</td>
<td>2.5</td>
<td>1.28</td>
<td>50</td>
<td>210</td>
<td>1.3</td>
<td>5</td>
<td>7</td>
<td>2.4</td>
<td>11.4</td>
</tr>
<tr>
<td>5</td>
<td>1.88</td>
<td>56</td>
<td>110</td>
<td>2.0</td>
<td>2</td>
<td>3</td>
<td>2.0</td>
<td>9.3</td>
<td></td>
</tr>
</tbody>
</table>

The rheometer torque correlates with the total network density in a linear fashion, which is in agreement with a previous real-time NMR study\(^{40}\) and supports the use of rheometer torque in rubber technology. The same holds for the modulus at 100 %, which is consistent with the standard rubber elasticity theory.
The elongation at break and the compression sets at 23 and 70 °C decrease upon increasing crosslink density, although in a non-linear fashion in agreement with general experience in rubber technology. The poor correlations of the tensile strength at break and the tear strength with the crosslink density are probably due to the defects or imperfections in the network in combination with the complex origin of ultimate mechanical properties.

### 3.4 Conclusions

Application of $T_2$ relaxometry to a series of peroxide-cured EP(D)M samples with different diene and peroxide levels has allowed a quantitative determination of the total crosslink density. The results presented in this work are relevant for a better understanding of the elastomer materials.
The respective contributions from temporary and trapped chain entanglements, as well as two types of chemical crosslinks originating from either combination of macro-radicals or addition of macro-radicals to the double bonds of the EPDM diene termonomers have been resolved. The peroxide crosslinking efficiency is $\approx 50\%$. The conversion of the diene is determined by both peroxide and diene contents, with a maximum of 47\% for 1.9\% ENB-EPDM and 24\% for 9\% ENB-EPDM. The latter was found to be consistent with the diene conversion estimated from MAS $^1$H NMR spectroscopy and Raman spectroscopy. The total network density, as determined from the $T_2$ relaxometry, correlates well with several common physical properties as measured for the peroxide-cured EP(D)M.

### 3.5 References

Solid-state NMR study on chemical crosslinks, chain entanglements and network heterogeneity in peroxide-cured EPDM rubber


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Chapter 4

Mechanism of peroxide crosslinking of EPDM rubber investigated by solid-state $^{13}$C NMR spectroscopy

Abstract

$^{13}$C labeled ENB-EPDM was cured with peroxide in steps of 3 minutes at 175 °C and the subsequent states of the material investigated by use of MAS $^{13}$C NMR spectroscopy and $^1$H NMR $T_2$ relaxometry to compare the conversion of the ENB unsaturation and the crosslink formation as a function of time. The results indicate that the initial network formation is dominated by combination of EPDM macroradicals produced by the peroxide decomposition, while in a later stage addition of macroradicals to the ENB unsaturation takes over. The selective $^{13}$C labeling of the C2/C8 olefinic carbon atoms in ENB permitted the new chemical structures formed by peroxide curing to be studied with MAS $^{13}$C NMR including the so called INADEQUATE technique. This technique selects neighboring $^{13}$C-$^{13}$C spin pairs only, and suppresses the natural-abundance $^{13}$C NMR signals of the ethylene and propylene moieties. The ENB unit is involved in the crosslinking reaction not only via addition to the pendant, but also via the allylic positions, resulting in new structures with the unsaturation intact. The latter represents a novel pathway to be added to the generally accepted mechanism of peroxide curing.

* this chapter is partly reproduced from: Orza, R.A.; Magusin, P.C.M.M.; Litvinov, V.M.; Duin van, M.; Michels, M.A.J.; to be submitted.
4.1 Introduction

Ethylene-propylene copolymers (EPM) and ethylene-propylene-diene ter-polymers (EPDM) are among the most versatile synthetic rubbers.\textsuperscript{1,2,3} In EPDM the ethylene and propylene co-monomers form a saturated polymer backbone with randomly distributed, non-conjugated diene monomers, which provide unsaturations attached to the main chain. The physical, thermal and chemical properties of EPDM can be tuned by adjusting the copolymer structure, the diene type and content and the molecular weight distribution. Incorporation of the diene monomer in EPDM enables sulfur vulcanization and enhances the peroxide curing efficiency.\textsuperscript{4}

Upon crosslinking of EPDM rubber, chemical links are formed between the polymer chains,\textsuperscript{4} improving both the tensile and elastic properties of the rubber. Sulfur vulcanization results in sulfur crosslinks between the polymer chains, providing inter-chain bonds which are more flexible but have limited thermal stability. As the number of sulfur atoms in a sulfur crosslink increases, the thermal stability decreases. Still, sulfur vulcanization is a robust technology and is practiced in a wide variety of vulcanization technologies, such as compression and injection molding, extrusion and hot air autoclaves. A major advantage of sulfur vulcanization is that by varying the sulfur chemicals formulation, the crosslinking kinetics and the final crosslink density can be tuned to a broad range of crosslinking technologies and applications. As opposed to sulfur vulcanization, the crosslinks provided by peroxide cure consist of carbon-carbon bonds, which have similar bond strength as the C−C bonds in the polymer backbone. Therefore, peroxide cure provides better heat aging properties and high-temperature compression set. However, peroxide cure in contact with air results in products with sticky surfaces, which is probably due to oxygen inhibition of the free-radical crosslinking at the surface, degradation of polymer chains and/or formation of polar oxidation products. Thus, unlike sulfur vulcanization peroxide cure cannot be performed in hot-air autoclaves.

Peroxide crosslinking of EP(D)M covers about 15 % of the commercial applications because of the enhanced performance in high temperatures. The generally accepted mechanism of peroxide crosslinking of EPDM is shown in Fig. 4.1.1.\textsuperscript{4} It is initiated by the thermal decomposition of the peroxide, which results in the formation of two radicals, which subsequently abstract H atoms from the EPDM polymer, yielding macro-radicals. The macro-radicals can give rise to crosslinks in two ways. First, two EPDM macroradicals can combine, yielding direct C−C crosslinks between the two polymer chains. Second, an EPDM macroradical can add to a residual EPDM
unsaturation. The intermediate radical undergoes hydrogen transfer, yielding a crosslink with a diene monomer unit between the two polymer chains and a new macroradical that can react again.

In our previous work (see Chapter 3) on peroxide-cured EPDM rubber, the crosslink density and network heterogeneity have been studied. For EPDM/peroxide compositions representative for industrial applications the peroxide efficiency was shown to be ~50 %, the diene conversion was up to 40 % and the contribution of addition crosslinks to the total crosslink density was up to 40 %, the latter two depending on the peroxide content and the diene monomer type and content.

Figure 4.1.1 Mechanism of peroxide curing of EPDM (For convenience, the mechanism is shown for a second time, from Chapter 3.1)\textsuperscript{4,5}
The aim of this work is to study the chemical structures formed upon peroxide cure of EPDM with ENB as third monomer in more detail and, thus, to elaborate on the mechanism shown in Fig. 4.1.1. A full understanding of the chemical reactions occurring during peroxide crosslinking of EPDM is of importance for studying peroxide crosslinking kinetics to obtain structure-properties relationships for the vulcanizates. Two different NMR methods have been used to study the chemical structures formed and the network density, viz. $^{13}$C NMR spectroscopy and $^1$H NMR $T_2$ relaxometry, respectively. By monitoring the intensity of the olefinic $^{13}$C resonances of the ENB third monomer, the ENB conversion can be followed as a function of the curing time, and correlations with the crosslink density, as determined by the $T_2$ relaxation analysis, can be established. Deviations from the expected correlation will be explained by the formation of new crosslink and oxidation products, which have not been identified before. Magic-angle spinning $^{13}$C NMR was used to identify the chemical structures formed in peroxide-cured EPDM. The use of EPDM with $^{13}$C ENB enriched at the C2−C8 double bond positions leads to strongly enhanced NMR signals, and facilitates a successful characterization of new structures involving the diene unsaturation. In addition, the double-labeling at the neighboring C2 and C8 positions permitted the use of NMR techniques with suppression of the natural-abundance $^{13}$C background such as INADEQUATE, as was shown in earlier studies on sulfur vulcanization and on resol cure of labeled EPDM.

4.2 Experimental

4.2.1 Samples

$^{13}$C labeled ENB-EPDM

The [2,8-$^{13}$C2] ENB-EPDM rubber used in this study has been synthesized by W. Heinen et al. It has an ethylene to propylene ratio of $\sim$ 1.8, an ENB content of $\sim$ 8 wt.-% ($\approx$ 670 mmol/kg) and an $M_w$ of $4.8\times10^5$ g/mol. ENB is incorporated in the polymer through its endocyclic C5/C6 double bond. Because of the limited quantity of labeled EPDM available, the EPDM/peroxide material was prepared on a small scale via a solution route and one sample was used for step-wise vulcanization. NMR experiments were performed after each vulcanization step. 100 mg of EPDM compound with 4.4 wt. % di(tert-butylperoxyisopropyl)benzene from Across (see Fig. 4.2.1.1) was prepared by dissolution in hexane followed by evaporation and drying at 90°C.
under vacuum. Crosslinking was performed in a hot press at 175°C for 3, 6, 9 and 19 minutes. The peroxide half life time at 175°C is 1 minute.\textsuperscript{8}

![Chemical structure of di(tert-butylperoxyisopropyl)benzene](image)

**Figure 4.2.1.1** Chemical structure of di(tert-butylperoxyisopropyl)benzene

*Model compound sample*

The model compound sample consisted of a mixture of 0.551 g 5-methylnonane (model for EPM) and 0.060 g hydrogenated ENB\textsuperscript{9} (model for ENB in EPDM) with 0.030 g di(tert.butyl peroxyisopropyl)benzene as peroxide. The sample was heated for 30 minutes in an oil bath at 185°C. As a result, the peroxide is fully decomposed.

**4.2.2 NMR techniques**

**4.2.2.1 $^{13}$C NMR Spectroscopy**

Magic-angle spinning (MAS) $^{13}$C NMR spectra were recorded on a Bruker DMX500 spectrometer equipped with a 4-mm MAS probehead and operating at a $^{13}$C NMR frequency of 125 MHz. Direct excitation $^{13}$C NMR spectra with proton decoupling were recorded by use of the Hahn-echo pulse sequence $90^\circ-\tau-180^\circ-\tau$ with a $90^\circ$ pulse of 5 $\mu$s and echo time $2\tau = 6$ $\mu$s. The relaxation delay between subsequent scans was 5 s, which in the initial test experiments proved to be long enough for quantitative measurements. The experiments were performed at room temperature and at 90°C. The $^{13}$C NMR signal of adamantane at 38.56 ppm was used as a reference. The sample rotation rate was 4 or 8 kHz.

**4.2.2.2 1D-INADEQUATE**

The experimental conditions for 1D-INADEQUATE are described in Chapter 2.2.6.
4.2.2.3 $^1$H NMR Hahn-echo relaxometry

The experimental conditions for $^1$H NMR transverse magnetization relaxation and the relation of the latter to crosslink density are described in Chapter 2.2.1.

4.3 Results and discussion

4.3.1. Crosslink density and conversion of the third monomer by $^1$H NMR relaxometry and $^{13}$C NMR spectroscopy

Solid-state $^1$H NMR transversal relaxation yields detailed insight into the network structure of crosslinked rubbers. $^5,^{10,11,12,13}$ $T_2$ relaxation is mainly determined by the anisotropy of the chain mobility and, thus, strongly affected by the crosslink density. The total network density, including the contributions of temporary and trapped chain entanglements, can be calculated from the $T_{2\text{pl}}$ value for peroxide-cured EPDM rubber, as described in Chapter 2.2.1. For the present study, a stepwise crosslinking has been performed in order to follow both the crosslink density and the third monomer conversion as a function of time.

![Graph showing ENB conversion ($^{13}$C NMR spectroscopy) and crosslink density ($^1$H NMR $T_2$ relaxation) for peroxide-cured $^{13}$C labeled EPDM as a function of time at 175 °C.]

Figure 4.3.1.1

ENB conversion ($^{13}$C NMR spectroscopy) and crosslink density ($^1$H NMR $T_2$ relaxation) for peroxide-cured $^{13}$C labeled EPDM as a function of time at 175 °C.
From the relaxation experiments the total network density can be calculated, and by subtracting the entanglement density, the total chemical crosslink density determined. As entanglement density, we use the value for 9 % ENB-EPDM studied in chapter 3, 230 mmol/kg, which was obtained by extrapolating the network density to zero peroxide level. The experimental crosslink density at time zero has a substantial error because the experiment performed for the non-crosslinked rubber at 90 °C is not the most accurate estimation of the entanglement density. Therefore it is simply taken as zero. The evolution of the chemical crosslink density as a function of time is shown in Fig. 4.3.1.1.

The time dependence of the crosslink density derived from $^1$H NMR $T_2$ relaxation shows that network formation follows a concave curve and is completed after approximately 10 min at 175 °C, which is consistent with the half life time of 1 min of the peroxide at 175 °C. The final crosslink density is in fair agreement with extrapolated data to 4.5 phr peroxide as presented in our previous study. $^{5}$

$^{13}$C NMR spectroscopy is useful for the structural elucidation and quantification of the composition of polymeric compounds. $^{14,15}$ MAS $^{13}$C NMR spectra of the stepwise crosslinked $^{13}$C labeled EPDM were recorded at 90 °C. The EPDM chain mobility at this temperature reduces the $^{13}$C NMR linewidth which leads to a significant gain in chemical resolution. As a result of the $^{13}$C labeling, the resonances of the unsaturated C2 and C8 atoms of ENB, at 111 and 147 ppm, respectively, are largely enhanced relative to the aliphatic resonances at 20-50 ppm (Fig. 4.3.1.2).

As shown in Fig. 4.1.1, peroxide cure of EPDM proceeds via combination and addition reactions, the latter resulting in the conversion of the EPDM unsaturation. The intensities of the two olefinic peaks upon crosslinking have been followed in time to determine the conversion of the ENB unsaturation, as shown in Fig. 4.3.1.3.

Indeed, the intensities are decreasing with increasing curing time. From the relative decrease of the peak intensities and the starting ENB content, the conversion of the ENB unsaturation can be calculated in similar units as the crosslink density derived from $^1$H NMR $T_2$ relaxometry (mmol/kg). The data plotted in Fig. 4.3.1.1 are averages for the C2 and C8 peaks. An S-shaped conversion profile is observed, reaching a plateau at $\sim$15 min. Although the relative errors in the crosslink density calculated from $^1$H NMR $T_2$ relaxation (5 % experimental and 10 % model-related errors) and in the ENB conversion estimated from the olefinic $^{13}$C NMR signals (levels
Figure 4.3.1.2 $^{13}$C NMR spectra of: (a) crosslinked non-labeled EPDM, (b) non-crosslinked $^{13}$C labeled EPDM mixed with the peroxide, (c) crosslinked $^{13}$C labeled EPDM and (d) INADEQUATE-crosslinked $^{13}$C labeled EPDM
Mechanism of peroxide crosslinking of EPDM

Figure 4.3.1.3 Olefinic $^{13}$C NMR spectra of $^{13}$C labeled EPDM crosslinked with peroxide at 175 °C as function of time. To avoid further crosslinking during the NMR measurement the spectra have been recorded at room temperature. The linewidth at room temperature is bigger than at 90 °C (see Fig. 4.3.1.2). As a result, the doublet fine structure of the resonances is not recognizable.

off at 15 % upon increasing curing time) are significant, it may still be concluded that the crosslink density and the ENB conversion behave differently as a function of time.

The crosslink density is higher than the ENB conversion over the whole time interval, although they approach each other upon full curing. The crosslink density is increasing faster than the conversion of the ENB unsaturation. However, during the later stages of curing the ENB conversion is still continuing, while crosslink formation has leveled off. The fast network formation relative to the double bond conversion indicates that the initial crosslinking is dominated by combination of the macro-radicals produced after the peroxide decomposition, while at a later stage addition of macroradicals to the ENB unsaturation takes over. Thus, the balance between the combination and addition pathway in the peroxide-cure mechanism (Fig. 4.1.1) changes with time. This makes sense, because immediately after the peroxide decomposition in the first minutes, EPDM macroradicals are formed, and at their initial concentration there is a relatively high probability that these combine. Later, when the
concentration of macro-radicals has become less, they live long enough to encounter an ENB unit and add to the double bond.

At first sight it may seem from the comparable densities of crosslinks and converted ENB units after 15 minutes (Fig. 4.3.1.1) that in the final stage almost all crosslinks have been formed via addition. However, as followed from the $T_2$ analysis for fully cured EPM (without ENB) in Chapter 3, at 4.5 phr peroxide the density of crosslinks produced via combination equals 130 mmol/kg. Thus, according to the additive model that proved to be successful in Chapter 3, the specific crosslink density arising from the addition route in the fully cured EPDM sample, studied in the present chapter, equals $400 - 130 = 270$ mmol/kg, which is significantly lower than the final ENB conversion.

Thus, there is a discrepancy between the density of crosslinks via addition, as estimated from the difference between crosslink density between EPDM and EPM, on the one hand, and the ENB conversion, measured with $^{13}$C NMR, on the other. A possible explanation follows from a quick inspection of the $^{13}$C NMR spectra of the crosslinked $^{13}$C labeled EPDM (Fig. 4.3.1.2), which does not only show new aliphatic C–C signals (40-50 ppm), but also new alcohol or ether signals (60-80 ppm), as well as new olefinic (100-160 ppm) and carbonyl (160-200 ppm) resonances. Obviously the ENB unsaturation is not only converted to saturated crosslinks via the addition pathway, but other reactions also occur, which contribute to the conversion of the ENB unsaturation, as well.

For a better understanding of the crosslinking mechanism and to explain the discrepancy between crosslink density and ENB conversion, the MAS $^{13}$C NMR spectra of the labeled ENB-EPDM have to be interpreted in more detail.

### 4.3.2 $^{13}$C NMR characterization of the structures formed upon crosslinking

The major goal of this study is to get insight in the structures of the chemical crosslinks and other products formed during peroxide cure of EPDM. The unsaturation of the ENB is essential in peroxide crosslinking, but because of the low content (usually less than 10 %) it is very difficult to characterize the reaction products. This is why $^{13}$C labeling is important, since it allows a direct study of the atoms involved in the crosslinking of the peroxide-cured EPDM. The
availability of the EPDM with the $^{13}$C labels at the C2/C8 double bond positions in ENB offers a unique opportunity to directly detect reaction products during peroxide crosslinking with $^{13}$C NMR. The assignment of the new signals in the spectra was facilitated by the availability of the NMR spectra of the corresponding non-labeled and labeled compounds. In earlier studies not much attention has been given to these new resonances. We will address this subject in the present chapter.

The $^{13}$C NMR spectrum of crosslinked labeled EPDM is shown in Fig. 4.3.2.1. The spectrum is complex as a result of the various chemical structures formed upon the curing the rubber chains with peroxide. The incorporation of the $^{13}$C labels gives rise to strong signals of the olefinic ENB carbons at 110 and 147 ppm (Fig. 4.3.1.2a and 4.3.1.2b). At higher expansion a doublet splitting is visible, caused by the $^{13}$C–$^{13}$C $J$ coupling over the double bond. The signal intensities of the labeled olefinic carbons are similar to the natural-abundance $^{13}$C NMR signals of the aliphatic carbon atoms in the rest of the EPDM chain. As shown in Fig. 4.1.3.1.2d, these natural-abundance signals can be suppressed by use of INADEQUATE NMR technique, which selects
the signals of $J$-coupled $^{13}$C–$^{13}$C spin pairs only (Chapter 2). The suppression is based on the fact that the statistical occurrence of natural-abundance $^{13}$C–$^{13}$C pairs at neighboring positions along the chain is extremely low. In addition to the two major olefinic signals, partially overlapping weaker signals are present in the spectrum of $^{13}$C labeled EPDM before crosslinking. The overlapping doublets around 111 and 147 ppm are attributed to the presence of both the $E$ and $Z$ isomers of the ENB in the EPDM.\(^7\)

The spectra of the labeled ENB-EPDM after crosslinking shown in 4.3.1.2c contain new signals. To exclude that these merely arise from the decomposed peroxide a model compound prepared form 5-methylnonane, hydrogenated ENB and peroxide was heated to 185 °C and the resulting material with the decomposed peroxide were investigated with $^{13}$C NMR. The resulting spectrum of the model compound contains various signals in the aliphatic, aromatic and carbonyl regions. However, none of model-compound signals coincides with relevant new EPDM signals appearing after crosslinking (vide infra). So, all new signals observed in the EPDM spectrum are related to EPDM structures rather than peroxide decomposition products.

The $^{13}$C NMR spectrum after crosslinking is complex and it is hardly possible to assign individual peaks. Instead, we will separately discuss different groups of resonances. We have used group-contribution calculations (ACD Labs) to elucidate the structures formed upon crosslinking. The discussion will concentrate on the clusters of new $^{13}$C NMR resonances.

ALIPHATIC REGION (0 – 40 ppm)
As shown in Fig. 4.3.2.1, the spectrum is characterized by the strong aliphatic peaks (10-40 ppm) that are readily assigned to the EP backbone\(^20\) (which will not be discussed in detail here) and by the peaks of saturated carbons (40-65 ppm) as a result of the addition reaction. The aliphatic EPM part of the NMR spectrum appears unchanged after crosslinking. This is expected, because the amount of ENB involved in the system is low. Even in the INADEQUATE spectra, i.e. with suppression of the natural-abundance signals, no new aliphatic peaks are observed after crosslinking, at least not with significant intensities above the INADEQUATE error level associated with the imperfect suppression of the $^{13}$C background signals (not shown). The NMR signals from the allylic carbon atoms of cured ENB may be obscured by the other large signals from the aliphatic carbons in the ethylene and propylene monomeric units of EPDM.

OLEFINIC REGION (100 -150 ppm)
In addition to the above discussed olefinic signals already visible for non-crosslinked $^{13}$C labeled EPDM, new olefinic peaks can be seen at strong magnification of the spectra. The magnified
165-100 ppm olefinic range is shown in Fig. 4.3.2.2. Resonances of labeled carbons are well distinguishable in the spectra before and after crosslinking. In addition to the signals from the $E$ and $Z$ isomers of the ENB third monomer (Fig. 4.3.2.2b), new resonances of the structures with intact unsaturation are present around in this spectral range.

Pairs of doublets show up in the olefinic region at 115, 142 and 155 ppm. Clearly, these signals prove that the double bond is intact, but the chemical structure near the double bond has changed.

![Figure 4.3.2.2 Olefinic region of $^{13}$C NMR spectra of $^{13}$C labeled EPDM: (a) before crosslinking (with unreacted peroxide), (b) after crosslinking and solvent extraction of the peroxide decomposition products and (c) model compound sample with decomposed peroxide.](image)

These results provide strong evidence for a third reaction pathway for the peroxide crosslinking of EPDM, namely crosslinking after radical formation at the allyl positions C3 and C9 next to the double bond in the ENB units. Hydrogen atoms at allyl positions are known to be relatively
easy to abstract by radicals. On the basis of chemical-shift prediction calculations we assign the new signals on the downfield side (higher shift values) of the 147 ppm line to olefinic C2 carbons with crosslinks at the C3 position, and those at the upfield side to C2 carbons with crosslinks at the C9 position. Both C3 and C9 crosslinks give rise to new C8 signals downfield from the initial signal position.

CARBONYL REGION (> 160 ppm)

The termonomer content of EPDM is important for peroxide curing since this is the source of easily abstractable hydrogen atoms which are useful in crosslinking. The unsaturation has a significant impact on the resistance to aging as well. Upon exposure to high temperature a keton resonance is observed around 207 ppm (see Fig. 4.3.2.3c).

*Figure 4.3.2.3* Carbonyl region of $^{13}$C NMR spectra of EPDM: (a) crosslinked non-labeled, (b) non-crosslinked $^{13}$C labeled air-exposed at high temperature, (c) crosslinked $^{13}$C labeled, (d) INADEQUATE for crosslinked $^{13}$C labeled, and (e) the model compound sample.
As also confirmed by the INADEQUATE spectrum (Fig. 4.3.2.3d) this keton arises from oxidation of the double bond reaction, but the neighboring $^{13}$C atoms stay still connected. Also carboxylic signals are observed between 175 and 180 ppm. The fact that these are only visible for

![Graph](image)

**Figure 4.3.2.4** Aliphatic region of $^{13}$C NMR spectra of EPDM: (a) crosslinked non-labeled, (b) non-crosslinked $^{13}$C labeled, (c) crosslinked $^{13}$C labeled, (d) INADEQUATE for crosslinked $^{13}$C labeled and, (e) model compound sample.
the $^{13}$C labeled samples, but do not show up in the INADEQUATE spectrum, indicates that this type of oxidation cleaves ENB at the double bond position. There are two types of oxidation: ENB can either be oxidized directly as a result of exposure to oxygen, or the carbonyl structures can be formed as an indirect result of the peroxide. In the latter case oxygen reacts with the peroxide-induced polymer radicals before these can couple and form crosslinks. The product formed can further decompose on heating to break the polymer backbone. The termonomer thus offers sites that are readily oxidized and can yield products that alter the properties of the rubber. The only effective way to avoid this would be to exclude oxygen from the crosslinking press.

ALCOHOL REGION (60-85 ppm)

Small new signals are also present in the 60-85 ppm range after crosslinking. These are resonances that can be related again to the oxidation. The new alcohol signals are larger than some of the new signals associated with the crosslink structures. This could mean that the amount of oxidation may be larger than the amount of crosslinking. There are two possibilities to form such oxidation products: the oxidation of the EPM chain and the oxidation of the double bond of the third monomer in the presence of peroxide. The peroxide involves the abstraction of the most labile hydrogen atoms. Two types of labile hydrogen atoms are present in EPDM: the one on the tertiary carbon of propylene units and the C atom in position $\alpha$ to double bonds of ENB. ENB, as it is incorporated in the EPDM, can be oxidized also due to the presence of oxygen in the rubber sample. All the signals that are related to the labeled carbons can be found in the INADEQUATE spectrum (Fig. 4.3.2.4d). Since this type of experiment is selecting only the signals from neighboring $^{13}$C atoms, the new signals in the 60-85 ppm range must be associated with alcohols at the (labeled) C2 and C8 positions in the ENB units.

![Figure 4.3.2.5](image)

**Figure 4.3.2.5** Aliphatic region of $^{13}$C NMR spectra of crosslinked EPDM: (a) one step and (b) step-wise
Taking in account that the amount of sample used for these experiments is small and that the compound has been crosslinked in steps, we show in Fig. 4.3.2.5 the comparison with the sample crosslinked in one step. As expected, the spectrum of the latter shows less intensity for the oxidized structures. It is also a proof that the oxidation signals for the step-wise vulcanized sample are caused by the step-wise sample preparation (too much contact with air).

### 4.3.3 Reaction mechanism

$^{13}$C NMR spectroscopy of peroxide cured labeled EPDM discussed above has provided information on the structure formed during peroxide crosslinking. In this process, thermal energy causes the oxygen-oxygen bond in the peroxide molecule to break, yielding two radicals. These radicals abstract H-atoms from the EPDM polymer, both at the CH$_2$ and CH units in the EPM main chain and at the allylic positions of the diene unit, yielding EPDM alkyl and allyl macro-radicals. Via combination reactions, the two radicals come into contact and form a covalent bond or crosslink between the polymer chains. The allylic H-atoms of the diene monomer will have a higher intrinsic reactivity for H-abstraction than the aliphatic H-atoms of the EPM chain. The addition reaction reduces the amount of unsaturation by the attachment of the radical to one of the carbon atoms involved in a double bond. The conversion of the ENB unsaturation observed in our present study is consistent with the crosslinks via addition as shown in Fig. 4.1.1. Obviously, the combination reaction as shown in Fig. 4.1.1 does not involve the labeled ENB unsaturation and thus, the combination structures formed are not observed by $^{13}$C NMR. The new olefinic structures indicate that addition reactions occur in close proximity of the ENB unsaturation, but without the unsaturation being consumed. Most probably, H-abstraction by the primary and secondary peroxide-derived radicals not only occurs from the EPM hydrocarbon backbone, but also from the ENB allylic positions C3 and C9. Combination of these allylic radicals with other allylic radicals or with EPM backbone allyl radicals results in crosslinks involving the ENB unsaturation without consuming it. Thus the mechanism as shown in Fig. 4.1.1 has to be expanded (Fig. 4.3.3.1).

A recent low molecular weight model study, using hydrogenated ENB and alkanes as low molecular weight models for the EPM chain and ENB in EPDM, respectively, confirms that combination crosslinking involves both allyl and alkyl radicals, yielding ~25 % alkyl/alkyl, ~25 % allyl/allyl and ~50 % allyl/alkyl combination crosslinks. Of course, it is well known that
allylic H-atoms are more susceptible towards H-abstraction than aliphatic H-atoms, because of resonance stabilization of the former. However, since alkyl hydrogen occurs by far more often in EPDM, the difference in reactivity on a molecular basis is not that large.

Figure 4.3.3.1 Mechanism for peroxide crosslinking of EPDM, including EPM and diene derived macro-radicals.

4.4 Conclusions

We have cured $^{13}$C-labeled ENB-EPDM with peroxide in a stepwise manner and investigated the subsequent crosslinking states by use of MAS $^{13}$C NMR spectroscopy and $^1$H NMR $T_2$ relaxometry. Comparison of the ENB conversion and the crosslink formation as a function of
time indicates that the initial network formation is dominated by combination of the macro-
radicals produced by the peroxide decomposition. In a later stage addition of macro-radicals to
the ENB unsaturation takes over. The availability of ENB-EPDM with $^{13}$C labels at the olefinic
C2 en C8 positions in ENB has offered a unique opportunity to study the new chemical
structures under peroxide curing which involve the ENB unsaturation. A special NMR
technique, INADEQUATE, was used, which is selective for neighboring $^{13}$C−$^{13}$C spin pairs
only, and filters away the natural abundance $^{13}$C NMR signals of the ethylene and propylene
moieties. As turns out, the ENB unit is not only involved in the generally accepted crosslinking
pathway via addition, but also in a novel pathway in which crosslinking occurs via the allylic
positions.

### 4.5 References

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Chapter 5

Effect of coagents in peroxide - cured EPDM rubber

Abstract

Coagents are used to increase the peroxide efficiency and reach improved mechanical properties. The effect of four different coagents, N,N’-m-phenylenebismaleimide (HVA-2), triallylcyanurate (TAC-70), zinc dimethacrylate (ZDMA) and trimethylolpropane trimethacrylate (TRIM), has been investigated in EPM and EPDM by use of $^1$H NMR relaxometry, $^{13}$C NMR spectroscopy and mechanical measurements. The results show that TAC and HVA-2 have an increasing effect on the crosslink density, while TRIM and ZDMA had hardly and decreasing effect, respectively. The latter results are unexpected, but the network density determined with NMR is also confirmed by the mechanical properties. Small coagent signals can be observed with MAS $^{13}$C NMR prior to the crosslinking. The disappearance of these signals after crosslinking shows that the coagents are chemically converted in the process. No new coagent signals are observed in the $^{13}$C NMR spectrum after crosslinking, which indicates that the coagents become scrambled over various chemical structures at too low concentration to be observable with NMR.
5.1 Introduction

EPDM rubber is one of the most used synthetic rubbers for light-, ozone- and heat-resistant applications. The properties of this elastomer can be modified by adjusting the copolymer structure, including the ethylene/propylene ratio and the content and type of diene. EPDM can be crosslinked by both sulfur and peroxide curing agents. Traditionally, sulfur vulcanization is applied, which however suffers from S-S bond cleavage at elevated temperatures. Peroxide cure results in more thermally stable networks. Together with the peroxides coagents can be added to improve the crosslinking efficiency.$^{1,2}$ The appropriate co-agent in combination with a peroxide can improve properties such as dynamic flexibility, tear resistance, and tensile strength to a level comparable or superior to those of sulfur-vulcanized systems, but with much better heat stability.$^3$ The use of coagents in peroxide-cured formulations has enlarged the range of applications of the corresponding crosslinked rubber. In addition, by applying a coagent the level of relatively expensive peroxide can be reduced, whilst maintaining the crosslink density.

Coagents are multi-unsaturated compounds, highly reactive towards free radicals. Usually, coagents for peroxide crosslinking are divided in two classes:$^4$

Type I: Addition and hydrogen abstraction reactions: these coagents 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 the onset of crosslinking takes place very fast, which sometimes can be a disadvantage. By using this kind of coagents not only the rate of cure is increased, but also the crosslink density. A disadvantage of some Type I co-agents is the low compatibility with the polymer matrix due to their high polarity. Some examples of Type I co-agents are: acrylates, methacrylates, the corresponding zinc salts and bismaleimides.

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 coagents. The use of these co-agents leads to an increase in crosslink density of the vulcanizates but, unlike Type I, they are not capable of increasing the cure rate. Due to their low polarity, these co-agents usually have a good compatibility with elastomers. Some examples are: high-vinyl 1,2-polybutadiene, divinylbenzene, allyl esters of cyanurates and sulphur.

Certain requirements for elastomers have lately become important to the rubber industry. Some of these issues concern higher temperature resistance for automotive applications, compounding without oil and reduction of toxic and volatile species in mixing, milling and molding operations.
As far as the effect of the different types of coagents on processing is concerned, it appeared that usually allyl-containing derivatives, methacrylates and polymers with high vinyl content will reduce the viscosity of a rubber compound.

These low molar mass compounds act, more or less, as a plasticizer and facilitate easier processing of the rubber compound. In general, methacrylate compositions can be expected to exhibit an enhanced tendency to scorch, whereas, allyl-containing compounds behave more or less indifferently.11

The way in which coagents affect the peroxide crosslinking mechanism and efficiency have been a topic of debate for many years. According to some authors, the coagent forms crosslinks without the consumption or deactivation of macroradicals. Therefore, the links formed by coagent molecules connected to two or three polymer chains can be considered as extra crosslinks.5 Most of the coagents are relatively polar materials and are not readily miscible with non-polar rubber formulations.6,7 Therefore, a significant portion of the coagent is anticipated to phase separate into distinct domains, where homopolymerization will occur.4 The total concentration of curatives seldom exceeds the peroxide level. A wide range of coagents is available to effectively boost the peroxide curing efficiency.8

There are various possible chemical mechanisms for coagents to react. Since all common coagents contain terminal unsaturations, one may expect addition, abstraction and radical polymerization reactions as the principal mechanisms by which coagents react during peroxide cure of a rubber compound. This has been confirmed by studies in which loss of coagent unsaturation during peroxide cure has been observed.9,10 Depending on their chemical class, coagents react in peroxide-crosslinked unsaturated elastomers either by addition and hydrogen abstractions (e.g., [meth]acrylate compounds), or by an addition reaction only (e.g. allyl-containing compounds and sulfur).11 Detailed insight in how coagents enhance the crosslink density during peroxide cure is still lacking. The occurrence of side reactions, such as “alternating intra-molecular polymerization or cyclopolymerization reaction” in the case of TAC and other di/tri allyl-containing compounds, further complicates the chemistry.12 In fact, the residual diene unsaturation in EPDM can be viewed as a sort of coagent already connected to the rubber chain. Actually diene and coagents will compete for the same macroradicals.

The aim of this study is to investigate the effect of different types of coagents on the density and heterogeneity of the network, as well as the chemical structures formed in peroxide-cured
Chapter 5

EPDM. The various EPDM-coagent systems have been characterized by means of $^1$H NMR relaxometry and MAS $^{13}$C NMR spectroscopy and mechanical measurements.

5.2 Experimental section

5.2.1 Samples composition and preparation

The chemical composition of the samples consisting of EPM (K3200A – 0 % ENB) and EPDM (K4802 - 4.5 % ENB) both produced by DSM Elastomers B.V., cured with di(tert.butyl peroxy isopropyl)benzene and a coagent, is given in Table 5.2.1.1. The peroxide was used as a 40 % master-batch (Perkadox14-40 MB-GR, from Akzo Nobel). Four types of coagents have been used: N,N’-$m$-phenylenebismaleimide (HVA-2), triallylcyanurate (TAC-70), zinc dimethacrylate (ZDMA) and trimethylolpropane trimethacrylate (TRIM). Their chemical structures are shown in Fig. 5.2.1.1.

<table>
<thead>
<tr>
<th>EP(D)M</th>
<th>HVA (phr)</th>
<th>TAC (phr)</th>
<th>ZDMA (phr)</th>
<th>TRIM (phr)</th>
</tr>
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<td>+Px14-40</td>
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<td>1</td>
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<td>2.5</td>
<td>2.5</td>
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</tr>
</tbody>
</table>

The peroxide and coagent levels are given in parts per hundred rubbers (phr). For the EPM and EPDM series, the peroxide content was chosen to be 2.5 and 5 phr, based on the common industrial practice. The constituents were mixed in the EP(D)M on an open mill at low temperatures and the compounds were crosslinked in a hot press at 175 °C for 17 minutes, providing full cure to all samples.
Coagents effect on EPDM network density and properties

Figure 5.2.1.1 Chemical structures of the coagents used: (a) HVA-2, (b) TAC, (c) ZDMA, and (d) TRIM

5.2.2 $^1$H NMR Hahn-echo relaxometry

The experimental conditions for $^1$H NMR transverse magnetization relaxation and the calculation of the crosslink density are described in Chapter 2.2.1.

5.2.3 $^{13}$C NMR spectroscopy

Magic-angle spinning (MAS) $^{13}$C NMR spectra were recorded on a Bruker DMX500 spectrometer at a $^{13}$C NMR frequency of 125 MHz. A 4-mm MAS probehead was used with a sample rotation of 8 kHz. The spectra were acquired by means of a single-pulse excitation with a 90° pulse of 5 µs and recycle delay time of 5 s, which proved to be long enough for quantitative measurements. The experiments were performed at room temperature and 90 °C for the non-crosslinked and crosslinked samples, respectively.

5.2.4 Mechanical measurements

The compounds were fully cured in an MDR 2000 E rheometer from Dynisco (formerly Alpha Technologies) at 175 °C to measure the increase in torque during curing, according to ISO 6502. The vulcanizates were characterized by measurement of hardness, tensile properties and
compression sets at 23 °C and 70 °C according to DIN53505, ISO37 and ISO815, respectively.\textsuperscript{13} For the modulus at 100 % elongation, the tensile strength and the elongation at break, the median value of 5 experiments is presented.

### 5.3 Results and discussion

#### 5.3.1 Total network density

The primary objective of this study is to investigate the effect of different types and levels of coagents on the crosslink density and network heterogeneity of peroxide-cured EPM and EPDM rubber. The network density has been obtained from the $T_2$ relaxation for samples without and with HVA-2, TAC, ZDMA and TRIM, as described in Chapter 2.2.1. As we will demonstrate later, the NMR experiments show that for EPM the crosslink density has increased for all the four coagents. The same behavior occurs for the EPDM series in the presence of TAC and HVA-2, whereas, unexpectedly, the crosslink density is decreased for ZDMA and there is hardly any effect of TRIM.

To exclude preparation-related errors, the samples with ZDMA and TRIM which show the reduction in crosslink density have been prepared in duplo and measured according to the same procedure. Within experimental error the results show the same effect for the duplo samples. The values obtained for the total crosslink density are shown in Table 5.3.1.1 for comparison. These results are confirmed also by mechanical properties that have been measured for all the samples. The values of torque, hardness, tensile strength, modulus, elongation at break, tear strength and compression sets at 23 and 70 °C are given in Table 5.3.1.2

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>$D_{tot}$ (mmol/kg)</th>
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<tr>
<td></td>
<td>1\textsuperscript{st} set</td>
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<tr>
<td>EPM</td>
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<tr>
<td>EPDM</td>
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<td>EPDM + 1 phr TRIM</td>
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<tr>
<td>EPDM + 2.5 phr TRIM</td>
<td>331</td>
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</tbody>
</table>

Table 5.3.1.1 Total crosslink density for the two sets of samples in the presence of ZDMA and TRIM
Table 5.3.1.2 Mechanical properties for the two sets of samples, in the presence of coagents. The second set consists of the duplo samples with ZDMA and TRIM.

<table>
<thead>
<tr>
<th>Set</th>
<th>Coagent</th>
<th>Torque (Nm)</th>
<th>Hardness (ShA)</th>
<th>Tensile strength</th>
<th>M100 (MPa)</th>
<th>Elong. at break (%)</th>
<th>Tear strength (N)</th>
<th>CS 23 (%)</th>
<th>CS 70 (%)</th>
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</thead>
<tbody>
<tr>
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<td>HVA-2</td>
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<tr>
<td></td>
<td>TAC</td>
<td>1.15</td>
<td>47.1</td>
<td>1.5</td>
<td>1.1</td>
<td>211</td>
<td>9.4</td>
<td>6.6</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>ZDMA</td>
<td>1.48</td>
<td>50.8</td>
<td>1.8</td>
<td>1.3</td>
<td>229</td>
<td>11.3</td>
<td>5.2</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td>ZDMA</td>
<td>1.41</td>
<td>50.8</td>
<td>2</td>
<td>1.2</td>
<td>268</td>
<td>11.7</td>
<td>6.1</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>TRIM</td>
<td>1.55</td>
<td>51.6</td>
<td>1.9</td>
<td>1.3</td>
<td>217</td>
<td>11.1</td>
<td>4.3</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>TRIM</td>
<td>1.56</td>
<td>51.9</td>
<td>2.1</td>
<td>1.3</td>
<td>221</td>
<td>11.8</td>
<td>5.6</td>
<td>7.5</td>
</tr>
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<td>2nd</td>
<td>ZDMA</td>
<td>1.65</td>
<td>51.8</td>
<td>1.9</td>
<td>1.2</td>
<td>241</td>
<td>11.2</td>
<td>3.9</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>ZDMA</td>
<td>1.59</td>
<td>51.7</td>
<td>2</td>
<td>1.2</td>
<td>234</td>
<td>12.5</td>
<td>5.1</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td>TRIM</td>
<td>1.72</td>
<td>52.5</td>
<td>1.8</td>
<td>1.3</td>
<td>196</td>
<td>10.9</td>
<td>3.2</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>TRIM</td>
<td>1.77</td>
<td>54</td>
<td>2</td>
<td>1.4</td>
<td>166</td>
<td>11.9</td>
<td>3.8</td>
<td>7.1</td>
</tr>
</tbody>
</table>

It is unexpected to obtain hardly any effect of TRIM and a decreasing effect of ZDMA on $D_{tot}$. These limited effects could have the following explanations. The peroxide-cured EPDM rubber was shown to result in a very heterogeneous network, even without adding the coagents. The coagents have the tendency to homopolymerize and therefore they can generate an additional heterogeneity by competing for the unsaturation of the diene monomer and the one of the coagent. This will result in an inefficient use of the radicals. Another comment that we can make is that we have used non-filled (e.g. carbon black) compounds. In commercial applications there is always a substantial amount of carbon black mixed into the EPDM. This filler behaves far more polar than the EPDM and therefore will also have a dispersing or compatibilizing effect on the coagents to reduce the amount the amount of clustering by homopolymerization.

It was found in a previous work that also other coagents, like the bis(allyl)ether of ethylene glycol, AEGA (CH$_2$=CHCH$_2$-O-CH$_2$CH$_2$O-CH$_2$CH=CH$_2$) and the bis(allyl)ether of 1,4-butandiol, ABUGA (CH$_2$=CHCH$_2$-O-(CH$_2$)$_4$-O-CH$_2$CH=CH$_2$), hardly improve the crosslinking efficiency.$^5$ Because IR spectra did not show visible absorbances of the coagent, it was concluded that these coagents evaporated as a result of their high volatility. Furthermore, it has been found that that at low coagent concentrations the equilibrium-swelling ratio remained constant or was slightly increased, indicating similar or slightly decreased network density. This effect was explained by different reactions of allyl groups towards macroradicals at various
coagent concentrations. When the largest part of the coagent was molecularly dispersed (< 10 phr), radical transfer or rearrangement reactions may prevail, whereas radical addition reactions may dominate when the coagent resides predominantly in domains.\(^5,14,15,16,17,18\) In these domains, a substantial part of the peroxide would dissolve, causing thermosetting of coagent molecules during crosslinking, without efficient co-curing of the EPDM matrix. Thus, when large coagent domains are present, a considerable amount of the crosslinker is concealed from the elastomer, leading to inefficient crosslinking.

Loan\(^19\) and also Baldwin et al.\(^20\) suggested that TAC reacts in EP(D)M peroxide cures via hydrogen transfer of the coagent allyl moieties to macroradicals. This conclusion was adopted by Keller without any experimental support.\(^21\) Simůnková et al.\(^22\) studied the peroxide crosslinking of PE in the presence of various coagents by sol-gel analysis and vulcametry. They concluded that TAC was incorporated as single coagent bridges, according to a radical addition-abstraction mechanism. According to this mechanism, an allyl moiety is added to a macro-radical, followed by a fast hydrogen abstraction from the polymer matrix, after which repeating of this reaction sequence with a second or third allyl moiety of the same TAC molecule yields a single coagent bridge.

As generally recognized nowadays, coagents can homopolymerize in domains which may be crosslinked with the polymer matrix at the interface.\(^23,24\) The main question is whether various coagents crosslink with the polymer and enhance efficiently the crosslink density. As shown in previous chapters, EPDM is already a complex system without coagents.\(^25\) When adding the coagents to the network, three competing reactions take place: combination of macroradicals, addition to the diene unsaturation and addition to the coagent unsaturation. In this situation, the reaction mechanism becomes complex due to the different reaction rates and the complex kinetics. The different reactivity of the different types of coagents can have an effect on the different reaction pathways. All these can create an additional heterogeneity of the network, in efficient or inefficient ways.

**5.3.2 Coagent efficiency from \(^1\)H NMR \(T_2\) relaxometry**

The total crosslink densities of crosslinked EPM and EPDM obtained from \(^1\)H NMR relaxometry \((D_{tot}, \text{mmol/kg})\) that are determined for the various types of coagents and 2.5 phr peroxide, are plotted as function of the coagent content in Fig. 5.3.2.1. The value of \(D_{tot}\) is composed of
chemical crosslinks and chain entanglements. The number of chain entanglements has been determined for the rubbers without coagents and equals 202 mmol/kg for EPM and 263 mmol/kg for EPDM.

In Chapter 5.3.1 we have shown good reproducibility of results by comparing the data for the duplo samples. In the above mentioned results, EPM and EPDM samples were cured with 5 phr and 2.5 phr peroxide, respectively, according to the common industrial practice. For a better estimation of the coagent efficiency it is fair to compare sets of samples containing the same peroxide level. For better comparison, a new series of EPM samples has been prepared with 2.5 phr peroxide. In practice, when a coagent is used together with EPDM, a lower peroxide content is needed. Fig. 5.3.2.1 shows the total crosslink density for the mentioned compositions. In this case, again, it is found that all coagents show an increase in $D_{tot}$ in the case of EPM.

The coagent efficiency, in the case of peroxide cured EPDM, is lower when compared with the corresponding EPM samples. This is probably due to the inefficient use of the peroxide in the presence of coagents. Analogous to the reaction mechanism proposed for crosslinking of EPDM in our previous study, the crosslinks can be formed via combination and addition reactions. In the case of radical combination, two EPDM macroradicals are combined, yielding direct C–C links between the two EPDM chains. Via the addition route, an EPDM macroradical can add to a residual unsaturation of EPDM or to the one of the coagents. The reaction mechanism is

![Figure 5.3.2.1 Total crosslink density for varied coagent content for EP(D)M cured with 2.5 phr peroxide](image-url)
relatively straightforward in the case of EPM. It does not contain the third monomer and therefore, only the unsaturation of the coagents will be involved in the crosslinks between coagent molecules formed via this pathway. If coagent molecules are not uniformly distributed on the molecular level in the rubber matrix, it would result in large network heterogeneity. Highly crosslinked coagent domains could form multifunctional network junctions reducing an efficient network density of EPDM even at high conversion of coagent double bonds. It is noted that \(^1\)H NMR \(T_2\) relaxometry reflects the weight-average molar mass of the network chains, since short network chains contain obviously less hydrogen atoms. Therefore, highly crosslinked domains provide a relatively smaller contribution to \(D_{tot}\) than to long network chains. In the EPDM case competition takes place between unsaturations of EPDM diene monomers and the ones of coagents. This could result in a larger fraction of crosslinks between EPDM chains relative to linkages between coagent molecules.

For the EPM samples we were able to estimate the efficiency of the coagent, based on the additivity model described in Chapter 3. The equation for EPM samples now becomes:

\[
D_{CC} = D_{CC\,comb} + D_{CC\,add\,coag}
\]  

(5.1)

where \(D_{CC\,comb}\) is the amount of crosslinks formed via combination reactions and \(D_{CC\,add\,coag}\) is the amount of crosslinks formed by the contribution of coagent via the addition pathway. \(D_{CC\,comb}\) has been determined (31 mmol/kg) for the EPM sample without coagent, cured with the same amount of peroxide. Comparing the obtained chemical crosslink density with the one for the corresponding EPDM sample without coagent, the coagent efficiency for EPM can be calculated in terms of mmols coagent or unsaturations of coagent per kg of EPDM. It is defined as the number of crosslinks formed via addition to the coagent over the amount of coagent in mmols. The efficiencies obtained for EPM cured with 2.5 and 5 phr peroxide are given for different coagents in Table 5.3.2.1.

As can be seen in Fig. 5.3.2.2, the highest efficiency, 32 %, is found for TAC while it decreases with increasing coagent content for all samples. When 5 instead of 2.5 phr peroxide was used the highest efficiency for TAC was 23 %. The loss of the efficiency is probably caused by more side-reactions which will not result in real crosslinks. It is not possible to make the same type of
calculations for the EPDM samples because it is impossible to distinguish between the two types of addition reactions.

Table 5.3.2.1 Total crosslink density, chemical crosslink density and coagent efficiency for various compositions of EP(D)M samples. Density of chain entanglements of 202 and 263 mmol/kg for EPM and EPDM, respectively, contribute to \( D_{\text{tot}} \).

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>( D_{\text{tot}} ) (mmol/kg)</th>
<th>( D_{\text{CC}} ) (mmol/kg)</th>
<th>( D_{\text{CC add coag}} ) (mmol/kg)</th>
<th>Efficiency of coagent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPM with 2.5 phr Px</td>
<td>233</td>
<td>31</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>EPM + 1 phr HVA</td>
<td>243</td>
<td>42</td>
<td>11</td>
<td>14</td>
</tr>
<tr>
<td>EPM + 2.5 phr HVA</td>
<td>254</td>
<td>52</td>
<td>21</td>
<td>11</td>
</tr>
<tr>
<td>EPM + 1 phr TAC</td>
<td>271</td>
<td>70</td>
<td>39</td>
<td>32</td>
</tr>
<tr>
<td>EPM + 2.5 phr TAC</td>
<td>278</td>
<td>76</td>
<td>45</td>
<td>15</td>
</tr>
<tr>
<td>EPM + 1 phr ZDMA</td>
<td>246</td>
<td>44</td>
<td>13</td>
<td>15</td>
</tr>
<tr>
<td>EPM + 2.5 phr ZDMA</td>
<td>263</td>
<td>62</td>
<td>31</td>
<td>15</td>
</tr>
<tr>
<td>EPM + 1 phr TRIM</td>
<td>244</td>
<td>43</td>
<td>12</td>
<td>13</td>
</tr>
<tr>
<td>EPM + 2.5 phr TRIM</td>
<td>244</td>
<td>43</td>
<td>12</td>
<td>5</td>
</tr>
<tr>
<td>EPM with 5 phr Px</td>
<td>257</td>
<td>56</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>EPM + 1 phr HVA</td>
<td>272</td>
<td>71</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>EPM + 2.5 phr HVA</td>
<td>273</td>
<td>72</td>
<td>16</td>
<td>9</td>
</tr>
<tr>
<td>EPM + 1 phr TAC</td>
<td>285</td>
<td>83</td>
<td>27</td>
<td>23</td>
</tr>
<tr>
<td>EPM + 2.5 phr TAC</td>
<td>298</td>
<td>96</td>
<td>40</td>
<td>13</td>
</tr>
<tr>
<td>EPM + 1 phr ZDMA</td>
<td>264</td>
<td>62</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>EPM + 2.5 phr ZDMA</td>
<td>276</td>
<td>75</td>
<td>19</td>
<td>9</td>
</tr>
<tr>
<td>EPM + 1 phr TRIM</td>
<td>262</td>
<td>60</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>EPM + 2.5 phr TRIM</td>
<td>261</td>
<td>60</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>EPDM with 2.5 phr Px</td>
<td>363</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPM + 1 phr HVA</td>
<td>367</td>
<td>104</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPM + 2.5 phr HVA</td>
<td>384</td>
<td>121</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPM + 1 phr TAC</td>
<td>373</td>
<td>110</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPM + 2.5 phr TAC</td>
<td>385</td>
<td>122</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPM + 1 phr ZDMA</td>
<td>358</td>
<td>94</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPM + 2.5 phr ZDMA</td>
<td>347</td>
<td>84</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPM + 1 phr TRIM</td>
<td>361</td>
<td>97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPM + 2.5 phr TRIM</td>
<td>365</td>
<td>102</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The improvement of the crosslinking efficiency for EPM can be explained by the favorable influence that coagents exhibit in suppressing unwanted side reactions of polymer radicals. The most common side reactions to be expected are disproportionation and scission of the polymer radical. In case of a disproportionation reaction (the chemical reaction in which the same compound is simultaneously reduced and oxidized), one H atom is transferred from one polymer...
radical to another, instead of establishing a crosslink between the two polymer chains. This results in the formation of one saturated and one unsaturated chain unit in the polymer molecule. Although the latter species may act as a weak coagent, the overall result is the loss of one peroxide moiety.

![Chemical crosslink density for varied coagent content for the EP(D)M cured with different peroxide levels](image)

**Figure 5.3.2.2** Chemical crosslink density for varied coagent content for the EP(D)M cured with different peroxide levels

A chain scission reaction (the breaking of a molecular bond causing the loss of a side group or shortening of the overall chain) requires the presence of two adjacent propylene moieties. The C-C bond between the secondary and tertiary C atoms next to the tertiary C atom carrying the radical is broken up. The final result is the formation of two shorter chains, one with a terminal double bond and one with a radical C atom. This also eventually results in a less efficient crosslinking reaction.

### 5.3.3 Correlation of the network density with mechanical properties

The effect of coagents on vulcanizate properties can be considerable and depends not only on the type of coagent used, but also on the type of polymer and the type of crosslinking peroxide.\(^{26}\)
With respect to mechanical properties of the rubber compound after cure, a marked influence of coagents is known, which is usually reflected by increased hardness and modulus values, whereas the elongation at break is reduced.

Upon application of coagents the compression set is usually improved. The combination of good processability and high hardness before and after crosslinking can be achieved by combining an elevated level of methacrylate coagents and a peroxide-based cure system.27

Differences in the network heterogeneity, i.e. the spatial distribution of the crosslinks and the presence of defects in the network structure, will have a large influence on mechanical properties. Therefore, the relationships between the average crosslink density as determined by NMR and the physical properties are not always straightforward. Nevertheless, some correlations can be established.

Fig. 5.3.3.1 shows the all the physical properties measured for all the crosslinked samples at different peroxide and coagent levels versus the total crosslink density as determined by NMR. Although the data for the EPM and EPDM samples in Fig. 5.3.3.1 fall apart, the crosslink density turns out to be the single factor determining the mechanical properties, within experimental errors, irrespective of the type of co-agent.28 In Chapter 3 was shown that even across a series of EPDM samples with different diene type and concentration and different peroxide contents the physical properties correlated well with the total network density determined from NMR, in a way consistent with existing network models. This conclusion can now be expanded to compounds with coagents.

The rheometer torque is a quantitative means to measure the crosslink density of the cured samples. The rheometer torque correlates with the NMR total network density in a linear fashion. In the case of coagent containing samples (Fig. 5.3.3.1a) a linear behavior holds also for all samples.

It appears first from the results that considerable differences exist between various EPM and EPDM types. Elastomers crosslinked in the presence of coagents show higher modulus and hardness than in absence (see Fig. 5.3.3.1b and 5.3.3.1d), except the EPDM samples containing ZDMA. Also enhanced compression sets (see Fig. 5.3.3.1g and Fig. 5.3.3.1h) are obtained for TAC and HVA-2 as a sign of a higher state of cure. The changes in tensile strength (Fig. 5.3.3.1c) are small since modulus increase leads to a decrease in elongation at break (Fig.
5.3.3.1e). In most cases, tensile strength of peroxide-cured compounds is barely influenced by the addition of the coagents.

![Graphs](image-url)

**Figure 5.3.3.1 (i)** Correlation between the total crosslink density and mechanical properties (torque, hardness, tensile strength, and modulus at 100 % elongation). The dotted line is guide to the eye.

The increase of the network chain length between crosslinks due to homopolymerization of coagents may lead in certain cases to higher elongation (Fig. 5.3.3.1e) at a given modulus.

The poor correlations of the tensile strength at break (Fig. 5.3.3.1c) and the tear strength (Fig. 5.3.3.1f) with the crosslink density are probably due to differences in network heterogeneity in the series of samples as well as the complex origin of ultimate mechanical properties.
5.3.4 Chemistry of crosslinking in the presence of coagents

$^{13}$C NMR spectroscopy is useful for the structural elucidation of polymeric compounds. $^{29,30}$ One goal of this part of the study is to get insight in the structures of the chemical crosslinks and other products formed during coagent assisted peroxide cure of EP(D)M, and to possibly detect new types of structures formed after crosslinking EPDM in the presence of coagents. We have recorded spectra for the compounds before and after crosslinking in order to follow the
conversion of the added coagents. Spectra of the non-crosslinked samples were recorded at room temperature in order to avoid any crosslinking reactions during the measurement. A detailed study of the diene conversion is presented in Chapter 4 of this thesis where we highlight the new types of chemical structures formed after crosslinking.

The main emphasis is on the EPDM containing TRIM and ZDMA because of the unexpected results from $T_2$ relaxometry, namely a decrease in the network density in the presence of these coagents (see Fig. 5.3.4.1 and 5.3.4.2, respectively).
Figure 5.3.4.2 $^{13}$C NMR spectra of the pure ZDMA coagent and EPDM sample containing ZDMA, before and after crosslinking, as indicated for every spectrum. Multiplication factors are given on the right-hand side of the figure.

All spectra are characterized by the strong aliphatic peaks (10-40 ppm) that are readily assigned to the EPM backbone $^{31}$ and will not be discussed in detail here. The aliphatic part of the NMR spectrum appears unchanged after crosslinking. This is as expected, because the amount of ENB and coagents involved in the system is low: 4.5 % ENB and 1 and 2.5 phr coagent. Another characteristic of all the spectra shown in the following figures is the presence of the C2 and C8 olefinic carbons at about 111 and 147 ppm. Again, conversion of this unsaturation is not discussed here.

For comparison we have recorded the $^{13}$C spectrum of the pure TRIM coagent at room temperature. It is characterized by the existence of the aliphatic and three intense olefinic, ester and carbonyl peaks. The same three peaks are found back in the non-crosslinked sample, as a
proof that the coagent has been incorporated in the rubbery matrix. The same position is found for the peaks at 125, 136 and 166 ppm. If compared to the spectrum after crosslinking, only the peaks from the diene third monomer are observed in the olefinic range, due to incomplete conversion.

![Figure 5.3.4.3](image)

**Figure 5.3.4.3** $^{13}$C NMR spectra of the EPDM sample containing TAC, before and after crosslinking, as indicated for every spectrum. Multiplication factors are given on the right-hand side of the figure.

Even in the spectrum recorded at 90 °C there are no new signals from structures in which the unsaturation of the coagent could be involved. This is probably caused by the large variety of chemical structures formed, and the resulting “scrambling” of NMR intensity below the spectral noise level. Note also that we have used small amounts of coagents to avoid the formation of phase-separated homo-polymerized coagent domains. The explanation for the lack of density enhancement in the case of TRIM assisted EPDM could be that the unsaturation of TRIM is inefficiently used together with the peroxide, without forming crosslinks that will contribute to the mechanical properties.

The same procedure has been followed for the sample containing the highest amount of ZDMA (see Fig. 5.3.4.2). The pure coagent was dissolved in ethanol. The spectrum shows two intense peaks that are assigned to the solvent used and other weak signals at 123, 133 and 175 ppm. The
intensity is low already in the pure coagent. For this sample it was also difficult to identify new structures formed after crosslinking. One explanation could be that ZDMA is a Zn salt and does not dissolve in the rubber.

Figure 5.3.4.4 $^{13}$C NMR spectra of the EPDM sample containing HVA-2, before and after crosslinking, as indicated for every spectrum. Multiplication factors are given on the right-hand side of the figure.

For the case of TAC (Fig. 5.3.4.3) and HVA-2 (Fig. 5.3.4.4) the recorded spectra show the presence of the coagent in the non-crosslinked compound, but no clear evidence after crosslinking. Also in view of the low concentration of coagent it is possible that very low amounts of new structures are formed and that these could not be detected with $^{13}$C NMR spectroscopy.

5.4 Conclusions

The results of the experiments described in this chapter show that the presence of the coagents TAC and HVA-2 in the EPDM network have an increasing effect on the network crosslink density. The TRIM has hardly any influence, whereas ZDMA had a decreasing effect. These results were explained by the fact that the peroxide has been inefficently used in the latter two
cases. In the case of TRIM assisted EPDM curing, the unsaturation is probably used together with the peroxide, without forming crosslinks that will contribute to the mechanical properties. The results obtained from $T_2$ relaxometry correlate well with the mechanical properties. Small coagent signals are visible in the MAS $^{13}$C NMR spectra of EPDM coagent mixtures prior to the crosslinking. These signals disappear upon crosslinking, which shows that the coagents are chemically converted. The fact that no new $^{13}$C NMR signals are observed is interpreted as a sign that the coagents are not converted into unique reaction products, but become scrambled over various chemical structures at too low concentration to be NMR detectable.

5.5 References

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Chapter 6

EPDM-carbon black interactions and network structure in relation to stress - strain behavior

Abstract

$^1$H NMR relaxometry has been applied in order to determine the effect of carbon black on the molecular mobility of the polymer chains in EPDM compounds and the corresponding sulfur vulcanisates. The crosslink density of filled EPDM was investigated as a function of the filler type and amount. The EPDM adsorption on carbon black surface creates physical junctions which will contribute to the total network density. This contribution is small compared to that of the chemical crosslinks and chain entanglements, and is found to increase at increasing filler content and specific surface of the carbon black. The presence of the immobilized adsorption layer at the carbon black surface is proven by DQ filtered $T_2$ relaxation and spin-diffusion experiments.
6.1 Introduction

Technical elastomers represent an important class of materials with a large number of applications. The macroscopic properties of these materials can be modified by changing the crosslink density and the curing and post-curing conditions, by the addition of different types of filler particles and by tuning their distribution by modification of filler surface. The addition of fillers in rubbery materials contributes not only to the enhancement of the mechanical properties, but also to a decrease in the cost of the end-products. The presence of carbon black implies an increase in mechanical strength (for example tensile strength) in the vulcanisates, an increased stiffness and hardness of the cured products. The main contribution to mechanical properties is due to the filler volume effect and filler-filler interactions. Carbon black has little chemical interaction with aliphatic rubbers such as EPDM. The carbon black particles also physically limit the mobility of the rubber chains due to chain adsorption in the direct vicinity. The physical interactions of the rubber chains with the filler surface can provide quasi-permanent junctions in the rubber matrix, which are not removed even after extensive solvent extraction.\textsuperscript{1,2}

The generic term “carbon black” today refers to a group of industrial products consisting of furnace blacks, channel blacks, thermal blacks, and lampblacks. They are materials composed essentially of elemental carbon obtained by partial combustion or thermal decomposition of hydrocarbons in the form of near-spherical particles of colloidal sizes,
fused mainly into particle aggregates. Table 1 gives examples of a few commercial carbon blacks together with their typical average surface area as measured by nitrogen adsorption (N$_2$SA), and particle size ranges.$^{3,4}$

The performance, failure properties and appearance of a rubber product are influenced significantly by the amount of filler, its type and the dispersion of filler in the rubber. The incorporation of the filler in the rubbery matrix takes place as described in the next four steps. The first step consists in forcing the polymer into the interstices of the carbon black agglomerates to effectively encapsulate the filler. In the second step, de-agglomeration, the agglomerate size is reduced by shear forces. In the third step the individual aggregates/smaller size agglomerates are distributed throughout the polymer matrix by random patterns of mechanical mixing. The inter-aggregate separation and filler network characteristics are determined by the dispersivity of the filler within the matrix. In reality, all the stages overlap but their relative importance changes as the mixing process continues.

At the same filler concentration the effect of different carbon blacks on rubber properties are dominated by differences in carbon black-carbon black interactions and by the carbon black specific surface area (the total exposed carbon black surface per unit mass of rubber) and structure.

![Diagram](image)

**Figure 6.1.1** A simplified graphic representation of EPDM chains at the carbon black surface: low mobile monomer units (filled circles) in the carbon black-rubber interface and mobile chain units outside of the interface (open circles). The low mobile chain fragments in the interface provide adsorption network junctions for the rubber matrix. Free rubber chains can be extracted in a good solvent.
With regard to rubber-filler interactions, there is supporting evidence for the view that complex adsorption processes take place between the surface of filler particles and rubber chains. Fig. 6.1.1 shows a schematic representation of the EPDM chains near the surface of carbon black. Two microregions with strongly different local chain mobility are present in the filled rubbers: the relatively immobile rubber chain fragment which covers the filler surface (called adsorption layer) and the mobile elastomer matrix outside of this rubber-filler interphase. The rubbery fraction with carbon black is called bound rubber, contrary to the extractable rubber. Because of the physical adsorption of the elastomer chains to the filler surface, the filler particles are “glued” in the rubber matrix. Rubbery chains with multiple adsorption junctions at the filler surface cannot be extracted even at prolonged extraction in a good solvent. The filler aggregates, which are covered by the interface, can be considered as multifunctional, physical crosslinks, which provide a significant amount of adsorbed physical junctions for the elastomer matrix in close proximity to the carbon black surface.

To produce elastomers with relevant mechanical properties, the polymer chains must be chemically crosslinked. In the rubber industry accelerated sulfur vulcanization systems are generally used.

Despite numerous investigations of carbon black filled rubber by diverse techniques including mechanical tests, thermal and sorption analysis and spectroscopic methods, the molecular origin of the reinforcement effect is still under discussion. NMR methods have also been used to study the matrix-filler interface (e.g., assessment of the degree of immobilization of rubber chains, the thickness of the rubber-filler interface, the structure of the physical network, etc) and are commonly used to characterize mobility in heterogeneous polymer samples. Previous studies on filled elastomers have shown that polymer chains have a strongly diminished mobility in the neighborhood of the filler particles. Wang et al. reported for the first time the use of $^1$H multiple-quantum NMR for investigating the heterogeneity in segmental chain order of grafted polymers.

$T_2$ relaxation and Double-Quantum (DQ) type of experiments have been used to study the structure of the physical network that is formed due to chain adsorption. The methods are
based on the sensitivity to the conformational mean position of the network chains, which are formed by chemical crosslinks and physical network junctions.

The formation of immobilized adsorbed rubber layer at the surface of carbon black and which is formed due to the adsorption interactions is studied with DQ NMR and spin-diffusion experiments on bound rubber. The effect of the amount and type of carbon black on the density of physical (adsorption) junctions is studied on non-crosslinked samples. The density of chemical crosslinks is determined for the EPDM-carbon black vulcanisates.

6.2 Experimental section

6.2.1 Sample composition and preparation

K4802 from DSM (4.5 % ENB) is the EPDM grade that has been used for the preparation of the filled samples. The carbon blacks used were rubber grade furnace black N: N990, N550, N330 and N115 from Cabot Corporation. The rubber was extensively mixed with the carbon blacks and the vulcanization agents on a laboratory rolling mill at 100°C. A procedure of repetitive cutting and milling of the rubber strips was used to ensure a good carbon black dispersion. The carbon black content was varied from 20 up to 160 phr (weight parts of carbon black per hundred weight parts of rubber). For various calculations performed later on, the density of carbon black and EPDM of 1.8 g/cm³ and 0.854 g/cm³, respectively, was used. The resulting EPDM master batches with different amounts and types of carbon black were crosslinked using by sulfur and peroxide cure. The recipe for the vulcanisates contains sulfur, zinc oxide (ZnO), stearic acid, mercaptobenzothiazole (MBT-80) and tetramethyluram disulfide (TMTD-80). The peroxide-crosslinked samples were prepared as described in Chapter 3.2.1.

Preparation of the bound rubber

When an elastomer and the reinforcing filler are mixed, part of the rubber cannot be extracted even after a prolonged extraction in a good solvent mainly due to the physical adsorption and possibly a small amount of chemical crosslinks and/or grafting of rubber chains to the filler surface. Bound rubber is, by definition, the weight percent of non-extractable rubber relative to its amount in the master-batch. Free rubber is the elastomer
matrix outside of the adsorbed rubber. According to previous studies\textsuperscript{25,26} the amount of bound rubber depends on the extraction time and temperature and to a small extent on the quality of the solvent used for the extraction. Preparation of bound rubber was performed as follows. The master-batch (60 phr N115) was cut into approximately 1 mm\textsuperscript{3} pieces. About 1 g of the compound was subsequently immersed in o-xylene. The extraction of the free rubber was carried out for 30 days at room temperature. To prevent a possible degradation and/or crosslinking of the rubber due to the radicals on the carbon black surface, 0.1 wt. % of a stabilizer, 2,6-di-tert-butyl-p-cresol (DTPC) was added to the solvent. The rubber was decanted every day in the first week and a fresh solvent together with the stabilizer was added. The solvent was replaced after each three days during following 23 days of extraction. After the extraction was finished, the bound rubber was decanted and immersed in pentane twice for two days. Afterward, the bound rubber was dried for one day in an oven at 60 °C in a vacuum at 5 mB. A small flow of nitrogen was used during drying.

6.2.2 NMR experiments

The NMR experiments of samples containing different amounts of carbon black were performed on a Bruker Minispec MQ-20 spectrometer operating at a proton frequency of 20 MHz. This spectrometer was equipped with a BVT-3000 variable temperature unit. The temperature gradient and stability was about 1°C. The experiments have been performed at 90°C. The dead-time of the receiver and duration of the 90° and 180° pulses were 9 µs, 2.8 µs and 5.2 µs, respectively.

6.2.2.1 \textsuperscript{1}H NMR solid- and Hahn-echo experiments

Three types of NMR experiments have been performed for an accurate study of the mobile and immobile fractions in filled EPDM: FID (Free Induction Decay), SEPS (Solid-Echo Pulse Sequence) and HEPS (Hahn-Echo Pulse Sequence)\textsuperscript{27}. In the FID experiment, the free induction decay was recorded after a 90° pulse-excitation [90° – dead time – acquisition of the amplitude $A(t)$ as a function of time $t$ after the 90° pulse]. Knowledge of the FID shape for the immobilized fraction is required for accurate
deconvolution of the FID into components corresponding to immobilized and mobile rubber fractions. The shape of the FID for the immobilized fraction was determined by SEPS.

The SEPS $[90^\circ_x - \tau - 90^\circ_y - \tau - \text{acquisition}]$, with $\tau = 10 \mu$s, was used to record the initial part of the magnetization of the immobilized fraction of the bound rubber. The echo decay was recorded starting from the echo maximum, time $t = 0$. The SEPS has the advantage of avoiding the dead-time of the spectrometer. It allows the accurate measurement of the shape of the initial part of the FID at short times. $T_2$ relaxation up to about 100 $\mu$s was measured by this pulse sequence. The analysis of the FID, as recorded using the SEPS, has shown that the FID shape for the adsorption layer in the bound rubber is close to Gaussian. However, the SEPS does not eliminate the effect of inhomogeneity of the magnetic field $B_0$ itself and the large inhomogeneity of $B_0$ within a sample volume that arises from an inhomogeneous magnetic susceptibility of the heterogeneous sample. For this reason, SEPS as well as FID experiments cannot be used for an accurate determination of the $T_2$ relaxation times longer than about 100 $\mu$s, typical for mobile rubber chains. Therefore, the HEPS $[90^\circ_x - t_{HE} - 180^\circ_y - t_{HE} - \text{acquisition of the amplitude of maximum echo}]$ was used to record the slow part of the $T_2$ relaxation decay for the mobile rubber fraction, where the $t_{HE}$ was varied between 35 $\mu$s and 400 ms. The HEPS makes it possible to eliminate the magnetic field and chemical shift inhomogeneities and to accurately measure the $T_2$ relaxation time for the mobile region only. The HEPS experiments were performed under the same conditions as described in Chapter 2.2.1.

Molecular mobility in filled rubbers is largely heterogeneous at temperatures far above $T_g$, as shown by $T_2$ relaxometry. In our measurements we describe the experimental relaxation with a bi-exponential function, indicating the molecular scale heterogeneity of the EPDM chains in the filled rubber. The fitting function used for the fit of all the experiments is: $A(t) = A_0 \exp(-t/T_{2A})^2 + B_0 \exp(-t/T_{2B})$. In most cases, the $T_2$ values given are the weight averages of the values ($T_2^\text{av}$). The two components are assigned to different EPDM fractions: the immobilized EPDM chain fragment at the carbon black surface, and the elastomer matrix outside this interface. The chain mobility in these two fractions is different: the less mobile the chains are, the smaller the $T_2$ value.
6.2.2.2 $^1$H NMR DQ experiments

The proton DQ build-up curve was recorded using the following pulse sequence: $[90^\circ_x - t_{ex} - 90^\circ_x]_{EX} - [t_{DQ}]_{EV} - [90^\circ_y - t_{ex} - 90^\circ_y]_{RE} - t_z - [90^\circ_x - (\text{acquisition of the amplitude } A(t) \text{ of the transverse magnetization})]_{DE}$ (see Fig. 2.2.2.1 in Chapter 2). The subscripts EX, EV, RE and DE stand for excitation, evolution, reconversion and detection periods, respectively. The initial amplitude $A(0)$ of the transverse magnetization which was determined by a least squares fit of the FID, was measured as a function of the excitation time, $t_{ex}$. The signal amplitude is underestimated using this pulse sequence because resonance offsets and differences in the chemical shift for different types of protons are not compensated. Therefore, this pulse sequence was only used for estimating the shape of the DQ build-up curves.

6.2.2.3 $^1$H NMR DQHE experiments

A DQ filtered Hahn-echo experiment was performed using the pulse sequence below: $[90^\circ_x - t_{ex}/2 - 180^\circ_x - t_{ex}/2 - 90^\circ_x]_{EX} - [t_{DQ}]_{EV} - [90^\circ_y - t_{ex}/2 - 180^\circ_y - t_{ex}/2 - 90^\circ_y]_{RE} - t_z - [90^\circ_x - t_{HE} - 180^\circ_y - t_{HE} - [\text{acquisition of the amplitude } A(t) \text{ of an echo maximum}]_{DE}$ (see Fig. 2.2.3.1 in Chapter 2). The first $90^\circ_x$ and $90^\circ_x$ pulses in both pulse sequences excite DQ coherences that evolve for time $t_{DQ}$, which was set to 5 µs. The DQ coherences are converted by $90^\circ_y$ and $90^\circ_y$ pulses to the z-polarization. The $180^\circ$ refocusing pulses in the middle of the excitation and the reconversion periods eliminate the effects of resonance offsets and differences in the chemical shift for different types of protons. After a delay time $t_z$ of the DQ filter, the HEPS was applied. It should be noted that the condition of selecting the isotropic powder average dipole-dipole interactions is broken for short DQ times. Simply, the magnetization of the segments with (residual) coupling tensors oriented along $B_o$ is enhanced, as compared to the other orientations, especially those at the magic angle. Therefore, a sufficiently long delay time $t_z$ is required for proper redistribution of the magnetization between chains with different direction of the end-to-end vector with respect to the $B_o$. The redistribution of the magnetization is effective on distances that are comparable with the scale of spin diffusion and/or translational chain mobility within time $t_z$. The time $t_z$ was set to 5 ms. Experiments with
different $t_x$ times have shown that 5 ms was sufficient for the redistribution of the magnetization over all rubbery chains either due to spin diffusion or large spatial-scale chain mobility.\textsuperscript{29} Thus, by a proper choice of the excitation time, the decay of the transverse magnetization of rubbery chains with different molecular mobility and, consequently, of the strength of the dipole-dipole interactions can be selected.\textsuperscript{30,31,32,33,34} This experiment was used to measure the decay of the transverse magnetization relaxation of the rubbery matrix in the bound rubber and unfilled EPDM.

\subsection*{6.2.2.4 $^1$H NMR DQ spin diffusion experiments}

Spin-diffusion experiments with a double-quantum (DQ) dipolar filter were performed to prove the existence of immobilized adsorption layer in the filled compound. Proton spin-diffusion data were recorded by using the pulse sequence $[90^0_x - \tau - 90^0_x - t_{DQ} - 90^0_x - \tau - 90^0_x - t_d - 90^0_x - FID]$ with $\tau$ the excitation time and $t_d$ the spin-diffusion time. The evolution time of the DQ coherences is $t_{DQ}$, which was taken as 5 $\mu$s in all experiments. The DQ filter selects at short excitation times mainly the signal from the least mobile chain fragments in immobilized adsorption layer. The excitation time of 15 $\mu$s was used in the experiment.

\subsection*{6.2.3 Dynamic Flocculation Model\textsuperscript{36}}

In order to correlate the results obtained by use of solid-state NMR with the physical properties of the filled EPDM, we have used the analysis of the stress-strain curves with the so-called Dynamic Flocculation Model developed by Klüppel et al.\textsuperscript{36} The experimental data and their analysis were kindly provided by Manfred Klüppel. The model combines well established concepts of rubber elasticity with a micro-mechanical approach of dynamic filler flocculation in cyclically strained rubbers at different elongations.\textsuperscript{36,37} The method focuses on a recently developed micro-mechanical model of deformation of filled rubber. The stress response of a filler reinforced strained rubber sample can be derived from the following mesoscopic phenomena: with increasing strain of a virgin sample, a successive breakdown of filler clusters takes place under the
exposed stress onto rubber. This process begins with the largest clusters and continues up to a minimum cluster size $\xi$. During the strain decrease cycles, complete re-aggregation takes place, but the filler-filler bonds that are formed again after once being broken are significantly weaker than the original ones. At subsequent stress-strain cycles of a pre-strained reinforced sample, two micro-mechanical mechanisms are distinguished:

(1) Hydrodynamic reinforcement of the rubber matrix by the fraction of rigid filler clusters with strong filler-filler bonds that have not been broken during previous deformations. Hydrodynamic reinforcement is determined by the volume fraction of the filler regardless broken and non-broken bonds.

(2) Cyclic breakdown and re-aggregation of the remaining fraction of more fragile filler clusters with weaker filler-filler bonds.

The fraction of rigid filler clusters decreases with increasing pre-strain, while the fraction of fragile filler-clusters increases. The break-down into rigid and fragile filler cluster units is illustrated in Fig. 6.2.3.1.

The soft bonds bend substantially in the stress field of the rubber, implying that their contribution to hydrodynamic reinforcement is relatively small. The mechanical action of the fragile filler clusters refers primarily to a visco-elastic effect, since any type of cluster that is stretched in the stress field of the rubber stores energy that is dissipated when the cluster breaks. This mechanism leads to a filler-induced visco-elastic contribution to the total stress that significantly impacts the internal friction of filled rubber samples. Note
that this kind of visco-elastic response is present also in the limit of quasi-static deformations, where no explicit time dependency of the stress-strain cycles is taken into account. According to these considerations, the apparent stress consists of two contributions: (1) the stress contribution of the rubber matrix, including the hydrodynamic reinforcement and (2) the stress contribution of the strained and broken filler clusters, which are weighted with the effective filler volume fraction $\Phi_{\text{eff}}$.\textsuperscript{35,36,37,38}

### 6.3 Results and discussion

#### 6.3.1 Adsorption layer

As stated above, physical adsorption of the elastomer chains to the surface of the fillers causes immobilization of the rubber chains adjacent to the filler surface. The two fractions with different local chain mobility present in the filled rubbers are the immobilized thin rubber layer around the filler particles and the mobile rubber matrix outside of this interface. Large spatial scale chain mobility in the rubbery matrix decreases in the presence of carbon black, as discussed above. To obtain unambiguous information about the amount of immobilized layer in a carbon black filled sample, we have performed extraction for the sample containing 60 phr carbon black N115, as described in the experimental section. We have recorded NMR experiments for this bound rubber. The bound rubber contains 300 phr filler after extraction. The fraction of immobilized EPDM should be sufficient for an accurate study by $^1$H NMR relaxometry because of high filler content in the bound rubber.

Another possibility to evaluate the presence of the adsorption layer and its thickness is the DQ spin diffusion experiment. Fig. 6.3.1.1 shows the FIDs obtained at four different mixing times.

The spin diffusion experiments are used in this case as proof that, indeed, the immobilized layer of the adsorbed EPDM is formed at the surface of carbon black. It can be seen that as a function of the mixing time the shape of the decays is changing. The intensity of the component with short $T_2$ decreases with increasing mixing time, whereas the fraction of the component with long decay time increases. This behavior is typical for spin-diffusion of polymers composed of rigid and soft domains.\textsuperscript{34} Quantitative analysis of
the spin-diffusion data requires a new theoretical model for this specific type of heterogeneous material. This could be a subject for future studies.

![Graph showing spin diffusion FIDs at different mixing times for the bound rubber.](image)

**Figure 6.3.1.1** Spin diffusion FIDs at different mixing times for the bound rubber.

It should be noted that when analyzing this type of experiment, other phenomena should also be discussed in relation to the fast decaying component in FIDs shown above: the magnetic field gradients introduced by the filler particles and the paramagnetic impurities from carbon black itself and from free radicals that could be caused by milling. In filled rubbers, magnetic susceptibility differences between carbon black and rubber lead to an inhomogeneity in $B_0$ at the rubber-filler interface. Since our experiments were performed with low-field NMR relaxometry, this effect could be neglected in accordance with results of a previous study of similar materials. Another study of carbon black filled rubbers has shown that the paramagnetic impurities are not the origin of the fast-decaying component. In addition, the two component NMR relaxation behavior is also observed for silica-filled PDMS, which apparently contains less paramagnetic impurities that the carbon black elastomers. Thus, the fast decaying component in the filled EPDM would appear to be caused by the motional constraints for the EPDM chains at the filler particles.
Advanced NMR experiments are used to confirm the existence of the immobilized layer on the carbon black surface. Using the DQ filter, the adsorbed rubber fraction can be selected by a proper choice of the excitation/reconversion time, $t_{ex}$. In the present study, the DQ filter is used to enhance the selectivity of the $T_2$ relaxation experiment to different micro-regions in the filled rubbers. To determine the optimum $t_{ex}$, a DQ build-up is recorded for both the non-filled and bound rubbers. The initial amplitude of the FID in the DQ experiment is shown in Fig. 6.3.1.2 as a function of the excitation time $t_{ex}$. The DQ build-up curves show two maxima for the bound EPDM. The first maximum is observed at $t_{ex} \approx 30 \mu s$. Such a short excitation time is typical for crystalline phases in semicrystalline polymers. Therefore, this maximum is assigned to the low mobile adsorption layer (EPDM – carbon black interface) in the bound rubber (Fig. 6.1.1.). The second maximum is situated at 0.3 ms. The broad maximum originates from the EPDM matrix outside of the interface. It should be noted that the maximum for the rubber compound without carbon black is situated at 0.5 ms and after incorporating the carbon black is shifted to 0.3 ms, which is a value similar to that for weakly crosslinked rubber. Thus, the presence of carbon black causes large immobilization of chain fragments on the carbon black surface. The adsorbed chain fragments form physical EPDM-carbon black junctions that increase the anisotropy of chain motions in the rubber matrix outside the adsorption layer.

To enhance the selectivity, and for the reliability of data analysis, two additional types of experiments are used: DQ FID and DQHEPS. The excitation times used for the two pulse sequences were: 15 $\mu$s for the DQ FID and 300 and 500 $\mu$s for the DQHEPS. The NMR signal is largely enhanced for the low mobile materials at short excitation time, whereas at long excitation times mainly a signal from soft-rubbery materials is detected. Fig. 6.3.1.3 shows the experimental curves for the bound and non-filled rubbers respectively. By comparing the normalized DQ FID of both samples in the graphs of Fig. 6.3.1.3, one can see that the normalized amplitude of DQ FID is about ten times smaller for the non-filled compound, whereas for the normalized DQHEPS both samples show almost the same value. Also, large changes can be noticed in the shape of DQ FID for the bound rubber.
Figure 6.3.1.2 DQ build-up for non-crosslinked rubber with and without carbon black at 90 °C. The bound rubber contains 300 phr N115. The expansion on the right side shows the presence of a shoulder at 30 µs, assigned to the immobilized EPDM–carbon black interface.

As can be seen in the figure (a), the decay for the bound rubber consists of two distinct components with strongly different decay times. The mean decay time of the components with short and long decay time is typical for the relaxation of rigid and soft materials, respectively.

The rigid fraction originates from the EPDM chain fragments adjacent to the carbon-black surface. These fragments have low molecular mobility due to EPDM–carbon black adsorption interactions and entropy constraints for chain dynamics in close proximity to the filler surface.¹⁷ DQ FID of non-filled EPDM is similar to the relaxation component with a long decay time for bound rubber. We have obtained the best fit of the DQ FID signal for bound rubber using a linear combination of a Gaussian and an exponential function. The values obtained from fitting show two fractions with relative intensity of 65 % ($T_2 = 24$ µs) and 35 % ($T_2 = 207$ µs). The other fraction has a small value of 24 µs, indicating that the units in the adsorption layer are substantially immobilized. Therefore, highly restricted anisotropic chain mobility occurs in the adsorbed rubber fraction which provides physical junctions in the rubber matrix (Fig. 6.1.1) that will contribute to the total crosslink density in filled vulcanizates. These physical junctions increase the
anisotropy of chain motions as it follows from the shift of the DQ build-up maximum from 500 $\mu$s for unfilled EPDM to 300 $\mu$s for bound rubber.

Figure 6.3.1.3 DQ FID and DQHE decays for (a) the extracted filled and (b) non-filled samples. The DQ FID and DQHEPS data have been normalized to the initial amplitude of the FID for each sample.

The thickness of the EPDM-carbon black interface in the bound rubber can be estimated from the value obtained for the fraction of chain units in the interfacial layer, the specific surface and the volume fraction of carbon black. The thickness of this interfacial layer is estimated to be about 0.6 nm if is assumed that the entire carbon black surface is covered by a uniform EPDM layer of a constant thickness. Since not all carbon black surface is available for chain adsorption because of carbon black aggregation, the thickness of the adsorption layer should be somewhat larger. The amount of the adsorption layer is very small in all compounds even at high loading and high specific surface of carbon black. Therefore, direct impact of this layer on properties would be small. However, an indirect effect will be due to the formation of the physical junctions that form quasi-permanent network in the rubber matrix in the proximity of carbon black aggregates. This network can be destroyed under deformation due to slippage of the physical junctions.

For the same bound rubber we can estimate the average number of chain units per single adsorption junction $N_{C-C \text{ bonds adsorbed}}$ based on Eq. 6.1:

$$\% \text{EPDM immobilized} = \frac{N_{C-C \text{ bonds adsorbed}}}{(N_{C-C \text{ bonds adsorbed}} + N_{\text{phys}})} \times 100\%$$  (6.1)
where $N_{phys}$ is the molecular weight between adjacent physical network junctions along the EPDM chains in bound rubber. In this way, based on the 23% fraction of immobilized chains in the bound rubber, we estimated that about nine monomer units are involved in one adsorption junction.

### 6.3.2 Carbon black–EPDM rubber interaction in compounds

Carbon black filled rubbers have a complex structure. The molecular-scale morphology of the rubber matrix depends on the following factors: (i) the chemical heterogeneity of the unfilled elastomers (ii) the morphological heterogeneity of filled rubbers due to a spatially heterogeneous distribution of the filler particles and their agglomeration, (iii) heterogeneous distribution of the chemical crosslinks in the rubbery matrix, and (iv) the elastomer/filler interface.  

The amount of immobilized adsorption layer is small (1-2%) in all master batches and vulcanizates. This did not allow to perform accurate analysis of chain mobility in the adsorption layer using $T_2$ relaxation experiments. Moreover, the density of physical junctions is also rather small. The amount of adsorption layer and the density of adsorption junctions are significantly larger in bound rubber.

Figure 6.3.2.1 shows the $T_2$ relaxation decays for the non-filled EPDM and the rubbery matrix of bound rubber. In the presence of carbon-black particles in the rubber, the overall $T_2$ value has decreased about three times as compared to the compound without carbon black. This means that EPDM chain fragments that are immobilized at the carbon black surface act as physical network junctions increasing the anisotropy of chains motion in the rubbery matrix in the close proximity to the filler surface. Quantitative information about the adsorption layer is not provided by the Hahn-echo experiments.

The adsorption layer is investigated later on, in Chapter 6.3.1.

The $T_2$ values of the filled and non-filled samples containing the same amount of vulcanization recipe are used for determining the density of adsorption network junctions that are formed in the rubber matrix of filled EPDM (see Fig. 6.1.1).
Figure 6.3.2.1 $^1$H transverse magnetization decays at 90°C normalized to the initial amplitude of FID for the non-filled compound and bound rubber. The decays were measured with HEPS.

Assuming simple additivity of the entanglement density and the physical network junctions, we can estimate the effect of physical junctions that increase anisotropy of chain motions, causing a decrease in $T_2$:

$$\frac{1}{T_2} = \frac{1}{T_2} - \frac{1}{T_2}$$

where $T_2^{filled}$ and $T_2^{unfilled}$ correspond to the $T_2$ of the filled and non-filled compounds, respectively. The $T_2^{phys}$ obtained is related to the volume average amount of EPDM-carbon black physical junctions formed in the filled compounds as described in Chapter 2.2.1. It should be mentioned here that the functionality of the physical junctions is “ill defined”. We have used the formal way (see Chapter 2.2.1) to calculate the amount of physical network junctions.

Analysis of the experimental data indicates that at increased filler content, the chain mobility in the filled rubber decreases, except for the N990 filled EPDM samples, where the effect of carbon black on $T_2$ relaxation is hardly observed. The density (volume average) of physical EPDM-carbon black junctions has been estimated for all the filled
compounds. The composition of these samples and the carbon black content are given in Table 6.3.2.1. The values obtained for the physical junction density \(D_{\text{phys}}\) and the total and chemical network density \(D_{\text{chem}}\) for the vulcanizates filled with different types of carbon blacks at varied concentrations, are given in the same table. \(D_{\text{chem}}\) was obtained from

\[
\frac{1}{T_{2}^{\text{chem}}} = \frac{1}{T_{2}^{\text{vulc}}} - \frac{1}{T_{2}^{\text{non-vulc}}} \quad (6.3)
\]

where \(T_{2}^{\text{vulc}}\) and \(T_{2}^{\text{non-vulc}}\) correspond to the \(T_{2}\) of the vulcanized and non-vulcanized compounds, respectively. The results for \(D_{\text{tot}}\) and \(D_{\text{chem}}\) are given in Table 6.3.2.1.

Figure 6.3.2.2 shows the values of \(D_{\text{phys}}\) as function of the amount of carbon black for different types and sulfur content in the filled non-crosslinked compounds. \(D_{\text{phys}}\) increases at increasing carbon-black content. At the same concentration of carbon black \(D_{\text{phys}}\) is increasing with increasing carbon black surface area (N115 > N330 > N550). \(D_{\text{phys}}\) increases with the amount of carbon black and its values reaches \(\sim 35 \, \text{mmol/kg}\) at highest carbon black content. It appears that \(D_{\text{phys}}\) is slightly affected by the amount of the
vulcanization recipe, possibly due to the competing adsorption of EPDM chain and vulcanization compounds in the recipe.

Once the surface area is increasing through a higher contact area (a consequence of the filler content as well), the mean density of the adsorption junctions in the rubber matrix is also increased. The filler effect is small in all compounds when compared to the entanglement density: about 260 mmol/kg for EPDM as such. In summary, the density of the EPDM-carbon black increases with increasing the specific surface and amount of carbon black, as well as preparation procedure. However, direct contribution of physical EPDM – carbon black junctions to the mechanical properties via additional crosslinks will be small since the density of chemical junctions and chain entanglements is significantly larger. Indirectly, EPDM-carbon black interactions could influence the breakdown of the carbon black aggregates during deformation of filled rubbers.

The motion of the free chain is not much influenced by the N990 carbon black filler, as a result of its low surface area per EPDM unit volume. In the literature it is already described how the chain dynamics are affected in the vicinity of filler particles and that the remaining components are only weakly affected.\textsuperscript{17,43,44}

We therefore conclude that the density of the adsorption junctions in the rubbery matrix increases with increasing carbon-black surface area and with increasing filler content.

The effect of carbon black agglomeration on $D_{\text{phys}}$ can be estimated using the maximum possible EPDM – carbon black area per unit volume of elastomer:

$$\Psi = \nu \varphi S_{sp} / (1 - \nu) \quad (6.4)$$

where $\nu$ is the volume fraction, $\varphi$ is the specific density and $S_{sp}$ is the specific surface of carbon black.
Table 6.3.2.1 Network densities for the carbon black filled samples

<table>
<thead>
<tr>
<th>Carbon black type</th>
<th>Crosslinker amount (phr)</th>
<th>$D_{\text{phys}}$ compounds (mmol/kg)</th>
<th>$D_{\text{tot}}$ vulcanizates (mmol/kg)</th>
<th>$D_{\text{chem}}$ vulcanizates (mmol/kg)</th>
</tr>
</thead>
<tbody>
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<td></td>
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<td>200</td>
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<td></td>
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<td>276</td>
</tr>
</tbody>
</table>
Fig. 6.3.2.3 shows the dependence of the amount of physical junctions formed in the filled compounds on the maximum possible carbon black contact area\textsuperscript{17} for the different types of carbon blacks. Even if the samples contain different loading of carbon black, the results follow the same trend. The exception is for the two samples containing 60 phr carbon black N115, represented by the open triangle and circle, due to a possible larger agglomeration of the carbon black aggregates. The slope is comparable for the other samples, contrary to results from a previous study.\textsuperscript{17} This suggests that mixing procedure can influence the structure of the physical network.

### 6.3.3 Effect of carbon black on network density for different types and amounts of CB in EPDM vulcanizates

The network structure in filled EPDM vulcanizates was studied to establish structure-properties relationships. The mean $T_2$ relaxation time for the rubbery matrix in filled vulcanizates has been used to calculate the total network density and the contribution to
its value from chemical crosslinks, EPDM – carbon black adsorption junctions and chain entanglements.\textsuperscript{45}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.3.3.1}
\caption{Total network density for three types of carbon black at three concentrations of sulfur vulcanization recipe}
\end{figure}

$D_{phys}$ has been estimated from the compounds by comparing the $T_2$ values for the nonfilled and filled master batches prior to vulcanization. The same procedure can be applied to calculate the density of chemical crosslinks, $D_{chem}$, by comparing now the values for the same master batch before and after vulcanization.

Assuming additivity of different types of network junctions to the total network density and consequently to the transverse magnetization relaxation, one can determine the value of $T_2^{chem}$ that is related to the mean-molar mass between chemical crosslinks in filled EPDM vulcanizates:

$$\frac{1}{T_2^{chem}} = \frac{1}{T_2^{vulc}} - \frac{1}{T_2^{comp}}$$ \hspace{1cm} (6.5)

The density of chemical crosslinks ($D_{chem}$) is calculated from $T_2^{chem}$ as described above. If we assume that the chain entanglements, adsorption junctions and chemical crosslinks are
decoupled and knowing that the entanglement density is independent of the carbon black content, the following equation is valid:

\[ D_{\text{tot}} = D_{\text{ent}} + D_{\text{phys}} + D_{\text{chem}} \]  \hspace{1cm} (6.6) 

\( D_{\text{phys}} \) and \( D_{\text{chem}} \) are calculated from \( 1/T^2_{\text{phys}} \) and \( 1/T^2_{\text{chem}} \) values (see Eq. 6.5) as described above. Based on Eq. 6.6, an entanglement density of 230 mmol/kg was obtained, which is in good agreement with our previous results for the non-filled EPDM.45

The total network density and contribution to it from the chemical crosslinks and EPDM - carbon black adsorption junctions are given in Table 6.3.2.1. Fig. 6.3.3.1 shows the total network density as function of sulfur level and carbon black loading. It appears that \( D_{\text{tot}} \) increases with increasing sulfur content and is hardly influenced by the filler content at loadings up to 40 phr. It appears that efficiency of vulcanization decreases with increasing carbon black content. However, \( D_{\text{tot}} \) value is not proportional to the amount of vulcanization recipe. The physical EPDM – carbon black junctions contribute to the total network density at high carbon black content (80 phr) and at higher specific surface of carbon black.

6.3.4 Correlation with mechanical properties

It is known that the incorporation of carbon black in an elastomer can improve the mechanical properties. The technique developed by Klüppel et al is based on the typical stress softening effect of filled rubber under the uniaxial stress-strain measurements.35 The strain regime is up to about 100 % where the strongly non-linear visco-elastic behavior of filler reinforced elastomers is generally referred to as a breakdown of the filler network. The stress-strain curves are analyzed in terms of crosslink density (see paragraph 6.2.3) and compared in this study with the network density obtained from NMR analysis.

Examples of stress-strain curves of the samples with 60 phr of carbon black N330 and N115 and corresponding fits are shown in Fig. 6.3.4.1. The measurements have been
performed with dumbbells shaped samples. The up- and down cycles are depicted (symbols) together with the obtained parameters as shown in the inserts.

The main parameters are obtained from the fitting procedure which is performed in several steps. First, all the parameters, except $G_e$ – entanglement density (0.6 MPa) and $c$ – universal scaling factor (0.83), are taken as free fitting parameters. In a next step, the

![Figure 6.3.4.1](image) Uniaxial stress-strain cycles of EPDM samples filled with 60 phr carbon black and fittings (red lines) with the stress softening model. The obtained fitting parameters are listed in the graphs.

stress-strain cycles are fitted again and $x_0$ – mean cluster size, $s_v$ – failure stress of virgin filler-filler bonds, $s_d$ – tensile strength of the damaged filler-filler bonds, $n$ – number of chain segments between trapped entanglements, $\phi_{eff}$ – effective filler volume fraction and $\nu$ – effective chain density are determined. The mechanically effective chain density of filled rubbers is assumed to consist of two parts: the chain density associated with polymer network junctions (crosslinks and trapped entanglements) and the additional chain density $\nu$ resulting from polymer-filler couplings.

Table 6.3.4.1 shows the values obtained for the total network density $D_{tot}$ as determined from $T_2$ relaxation and for the effective chain density $\nu$ as determined using the dynamic flocculation model, at different compositions. Both parameters are increasing at higher loading and higher specific surface. For convenience we have converted the unit mol/m$^3$ in mmol/kg for the mechanically effective chain density. Usually, $\nu$ is composed of contributions from crosslinks points, trapped entanglements, and network links on the
filler, whereas $D_{tot}$ includes the contributions from chemical crosslinks, physical junctions and permanent and temporary entanglements.

**Table 6.3.4.1** Network density for carbon black filled samples as determined from $T_2$ relaxation and dynamic flocculation model

<table>
<thead>
<tr>
<th>Carbon black type</th>
<th>Crosslinker amount (phr) (%)</th>
<th>$D_{tot}$ vulcanizes (mmol/kg)</th>
<th>$\nu$ (mmol/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>N550</strong></td>
<td>20 50</td>
<td>355</td>
<td>252</td>
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<td>100</td>
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<td></td>
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<td>0 50</td>
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</tr>
<tr>
<td></td>
<td>200</td>
<td>494</td>
<td>370</td>
</tr>
</tbody>
</table>

Contrary to the chain densities obtained from NMR, the densities from mechanical measurements increase with filler loading and they are found to be systematically larger than the NMR data. This indicates that the NMR method is not very sensitive for the coupling of the chains to the filler surface. A more pronounced effect of polymer filler interaction is seen in Fig.6.3.2.1 for the extracted samples.
6.4 Conclusions

The crosslink density of carbon black filled EPDM samples was investigated as a function of vulcanization recipe, the filler amount and of the filler type by means of low field $^1$H NMR relaxometry. It is shown that in addition to the chemical crosslinks and chain entanglements, physical junctions by adsorption of EPDM on carbon black contribute to the total network density at high filler content and at higher specific surface. The influence of the filler type on the mobility of the chains was compared for different types of carbon black. The immobilization effect is increasing with increasing amount of filler. At the same time the contribution of physical junctions in the filled compounds has been estimated. The effect increases with increasing the specific surface but it is small compared to the amount of entanglements and the amount of chemical crosslinks. DQ-filtered $T_2$ relaxation analysis and spin-diffusion experiments prove the existence of an immobilized rubber layer on the surface of carbon black. The minimum thickness of the adsorption layer was estimated to be 0.6 nm and in average about 9 monomer units form a single adsorption junction. Quantitative determination of the thickness of the adsorption layer from spin-diffusion experiments requires more detailed investigation and the development of a new model for the case of filled elastomers.

6.5 References

12 Donnet, J.B., *Compos. Sci. Technol.*, 2003, 63, 1085
Chapter 7

Conclusions

NMR together with other techniques has been successfully applied to investigate peroxide-cured EPDM rubber with respect to network density and network heterogeneity, as well as crosslinking chemistry. The effect of coagents and fillers is studied in order to obtain information about the rubbery network in the presence of these chemicals. Several experiments have probed different aspects of the network structure and dynamics of the polymer chains at the molecular level. These results have been correlated with the mechanical properties. New NMR methods have been developed and applied on these systems. The main conclusions of this work are summarized as follows:

- **Chapters 1** and **2** provide the introduction in the field of elastomers and the NMR techniques that have been used, respectively.

- In **Chapter 3** we have investigated the effect of the amount of peroxide and the type and content of diene third monomer on the network density. $^1$H $T_2$ relaxometry proved to be a useful method to quantitatively characterize total crosslink density and the contribution to it of temporary and trapped entanglements. The effective Hahn-echo decay rate $1/T_2$ reflects the volume-average network density, which correlates well to mechanical properties, such as torque and modulus. At low peroxide levels the observed decay rates all depend linearly on the initial peroxide content for the various types and levels of diene probed. The chain-entanglement density estimated from the intercept, i.e. in the limit of zero peroxide content, agrees with published neutron-scattering values. The slope reflects the peroxide-induced chemical crosslinks per peroxide unit. The peroxide crosslinking efficiency estimated in this way is $\approx 50\%$. The role of the termonomer 5-ethylidene-2-norbornene (ENB) in ENB-EPDM can be
Chapter 7

estimated by comparing network densities in EPDM and EPM at the same peroxide level. Subsequent comparison of the network-density increase in EPDM (relative to EPM) with the diene content prior to the peroxide cure indicates how many diene monomers were actively involved in the network formation. At the highest peroxide level probed (5 phr) the increased crosslink density in 1.9 % and 9 % ENB-EPDM relative to EPM respectively corresponds to 47 and 24 % of the ENB content. For 9 % ENB-EPDM the crosslink numbers correlates well to the diene conversion estimated from the reduction of the olefinic signals in MAS ¹H NMR and Raman IR spectra. At first sight this seemed to confirm the accepted view that the main role of termonomers is to offer addition sites for the peroxide-induced EPDM macroradicals. However, this hypothesis turns out to be too simple based on the ¹³C NMR analysis in Chapter 4 (see below). By comparing $T_2$ relaxation times in solid and swollen EPDM we can distinguish between the contributions of temporary and trapped entanglements. The availability of a relatively large set of EP(D)M materials with varying peroxide and diene content allowed us to resolve the respective contributions from temporary and trapped chain entanglements, as well as two types of chemical crosslinks originating from either combination of macro-radicals or addition of macro-radicals to the double bonds of the EPDM diene termonomers.

The shapes of the Hahn-echo decays of both solid and swollen EPDM suggest strong network heterogeneity. This heterogeneity has been investigated by use of double-quantum filtered $T_2$ relaxometry, a novel NMR technique developed in the context of this project.

- **Chapter 4** provides information about the reaction mechanism of peroxide cure. ¹³C NMR spectroscopy provides an excellent tool for studying peroxide crosslinking of labeled EPDM. The basic three-step radical crosslinking reaction is complicated by several competing reactions that affect the crosslinking process. The contribution of these reactions is important for the optimization of the peroxide-cure. By investigating EPDM with ENB ¹³C-labeled at the olefinic C2 and C8 position, the signal/noise ratio of the ¹³C NMR spectra was greatly enhanced, and the fate of the double bond during peroxide cure could be
Conclusions

monitored with a highly selective $^{13}$C NMR experiment based on the scalar $^{13}$C-$^{13}$C coupling (INADEQUATE). As turns out, the ENB unit is not only involved in the crosslinking reaction via addition to the pendent unsaturation, but also via the allylic positions, resulting in new structures with intact unsaturation. The observed carbonyl moieties are the result of oxidation of the double bond and artifacts of the experimental method applied. Combination of the allylic radicals with other allylic radicals or with EPM backbone allyl radicals results in crosslinks involving the ENB unsaturation without consuming it. We therefore propose new reaction pathways to be added to the accepted reaction mechanism for peroxide curing.

- **In Chapter 5** we investigate the effect of four common coagents on peroxide-cured EPDM. The results show an increasing effect on the network crosslink density in the presence of the coagents triallylcyanurate (TAC) and N,N'-m-phenylenebismaleimide (HVA-2). Trimethylolpropane trimethacrylate (TRIM) and zinc methacrylate (ZDMA) also promote crosslinking in EPM, but for EPDM TRIM has hardly any influence, while ZDMA has even a decreasing effect. These unexpected results for TRIM and ZDMA in EPDM indicate that the peroxide has been inefficiently used in these systems. In EPDM TRIM may perhaps consume the peroxide without forming crosslinks that will contribute to the mechanical properties. ZDMA is a salt and does not mix well with the apolar EPDM matrix.

- **Chapter 6** explores the EPDM-carbon black interactions and network structure in relation to stress-strain behavior. The crosslink density of carbon black-filled EPDM samples was investigated as a function of vulcanization recipe, filler amount and filler type by means of low-field $^1$H NMR relaxometry. In addition to the chemical crosslinks and chain entanglements already present in non-filled EPDM, physical junctions due to adsorption of EPDM onto carbon black physical junctions contribute to the total network density at high filler content and higher specific surface. The contribution of the physical junctions in the filled compounds has been also estimated on the basis of a model. The chain-immobilization effect observed with $T_2$ relaxometry increases with increasing specific surface but it is small compared to the contribution of entanglements and
of chemical crosslinks. The presence of an immobilized adsorption layer at the surface of carbon black was proved by DQ filtered $T_2$ relaxation analysis and by spin-diffusion experiments, but quantitative determination needs a new theoretical model for this specific type of heterogeneous material.

- The present Chapter 7 summarizes the main conclusions obtained in this project by using solid state NMR
- The Appendix highlights the results obtained for both sulfur- and peroxide-cured samples by $^1$H multiple-quantum NMR, a novel NMR technique implemented in the context of this DPI Corporate Research project. The technique yields insight into the network distribution as a function of initial sulfur and peroxide content. Interesting differences between sulfur- and peroxide cured EPDM have been observed, which may well be related to the different nature of the two types of curing.

In summary, we have demonstrated that NMR is a versatile tool to elucidate the 3D network structure of non-transparent crosslinked polymers.
Elastomers are an important class of materials with a large number of applications. Since EP(D)M rubbers have no double bonds in the backbone of the polymer chains, are less sensitive to oxygen and ozone and have high UV-resistance. Other excellent properties of these rubbers are high resistance to acid and alkali, insulation properties, and high and low temperature performance.

**Chapter 1** provides the introduction in the field of elastomers. Crosslinking is a process of chemically producing network junctions by the insertion of crosslinks between the polymer chains. The presence of diene termonomers generally improves the crosslinking efficiency. Increasing the amount of diene results in increased crosslink densities and, thus, in corresponding changes in mechanical and elastic properties. The first and by far the most important crosslinking agent is sulfur, which is relatively inexpensive and yet vital to the rubber industry. Although sulfur is the best known and most used vulcanizing agent, there is another class of crosslinking agents known as peroxides. Peroxides typically react with the elastomer chains by removing hydrogen atoms from the carbon backbone of the polymer and the crosslink results to be carbon to carbon link, which is stronger than a sulfur-carbon link and more thermally stable. The characterization of rubbery networks using different techniques is discussed.

**Chapter 2** describes the NMR techniques that have been used for the investigation of EPDM rubber. Several methods like transverse $^1$H NMR relaxation, $^1$H and $^{13}$C NMR spectroscopy and multiple quantum experiments have been used to probe different aspects of the network structure and dynamics of the polymer chains at the molecular level.

Mechanical properties of crosslinked elastomers are influenced not only by the volume average crosslink density but also by network heterogeneity. In **Chapter 3** we show that in the case of peroxide-cured EPDM, the network has a complex structure with various
types of chemical crosslinks formed via addition and combination reactions, as well as both temporary and trapped entanglements. Usually, additional components such as residual sol, dangling chains, chain loops and differences in the distribution of the crosslinks may be present. A good correlation with mechanical properties is established.

In Chapter 4 the chemistry of peroxide cure is investigated. A more detailed reaction mechanism is given, based on results obtained using $^{13}$C NMR spectroscopy and 1D INADEQUATE for EPDM with $^{13}$C labeled ENB (5-ethylidene-2-norbornene). We have found new structures with intact unsaturations showing that the ENB unit is involved in the crosslinking reaction not only via addition to the pendant unsaturation, resulting in saturation, but also via the allylic positions.

The use of co-agents together with the peroxides can result in improved crosslink density.

In Chapter 5 the effect of different types of coagents on network density and network heterogeneity is investigated. The crosslink density and network heterogeneity are compared for different types of coagents at different compositions for the peroxide-cured EPDM. The results in this chapter show that the presence of the coagents TAC and HVA-2 in the EPDM network have an increasing effect on the network crosslink density. The TRIM has hardly any influence, whereas ZDMA had a decreasing effect. The results obtained from $T_2$ relaxometry correlate well with the mechanical properties.

In the case of filled rubbers the network structure is additionally complicated. Chapter 6 deals with the effect of carbon black on EPDM sulfur vulcanisates. It is shown that in addition to the chemical crosslinks and chain entanglements, physical junctions by adsorption of EPDM on carbon black contribute to the total network density at high filler content and at higher specific surface. Using DQ filtered $T_2$ relaxometry and spin-diffusion we have shown the presence of an immobilized adsorption layer at the surface of carbon black. Quantitative determination of the thickness of the adsorption layer from spin-diffusion experiments requires more detailed investigation and the development of a new model for the case of filled elastomers.

The last chapter of the thesis, Chapter 7, summarizes the main results obtained in this project by use of both high- and low-field solid state NMR.
Appendix

Difference in network heterogeneity between sulfur- and peroxide-cured EPDM investigated with double-quantum $^1$H NMR

Five sulfur-cured and three peroxide-cured EPDM systems with respectively different sulfur and peroxide levels were studied with DQ $^1$H NMR and $^1$H NMR $T_2$ relaxometry.

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<th>S2994</th>
<th>S2995</th>
<th>S9301</th>
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<td>0.8</td>
<td>1.2</td>
<td>1.5</td>
<td>4.5</td>
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</table>

<table>
<thead>
<tr>
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<th>T1076</th>
<th>T1081</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial peroxide content (phr)</td>
<td>1.25</td>
<td>2.5</td>
<td>5</td>
</tr>
</tbody>
</table>

DQ build-up curves were obtained using the multi-pulse method described in Chapter 2.2. Both the DQ build up $S_{DQ}$ and the reference decay $S_{ref}$ were recorded. Fig. 1 shows the $S_{DQ}$, $S_{ref}$ and the sum $S_\Sigma = S_{DQ} + S_{ref}$ as a function of evolution time $\tau_{DQ}$ (which equals twice the excitation and reconversion time $\tau_{ex}$). For comparison also (the curve fits to) the Hahn-echo decays of the same samples are shown. $S_{ref}$ and $S_{DQ}$ show the typical decay - and build-up behavior, respectively. For an isotropic ensemble of isolated spin pairs without relaxation and spin diffusion, $S_{ref}$ and $S_{DQ}$ should approach each other at sufficient long evolution time. This is indeed observed for the sulfur-cured systems, but not for peroxide-cured EPDM, where $S_{ref}$ is always bigger than $S_{DQ}$. Apparently the latter contains a comparably large fraction (~10 % monomer units, *vide infra*) of mobile chain fragments, such as long network chains or “dangling ends”. The DQ build-up rate of these fragments is low compared to the overall loss of coherence due to $T_2$ relaxation. As a result, these mobile chain fragments will only contribute to $S_{ref}$ and hardly to $S_{DQ}$, which causes $S_{ref}$ to be systematically larger than $S_{DQ}$ even at long DQ evolution time.
The loss of overall coherence is reflected by the decay of $S_\Sigma$. The observed sum-intensity decays (~5 ms) are always slower than the corresponding Hahn-echo decays (~1 ms).

**Figure 1** $S_{DQ}$, $S_{ref}$ and the sum $S_\Sigma$ as a function of evolution time $\tau_{DQ}$

This shows that the “true” incoherent $T_2$ relaxation is not the same as the $T_2$ relaxation defined by the Hahn-echo decay. This makes sense, because the latter is supposedly dominated by coherent dipolar dephasing, which is the basis for interpreting Hahn-echo
Appendix

decay rates in terms of network density in crosslinked rubbers. Indeed, the Hahn-echo decays for the differently crosslinking samples correlate well to the corresponding decays $S_{\text{ref}}(t_{DQ})$, which are dominated by dipolar dephasing as well.

![Figure 2 Normalized DQ build-up curves](image-url)
The difference between $S_{ref}$ and $S_{DQ}$ at long time is a signature of “incoherent” components, of which the loss of overall coherence is faster than the build-up of DQ coherence. To remove these components from the NMR data we have therefore fitted a bi-exponential model to the difference intensity $S_{ref} - S_{DQ}$ over the range 5 – 18 ms, and used this to normalize the DQ build up according to (Chapter 2):

$$S^{N}_{DQ}(\tau_{ex}) = \frac{S_{DQ}(\tau_{ex})}{S_{LM}(\tau_{ex}) + S_{DQ}(\tau_{ex}) - a \exp(-\tau_{ex} / T_{2a}) + b \exp(-\tau_{ex} / T_{2b})}$$  \[1\]

**Figure 3** Build-up curves for sulfur vulcanized samples

**Figure 4** Build-up curves for peroxide cured samples

The bi-exponential correction is negligible for the sulfur-cured EPDM, and corresponds to the removal of ~10 % of the initial intensity for the peroxide-cured EPDM, with a tendency to decrease at increasing peroxide-level (Fig. 1).
The normalized DQ build-up curves are depicted up to 5 ms in Fig. 2. As expected, the DQ build-up becomes faster at higher sulfur and peroxide levels. The respective shapes reflect the underlying distribution of residual dipole coupling constants. Before giving a detailed analysis in terms of specific distribution models, we note an interesting shape similarity among the build-up curves of the sulfur-cured EPDM systems when plotted along a logarithmic time axis (Fig. 3a).

Up to 1.5-phr sulfur the curves coincide upon scaling the evolution time (Fig. 3b). The same is true for peroxide-cured EPDM up to peroxide levels of 2.5 phr (Fig. 4). The faster the DQ build-up, the bigger the required scaling factor, which thus represents a "relative build-up rate" $R_{DQ}$. Arbitrarily taking the curve of 1.25-phr peroxide-cured EPDM as the reference, we have determined the time-scaling factors of the other curves with respect to this curve. There is a systematic shape difference between sulfur- and peroxide-cured EPDM, which cannot be removed by time scaling (Fig. 5). This makes comparison of the relative build-up rates between sulfur- and peroxide-cured EPDM slightly ambiguous, but a rough comparison is still possible.

![Figure 5](image)
RDQ depends similarly on the sulfur and peroxide levels as the (weighted-average) Hahn-echo decay rate $R_2 = 1/T_2$ (Fig. 6a). As we have shown before in Chapter 4, for the network density derived from $R_2$, we observe a linear trend for peroxide-cured EPDM. For sulfur-cured EPDM $R_2$ and $RDQ$ follow a kind of saturation curve, indicating that at high sulfur-levels ($> 4$ phr) the content of third monomers become limiting for the crosslink density. Sulfur- and peroxide-cured EPDM appear to have similar $R_2$ values, as

**Figure 6** Different correlations between $1/T_2$, relative DQ build-up rate and M100 for both sulfur and peroxide cured samples
well as similar $R_{DQ}$ values, at low crosslink density. This is consistent with the picture that in this range the network density is dominated by quasi-permanent entanglements, independent of whether EPDM is sulfur or peroxide cured. Thus, we have no indication that $R_2$ and $R_{DQ}$ behave significantly different with respect to these entanglements. The similar dependence of $R_2$ and $R_{DQ}$ on the sulfur- or peroxide levels is also clear from the linear correlations between the two (Fig. 6b). Sulfur- and peroxide-cured EPDM show different slopes, which may reflect the difference in the underlying network topology. Peroxide can generate radicals anywhere along the EPDM chains, whereas sulfur requires the third monomer to generate crosslinks. Interestingly, the linear correlations between $R_2$ and $R_{DQ}$ for sulfur and peroxide-cured EPDM cross each other at $R_{DQ} = 0$ and a positive value $R_2^* \sim 300$ s$^{-1}$. This may indicate that the entanglements, which determine $R_2$ and $R_{DQ}$ in the absence of chemical crosslinks, may be different. Alternatively, $R_2^* = 1/T_2^{BWR}$ may represent the Bloch-Wangsness-Redfield contributions$^{1,2}$ to $T_2$:

$$\frac{1}{T_2^{\text{eff}}} = \frac{1}{T_2^{BWR}} + \frac{1}{T_2^{\text{coh}}}$$  \[2\]

where $1/T_2^{\text{coh}}$ denotes the decay rate of the Hahn echo under the influence of the coherent dipolar dephasing.

Since $R_2$ and $R_{DQ}$ appear to follow different slopes for sulfur- and peroxide-cured EPDM, one could wonder which of the two, $R_2$ or $R_{DQ}$, correlates best with the macroscopic mechanical properties. The ideal behavior would be an NMR parameter predicting, e.g., the modulus, independent of the applied curing method. Fig. 6d shows plots of the modulus at 100 % elongation (M100) versus either $R_2$ or $R_{DQ}$. For each of the curing types there is a linear correlation between the modulus and $R_2$ and $R_{DQ}$, respectively. However, for neither $R_2$ nor $R_{DQ}$ the curing-type dependence disappears. This confirms that the $R_2$ and $R_{DQ}$ difference between sulfur- and peroxide-cured networks is not so much caused by NMR artifacts related to the selected NMR parameter, but may actually be related to the even qualitatively different types of networks formed.

After this essentially model-free analysis we have also analyzed the DQ build-up curves in terms of mono- and bi-modal Gaussian distributions:
with \( n = 1 \) or \( 2 \), respectively, and in the latter case \( f_1 + f_2 = 1 \). This distribution can be convoluted with the Gaussian initial behavior of the DQ build-up curves for an isotropic ensemble of isolated spin pairs with identical residual couplings \( D \):

\[
S_{DQ}^N(D, \tau_{DQ}) \approx 0.5 \left\{ 1 - \exp\left( -0.4D^2\tau_{DQ}^2 \right) \right\}
\]

which yields an analytical DQ build-up curve of the form:

\[
S_{DQ}^N(D_{av}, \sigma, \tau_{DQ}) \approx 0.5 \sum_{k=1}^{n} f_k \left\{ \exp \left( \frac{0.4(D_0^{(k)})^2\tau_{DQ}^2}{1 + 0.8\sigma_k^2\tau_{DQ}^2} \right) \right\} \left( 1 - \frac{\sqrt{1 + 0.8\sigma_k^2\tau_{DQ}^2}}{\sqrt{\langle D^2 \rangle}} \right)
\]

The model curve described by Eq. 5 has five fit parameters.

Mono-modal curves based on Eq. 5 fit well to the initial part of the DQ build-up curves of the peroxide-cured EPDM (Fig. 2, right hand side). Note that monomodal does not mean here homogeneous. The distribution is very broad, but homogeneous in a sense that there are no well-defined sub-regions, only smooth variations. Given the weak justification for Gaussian behavior at long evolution time, the least-square fit was actually up to 2 ms only, but the later parts of the curve are also reasonably described by the curves with fit parameters determined from the initial part. The two-parameter fit suggests that the distribution center is close to the origin compared to the distribution width. We have therefore assumed \( D_0 = 0 \) and left only \( \sigma \) as the single fit parameters, which yields an equally good fit. To properly normalize a Gaussian centered at the origin over \( D > 0 \), we have corrected Eq. 5 with a factor 2. For a half-Gaussian distribution with the maximum at 0, the average \( D \) value \( D_{av} = \langle D \rangle \) is given by \( \sigma/\sqrt{\pi} \) and the width \( \delta = \sqrt{\langle D^2 \rangle} \) by \( \sigma/\sqrt{2} \). At increasing peroxide content the width of the half-Gaussian increases,
but the maximum stays at 0. This indicates that the network chains become shorter at increasing peroxide content, but there is always a significant fraction with long chain segments ($D_{res} = 0$) even at high peroxide content (Figs. 7, 8). Such network structure

![Graph](image)

**Figure 7** Different correlations between relative DQ build-up rate and $D_{av}$ and $\delta$; distribution curves are also shown for both sulfur and peroxide cured samples.
could indicate a tendency of peroxide to cluster together, leaving part of the EPDM chains non-crosslinked. Chain reactions (formation of multifunctional crosslinks by double-bond polymerization) may also play a role in peroxide-cured systems and may lead to the overall much broader distributions.

In contrast to the peroxide-cured samples, mono-modal curves based on Eq. 5 do not fit well to the DQ build-up curves for the sulfur-crosslinked EPDM systems (Fig. 2, left hand side). Bi-modal distributions consisting of a broad Gaussian centered at 0 and a

![Distribution curves for sulfur and peroxide crosslinked samples](image)

**Figure 8** Distribution curves are for both sulfur and peroxide cured samples.
narrow Gaussian with variable center and width (all together 4 fit parameters) fit better. In this case both the center and the width of the narrow Gaussian component increases at increasing sulfur content (Fig. 8). Perhaps sulfur mixes better and forms crosslinks more homogeneously along the chain. We have also observed (not shown) the very same trend in NR crosslinked by sulfur vs. peroxide. An additional relevant difference between sulfur- and peroxide-crosslinking may be that the first requires unsaturated functions (which are randomly distributed along the EPDM chain), whereas peroxide radicals create crosslinks anywhere along the chain plus possible chain reactions. So, even if sulfur reactants would tend to cluster, no big crosslink heterogeneity could arise, since the unsaturated third monomers are homogeneously distributed along the polymer chain.

**References**

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Ramona Orza
Curriculum Vitae

The author of this thesis was born on July 17\textsuperscript{th} 1980 in Gherla, Romania. After her graduation from high-school in 1999, she continued studying Medical Physics at the Babes-Bolyai University in Cluj-Napoca. She obtained her Masters’ degree in 2004 after completion of the thesis “NMR Investigation of silicon breast implants and elastomers” in the group of Prof. dr. B. Blümich. In November 2004 she started her PhD-study in the Inorganic Chemistry and Catalysis group of the Eindhoven University of Technology, under the supervision of Prof.dr. M.A.J. Michels. Her research was aimed at the investigation of peroxide crosslinking of EPDM rubber by solid-state NMR. The most important results of the research project DPI #511 are described in this thesis.
1. *Multispin moments edited by multiple-quantum NMR: application to elastomers*

2. *Network density and diene conversion in peroxide-cured gumstock EPDM rubbers. A solid-state NMR study*

3. *Solid-state $^1$H NMR study on chemical crosslinks, chain entanglements and network heterogeneity in peroxide-cured EPDM rubbers*

4. *Mechanism of peroxide crosslinking of EPDM rubber*

5. *Mechanism of peroxide crosslinking of EPDM rubber investigated with $^{13}$C NMR spectroscopy*

6. *EPDM – carbon black interactions and network structure in relation to stress-strain behavior*
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