High Pressure Vulcanization

Crosslinking of Diene Rubbers Without Vulcanization Agents

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Stockholm 1998

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ABSTRACT

High pressure vulcanization (HPV) is defined in this thesis as crosslinking of rubber materials at elevated pressure and temperature, without the use of any vulcanization agents. This is a totally new vulcanization technique, not used in the industry today. The HPV technique, however, has an interesting potential since no hazardous chemicals need to be handled, the vulcanization fumes contain no derivatives from a vulcanization system, and the resulting material does not contain any additives. The phenomenon that certain rubber materials can be crosslinked in this way was observed already in the 1960s, but there has been a lack of knowledge of the underlying reaction mechanisms, kinetics, the resulting network structure, and also the correlation between the molecular structure and the physical properties of these materials. The purpose of this thesis is to increase the knowledge of high pressure vulcanization, with respect to reaction kinetics and mechanisms, network structure and physical properties.

A low cis-polybutadiene was used as a model material for crosslinking at high pressure (10-290 MPa) and temperature (240-250°C), and comparisons were made with peroxide vulcanizates. Both unfilled and carbon black filled samples were studied. Nitrile- and styrene-butadiene rubber were also crosslinked successfully. Crosslink density is a central concept in this thesis and was evaluated by swelling measurements. The microstructural changes occurring during vulcanization were studied by Fourier Transform Infrared Spectroscopy (FTIR) and ^{13}C solid state nuclear magnetic resonance (NMR). The mechanical properties were investigated by dynamic mechanical thermal analysis (DMTA), tensile testing, and permanent set and stress relaxation measurements.

The progress of the reaction proved to be well controlled by the treatment time, temperature and pressure, resulting in materials with widely different properties within one single compound due to the possibility of controlling the crosslink density during the vulcanization process. The reaction mechanism was shown to be of a radical type, and vinyl unsaturations in the polybutadiene are consumed concurrently with the crosslink formation. The effect of pressure on the reaction is a decrease in molecular mobility, which results in higher crosslinking reaction rate due to a decrease in termination reactions. When a carbon black filler is introduced, the number of polymer-filler interactions is increased due to the ability of the polymer to penetrate the carbon black structure under pressure. The mechanical properties are as good as those of peroxide vulcanizates, and especially the resistance to deformation in service-use at elevated temperatures suggests that the resulting material may be used in gasket and seal applications. In spite of the difficulties of mould sealing that arise at elevated pressures, it was possible to obtain vulcanized samples by common injection moulding with properties comparable to those obtained by traditional vulcanization.

Keywords: High Pressure Vulcanization, Vulcanization, Crosslinking, Pressure, Elevated Temperature, Polybutadiene, Carbon Black, Rubber-Carbon Black Interactions, Crosslink Density, Peroxide Vulcanization, Injection Moulding, Nitrile-Butadiene Rubber.

LIST OF PAPERS

This thesis is a summary of the following papers:

I M. Bellander, B. Stenberg, S. Persson, *Crosslinking of Polybutadiene Rubber Without any Vulcanisation Agent,* Polymer Engineering and Science **38** (1998) 1254.

II M. Bellander, B. Stenberg, S. Persson, *Influence of Oxidised Carbon Black on the Degree of Cure in Polybutadiene Crosslinked by High Pressure Vulcanisation,* Kautschuk Gummi Kunststoffe **51** (1998) 512.

III M. Bellander, B. Stenberg, S. Persson, *Heterogeneities in Polybutadiene Network Structures Formed During High Pressure and Peroxide Vulcanisation,* Kautschuk Gummi Kunststoffe, submitted (1998).

IV M. Bellander, B. Stenberg, S. Persson, *Network Structure and Reaction Mechanisms in High Pressure and Peroxide Vulcanization of Polybutadiene: Microstructural Changes Studied by ^{13}C Solid State NMR,* Journal of Applied Polymer Science, submitted (1998).

V M. Bellander, B. Stenberg, S. Persson, *Effect of Temperature and Pressure on Carbon Black Reinforcement,* Plastics, Rubber and Composites Processing and Applications, submitted (1998).

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1. INTRODUCTION

Purpose of the Study

Ever since the 1830s, when Charles Goodyear invented the vulcanization of natural rubber with sulphur, the main idea in crosslinking rubber materials has been to add some reactive species to interconnect the polymer chains. However, some polymers can crosslink only by means of heat, without any vulcanization agents. This fact has been known for a long time but has not been considered as a potential process for the production of rubber products, partly due to the low reaction rate. If, however, certain rubber materials are concurrently subjected to an elevated pressure, they will crosslink at a rate comparable to commercial vulcanization processes used today. This technique, called high pressure vulcanization (HPV), has been investigated very sparsely, and neither the underlying reaction mechanisms nor the network structure have been clarified, including its effect on the physical properties of the resulting material.

The purpose of the work that has been performed during the last four years, resulting in this thesis, can be summarized in the following way:

- To understand the mechanisms of the crosslinking reaction in HPV, and establish the structure of the resulting network.
- To characterize the mechanical properties of rubber materials crosslinked by HPV.
- To correlate the network structure and the physical properties shown by materials crosslinked by HPV.
- To increase the knowledge of the effect of carbon black fillers on the crosslinking reaction in HPV.
- To increase the knowledge of the effect of pressure on the interactions between polymer and filler.

Rubber Materials

Rubber materials are without any doubt a prerequisite for the life we live today in the civilized world. Imagine just how it would be to travel without tyres on the wheels of your car or bicycle. The worldwide consumption of rubber materials in 1997 was 15.9×10^6 tonnes. This equals the weight of 640 000 soil-transporting normal-size lorries, which would create a line from the pole to the equator. 38% of the rubber materials were made from natural rubber, and the total annual increase is around 2 % *[Seifert, 1998]*.

A rubber material consists of many different components, of which the polymer itself is the most important in determining the final properties and performance. Most rubber materials contain a filler, such as carbon black (Swedish: *kimrök*), silica, clay or whiting. The role of the filler is to tailor the properties of the final product, but in the beginning it was also used to reduce cost of the compound. In addition to the polymer and filler, a rubber material also contains a vulcanization system, which includes crosslinking agents, accelerators, activators (zinc oxide and stearic acid) and retarders of the crosslinking reaction. The composition of the vulcanization system can be varied endlessly and will determine both the properties of the vulcanized material and the characteristics of the crosslinking process. These three main components – polymer, filler and vulcanization system – form the basis of a rubber material. To satisfy further demands, both on the manufacturing process and on the final properties, a number of additives are used. These may be antidegradants (antioxidants, antiozonants, waxes, etc.), processing aids (oils, plasticizers), diluents, pigments, and specific additives (blowing agents, fungicides, etc). For more details about the compounding of rubber materials, the interested reader is referred to textbooks by e.g. Hepburn and Blow *[Hepburn and Blow, 1982]*, Morton *[Morton, 1987]*, Swedish Institution of Rubber Technology *[Swedish Institution of Rubber Technology, 1996]*, and Mark et al. *[Mark et al., 1994]*.

The choice of polymer in rubber compounding is often governed by a mix of performance and price. Bulk polymers such as natural rubber (NR), styrene-butadiene rubber (SBR), and butadiene rubber (BR) are cheap, but do not have super properties regarding thermal, oxidative, oil and chemical resistance. On the other hand, high performing polymers such as fluorocarbon and silicone rubber are expensive. Between these two extremes are polymers which can be considered as compromises, e.g. nitrile-butadiene rubber (NBR) ethylene-propylene-diene rubber (EPDM), and butyl rubber (IIR). The following paragraphs contain more detailed descriptions of the polymers used in the reasearch leading to this thesis.

Butadiene Rubber (BR)

Butadiene rubber, or polybutadiene, is mainly produced by solution polymerization, even if there are some grades that are produced by emulsion polymerization. The chemical structure of BR is shown in Figure 1.1 and is worth some further comments.

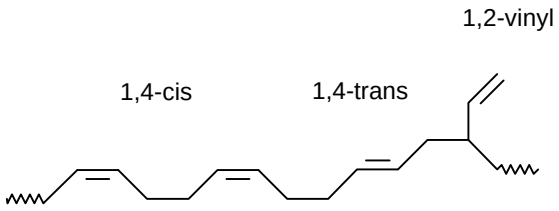


Figure 1.1. Chemical structure of butadiene rubber.

The butadiene monomer can be incorporated either by 1,4-addition, yielding the cis- or trans-stereoisomer, or by 1,2-addition yielding a pendant vinyl unit. This vinyl unit can be either syndiotactic, isotactic, or atactic, but only the latter has been reported to appear in anionic polymerization *[Morton and Fetters, 1975]*, one of the important reaction paths. The relative amount of each kind of unsaturation and the order in which they appear in the main chain depend on many factors, such as type of catalyst, solvent, monomer/initiator ratio, and polymerization temperature. A structure of 30% cis, 62% trans and 8% vinyl may be obtained by lithium-catalysed anionic polymerization in hexane at 20°C. By simply changing the solvent to a more polar one, tetrahydrofuran, the microstructure will consist of 6% cis, 6% trans and 88% vinyl *[Hargis et al., 1987]*. High cis-BR may be obtained by using e.g. a cobalt catalyst, yielding >99% cis structures *[Morton, 1987]*.

The microstructure affects many different properties of BR. By increasing the vinyl content, the T_g is increased; see Table 1.1. This increase in vinyl content impairs the abrasion resistance of the final material. Polybutadiene is seldom used alone, but most often mixed with other polymers such as styrene-butadiene (SBR) and natural rubber (NR). In addition to tyres, polybutadiene is used for production of e.g. high resilience playballs *[Brydson, 1988]*.

Table 1.1. Typical T_g-values of different polybutadienes.

Polybutadiene	T_g (°C)
cis	-113[a]
trans	-88[a]
vinyl, atactic	-4[a]
38% cis, 51% trans, 11% vinyl	-80[b]

[a] According to reference *[Hargis et al., 1987]*

[b] Present work, tanδ peak in DMTA measurements of very slightly crosslinked polybutadiene.

Nitrile-Butadiene Rubber (NBR)

Nitrile-butadiene rubber is a copolymer between acrylonitrile and butadiene, and the structure can be written as in Figure 1.2. It is produced mainly by emulsion polymerization, and the butadiene unit may be incorporated in the cis, trans or vinyl configuration, where the latter is favoured by increasing the polymerization temperature.

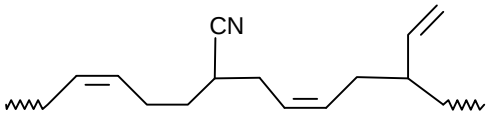


Figure 1.2. Chemical structure of nitrile-butadiene rubber.

NBR is best known for its oil resistance, which has made it useful in applications such as hoses, seals and gaskets in contact with oils. The oil resistance improves with increased acrylonitrile content, but at the same time the rubber becomes much stiffer. In commercial NBR, the acrylonitrile content is between 15-50% (w/w) *[Brydson, 1988], [Hepburn and Blow, 1982]*.

Network and Crosslink Density

Network

A polymer network can be defined as a system of many long polymer chains that are connected to each other through chemical bonds, so-called crosslinks, resulting in a three-dimensional structure (see figure 1.3.). Three requirements have to be fulfilled for a material to show rubber-like properties *[Treloar, 1975]*:

(1) the presence of long chain-like molecules with freely rotating links;
(2) weak secondary forces between the molecules;
(3) an interlocking of the molecules at a few places along their length to form a three-dimensional network.

Through the introduction of crosslinks, the chains are prevented from sliding from each other and the rubber becomes elastic. Besides *chemical crosslinks*, *chain entanglements* contribute to the elasticity of the polymer network. They can be of either a permanent or a temporary nature. The concept of entanglements has been discussed, and even questioned, during many decades. However, today it is more or less accepted that entanglements contribute to the elastic forces in rubber materials *[Boyd and Phillips, 1993]*. When a filler is introduced, *polymer-filler interactions* appear and will also contribute to the three-dimensional network. Opposing these three mechanisms of networking are *loose chain ends* and *elastically ineffective loops*. The former increase the free volume of the material by their non-restricted mobility (no crosslinks that tighten the chain end). Chain loops may be formed during vulcanization and will lower the number of elastically effective chains in the material.

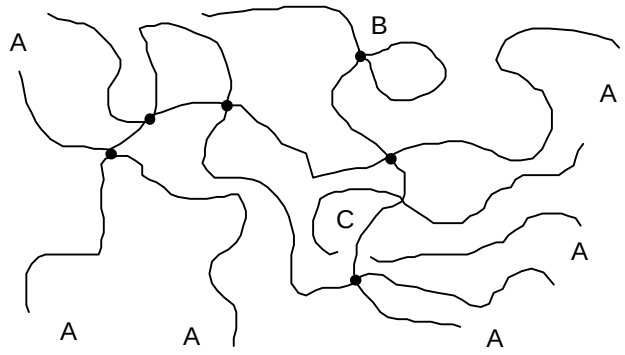


Figure 1.3. Model of a rubber network. A - loose chain ends, B - elastically inactive loop, C- chain entanglement, λ - chemical crosslink.

Crosslink Density

The term *crosslink density*, which will be used frequently in this thesis, deserves a more elaborate explanation. It can be expressed as the number of crosslink points or number of elastically effective chains per unit volume. Theses two quantities are proportional to each other, and their exact relationship depends on the functionality of the crosslink points, i.e. the number of chains that radiate from the crosslink. Henceforth crosslink density will be defined as the number of *crosslink points* per unit volume. Furthermore, crosslink density is inversely related to the average molecular weight of the chains between the crosslinks, which is also a way to express the network properties. The value of crosslink density may be in the order of 10^{-3} to 10^{-5} mol/cm^3 for a typical rubber material, corresponding to 15 to 1500 monomer units between the crosslinks. Crosslink density is fundamental for polymeric networks, as it determines many physical properties of the resulting material *[Coran, 1994]*. Figure 1.4 shows how some properties of a rubber material generally depend on the crosslink density.

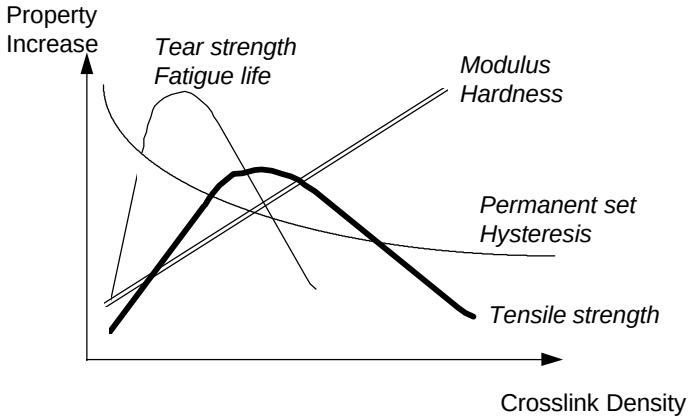


Figure 1.4. The dependence of some properties of a rubber material on crosslink density.

Determination of Crosslink Density

Crosslink density can be measured in principally three different ways:

(1) By stress-strain measurements, evaluation by the Mooney-Rivlin equation *[Mooney, 1940], [Rivlin, 1948]*.
(2) By determination of the elastic modulus at a certain temperature in the rubbery plateau zone *[Saville and Watson, 1967]*.
(3) By swelling measurements, using the Flory-Rehner equation *[Flory and Rehner, 1943]*.

The values thus obtained must be handled with care, as the methods are not absolute but have to be calibrated in some way. The different methods will give different results partly due to the time scale of the measurements *[Hagen et al., 1996]*. Swelling measurement, which is an equilibrium method, will have lower contributions from entanglements, as the time scale of the

experiment permits disentanglement of temporary entanglements. DMTA measurements, on the other hand, which are often performed at a frequency of 1 Hz, will show a much larger proportion of entanglements as there is not time enough for disentangling. However, measurement of crosslink density is valuable, especially for relative comparisons of similar rubber materials. In the research for this thesis swelling measurements have been used throughout to establish the degree of crosslinking.

Crosslink density can further be divided into two sub-parts: *chemical* and *physical* crosslink density. The former is the contribution of the pure chemical crosslinks that result when a rubber material is vulcanized. The physical crosslink density is composed of both chemical crosslinks and chain entanglements, and is the crosslink density that is physically measured by e.g. stress-strain measurements. It is very difficult to distinguish between these two quantities, as there are very few techniques apt to measure such low concentrations as the chemical crosslinks show. One way to quantify chemical crosslink density is by stoichiometric calculations of the crosslinking reaction, as Moore and Watson *[Moore and Watson, 1956]* did for a peroxide crosslinked natural rubber. They constructed a calibration curve of physical versus chemical crosslink density.

Vulcanization

General

Vulcanization (from *Vulcanus*, the Roman god of fire and smithery) is the process whereby viscous and tacky raw rubber is converted into an elastic material through the incorporation of chemical crosslinks between the polymer chains. Hereafter the word vulcanization will be used interchangeably with *crosslinking* and *curing*. The invention of vulcanization is ascribed to Charles Goodyear, who in the late 1830s heated rubber in contact with sulphur and found that it became an elastic, non-sticky material. Since then the vulcanization technique has been developed enormously, to fit new materials and to meet the demands of modern production of rubber materials. However, sulphur is still the most frequently used vulcanization agent for rubbers containing unsaturations.

Sulphur vulcanization always includes the use of accelerators, to speed up the crosslinking process, which would otherwise take many hours to perform. Depending on the amount of accelerator used, different lengths of sulphur crosslinks are obtained; see Table 1.2. Moreover, the final properties of the vulcanizates will differ depending on the type of vulcanization system used. A conventional system will give better mechanical properties, such as tensile strength, than an EV system. On the other hand, the ageing properties will be the opposite since in this respect the EV system is superior to the conventional system. The semi EV system is a compromise and exibits intermediate properties in both cases. *[Southern, 1979]*.

Table 1.2. Different systems in sulphur vulcanization

Type of system	Sulphur/accelerator ratio	Type of crosslinks
Conventional	>2	-S_x-, cyclic sulphides
Semi EV	~1-2	C-S_2-C, C-S-C
EV	<0.3	C-S-C, C-S_2-C, C-C

Other types of vulcanization systems are peroxides, which are used in the crosslinking of e.g fluorocarbon, silicone, and some diene rubbers, metal oxides (chloroprene rubber), diamines (fluorocarbon rubbers), maleimides (chlorosulfonated polyethylene), isocyanates (polyurethane rubber), nitroso compounds (butyl rubber), polymethylol-phenol resins (butyl rubber), and crosslinking with β– (electron beam) or γ–radiation. A characteristic of all these types of vulcanization systems (except for the radiation-curing) is that they involve the use of reactive chemicals, often of low molecular weight. This means that they must be handled with care for environmental and health reasons.

Peroxide Vulcanization

Peroxides may be used for crosslinking of slow reacting rubbers, such as some fluorocarbon rubbers, silicone rubbers and ethylene propylene rubbers. They are also applicable for crosslinking of polydienes when the ageing properties are of importance, as they involve formation of stable carbon-carbon crosslinks. The reason why carbon-carbon bonds are more stable than sulphur-sulphur bonds appears from Table 1.3, which shows the bond dissociation energy of different crosslinks. The properties of peroxide vulcanizates are often very similar to radiation crosslinked materials, which is due to the fact that both curing systems result in carbon-carbon crosslinks.

Table 1.3. Bond dissociation energy of different crosslinks *[Brydson, 1988]*.

Type of crosslink	Bond dissociation energy (kJ/mol)
C-C	346
C-S-C	272
CS-SC	270

A number of different peroxides is available for vulcanization applications. Of these dicumyl peroxide is one of the most frequently used. Others are benzoyl peroxide, 2,4-chlorobenzoyl peroxide, and tertiary butyl perbenzoate peroxide. Dicumyl peroxide, which will be the only peroxide discussed from here on, is cleaved thermally to give two radicals that can initiate the crosslinking reaction. It is often this step that determines the rate of the crosslinking reaction, and the temperature dependence of the half-life of the peroxide displays a logarithmic behaviour (log*(half-life)* μ *1/T*) *[Amberg, 1964]*.

Peroxide crosslinking has been known since the beginning of this century, and the reaction mechanisms have been studied by several authors. Loan *[Loan, 1967]* wrote a comprehensive review of peroxide vulcanization of elastomers, and one year later van der Hoff wrote a more specific review of radical crosslinking of polybutadienes *[van der Hoff, 1968]*. Peroxide crosslinking of polydienes takes place either through an *abstraction-combination* or an *addition* mechanism; see Figure 1.5. The former starts with the abstraction of an unstable

hydrogen, preferably an allylic hydrogen atom, by the peroxide radical. Then the polybutadiene radical formed combines with another polybutadiene radical, resulting in a carbon-carbon crosslink. The addition mechanism may start with the same step, or as indicated

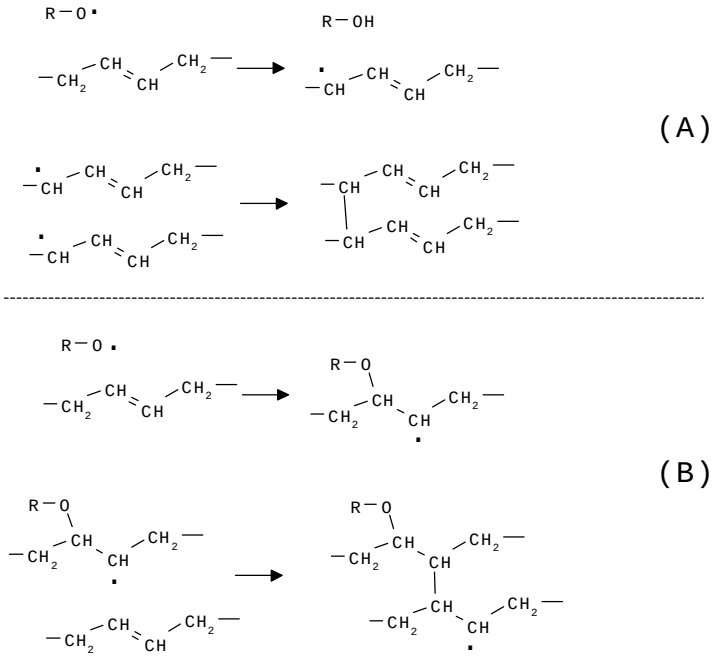


Figure 1.5. Reaction mechanisms in peroxide vulcanization of polydienes. (A) abstraction-combination mechanism, (B) addition mechanism.

in structure (B) in Figure 1.5, with the addition of the peroxide radical to a double bond in the polymer chain. The subsequent step is addition of the polybutadiene radical formed to a double bond in a nearby chain. This addition step can be repeated as long as there are reactive sites left in the vicinity, resulting in new intermolecular bonds. In this way, every initiating radical may generate numerous crosslinks, and the number of crosslinks formed per peroxide molecule, often referred to as *crosslinking efficiency*, may attain values of up to one hundred.

In peroxide crosslinking of polybutadiene, the microstructure is of great importance for the crosslinking efficiency. For example, cis-polybutadiene has a crosslinking efficiency around 10 *[Loan, 1963]*, and a polybutadiene with vinyl content increasing from 10% to 98% shows a rise in crosslinking efficiency from 2 to around 100 *[Loan, 1967]*. Further, the crosslinking of polybutadienes with varying vinyl content displays a strange temperature behaviour. For a polybutadiene with 79% vinyl content, the crosslinking efficiency increases from 18 to 45 when the temperature is increased from 115°C to 160°C, while an 11% vinyl polybutadiene shows a decrease in efficiency from 50 to 22 over the same temperature range *[Loan, 1967]*. From this it is clear that the vinyl content plays a very important role in peroxide vulcanization of BR, and there is no doubt that the addition reaction has a key role.

Of later years, the mechanisms of peroxide crosslinking of polydienes have again been focused. Gonzales et al. *[Gonzales et al., 1992 a and b]* proposed that a kind of heterogeneity was

formed during peroxide crosslinking of natural rubber. DMTA measurements showed that a second tanδ peak, on the high temperature side of the original peak, appeared at peroxide levels (dicumyl peroxide) of 3.0 phr. This was ascribed to regions containing more densely crosslinked chains with slightly lower mobility than the main part of the network. These densely crosslinked regions were explained as due to the addition mechanism, leading to many crosslinks in the vicinity of the initiating radical. This heterogeneity can be viewed schematically in Figure 1.6.

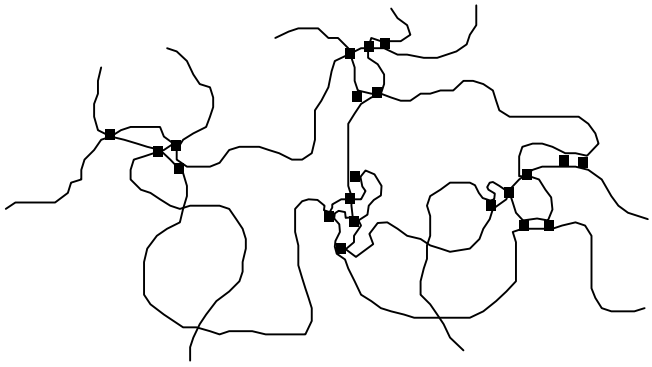


Figure 1.6. Heterogeneity of crosslinks in a rubber network.

When an active filler was added, such as carbon black, the second transition disappeared *[Gonzales et al., 1994]*. This was claimed to be caused by some kind of interaction of the carbon black with the crosslinking reaction. The importance of the addition mechanism was further investigated for polybutadiene, styrene-butadiene rubber and polychloroprene *[Gonzales et al., 1996]* and it was generally concluded that at low temperatures and a low concentration of peroxide, the abstraction mechanism dominates, while the addition mechanism dominates at higher temperatures and at an elevated peroxide concentration. As an additional tool, ^{1}H NMR was used to study the degree of crosslinking in NR vulcanizates *[Gonzales et al., 1998]* and led to the same conclusion about the importance of the addition mechanism.

State of Cure

The degree of crosslinking during vulcanization of a compound can be represented by its vulcanization curve, which shows some property proportional to the degree of crosslinking versus vulcanization time. This is done as a routine measurement (e.g. by oscillating disc or moving die rheometer) in the rubber industry and is of paramount importance in order to obtain products vulcanized to an optimum level. Typical vulcanization curves may look as in Figure 1.7. The upper curve (A) shows a marching behaviour that can be observed for chloroprene rubber and SBR-based compounds. (B) is the ideal behaviour where the cure level reaches a plateau level, typically for NBR, and (C) shows reversion, a phenomenon that appears for e.g. NR vulcanized with a conventional sulphur system *[Crowther et al., 1988]*. The time from the start of the measurement to the onset of the crosslinking process (i.e. when the increase in the curve starts) is called *scorch time [Hepburn and Blow, 1982]*.

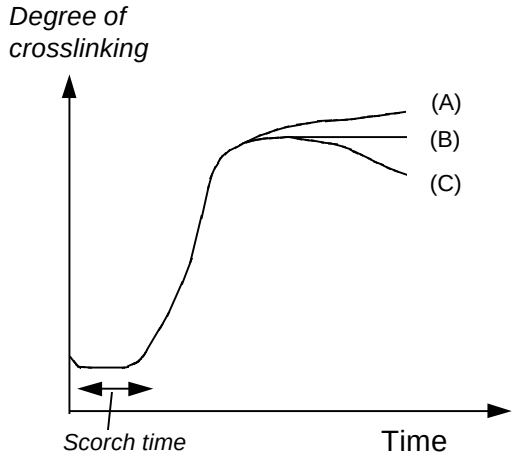


Figure 1.7. Vulcanization curves showing (A) - marching behaviour, (B) - plateau level, and (C) - reversion

Carbon Black

Carbon black is today the most utilized filler in the rubber industry, mainly due to its unique ability to reinforce the rubber material, resulting in enhanced mechanical properties *[Wang et al., 1991]*. Carbon black also improves the ageing resistance of the rubber material. This is due to the ability of carbon black to absorb UV light, which otherwise would be absorbed by the polymer and initiate photo-oxidative reactions leading to deterioration *[Hawkins and Winslow, 1965]*.

Carbon black is produced by incomplete combustion of a carbon source, such as oil or gas. This can be achieved by different processes, of which the furnace process is the most common today *[Donnet et al., 1993]*. The characteristics of carbon black are strongly dependent on the process used, and by controlling the manufacturing conditions a huge number of carbon black grades can be obtained. The nomenclature of different carbon blacks has been a little confusing, but now the ASTM system has been widely accepted, even if it is not perfect. In this system every grade of carbon black has a letter followed by three digits. The letter is S or N, referring to *Slow curing* (acidic carbon blacks) or *Normal curing* (basic or neutral carbon blacks). The first digit gives the size range of the primary particles, and the last two digits are arbitrarily chosen to distinguish between carbon blacks with the same primary particle size but a different structure. An example is N220, which is a normal curing carbon black with particle size 20 to 25 nm and a high structure *[Swedish Institution of Rubber Technology, 1986]*.

In spite of the enormous research spent to characterize and describe carbon black in an objective way with some kind of universal parameters, there are still many questions left about the exact nature of carbon black particles. Carbon black is composed of primary particles with a size of ~10-500 nm, depending on grade. These primary particles are clustered together to aggregates (primary structure) of varying sizes, up to several hundred nm. The aggregates can in turn be fused together by van der Waals interactions to form agglomerates (secondary

structure) *[Donnet et al., 1993]*. This hierarchic morphology of carbon black particles can be viewed in Figure 1.8.

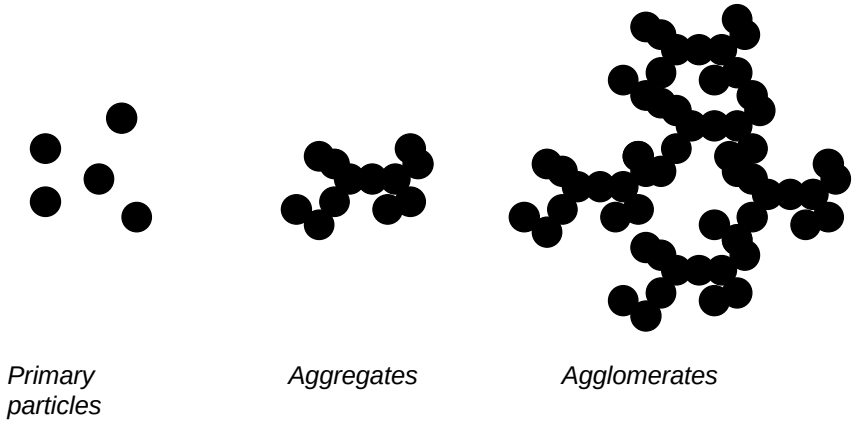


Figure 1.8. The different levels of carbon black morphology. Primary particles - aggregates - agglomerates.

There are several important parameters used today to describe a carbon black grade. The *specific surface area* can be measured by N_2-adsorption, and is one of the most basic parameters. It may vary from a few to several hundred m^2/g. The *structure* is measured by DBP-absorption (dibutylphtalate), expressed in $cm^3/100$ g, and reflects the bulkiness of the aggregates. The high reinforcing ability of carbon black is due to the *surface activity*. The surface of the primary particles consists of crystalline regions with a two-dimensional order, almost like graphite. The size of the crystallites is of the order of 15 Å (N121 carbon black) *[Ayala et al., 1991]*. At the edges of the crystallites the structure becomes disordered and the carbon is present in an amorphous state. It is here where the clue to the carbon black surface activity can be found. In the amorphous regions a number of different functional groups exists, e.g. carboxyls, phenols, lactones, carbonyls and pyrones *[Papirer et al., 1987]*. The presence of quinone-like structures has also been proposed *[Rivin, 1962]*.

The surface of the primary particles is by no means smooth. Throughout its history, carbon black has been reported to have pores. The porosity can be either open or closed *[Hess and Herd, 1993]*. The open pores are of undefined shape, of the size of a few nm, and accessible to the surface. The closed pores on the other hand, do not have access to the surface of the particles. However, it must be mentioned that in recent years, it has been questioned whether the carbon black surface shows porosity at all *[Gerspacher et al., 1995]*. Even if there have been some controversies whether carbon black particles are microporous on the surface or not, there is no doubt that there are geometrical variations on the surface, as demonstrated by e.g. AFM and STM *[Donnet and Wang, 1995]*. Furthermore, the concept of *fractal geometry* has been used to characterize carbon black and can be applied to different levels of the carbon black morphology. The shape of the aggregates can be described by one fractal dimension, and it has been shown that it varies between different grades of carbon black *[Gerspacher, 1992]*. By contrast, the fractal dimension of the surface of the primary particles has been found not to vary in this way *[Gerspacher and O´Farrell, 1991]*.

By heating carbon black in inert atmosphere, at temperatures of ~1500°C, most of the surface groups are burned off, and the crystallites become larger *[Ayala et al., 1991]*. This graphitized carbon black, as it is usually called, shows very low surface activity compared to original carbon black and well illustrates the importance of the surface groups. The opposite can also be done, by oxidative treatment of carbon black (thermally or chemically) resulting in increased surface activity. However, the surface activity cannot be considered without specifying what kind of substrate it is supposed to be reactive against. Oxidation of carbon black may lead to increased reactivity against polar polymers, while the opposite is true for non-polar polymer types. The thermal oxidation of carbon black has been shown to lead to hollowing of the particles *[Ladd and Ladd, 1961]*, in extreme cases leaving primary particles with a shell-looking structure. In this way, the surface area of the oxidized carbon black may be increased. If the oxidation is performed by chemical treatment (nitric acid or ozone), the surface area is left almost unchanged, and only the surface chemistry of the carbon black is changed *[Sweitzer et al., 1961], [Gessler,1964 a], [Gessler,1964 b], [Serizawa et al., 1983], [Roychoudhury, 1994]*.

Compounding and Processing

Manufacturing of rubber products involves the following main steps: Mixing, shaping, and vulcanization. In the mixing step, the aim is to get all ingredients dispersed homogeneously. Especially the carbon black has to be well dispersed. During mixing of carbon black with rubber, the carbon black particles are wet by the rubber and interactions between the two phases are developed (bound rubber, see section ”Rubber-Carbon Black Interactions”, p. 13). The following step is shaping of the final product. This can be done either continuously, in which case extrusion is the most common process, or intermittently, by some kind of moulding process. The oldest moulding technique, and still very much used, is *compression moulding*. The material is inserted manually into the hot mould, which is divided into two halves. Then the mould is closed and the rubber flows out into all cavities and vulcanization takes place. *Transfer moulding* looks almost the same, with the only exception that the material is transferred (injected) into the mould cavity through a sprue from a pre-chamber. *Injection moulding* is the most automated moulding technique and functions almost like injection moulding of thermoplastics. The rubber material is fed into a reciprocating screw, which rotates slowly backward as the rubber is conveyed in frontal direction. Then the screw is pushed forward and the material flows through the nozzle, runner, sprue and gate into the hot mould. When the rubber product has vulcanized enough to be stable in shape, the mould is opened and the product ejected. In rubber moulding it is very difficult to avoid flash formation, and therefore most products must be deflashed after moulding. The pressure in rubber injection moulding may be up to 250 MPa, measured as nominal injection pressure of the machine. However, the pressure reaching the mould is much lower, and this pressure drop is dependent on the flow length before the rubber reaches the mould. In the mould there is also a large pressure drop, which decreases the pressure at the outer edges to a minimum *[Isayev at al., 1994]*.

Carbon Black Reinforcement

There are mainly four different mechanisms that are responsible for the reinforcing action of carbon black in rubber materials:

- The hydrodynamic effect
- Rubber-carbon black interactions
- Occluded rubber
- Filler networking

The hydrodynamic effect has its origin in the viscosity of fluids. If a particle is introduced into a fluid, the flow field is perturbed in relation to that of the pure fluid, increasing the viscosity *[Funt, 1988]*. It was originally stated by Einstein in 1906 *[Einstein, 1906]* through the equation

$$h_f = h_u(1+2.5c) \qquad (1.1)$$

which describes how the viscosity of a fluid, h_u, is changed to h_f with the introduction of spherical particles at a concentration c. In terms of carbon black filled rubber it may be explained as a reduction in the volume fraction of the soft part (the rubber), and this increases the modulus of the material. The *rubber-carbon black interactions* improve the adhesion between polymer and filler and thereby prevent large scale molecular slippage. These interactions are full of nuances and will be treated separately in the next section. *Occluded rubber* refers to the rubber that is hidden within the carbon black aggregates, not available for deformation on loading a rubber material *[Wolff and Wang, 1993]*. This partially immobilized rubber behaves more like the filler than the polymer matrix. Occlusion of rubber is a somewhat strange concept, as it is quite difficult to define what is meant by ”within the aggregates”. Finally, *filler networking* is the agglomeration of carbon black aggregates into a kind of network of filler particles. The aggregates are held together by London/van der Waal type of forces and will be effective only if the deformation is small. In the case of large deformations, they will break and the modulus will decrease (for further information see the section ”Dynamic Mechanical Properties of Rubber Materials”). Reinforcement of rubber materials is a large area of research and many books have been written on the topic or part of it *[Kraus, 1965], [Donnet et al., 1993], [Donnet and Voet, 1976] [Mark et al., 1994], [Hepburn and Blow, 1982]*.

Rubber-Carbon Black Interactions

As mentioned earlier in this chapter, it is the reinforcing properties of carbon black that have made it such an attractive filler for rubber materials. It was also mentioned that the reinforcement emanates partly from the great ability of the carbon black particles to interact with the polymer chains. Whether these interactions are of a physical or chemical nature has not been fully understood yet. It is also of importance that many carbon blacks have a very high specific surface area, which makes the interface between polymer and filler very large and thus increases the number of interactions.

The most common concept when speaking about polymer-filler interactions is *bound rubber*. Above a certain critical level of carbon black loading, a coherent gel is formed (before any vulcanization has taken place and before any vulcanization agents have been added) as a result of interactions between the polymer and the carbon black. Bound rubber is defined as the portion of polymer that cannot be extracted by a good solvent. A closely related concept is the *rubber shell*, which is the polymer layer around the carbon black particle with restricted mobility due to the interaction with the particle surface. It can be measured by e.g. NMR. The difference between bound rubber and rubber shell is in the way of measuring it. It is enough for a polymer chain to contribute to the bound rubber by a single attachment at one end of the chain. On the other hand, only part of a chain may contribute to the rubber shell, while another part of it does not, due to differences in mobility within the same molecule. The amount of bound rubber formed depends on many factors, such as specific surface area, structure, and surface chemistry of the carbon black, and on the type of polymer *[Blow, 1973]*. It is important to stress that the bound rubber is measured in unvulcanized compounds, after mixing. During vulcanization, new kinds of interactions may take place. Because of that, care must be taken when results from bound rubber measurements are translated into terms of reinforcement; a high bound rubber value does not necessarily mean good reinforcement of the final vulcanized material.

The nature of the interactions resulting in bound rubber has been penetrated in many studies, but there is still no single picture of the interface. It is often mentioned that chemisorption or very strong physical adsorption are the main mechanisms *[Leblanc and Hardy, 1991]*. One interesting discovery by Wolff and co-workers *[Wolff et al., 1993]* was that almost all bound rubber could be extracted when the temperature of the leaching increased. This suggests that bound rubber is mainly a physically controlled phenomenon. Nevertheless, the surface chemistry of carbon black plays an important role in bound rubber formation. Gessler *[Gessler, 1969]* suggested that carboxylic acid groups participate chemically in the interaction between butyl rubber and oxidized carbon black, through a nonradical mechanism. Bound rubber values for samples containing oxidized black were significantly higher than for those contaning standard black, both after mixing only and after mixing and heat treatment at 150°C for 45 min. Sweitzer et al. *[Sweitzer et al., 1961]* earlier found that oxidized carbon black *does not* have any significant effect on the reinforcing properties of vulcanized natural rubber or SBR. The only effect seen was retarded cure, to a higher extent for sulphur than for peroxide. In contrast to Sweitzers finding, Serizawa and co-workers *[Serizawa et al.,1983]* demonstrated that oxidized carbon black led to higher amount of bound rubber in natural rubber mixed with SAF (N110) carbon black. Furthermore, the importance of surface groups, especially ones containing oxygen, has been demonstrated by Vidal et al. *[Vidal et al., 1991]*. They deactivated carbon blacks by grafting alkyl chains (esterification reactions) onto the surface, and then measured the mechanical properties of the vulcanizates (peroxide curing). After deactivation, the mechanical properties were significantly lower than for compounds containing non-modified carbon blacks. When using epoxidized and carboxylated rubbers, the possibilities of chemical interactions between polymer and filler are increased, as shown by Manna et al. *[Manna et al., 1997]* for epoxidized NR, Bandyopadhyay et. al. for carboxylated NBR *[Bandyopadhyay et al., 1995], [Bandyopadhyay et al., 1996]*. Increased interactions between filler and polymer have also been reported for chlorosulfonated polyethylene by Roychoudhury and co-workers, who oxidized carbon black with ozone *[Roychoudhury et al., 1994]*.

Bound rubber formation is not only determined by the nature of polymer and carbon black surface; the molecular weight of the polymer is also of importance. The higher molecular weight portions of the polymer are preferentially adsorbed to the filler surface *[Kraus and Gruver, 1968]*. Moreover, bound rubber formation is a kinetically controlled phenomenon. The first chains to be adsorbed are those with the lowest molecular weight, and gradually they are exchanged for higher molecular weight chains *[Meissner, 1993]*. An additional kinetic aspect of bound rubber formation is that the amount of bound rubber formed is increasing steadily from the time of mixing to many weeks after it, finally reaching some kind of equilibrium value. By heating the rubber-carbon black mix, this equilibrium is reached faster *[Kraus, 1967]*. However, care must be taken so that other reactions do not take place at the elevated temperature, such as chain scission or crosslinking of the polymer.

Bound rubber measurement is still the most used technique for investigation of reinforcement and rubber-filler interactions. However, NMR techniques have become more frequently used, providing new interesting knowledge about the interface between filler and polymer. By measuring the T_2 (spin-spin) relaxation times of protons, a great deal of information about the mobility of the chains closest to the filler particle can be obtained. Kaufman et al. *[Kaufman et al., 1971]* showed that two regions with different mobility could be detected in the bound rubber, i.e. the part of the rubber-carbon black mix that could not be extracted by a good solvent. The region with the lowest mobility is formed from the chain segments that are closest to the point of interaction with the filler surface. The other region belongs to chain segments and chains at some distance from that point. Figure 1.9 shows a generalized picture of the two layers with different mobility that are closest to the carbon black particle. The ”free” rubber is also indicated, i.e. the part of the rubber that is not influenced at all by the carbon black.

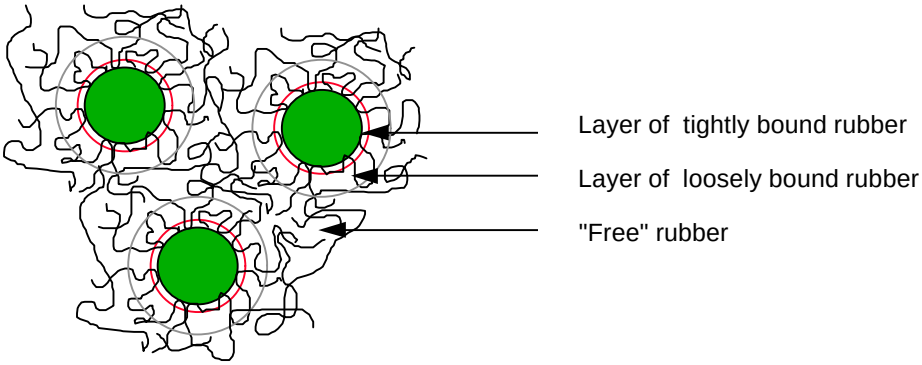


Figure 1.9. Model of bound rubber with the two regions of different mobility. The carbon black particles have been drawn as single primary particles for convenience.

O´Brien et al. *[O´Brien et al., 1976]* applied this model to a cis-polybutadiene filled with different carbon blacks at loadings up to 100 phr, and measured T_1 and T_2 NMR relaxation times. They considered the model as a realistic way of representing the bound rubber and concluded that the inner layer accounts for ~1/5 of the total bound rubber layer thickness. Further they found that the introduction of filler leaves the T_g of the polymer almost unchanged.

Pressure Effects on Rubber-Carbon Black Compounds

When a rubber polymer is mixed with carbon black, the filler particles will get dispersed and wet by the polymer. However, as carbon black has a very complicated morphology and often a high structure, there will be space inside the rubber-carbon black composite where the polymer does not have access. This is illustrated in Figure 1.10, which shows the density of a polymer-carbon black mix (SBR-N330) versus composition *[Schilling et al., 1974 a]*. At elevated pressure (1.9 GPa) the density is much higher, since both the polymer and the carbon black get compressed. Moreover, the density increases as the amount of carbon black increases (higher density than the polymer). However, when the composition is around 80% carbon black, the linear increase of the 1.9 GPa curve deviates since the polymer cannot fill all empty space in the sample. There will consequently be pores in the sample, even when the sample is under pressure. At 0 GPa, i.e., after compression and release of the pressure, this deviation appears at a much lower carbon black loading (around 20%). In the range 0-20% carbon black, the samples will exhibit almost no porosity after compression as the polymer fills the empty room. At higher concentrations, on the other hand, there is not polymer enough to fill the empty space between the carbon black particles, leading to lower densities.

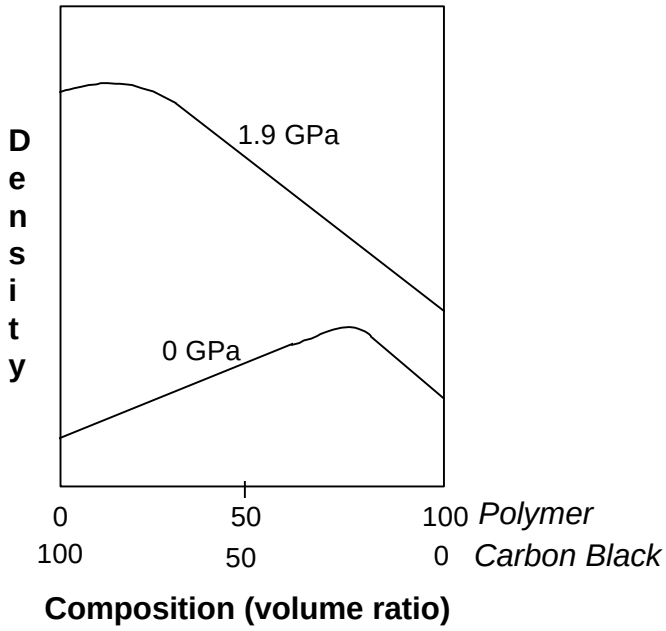


Figure 1.10. Density of polymer carbon black composites as a function of composition. The curve 0 GPa represents the density of samples at amospheric pressure, previously compressed at 1.9 GPa. The 1.9 GPa curve represents the density of samples under pressure.

Furthermore, the result of elevated pressure on a polymer carbon black composite is that the samples become almost like vulcanizates, even if they are treated at a tepid temperature. This is due to the strong chemisorptive bonds that are evolved. The fact that these bonds are not of a purely physical nature is demonstrated by their ability to withstand leaching in boiling toluene for 24 h *[Schilling et al., 1974 c]*. Another indication that not purely physical processes are taking place is that unsaturated rubbers behave differently from saturated ones when subjected to pressure. The latter do not show the same interaction ability with carbon black as unsaturated polymers under the influence of elevated pressure *[Angerer and Schilling, 1975]*.

Carbon black types other than N330 have also been investigated, and the number of interactions between polymer and filler varies with the characteristics of the black. However, the general behaviour described above tends to be valid *[Angerer and Schilling, 1975]*.

Pressure Effects in Polymers

Rubber materials are generally regarded as incompressible substances, with a Poisson´s ratio of 0.5. This means that when a rubber sample is stretched or compressed, the ratio, as regards dimensional change, of longitudinal to transversal direction is constant and there is no volume change of the test piece. However, at hydrostatic pressures of several hundred MPa, volumetric changes occur, which have appreciable effects on some properties, e.g. modulus, electrical conductivity, heat capacity, and specific volume.

In the study of pressure effects on rubber materials a number of techniques have been used. Anderson et al. *[Anderson et al., 1969]* investigated the pressure dependence of molecular motions in NR, IIR, BR and EPDM in terms of NMR T_1-relaxation times (spin-lattice relaxation time), which involve relaxation processes in the range of MHz. The T_1 curve versus temperature was shifted when an elevated pressure (68 MPa) was applied. However, this was observed only at higher temperatures, where main chain segments were responsible for the relaxation processes. At low temperatures, where only small scale motions such as rotation of methyl groups in natural rubber are involved, the T_1 curves for the different pressures coincided. Thus, main chain segment motions appear to be much more pressure sensitive than small scale motions such as rotation of methyl groups. Dynamic mechanical analysis of natural rubber under pressure (0.1-140 MPa) has shown that the modulus curve is shifted to higher temperatures as the pressure is increased *[Billinghurst and Tabor, 1971], [Parry and Tabor, 1973]*. The same is applicable to the dielectric properties, where the curves for the dielectric constant and dielectric loss are shifted towards higher temperatures *[Dalal and Phillips, 1983]*. The pressure range in this study was 0.1-380 MPa. Furthermore, the thermal properties of rubber materials have been examined and they are also sensitive to pressure changes. The thermal conductivity of natural rubber increases linearly with pressures up to 200 MPa *[Andersson, 1976]*. Butyl-ethylene-propylene diene, and nitrile-rubber showed a similar behaviour, and a dependence of same order of magnitude as applies to natural rubber. Sandberg and Bäckström *[Sandberg and Bäckström, 1979]* measured the heat capacity and thermal conductivity of both crosslinked and unvulcanized natural rubber under pressures up to 1 GPa. At high pressures the vulcanized rubber was less pressure sensitive, and the increase in thermal conductivity levelled off from that of the raw rubber.

All the properties described are dependent on the mobility of the polymer molecules, which is affected by pressure changes. In this connection, the concept of free volume becomes relevant. The free volume of a polymer is the space not occupied by the polymer chains, and can be looked upon as mobile holes jumping around in the structure making it easier for the chains to take new conformations *[Meares, 1965]*. When the temperature decreases, the concentration of holes becomes lower, and at T_g there is not enough empty space for large scale motions of chain segments. The critical volume needed for a certain process to take place is referred to as the *activation volume*. The value of the activation volume is dependent on the size of the motion. Glass transitions may have an activation volume of 100-500 cm^3/mol, while that of small-scale motions such as rotation of methyl groups is in the order of 10-40 cm^3/mol *[Kovarskii, 1993]*. The effect of pressure is to decrease the free volume, which will aggravate

the chain motions. This will shift the T_g towards higher temperatures, as the decrease in free volume due to the pressure must be compensated for by an increase in temperature. The shift in T_g of polymers under pressure varies, depending on the type of polymer, and for natural rubber $\partial T_g/\partial p$ is of the order 170 K/GPa *[Sandberg and Bäckström, 1979]*. However, it must be mentioned that the value also depends on the method used for determination.

Effect of Pressure on Traditional Vulcanization

As stated above, the effect of pressure on traditional vulcanization is dependent on the type of polymer. Sulphur vulcanization of SBR under pressure will result in a material with higher modulus as the pressure is increased *[Wilkinson and Gehman, 1949]*, *[Isayev and Kochar, 1984]*. Natural rubber will behave differently and show a lower modulus increase with increasing pressure, as shown by Wilkinson and Gehman *[Wilkinson and Gehman, 1949]*. They speculated that this more retarded behaviour, compared to SBR, was due to the controlling influence of a reaction with a negative pressure coefficient. The properties of vulcanizates resulting from sulphur vulcanization under pressure were investigated more thoroughly by Isayev and Kochar. Tensile properties, permanent set, dynamic modulus, abrasion resistance, and hardness were measured, and it was found that the vulcanizates formed under elevated pressure showed lower permanent set and hysteresis, even for samples with equal crosslink density.

Radiation crosslinking, which involves different mechanisms from those in sulphur vulcanization, has also proved to be very sensitive to pressure. Cis-polybutadiene crosslinked by γ-radiation yielded a 30-fold increase in crosslink density when the pressure was increased from atmospheric to 890 MPa *[Sasuga and Takehisa 1975]*. EPDM and SBR also exhibited a pressure dependence, but not so pronounced as that of polybutadiene. The reason for the increase in crosslink density as a result of pressure is variation in molecular mobility. When the pressure increases, the molecular mobility decreases as a result of decreased free volume, and this prevents long range motions. The obstructed long range motions will decrease the termination rate of radicals by combination. Instead of being terminated, they react with nearby unsaturations, creating a polymerization crosslinking. The pressure will also reduce the distance between the chains, which may increase the reactivity of the addition to a nearby double bond *[Sasuga and Takehisa 1975]*.

High Pressure Vulcanization

High Pressure Vulcanization (HPV) will be defined in this thesis as vulcanization at elevated pressure and temperature, without any vulcanization chemicals present. For a polybutadiene, the typical pressure and temperature for obtaining a reaction rate that is of technical interest is 200-300 MPa and 240-250°C. The fact that certain unsaturated rubbers undergo crosslinking when heated, without any crosslinking agents, have been known since the 1930s *[Luttropp, 1958]*. When butadiene-based polymers are heated in the absence of air, they harden gradually, while natural rubber becomes softer due to chain scission. The mechanisms of these reactions, and other reactions taking place in polybutadiene at elevated temperature are treated on page 20. Luttropp *[Luttropp, 1958]* investigated the thermal vulcanization (thermovulcanizates) of carbon black filled styrene- and nitrile-butadiene rubbers and compared them with sulphur vulcanizates. When the polymers were heated to 195°C for 4 h in absence of crosslinking agents, they became fully vulcanized. The comparisons involving abrasion resistance, rebound

elasticity and surface crack growth were in favour of the thermovulcanizates while their tensile strength in general was somewhat inferior. Moreover, their swelling resistance was weaker, indicating a lower degree of crosslinking. In the absence of carbon black, the crosslinking reaction was shown to take place at a lower rate.

Okhrimenko *[Okhrimenko, 1960]* described the vulcanization of SKB (Russian abbreviation for sodium catalysed polybutadiene) rubber under high pressure, both in presence and absence of vulcanization agents. The pressure range was up to 1 GPa and the temperature was 120-240°C. The number of unsaturations was shown to decrease as the degree of crosslinking rose, and it was concluded specifically that the reactivity of the polymer in HPV is dependent on the amount of pendant unsaturations (1,2-vinyl units). When dicumyl peroxide was added, it led to an ultrarapid crosslinking reaction. Artemov and co-workers *[Artemov et al., 1979]* investigated the chemical changes taking place in nitrile rubber at high pressure (7.5-500 MPa) and temperature (150-250°C). Crosslinks were formed, and the main chain unsaturations were consumed together with the nitrile groups, the latter probably forming cyclic structures.

A broad investigation of different polymers useful for HPV was performed by Frenkin et al. *[Frenkin et al., 1984],* who stated that all unsaturated rubbers are possible to crosslink without any vulcanization agents, and that vulcanizates formed under high pressure have good heat resistance. They used sodium-catalysed polybutadiene as a model material for more detailed studies of the crosslinking reaction and found it to be a first order reaction. They also found that there is both a critical pressure and a critical temperature below which the crosslinking takes place very slowly. Just like Luttropp in the case of crosslinking without vulcanization agents, but in the absence of elevated pressure, Frenkin and co-workers noticed that carbon black accelerates the crosslinking reaction. The crosslink densities achieved varied very much, and the hardest samples became glassy and showed no transitions up to 180°C, almost like an ebonite looking material. A patent describes the vulcanization of unsaturated elastomers with sulphur and peroxide at 200-250°C and 0.3-1.0 GPa, in order to achieve a rubber material with improved permanent set *[Vinogradov, Patent, 1975]*. The thermo-mechanical properties of polybutadiene crosslinked by HPV have also been investigated by Lavebratt et al. *[Lavebratt et al., 1990]*. The dynamic stress relaxation rate of carbon black filled polybutadienes was shown to be very low compared to peroxide crosslinked ones, and a radical mechanism for the crosslinking reaction was proposed where the 1,2-vinyl unsaturations were important.

Recently, Zeng and Ko *[Zeng and Ko, 1998]* examined the thermal crosslinking of cis-1,4-polybutadiene at ultrahigh pressures. The pressure applied was extremely high, 4.0 GPa, resulting in brittle materials showing no glass transition. However, when the temperature was lowered from 180°C to 120°C the resulting material after 10 min pressure treatment was rubber-like. FTIR and NMR analyses pointed to consumption of unsaturations, and the network structures formed could be discerned in the NMR spectra.

To summarize the section High Pressure Vulcanization, the following schematic comparison between HPV and traditional vulcanization may be relevant (table 1.4). However, it must be stressed that all figures given are very rough.

Table 1.4. General comparison between HPV and traditional vulcanization.

	HPV	Traditional Vulcanization
Temperature	240-250°C	140-180°C
Pressure	100-300 MPa	->15 MPa
Vulcanization Time	2 min ->	1 min ->
Type of polymer	Unsaturated	All

Polybutadienes at Elevated Temperature

The behaviour of polybutadiene at elevated temperature, in inert atmosphere or in vacuum, has been the subject of many studies. Two different regions may be discerned: pyrolytic and non-pyrolytic, the latter at temperatures below 300°C and the former above. Under pyrolytic conditions weight loss is evident, resulting in volatile species, e.g. vinyl cyclohexene and butadiene monomer from depolymerization reactions *[Golub, 1982], [Brazier and Schwartz, 1978]*. At temperatures below 300°C isomerization, cyclization and crosslinking are the main reactions *[McCreedy and Keskkula, 1979]*. Cis-1,4-polybutadiene shows cis/trans isomerizations a temperature of 200°C *[Golub and Gargiulo, 1972]*, but there is no consumption of unsaturations at that temperature. However, 1,2-polybutadiene (~95% vinyl groups) shows consumption of vinyl groups at 220°C at a rate which increases with the temperature. The kinetics follows a second-order reaction, yielding an Arrhenius activation energy of 141 kJ/mol *[Golub, 1974]*. These different behaviours between 1,4 and 1,2-polybutadiene accentuate the importance of the microstructure to chemical reactions in polybutadiene systems. Further, if the microstructure is a mixture of all isomers, with a vinyl content around 10%, crosslinking occurs as a result of thermal treatment already at 200°C, but at a very low rate. At 230°C, vinyl unsaturations are consumed and the polymer becomes unsolvable after 2.5 h treatment due to crosslinking. This reaction follows a first order reaction with an activation energy of 63 kJ/mol *[Grassie and Heaney, 1974]*. It has been suggested that the mechanism causing this loss of unsaturations is a non-radical intermolecular addition from a vinyl group to a methylenic carbon in α-position to a main chain unsaturation *[Grassie and Heaney, 1974]*. By contrast, Golub *[Golub, 1981]* found the loss of vinyl unsaturations to follow a second order reaction with an activation energy of 142 kJ/mol. In addition to the loss of double bonds, methyl groups were found to be produced. The suggested reaction mechanism was according to the following scheme (Figure 1.11):

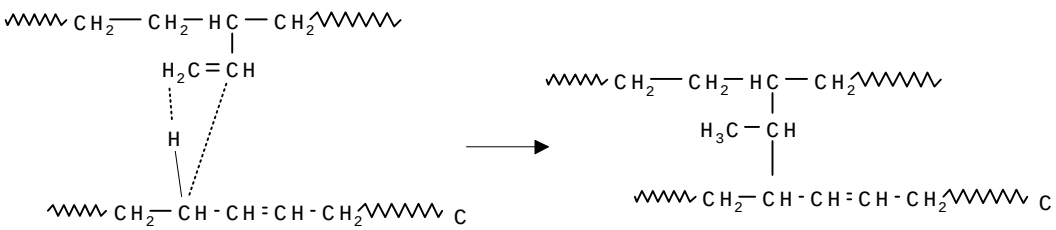


Figure 1.11. Reaction mechanism for the thermal crosslinking of polybutadiene with 10% vinyl content, according to Golub *[Golub, 1981]*.

This reaction mechanism was further emphasized by Doskocilová and co-workers *[Doskocilová et al., 1993], [Schneider et al., 1993],* who used of FTIR and ^{13}C solid state NMR of polybutadiene, containing 11% vinyl units, heated at 200 and 250°C for 2.5 to 4 h. They also pointed out that crosslinking was the main route for the loss of unsaturations.

Dynamic Mechanical Properties of Rubber Materials

The dynamic mechanical properties of rubber materials are of very great importance from a practical point of view, e.g. in tyre and damping applications. Typical DMTA curves are shown in figure 1.12.

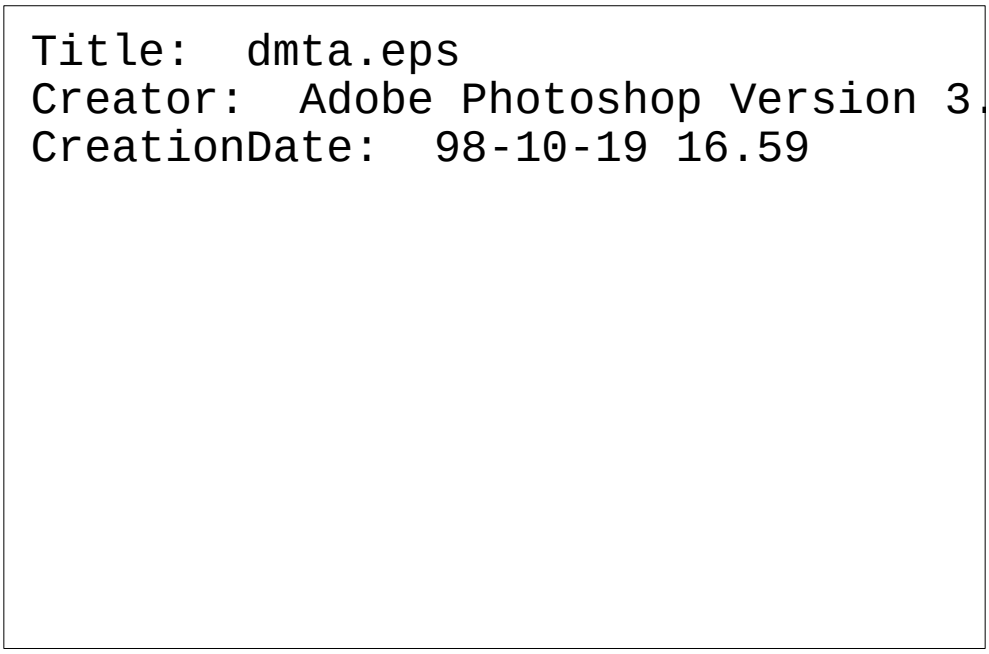


Figure 1.12. Dynamic modulus and tanδ for high pressure vulcanized polybutadiene with varying crosslink density (from swelling measurements): (a) 0.91×10^{-4} mol/cm^3; (b) 4.1×10^{-4} mol/cm^3; (c) 6.0×10^{-4} mol/cm^3; (d) 15×10^{-4} mol/cm^3. Measured by the author.

When the crosslink density increases, the tanδ peak is shifted towards a higher temperature, and the peak value is lowered. The lower the tanδ value is, the lower are the mechanical losses in the material (tanδ=E´´/E´, where E´´ is the loss modulus and E´ is the storage modulus). The peak also becomes broader as a result of a wider distribution of chain lengths between the crosslink points *[Nielsen and Landel, 1994]*. If a filler is introduced, the behaviour becomes more complicated. Depending on factors such as adhesion between the filler and the polymer, agglomeration of filler particles, changes in polymer conformation and morphology, the damping peak may be shifted and altered in intensity. Due to the immobilization of polymer chains at the surface of a carbon black particle, the T_g of the chains may be expected to rise. However, this is only a small fraction of the polymer, and therefore the macroscopically shown T_g of the sample does not change to any great extent.

The dynamic modulus of a carbon black filled rubber material display a very strong deformation amplitude dependence (non-linear properties), a phenomenon which often is referred to as the *Payne effect*. It is observed as a drastic drop of the storage modulus when the strain amplitude is increased, typically in the range of 0.1-10%. The drop may be as large as 90%. The interpretation of this modulus drop is that the carbon black agglomerates, held together by weak dispersion forces, are broken as the deformation increases. A qualitative description of this phenomenon is given in Figure 1.14, after Medalia *[Medalia, 1968]*.

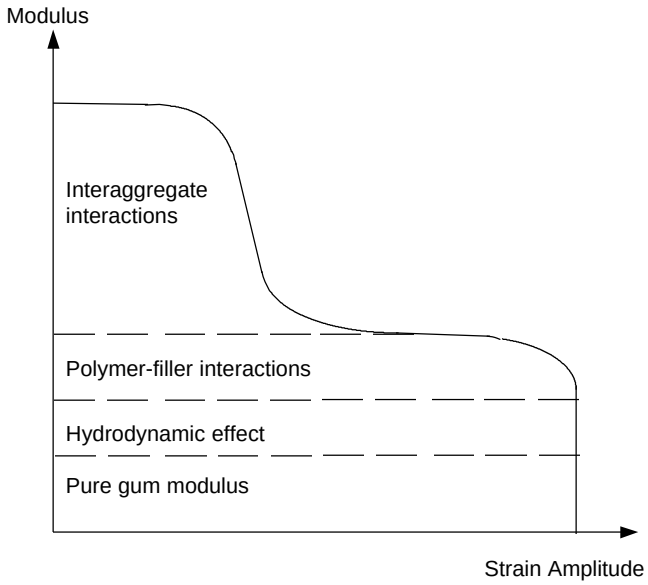


Figure 1.14. A qualitative interpretation of the Payne effect.

This interpretation has been valid and accepted for many decades, also supported by electrical measurements reflecting the conductivity of the rubber material. Electrical conductivity in carbon black filled rubber materials is due to a tunnelling effect between aggregates, and was shown to follow the decrease in modulus with increased strain *[Payne, 1965]*. In recent years, this interpretation has been questioned, and Göritz and co-workers have emphasized that molecular slippage of chains from the filler particles is the main reason for the modulus drop *[Göritz and Maier, 1996]*. In addition to this, Freund and Niedermeier *[Freund and Niedermeier, 1997]* have suggested that both molecular slippage and disagglomeration of carbon black are responsible for the Payne effect.

2. EXPERIMENTAL

MATERIALS

Butadiene Rubber (BR)

The butadiene rubber used in the experiments was Buna CB55, which is a lithium-catalysed solution-polymerized commercial grade from Bayer AG. The molecular weight is 1×10^5 mol/cm^3, the density 0.91 g/cm^3, and the microstructure consists of 51% trans, 38% cis and 11 % vinyl, respectively. The polymerization of butadiene in solution, with lithium as catalyst, yields a polymer with the different unsaturations incorporated in a random manner *[Clague et al., 1974]*. The polybutadiene was used both unfilled and filled with carbon black, up to 45 phr. The different carbon blacks are listed further on in this chapter.

Nitrile-Butadiene Rubber (NBR)

The only NBR compound used was a mix of two different nitrile-butadiene rubber polymers, containing 28% and 34% acrylonitrile respectively. The total composition of the NBR compound is given in Table 2.1.

Table 2.1. Composition of NBR compound

Component	Amount in phr (parts per hundred rubber)
NBR (acrylonitrile content 28%)	50
NBR (acrylonitrile content 34%)	50
Carbon black N550	47
Carbon black N990	28
Stearic acid	0.6
ZnO	5
Wax, microcrystalline, *Antilux 654*	1
TMQ[a], *Vulkanox HS/LG*	1.5
Imidazole[b], *Vulkanox MB2/MGC,*	1.5
Ether - thioether[c], *Vulkanol OT*	10.4

[a] Antioxidant, poly-2,2,4-trimethyl-1,2-dihydroquinoline.
[b] Antioxidant, methylmercaptobenzimidazole
[c] Plasticizer

Carbon Black

All carbon blacks used were of commercial grades. However, in some experiments the N220 carbon black was modified after manufacture to change the surface chemistry of the particles. *Oxidation* was performed through thermal treatment at 400°C in air for 24 hours. *Graphitization* was achieved by heating the carbon black in inert atmosphere (ca 1500°C) to burn off most of the active sites on the particle surface. Table 2.2 lists some typical properties of the carbon black used, according to Hess and Herd *[Hess and Herd, 1993]* unless otherwise stated.

Table 2.2. Typical characteristics of the carbon black used, according to Hess and Herd *[Hess and Herd, 1993]* unless otherwise stated.

Carbon Black Type	Surface area (m^2/g, N_2-adsorption)	DBP-absorption ($cm^3/100$ g)	Base adsorption[a] (meq/g)
N220	114[b]	114	0.33
N220 oxidized	-	-	0.63
N220 graphitized	-	-	0.11
N550	39	122	-
N660	36	91	-
N990	9	38	-
Monarch 1300	560 [b]	-	-

[a] Base adsorption was measured by neutralization in 0.6 molar sodium hydroxide solution for 7 days.
[b] Supplier values.

Chemicals and Solvents

The chemicals used in the NBR and BR compounds were commercial rubber grade chemicals. *Dicumyl peroxide* was used for peroxide crosslinking of some polybutadiene samples. It was used in the form of DiCup 40, which is a commercial grade and consists of dicumyl peroxide

adsorbed on a silica carrier yielding a powder with 40 % peroxide content. The *hindered phenol* used was Irganox 1098, which is N, N´-hexamethylene bis(3,5-di-tert-butyl-4-hydroxy-hydrocinnamamide) and acts as a radical scavenger. *N-heptane, toluene,* and *methylene chloride* used for swelling and bound rubber measurements were of bulk quality, normally used as solvents for syntheses.

Sample Preparation

Mixing

The *polybutadiene compounds* were mixed on an open two-roll mill, laboratory scale (batch size around 50-150 g), until the ingredients were well dispersed. The *NBR compound* was mixed in a large-scale internal mixer at Skega AB and then flattened out on a two-roll mill.

High Pressure Treatment

The high pressure treatment was performed in an electrically heated plunger type mould, see Figure 2.1. To avoid rubber leakage, the mould was sealed with two piston rings at the bottom. The rubber was then put into the hot mould and allowed to equilibrate for 6 min. This delay before applying the pressure was to avoid any temperature gradient in the sample. The plunger was then forced down by means of a mechanical press, adjustable to give pressures in the mould cavity from 30 to 290 MPa. The pressure was then kept as constant as possible for different lengths of time, hereafter referred to as vulcanization time, ranging from 0 to 50 minutes. After releasing the pressure, the sample was immediately demoulded. The sample thus obtained was a circular disc with a diameter of 45 mm and a height of about 8-9 mm, the latter depending on the amount of material inserted. The pressure was not measured inside the mould, but calculated from the applied force of the mechanical press and the cross-section area of the mould.

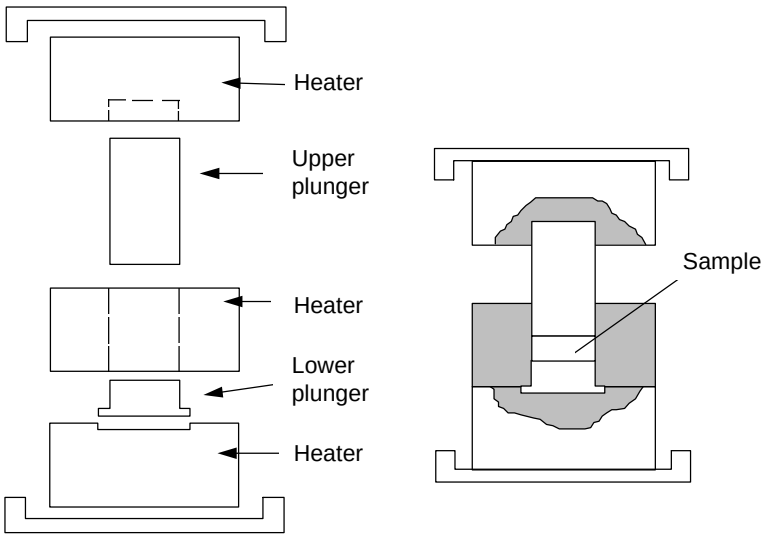


Figure 2.1. Plunger type mould used for the high pressure treatment.

Peroxide Vulcanization

Peroxide vulcanization was performed in the same mould as the high pressure treatment, at temperatures from 170°C to 240°C and a pressure of ~10 MPa. Some of the peroxide vulcanizates were also treated at an elevated pressure (indicated when used).

Analytical Techniques

Swelling

The polybutadiene was swelled to equilibrium in n-heptane. It was shown that 24 h was enough to reach equilibrium for the geometries used, which were rod-shaped specimens (three specimens from every sample), approximately 1.5×1.5×15 mm and cut out from the lower 2 mm layer of the disc-shaped sample in the case of high pressure treatment. The nitrile-butadiene rubber was swelled in methylene chloride, also for 24 hours. All samples were weighed, first before swelling, then in a swollen state after wiping off the excess of solvent, and finally after drying to constant weight. The values obtained were used to calculate the crosslink density by using the Flory-Rehner equation *[Flory and Rehner, 1943]*

$$n_{phys} = \frac{1}{2 \cdot V_S} \cdot \frac{\ln(1 - v_r) + v_r + c \cdot v_r^2}{v_r^{1/3}} \qquad (2.1)$$

where ν_{phys} is the number of crosslink points per unit volume (including chemical and physical interactions), V_s is the molar volume of the solvent, χ is the interaction parameter and v_r is the volume fraction of rubber in the swollen gel, calculated as

$$v_r = \frac{m_{dried} / r_{pol}}{\frac{m_{swollen} - m_{dried}}{r_s} + \frac{m_{dried}}{r_{pol}}} \qquad (2.2)$$

where m_{dried} is the weight of the dried specimen, $m_{swollen}$ is the weight of the swollen polymer, ρ_{pol} the density of the polymer, and ρ_s the density of the solvent. For convenience, the functionality of the crosslinks is set equal to four, which in fact is a reasonable assumption.

The χ-value used for polybutadiene was $\chi = 0.37 + 0.52\ v_r$ according to Kraus *[Kraus, 1963]*, who investigated the swelling behaviour of lithium-catalysed polybutadiene with the same microstructure as used in the present study. The χ-value used for nitrile-butadiene rubber was 0.314, according to Sheehan and Bisio *[Sheehan and Bisio,1966]*.

In the carbon black filled samples, the filler was considered to be inert to swelling, and compensation was not made for rubber-filler interactions. The crosslink density values reported for these, are thus a measure of chemical and physical crosslinks, the latter including entanglements as well as filler-polymer interactions.

Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra were recorded on a Perkin Elmer 1760X FTIR as ATR measurements, using a KRS-5 crystal and a TGS detector. The angle of the incident beam was 45°, the resolution 4 cm^{-1} and the number of scans was set to 20. As ATR is a surface sensitive technique, newly cut surfaces were used for each measurement. Slices were taken from the lower 2 mm of the vulcanized disc shaped samples.

The following peaks were chosen for the evaluation of the number of unsaturations consumed (polybutadiene): 720 cm^{-1} (C-H bending in cis units), 911 cm^{-1} (C-H bending in vinyl units), 965 cm^{-1} (C-H bending in trans units), and 1435 cm^{-1} (CH_2-bending) *[Nakanishi, 1962], [Hampton, 1972]*. The ratio of the peak height of the unsaturations to the peak height of the CH_2-bending peak was used to calculate the number of double bonds consumed. It was assumed that the original numbers of the respective unsaturations was according to the supplier values.

Nuclear Magnetic Resonance (NMR)

^{13}C solid state NMR-spectra were recorded on a Chemagnetics 400 MHz at ambient temperature during proton decoupling. Magic angle spinning (MAS) at 12 kHz was applied on the 4 mm ZrO rotor containing the sample. Comparisons with spectra using Cross Polarization (CP) showed no differences, so 90° single pulse experiments were used. The pulse repetition time was 9 s, and 128 FIDs were accumulated before processing the spectra into the shift domain.

Dynamic Mechanical Thermal Analysis (DMTA)

The dynamic mechanical measurements were performed on a DMTA Mark II, from Polymer Laboratories, working in the bending mode (single cantilever) at 1 Hz. The strained samples had cross-sections of approximately 2×2 mm and a length of 5 mm. The deformation was varied between 16 and 256 μm during the strain amplitude scans (Paper II), yielding strains between 0.22 and 5.12%, and the temperature was kept constant at 25°C. The temperature scans (Paper III) were performed at a heating rate of 2°C/min, and liquid nitrogen was used as cooling medium.

Stress Relaxation

Stress relaxation measurements of the high pressure vulcanized samples were performed in compression mode at room temperature in an Instron 5566. Cylindrical specimens of diameter 10 mm and height 5 mm were subjected to 15% compression, and the resulting stress was recorded during 15 min. In such short times, only physical processes are responsible for the stress relaxation, both in compression and elongation. As shown by Cotten and Boonstra *[Cotten and Boonstra,1967]*, rubber materials containing various fillers obey the following empirical law

$$F_t = F_0 \times t^{-n} \qquad (2.3)$$

where F_t is the force at time t, F_0 the force 1 min after compression/elongation, and n is defined as the stress relaxation rate. The stress decay was plotted as $\log(100 \times F_t/F_0)$ versus

logarithmic time. The stress relaxation rate was determined from the slope of the linear curves obtained, by linear regression.

Permanent Set

The permanent set was measured on cylindrical samples of 9 mm diameter and 10 mm height, compressed 15% and subjected to 100°C for 24 h. The test specimens were allowed to rest for 30 min at ambient temperature before measuring the dimension. The permanent set was calculated as percent remaining deformation.

Tensile Testing

All tensile testing was performed at room temperature at a strain rate of 500 mm/min. Dog bone shaped test specimens with a length of 45 mm were used. The samples from the plunger type mould were tested in an Instron 5566, while the injection moulded high pressure vulcanized samples were tested on a Monsanto Tensometer 10 at Skega AB, Ersmark.

Hardness

Hardness was measured as Shore A with a dead weight durometer from Zwick & Co. KG, on the bottom side of the vulcanized disc-shaped sample.

Gravimetric Density

Gravimetric density was measured in a density gradient column, containing water and $CaNO_3$. Small pieces of the rubber samples, approximately 0.1-0.2 g, were slowly submerged in the column, and simultaneous calibration was obtained using glass bullets with exactly determined density.

Bound Rubber

Bound rubber was measured by immersing a piece of 0.5-1 g of the mixed, unvulcanized rubber compound in toluene or n-heptane for 72 or 96 hours at room temperature. After that period the sample was dried to constant weight. The bound rubber was calculated as the percentage of remaining polymer in the polymer-carbon black composite.

$$BoundRubber = 100 \times \frac{m_{rem}}{m_{pol}} \qquad (2.4)$$

where m_{rem} is the mass of the remaining polymer in the composite and m_{pol} is the mass of polymer in the sample before leaching.

Carbon Black Acidity - Degree of Oxidation

The degree of carbon black oxidation was measured by base adsorption. Actually this is a measure of acidity, but this is accurate enough to verify changes of the carbon black surface due to oxidative treatment. 1 g of carbon black was stirred in a 0.6 molar sodium hydroxide solution for 7 days. Then the slurry was centrifugalized and the resulting solution was titrated with hydrochloric acid. The base adsorption was calculated as mmole neutralized hydroxide ions per gram carbon black (meq/g).

3. RESULTS AND DISCUSSION

Time, Temperature and Pressure Dependence

Vulcanization curves are very common in the characterization of the cure behaviour of a rubber compound and show the increase in crosslink density during the vulcanization. Figure 3.1 shows crosslink density, measured by swelling, versus vulcanization time of the high pressure vulcanization (HPV) for a pure butadiene rubber (no vulcanization agents) treated at 240°C and 250°C and at a pressure of 290 MPa. As can be seen, no final degree of crosslinking is reached. Instead there is a continuous increase, a so-called marching crosslink density is obtained, and this process will continue until all reactive sites in the polymer are consumed. This is quite different from conventional vulcanization, i.e. vulcanization with chemical crosslinkers, where the degree of crosslinking is determined mainly by the amount of chemicals added and only to some extent by the processing conditions.

Frenkin and co-workers concluded that the kinetics in high pressure vulcanization of polybutadiene follows a first order reaction *[Frenkin et al., 1984]*, a statement which cannot be confirmed here. According to the values in figure 3.1 there is no simple kinetic expression for the reaction progress, which indicates that different processes determine the reaction rate, each to a varying extent during the vulcanization. This is understandable, as the mobility of the polymer chains is reduced with the formation of crosslinks. This reduction may affect the rate of certain reactions, and as the mobility decreases over the time when crosslinks are formed, different processes may be rate-determining at different extent of reaction. However, mathematical expressions can be fitted to the points in figure 3.1, such as the power law:

$$n = n_0 \cdot t^n, \qquad (3.1)$$

where n is crosslink density at time t, n_0 crosslink density at time t_0, and n a constant, here defined as the *reaction rate*. Thus, if $\log(n/n_0)$ is plotted versus $\log(t)$, linear curves will result from which the reaction rate can be determined. The values obtained by linear regression are 0.327 at 240°C and 0.351 at 250°C respectively. In these calculations t_0 was set to 0.01 min (the first point), and n_0 to 6.25×10^{-6}, the latter an average value of the two temperature series as the crosslink density of these samples was difficult to determine due to the low level.

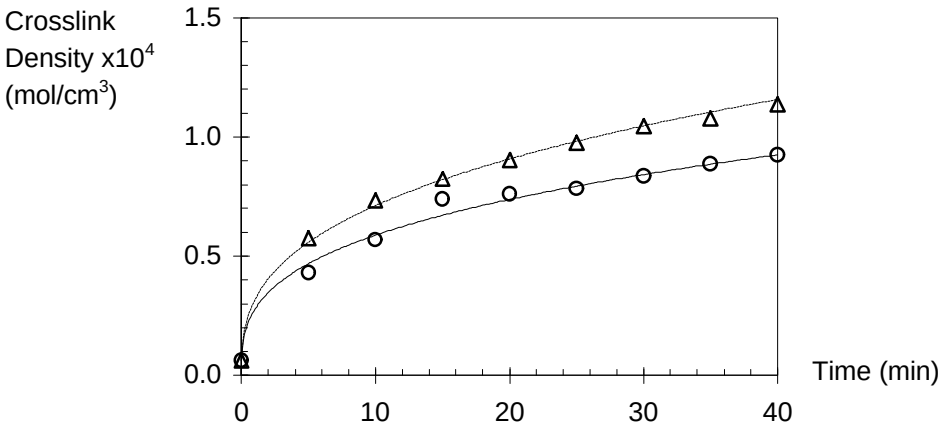


Figure 3.1 Crosslink density, measured by swelling, versus vulcanization time for pure polybutadiene high pressure vulcanized at 240°C (—○—) and 250°C (—Δ—) at a pressure of 290 MPa. Each point represents one vulcanized sample (**Paper I**).

Furthermore, the degree of pressure will affect the vulcanization rate. This can be seen in Figure 3.2, which shows crosslink density versus pressure; In (a) the material is unfilled polybutadiene and in (b) a nitrile rubber filled with carbon black. In both cases, the crosslink density increases continuously in the pressure interval investigated. The crosslink density values obtained for each material cannot be compared as these material belong to two totally different systems, each with its own set of empirical parameters for the calculation of crosslink density on the basis of swelling measurements. The mechanisms behind the increase in crosslink density will be discussed further on in this thesis, but it should be noted that the pressure dependence exists in both filled and unfilled materials. Carbon black will contribute to crosslink density with an extra amount due to the possibilities of increased polymer-filler interactions at elevated pressure, which will also be demonstrated further on.

The fact that the reaction rate increases continuously with the pressure is of practical importance, since there is no treshold pressure to be reached for the reaction to take place at a high rate. Frenkin and co-workers *[Frenkin et al., 1984]* stated that there is both a critical pressure and a temperature below which the high pressure vulcanization reaction takes place at a negligible rate. The existence of a true critical pressure cannot be supported by the results in Figure 3.2 a) and b), and when polybutadiene samples were treated at 290 MPa between temperatures of 200-260°C, a continuous increase in the crosslink level was found. There was no temperature region where the reaction seemed to accelerate drastically. At 200°C, the samples were almost soluble in n-heptane, and as the vulcanization temperature was increased, the samples became harder and harder (constant vulcanization time), and were finally like

common vulcanizates. Thus, it is a matter of definition where the reaction rate becomes ”non-negligible”, and the terms critical pressure and temperature lose their meaning.

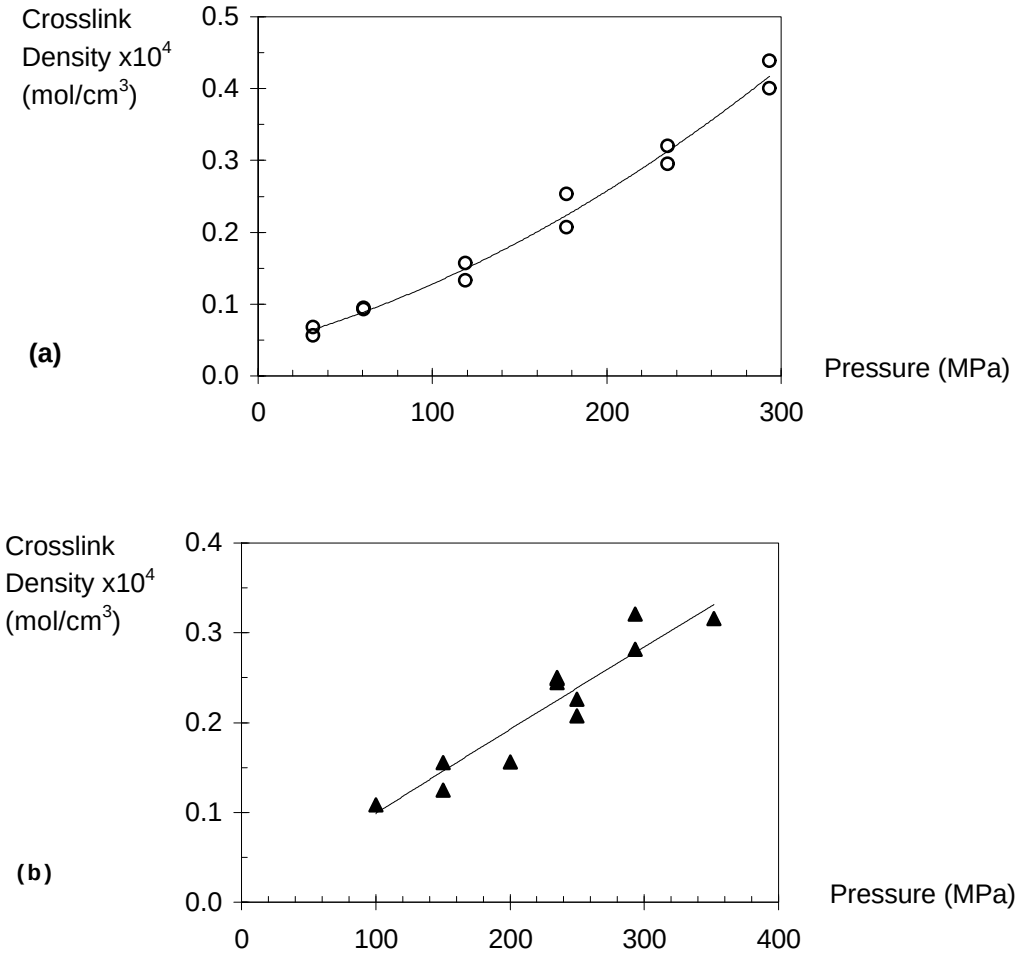


Figure 3.2. Crosslink density versus vulcanization pressure for (a) polybutadiene treated at 240°C for 5 min (**Paper I**), (b) nitrile rubber filled with carbon black treated at 250°C for 3 min.

To summarize, there are some interesting points to keep in mind concerning HPV. As no vulcanization chemicals are added, the final degree of crosslinking can be varied enormously within one single compound. Thus, the use of only one compound can give a material with widely different properties, only by adjustment of the processing parameters: *time*, *temperature* and *pressure*.

Moreover, the *scorch problem is eliminated* in high pressure vulcanization, as the elevated pressure and temperature must be applied simultaneously to obtain crosslinking. The rubber compound may be held at an elevated temperature without any crosslinking taking place, which is totally different from conventional vulcanization with chemical crosslinkers.

Network Structure and Reaction Mechanisms

Radical Reaction

In the history of HPV, it was suggested already by Ohkrimenko *[Okhrimenko, 1960]* that the reaction proceeds via a radical mechanism. However, few explicit data have been presented, and in the light of Doskocilova´s work *[Doskocilová et al., 1993]*, which suggests that a non-radical reaction is responsible for the thermal crosslinking of polybutadiene (without pressure: in vacuum), the establishment of whether a radical reaction is involved or not is of fundamental interest. Figure 3.3 shows the effect of a radical scavenger on crosslink density after crosslinking of polybutadiene by HPV at 240°C and different pressures. The radical scavenger used was Irganox 1098, which is a hindered phenol: N, N´-hexamethylene bis(3,5-di-tert-butyl-4-hydroxy-hydrocinnamamide), commonly used as an antioxidant. The presence of the scavenger lowers the crosslink density significantly over the whole pressure range which shows that a radical reaction is at least partially responsible for the crosslink formation. At temperatures around 240°C, it is expected that radical formation takes place due to the high thermal energy, e.g. by cleavage of allylic hydrogen bonds which are present in large quantities in polybutadiene.

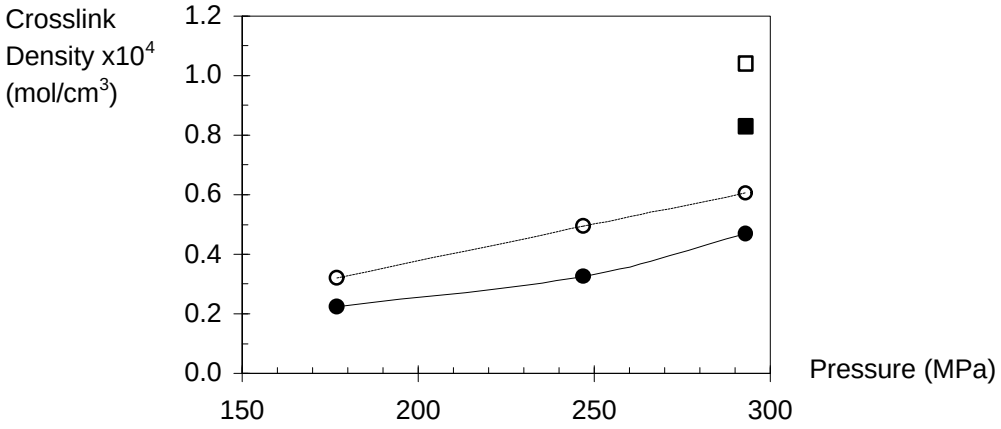


Figure 3.3. Effect of a radical scavenger on crosslink density in polybutadiene samples crosslinked by HPV at 240°C, for 30 min: without scavenger (o) and with scavenger (ν), for 5 min: without scavenger (○) and with scavenger (λ) (**Paper IV**).

Oxidative Reactions

A temperature of 240°C is much above the highest intermittent usability temperature for polybutadiene. Beside thermal rearrangements of the polymer chain, thermooxidative degradation may be expected in the presence of oxygen. However, FTIR studies indicate no absorption increase in the region around 1690-1730 cm^{-1} due to formation of carbonyls which is associated with thermooxidative reactions. It is true that the surface of the vulcanized samples shows some absorption in the carbonyl region, but not more than that of a peroxide-vulcanized sample. The surface of a rubber material is always exposed to oxygen and will form an oxidation skin containing carbonyls. Furthermore, the oxidation skin lowers the diffusion rate of oxygen into the matrix. This is a well-known phenomenon and has been observed in e.g.

bridge pads which after being in service for 100 years have an oxidized surface layer but an almost unchanged core *[Stevenson and Campion, 1992]*. Thus, the interior of the polybutadiene remains intact in the sense of thermooxidative degradation, which is explained by the inability of oxygen to diffuse into the rubber matrix during vulcanization. The small amount of oxygen that is always dissolved in a polymer will probably react, but the concentration is so low that the products formed cannot be detected by FTIR.

An interesting observation is that an increase in the amount of oxygen dissolved in the polymer leads to a higher crosslink density. By subjecting a polybutadiene sample to a pure oxygen atmosphere at a pressure of 2 MPa before the crosslinking process, the amount of dissolved oxygen will increase. This is a reversible process, and the oxygen will diffuse out of the polymer when the sample is again in the normal atmosphere *[Stenberg and Dickman, 1983]*. Figure 3.4, where the time scale on the x-axis represents the time between the oxygen treatment and the vulcanization, shows the the resulting crosslink density when the polybutadiene has been kept in oxygen atmosphere at 2 MPa for 24 h before the high pressure vulcanization is performed. The resulting crosslink density increases significantly due to the higher amount of dissolved oxygen.

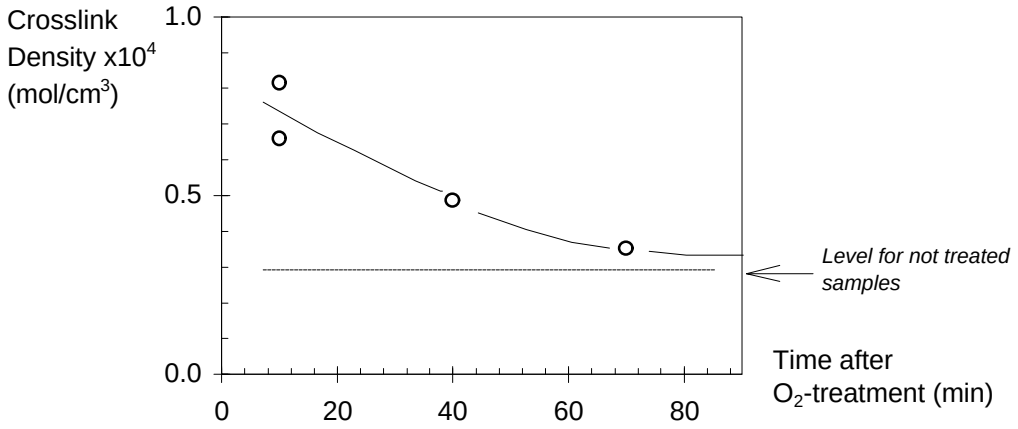


Figure 3.4. The effect of oxygen treatment before crosslinking by HPV for 10 min at 290 MPa, 240°C (—○—) treated in an oxygen atmosphere. The broken line (---) represents the crosslink level for samples not treated in oxygen before crosslinking (unpublished data).

However, the effect decays rather fast, and after 70 min in the ambient atmosphere, the crosslink density level is almost at the same level as without the treatment. The increase in crosslink density has two reasonable explanations, either a *physical* one or a *chemical* one. The physical explanation is that the oxygen molecules occupy part of the free volume in the system, and thereby decrease the mobility of the polymer, which leads to an increased rate of the crosslinking reaction. This mobility aspect will be discussed and explained in more detail further on. The chemical explanation is that the oxygen causes a chemical reaction which by creating new radicals in an autocatalytic way leads to more crosslinks.

Depletion of Unsaturations.

The fact that radicals are involved in the formation of crosslink undoubtedly invites comparison with peroxide vulcanization, which is also a radical reaction. In the addititon mechanism for

peroxide vulcanization of diene rubbers, unsaturations are consumed as a result of the polymerization type of crosslink formation. FTIR studies of HPV crosslinked polybutadiene show that the vinyl units were consumed while no significant changes in the number of main chain unsaturations (cis and trans) could be seen. This is also true for peroxide vulcanization of the same polybutadiene. Figure 3.5 shows the amount of reacted vinyl groups (FTIR measurements) versus crosslink density (swelling measurements) for the polybutadiene model material vulcanized by peroxide and HPV. It can be seen that the vinyl units are consumed at a rate which is of the same order as the rate by which crosslinks are formed, and there is no significant difference between the peroxide and HPV crosslinked materials. The crosslink densities are not to be taken to be true absolute values, as the interaction parameter used in the Flory Rehner equation is an empirical factor, often very temperature sensitive, and different solvents may give very different values of the crosslink density. In spite of this uncertainty in absolute crosslink densities, it is clear that crosslink formation and loss of vinyl unsaturations are closely connected to each other.

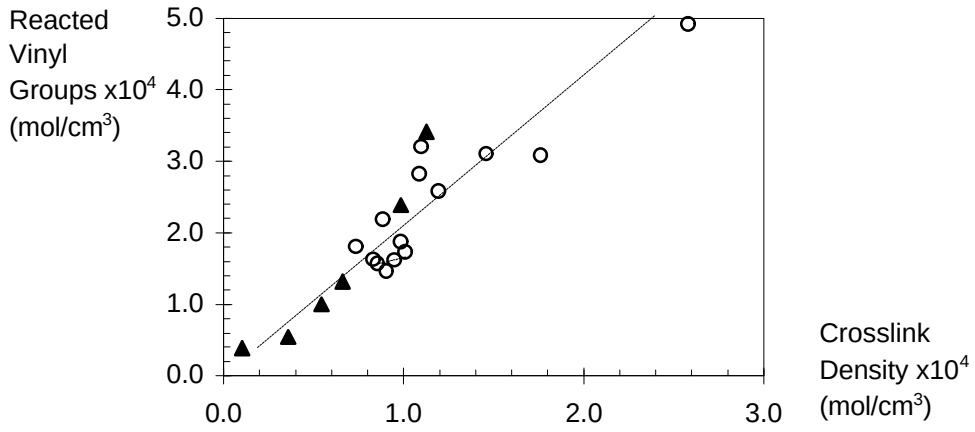


Figure 3.5. Number of reacted vinyl unsaturations (measured by FTIR) versus crosslink density (swelling measurements) for peroxide (○) and HPV (σ) crosslinked polybutadiene. Vulcanization temperature 170°C for the peroxide vulcanizates and 240-250°C for the HPV material, the latter at a pressure of 290 MPa. The crosslink density of the peroxide vulcanizates has been varied by different amounts of peroxide (**Paper III**).

As the unsaturations are consumed, some kind of new structures must be formed. However, no new peaks can be found in the FTIR spectra of polybutadiene samples crosslinked by HPV. The reason for this is probably that many different structures are formed, each yielding changes in the spectra that are lower in intensity than the corresponding change of the vinyl peak. Besides formation of crosslink structures, cyclization reactions and isomerizations may take place, which will be discussed further on.

The depletion of unsaturations is further evidenced by ^{13}C solid state NMR analyses. Figure 3.6 shows the olefinic region in NMR-spectra of polybutadiene, and indicates a decrease in the intensities of the vinyl units upon crosslinking. Calculation of the areas under the peaks gives a better picture of the disappearance of the vinyl units. The area under the vinyl peaks indicated

in figure 3.6 decrease to around 55-65% of their original value, corresponding to 8.2-6.4×10^{-4} mol/cm^3 of reacted vinyl units, while the crosslink density of the vulcanized sample is 1.28×10^{-4} mol/cm^3. If these figures are compared to the plotted values in Figure 3.5, it appears that the consumption of unsaturations is probably somewhat overestimated in the NMR measurements compared to the FTIR measurements.

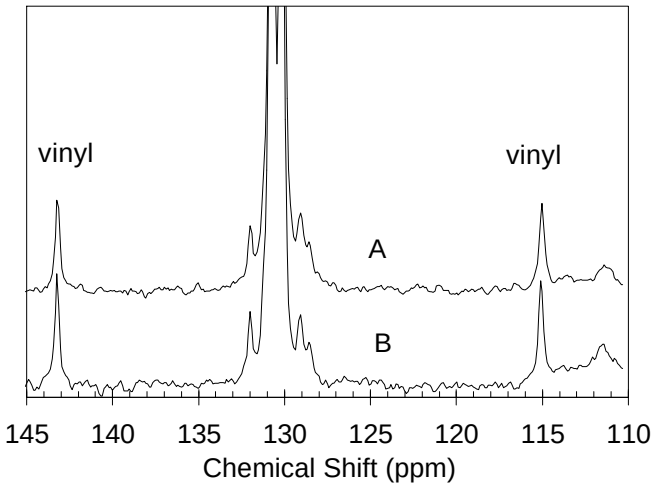


Figure 3.6. The olefinic region of ^{13}C solid state NMR-spectra (MAS) of polybutadiene crosslinked with HPV (A) and uncrosslinked (B). Vulcanization performed at 250°C and 290 MPa for 20 min (**Paper IV**).

Furthermore, the cis- and trans-contents do not change during the vulcanization according to the NMR measurements. Cis/trans isomerizations, which are common in sulphur vulcanization of natural rubber, have been shown to take place in polydienes only through the influence of an elevated temperature *[Golub, 1972]*. The fact that no cis/trans isomerizations are observed during HPV may be due to the cis/trans ratio being almost at an equilibrium value already in the untreated polybutadiene. The cis/trans ratio of γ-radiation crosslinked cis-polybutadiene is around 0.6 *[O´Donnell and Whittaker, 1992]*, which is somewhat different from the cis/trans ratio of 0.75 shown by the polybutadiene used in this thesis. However, the cis/trans ratio of photo-isomerized polybutadiene has an equilibrium value of 0.25 *[Brydson, 1978]*, which is still more different. Either the cis/trans isomerizations are prevented by the elevated pressure, or the cis/trans ratio of a polybutadiene with 11% vinyl units is significantly different from that of a polybutadiene without vinyl units.

In addition to cis/trans isomerizations, formation of methyl groups has been observed with FTIR when polybutadienes with varying vinyl content are heated *[Golub, 1982]* as well as crosslinked by peroxides *[Patterson and Koenig, 1984]*. These methyl groups are associated with inter- or intra-molecular cyclization reactions. They can also be due to chain scission resulting in new chain ends. In the high pressure treated polybutadiene samples, no formation of methyl groups could be found, either by FTIR or NMR measurements. This has also been shown for polybutadiene crosslinked by γ-radiation *[O´Donnell and Whittaker, 1992]*, pointing towards similarities between HPV and radiation crosslinking.

Concerning carbon black filled samples, studies of the microstructure by spectroscopic techniques have been difficult to perform due to the high absorption of carbon black. However, the development of new techniques has facilitated the studies of the microstructure even in carbon black filled samples. ^{13}C solid state NMR with magic angle spinning yields highly resolved spectra of unfilled as well as filled samples. This makes it possible to compare the microstructural changes in pure polymer samples with those in carbon black filled ones, in order to get an indication if the filler affects the crosslinking reaction. Figure 3.7 shows the ^{13}C solid state NMR spectra of carbon black filled (45 phr N220) polybutadiene crosslinked by HPV and peroxide, compared to that of an uncrosslinked sample. The resolution is generally somewhat lower than that for the unfilled samples, but still the original peaks can be identified and quantified. The same main changes as for the unfilled samples can be seen; the cis and trans unsaturations remain intact while the vinyl unsaturations are consumed during the crosslinking. The spectra of the carbon black filled samples have broader peaks compared to the unfilled, which is due to the increased rigidity of the filled samples. An additional observation in figure 3.7 is the increase in the peak at 111 ppm, a peak which could not be associated with any structure.

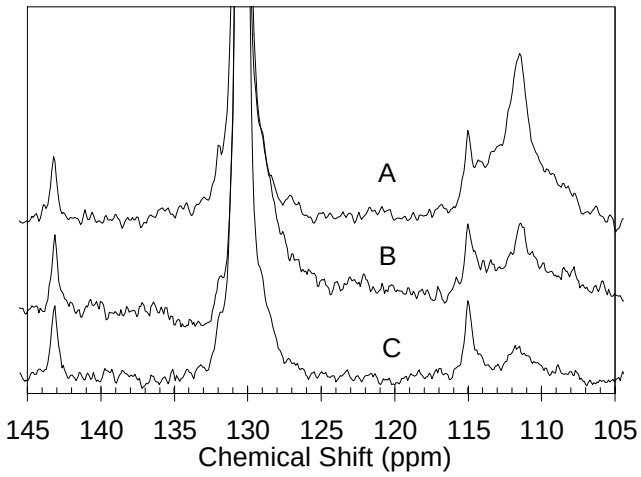


Figure 3.7. The olefininc region of ^{13}C solid state NMR (MAS) spectra of carbon black filled (45 phr) polybutadiene crosslinked by HPV at 250°C and 290 MPa (A), peroxide crosslinked at 170°C (B), and uncrosslinked (C) (**Paper IV**).

Reaction Mechanism

Based on the observations with a radical scavenger present during the high pressure vulcanization, and the microstructural changes studied by means of FTIR and NMR, a suggestion about the reaction mechanism can be made. The main mechanism is probably a radical mechanism, very similar to peroxide and radiation crosslinking. The initiation step involves thermal cleavage of an allylic hydrogen, yielding a polymeric radical of the same type as in peroxide crosslinking of diene rubbers. This is shown in Figure 3.8 with the cleavage of the allylic carbon-hydrogen bond in a methylene unit located between a main chain unsaturation and a vinyl unit. Allylic hydrogens have low bond dissociation energy, 355 kJ/mol compared to 410 kJ/mol for a methylenic hydrogen *[Carey and Sundberg, 1984]*, due to the fact that the created radical is delocalized.

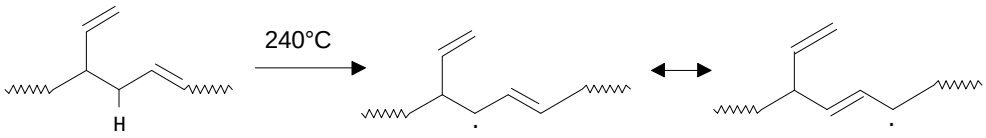


Figure 3.8. Initiation of the crosslinking reaction in high pressure vulcanization **(Paper IV)**.

The polymer radical may then propagate by addition as shown in Figure 3.9, resulting in a crosslink simultaneously with the consumption of an unsaturation. Another probable reaction is the combination of two radicals, also yielding a crosslink, but this reaction does not consume double bonds, which makes the addition mechanism the more likely one.

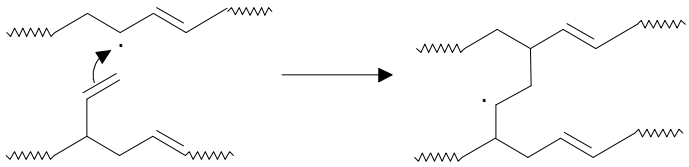


Figure 3.9. One possible propagation route in high pressure vulcanization **(Paper IV)**.

The radical formed after the first addition step may then propagate further with the consumption of new unsaturations, principally by vinyl units as shown by the FTIR and NMR studies. This results in a kind of polymerization reaction, and the network resulting from such a reaction is shown in Figure 3.10.

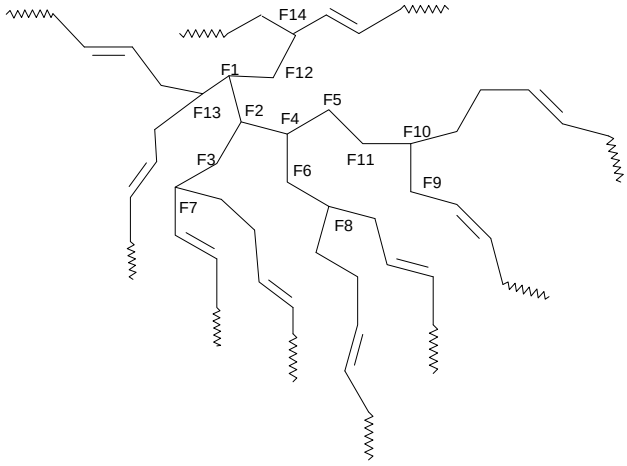


Figure 3.10. The network structure resulting from the addition of radicals to vinyl units in polybutadiene (four steps). The abbreviations are used in the prediction of chemical shifts (**Paper IV**).

This kind of reaction may take place at high temperatures, >200°C for a polybutadiene. However, one important question remains to be answered, namely why the pressure accelerates the crosslinking reaction. As has been described in the introductory section of this thesis, a hydrostatic pressure decreases the segmental mobility of the polymer due to a

reduction of the free volume, and the decrease in mobility prevents long range motions of the polymer chains. A prerequisite for radicals to be terminated by combination (cf. the abstraction-combination mechanism in peroxide vulcanization) is that two polymer radicals are able to coincide with each other. This is very unlikely to happen if the chains are not mobile enough on the segmental level. Thus, an increased pressure will lead to a lower rate of radical termination by combination owing to decreased mobility. Another way of expressing this phenomenon is that the lifetime of the radicals is increased and that the concentration of radicals will increase with the pressure. A created polymer radical will have time to perform a large number of addition steps before termination occurs, which can be expressed as an increase in the so-called kinetic chain length. While the termination rate decreases, the propagation reaction rate may show an increase as the polymer chains are fused closer to each other, leading to increased reactivity *[Sasuga and Takehisa, 1975]*.

The fact that the vinyl units are essential can also be explained in terms of mobility. As the pressure increases and the free volume decreases, motions with a large activation volume will be impeded very much, whereas motions with a low activation volume, such as rotation of a side group, are not affected by the decrease in free volume *[Kovarskii, 1993]*. There may also be a steric effect involved, as the vinyl units protrude from the main chain and are likely to be more accessible to reactive species in the vicinity.

In the suggested network structure (figure 3.10), the carbon atoms involved in the crosslinks may give rise to new resonances in the ^{13}C NMR spectra. The chemical shift of these resonances can be predicted by means of addition rules, e.g. those suggested by Lindeman and Adams *[Lindeman and Adams, 1971]*. The calculated chemical shifts of the carbon atoms indicated in figure 3.10 are tabulated in table 3.1.

Table 3.1. Chemical shift of resonances in the proposed network structure, calculated by means of the addition rules given by Lindeman and Adams *[Lindeman and Adams, 1971]* (**Paper IV).**

Carbon	Calc. shift (ppm)
F1	37.9
F2	37.9
F3	34.3
F4	35.4
F5	30.1
F6	36.8
F7	35.0

Carbon	Calc. shift (ppm)
F8	35.0
F9	34.5
F10	37.1
F11	32.3
F12	34.4
F13	31.4
F14	35.0

The main conclusion from this calculation is that many different peaks may appear, each of a low intensity, much lower than would be the case if there was only one single resonance resulting from the crosslinks. Together with the fact that the concentration of crosslinks is low (10^{-3}-10^{-5} mol/cm^3), it is clear that the detection of crosslinks is very difficult, and the intensities of the resonance peaks of the crosslinks are close to the detection limit of the NMR technique. The region where these peaks are expected to appear is around 30-38 ppm, which makes it likely that many peaks will overlap with already existing resonances. It is relevant to

point out that the agreement between predicted and observed shifts is in the order of +/-1 ppm (see paper IV). An enlargement of the alifatic region of the NMR spectra of high pressure vulcanized and unvulcanized polybutadiene is shown in figure 3.11. As can be seen, the spectra before and after crosslinking are very similar. However, some indications of spectral changes can be noticed, indicated by arrows in the figure, at 29.5, 31, 36, 41, and 46-47 ppm. These are in the range of the predicted shifts, based on the suggested network structure. Zeng and Ko *[Zeng and Ko, 1998]* found that cis-polybutadiene crosslinked under a pressure of 4 GPa and a temperature between 140°C and 180°C showed a new broad resonance band between 30 and 50 ppm. These were, however, highly crosslinked samples of a glassy nature. Radiation crosslinked cis-polybutadiene was analyzed by Barron and co-workers *[Barron et al., 1985]*, and new peaks were developed at 45.8 ppm ascribed to tertiary carbons at the crosslink sites and at 30.5 and 28.2 ppm ascribed to methyl groups adjacent to crosslinks, respectively. Moreover, crosslinked structures in photo-oxidized polybutadiene with a microstructure similar to that used in the present study have been identified as new peaks at 29.5, 36.1, 37.9, 40.0, 41.4, and 42.0 ppm in the ^{13}C NMR spectra *[Adam et al., 1991]* of swollen networks. In the same study, spectra from solid state measurements of both photo-oxidized and peroxide crosslinked polybutadiene (1-5% dicumyl peroxide) showed weak peaks at 34.2, 36.0, and 42.0 ppm for the former and a shoulder around 50 ppm for the latter, all ascribed to crosslinked structures. All these observations are in agreement with the changes seen in figure 3.11, and it is reasonable to assume that at least some of the new resonances in high pressure vulcanized polybutadiene originate from the crosslinks formed.

Even if the new peaks could not be ascribed to some specific structures, they are in the region where crosslinked structures are expected to appear. They are also in agreement with observations of peroxide, photo, and radiation crosslinked polybutadiene, which makes it likely that the network structures formed in high pressure vulcanization are similar to these. Finally, it is worth noting that oxygen bridges (C-O-C and C-O-O-C), which have absorption peaks around 70 ppm *[Adam et al., 1991]*, could not be detected in the HPV materials.

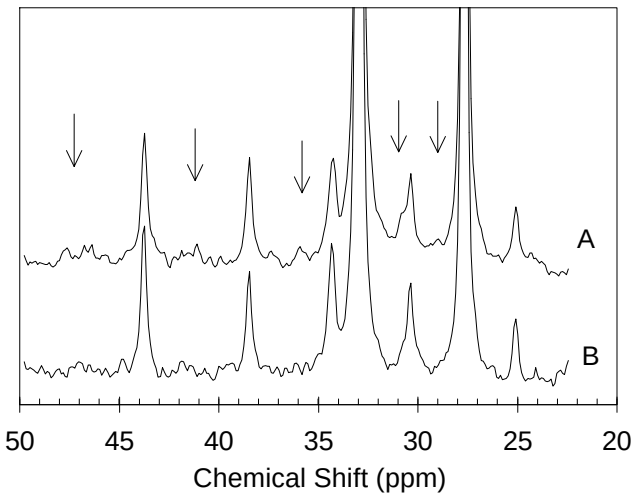


Figure 3.11. The alifatic region of ^{13}C NMR-spectra of polybutadiene, HPV crosslinked (A) and uncrosslinked (B) (**Paper IV**).

Thus, it can be concluded that the crosslinks formed during high pressure vulcanization are carbon-carbon crosslinks, quite similar to those resulting from peroxide and radiation crosslinking. This means that HPV crosslinks are much more resistant to degradation than sulphur crosslinks. It is also reflected in the fact that high pressure vulcanization shows no reversion, which is a great problem in sulphur vulcanization.

Network Heterogeneity

As a result of the addition mechanism, which creates many crosslinks in a very small spatial surrounding, the network formed may exhibit heterogeneities. This has not been investigated for HPV, while it has been observed for peroxide vulcanization of polydienes, as mentioned in the Introduction. Heterogeneities in the network structure may be revealed by e.g. DMTA measurements.

Figure 3.12. shows the glass transition temperature, here defined as the position of the tanδ peak in DMTA measurements, versus crosslink density and it increases with the degree of crosslinking. This behaviour is due to the fact that crosslinks in general impart the segmental motions associated with glass transition *[McCrum et al., 1967]*. Furthermore, no significant changes between the two crosslinking systems can be seen. Different crosslinking systems may give rise to unequal shifts in the glass transition as the crosslink density is changed, due to varying mobility of the crosslinks (different length and flexibility) *[Hagen et al., 1996]*. The fact that HPV and peroxide crosslinking display similar behaviour is explained by the formation of carbon-carbon crosslinks in both cases, so there is no difference between the two systems investigated regarding the mobility of the crosslinks. It can also be mentioned that possible cyclization reactions would stiffen the main chain, thereby increasing the glass transition temperature. As there are no differences between the two crosslinking systems seen in figure 3.12, it is reasonable to assume that there are no differences in the extent of cyclization reactions.

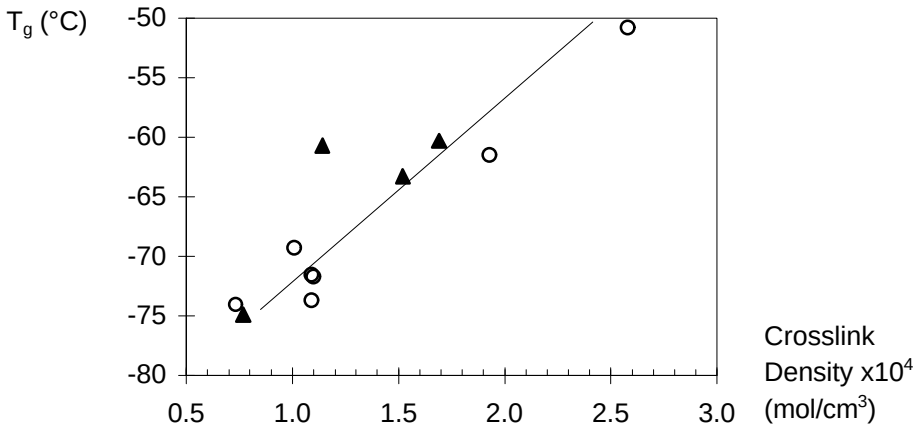


Figure 3.12. T_g versus crosslink density for polybutadiene crosslinked by peroxide (○) at 170°C, and HPV (σ) at 240-250°C and 290 MPa for different lengths of time. Frequency 1 Hz (**Paper III**).

The peroxide most often used in the crosslinking of rubber materials is dicumyl peroxide, which is not perfectly dissolved in a non-polar matrix such as polybutadiene, but will tend to

agglomerate. This effect can be reduced by the use of dispersion agents, such as silica, where the peroxide molecules are adsorbed upon the surface. This is the form of dicumyl peroxide which is used most frequently in rubber industry today. In spite of the dispersion agent, the peroxide molecules will not be present in the rubber matrix in a spatially random way, as each silica particle will contain many peroxide molecules within a very small volume. HPV on the other hand, will create initiating radicals in a spatially random fashion, just as in radiation crosslinking. The difference in distribution of radicals between peroxide and HPV can be viewed in a qualitative way as in Figure 3.14. These differences in the initiating mechanism may be detected in terms of unequal elastic properties, as the distribution of the length of the load-bearing segments will vary.

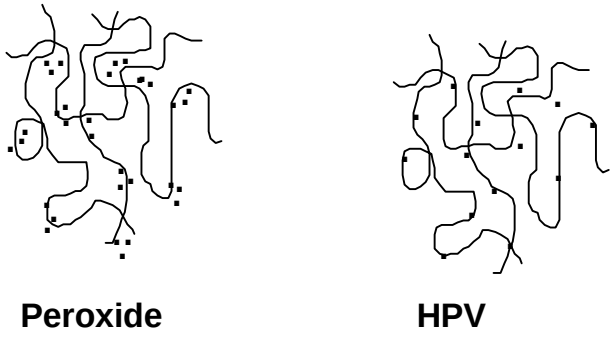


Figure 3.14. A qualitative description of the differences in distribution of radicals (•)during the initiation of peroxide and HPV crosslinking.

Figure 3.15 shows the tanδ value versus crosslink density for HPV and peroxide vulcanizates. There is a significant difference between the two vulcanizates. The HPV samples have a lower tanδ value than the peroxide samples when compared at equal crosslink density. A lower tanδ means less energy losses in the material. It can also be expressed as an increase in elasticity. This may be due to a more equal distribution of chain lengths between the crosslink

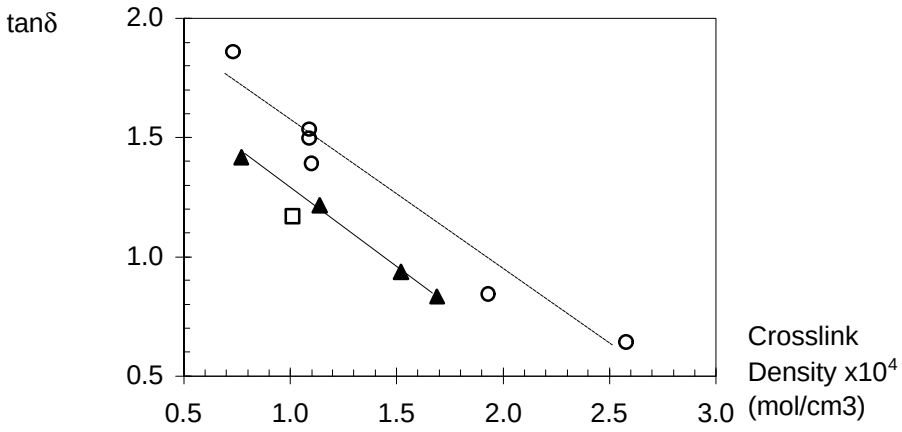


Figure 3.15. tanδ peak value versus crosslink density for polybutadiene crosslinked by HPV (σ), peroxide (○) (The same samples as in Figure 3.12), and peroxide vulcanization at 240°C and 290 MPa (o). Frequency 1 Hz (**Paper III**).

points, and is just what may be expected, as the initiation takes place in a totally random way for HPV. The unfilled square (o) in figure 3.15 represents a peroxide vulcanizate crosslinked at 240°C and 290 MPa. Under these conditions, both peroxide molecules and the thermal energy (the only initiation route in HPV) will create radicals. The thermally initiated radicals will have spatially random distribution and make the crosslinks more evenly distributed. Thus the polybutadiene peroxide vulcanized at 240°C will show properties more like an HPV crosslinked material than a peroxide crosslinked one.

Effect of Carbon Black

In this section the effect of carbon black on rubber materials treated at elevated pressure will be discussed. It contains studies of samples with the following two main characteristics:

- Unvulcanized samples of a mainly viscous character
- Vulcanized samples of an elastic character

The reason why unvulcanized samples are studied is the difficulty of differentiating between true polymer-polymer crosslinks and polymer-filler interactions. It must also be mentioned that there is no distinct border-line between unvulcanized and vulcanized samples in high pressure vulcanization, but there is a successive transition from viscous to elastic samples and vice versa.

Increase in Polymer-Filler Interactions - Penetration

As described in the introduction, the ability of carbon black to form interactions with the polymer is of importance for the properties of a rubber material. One of the relevant factors in determining the reinforcing capability is the bound rubber. Figure 3.16 shows the effect of pressure and temperature on the amount of bound rubber for a polybutadiene containing 45 phr N220. The samples, without any vulcanization agents or other additives, were kept under pressure for 15 min. The bound rubber increased steadily with the treatment temperature, finally reaching abnormally high values of 90-95%. Normal bound rubber values in the case of carbon black loadings of 50 phr may be around 35% *[Boonstra, 1982]*. The common picture of bound rubber formation is, that it is a dynamic process going on for up to 30-50 days after mixing, finally reaching a kind of equilibrium value *[Leblanc and Hardy, 1991]*. During this time the lower molecular weight chains, which are adsorbed first, are replaced by the higher ones.

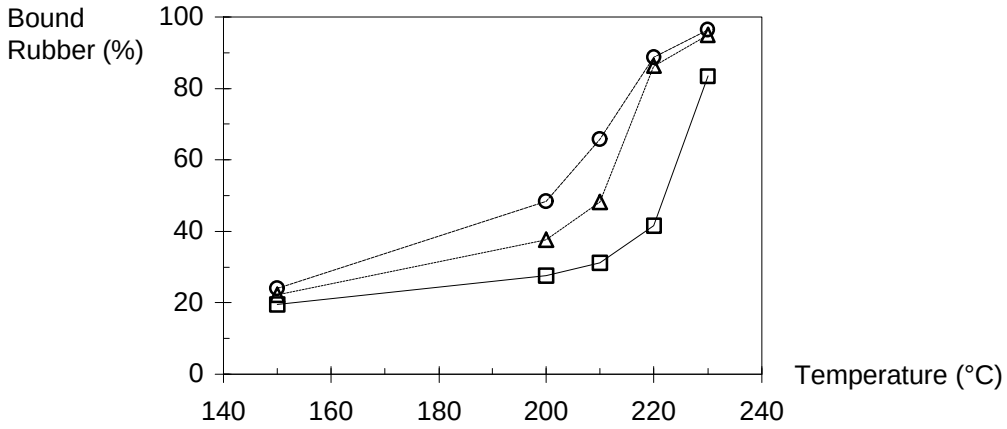


Figure 3.16. Bound rubber versus treatment temperature for a polybutadiene filled with 45 phr N220. Treatment pressures 10 MPa (—o—), 180 MPa (—Δ—), and 290 MPa (—○—) for 15 min (**Paper V**).

This process is accelerated by an increase in temperature. However, this traditional picture is valid for moderate temperatures, up to 100-150°C, where the main mechanism of attachment between polymer and filler is of a physico-chemical nature. At higher temperatures, it is likely that other kinds of interaction may take place between the polymer and filler, including covalent chemical bonds. The pressure may also contribute to the high bound rubber values, which will be discussed further on. It is also possible that chemical crosslinking between polymer chains may contribute to the high bound rubber values. Spontaneous crosslinking between unsaturated polymer chains may occur very slowly already at temperatures around 210-220°C, even if the extent of crosslinking is not of any technical importance. Thus, the abnormal high bound rubber values shown in figure 3.16 may be explained by the following:

1) Increased number of interactions between polymer and filler owing to some new kind of reactions facilitated by the elevated temperature and pressure.
2) Formation of polymer-polymer crosslinks, few in number but enough to create an infinite, three-dimensional network including the filler particles attached to polymer chains.

Also revealed in Figure 3.16 is the effect of increased pressure on the amount of bound rubber. At 150°C there is a small, but significant difference in the amount of bound rubber between the pressures applied. At 210°C and 220°C the difference is even more pronounced, while at the highest temperatures shown it is levelled off.

Most carbon blacks, including N220, have an irregular morphology both on the primary particle level (surface irregularities) and the aggregate level. When a polymer and a carbon black are mixed, the polymer wets the carbon black surface and interactions are evolved. However, due to the complicated morphology of carbon black, it is likely that not all of the surface is accessible to the rubber molecules. When the composite is subjected to an elevated pressure, this may be changed, and the polymer will be able to penetrate the unoccupied space to a much higher extent. This leads to an increased number of polymer-filler interactions and is reflected in the higher bound rubber values as the pressure is increased. Specifically at the lower temperature investigated, i.e. 150°C, this is probably the main reason for the pressure dependence of the bound rubber. The large difference observed at 210-220°C may, in addition, have the explanation that polymer-polymer crosslinks are formed. This is known to be a pressure sensitive reaction, as shown on p. 31 in this chapter, and forms the basis of high pressure vulcanization. Even if temperatures around 210-220°C have not been considered interesting in HPV (of polybutadiene) from a technical point of view, the extent of crosslinking that takes place may be enough to cause large changes in bound rubber measurements.

The view that rubber molecules penetrate the empty space in rubber-carbon black compounds to a higher extent at elevated pressures, is supported by the results shown in Figure 3.17. Here the gravimetric density is plotted versus treatment pressure, for different temperatures, and it increases with treatment pressure for all temperatures. This indicates that the rubber penetrates and fills the empty space in the composite. The fact that there is empty space, or ”pores” in the rubber-carbon black compound (the term ”pores” is not to be confused with the pores of the carbon black particle itself) is also displayed in Figure 3.17. The highest measured density of

the pressure-treated samples was slightly above 1.06 g/cm^3 , while the theoretical density (calculated, not measured) for polybutadiene filled with 45 phr N220 is 1.10 g/cm^3, based on a carbon black density of 2.0 g/cm^3 . The density value of the carbon black was taken from measurements with helium *[Hess and Herd, 1993]*. This difference shows that there must be a great deal of empty space inside the polymer-carbon black composite which may be filled with polymer when subjected to an elevated pressure. This is in accordance with Schilling and Angerer´s study, where the density and porosity of rubber-carbon black mixes were shown to be strongly dependent on the applied pressure *[Schilling et al., 1974 a]*.

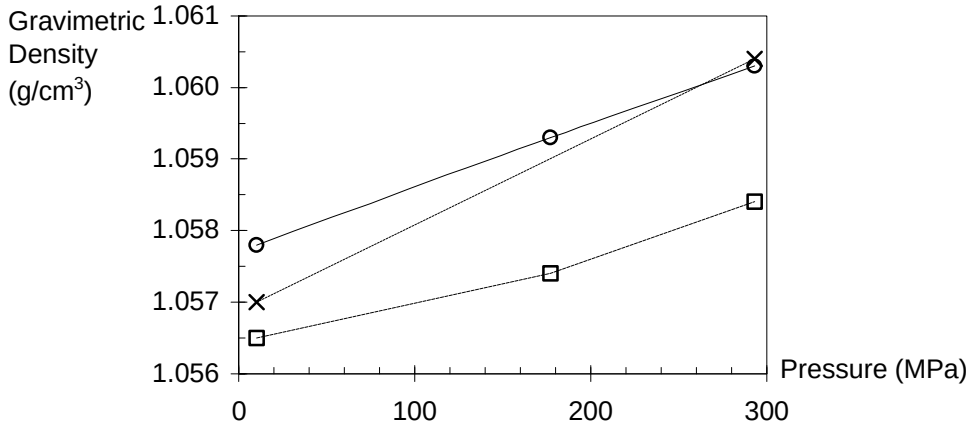


Figure 3.17. Gravimetric density versus treatment pressure. Polybutadiene filled with 45 phr N220 and subjected to pressure for 15 min at different temperatures: 150°C (o), 220°C (×), and 230°C (○) (**Paper V**).

As mentioned earlier, the formation of bound rubber is a kinetic process that can be in progress for many weeks, and if the temperature increases, it accelerates. The pressure treated samples also displays a kinetic behaviour, in the sense that the bound rubber increases with time under pressure. Figure 3.18 shows the bound rubber versus gravimetric density of

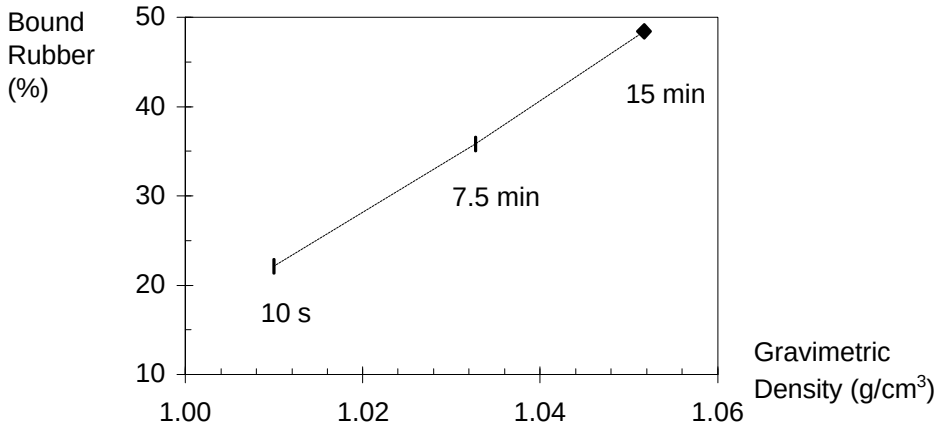


Figure 3.18. Bound rubber versus gravimetric density for a polybutadiene filled with 45 phr N220, treated at 200°C and 290 MPa for different lengths of time: 10 s, 7.5 min, and 15 min respectively (**Paper V**).

samples pressure-treated for different lengths of time. There is an obvious relationship between the two quantities, which strengthens the suggestion that polymer under the influence of hydrostatic pressure penetrates into the otherwise unattainable regions of carbon black. When the molecules reach these regions, new surfaces become available for interactions, irrespective of what kind these interactions may be, i.e. of adsorption or covalent type, and the bound rubber values increase.

In addition to the density and bound rubber measurements of pressure treated polymer-filler samples, measurements of the dynamic storage modulus provide some further information. As seen in figure 3.19 there is no increase in modulus between treatment temperatures of 150°C and 200°C, while the bound rubber values are affected in this interval. When the temperature reaches 220°C, where it is likely that some polymer-polymer crosslinks are formed, the modulus increases drastically. Thus, the effect of temperature on the properties of polymer carbon black composites is that the formation of an infinitely three-dimensional network starts at temperatures around 210-220°C, and is first seen by an increase in bound rubber. Later on, at slightly higher temperatures, the modulus is affected and the samples become almost like a vulcanized material.

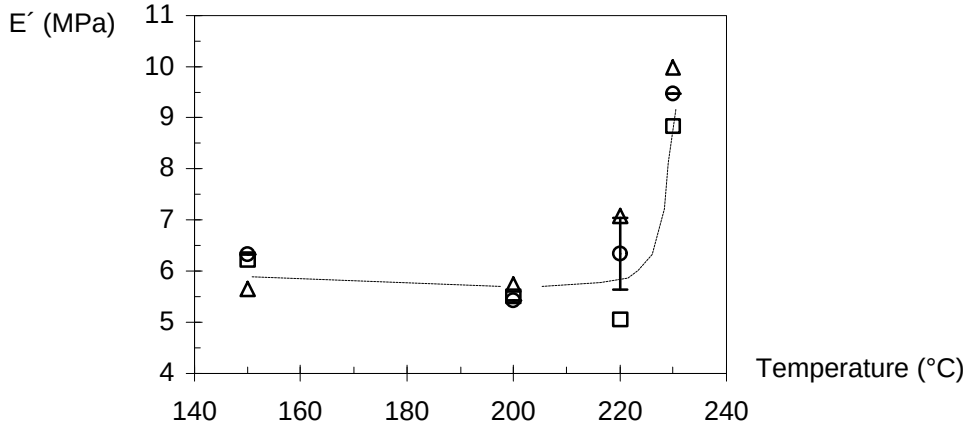


Figure 3.19. Dynamic storage modulus at 27°C and 0.22% strain versus treatment temperature for different pressures: 10 MPa (o), 180 MPa (Δ), and 290 MPa (○). Frequency 1 Hz. The error bar indicated is representative of all points (**Paper V**).

This section has shown that the polymer-filler interactions increase in unvulcanized samples with both pressure and temperature. As temperature and pressure are increased, the samples become more and more like vulcanizates, and there is no distinct borderline between vulcanized and unvulcanized samples, but a continuous transition. The effect of pressure is probably an increase in the penetration of the polymer into the empty space of the carbon black structure, while increased temperature facilitates chemical reaction between both polymer chains and polymer chains and filler particles.

Rubber-Carbon Black Interactions in Vulcanized Samples

When carbon black is added to a rubber material, the measured crosslink density increases due to the formation of polymer-filler attachments which act almost like crosslinks and restrict the swelling of the polymer. In fully crosslinked samples, the number of interactions is expected to

increase due to the elevated pressure, just as is the case of the less crosslinked (or totally uncrosslinked) samples discussed in the previous pages.

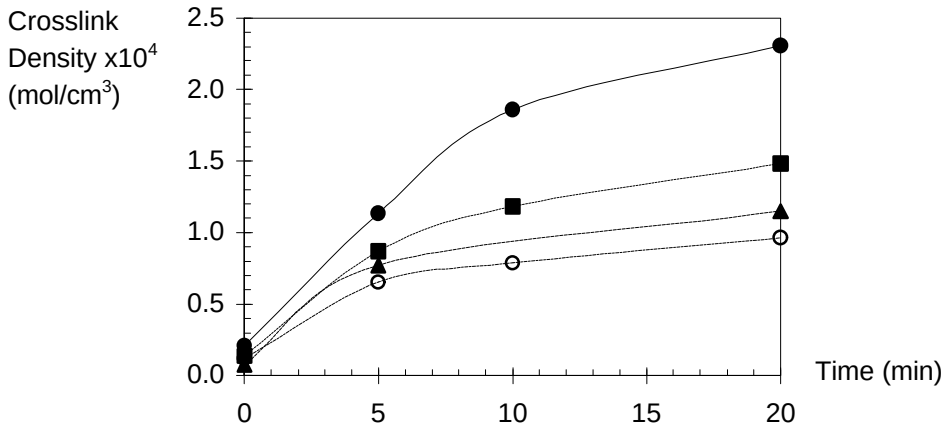


Figure 3.20. Crosslink density versus vulcanization time for high pressure vulcanized polybutadiene with different contents of carbon black: 0 phr (○), 15 phr (σ), 30 phr (ν), and 45 phr (λ). Pressure 290 MPa and temperature 250°C (unpublished data).

Figure 3.20 shows the effect of carbon black on the crosslink density of samples crosslinked by HPV for different lengths of time. The compounds containing carbon black display the same behaviour as the unfilled samples: a marching crosslink density. The difference in crosslink density between filled and unfilled samples is due to the restricted swelling of the polymer layer closest to the filler particles, and can be regarded as an amount of extra network material. This amount increases with carbon black loading, which reflects the increased interface area between polymer and filler. The carbon black may also increase the number of polymer-polymer crosslinks in some catalytic way, also resulting in more restricted swelling. However, it is impossible to determine the origin of the measured increase in crosslink density only from swelling measurements.

Despite these difficulties in determining the origin of the measured increase in crosslink density, valuable information can be obtained from samples treated at different pressures. Unfilled samples will show only the pressure sensitivity of the polymer-polymer crosslink reaction (cf. figure 3.2 b), while filled samples will also include the polymer-filler reactions and the possible increase in the polymer-polymer crosslinks due to a catalytic effect of the carbon black. Figure 3.21 shows the difference between filled (45 phr N220) and unfilled samples vulcanized at different pressures, normalized with respect to the samples crosslinked at the lowest pressure. The amount of extra network material increases almost linearly with the pressure, showing that the increase in measured crosslink density is pressure sensitive. Figure 3.16 showed that the formation of bound rubber is pressure sensitive, due to the possibility of increased interaction surface area at elevated pressures. With that observation in mind, it is clear that at least part of the increased difference in figure 3.21 is due to increased carbon black interactions, but the catalytic concept cannot be rejected.

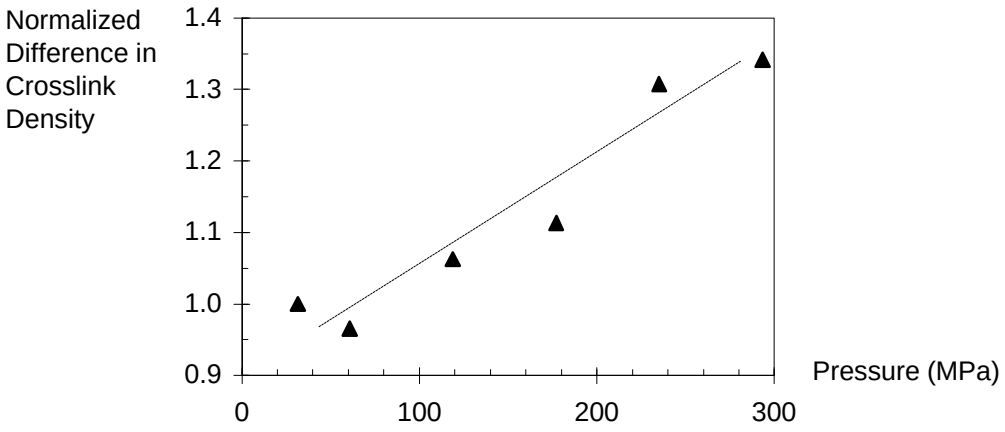


Figure 3.21. Normalized difference in crosslink density between filled (45 phr N220) and unfilled polybutadiene treated at different pressures. Treatment temperature 240°C for 5 min. Normalized with respect to the lowest pressure (**Paper I**).

Graphitized and Oxidized Carbon Black

The amount of rubber-filler interactions is strongly dependent on the surface activity of the carbon black, which in turn can be changed by thermal treatment. Graphitized carbon blacks exhibit very weak interactions and do not alter the swelling behaviour of the vulcanized sample, compared to an unfilled one. On the other hand, oxidized carbon blacks have a larger amount of active surface groups, which may increase the interactions with the polymer. Whether this happens or not is dependent on the type of polymer; different polymers may display diverging behaviour with respect to the effect of oxidized carbon black on the polymer-filler interactions. Table 3.2 shows the amount of bound rubber for polybutadiene mixed with 45 phr oxidized, graphitized and untreated N220 carbon black, respectively. There is no doubt that the rubber-carbon black interactions increase as a result of the oxidative treatment (thermal oxidation in air at 400°C). Also shown is the bound rubber for the compound with Monarch 1300, which is a very high surface area carbon black (560 m^2/g) with a high content of surface groups, mainly oxygen functionalities.

Table 3.2. Bound rubber for polybutadiene-carbon black mixes (45 phr) (**Paper II**).

Carbon Black	Bound Rubber (%)
Graphitized N220	12.9
Untreated N220	27.2
Oxidized N220	37.8
Monarch 1300	39.7

When these compounds are crosslinked by HPV, the resulting crosslink densities are as shown in Figure 3.22, which also displays the crosslink densities of the same compounds crosslinked by means of 3 phr dicumyl peroxide. The abscissa represents the base adsorption of carbon blacks, indicating the differences in surface activity. The mixes are in the order of increasing base adsorption: graphitized, untreated, oxidized, and finally Monarch 1300. The two different

vulcanization systems display totally different behaviour. The peroxide vulcanizates show decreasing crosslink density with an increased

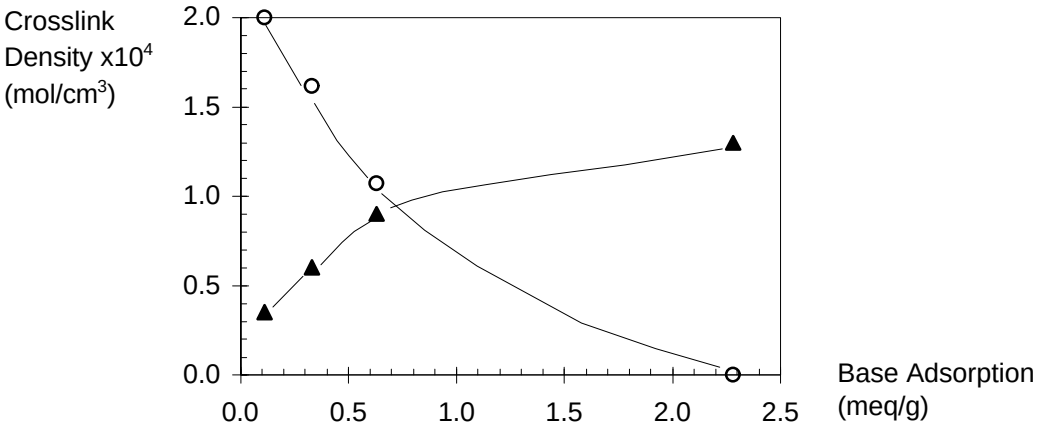


Figure 3.22. Crosslink density versus base adsorption of the carbon blacks used for HPV (σ) and peroxide (○) crosslinking. Carbon blacks used, from the left to the right in the figure: graphitized N220, N220, oxidized N220, and Monarch 1300 (**Paper II**).

degree of oxidation of carbon black, while the HPV samples show the opposite. The reason why the peroxide vulcanizates decrease in crosslink density is that the active groups on the carbon black surface are able to decompose the peroxide molecules before they are decomposed into radicals. Alternatively, they can quench the radical reactions after they have been initiated *[Coran, 1994]*. Thus, the crosslinking reactions are prevented more effectively by an increased number of surface groups on the carbon black. In the extreme case of Monarch 1300, which has an oxygen content around 12%, the result is an unvulcanized piece of material which falls apart when touched and dissolves totally in a good solvent. Contrary to this, the HPV samples show an increase in crosslink density with an increased degree of oxidation of the carbon black. The explanation is that the crosslinking reactions are not disturbed by the presence of active surface groups. Instead, these groups increase the number of polymer-filler interactions, as indicated by the bound rubber values. However, there are probably not only physicochemical types of interactions that are involved, but also some covalent bonds as a result of the elevated temperature (240°C). This view, that the polymer-filler interactions play a relatively important role, is strengthened by the fact that HPV of the compound with Monarch 1300 yields a vulcanized material with pronounced rubber properties, which is not the case with peroxide vulcanization. The extremely high surface area facilitates a large extent of polymer-filler interactions especially under pressure, where the penetrating ability of the polymer is increased.

The strain amplitude dependence of the dynamic modulus also shows some interesting features of materials vulcanized by high pressure. The non-linearity of carbon black filled rubber materials is characterized by a large drop in the modulus when the strain amplitude is increased, called the Payne effect. It is often given as a $\Delta E'$-value, which is the difference between the modulus at low and high strain, respectively. The modulus of HPV and peroxide crosslinked materials containing different carbon blacks was measured, varying the strain amplitude between 0.22% and 5.12% (peak to peak strain, bending mode). Figure 3.23 shows

$\Delta E'$-values ($\Delta E' = E'_{0.22}-E'_{5.12}$) of the samples with different N220 carbon blacks, normalized to the sample with graphitized carbon black.

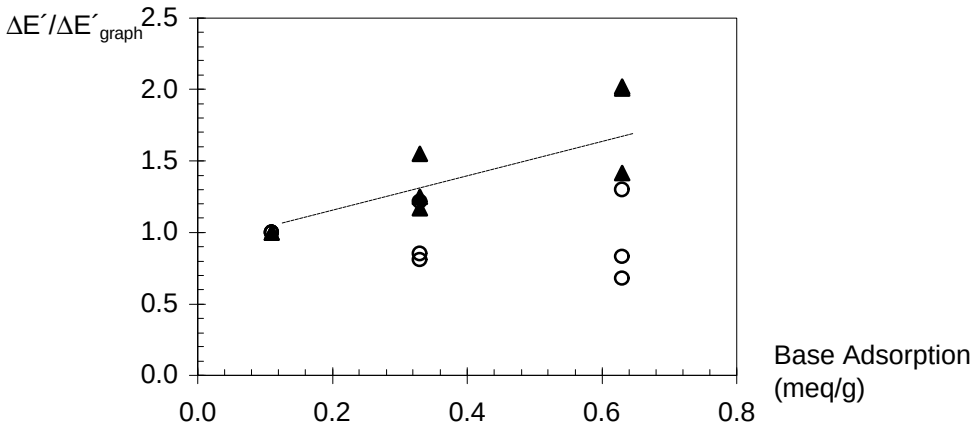


Figure 3.23. Normalized $\Delta E'$ versus base adsorption for HPV (σ) and peroxide (○) crosslinked samples with 45 phr of different carbon blacks: N220 graphitized, N220 untreated, and N220 oxidized. $\Delta E' = E'_{0.22}-E'_{5.12}$. (**Paper II**).

$\Delta E'$ increases with the base adsorption for the HPV samples, while the peroxide vulcanizates display a somewhat ambiguous behaviour. The increase for the HPV samples is quite unexpected, as the number of polymer-filler interactions increases with a higher degree of oxidation of carbon black. More polymer-filler interactions lead to less interaggregation of the carbon black particles (filler networking) as the polymer layer around them decreases their ability to get fused together. The traditional interpretation of the Payne effect is that filler-filler interactions are broken as the strain amplitude increases. According to this interpretation, the $\Delta E'$-values in Figure 3.23 should decrease with higher degree of oxidation, but this cannot be observed. However, the Langmuir-adsorption based theory proposed by Göritz and Maier *[Göritz and Maier, 1996]* may serve as an explanation of the results in figure 3.23. According to this theory, the Payne effect is due to polymer-filler slippage. Since the number of polymer-filler interactions increases (for polybutadiene) with an increased degree of oxidation of the carbon black, and the polymer-filler interactions in general are of high importance in high pressure vulcanized samples, this would be observed as a higher modulus drop during a strain amplitude scan according to Göritz and Maiers explanation of the Payne effect, and this is also what is seen in figure 3.23.

Mechanical Properties

The following section will be a short summary of the mechanical properties of samples vulcanized by HPV, in some cases compared with peroxide vulcanizates. The mechanical properties of rubber materials in general have been extensively studied and discussed in many textbooks *[Mark et al., 1994], [Gent, 1992], [Hepburn and Reynolds, 1979], [Hepburn and Blow, 1982]*.

Stress Relaxation

The stress relaxation properties are often essential for rubber materials, e.g. in sealing applications. Both physical and chemical processes are responsible for the stress decay upon constant deformation, including mechanisms such as disentanglement, chain slippage, chain and crosslink scission and formation of new crosslinks. At moderate temperatures and during short lengths of time, the physical processes dominate and thermooxidative reactions can be neglected *[Stevenson and Campion, 1992]*. Figure 3.24 shows the stress relaxation rate for peroxide and HPV crosslinked polybutadiene samples filled with 45 phr N220 carbon black and subjected to 15% compression for 15 min at 25°C (physical stress relaxation). The stress relaxation rate has been plotted versus crosslink density as it depends on the number of load-bearing segments in the rubber sample (correlated with the crosslink density).

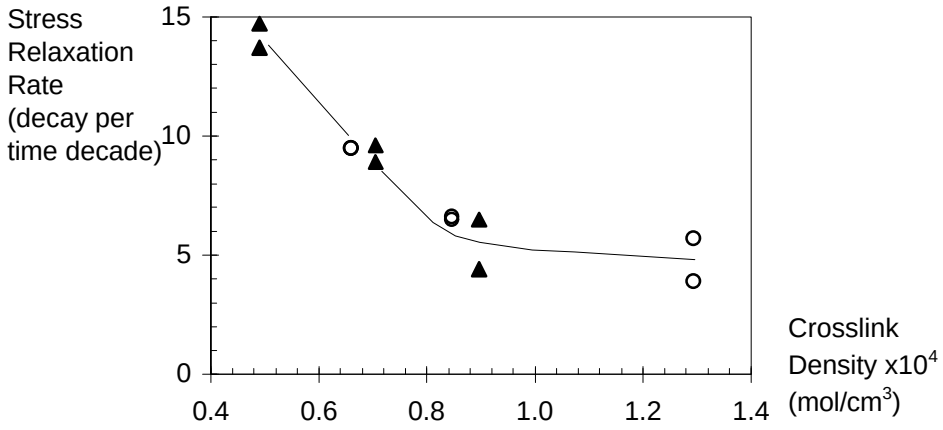


Figure 3.24. Stress relaxation rate (at 25°C) versus crosslink density for polybutadiene filled with 45 phr N220 carbon black crosslinked by HPV (σ) and peroxide (○). HPV performed at 290 MPa and 240°C for 3, 5 and 10 min respectively. Peroxide content 0.7, 1, and 2 phr, samples vulcanized for 12 min at 170°C (**Paper I**).

Peroxide vulcanizates are known for their good stress relaxation properties, especially at elevated temperatures, and it is obvious from the figure that the HPV samples show as good properties as the peroxide samples. This is valid at ambient temperature, but it may change at elevated temperatures. It has also been shown to be valid for high pressure vulcanized polybutadiene subjected to a dynamic stress during a long time and at an elevated temperature *[Lavebratt et al., 1990]*. The reason why samples crosslinked under the influence of an elevated pressure are as good as peroxide vulcanizates, or even better, may have the following explanations:

(1)There is an increased number of strong polymer-filler interactions due to the elevated pressure, which decreases the slippage between chain segments and filler surface;

(2)The network is formed when the material is compressed, i.e. the interconnecting forces are evolved in a state which is favourable to subsequent deformations; cf. the Tobolsky two-network theory *[Tobolsky, 1960], [Stevenson and Campion, 1992]*.

Permanent Set

The permanent set is often used as an industrial standard and is not necessarily correlated to the stress relaxation properties. The set is measured after a certain time of recovery, while the stress relaxation is measured continuously, during the deformation. The recovery of the samples applied to permanent set tests may be opposed by crosslinks that may form in the deformed state. In peroxide vulcanizates this may be due to reactions involving rests of peroxides. In the case of HPV materials, no crosslinking reactions are supposed to take place in the deformed state, since there are no reactive species that can cause crosslinking. Thus, the permanent set is expected to be lower for HPV materials than for peroxide vulcanized ones.

Figure 3.25 shows the results of permanent set measurements of samples subjected to 25% compression at 100°C for 24 hours. The compounds used are not the same as for the stress relaxation measurements, so the absolute values of the crosslink densities are not comparable. However, the same trend as shown in the stress relaxation measurements with a decrease at higher crosslink densities can be seen. In addition, the HPV material is better than the peroxide vulcanizate, based on the observations in Figure 3.25. This suggests that HPV materials are very useful for e.g. sealing applications at somewhat elevated temperatures.

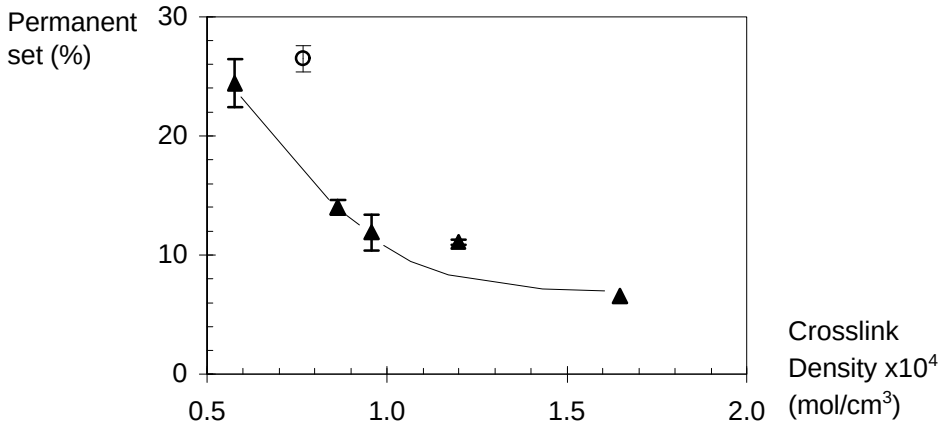


Figure 3.25. Permanent set for polybutadiene filled with 45 phr N220 carbon black, vulcanized by HPV (σ) and dicumyl peroxide (○). Error bars represent +/- standard deviation. HPV performed at 290 MPa and at temperatures of 240°C (0.5-20 min vulcanization time) and 260°C (5 min vulcanization time, the highest crosslink density) (unpublished data).

Hardness

The hardness of rubber materials is measured very quickly and easily and reflects the value of the modulus. The modulus is in turn affected by factors such as presence of fillers, plasticizers,

and the crosslink density of the rubber matrix. The hardness of HPV crosslinked butadiene rubber filled with 45 phr N220 carbon black is shown in Figure 3.26. As can be seen, it increases drastically within the first 5 min of the vulcanization reaction, and the behaviour is almost the same as for the crosslink density measured by swelling (Figures 3.1 and 3.20).

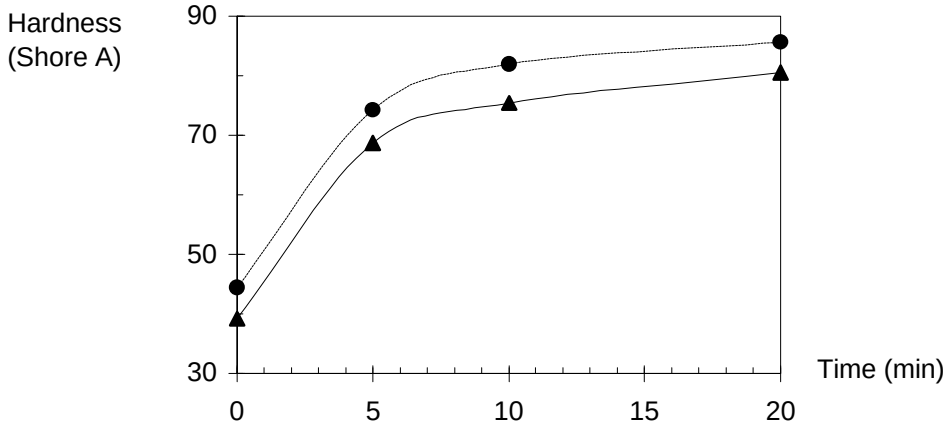


Figure 3.26. Hardness versus vulcanization time for polybutadiene filled with 45phr N220. Treatment pressure 290 MPa and temperature 240°C (σ) and 250°C (λ) (**Paper I**).

Tensile Strength

The tensile strength of rubber materials generally depends on their crosslink density in a somewhat strange way, showing a maximum for intermediate degrees of crosslinking. Figure 3.27 shows that the HPV materials (filled with 45 phr carbon black) have properties comparable to those of peroxide vulcanizates. The absolute values of the stress at break are quite low, the highest value shown is around 11 MPa, as compared to a sulphur vulcanized polybutadiene which may have a stress at break value that is much higher. This, however, is expected as the crosslinks in high pressure vulcanized rubber materials contain carbon-carbon bonds which are inferior to sulphur crosslinks *[Southern, 1979]*.

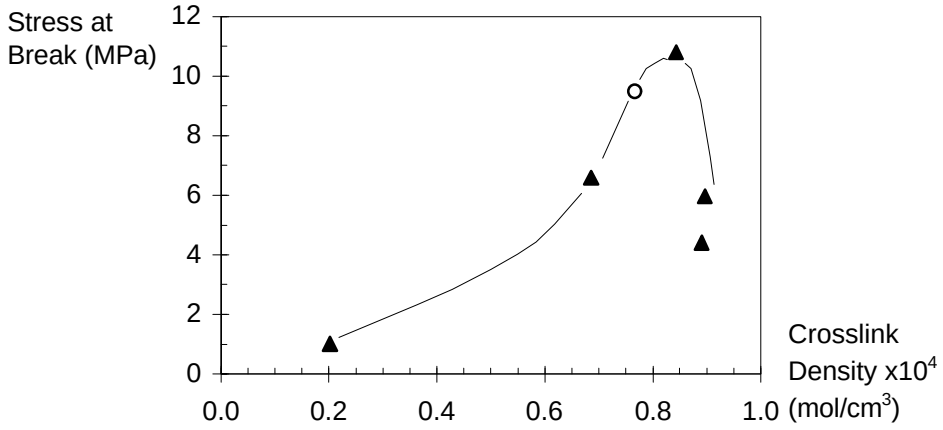


Figure 3.27. Tensile strength (stress at break) for HPV (σ) and peroxide (○) vulcanized polybutadiene filled with 45 phr N220 (unpublished data).

Summary of Mechanical Properties

To conclude this section, it is obvious that rubber materials crosslinked by high pressure vulcanization have mechanical properties comparable to, or sometimes even superior to, those of peroxide vulcanizates of the same materials. This suggests that HPV materials may be of importance in certain applications such as seals and gaskets.

Injection Moulding

Injection moulding machines of today have the characteristics needed for high pressure vulcanization, with injection pressures of up to 250 MPa *[Maplan, 1998]*. To be successful, however, there are some critical points which must be taken into consideration. The first point is the sealing of the mould, since the pressure utilized will cause the rubber compound to extrude via the parting line between the mould halves if the mould deflection becomes to large. The second point is that the presence of pressure gradients inside the mould cavity will result in products with uneven properties, since the crosslinking reaction is pressure sensitive.

Some preliminary tests were performed with a 250 tonne Werner & Pfleiderer injection moulding machine at Skega AB, Ersmark, with a mould yielding 1 cm thick circular discs with a diameter of 10 cm. The mould was specially constructed to eliminate leakage of rubber. A nitrile rubber compound was used, and in spite of appreciable leakage from the mould, a vulcanized sample was obtained. The temperature of the mould was set to 250°C, the injection pressure was 250 MPa, and the mould was closed for 3 min. The part obtained from the mould cavity showed a hardness value of 63 Shore A. The tensile properties of the flash that surrounded the circular disc were measured and the results are shown in Figure 3.28. For the sake of comparison, an identical nitrile rubber compound was vulcanized with sulphur and accelerators. The results showed that both the flash and the sample were fully vulcanized and had really good mechanical properties.

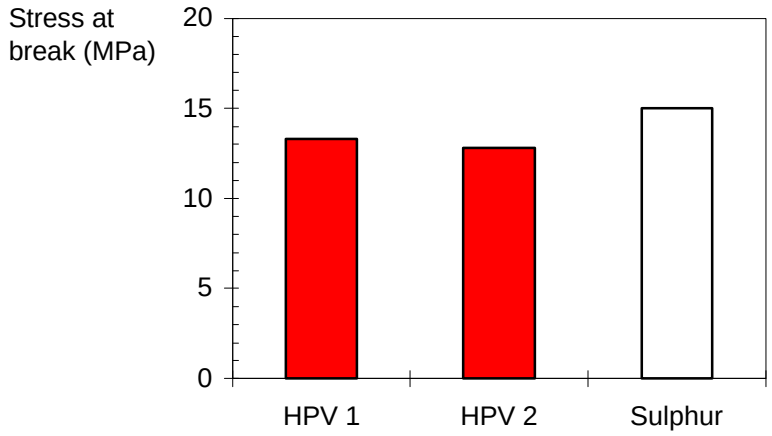


Figure 3.28. Tensile properties of the flash of two injection moulded samples. Nitrile rubber compound vulcanized for 3 min at 250°C with an injection pressure of 250 MPa samples (HPV 1 and HPV 2). In addition a sample of the same nitrile rubber compound, but vulcanized in a conventional way with a sulphur curing system (Sulphur) (unpublished data).

In addition, some further preliminary tests were performed with a polybutadiene filled with 45 phr N220 (no additives at all). The result was a fully vulcanized sample, but in the striving to construct a sealed cavity, it was found to be impossible to demould the sample automatically as the mould halves were jammed. This is an example of the problems that may arise in high pressure vulcanization with injection moulding machines.

High Pressure Vulcanizable Rubber Materials

The polymer mainly investigated for the purpose of this thesis has been polybutadiene with a specific microstructure. However, tests have been performed with other polymers. Nitrile rubber was successfully used in the injection moulding tests, and also in the investigation of the pressure dependence of the HPV crosslinking reaction. Frenkin and co-workers suggested that nitrile-butadiene rubber is easily crosslinked by high pressure vulcanization already at temperatures around 150°C *[Frenkin et al., 1984]*. This seems reasonable as the nitrile rubber compound was crosslinked very quickly at 250°C in the injection moulding experiments. They also concluded that all rubbers containing unsaturations can undergo high pressure vulcanization.

According to the suggested reaction mechanism, most butadiene-based polymers should be able to crosslink by means of HPV. There are two main prerequisites for success: the presence of bonds that can be broken thermally (without deteriorating the polymer chain), thus generating radicals, and double bonds over which the radicals may propagate by addition. If this propagation cannot take place, the reaction will probably not be so pressure sensitive. In this thesis it has been demonstrated that only vinyl unsaturations in the polybutadiene take part in the addition reaction. However, Zeng and Ko *[Zeng and Ko, 1998]* showed that cis unsaturations were consumed when a high cis-polybutadiene was crosslinked at 4 GPa and temperatures around 160-180°C, without any vulcanization agents.

The prerequisites for successful HPV crosslinking are fulfilled in e.g. styrene-butadiene rubber, which contains butadiene units with both main chain and pendant (vinyl) unsaturations, and this rubber has also been shown to be crosslinked in the absence of vulcanization agents. Europrene 1609, which is a masterbatch of SBR, 40 phr N110 carbon black, and 5 phr HA-oil, was treated at 240°C and 290 MPa for 5 min. The result was an elastic rubber material with increased hardness compared to the untreated sample. No further investigations were made concerning the properties of the resulting material, but there is no doubt that the crosslinking was successful. A silicone rubber (with vinyl groups) was tested without any success; no tendency to crosslinking could be seen. The same result was obtained with an ethylene-propylene-diene rubber (EPDM) with ethylidene norbornene (ENB) as diene monomer, and when the samples were immersed in n-heptane they were totally dissolved. However, when the EPDM containing ENB was mixed with an EPDM containing hexadiene, a very sligthly gelled sample was obtained.

4. CONCLUSIONS

This thesis has demonstrated that it is possible to crosslink certain rubber materials without using any vulcanization agents, merely by an elevated pressure and temperature, a process which is called high pressure vulcanization (HPV). Butadiene-, nitrile- and styrene-butadiene rubber have been crosslinked successfully, and the polybutadiene was chosen as a model material for further studies of the crosslinking reaction mechanisms and the resulting network structure of HPV.

- The reaction mechanism was shown to be of a radical type, and the crosslink formation involves the consumption of vinyl unsaturations by an addition mechanism. The reaction rate increases continuously with the applied pressure and temperature, in the ranges 10-290 MPa and 200-260°C which are the intervals that have been studied. Because of this, the final crosslink density and consequently the physical properties of the vulcanized sample, can be easily adjusted during the processing by the parameters time, temperature, and pressure. Thus, one single compound can give products with widely different properties. The microstructural changes occurring during vulcanization of both unfilled and carbon black filled samples were studied by means of ^{13}C solid state nuclear magnetic resonance (NMR) and, in the case of the former, also by means of infrared spectroscopy (FTIR).

- The presence of carbon black increases the measured crosslink density, due to an increased number of polymer-filler interactions facilitated by the elevated pressure and temperature. This is a result of the ability of polymer to penetrate the carbon black structure when a sample is subjected to an elevated pressure. Furthermore, vinyl unsaturations are consumed also in carbon black filled samples, which causes the reaction mechanism to seem unchanged in the presence of carbon black.

- Dynamic mechanical thermal analysis (DMTA) of unfilled polybutadiene revealed that its network structure is of a more homogeneous nature than that of peroxide vulcanizates, as the radicals resulting in crosslinks are thermally initiated in a spatially random fashion, similar to radiation crosslinking, while the peroxide molecules are easily clustered together, even in the presence of dispersion agents.

- The mechanical properties of the resulting vulcanizates are as good as those of peroxide vulcanizates of the same material. Moreover, the thermomechanical properties seem to be superior to those of the peroxide vulcanized material.

- Some preliminary tests have shown that it is possible to injection mould rubber samples with HPV; however, there are some difficulties with the mould construction that have to be overcome.

The high pressure vulcanization technique offers the possibility to crosslink certain rubber materials in an environmentally friendly way. The technique does not include any handling of hazardous chemicals, and the vulcanization fumes contain no accelerators or derivatives of the vulcanization system. Moreover, it results in rubber materials without any additives that can be leached to the surrounding.

5. SUGGESTIONS FOR FUTURE WORK

This thesis has only scrathed the surface of an enormous research area. Therefore, suggestions for future work would form a never ending list. In spite of this, there are some phenomena which in the light of this thesis are especially worth mentioning.

- The role of molecular oxygen in the crosslinking reaction did not get an unambiguous explanation. Further experiments with inert gases may show if the effect is of a chemical or a physical nature.

- The interface between polymer and carbon black filler subjected to elevated pressure is worth investigating more in detail. NMR T_2-relaxation time studies may show if the number of chains with strongly restricted mobility, closest to the filler particles, is increased. This would give a still better view of the suggested penetration of polymer into the unattainable regions of the rubber-carbon black composite. Furthermore, bound rubber measurements with hot solvents, at different temperatures, could reveal the distribution in bond strength of the carbon black trapped rubber.

- The ageing and electrical properties of HPV materials are expected to be different from those of traditional, e.g. peroxide, vulcanizates. This is due to the fact that the vulcanization system introduces foreign polar groups into the material, which may act as initiation sites for degradation or increase the electrical conductivity of the rubber material, leading to disruptive discharges in the products that are in use.

- It would be of interest to investigate the effect of pressure on vulcanizates containing significant amount of recycled rubber, preferably powdered rubber. Due to the increased penetration ability of polymer, it is likely that the mechanical properties of these materials would differ from those of rubber materials treated only at normal curing pressures.

- A mild pressure treatment of thermoplastic elastomer (TPE) containing vulcanizable sites would probably create a loose network. Properties such as set and chemical resistance would be improved much, without losing the possibility to melt and reshape the material after use (cf. dynamic vulcanization).

- The great potential of high pressure vulcanization is that other polymers than polybutadiene, which has only been used as a model material in this work, could be used. Blends of polymers with suitable microstructure would probably facilitate the crosslinking of many other types of rubber materials, without the use of any vulcanization chemicals. The possibility of synthesizing new polymers with a microstructural architecture suitable for high pressure vulcanization must be the utmost aim, yielding rubber materials that have widely designable properties and can be crosslinked without any hazardous chemicals, only utilizing the inherent reactivity of the polymers.

6. ACKNOWLEDGEMENTS

First of all I would like to thank my supervisor Associate Professor Bengt Stenberg for accepting me as a graduate student, introducing me to this field of the polymer science, and his enthusiasm and guidance throughout this work.

I also wish to thank Professor Ann-Christine Albertsson, head of the Department, for her work keeping the Department of Polymer Technology a prominent scientific working place. I also thank Professor Emeritus Bengt Rånby for his pioneering work in Polymer Technology in Sweden, and Professor Ulf Gedde, Professor Anders Hult, Professor Jan-Fredrik Jansson, and Professor Sigbritt Karlsson for their work in creating a stimulating research atmosphere.

I wish to thank Dr. Sture Persson at Skega AB, for his enthusiasm and good advices in the field of rubber technology, always being ready for valuable discussions, even in the darkest world of carbon black.

Furthermore I wish to thank for financial support from NUTEK (the Swedish Board for Technical and Industsrial Development).

I thank Torgny Karlsson at the University of Stockholm for taking time to assist with the NMR measurements, and Sven Jacobson and my mother for the linguistic correction.

I would like to thank all graduate students and the personnel at the Department, all included, for making it a good place to work at.

Thanks to Associate Professors Torbjörn Reitberger and Björn Terselius for their good advices to my work, and for all their day and night discussions about everything from hydroxyl radicals to javelin-throwing. The Rubber Group, former and present members: thank

you for always being so flexible and creating super-duper evenings-after-scientific-meetings, in Åre, in the Archipelago of Stockholm, at the Department etc.

Special thanks to Karin *the Somersault* Jacobson, Gustav *Emergency Shower, Where-is-the-wasp?, The Soya Man and Chef of Horror Cooking, I-will-be-there* Ahlblad, Dan *Innocent Four-child-dad* Forsström, Tomas *High Water, Wine Master, Would-I-have-done-that?* Forsss, Pontus *G-M* Nordberg, Anna *Always Happy* Kron, Johan *Get a Secretary* Haasum, Ronnie *Cauliflower and Broccoli, Never-say-no* Palmgren, Thierry *Whiskey Chicken* Glauser, Kajsa *Sumo* Stridsberg, Henrik *Just Perfect* Ihre, Jonas *Boxer* Örtegren, Philippe *Jag-fattar-ingenting* Busson, Micke *Billy* Hedenkvist, Henrik *Microwave Master* Hillborg, Pontus *Almost Microwave Master* Alm, Patrik *Don´t -ever-get-tired-at-knäckebröd-and fil* Rosén, and Per-Anders *Happy Hudik* Högström.

Thanks to former and especially present members of ABB, I will come back for inspections, so keep the beer assortment good!

Almost Almost Finally I would like to thank all friends and relatives for their curiosity about my work, I will do my best to translate this thesis into understandability for you.

Almost Finally I would like to thank Pia for your patience during the preparation of this thesis. You are the joy in my life - without your love I would never have done this!

Finally I would like to thank my mother and father that they 28 years ago were not so familiar with rubbers as I am today.

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