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Crosslink Density Distributions in Natural Rubber/Nitrile Rubber Blends

by

Michael Victor Lewan

A Doctoral Thesis

Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy

Institute of Polymer Technology and Materials Engineering of the Loughborough University of Technology

April 1995

© by Michael Victor Lewan 1995
This thesis is dedicated to Chris J. Lewan
Abstract

Crosslink Density Distributions in Natural Rubber/Nitrile Rubber Blends

An NMR technique has recently been developed to determine the crosslink density in each phase of a polymer blend. This work uses the NMR method to study natural rubber (NR)/acrylonitrile butadiene rubber (NBR) blends, in order that the cure system used to vulcanize such blends can be optimized.

A standard injection moulding cure system for NR/Perbunan N1807 (18% acrylonitrile content) gave much more crosslinking in the NBR phase. To reduce this imbalance a less polar analogue of the accelerator was used, resulting in a more even distribution of crosslinks but still with a bias towards the NBR.

When a higher acrylonitrile rubber, Breon N41 (41% acrylonitrile), was used, its greater polarity increased the bias towards NBR crosslinking in blends cured with the original accelerator. However, with the less polar accelerator the maldistribution was reversed, with the bias now in favour of the NR phase.

For both of the NR/NBR blends the less polar accelerator gave a better balance of crosslinks between the phases, and consequently the tensile properties of the blends improved.

Chemical probe treatments were used to investigate the nature of the crosslinks in both phases of the blends. For the NR/Perbunan blends the less polar accelerator resulted in crosslinks containing longer sulphur chains, and this more polysulphidic nature together with the more even distribution of crosslinks, gave better tensile properties. For the NR/Breon blends the accelerator with lower polarity produced a network comprising mainly short sulphur crosslinks. This less polysulphidic network would be expected to have given lower strength properties, but for the concomitant change in crosslink distribution. Because the crosslink density in the NR phase was raised to a reasonable level, and the crosslink density in the NBR phase reduced, the properties of NR dominate in 50/50 blends and a higher tensile strength results.
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Chapter 1

Introduction and background

1.1 Introduction

The reason for combining natural rubber (NR) and acrylonitrile butadiene rubber (NBR) is to produce a blend which has the best properties of each constituent. Unfortunately the produced blends have not had the desired properties, and one of the major reasons put forward for this is the poor interfacial adhesion between the phases due to their large differences in solubility parameters. This was investigated using differential swelling measurements, and the result was that poor interfacial adhesion did exist. However this technique made the assumption that the presence of one of the rubbers did not affect the degree of crosslinking attained by the other rubber, which is erroneous. A method to assess the degree of crosslinking in a vulcanizate is the measurement of the peak width (H%) of an olefinic signal obtained from a continuous wave $^1$H NMR spectrum of a vulcanizate swollen to equilibrium. This technique can also be employed to obtain estimates of the crosslinking in individual phases of a blend. The advantage of this method is that H% is only slightly dependent on the degree of swelling to less than equilibrium and so the major factor in the determination of H% is the crosslink density of the rubber. Any minor effect on the swelling behaviour of the phases due to differences between the rubbers, such as polymer-solvent interaction parameters or degree of crosslinking, will not affect the estimates of the crosslink densities for the individual phases.

The combination of the swelling technique and the estimates of the degree of crosslinking in the phases of the blends showed that the interfacial adhesion in the blends of NR and low acrylonitrile NBR (Perbunan N1807 - 18% acrylonitrile content) was not lacking. But Tinker also showed that blends containing a minor proportion of NR and vulcanized with S/TMTM
may show cohesive failure of the NR phase when the NBR phase is highly swollen, due to the low degree of crosslinking in the NR.

The original work carried out by Tinker used tetramethylthiuram monosulphide (TMTM) as the accelerator in the vulcanizate, while for this thesis the very similar disulphide (TMTD) was used, as well as N,N'-dioctadecyl N,N'-diisopropylthiuram disulphide (ODIP). The main difference between these two accelerators is the two octadecyl groups, which are long aliphatic chains, on the ODIP. The reason for using the latter accelerator is that it is hoped that the longer chains will make it more soluble in the NR phase, and thus may result in a redistribution of the crosslink density. A range of polymer ratios between NR and NBR is investigated to see how the distribution of crosslinks changes. A higher acrylonitrile NBR (Breon N41 - 41% acrylonitrile content) is also investigated to see how replacing the Perbunan in the blends with a more polar rubber affects the distribution of the crosslinks.

The initial work was carried out on a Perkin-Elmer R32 (90MHz) continuous wave NMR spectrometer, but due to the acquisition of a new General Electric QE300 (300MHz) machine, the analysis was transferred.

By incorporating the data obtained from chemical probe treatments in which specific sulphidic crosslinks are cleaved in order to determine their sulphidic ratios, the efficiency of the vulcanization can be studied by determining how the combination of two polymers affects their individual poly-: di-: monosulphide crosslink ratios. This leads towards the optimization of the properties of natural rubber blends by control of the type of crosslinking in the components of the blend.

Differential scanning calorimetry is employed as another physical measurement of the blends which is not dependent on phase morphology. While there are other factors which can influence the $T_g$ of a vulcanizate, it is thought that the crosslink density will also be a contributing factor in a series of similar blends.

The phase morphology is also investigated to determine the changes that occur when the polymer ratio of the compounds in the blends is altered. From the phase size, curative and
filler distribution and the information obtained from the NMR work, explanations for the properties of the blends can be obtained.

1.2 Literature Review

1.2.1 Natural Rubber

Raw natural rubber is either prepared by the smoked sheet or the hevea crumb process from field latex. The rubber consists mainly of linear cis-1,4-polyisoprene with a number average molecular weight of about $10^5-10^6$. It has low mechanical strength and exhibits plastic flow but when vulcanized it takes on the properties of high elasticity and high strength which make it a good 'general purpose' material. Elemental sulphur, organic accelerator (usually a sulphenamide) and activators such as zinc oxide and a long chain fatty acid are mixed with the masticated rubber. It is moulded under pressure into a stable, elastic and resilient material. In this vulcanization reaction, the polyisoprene molecules are crosslinked into a three dimensional, covalent bonded network.

![Diagram of crosslink types in a rubber network](image)

Figure 1.1. Types of crosslink in a rubber network.
The sulphide linkages are randomly formed between isoprene units of nearby rubber chains at a few points along each molecule. These sites occur at carbon atoms α-methyllic or α-methylenic to the double bonds. The three types of sulphidic crosslink are mono- \((RS_1R, R = \text{rubber hydrocarbon})\), di- \((RS_2R)\) and poly- sulphides \((RSS_xSR\) where \(x \geq 1\)). The sulphur can also be involved in other bonds such as intramolecular mono- and disulphidic cyclic sulphides and in pendant groups of the \(RS_xX\) type where \(X\) is an accelerator and \(y \geq 1\). Also present are conjugated dienes and trienes in the main-chain. The non-network materials include unreacted vulcanizing ingredients and vulcanization products.

The vulcanization procedure changes the rubber from a collection of flexible linear chain molecules that do not interact very strongly with their neighbours to a pseudo lattice structure due to crosslink being inserted into the network.

![Figure 1.2. Rubber structure before vulcanization (a) and after vulcanization (b).](image)

- random coiled conformation due to thermal mobility
- crosslinked rubber
- ○ - crosslinks
- ∼ - network chain
- ♂♂ - chain ends

Figure 1.2. Rubber structure before vulcanization (a) and after vulcanization (b).
In a network formed from a rubber of infinite molecular weight the chain ends are ignored. In this case the number of crosslinks per unit volume is related to the number of network chains per unit volume by the functionality of the crosslink. Thus if the crosslink binds together four network chains, e.g. functionality 4, there are twice as many network chains as crosslinks for the whole network.

![Figure 1.3. Rubber crosslinks of functionality four.](image)

For crosslinks of functionality six there will be three network chains per crosslink.

![Figure 1.4. Rubber crosslinks of functionality six.](image)

Thus in the absence of knowledge of crosslink functionality the density of the network chains cannot be related to the density of the crosslinks.

Chain entanglements also result in a lack of correspondence between the density of crosslinks and the density of network chains when they are estimated by physical methods. A dual loop
such as shown in Figure 1.5a becomes a permanent structure when crosslinks are added (Figure 1.5b).

![Diagram](image)

Figure 1.5. Dual loop without crosslinks (a) and with crosslinks (b).

Taking $M_c$ as the number average molecular weight of a network chain between two adjacent crosslinks and $N$ as the Avogadro number, then there are $2M_cN^{-1}$ grams of rubber containing one crosslink, or one gram of rubber contains $N/2M_c$ crosslinks, which can also be stated as $1/2M_c$ gm molecules of crosslinks.

1.2.2 Accelerated Sulphur Vulcanization

Accelerated sulphur vulcanization was discovered by Goodyear and Hancock in the 19th Century and is still the most widely used crosslinking method. A vulcanizing system comprises of a mixture of additives required to vulcanize an elastomer. The three main classes of chemicals used for curing in this vulcanizing system are vulcanizing agents, accelerators and activators.
(i) Vulcanizing Agents

These are chemicals which can initiate the chemical crosslinking of the rubber molecules leading to the formation of a three-dimensional network. The most common is sulphur.

(ii) Accelerators

These are substances which can increase the rate of sulphur combination with rubber. They are capable of promoting more efficient use of sulphur for crosslinking, thereby improving the properties of the vulcanizates. They are also used to shorten the period of vulcanization and are themselves stimulated by activators. Most of the accelerators used are organo-nitrogen or organo-sulphur compounds like amines, guanidines, thioureas, thiazoles, sulphenamides, thiram, dithiocarbamates and xanthates. They are normally used in combination with metal oxides and stearic, oleic, lauric, palmitic or myristic acids.

(iii) Activators

These are used to increase the vulcanization rate. They activate the accelerators which become more efficient. There are two groups of activators:

(a) inorganic compounds consisting mainly of metal oxides such as zinc oxide, calcium oxide, lead oxide, magnesium oxide and alkali carbonates,

(b) organic carboxylic acids.

Apart from the above compounding ingredients, a mix may contain others, e.g. fillers, reinforcing agents, antidegradants, retarders and softeners.

Sulphur vulcanization systems can be divided into three different types based on the ratio of accelerator concentration (A) to sulphur concentration (S).
(i) **Conventional Vulcanizing Systems (C.V.)**

The A/S ratio is low, with a range from 0.2 to 0.7. The crosslinks are mainly poly- and disulphidic with a small number of monosulphidic crosslinks at optimum cure.

**Typical C.V. system:**

\[ S = 2.5, \text{CBS} = 0.6, \text{ZnO} = 5.0, \text{Fatty acid} = 0.7 \text{ (all parts per hundred rubber, p.p.h.r.)} \]

- **S** = sulphur
- **CBS** = N-cyclohexylbenzothiazole-2-sulphenamide
- **ZnO** = zinc oxide

(ii) **Efficient Vulcanizing Systems (E.V.)**

The A/S ratio is high, with a range from 4 to 15. At optimum cure, the crosslinks are mainly monosulphidic with di- and polysulphidic types.

**Typical E.V. system:**

\[ S = 0.4, \text{CBS} = 6.0, \text{ZnO} = 5.0, \text{Fatty acid} = 1.0 \text{ (all p.p.h.r.)} \]

(iii) **Semi-efficient Vulcanizing Systems (S.E.V.)**

The A/S ratio is between 0.6 and 2.5. Vulcanizates in these systems have network structures and thermal stability intermediate between those of CV and EV systems.

**Typical S.E.V. system:**

\[ S = 1.8, \text{CBS} = 1.0, \text{ZnO} = 5.0, \text{Fatty acid} = 1.4 \text{ (all p.p.h.r.)} \]
1.2.3 Mechanism of Accelerated Sulphur Vulcanization

Accelerator, Fatty acid, Zinc Oxide

Accelerator Complex

S₈

Active Sulphurating Agent

RH (rubber hydrocarbon, H = allylic hydrogen in a methyl or methylene position)

Rubber Bound Intermediate (R-Sₓ-X)

Initial Polysulphidic Crosslinks (R-Sₓ-R)

Lability and Interchange

Crosslink Shortening

Thermal Elimination

Poly-sulphides

Di-sulphides

Mono-sulphides

Conjugated Alkenes

Cyclic sulphides

Figure 1.6. The reaction route of accelerated sulphur vulcanization of rubber.
(A) A species which reacts with RH to form C-S bonds.

(B) Immediate precursor to crosslinks which the rubber bound intermediate forms either by disproportionation reaction between two intermediates or by reaction of intermediate compound with rubber hydrocarbon.

\[ X = \text{accelerator or S donor fragment, } y \geq 2. \]

(C) Thermally unstable and chemically reactive and subject to a number of competing reactions, the relative rates of which depend on the detailed structure of the crosslink termini, the concentration of various accelerator derivatives and zinc compounds, and the temperature of vulcanization.

Most reactions proceed at broadly comparable rates in the normal temperature range of vulcanization of dry rubber (140° - 180°C) thus none of the steps are completed before the succeeding steps are well underway.

At the beginning the zinc oxide, fatty acid and accelerator form a zinc/accelerator complex whose solubility is increased by the chelating of an amine or carboxylate ligand to the zinc atom. Taking the 2-morpholinylbenzothiazole sulphenamide as an example, the morpholinyl complex of zinc mercaptide of 2-mercaptobenzothiazole (MBT) is formed.

![Figure 1.7. The morpholinyl complex of zinc mercaptide of 2-mercaptobenzothiazole.](image)

Figure 1.7. The morpholinyl complex of zinc mercaptide of 2-mercaptobenzothiazole.
The complex reacts with the eight atom rings of elemental sulphur to form an active sulphurating agent for the rubber hydrocarbon. The $S_8$ ring is thought to attack the sulphur atom of the accelerator complex nucleophilically and thus produce sulphur chains of varying length.

\[
\text{Figure 1.8. Production of the sulphur chain.}
\]

The active sulphurating agent then attacks the rubber hydrocarbon to form polysulphidic pendant groups - $RS,SX$, which are thought to be the precursors of crosslinks. This rubber bound intermediate is formed by the nucleophilic attack on the $\alpha$-carbon atom by the terminal persulphenyl anions in the sulphurating complex. This is followed by the simultaneous displacement of the hydride ion towards the penultimate persulphenyl cations and the formation of zinc sulphide.

\[
\text{Figure 1.9. Formation of the precursors of crosslinks.}
\]
Depending on the steric accessibility of the α-carbon atom, the polarizability of the rubber hydrocarbon bonds and the electronic distribution of the sulphurating complex, the substitution takes place either at α-methylic or α-methylenic carbon atoms. Thus if the terminal persulphenyl anion has high nucleophilicity, the substitution occurs at the least sterically hindered α-methylic carbon atom. Alternatively, if the penultimate persulphenyl cations are highly electrophilic, the substitution should occur at the more polarizable α-methylenic positions.

![Diagram of structures](image)

**Figure 1.10.** Structures observed from the sulphuration of 2-methylpent-2-ene in the presence of CBS (N-cyclohexylbenzothiazole-2-sulphenamide).

The initial formation of crosslinks is thought to have resulted either from the disproportionation between pendant accelerator intermediates on nearby chains or by the direct reaction of the intermediate with the rubber hydrocarbon. Porter stated that the initial polysulphidic crosslinks underwent one of three alternatives:

1. **Desulphuration**, resulting in progressive shortening of the crosslinks to eventually form unreactive monosulphidic crosslinks, or

2. the thermal elimination with the formation of cyclic mono- and disulphides, conjugated diene and triene, and zinc sulphide, or

3. interchange reaction between polysulphidic crosslinks at their points of attachment to the sulphur chains. However this can lead to stress relaxation and permanent set in the deformed vulcanizate.
These competing reaction paths of the polysulphidic crosslinks affect the strength properties of the accelerated sulphur vulcanizates of natural rubber. Its relative weakness in bond strength allows an interchange mechanism in which a localised stress build-up is relieved during deformation and hence ensures that the high strength of an accelerated sulphur vulcanizate is reached.

As can be seen, accelerated sulphur vulcanizates have a wide variety of network structures which can be obtained by varying factors such as the sulphur : accelerator ratio, type of accelerator and the vulcanization conditions.

1.2.4 Crosslink Density

Three things contribute to the degree of physically effective crosslinks in the rubber vulcanizate:

(i) the degree of chemical crosslinking

(ii) the degree of physical entanglements

(iii) the negative contributions from the free chain ends and the intramolecular cyclic links.

The degree of physically effective crosslinks can be obtained from stress-strain measurements. From the statistical theory of rubber-like elasticity, which is based on network models of the vulcanized state and which gives quantitative expressions to elastic swelling and related properties, it is shown that the force per unit area, $F$, required to maintain a perfect elastic network at a small extension ratio, $\lambda$ (extended length / initial length), is given by,

$$F = \rho RT M_{cphy}^{-1}(\lambda - \lambda^{-2})$$

(M$_{cphy}$ = number average molecular weight of the rubber chains between two physically effective crosslinks)
\[ \rho = \text{density of the vulcanizate} \]
\[ R = \text{gas constant} \]
\[ T = \text{absolute temperature} \]

Gumbrell, Mullins and Rivlin\textsuperscript{17} and Gee\textsuperscript{18} found that there were departures from this theory if dry or lightly swollen rubbers were stretched instead of highly swollen ones. These departures can be described in terms of a single parameter \( C_2 \) which had a large magnitude in dry rubber but decreased to zero at high degrees of swelling. In fact the decrease occurred linearly with decrease in volume fraction of rubber in the swollen gel. The value of \( C_2 \) was also found to be independent of the nature of the rubber polymer, of the degree of vulcanization and of the nature of the swelling liquid. The explanation of the divergencies described by the term \( C_2 \) is not clearly known, but a reasonable assumption is that it relates to the restriction in the number of possible configurations of the molecular chains. This restriction would be less in the swollen state than in the dry state, and in highly swollen rubber, deviations from ideal behaviour due to this cause will be small.

It has been shown that the stress-strain data for the dry natural rubber networks can fit the Mooney-Rivlin expression\textsuperscript{19-23} over a range of up to \( \lambda = 2 \).

\[ F = 2(C_1 + C_2\lambda^{-1})(\lambda - \lambda^2) \quad (2) \]

\( C_1, C_2 \) = elastic constants.

For natural rubber vulcanizates it has been shown that \( C_1 \) is independent of the degree of swelling (as seen by \( C_1 \) values agreeing very well with those obtained from stress-strain data on networks highly swollen with a liquid). By comparing equations (1) and (2) it can be shown that

\[ C_1 = \rho RT(2M_{c,phy})^{-1} \quad (3) \]

When the crosslink functionality is four the \((2M_{c,phy})^{-1}\) is equal to the physically effective
crosslink density and can easily be derived from measurement of force in simple extension$^{24,25}$. It has been shown$^{26}$ that for nitrile rubbers the $C_1$ values measured from stress-strain in tension on dry samples are unreliable when dealing with low crosslink densities.

Stress-strain measurements are made at temperatures close to $25^\circ C$ ($\pm 5^\circ C$) to avoid correction for thermal expansion, and $C_1$ terms corrected to $25^\circ C$ by the calculation:

$$C_{1,RV} = C_1(\text{measured at } T^\circ C) \times \frac{298}{(273 + T)}$$

$C_{1,RV} = C_1$ of rubber vulcanizates.

The correction for the stiffening effect of non-reinforcing particle fillers is made by using the Guth and Gold relationship$^{27}$.

An alternative technique to determine the value of $\langle M_r \rangle$ is the equilibrium swelling of a rubber network in a non-volatile solvent. Flory and Rehner$^{28,29}$ gave a statistical mechanical treatment of swelling when they combined an expression for the free energy of mixing with the elastic free energy of the swollen rubber, as obtained by the stored energy function of the statistical elastic theory:

$$-\ln(1 - v_r) - v_r - \chi v_r^2 = V_o M_c^{-1} \rho v_r^{1/3}$$  \hspace{1cm} (4)

$V_o$ = molar volume of the swelling liquid

$\rho$ = density of the rubber

$\chi$ = rubber-liquid interaction constant (found by using $\langle M_r \rangle$ values obtained by independent methods e.g. stress-strain measurements and corresponding values of $v_r$, osmotic pressure measurements, etc.)

$v_r$ = volume fraction of the rubber network in the swollen gel
This equation is now expressed as:

\[ u = \frac{-[\ln(1-v_r) + v_r + \chi v_r^{1/2}]}{2V_0(v_r^{1/3})} \]  

(5)

where \( u = \) physical crosslink density

It was shown\(^{15,30,31}\) that for NR vulcanized with tertiary peroxides a consistent value of \( \chi \) is obtained for a wide range of \(<M,>\) values.

When using the swelling method, problems were found with \( \chi \). Moore and Trego\(^2 \) and Bobear\(^3 \) found that when using sodium di-n-butyl phosphite as a chemical probe reagent that \( \chi \) increased after its use and thus the use of the \( \chi \) value of the untreated network to estimate the number of crosslinks broken by the phosphite led to an appreciable error in the estimate for the networks examined. Other work has also shown that \( \chi \) depends on the degree of swelling\(^31 \) and degree of crosslinking\(^34 \). The latter authors also stated that when using a good solvent, e.g. chloroform for natural rubber and nitrile-butadiene rubber, that the dependence is very small with the overall effect being about a 5\% error in the crosslink density values. With a solvent that is not as good then unless \( \chi \) is known accurately or it is determined separately by an independent method, e.g. stress-strain measurements, then errors in the value of the physically effective crosslink density values are seen.

Bristow and Watson\(^11,35 \) carried out swelling measurements on vulcanized natural rubber and some synthetic rubbers in a wide range of solvents and derived values for \( \chi \). For NR and two NBRs (18\% and 41\% acrylonitrile content) they were 0.383, 0.251 and 0.241 respectively.

In the equilibrium swelling procedure to determine the volume fraction of rubber in the swollen gel, corrections should be made for the zinc oxide content in the vulcanizate. Ellis and Welding\(^36 \) found that because vulcanizates contain constituents additional to the main polymer, they could add about 10\% error to \( v_r \) estimates. To eliminate most of this error
only an approximate estimate of the allowance to be made was necessary, and for this they derived the equation:

\[
\nu_t = \frac{(D-FT)p^1}{(D-FT)p^1 + A_0 \rho_s^{-1}}
\]

\(D\) = dry weight of sample after swelling (to make allowances for material extracted during swelling)

\(F\) = weight fraction of insoluble component of the vulcanizate (weight of insoluble products/batch weight)

\(T\) = weight of sample before swelling

\((FT)\) = estimated weight of the insolubles

\(\rho\) = density of main polymer

\(\rho_s\) = density of liquid

\(A_0\) = weight of absorbed liquid corrected for swelling increment (which is the continuing degree of swelling with the length of immersion after the diffusion equilibrium is reached)

1.2.5 Chemical Crosslink Density

Mullins\(^{37}\) carried out comparisons between physical and chemical determinations of degree of crosslinking. He used the work of Moore and Watson\(^{38}\) who had analysed \(C_1\) data obtained on a large number of natural rubber networks of known chemical crosslinking concentrations, and found that the physical degree of crosslinking always exceeded the chemical degree of crosslinking, especially at low crosslink densities\(^{39}\), as shown in Figure 1.12.
Figure 1.12. Plot of physical crosslink density against chemical crosslink density. The explanation proposed for this difference was that the network was subjected to restraints other than those resulting from crosslinks. One suggestion was that chain entanglements would impose conformational constraints and behave elastically as if they were crosslinks. By taking into account the effect of chain entanglements and also the chain ends on the elastic constant $C_1$, Mullins proposed a semi-empirical relation for the NR network.

$$C_1 = [\mu RT(2\langle M_{c,chem} \rangle)^{-1} + 0.78 \times 10^5][1 - 2.3 \langle M_{c,chem} \rangle M_n^{-1}]$$  \hspace{1cm} (7)

$M_{c,chem}$ = number average molecular weight of the rubber chain between two chemical crosslinks

$0.78 \times 10^5$ = a correction term which includes the maximum contribution of entanglements
\[ M_n = \text{number average molecular weight of the rubber before vulcanization} \]

The equation gives the density of chemical crosslinks \((2M_{\text{chem}})^{-1}\) when \(M_n\) and \(C_1\) values are known and three criteria are met:

(i) the crosslink functionality is four

(ii) main-chain scission during vulcanization is negligible

(iii) the initial rubber chains are substantially unbranched.

When using the original raw vulcanizates the \(C_1\) value is called \(C_{1,\text{RV}}\) and by using the methods of Bristow and Porter\(^4\) these values can be converted into \(C_{1,\text{ERM}}\) (rubber network free from extraneous material but supercoiled relative to its state when prepared), and then into \(C_{1,\text{RH}}\) (the \(C_1\) of the rubber hydrocarbon component of the network). From these the equation for NR is altered to\(^15,37,38,42\):

\[ C_{1,\text{RH}} = \left\{ \rho RT(2M_{\text{chem}}^{\text{RH}})^{-1} + 0.78 \times 10^4 \right\} (1 - 2.3M_{\text{chem}}^{\text{RH}} M_n^{-1}) \quad (8) \]

\[ M_{\text{chem}}^{\text{RH}} = \text{number average molecular weight of the rubber hydrocarbon (RH) chain segments between chemical crosslinks.} \]

Using this, and specific cleavage of crosslinks, gives unambiguous information on the chemical crosslink structure.

### 1.2.6 Chemical Probes

A chemical probe reagent is defined\(^5\) as a reagent that reacts in a useful analytical way with a specific feature in the crosslinking network. It must also be introduced into the network homogeneously and when the reaction has been completed it must be easily removed. Therefore the reagent must be soluble in an inert organic solvent in order that a solution can
be made which can be swollen into the network. Ideally when the solvent is removed the reagent is still soluble and able to work in the dry network. A reagent that blooms to the surface of the network after it has been introduced in the solvent is not recommended. A probe should also not result in any change in the rubber network except for that which it was intended to change.

1. Sodium Sulphite

Dogadkin and Tarasova\textsuperscript{43} removed labile sulphur from organic polysulphides by treating finely divided vulcanizates with sodium sulphite, which converts the latter into thiosulphate, and also polysulphides into disulphides. The broken linkages may be polysulphidic, however, only a qualitative and not a quantitative value was obtained.

2. Zinc Sulphide

The same authors\textsuperscript{43} determined the amount of zinc sulphide in specimens of vulcanizates extracted with acetone, as an indirect method to determine the presence of disulphide bridges. This was based on earlier work which showed that the zinc sulphide content of a vulcanizate was equivalent to the content of disulphide bonds of the $R_1$-S-S-$R_2$ type\textsuperscript{44}.

3. Methyl Iodide

This reagent is easily swollen into the rubber network by warming under vacuum. It was introduced to estimate monosulphidic crosslinks in natural rubber\textsuperscript{45}.

Brown and Hauser\textsuperscript{46} found that methyl iodide formed addition compounds containing one or more iodine atoms with compounds like ethylene sulphide and organic disulphides, and that such types of sulphur combination could exist in vulcanized rubber, thus the methyl iodide test was proved unreliable for the study of sulphur linkages produced in vulcanization.

Selker and Kemp\textsuperscript{42,47} realising further research was needed, carried out reactions under purified nitrogen to eliminate decomposition of methyl iodide due to oxygen.
4. **Radioactive Sulphur**

Radioactive sulphur can be used in the analysis of networks for combined sulphur by relating the radioactive count for the extracted networks of radioactive sulphur enriched vulcanizates to the total combined sulphur. A major problem encountered with the radioactive sulphur technique is that there is not always a clear cut division between the di- and polysulphide linkages.

5. **Lithium Aluminium Hydride**

Lithium aluminium hydride is a powerful reducing agent and it was found that it reduces organic disulphides quickly and easily to give high yields of the mercaptan.

6. **Phenyllithium**

Phenyllithium and lithium aluminium hydride were used as chemical probes in sulphur vulcanizates of polybutadiene. The reactions of phenyllithium were similar to lithium aluminium hydride as it did not react with monosulphides but did cleave di- and polysulphidic links.

From models, and by relating their results to the rubber elasticity theory, Gregg and Katrenick obtained the actual network structures, and in doing so validated the method of counting elastically effective sulphur crosslinks in cis-1,4-polybutadiene vulcanizates by the theory of rubber elasticity through the Flory-Rehner equation and the Moore-Watson calibration curve.

7. **Triphenylphosphine**

Triphenylphosphine can be used to determine the amount of polysulphidic sulphur combined in a rubber network. Moore and Trego based this on previous research they had done which showed that triphenylphosphine desulphurates dialkenylpolysulphide and, in most cases,
alkyl-alkenyl polysulphides to monosulphides.

8. Trialkylphosphites

Closely related to triphenylphosphine chemically, are the esters of tervalent phosphorous acid i.e. the triaryl and trialkyl phosphites. These also react with polysulphides and desulphurate them to disulphides. Unlike triphenylphosphine, which has no action on simple disulphides, trialkylphosphites cleave simple disulphides. The trialkylphosphites have very good properties as network probes, and as their chemistry is known they can be used very effectively for removing polysulphidic sulphur. For both the triphenylphosphine and the trialkylphosphites the big disadvantage is the fact that they take so long to complete their reactions (e.g. 96 hours at 80°C).

9. Thiol-Amines

Thiol-amines are extremely useful reagents which can give quantitative estimations of the proportions of poly- and disulphidic crosslinks in a network. Campbell and Saville showed that a solution of propane-2-thiol (0.4M) and piperidine (0.4M) in n-heptane was able to cleave model di- and polysulphides very quickly at room temperature. Basically the reactions are sulphur-sulphur bond interchange reactions with a nucleophilic substitution by an alkane thiolate ion:

\[
R-S-H + R'-S-S-x-S-R' \longrightarrow R-S-S-R' + R'-S-S_x-S-H
\]

\[
R-S-H + R'-S-S-R' \longrightarrow R-S-S-R' + R'-S-H
\]

No reaction with monosulphides

**Figure 1.13.** The cleaving of sulphidic crosslinks using propane-2-thiol/piperidine probe reagent.

The reagent reacts at least one thousand times more slowly with disulphide than with
polysulphides under the same conditions, and in the time taken to change all the trisulphide they are basically unaffected. Use is made of this to cleave quantitatively the polysulphides. Butane-1-thiol (or hexane-1-thiol) and piperidine will, within a few hours at room temperature, cleave quantitatively di- and polysulphides. Assuming that carbon-carbon crosslinks are not present, then by knowing the number of original chemical crosslinks, as well as the fraction of those crosslinks cleaved by each reagent, the network can be established in terms of the number of poly-, di- and monosulphidic crosslinks.

A standardized procedure for the combined cleavage of di- and polysulphide crosslinks in vulcanizate samples was described by Campbell56.

To determine the crosslink concentration the samples underwent stress-strain measurements57 within 5 days of treatment. Oxidation of the rubber-bound thiol groups by atmospheric oxygen to reform disulphides was avoided by storing them in vacuo until immediately before measurements.

10. Sodium di-n-butylphosphite

Sodium di-n-butylphosphite (0.4M) in benzene has been used in a chemical probe32,59. It reacts with di- and polysulphides but not with carbon-carbon bonds or monosulphidic crosslinks. Therefore determination of the proportions of the original number of crosslinks which are cleaved by the separate treatment of a sulphur vulcanizate of natural rubber with; (i) sodium di-n-butylphosphite, and (ii) propane-2-thiol and piperidine, will yield estimates of the number of mono-, di-, and polysulphidic crosslinks in the network.

1.2.7 Effect of Crosslink Types on Strength

Bueche59 suggested a theory in which one of the basic postulates is that in order for a sample to break, conditions must be such that when one chain breaks the extra load thrown onto its near neighbours causes one of them to break. The effect of crystallites and filler particles is to decrease the additional load forced onto each of its neighbours when a segment breaks.
This makes possible the effective use of higher degrees of crosslinking.

Mullins\textsuperscript{60} and Cooper\textsuperscript{61} state that the differences in tensile strengths are due to differences in the chemical nature of crosslinks, a view which is based on the assumed difference in the mechanical strength of crosslinks being as shown in Figure 1.14, which is itself based on the thermal strength of these bonds from stress-relaxation studies.

\begin{align*}
C-C & > C-S-C > C-S_2-C > C-S_x-C
\end{align*}

\textbf{Figure 1.14. Mechanical strength of crosslinks.}

The crosslinks of lower strength result in stronger rubbers because breakage of the mechanically weak crosslinks relieves localized high stress concentrations giving a more uniform distribution of stress. The mechanically strong crosslinks do not give this stress relief and so in vulcanizates containing strong crosslinks the chains are subjected to extreme high stress which makes them more likely to break. This in turn puts extra stress on neighbouring chains and eventually leads to catastrophic rupture.

Bristow and Tiller\textsuperscript{62} found that a series of vulcanizing systems all followed the trend of tensile strength increasing and then decreasing as crosslink density increased. Natural rubber has a particularly high tensile strength due to its ability to crystallize on extension\textsuperscript{14,63-65}. Thus it was argued that any hindrance in this ability would decrease the tensile strength. This was found to be untrue for vulcanizates that had mainly polysulphidic crosslinks as they had an ability to confer high tensile strength\textsuperscript{66-69}. Proof of this was shown\textsuperscript{62} when the vulcanizates were treated with triphenylphosphine, which desulphurates all crosslinks to monosulphidic units. The decrease in tensile strength was quite marked and hence disagreed with observations made by Lal\textsuperscript{70}, and Lal and Scott\textsuperscript{71}, who argued that polysulphides were not essential for high tensile strength. Bristow and Tiller explained their results as being due to crosslink exchange under stress. The sulphur-sulphur bonds are mechanically weak compared to carbon-sulphur and carbon-carbon bonds and thus at high elongations and stored energies (easily attained in natural rubber vulcanizates due to the strain-induced crystallization) these bonds are able to rupture and reform in preferred configurations. A built in stress relaxation
bonds are able to rupture and reform in preferred configurations. A built in stress relaxation mechanism is provided which results in greater energy being required to reach final rupture. The difference seen with Lal and Scott’s work may be due to differences in curing recipes or in the probe treatment.

In stretched vulcanizates of butadiene copolymers, crystallization has not been detected by either x-ray or density methods\(^2\).

### 1.2.8 Blends

In this project the three rubbers to be used are a natural rubber (NR) and two synthetic rubbers (NBR).

The NR used is SMR L which is Standard Malaysian Rubber Light, the light referring to its colour. It is a rubber that has been purified but still contains 5 - 6% of non-rubbers. The chemical name is cis-1,4-polyisoprene (Figure 1.15a). The NBR rubbers used are copolymers of acrylonitrile and butadiene (Figure 1.15b). Perbunan N1807 has an acrylonitrile content of 18%, while Breon N41 has an acrylonitrile content of 41%.

![Chemical structures](image)

**Figure 1.15. The structure of NR and NBR.**

NR is the preferred material where a rubber product with high resilience and low heat build-up is needed or where green strength, tack and easy processing are desirable
at high temperatures than most other general purpose rubbers, and a high resistance to fatigue
during repeated flexing. Thus NR is used for heavy duty applications such as aircraft and
giant tyres where maximum strength and minimum heat build-up are required. The major
weakness of NR is its lack of resistance to environmental damage such as atmospheric
oxygen and ozone which cause weathering cracks. Although NR has little resistance to oils
it can resist certain chemicals such as inorganic acids which make it ideal for lining tanks in
the chemical process industry.

NBR is an oil resisting rubber and it is the acrylonitrile component that makes it so; the
higher the portion then the greater is its resistance. NBR is produced by emulsion
polymerisation which entails the monomer being dispersed in water as an emulsion. The oil
resistance of nitrile rubbers makes them ideal for oil hoses, oil seals, etc. Resistance to wear
is also good.

The blending together of two polymers is often attempted in order to obtain a material which
has a combination of the best properties of the constituent polymers. This does not often
occur for a few reasons\textsuperscript{73-76}, one of which is that there is little or no interfacial adhesion
between the components of the blend when there is a large difference between the solubility
parameters of the polymers. NR and NBR are two such rubbers and therefore the degree of
mixing at the interface in the blend is limited. However NR can be blended with NBR to
introduce a degree of resistance to swelling by fats and oils, or to increase damping\textsuperscript{44}. Many
properties of a blend depend upon the nature of arrangement of the two phases\textsuperscript{77}. One phase
could be dispersed in the matrix of the other one, in which case the matrix phase will
dominate the properties. Adhesion between the phases can be very important in terms of
mechanical properties. Curative migration can also affect the properties of the blend\textsuperscript{78-81}.

Nuclear magnetic resonance (NMR) spectroscopy has developed into an extremely powerful
analytical technique since its introduction in the early 1950s\textsuperscript{82}. When analysing accelerated
sulphur vulcanized rubbers it is not possible to utilise the sulphur atoms themselves because
the sulphur that forms crosslinks represents a low concentration of sulphur within the
crosslinked network, and this coupled with the naturally low abundance of the relevant
sulphur isotope ($^{33}$S) in elemental sulphur makes measurement difficult. Thus analyses are
confined to identifying hydrogen or carbon atoms adjacent to a crosslink.

Loadman and Tinker\textsuperscript{83} found that the width of a peak in a Continuous Wave Proton NMR spectrum of a vulcanizate swollen to equilibrium was related to the degree of crosslinking. Hence the crosslinking in individual phases of a vulcanized blend could be estimated\textsuperscript{84-87}. One of the blends that they investigated consisted of the rubbers NR and NBR.

The width of signals in NMR spectra of polymers is dependent on the mobility of the chains; signals broaden as mobility decreases. Using conventional solution NMR instruments, swollen vulcanizates have spectra which are much broader than those for small molecules, although the basic signals due to differing chemical structures are still largely resolved even in \textsuperscript{1}H NMR spectra. In this thesis, peak width is measured by the ratio of signal strength at a reference position on the side of the chosen signal to the peak signal strength, expressed as a percentage - H\%. It has been found that H\% not only correlates well with physical crosslink density of the vulcanizates, but also varies sufficiently over the range of interest to provide good estimates of crosslink density\textsuperscript{88}.

1.3. Aims of Investigation

NR/Perbunan N1807 blends with standard injection moulding cure systems, based on the accelerator TMTD (tetramethyl thiuram disulphide), have a maldistribution of crosslinks which favour the NBR phase. This results in poor service life. The purpose of the work undertaken here, is to investigate the distribution of crosslinks in NR/NBR blends, in order to attempt to reduce this undesirable bias, and thereby, improve the properties of the blend.

It is quite likely that in NR/NBR blends the TMTD accelerator is preferentially located in the NBR phase, due to the polymer polarities. This would also apply to the vulcanization intermediates, resulting in the much higher crosslinking of the NBR phase compared to the NR phase. If the accelerator is changed to one of lower polarity, then hopefully it, or its vulcanization intermediates, will be more evenly distributed between the rubber phases, and hence reduce the biasing of the crosslinking towards the NBR phase. The accelerator to be
used is ODIP (N,N'-dioctadecyl N,N'-diisopropyl thiuram disulphide), which is a less polar thiuram disulphide than TMTD, due to its very long aliphatic side chains.

To confirm the theory of polarity effects being the major influences in determining the crosslink distribution in NR/NBR blends, a nitrile rubber of much higher polarity than Perbunan N1807 was investigated. If polarity does not have an influence, then the distribution of crosslinks will be similar to that for NR/Perbunan blends. The higher polarity NBR chosen was Breon N41, which at 41% acrylonitrile content is a very high nitrile rubber.

Using the newly developed NMR technique, the crosslink density of each rubber phase will be investigated. The crosslink distribution will then be related to the physical properties of the blends. With the use of chemical probe treatment in conjunction with the NMR analysis, the crosslinks will then be classified into their respective poly-, di- and mono-sulphidic ratios to ascertain the efficiency of the vulcanization process, and also to relate these to vulcanizate properties.
Chapter 2

Materials and Experimental Method

2.1 Introduction

Both natural rubber (NR) and acrylonitrile-butadiene rubber (NBR) were used in the investigations described in this thesis. Standard Malaysian Rubber (SMR L) was used because of its cleanliness and its more widespread use than any other light coloured NR. The two NBRs chosen were Perbunan N1807 (18% acrylonitrile content) and Breon N41C80 (41% acrylonitrile content) which are classified as low and high acrylonitrile-NBR rubbers respectively.

2.2 Materials

The materials used in this project and the suppliers are listed alphabetically in Table 2.1.

2.3 Formulations (Tables 2.2 - 2.5)

The formulations of three series of compounds with varying degrees of crosslinking are given in Tables 2.2a - c for NR, Perbunan N1807 and Breon N41C80 respectively. Two thiram disulphide accelerators were used (Figure 2.1). The tetramethylthiuram disulphide (TMTD)/sulphur cure system was selected on the basis of its suitability for NBR, while the N,N'-dioctadecyl N,N'-disopropylthiuram disulphide (ODIP) accelerator was chosen because the long aliphatic chains would hopefully make it soluble in NR and thus result in a redistribution of the crosslink densities.
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<th>Supplier</th>
</tr>
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<td>Acetone, Analar</td>
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<td>BDH</td>
</tr>
<tr>
<td>Breon N41</td>
<td>41% acrylonitrile-butadiene rubber</td>
<td>B.P.</td>
</tr>
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<td>d-chloroform, 99.8 atom% D</td>
<td></td>
<td>Aldrich</td>
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<tr>
<td>Chloroform, Analar</td>
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<td>BDH</td>
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<td>Aldrich</td>
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<td>BDH</td>
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<td>BDH</td>
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<td>Aldrich</td>
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<tr>
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Table 2.1   Materials.
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Table 2.2a. Natural rubber formulations.
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<table>
<thead>
<tr>
<th>Mix No.</th>
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<th>8940</th>
<th>9013</th>
<th>9014</th>
<th>9038</th>
<th>9039</th>
<th>9040</th>
<th>9203</th>
<th>9204</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphur</td>
<td>1.5</td>
<td>2.25</td>
<td>1.5</td>
<td>1.5</td>
<td>4.0</td>
<td>5.0</td>
<td>6.0</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>TMTD</td>
<td>0</td>
<td>0</td>
<td>0.6</td>
<td>0</td>
<td>1.6</td>
<td>2.0</td>
<td>2.4</td>
<td>0.6</td>
<td>0</td>
</tr>
<tr>
<td>ODIP</td>
<td>1.93</td>
<td>2.9</td>
<td>0</td>
<td>1.93</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.93</td>
</tr>
<tr>
<td>Weight, g</td>
<td>112</td>
<td>114</td>
<td>111</td>
<td>112</td>
<td>114</td>
<td>116</td>
<td>117</td>
<td>111</td>
<td>112</td>
</tr>
<tr>
<td>Cure time, min</td>
<td>25.0</td>
<td>30.0</td>
<td>16.0</td>
<td>8.0</td>
<td>11.0</td>
<td>11.0</td>
<td>10.9</td>
<td>14.4</td>
<td>28.7</td>
</tr>
<tr>
<td>% Methanol extraction</td>
<td>6.4</td>
<td>7.0</td>
<td>5.5</td>
<td>6.5</td>
<td>6.4</td>
<td>6.3</td>
<td>6.5</td>
<td>5.1</td>
<td>5.5</td>
</tr>
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</table>

Table 2.2b. Perbunan N1807 formulations.
<table>
<thead>
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<th>Mix No.</th>
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<th>89011</th>
<th>89012</th>
<th>89033</th>
<th>89034</th>
<th>89035</th>
<th>89036</th>
<th>89037</th>
<th>89041</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphur</td>
<td>1.5</td>
<td>1.5</td>
<td>0.75</td>
<td>0.5</td>
<td>1.0</td>
<td>1.5</td>
<td>2.25</td>
<td>3.38</td>
<td>0.5</td>
</tr>
<tr>
<td>TMTD</td>
<td>0</td>
<td>0.6</td>
<td>0</td>
<td>0.2</td>
<td>0.4</td>
<td>0.6</td>
<td>0.9</td>
<td>1.35</td>
<td>0</td>
</tr>
<tr>
<td>ODIP</td>
<td>1.93</td>
<td>0</td>
<td>0.97</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.64</td>
</tr>
<tr>
<td>Weight, g</td>
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<td>110</td>
<td>111</td>
<td>112</td>
<td>113</td>
<td>110</td>
</tr>
<tr>
<td>Cure time, min</td>
<td>32</td>
<td>16</td>
<td>30</td>
<td>35</td>
<td>25</td>
<td>17.5</td>
<td>30</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>% Methanol extraction</td>
<td>7.0</td>
<td>3.2</td>
<td>9.4</td>
<td>6.2</td>
<td>6.1</td>
<td>6.1</td>
<td>5.9</td>
<td>5.6</td>
<td>6.8</td>
</tr>
</tbody>
</table>

Table 2.2c. Breon N41C80 formulations.
2.4 Mixing Technique

2.4.1 Single Polymers

Each rubber batch is prepared by weighing out the raw rubber and the initial ingredients (excluding curatives) as shown in Table 2.3.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>pphr</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubber</td>
<td>100</td>
<td>Polymer</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>2</td>
<td>Activator system</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Flectol Pastilles</td>
<td>1.5</td>
<td>Antioxidant</td>
</tr>
<tr>
<td>Batch Weight</td>
<td>108.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.3 Masterbatch formulations.
These amounts are based on parts per hundred rubber (pphr). A Banbury internal mixer is used to incorporate these ingredients into the rubber using the mixing cycle in Table 2.4.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>All pieces of rubber added and press firmly down</td>
</tr>
<tr>
<td>0.5</td>
<td>Add ingredients</td>
</tr>
<tr>
<td>2</td>
<td>Sweep powders down chute</td>
</tr>
<tr>
<td>2.5*</td>
<td>Dump rubber batch</td>
</tr>
</tbody>
</table>

* 3.5 for NBR

Table 2.4  Masterbatch mixing procedure for the internal mixer.

The rubber is added first to break the chunks up and allow easier mixing with the additives. The ingredients are added as a batch lot and are given two minutes for NR and three minutes for NBR to mix in with the rubber. The two minutes for NR was a standard time that had successfully been used before, but when this was used for NBR the powders were found not to have fully mixed into the rubber. Experimentation with a few NBR batches showed that a three minute mixing time was more appropriate. Cooling water is continuously pumped through the rotors due to the great heat generated from the shear stress being applied to the rubber. When the rubber batch had been dumped it was passed through a two roll mill a few times in order to sheet it out.
The addition of the curatives was carried out on a 12" x 6" two roll mill, in which the rotors were cooled so that the shear stresses produced in the rubber did not raise the temperature above 30°C. This was a convenient temperature which was hot enough to allow easier incorporation of the curatives into the rubber, while still being well below the vulcanization temperature to be used later, but also cool enough to be able to handle. The curatives were added according to the amounts shown in Table 2.2 which are all based on parts per hundred of the pure rubber. The curative levels were chosen so that when the samples were vulcanized, a wide range of crosslink densities could be achieved. This was necessary so that an accurate calibration curve could be generated for the future analysis of the crosslink densities in the individual phases of NR/NBR blends (see Chapter 5). The mixing for each rubber containing TMTD was 4 minutes, but for the ones containing ODIP the time taken was between 5 - 6 minutes due to the rubber being crumbly when the accelerator was first added. The rubber was finally sheeted out using a very tight nip between the rollers so that a good shear was obtained, thus ensuring that there was a good mix. The rubbers were allowed to rest for 24 hours to ensure completion of any distribution of curatives and also to allow time for the rubber to relax, before obtaining their cure times.

2.4.2 Blends

Work previously carried out by Tinker\(^4\) used a semi-EV system of sulphur and the accelerator tetramethylthiuram monosulphide (TMTM). For this thesis the curing system was slightly changed with the use of the very similar TMTD, so that a similar chemical structure to the other thiuram disulphide (ODIP) was achieved.

In order to study the blends and their crosslink densities, five different blend ratios were prepared that gave an even spread across the composition range (Table 2.5). Masterbatches were prepared as for the single polymers, and then the two rubbers were mixed together in their respective ratios on a two roll mill. Initially this was very difficult due to the incompatibility of the rubbers creating a flaky mixture. They eventually became coherent, i.e. produced one solid piece of rubber, after about 5 minutes. The addition of the S/TMTD curatives (Table 2.5) went very smoothly with easy incorporation into the rubber. The
<table>
<thead>
<tr>
<th>Mix No.</th>
<th>9111</th>
<th>9001</th>
<th>9002</th>
<th>9003</th>
<th>9004</th>
<th>9005</th>
<th>9109</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR Batch</td>
<td>21.7</td>
<td>27.1</td>
<td>38.0</td>
<td>54.3</td>
<td>70.5</td>
<td>81.4</td>
<td>92.2</td>
</tr>
<tr>
<td>Perbunan batch</td>
<td>86.8</td>
<td>81.4</td>
<td>70.5</td>
<td>54.3</td>
<td>38.0</td>
<td>27.1</td>
<td>16.3</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>TMTD</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Total Weight, g</td>
<td>111</td>
<td>111</td>
<td>111</td>
<td>111</td>
<td>111</td>
<td>111</td>
<td>111</td>
</tr>
<tr>
<td>Cure time, min</td>
<td>4.6</td>
<td>4.5</td>
<td>5.0</td>
<td>4.7</td>
<td>5.0</td>
<td>4.5</td>
<td>4.8</td>
</tr>
<tr>
<td>% Methanol extraction</td>
<td>5.4</td>
<td>5.3</td>
<td>5.0</td>
<td>4.7</td>
<td>4.5</td>
<td>4.3</td>
<td>4.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mix No.</th>
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<th>9006</th>
<th>9007</th>
<th>9008</th>
<th>9009</th>
<th>9010</th>
<th>9110</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR Batch</td>
<td>21.7</td>
<td>27.1</td>
<td>38.0</td>
<td>54.3</td>
<td>70.5</td>
<td>81.4</td>
<td>92.2</td>
</tr>
<tr>
<td>Perbunan batch</td>
<td>86.8</td>
<td>81.4</td>
<td>70.5</td>
<td>54.3</td>
<td>38.0</td>
<td>27.1</td>
<td>16.3</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>ODIP</td>
<td>1.93</td>
<td>1.93</td>
<td>1.93</td>
<td>1.93</td>
<td>1.93</td>
<td>1.93</td>
<td>1.93</td>
</tr>
<tr>
<td>Total Weight, g</td>
<td>112</td>
<td>112</td>
<td>112</td>
<td>112</td>
<td>112</td>
<td>112</td>
<td>112</td>
</tr>
<tr>
<td>Cure time, min</td>
<td>10.6</td>
<td>10.0</td>
<td>7.5</td>
<td>7.0</td>
<td>7.0</td>
<td>6.2</td>
<td>6.8</td>
</tr>
<tr>
<td>% Methanol extraction</td>
<td>6.3</td>
<td>6.2</td>
<td>6.1</td>
<td>6.0</td>
<td>5.4</td>
<td>5.4</td>
<td>5.7</td>
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</tbody>
</table>

**Figure 2.5a.** Formulations for NR:Perbunan Blends.

37
<table>
<thead>
<tr>
<th>Mix No.</th>
<th>9025</th>
<th>9026</th>
<th>9027</th>
<th>9028</th>
<th>9029</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR Batch</td>
<td>27.1</td>
<td>38.0</td>
<td>54.3</td>
<td>70.5</td>
<td>81.4</td>
</tr>
<tr>
<td>Breon batch</td>
<td>81.4</td>
<td>70.5</td>
<td>54.3</td>
<td>38.0</td>
<td>27.1</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>TMTD</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Total Weight, g</td>
<td>111</td>
<td>111</td>
<td>111</td>
<td>111</td>
<td>111</td>
</tr>
<tr>
<td>Cure time, min</td>
<td>17.5</td>
<td>13.8</td>
<td>12.0</td>
<td>8.5</td>
<td>7.6</td>
</tr>
<tr>
<td>% Methanol extraction</td>
<td>5.8</td>
<td>5.4</td>
<td>4.6</td>
<td>4.6</td>
<td>4.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
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<th>9032</th>
<th>9033</th>
<th>9034</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR Batch</td>
<td>27.1</td>
<td>38.0</td>
<td>54.3</td>
<td>70.5</td>
<td>81.4</td>
</tr>
<tr>
<td>Breon batch</td>
<td>81.4</td>
<td>70.5</td>
<td>54.3</td>
<td>38.0</td>
<td>27.1</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>ODIP</td>
<td>1.93</td>
<td>1.93</td>
<td>1.93</td>
<td>1.93</td>
<td>1.93</td>
</tr>
<tr>
<td>Total Weight, g</td>
<td>112</td>
<td>112</td>
<td>112</td>
<td>112</td>
<td>112</td>
</tr>
<tr>
<td>Cure time, min</td>
<td>22.5</td>
<td>17.5</td>
<td>12.5</td>
<td>11.0</td>
<td>9.7</td>
</tr>
<tr>
<td>% Methanol extraction</td>
<td>6.8</td>
<td>6.4</td>
<td>5.8</td>
<td>5.4</td>
<td>5.3</td>
</tr>
</tbody>
</table>

Figure 2.5b.  Formulations for NR:Breon Blends.
S/ODIP curatives resulted in an initial non-cohesion of the rubber to the roll, but this soon corrected itself.

2.5 Vulcanization

The assessment of curing characteristics was carried out on a Götffert Elastograph. This instrument consists of an oscillating disc in a heated cavity which contains the test sample (ca. 5g). The temperature was selected to be a typical processing temperature of 150°C. The torque on the disc is plotted continuously against time, and as vulcanization proceeds, the torque increases with increasing rubber stiffness, to produce its characteristic cure curve. Figure 2.2 shows a typical NR rheometer trace and Figure 2.3 shows a typical NBR rheometer trace.

Figure 2.2. A typical NR rheometer trace of torque rise against time.
For NR the time taken to obtain the maximum torque rise is taken as the maximum state of cure ($t_{\text{max}}$). Some of the NBR compounds produced 'marching' cures, where the torque continues to rise without any sign of falling. The cure times for these are taken at the point where the rise over one minute was less than 5%. A typical rheometer trace of an NR/NBR blend is represented in Figure 2.4.

Figure 2.3. A typical NBR rheometer trace of torque rise against time.
Vulcanized sheets (9" x 9" x 1mm) for crosslink density determination were produced using compression moulds in hydraulically operated presses, heated to 150°C. When the cure time was reached the samples were released from the mould and allowed to cool to room temperature.

2.6 Methanol Extraction

This process is carried out to ensure the cleanest olefinic peaks are produced in a $^1$H nmr spectrum of the vulcanizate. Any impurities which give signals that appear in the region of the spectrum being analysed will most likely affect the olefinic signals, especially if they are
directly interfering with them. Even indirect interference may cause problems, because even
though there are small quantities of low molecular weight impurities they have very sharp
signals and hence relatively high peak signal strengths. As the spectrum is selected between
the baseline and the highest signal, they will cause a reduction in the intensity of the other
signals.

Sections from the middle of the vulcanized sheet (to avoid end distortions) were cut out
(50mm x 50mm x 1mm) and accurately weighed. These were individually wrapped in lens
cleaning tissue, so that the samples did not stick together, and placed in a Soxhlet apparatus.
Boiling methanol was used to carry out the extraction of the mobile extra network materials.
After an overnight extraction the samples were dried down to constant weight in vacuo at
room temperature.

The percentage material extracted was calculated using the equation:

\[
\text{% material extracted} = 100 \times \frac{W_o - W_D}{W_o}
\]  

(9)

\begin{align*}
W_o &= \text{unextracted weight} \\
W_D &= \text{weight after extraction}
\end{align*}

The values are given in Table 2.2, and show that the mobile extra network materials form
between 3 - 8% of the vulcanizate.

2.7 Volume Swelling

A technique to determine the crosslink density of a single polymer vulcanizate is equilibrium
swelling of a rubber network in a non-volatile solvent. Flory and Rehner\textsuperscript{28,29} derived an
equation which shows the relationship between volume swelling and physical crosslink
density,
\[ u = -[\ln(1 - v_r) + v_r + \chi v_r^2]/2V_o(v_r^{12}) \]  
\hspace{1cm} (10)

- physical crosslink density (mol m\(^{-3}\))
- \(V_o\) = molar volume of the swelling liquid (8.0962 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \text{ for chloroform})
- \(\chi\) = polymer-liquid interaction parameter

Flory\(^{59}\) later modified this equation to:

\[ u = -[\ln(1 - v_r) + v_r + \chi v_r^2]/2V_o(v_r^{12} - v_r/2) \]  
\hspace{1cm} (11)

There is no experimental evidence to justify the use of equation (10) in preference to equation (11), or vice versa. Bristow\(^{59}\) has investigated the selection of the equation and provided evidence to support the Flory-Rehner equation (10) and so this is the one used for the purposes of this thesis.

The determination of the physical crosslink density is critically dependent on the value of the polymer-liquid interaction parameter, \(\chi\). \(\chi\) must first be determined accurately, by the substitution into equation (10), of known values of the crosslink density determined by an independent method. For vulcanizates, \(\chi\) can conveniently be determined by substituting \(C_1\) values (obtained from stress-strain measurements) (see section 3.4) and \(v_r\) values into equation (12):

\[ \chi = -[2V_o u(v_r^{12}) + \ln(1 - v_r) + v_r]/v_r^2 \]  
\hspace{1cm} (12)

Small pieces (ca. 0.2g) of the extracted vulcanizate were immersed in chloroform at 23°C for 48 hours, sufficiently long for equilibrium swelling to be obtained, and stored in the dark. The swollen pieces were removed, surface dried on filter paper, and weighed in closed vessels. The final weight was taken after the samples had dried down to constant weight. The volume fraction of rubber in the swollen gel was calculated from initial, swollen and dried weights, with corrections made for the zinc oxide content in the vulcanizate:
\[ V_3 = (\text{dried weight} - \text{original weight}) \times (\text{p.p.h.r of ZnO}) / \text{Formula weight} \]  
\[ \text{rubber density} \]

\[ V_3 = \text{volume of rubber network corrected for zinc oxide and extractable material} \]

\[ V_2 = \frac{\text{swollen weight} - \text{dried weight}}{\text{solvent density}} \]  

\[ V_2 = \text{volume of imbibed liquid} \]

\[ v_i = V_3(V_2 + V_3) \]  

\[ \text{(13)} \]

\[ \text{(14)} \]

\[ \text{(15)} \]

2.8 Differential Scanning Calorimetry

Differential scanning calorimetry was carried out on a Perkin-Elmer DSC7 machine to determine the \( T_g \) (glass transition temperature) values of the NR and NBR components in the blends, but first a range of the single polymers with different crosslink densities were analysed. This was done so that a calibration graph of \( T_g \) against crosslink density could be plotted, which would enable the crosslink densities of the individual phases of the blends to be calculated from their respective \( T_g \) values.

In order to calibrate the machine two standard transition values were required, and these were both obtained from cyclohexane. The transitions are its \( T_m \) (melting point) at \( 6^\circ C \) and a crystalline transition point at \(-87^\circ C\), and both these values were used in the calibration program so that the \( T_g \) of an NR sample could be obtained. If the value was \(-72^\circ C +/- 1^\circ C\) then the calibration was correct, but any further deviation meant a slight adjustment to the calibration figures was required. Previous work had been carried out using the \( T_g \) values of NR (\(-72^\circ C\)) and SBR (\(-60^\circ C\)) as the calibration points, but cyclohexane replaced these due to the greater accuracy of the transition points and its wider temperature range.

Each sample (ca. 20mg) was placed in a small metal container and enclosed in a temperature
controlled environment. The temperature was dropped to \(-110^\circ C\) with the aid of liquid nitrogen, and the sample left for a few minutes to properly adjust itself to the temperature. The sample was then heated at \(20^\circ/min\). and the temperature rise against energy difference plotted on a computer screen. The energy difference was between that of the sample in its container and an identical empty container which underwent the same temperature changes at the same time. The energy graph is straight to begin with but when the \(T_g\) of the sample is reached the trace rises and then levels off again (Figure 2.5). This is indicative of the energy increase required to convert the sample from a glass-like structure to a rubber-like one. By taking the intersection between the initial straight line and the steepest gradient of the transition slope, the \(T_g\) value was found. Any anomalies in the trace were usually due to crystallization of the sample, and this was eliminated by heating the sample to \(100^\circ C\) and then cooling very rapidly.

Figure 2.5. A dsc trace of heat flow against temperature rise for an NBR vulcanizate.
2.9 NMR Measurement

Loadman and Tinker\textsuperscript{13} have demonstrated that peak broadening in $^1$H nmr spectra of gum vulcanizates of NR and acrylonitrile-butadiene rubber can be used to estimate the degree of crosslinking in the individual phases of a blend of the two rubbers. Before the sample is analysed it has to be prepared and this was done by cutting slivers from the extracted vulcanizates (ca. 1mm x 1mm x 10mm) and placing them in deuterated chloroform (ca. 1cm$^3$) in a sealed tube which was stored in the dark. This was necessary since it has been shown that the peak width of swollen vulcanizates stored in daylight vary with time. After a period of 48 hours, which ensured that equilibrium swelling had been obtained, the sliver was cut to a width that enabled it to fit into an nmr sample tube and to be able to move freely in the deuterated chloroform solvent. A General Electric QE300 nmr spectrometer was used to obtain the $^1$H spectra as a free induction decay signal, and then Fourier transformation analysis was performed. The resultant signal was then available for manipulation to obtain an accurately phased spectrum. From this the peak width of the olefinic peaks could be determined and consequently the crosslink densities. This technique is discussed in detail in Chapter 5.

2.10 Stress-Strain

The stress-strain behaviour in practice of dry NR vulcanizates is well described, up to moderately high extensions, by the Mooney-Rivlin equation\textsuperscript{19, 23}:

$$F = 2A_o(C_1 + C_2\lambda^2)(\lambda - \lambda^2)$$  \hspace{1cm} (16)

$F$ = force  
$A_o$ = original cross-sectional area  
$\lambda$ = extension ratio  
$C_1, C_2$ = Mooney-Rivlin parameters

When the crosslink functionality is four, the $C_1$ term is equivalent to the physically effective
crosslink density of the rubber. Thus a graph of reduced stress, $F/2A_o(\lambda - \lambda^{-2})$ versus $1/\lambda$ should give a slope of $C_2$ and an intercept of $C_1$ on the ordinate (Figure 2.6).

![Figure 2.6 A typical Mooney-Rivlin plot.](image)

The single polymer vulcanizates underwent stress-strain analysis in order to obtain physically effective crosslink density values. This was done on the Greensmith’s apparatus at MRPRA, an in-house machine developed during the 1950’s, which stretches the rubber samples and balances the elastic force with weights. For this experiment the rubber test pieces were cut out using a "C_1" cutter, which is an instrument which has two sharp parallel blades that cut strips roughly 13cm long, and 3mm wide. The density and cross-sectional area (C.S.A.) of the strips are found by weighing a known length in air and in water. The latter weighing is carried out with the aid of a sinker since most of the samples float in water.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length of rubber sample</td>
<td>= l</td>
</tr>
<tr>
<td>Weight of rubber sample in air</td>
<td>= $W_1$</td>
</tr>
<tr>
<td>Weight of sinker in water</td>
<td>= $W_2$</td>
</tr>
</tbody>
</table>
Weight of sinker + rubber sample = \( W_3 \)

\[
\text{Density, } \delta, \quad = \quad \frac{W_1}{(W_1 + W_2 - W_3)}^* \\
\text{C.S.A} \quad = \quad \frac{W_1}{1 \times \delta}
\]  

* This is only true when the density of water is 1.0000g/cm\(^3\)

The Greensmith machine consists of a leaf-spring platform which is constrained to move against an electrical contact. The vertical displacement is less than 0.05mm. It has set stops which the rubber is extended to, and at each stop the upward force of the extended sample is measured by adding weights to the platform until the electrical connection is just made. The initial length of the rubber sample placed in the apparatus is just less than 9.945cm. This is determined by placing the sample in two clamps which have been positioned in two slots at a fixed distance apart. When the rubber is firmly in place it is placed in the apparatus to determine if the tension is correct. This is found by determining if an electrical connection has been made by the tension in the rubber pulling the bottom platform up. If there is no connection then the sample must be reclamped with more tension. If there is a connection then a small weight i.e. 2g is applied to the platform to determine if the tension is too tight. If there is no electrical connection then the rubber sample is under too much tension and so must be reclamped with more slack. With experience the reclamping is rarely done due to correct initial clamping. When the correct tension has been achieved the sample is allowed to relax for 15 mins.

There are two series of stops on the Greensmith machine, one set of six short stops (up to 10.46cm, corresponding to approximately 5% strain) and one set of 16 stops (up to 50cm or approximately 400% strain). The set of six stops was used to determine the original unstrained length of the sample, which is crucial in the \( C_1 - C_2 \) determination. This was found by extrapolating the force-extension points from these six stops (which are fairly linear in this region due to the obeyance of Hooke's Law) back down to the intercept on the abscissa, which is the original length of the sample. This procedure is now omitted so that more rubbers can be tested in a day. This was made possible due to a computer program by
Campbell\textsuperscript{24} which now determines the original length of the sample by a best fitting procedure of the Mooney-Rivlin plot\textsuperscript{19-23}.

The next 16 stops are used to obtain the points on the Mooney-Rivlin curve and hence the $C_1$ and $C_2$ values, except that only the first 10 of these stops are used because of the finite extensibility of the molecular backbone of rubber causing upturn in the Mooney-Rivlin curves. The rubber is stretched to each of the 10 stops and allowed to relax for 3 minutes prior to load measurement. This measurement is achieved by placing small weights on the platform so that the electrical connection is almost broken. This is indicated by a light, that is part of the electrical connection, just beginning to flicker, which means the force exerted by the weight in the balance pan is the same as the tension in the rubber sample. The time interval of 3 minutes is a compromise between an accurate load determination and the time scale of the experiment. This is necessary because initially the stress falls quicker than can be followed with the Greensmith apparatus. This is shown in Figure 2.7 were the rubber is put under a large stress when it is initially stretched, but very quickly relaxes before slowly reaching a fairly stable state. It is when the rubber has reached this last state that an accurate force determination can be made.

![Figure 2.7 Stress-relaxation of a vulcanizate in the Greensmith apparatus.](image)

\textbf{Figure 2.7 Stress-relaxation of a vulcanizate in the Greensmith apparatus.}
The stops are not separated linearly with distance but are spaced in equal steps of the reciprocal of the extension ratio, $\lambda$. The stops are separated by steps of 0.05 in $1/\lambda$, so that after 10 stops $1/\lambda = 0.5$ i.e. $\lambda = 2$ or the rubber is stretched to 100%, which takes 30 minutes.

The data are graphically represented in the form of a Mooney-Rivlin plot of $F/2(\lambda - \lambda^2)$ vs $1/\lambda$. According to the Mooney-Rivlin Equation this should be a straight line, with intercept $C_1$ and gradient $C_2$ and the actual unstrained length of the sample (which is undetermined) is obtained using a least square regressive analysis and allows the initial length, $l_0$, to vary from a start value at 9.945.

The temperature at which the stretching of the rubber took place was noted so that $C_1$ values could be corrected to 25°C.

$$C_{1, RV} = C_1(\text{measured at } T^\circ C) \times \frac{298}{(273 + T)}$$ \hspace{1cm} (19)

$C_{1, RV} =$ temperature corrected $C_1$ of rubber vulcanizate

### 2.11 Phase Morphology

Sections need to be thin enough (1 - 2μm) to give a two dimensional representative view of the morphology. A small piece was cut into a v-shape (1mm x 2mm) and sectioned on a cryoultramicrotome at least 20 - 30° below the lowest $T_s$ in the sample. Six sections were collected and from these three suitable ones were found that have an area that is representative of the phase morphology of all of them.

Prior to viewing the sample, it is mounted in a material that has a similar refractive index. This is called 'oiling' out and eliminates most of the knife marks.

A Leitz Ortholux 2 optical microscope was used to examine the samples. Thin sections of the polymer blends can give bright field images with little or no contrast between the components. Transmitted light phase contrast converts the refractive index differences in such
a specimen to light and dark image regions.

2.12 Network Visualization

The preparation of the samples for network visualization requires styrene swelling and polymerization of the styrene.

The vulcanizates are acetone extracted using a hot Soxhlet, and dried down to constant weight in vacuo. The vulcanizates are then swollen in a solution of styrene with dibutylphthalate (2% w/w) and dibenzoyl peroxide (1% w/w), in a sample tube stored in the dark, for sufficient time to ensure that equilibrium swelling is achieved (4 days). A small length of the rubber is cut off and placed in the bottom of a glycerine capsule. To this the styrene solution is added and a cap firmly fitted. The capsule is then placed in a heated oil bath (70°C) for 24 hours or until the solution has set. They are then heated in an oven at 90 - 100°C for 2 - 3 hours to ensure all the styrene has polymerized.

A piece of vulcanizate embedded in polystyrene is cut out and mounted for sectioning at room temperature using a LKB Ultratome V. This was cut using a 45° freshly cleaved glass knife at a 5° rake angle, and carried out at a rate of 0.5 mm/s using a thermal advance. Sections were collected on a surface of a water/ethanol trough and relaxed with a small amount of xylene vapour. Those judged to be of correct thickness were selected and collected on a nickel TEM (transmission electron microscope) grid, and stored in osmium tetroxide vapour two hours prior to examination. The sample is then examined using a Philips EM300 transmission electron microscope, and areas chosen that are representative of the rest of the blend.

2.13 Chemical Probe Treatment

Two chemical probe treatments were employed in order to determine the distribution of crosslink types in the polymer. Propane-2-thiol/piperidine in heptane was used to cleave
polysulphidic crosslinks, while hexane-1-thiol in piperidine was used to cleave both poly- and di-sulphidic crosslinks. In both treatments the vulcanizates were cut to a standard size that enabled stress-strain measurements to be carried out on the Greensmith apparatus.

**Propane-2-thiol/piperidine**

Four samples of the rubber were cut into parallel sided strips approximately 13cm long, and 3mm wide, and weighed. They were placed in a horizontal tube as below and a stream of nitrogen passed through.

![Diagram of horizontal glass tube](image)

100cm$^3$ of degassed heptane was poured through the middle tap, the nitrogen supply lowered to a steady stream, and the samples left overnight to swell.

The solvent was decanted off the rubber and replaced by 50cm$^3$ of propane-2-thiol (0.4M) and piperidine (0.4M) in heptane solution. The nitrogen supply was increased for two minutes to purge air from the tube and then turned off. During the two hours necessary for the probe to work, the solution was agitated a few times. The tube was emptied of the reagent and 50cm$^3$ of degassed light petroleum ether, bp 40-60°C, was added. This washing procedure was repeated five times during the day, with agitation of the tube in between times. Finally
the petrol and rubbers were poured out at the stoppered end, the rubbers removed with tweezers and placed on filter paper, where they were frequently turned so that the ends did not curl up. They were put into a vacuum desiccator covered with foil, to protect them from the heat and light of the sun, and dried to constant weight. The treated samples were then analysed to obtain their crosslink densities by stress-strain measurements.

**Hexane-1-thiol/piperidine**

![Diagram](attachment:image.png)

**Figure 2.9.** H-tube used for hexane-1-thiol probe treatment.

Four parallel sided strips (ca. 13cm long and 3mm wide) were placed in one arm of the H-tube above and 60cm³ of the hexane-thiol (1.0M) in piperidine solution added to the other side by tilting the tube. The tube was frozen in liquid nitrogen and then evacuated. When this was completed the tap to the vacuum was closed and the tube warmed up in water. This procedure was repeated three times to ensure complete solvent degassing. With the reagent in a frozen state, the tube was sealed, and placed in water to melt the reagent. The reagent was then poured into the arm containing the samples, and the 'H'-tube immersed in a water bath, set at 25°C, with the tube arm horizontal so that the samples stayed under the reagent.
After 48 hours the reagent was transferred to the other arm and frozen in liquid nitrogen so that the sealed end could be opened. With this done, the samples were transferred into the horizontal tube, used for the other probe treatment (Figure 2.7), and 100cm³ of petroleum ether, bp 40-60° added, and a steady nitrogen flow passed through. After eight washings with the degassed 40-60° petrol and an overnight soaking in degassed petrol, the samples were removed and dried on filter paper, with frequent turnings to avoid curling at the edges. These were then dried to constant weight in a vacuum desiccator before undergoing stress-strain measurement on the Greensmith instrument.
Chapter 3

Determination of Crosslink Densities in Single Polymers

3.1 Introduction

A satisfactory characterization of a rubber network requires the quantitative knowledge of the concentration of the crosslinks. The values of the crosslink concentration obtained from physical measurements, such as equilibrium stress-strain and swelling measurements are of the physical crosslink density. These values are greater than the chemical crosslink densities because they also take into account chain entanglements and chain ends. Chemical crosslink densities can be obtained from the Mullins equation, but this only applies to NR and so comparisons with NBR cannot be made. Calculation of the concentrations of physical crosslink densities is carried out for both NR and NBR (see Tables 3.1 - 3.3), and the basis for the procedures used in obtaining these values are discussed in Chapter 1. Some vulcanizates were used that had been produced by Brown so that a more comprehensive study could be performed.

When carrying out stress-strain analysis, vulcanizates are allowed to relax for 3 minutes before the load measurement is taken (section 2.10). For NR this is ideal as the vulcanizates are relaxing very slowly by this time. NBR has a much faster relaxation rate, and even after 3 minutes is still relaxing quite fast. This makes taking a load measurement very difficult, but with practice it can be achieved. To make the reading easier the vulcanizate can be allowed to relax for a longer period of time so that the rate of relaxation will be slower. Unfortunately this makes the experimental time per sample much longer, with the end result that fewer samples are analysed each day. A much less labour intensive procedure is determination of equilibrium volume swelling values and the conversion to crosslink densities using the Flory-Rehner equation (see section 3.4).
3.2 Stress-strain Measurement

The stress-strain measurements were carried out as described in Chapter 2 (section 2.10) on the Greensmiths apparatus. The units for physical crosslink density were required to be in mol/m$^3$ and so the values were converted (Tables 3.1 - 3.3).

3.3 Volume Swelling Measurement

The volume swelling experiment was carried out as previously described in Chapter 2 (section 2.7) with weighing of the sample before the experiment, when fully swollen in chloroform, and finally when dried down to constant weight.

Volume swelling measurements were carried out on rubber vulcanizates of NR, Perbunan and Breon, and the results are recorded in Tables 3.1 - 3.3 respectively.

3.4 Flory-Rehner Equation

The Flory-Rehner equation$^{28,29}$ can be used to convert $v_r$ values, obtained from equilibrium volume swelling measurements, into physical crosslink densities, providing the correct polymer-interaction parameter, $\chi$, is used (see Chapter 2 for more detail). In order to obtain this value, a series of vulcanizates, with a range of crosslink densities, must undergo both stress-strain analysis and volume swelling measurements. The results from both these procedures can then be incorporated into the Flory-Rehner equation and the $\chi$ value obtained. The $\chi$ values for NR, Perbunan and Breon are shown in Tables 3.1 - 3.3.
<table>
<thead>
<tr>
<th>Sample No.</th>
<th>n_{phys}^* (mol/m^3)</th>
<th>ν_r</th>
<th>χ</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSB 6.70</td>
<td>0.049</td>
<td>0.352</td>
<td></td>
</tr>
<tr>
<td>PSB 30.2</td>
<td>0.121</td>
<td>0.379</td>
<td></td>
</tr>
<tr>
<td>PSB 48.2</td>
<td>0.148</td>
<td>0.367</td>
<td></td>
</tr>
<tr>
<td>PSB 63.5</td>
<td>0.167</td>
<td>0.361</td>
<td></td>
</tr>
<tr>
<td>PSB 79.8</td>
<td>0.185</td>
<td>0.357</td>
<td></td>
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<td>PSB 110</td>
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<td>0.332</td>
<td></td>
</tr>
<tr>
<td>PSB 125</td>
<td>0.220</td>
<td>0.336</td>
<td></td>
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<tr>
<td>PSB 15.5</td>
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</tr>
<tr>
<td>PSB 37.3</td>
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</tr>
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</tr>
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<td>8924</td>
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</tr>
<tr>
<td>8926</td>
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<td>8927</td>
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<td>8947</td>
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<tr>
<td>9011</td>
<td>55.8</td>
<td>0.361</td>
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<tr>
<td>9012</td>
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<td>9017</td>
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<td>9201</td>
<td>92.8</td>
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<tr>
<td>9208</td>
<td>120</td>
<td>0.323</td>
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</tr>
</tbody>
</table>

PSB - spectra provided by Brown\textsuperscript{86} and analysed for this work.
* Derived from C\textsubscript{1} measurements

Table 3.1. Stress-strain and volume swelling data for Natural Rubber vulcanizates.
<table>
<thead>
<tr>
<th>Sample No.</th>
<th>( n_{\text{phys}}^* ) (mol/m(^3))</th>
<th>( v_r )</th>
<th>( \chi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>8913</td>
<td>28.2</td>
<td>0.0895</td>
<td>0.277</td>
</tr>
<tr>
<td>8914</td>
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<tr>
<td>8917</td>
<td>56.0</td>
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<tr>
<td>8928</td>
<td>4.81</td>
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<td>23.2</td>
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<td>9204</td>
<td>39.1</td>
<td>0.096</td>
<td>0.253</td>
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</tbody>
</table>

* Derived from \( C_1 \) measurements

Table 3.2. Stress-strain and volume swelling data for Perbunan vulcanizates.
<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$n_{phys}^*$ (mol/m³)</th>
<th>$v_r$</th>
<th>$\chi$</th>
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<td>0.130</td>
<td>0.326</td>
</tr>
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</table>

* Derived from C₁ measurements

Table 3.3. Stress-strain and volume swelling data for Breon vulcanizates.
3.5 Results and discussion

The $u$, $v$, and $\chi$ values for the NR, Perbunan and Breon vulcanizates are presented in Tables 3.1 - 3.3 respectively.

For all 3 rubbers the relationship between $u$ and $v_r$ is very similar (Figures 3.1 - 3.3). For low values of $v_r$ the dependence on $C_1$ is very small but the dependence increases with increasing values of $v_r$.

![Crosslink density versus volume swelling for NR vulcanizates.](image)

Figure 3.1. Crosslink density versus volume swelling for NR vulcanizates.
Figure 3.2. Crosslink density versus volume swelling for Perbunan vulcanizates.

Figure 3.3. Crosslink density versus volume swelling for Breon vulcanizates.
The $\chi$ values are however variable for each rubber (Figures 3.4 - 3.6). For NR, the relationship between $\chi$ and $v_r$ shows a trend of decreasing $\chi$ values with increasing $v_r$, but this is not so clear at low $v_r$ values (Figure 3.4).

![Graph showing $\chi$ versus $V_r$ for NR vulcanizates.](image)

Figure 3.4. $\chi$ versus $V_r$ for NR vulcanizates.

A mean value of 0.368 can be taken for $\chi$, but the accuracy of the vulcanizates with low or high $v_r$ values is then put into question.

Perbunan vulcanizates (Figure 3.5) give a few anomalous results but it is clear that there is no direct relationship between the $\chi$ and $v_r$ values.
Figure 3.5. $\chi$ versus $V_r$ for Perbunan vulcanizates.

Figure 3.6. $\chi$ versus $V_r$ for Breon vulcanizates.
A mean value of 0.286 for $\chi$ can be taken for Perbunan, but as the values for vulcanizates with similar $v$, values is so varied, the accuracy is not very good. Apart from one anomalous reading, Breon (Figure 3.6) has only small $\chi$ changes over a wide range of $v$, values. Thus the average value for $\chi$ of 0.305 can be used to give crosslink densities for vulcanizates that are accurate.

The $\chi$ values obtained above are different from those derived by Bristow and Watson$^{31,35}$ (NR, 0.383, 18% acrylonitrile content NBR, 0.251 and 39% acrylonitrile content NBR, 0.241). By comparing these values with those obtained from the analysis of a wide range of crosslink density vulcanizates it would appear that low crosslink density vulcanizates would give similar $\chi$ values to those obtained by Bristow and Watson. Other work has already shown that $\chi$ is dependent on the degree of swelling$^{31}$ and degree of crosslinking$^{49}$. Thus in order to obtain accurate crosslink density values for the single polymer vulcanizates, equilibrium stress-strain measurements, using the Greensmith apparatus, were carried out on all the vulcanizates.
Chapter 4

Blend Characterization

4.1 Introduction

In the studies of vulcanized elastomer blends it is commonplace for the materials to be characterized in respect of phase morphology. Techniques for studying the morphology of elastomer blends and the distribution of phases in blends have been established for some time. The most versatile method of elucidating the morphology of polymer blends is phase contrast microscopy, a method particularly suitable for gum blend systems.

NR and NBR are incompatible polymers and hence should exhibit two glass transition temperatures \( (T_g) \) at any blend composition. The \( T_g \) values of the phases should also increase with increasing crosslinking due to the restraining influence of the crosslinks, especially the chemical crosslinks\(^2\), and thus this method can be used as a way of comparing the crosslinking in the individual phases of a blend.

4.2 Phase Morphology

The phase texture of the NR/NBR blend vulcanizates were investigated by employing the normal procedure for the determination of phase texture. This was done by planing thin sections by cryo-ultramicrotomy, mounting them in polybutene and then examining them by phase contrast light microscopy. The polybutene was used in order to mask any irregularities on the surface of the sample i.e. scratching from knife marks and the dragging of filler particles across the surface. It can be used for this purpose due to its similar refractive index to natural rubber, which ensures no distortion when observing the sample, and also its non-
reactivity to rubber. Each micrograph obtained is of an NR/NBR blend and is at 500 times magnification. The phase sizes which are given are approximate as the measurements are taken from micrographs which show only a cross-section in two dimensions, whereas phase morphology is obviously three dimensional.

4.2.1 NR/Perbunan

The micrographs for these blends are all very similar, so the 50:50 NR:Perbunan blend accelerated with ODIP (vulcanizate 9008) has been chosen as a representative for the other samples, due to its greater clarity (Figure 4.1).

![Phase contrast micrograph of an NR/Perbunan blend.](image)

Figure 4.1. Phase contrast micrograph of an NR/Perbunan blend.
The dark areas are the Perbunan phase and the light areas the NR phase. The tiny black and white dots are the zinc oxide particles, which appear to be mainly visible in the NR phase. The phase sizes are very small, less than 1 μm, and in fact are on the limit of resolution. The small size means that diffusion of the curatives can take place quite easily within the vulcanization time.

4.2.2 NR/Breon

i) TMTD accelerated blends (Figure 4.2)

Vulcanize 9029 (75:25 NR:Breon) shows discrete Breon phases of approximately 9 μm in a continuous phase of NR. Increasing the Breon content in the blend to 50% (vulcanize 9027) gives larger Breon phases (approx. 20 μm) but they are still in a continuous NR phase. This is to be expected since in a 50:50 two polymer blend system the low viscosity component becomes the continuous phase and surrounds the high viscosity polymer zones. In a blend containing 75% Breon (vulcanize 9025), the NR becomes the discrete phase (approx. 8 μm) in a Breon matrix.

The phase sizes are much bigger than those seen in the NR/Perbunan blends due to the greater difference in solubility parameters, which means that there is the possibility that there may not be enough time for complete diffusion of the curatives to occur before the rubber is vulcanized.
Figure 4.2. Phase contrast micrographs of NR/Breon blends with TMTD.
ii) ODIP accelerated blends (Figure 4.3)

Vulcanizate 9034 (75:25 NR:Breon) Breon is the discrete phase (approx. 12μm) and NR the continuous phase. At 50% Breon in the blend (vulcanizate 9032) the two phases appear to show a degree of co-continuity, however the NR phase does seem to be more continuous. At 75% Breon content (vulcanizate 9030) the NR is the discrete phase (approx. 7μm) and Breon the continuous phase.
Figure 4.3. Phase contrast micrographs of NR/Breon blends with ODIP.
For the 75:25 NR:Breon blend the lighter areas are the lesser phase, which in this blend composition would represent Breon. Thus the Breon has changed from a dark to a light contrast. The NR phase also appears to have become darker. The crosslink densities of the ODIP accelerated blends compared to TMTD accelerated blends, (section 5.2.4 in Chapter 5) are much lower for Breon whilst those of NR stay approximately the same. Thus, NR may still be the same light shade as seen in the previous micrographs, but when placed alongside a lighter NBR phase the camera may have adjusted the contrast so it appears darker.

To try and explain the change in contrast of Breon brought on by the ODIP accelerator, it was decided to examine some of the above samples in their unvulcanized form. Four samples were chosen and these were the 25:75 and 75:25 NR:Breon blends with the TMTD and the ODIP accelerators. The micrographs showed that in all cases the NBR was the darker phase and NR the lighter phase, with the zinc oxide particles preferentially, but not exclusively, located in the NR phase. The micrographs of the blends containing TMTD were almost identical to their vulcanized counterparts so are not reproduced in this thesis, but the micrographs of the blends containing ODIP are shown in Figure 4.4 (samples 9030 and 9034). Thus it seems that the Breon crosslink density is so much lower when vulcanized with the ODIP accelerator, that a dramatic change in refractive index occurs.
Figure 4.4. Phase contrast micrographs of unvulcanized NR/Breon blends with ODIP.
4.3 Differential Scanning Calorimetry

The DSC measurements were carried out on a Perkin-Elmer DSC7 as described in Chapter 2, and the results are represented in graphical form of $T_g$ against NBR content in the blends (Figures 4.5 - 4.8).

4.3.1 NR/Perbunan

NR and Perbunan have $T_g$ values that are very close to each other, which means that determination of their individual values is slightly problematical. For single polymers an initial long straight baseline is taken to obtain the gradient of the transition slope, but in a blend consisting of close $T_g$ values there is only a short straight line between the ending of one transition and the beginning of the next. Thus any slight deviations within a short line would give large errors and hence necessitated a large number of repeat determinations.

i) TMTD accelerated blends  (Figure 4.5)

![Figure 4.5. Glass Transition Temperature versus Percentage NBR Content. NR/Perbunan - TMTD.](image-url)
The overall trend in $T_g$ values for the Perbunan phase is to decrease with increasing NBR content, with the largest differences occurring at lower NBR content. All the $T_g$ values are higher than that of the parent Perbunan vulcanizate. For NR the $T_g$ values change very little across the blend ratios but they appear to decrease with increasing NBR at low NBR content and increase at high NBR content, with a minimum around the even blend ratio. All the $T_g$ values for the NR phases are lower than the value for the parent NR vulcanizate.

ii) ODIP accelerated blends  (Figure 4.6)

![Figure 4.6. Glass Transition Temperature versus Percentage NBR Content. NR/Perbunan - ODIP.](image)

The Perbunan shows decreasing $T_g$ values with increasing NBR level at initially low NBR content, and then a slight increase in $T_g$ at high NBR content, but this is within experimental error. All the values are higher than the $T_g$ of the parent Perbunan vulcanizate. NR has very little change in the $T_g$ values but they do appear to decrease at low NBR content and increase at high NBR content, with the lowest value being at the 50:50 NR:NBR blend. The $T_g$ values are all very close to that of the parent NR vulcanizate.
Comparison of the two accelerator systems shows that the NR $T_g$ values, when the ODIP accelerator is used, are slightly higher than the comparable values with TMTD. The reverse is true for the Perbunan phase, which exhibits a large difference in $T_g$ values when it is the minor component in the blend, but above 50% NBR the values become very similar, irrespective of the accelerator used.

4.3.2 NR/Breon

The $T_g$ values of the individual phases are far enough apart so that a long straight baseline can be achieved between them, thus enabling greater reproducibility of the results.

i) TMTD accelerated blends  (Figure 4.7)

The change in the $T_g$ values for both the NR and Breon phases is very small. For NR there appears to be no change, within experimental error, with all the values being well below that of the parent NR vulcanizate, and close to that of unvulcanized rubber. For Breon the trend in the $T_g$ values is to decrease from low NBR content, to a minimum at 50% NBR and then slightly increase to a high NBR content. However, this slight upward trend could be within experimental error. All the values for the Breon phase in the blends are above that for the parent Breon vulcanizate.
Figure 4.7. Glass Transition Temperature versus Percentage NBR Content for
(a) Breon and (b) NR. NR/Breon - TMTD.
ii) ODIP accelerated blends  (Figure 4.8)

For the Breon phase the $T_g$ has a minimum value at the 65/35 NR/NBR ratio blend, with the values either side of this increasing, but their values are all lower than the $T_g$ of the parent vulcanizate. However, NR increases its $T_g$ value from -68°C in the single polymer vulcanizate, across increasing NBR content in the blends, to -62°C in the 25/75 NR/NBR blend, which is a very large change compared to the few degrees that it changed over the same blend ratio difference in the other systems. This dramatic change in the $T_g$ values is unique to this blend system.
Figure 4.8. Glass Transition Temperature versus Percentage NBR content for (a) Breon and (b) NR. NR/Breon - ODIP.
Comparison of the two accelerator systems shows that for NR the $T_g$ values of the ODIP accelerated system are higher than those for the TMTD accelerated system, especially so at higher NBR content of the blends. The $T_g$ values for Breon are however much lower for the ODIP accelerated blends.

4.4 Conclusions

For NR/Perbunan blends accelerated with TMTD, the Perbunan phase in the blends has much higher $T_g$ values than its parent vulcanizate, which suggests much greater crosslinking. Correspondingly, the lower $T_g$ values for the NR phase in the blends, compared to the parent vulcanizate, suggests less crosslinking. Thus a maldistribution of crosslinks is evident which favours the Perbunan phase.

The effect of changing the accelerator from TMTD to ODIP, is an increase in crosslinking in the NR phase and a decrease in crosslinking in the Perbunan phase, as shown by the higher $T_g$ values for NR and the lower $T_g$ values for Perbunan. In fact the $T_g$ values for the NR phase are now higher than or equal to that for the parent NR vulcanizate.

The phase sizes of the components in the NR/Breon blends are much larger than those in the NR/Perbunan blends, and therefore the initial distribution of the curatives is the dominating factor, and far outweighs any diffusion that may occur during vulcanization.

Changing the accelerator from TMTD to ODIP greatly alters the $T_g$ values for both the NR and Breon phases. While the $T_g$ values in the Breon phase drop to below the value of the parent Breon vulcanizate, the values for the NR phase rise above that of the NR parent vulcanizate.

A more comprehensive investigation is carried out on the behaviour of crosslinking in NR/NBR blends using $^1$H nmr analysis (Chapter 5).
Chapter 5

Determination of Crosslink Densities in Blends

5.1 Introduction

For the distribution of crosslinks, the application of a recent NMR technique employed by Loadman and Tinker\textsuperscript{3} is used to estimate the degree of crosslinking in the individual phases of blends of NR and NBR. The glass transition temperatures ($T_g$) of the blends are also used to determine the crosslink densities of the two phases of the blends, based on a derived correlation between $T_g$ and crosslink density for single polymer vulcanizates.

5.2 NMR Technique

5.2.1 Introduction

Loadman and Tinker\textsuperscript{3} have shown that peak broadening in the continuous wave $^1$H NMR spectrum of a swollen vulcanized blend can be used to estimate the degree of crosslinking of the individual phases. The method involved the estimation of a measure of peak width in the NMR spectrum of a swollen vulcanize, H%, and the determination of its empirical relationship to the degree of crosslinking of the rubber indirectly via parameters which either determine or reflect the degree of crosslinking. These include:

(a) measuring H% as a function of the amount of curative added,

(b) measuring torque rise in the evaluation of cure behaviour by the Monsanto ODR rheometer, and

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Assessment of the peak broadening as well as the correction terms used for each rubber, necessary because of overlapping of the olefinic signals of the two rubbers in the vulcanized blend, are discussed in detail below. Loadman and Tinker's results demonstrated that there is good correlation between H% and $v$, in chloroform for both NR and NBR gum vulcanizates.

5.2.2 Background

A suitable signal in the spectrum of each swollen rubber needed to be identified in order to measure the peak broadening. At first the signal from the methyl protons of NR were used and the peak broadening measured indirectly as the ratio of the height of the valley between this signal and that due to the methylene protons, to the height of the methyl signal. The technique was very sound for NR on its own but unfortunately when blended with other rubbers it was found that there was overlapping with the methyl and methylene signals. Instead the olefinic signal was used for both the NR and NBR evaluation (Figure 5.1).

\[
\text{CH}_3 \quad \text{H*} \quad \text{H*} \quad \text{H*} \quad \text{CN} \\
\downarrow / \quad \downarrow / \quad \downarrow / \\
\text{C = C} \quad \text{C = C} \quad \text{CH} \\
\downarrow \quad \downarrow \quad \downarrow \quad \downarrow \\
\sim \text{CH}_2 \quad \sim \text{CH}_2 \sim \quad \sim \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \sim \\
\text{NR} \quad \text{NBR}
\]

* olefinic protons

Figure 5.1 The structure of NR and NBR.

For NR, peak broadening was assessed indirectly as the ratio of signal strength at a chosen
reference point on the high field side of the peak to the signal strength at the peak. To overcome baseline deviation, the baseline was estimated by averaging the signal strength over 0.5 ppm at low field and then subtracting this from the signal strengths at the reference and peak positions before the ratio was calculated. This ratio is expressed as a percentage (H%, H = signal strength). As the crosslinking of the rubber increases the NMR peak becomes broader and hence H% increases.

Figure 5.2 NMR signals of the olefinic regions of NR and NBR.

Figure 5.2 is a diagrammatical representation of the NMR signals of the olefinic regions of NR and NBR, and of their relative chemical shift positions to each other. The positions of
the reference points, relative to the peak positions, for NR and NBR (a and e respectively) were chosen so that H% would give good differentiation between values for a wide range of crosslinking densities. The olefin signal of the butadiene rubber lies on the low field side of the olefin signal of NR, so in order to ensure the maximum discrimination between the blends, the reference position for the NBR was chosen on the low field side of its olefin peak.

When a blend of the two rubbers is analysed by NMR, the olefinic signals of the rubbers overlap and thus make estimation of the degree of crosslinking of the individual phases impossible by direct observation. A method was adopted that allowed contribution of the olefinic signal of one polymer, in the region of the signal for the other one, to be corrected for, and which was also independent of the proportion of the two polymers in the blend. This is done by relating the correction to the peak height and the peak broadening of the olefin signal of the rubber under study. Each rubber requires two correction terms, the first rubber will have one relating to the position of the peak of the second rubber, and also one to the chosen reference position of the second rubber.

With reference to Figure 5.2, the term used to make allowances for the contribution of the NR olefinic signal which is seen at the peak position of the NBR olefinic signal is

\[ P%H = 100 \times \frac{c}{b} \]  

and the term to allow for the contribution of the NR olefinic signal at the chosen reference position for the NBR olefinic signal is

\[ R%H = 100 \times \frac{d}{b} \]  

The correction terms for the contribution of NBR to the peak and the reference positions of the NR olefinic signal are:
The $P%H$ and $R%H$ values are plotted against $H%$ for a range of crosslink densities and the best-fit curve applied.

The $H%$ value for the individual phases of the blend must be calculated. First of all $H%$ is evaluated for one of the rubbers and the corresponding $P%H$ and $R%H$ values calculated from the second order polynomial equations. The correction factors to be applied to the signal at the peak and reference positions of the other rubber are calculated from the observed signal strength at the peak position for the original rubber. By subtracting the corrections from the appropriate observed signal strength for the second rubber, $H%$ and then the corresponding $P%H$ and $R%H$ can be calculated. From the corrected signal strength at the peak position for the second rubber, the magnitude of the corrections to be applied to the signal strengths of the first rubber can be calculated. By subtracting the corrections from the observed signal strengths of the first rubber, the whole procedure can be repeated until the $H%$ values for both rubbers do not vary by any significant amount. In this iterative procedure, after the initial step of the calculation for the first rubber, all the magnitudes of the correction terms are calculated from $P%H$, $R%H$ and the corrected signal strength at the peak position, and then these are subtracted from the observed signal strengths.

Loadman and Tinker\textsuperscript{83} demonstrated the method on a 60:40 NR:NBR blend and approached the analysis from both angles by using the NR as the first rubber in the procedure and then using NBR as the first rubber. Both gave the same values for $H%$. When performing duplicate runs they discovered that there was a certain disparity in their values for the NBR phase and this was put down to two factors:

(i) the correction term relationships of $P%H$ and $R%H$ against $H%$ did not cover a wide
enough range so that there was some uncertainty at high values of H%,

(ii) the magnitude of the peak broadening made the measurement difficult due to the signal strength being low.

Putting this disparity aside they still found the trend that the NBR phase had a greater H% and hence a greater degree of crosslinking. The NBR phase was crosslinked to a much higher degree than expected while the NR was crosslinked to a much lower degree.

When used in conjunction with chemical probe techniques investigations could be made into the effects of blending on the ratio of poly-, di-, and monosulphidic linkages.

The analysis of the blends takes place after they have been swollen in a suitable solvent for forty-eight hours to achieve equilibrium swelling. For the NR/NBR blends deuterochloroform was used as it has a similar interaction parameter with both rubbers. This was initially thought to be important, since excessive differential swelling could possibly cause distortion in the estimates of H%. On further investigation of the relation between H% and v, it was discovered that H% is only slightly dependent on the degree of swelling for Vulcanizates swollen to less than equilibrium\textsuperscript{66}.

5.2.3 Experimental

\textsuperscript{1}H NMR spectra of the single polymer vulcanizates of NR, Perbunan and Breon were obtained using a General Electric QE300 spectrometer. The original work was carried out on a Perkin-Elmer R32 NMR spectrometer that operates at 90MHz, but unfortunately it did not stay in operation for the duration of this study. Thus all the work was transferred to a new spectrometer, the QE300, that operates at 300MHz and the spectra produced were vastly superior to those obtained from the R32 spectrometer. Signal width is not only dependent on mobility of the polymer chains but also magnetic strength and other instrumental factors which affect resolution, so changing the NMR spectrometer was obviously going to affect the NMR spectra. The higher field strength produced much higher resolution (sharper signals),
but the width of the signal was still dependent on crosslink density. Thus the results obtained from the QE300 were very similar to those from the R32 (see section 5.2.4). For the purposes of this thesis a good correlation between H% and crosslink density was required. H% is obtained from selecting an arbitrary reference position from which to compare the height of the peak. By altering the reference position and acquiring different H% values, many graphs of H% against crosslink density could be plotted. The graph chosen was the one that gave the best relationship between H% and crosslink density. With this reference position, relative to the peak position, fixed for the appropriate polymer (NR +0.197ppm, Perbunan -0.123ppm and Breon -0.148ppm), it was necessary to obtain repeated spectra of each vulcanize so that H% values that agreed closely with each other could be obtained. Usually only 2 or 3 spectra were required to achieve this.

Another important factor in determining H% was the location of the olefinic peak. This does not represent a problem in the spectra of the single polymers, but in the spectra of the blends the overlapping signals will distort each other, and in some cases the peaks that are visible will not be the true peaks of the rubbers. Thus a procedure was required where the correct peak of the rubber could be determined. Each spectrum was examined to find the separation between a large standard peak and the olefinic peak. The standards looked at were the chloroform and TMS signals. However, it was found in most cases, apart from Breon, that these standard signals had secondary signals and that these gave consistent separations to the olefinic peaks, especially so in the case of the TMS secondary signal. The fact that these smaller signals change shape and position in synchrony with the polymer signals suggests that they originate from solvent within the swollen polymer. Thus the solvent is in the same environment as the polymer. Hence the location of the olefinic peak could be determined from the TMS secondary peak in the case of NR and Perbunan, and from the main TMS signal in the case of Breon.

In the NR/Perbunan blends only one TMS secondary signal is visible, despite the fact that both have secondary signals in the NMR spectra of their single polymers. This could mean that the magnetic environments of the solvent in both rubbers are so close that they cannot be separated.
The spectra of the blends have overlapping signals that have to be split into their respective polymers, and this is done by using the P%H and R%H values discussed earlier. Their equations are essential in determining the 'shape' of the olefinic signal so that the blends can be analysed by deconvolution. When the H% values of both phases have been determined then their crosslink densities can be worked out from the H% versus crosslink density graph.

5.2.4 Results and Discussion

Figures 5.3 - 5.5 are NMR spectra for single polymer vulcanizates of NR, Perbunan and Breon respectively.

Figure 5.3. 300MHz NMR spectrum of swollen NR vulcanizate.
Figure 5.4. 300MHz NMR spectrum of swollen Perbunan vulcanizate.

Figure 5.5. 300MHz NMR spectrum of swollen Breon vulcanizate.
The signals observed in the region of 4ppm to 7ppm are from the olefinic protons of unsaturated rubbers, and as can be seen they are well separated from other signals. Both NBR vulcanizates have several olefinic peaks and these correspond to the cis-1,4-, trans-1,4- and 1,2- isomers	extsuperscript{94}. The peaks at 0ppm and 7.2ppm are the tetramethylsilane and chloroform signals respectively, which both exhibit secondary peaks to the down field of their main peaks. The region between 1ppm and 3ppm has peaks due to the alkyl signals, and also sharp signals due to water and other low molecular weight impurities. The location of the olefinic peak is done by using the TMS secondary signal as the reference position for NR and Perbunan, and the TMS main signal as the reference for Breon:

\[
\begin{align*}
\text{NR olefinic peak location} &= \text{TMS secondary signal} - 5.13\text{ppm} \\
\text{Perbunan olefinic peak location} &= \text{TMS secondary signal} - 5.41\text{ppm} \\
\text{Breon olefinic peak location} &= \text{TMS} - 5.56\text{ppm}
\end{align*}
\]

Figures 5.6 - 5.9 are plots of P%H and R%H against H% for the respective single polymer vulcanizates.

![Graph](image)

**Figure 5.6.** Plot of P%H and R%H against H% for NR (corrections to Perbunan).
Figure 5.7. Plot of P%H and R%H against H% for NR (corrections to Breon).

Figure 5.8. Plot of P%H and R%H against H% for Perbunan (corrections to NR).
Figure 5.9. Plot of P%H and R%H against H% for Breon (corrections to NR).

The corrections for the other vulcanizates are stated to show which peak and reference positions were used to obtain the P%H and R%H values. These are only required for the vulcanizates which are to be blended together, which is why NR has corrections for both Perbunan and Breon. The equation for the relationships of P%H and R%H with H% is calculated by using GLIM (Generalised Linear Interactive Modelling System 3.77) a statistical modelling programme which fits an equation in terms of a constant and coefficients for the variables. The 'fit' for each equation is calculated using the t-test (a measure of the significance of each response coefficient), and when the criterion for this are met the curve is plotted.

NR
Corrected for Perbunan:

\[ P%H = -0.601 + 0.876H% - 0.00207H%^2 + 0.0000363H%^3 \]  

(24)
\[ R\% H = -0.490 + 0.354 H\% + 0.0000381 H\%^3 \] (25)

Corrected for Breon:

\[ P\% H = -0.803 + 0.474 H\% + 0.0000379 H\%^3 \] (26)

\[ R\% H = -0.4141 + 0.299 H\% + 0.00003888 H\%^3 \] (27)

**Perbunan**

\[ P\% H = 6.62 + 0.0622 H\% + 0.0208 H\%^2 - 0.000138 H\%^3 \] (28)

\[ R\% H = 3.59 + 0.504 H\% + 0.00292 H\%^2 \] (29)

**Breon**

\[ P\% H = 6.82 + 0.172 H\% + 0.0069 H\%^2 - 0.0000199 H\%^3 \] (30)

\[ R\% H = 0.903 + 0.187 H\% + 0.00431 H\%^2 \] (31)

Figures 5.10 - 5.12 show the dependence of peak width, H\%, on physical crosslink density for the gum vulcanizates of NR, Perbunan and Breon respectively.
Figure 5.10. Plot of H% against crosslink density for NR.

Figure 5.11. Plot of H% against crosslink density for Perbunan.
Figure 5.12. Plot of H% against crosslink density for Breon.

The points are the average crosslink density values obtained from equilibrium stress-strain measurements on the Greensmith apparatus, and the H% values obtained from $^1$H NMR measurement. At very high crosslink densities the relationship is not very good, with large changes in crosslink density only producing small changes in H%. For this study H% values encountered in the NR:NBR blends were not high enough to be in this region and so alteration of the reference position for determination of H% was not necessary. The GLIM programme was used to fit the best equation to the relationship between H% and crosslink density so that H% values obtained from the analysis of the individual phases of the blends could be converted into crosslink density values (v).

\[ H\% = 4.29 - 0.106v + 0.0185v^2 - 0.000108v^3 \]  

NR

H% = 4.29 - 0.106v + 0.0185v² - 0.000108v³  

(32)
\[ H\% = 6.80 + 0.482v + 0.00196v^2 - 0.0000130v^3 \]  

(33)

\[ H\% = 5.55 + 0.479v + 0.0735v^2 - 0.0000517v^3 \]  

(34)

Spectra for 50:50 NR:NBR blends containing both the TMTD and ODIP accelerators are shown in Figures 5.13 - 5.16.

Figure 5.13. NMR spectrum of a 50:50 NR:Perbunan blend containing the TMTD accelerator.
Figure 5.14. NMR spectrum of a 50:50 NR:Perbunan blend containing ODIP.

Figure 5.15. NMR spectrum of a 50:50 NR:Breon blend containing TMTD.
The peak widths show that NR is lightly crosslinked, while Perbunan is highly crosslinked. When altering the accelerator to ODIP (Figure 5.14) it is clear that the peak widths have changed for both NR and Perbunan, but in different ways. The NR peak width has increased, indicating greater crosslinking, while the Perbunan peak width has decreased, which indicates a lessening in crosslink density. At this stage without actual crosslink density values it is impossible to know how close the crosslink densities are between the two phases, but it is clear that the wide differences in crosslink densities between the two phases in the TMTD accelerated blend is much reduced in the ODIP accelerated blend.

Figure 5.15 is a spectrum of a 50:50 NR:Breon blend containing the TMTD accelerator. The peak widths show that NR is very weakly crosslinked, while Breon is very heavily crosslinked. When the accelerator is substituted with ODIP (Figure 5.16) there is a distinct reversal in the shape of the peak widths, with NR being much more crosslinked and Breon being much less crosslinked. The Breon phase has such a sharp peak that it must be very
lightly crosslinked.

From analysis of the NMR spectra of the NR:NBR blends to obtain their constituent H% values, the crosslink densities given in Figures 5.17 - 5.20 could be determined.

![Crosslink density graph](image)

Figure 5.17. Plot of crosslink density against NBR content for NR:Perbunan blends containing TMTD.

NR/Perbunan blends (Figure 5.17) clearly show a decrease in crosslink densities in the Perbunan phase as the amount of Perbunan in the blend increases, and an increase in crosslink densities within the NR phase as the NR level increases. This is because the increase in NR allows a greater proportion of the total curatives to diffuse into the NBR phase, as they are preferentially attracted to NBR. But as the NBR content decreases, the saturation point of the NBR phase is reached and thus fewer curatives can migrate to the NBR phase, so leading to an increase in the crosslink density of the NR phase. The Perbunan phase has greater crosslink density in the blends than it does in its parent vulcanizate, while the NR phase in the blends has lower crosslink densities than its parent vulcanizate, which again suggests the migration of curatives towards the NBR phase.
Figure 5.18. Plot of crosslink density against NBR content for NR:Perbunan blends containing ODIP.

The effect of changing the accelerator from TMTD to ODIP (Figure 5.18) is an increase in solubility of the curatives in the NR phase and a decrease in the NBR phase. However, this levelling-off effect is not complete as the crosslink densities of NR are still lower. The crosslink densities for the individual phases in the blends are still greater than the parent vulcanizate for Perbunan and lower than the parent vulcanizate for NR, but the differences are significantly less.
Figure 5.19. Plot of crosslink density against NBR content for NR:Breon blends containing TMTD.

The analysis of the NR/Breon blends with the TMTD accelerator (Figure 5.19), shows that the relationships of crosslink density with NBR content is the same as that for NR/Perbunan blends, but the difference between the two rubbers is more pronounced. This is due to the preferential distribution of the curatives (which are polar) into the Breon, which has a higher polarity compared to Perbunan. The crosslink densities of the Breon phase in the blends are much greater than that of its parent vulcanizate, while the NR phase in the blends has crosslink densities which are far below that of its parent vulcanizate, and in some cases the crosslink densities are so insignificant that this technique cannot accurately determine their values.
With the ODIP accelerated system (Figure 5.20), the maldistribution of crosslinks is completely reversed with the NR phase having crosslink densities close to that of the single NR polymer, and Breon having crosslink densities of about one-seventh that of the single polymer. Thus the less polar ODIP accelerator is more soluble in the less polar NR polymer.
5.3 DSC Technique

5.3.1 Introduction

The crosslink densities of the individual phases in NR/NBR blends can also be determined using DSC analysis. Calibration curves of $T_\delta$ against crosslink density are generated for the single polymers and then applied to the $T_\delta$ values obtained from the individual phases of the blends.

5.3.2 Experimental

With the previous work on the $T_\delta$ values of the blends already carried out (Chapter 4), only the $T_\delta$ values of the individual polymer vulcanizates were required. The vulcanizates underwent differential scanning calorimetry on the Perkin-Elmer DSC7, as described in section 2.8. The DSC technique is not a very accurate analytical tool and so a number of runs had to be carried out on each sample until duplicates within acceptable agreement were obtained.

When all the samples had been analysed, the calibration curves of $T_\delta$ against crosslink density were produced (Figures 5.21 - 5.23).

GLIM was used to produce the equations for the curves as described in section 5.2.4.
Figure 5.21. Plot of glass-transition temperature against crosslink density for NR.

Figure 5.22. Plot of glass-transition temperature against crosslink density for Perbunan.
Figure 5.23. Plot of glass-transition temperature against crosslink density for Breon.

5.3.3 Results and Discussion

NR

\[ T_g = -71.4 + 0.0398v + 0.000241v^2 \]  

(35)

Perbunan

\[ T_g = -59.4 + 0.00179v^2 - 0.00000662v^3 \]  

(36)

Brecon

\[ T_g = -22.5 + 0.0451v + 0.00000430v^2 \]  

(37)
Using the equations above, which are obtained from the calibration curves of $T_g$ against crosslink density (Figures 5.21 - 5.23), the $T_g$ values for the individual phases in the NR:NBR blends could be converted into crosslink density values (Figures 5.24 - 5.27).

**Figure 5.24.** Plot of crosslink density against NBR content for NR:Perbunan blends containing TMTD.
Figure 5.25. Plot of crosslink density against NBR content for NR:Perbunan blends containing ODIP.

Figure 5.26. Plot of crosslink density against NBR content for NR:Breon blends containing TMTD.
The discrepancies are very large in some cases but this is due to the very low slope of the plot of $T_s$ against crosslink density, so any small deviation in $T_s$ results in a large deviation in crosslink density.

In the NR/Perbunan blends containing the TMTD accelerator, the crosslink densities of both phases decrease with increasing NBR content of the blends, but the Perbunan phase always contains the greater crosslink density values due to the preferential distribution of curatives in the NBR phase. For the Perbunan component the DSC method shows little change in crosslink densities between the low NBR content blends, and a large difference in the crosslink densities between the high NBR content blends. The opposite trend is seen in the Perbunan phase when NMR analysis was carried out, while the NR phase shows the same trend in behaviour for crosslink densities using both analytical procedures.

The NR/Perbunan blends with the ODIP accelerator have very similar crosslink densities in both phases, which coupled with the large error bars makes it very difficult to differentiate
between them. The NMR work produced a similar situation but the crosslink densities of the two phases could just be resolved.

The NR/Breon blends with the TMTD accelerator show a similar trend for crosslink densities to that of the NR/Perbunan blends containing the same accelerator. The distribution of crosslink density between the phases of the NR/Breon blends with the ODIP accelerator now favours the NR phase. This reversal in the distribution of crosslinks is probably due to polarity affects, as described earlier. With increasing NBR content in the blends, the crosslink densities in both phases increase. This trend is also seen in the blend when analysed by NMR, but a discrepancy between the two arises in the level of increase seen in the NR phase. The blends analysed by DSC have the crosslink density of the NR phase increasing by about two and a half times over the range 0% to 75% NBR content, while the blends analysed by NMR have very little change in crosslink densities in the NR phase over the same range.

To investigate this discrepancy the two rubber phases were analysed by a new microscopy technique, 'network visualization', where the vulcanizate is swollen to equilibrium in styrene and the styrene polymerized. Ultra-thin sections were then taken from the resulting composite and stained with osmium tetroxide prior to viewing by transmission electron microscopy (TEM). A mesh structure comprising strands of rubber in a polystyrene matrix is revealed and the mean size of the mesh cells is correlated with the molecular weight between crosslinks, $M_c$. Furthermore, relatively large regions of polystyrene accumulate at weaknesses within the vulcanizate - around zinc oxide particles for instance or in the case of blends at weak interfaces.

The micrograph of the sample (Figure 5.28) is shown at a magnification of 230,000 times. The NBR phase is characterized by a larger mesh size and thicker mesh strands, which is to expected because work done by Cook has shown that the relationship between the mesh size and $M_c$ is dependent on the nature of the elastomer, in particular the difference between the solubility parameters of the rubber and polystyrene - the greater the difference the larger the mesh size for a given crosslink density. The difference is four times greater for Breon N41 than for NR. Strand size is believed to be similarly related to difference in solubility parameters of the rubber and polystyrene.
NR phase

NBR phase

0.1μm

Figure 5.28  TEM micrograph of a 25:75 NR:Breon blend accelerated with ODIP, prepared for 'network visualization'.

Without doing any measurements of the networks it is clear from previous work, that the crosslink density in the NR phase is much less than the 100 mol/m³ obtained from the DSC method and very close to the 50 mol/m³ from the NMR method.
Figure 5.29. TEM micrographs of NR vulcanizates prepared for 'network visualization' of crosslink densities; (a) 50 mol/m$^3$ and, (b) 100 mol/m$^3$. 

---

0.1μm
Figure 5.29 shows two micrographs of NR vulcanizates with crosslink densities of 50 and 100 mol/m³, and from these it can be seen that the former micrograph has mesh sizes that are similar to those of the NR phase in the 25:75 NR:Breon blend. Thus the styrene swelling coupled with TEM analysis, and the NMR analysis give very similar results for the crosslink density distribution in blends. The DSC analysis does not appear to be as accurate as the previous two methods and thus the results obtained from NMR analysis of the crosslink density distribution in the 25:75 NR:Breon N41 are taken as the most reliable. However, the apparent dependence of \(T_g\) on crosslink density is due to main chain modifications during sulphur vulcanization and therefore \(T_g\) is dependent on efficiency of vulcanization as well as the level of crosslink density (Appendix 1).

Further observation of the blend shows that there appears to be extensive voiding at the interfaces between phases. Figure 5.30a shows voiding at the interface between the rubbers as well as voiding within the NBR phase. Closer examination of this latter voiding shows that it is also occurring at an interface because there is a microdomain of NR present within the NBR phase. Figure 5.30b is a higher magnification micrograph and clearly shows the extensive separation with only occasional network material linking the two rubbers. This suggests very little crosslinking between the two rubbers and hence the blend may suffer from weak interfacial adhesion\(^8\).
Figure 5.30. TEM micrograph of a 25:75 NR:Breon blend prepared for 'network visualization'.
Chapter 6

Determination of Crosslink Types

6.1 Chemical Probes

A review of chemical probes is carried out in section 1.2.6. Probably the most useful chemical probes are the 'thiol-amine reagents' because they allow the quantitative estimation of the proportions of poly- and disulphidic crosslinks in a network. Campbell and Saville\textsuperscript{55} showed that an equimolar solution of propane-2-thiol and piperidine or hexane-1-thiol and piperidine is capable of cleaving model di- and polysulphides quite rapidly at room temperature. The propane-thiol/piperidine reagent reacts with disulphides at room temperature at least 1000 times more slowly than with trisulphides and use is made of this to cleave quantitatively the polysulphides. Hexane-1-thiol and piperidine cleave poly- and disulphides quantitatively, within a few hours at room temperature. Thus knowing the number of original crosslinks present as well as the fraction of these crosslinks cleaved by each of these reagents, it is possible to characterize the network in terms of the number of poly-, di- and monosulphidic crosslinks originally present.

6.2 Probe Treatment.

6.2.1 Introduction

The hexane-1-thiol probe was used to cleave the poly- and disulphidic crosslinks in the sample (reaction pathways 1 and 2, Figure 6.1), and thus the equilibrium stress-strain analysis carried out subsequently gives the physical crosslink density values associated with the
monosulphidic crosslinks. The propane-2-thiol probe reagent is used to cleave only polysulphidic crosslinks (reaction pathway 1, Figure 6.1), so that the physical crosslink densities associated with both the di- and monosulphidic crosslinks could be obtained.

1) \[ \text{RS}^- + \text{[SS]}^\text{x} \rightarrow \text{[SSr]} + \text{[SS]}^\text{x} \]

2) \[ \text{RS}^- + \text{[S]}^\text{L} \rightarrow \text{[SSr]} + \text{[S]}^\text{L} \]

\[ \text{RS}^- + \text{[S]}^\text{L} \rightarrow \text{no reaction} \]

Figure 6.1 Sulphidic crosslink cleavage.

Subtraction of the data from these two probe treatments would then reveal the physical crosslink density of the disulphidic linkages on their own. With this knowledge the physical crosslink density of the polysulphidic linkages could be obtained from the crosslink density of the untreated sample which contains all three types of sulphidic crosslinks. This is an approximation in the sense that it is the chemical crosslinks that are removed, and physical crosslink density is not proportional to chemical crosslink density.

6.2.2 Experimental

The single polymer vulcanizates successfully underwent propane-2-thiol treatment (see section 2.13) and their crosslink densities were determined from equilibrium stress-strain analysis using the Greensmith apparatus (see section 2.10). The initial probe treatment using hexane-1-thiol reagent (see section 2.13) showed immediately that the NR vulcanizates (samples 9011 and 9012) contained very little or no monosulphides at all, as they disintegrated in the solution. The remaining samples survived the probe treatment intact but only the Breon samples were strong enough to undergo equilibrium stress-strain analysis using the Greensmith apparatus. Thus as an alternative, NMR analysis (see section 5.2.3), was carried out in order to obtain the physical crosslink density data for the hexane-1-thiol treated
samples (Table 6.1). Consequently, as the two probe systems were being used in conjunction with each other, the analytical technique had to be kept the same, and thus the propane-2-thiol treated samples were also analysed using the NMR technique (Table 6.1).

<table>
<thead>
<tr>
<th>Rubber</th>
<th>SMR L</th>
<th>Perbunan</th>
<th>Breon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accelerator</td>
<td>TMTD</td>
<td>TMTD</td>
<td>TMTD</td>
</tr>
<tr>
<td>Sample No.</td>
<td>9011</td>
<td>9013</td>
<td>8935</td>
</tr>
<tr>
<td>Untreated</td>
<td>55.9</td>
<td>53.6</td>
<td>62.6</td>
</tr>
<tr>
<td>Propane-2-thiol treatment</td>
<td>25.4</td>
<td>43.7</td>
<td>89.2</td>
</tr>
<tr>
<td>Hexane-1-thiol treatment</td>
<td>0</td>
<td>31.0</td>
<td>75.3</td>
</tr>
</tbody>
</table>


The problem encountered with the NBR vulcanizates was that they took a long time to achieve constant weight when drying, after both probe treatments. For the Breon samples a period of 3 months in vacuo was common. The resulting crosslink densities showed that this had a deleterious affect because the values measured were greater than those before probe treatment. While only two samples showed this increase it cast doubt on the validity of the other values. A study of the effect of time using NMR analysis of the samples as they dried over a 3 month period, clearly showed an increase in crosslink densities, but the largest increase occurred within the first two weeks (Figures 6.2 and 6.3).
Figure 6.2. Crosslink density variation with time of propane-2-thiol treated vulcanizates.

Figure 6.3. Crosslink density variation with time for hexane-1-thiol treated vulcanizates.
The factor that needed to be eliminated was the drying period. A lot of stress can be applied to a sample during drying due to the outer layer drying before the inside does. Thus the samples had to be analysed while still in the swollen state. This did not present a problem on further NMR analysis but meant that neither the stress-strain nor the volume swelling methods could be carried out.

The method adopted was washing the probed samples with chloroform instead of petroleum spirit (see section 2.13). This kept the samples swollen and also made it possible to solvent exchange the chloroform with deuterochloroform in order to prepare the samples for NMR analysis. The results from this experiment were very good (Table 6.2a) and the same procedure was applied to the 50:50 NR:NBR blends (Table 6.3a). Due to the collapse of the NR vulcanizates after the hexane-1-thiol probe treatment, new vulcanizates were produced (9207 and 9208) with triple the curative levels of the originals (9011 and 9012). It was hoped that by doing this that proportionately more monosulphidic crosslinks would be produced and hence the rubbers would survive the hexane-1-thiol treatment. As the curatives had been increased proportionately then the ratio of the crosslinks within the vulcanizates should still be roughly the same and so comparisons could still be made.
### Table 6.2a. Crosslink densities for single polymer vulcanizates before and after chemical probe treatment.

<table>
<thead>
<tr>
<th>Rubber</th>
<th>SMR L</th>
<th>Perbunan</th>
<th>Breon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accelerator</td>
<td>TMTD</td>
<td>ODIP</td>
<td>TMTD</td>
</tr>
<tr>
<td>Sample No.</td>
<td>9207</td>
<td>9013</td>
<td>8935</td>
</tr>
<tr>
<td>Untreated</td>
<td>106</td>
<td>53.6</td>
<td>62.6</td>
</tr>
<tr>
<td>Propane-2-thiol treatment</td>
<td>39.4</td>
<td>20.2</td>
<td>38.5</td>
</tr>
<tr>
<td>Hexane-1-thiol treatment</td>
<td>0</td>
<td>21.8</td>
<td>28.5</td>
</tr>
</tbody>
</table>

### Table 6.2b. Percentage of crosslink types for single polymer vulcanizates.

<table>
<thead>
<tr>
<th>Rubber</th>
<th>SMR L</th>
<th>Perbunan</th>
<th>Breon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accelerator</td>
<td>TMTD</td>
<td>ODIP</td>
<td>TMTD</td>
</tr>
<tr>
<td>Sample No.</td>
<td>9207</td>
<td>9208</td>
<td>9013</td>
</tr>
<tr>
<td>Polysulphides</td>
<td>63%</td>
<td>59%</td>
<td>38%</td>
</tr>
<tr>
<td>Disulphides</td>
<td>37%</td>
<td>0%</td>
<td>16%</td>
</tr>
<tr>
<td>Monosulphides</td>
<td>0</td>
<td>41%</td>
<td>46%</td>
</tr>
</tbody>
</table>

Table 6.2a. Crosslink densities for single polymer vulcanizates before and after chemical probe treatment.

Table 6.2b. Percentage of crosslink types for single polymer vulcanizates.
### Table 6.3a. Crosslink densities for 50:50 NR:NBR blends before and after chemical probe treatment.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>9003</th>
<th>9008</th>
<th>9027</th>
<th>9032</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accelerator</td>
<td>TMTD</td>
<td>ODIP</td>
<td>TMTD</td>
<td>ODIP</td>
</tr>
<tr>
<td>Rubber</td>
<td>Perb.</td>
<td>NR</td>
<td>Perb.</td>
<td>NR</td>
</tr>
<tr>
<td>Untreated</td>
<td>86.0</td>
<td>21.2</td>
<td>57.0</td>
<td>43.9</td>
</tr>
<tr>
<td>Propane-2-thiol treatment</td>
<td>74.3</td>
<td>0</td>
<td>35.0</td>
<td>0</td>
</tr>
<tr>
<td>Hexane-1-thiol treatment</td>
<td>39.1</td>
<td>0</td>
<td>22.5</td>
<td>0</td>
</tr>
</tbody>
</table>

### Table 6.3b. Percentage of crosslink types for 50:50 NR:NBR blends.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>9003</th>
<th>9008</th>
<th>9027</th>
<th>9032</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accelerator</td>
<td>TMTD</td>
<td>ODIP</td>
<td>TMTD</td>
<td>ODIP</td>
</tr>
<tr>
<td>Rubber</td>
<td>Perb.</td>
<td>NR</td>
<td>Perb.</td>
<td>NR</td>
</tr>
<tr>
<td>Polysulphides</td>
<td>14%</td>
<td>100%</td>
<td>39%</td>
<td>100%</td>
</tr>
<tr>
<td>Disulphides</td>
<td>41%</td>
<td>0%</td>
<td>22%</td>
<td>0%</td>
</tr>
<tr>
<td>Monosulphides</td>
<td>45%</td>
<td>0%</td>
<td>39%</td>
<td>0%</td>
</tr>
</tbody>
</table>


Table 6.3b. Percentage of crosslink types for 50:50 NR:NBR blends.
6.3 Results and Discussion

The time study on the propane-2-thiol treated vulcanizates (Figure 6.2) showed that during the 85 days the crosslink densities of Perbunan and Breon vulcanizates increased very slightly but the change was within experimental error. However the NR vulcanizates had an increase in crosslink densities of one-and-a-half times that of their initial values over 85 days, with the greatest increase coming within the first two weeks. The original analysis carried out on the probe treated samples was done on the vulcanizates when they had dried down to constant weight. In the case of the NBR vulcanizates this usually took over 2 months which this study has shown does not make any significant difference to the crosslink density values. The NR vulcanizates were usually analysed within the first two weeks, due to their short drying down period, which the time study has shown is the period when the crosslink density increases the most, and thus the crosslink densities recorded would be too high (Table 6.1).

The time study on the hexane-1-thiol treated vulcanizates (Figure 6.3) showed that the crosslink density values of all the vulcanizates increased significantly with time. The crosslink densities of the NBR vulcanizates increased by almost two fold over 76 days, while in the same time period the crosslink density of the NR vulcanize, accelerated with TMTD, increased from an amount very close to zero, to 44 mol/m³, with the greatest increase coming within the first two weeks. The ODIP accelerated NR vulcanizate disintegrated during treatment due to the lack of monosulphidic crosslinks. These results show that the previous analysis of hexane-1-thiol treated samples would have produced erroneously high crosslink density values because they were all analysed after drying down to constant weight (Table 6.1).

The increase in crosslink densities of the vulcanizates after probe treatment can be explained by oxidation of the rubbers. Once the vulcanizates have undergone probe treatment, pendant thiol groups are left in the rubber network and these can oxidize to reform to sulphidic linkages (Figure 6.4).
Using the technique of washing the probe treated samples with chloroform and then solvent exchanging with deuterochloroform ready for NMR analysis, avoided any drying period and also kept the vulcanizates swollen so that no deleterious affects from drying were incurred. The results are shown in Table 6.2a. The crosslink densities of the Perbunan vulcanizates after hexane-1-thiol probe treatment are higher than after propane-2-thiol probe treatment, but the difference is so small as to be well within experimental error and thus the two values can be assumed to be the same. Comparison of Tables 6.1 and 6.2a clearly shows the difference in the crosslink densities after probe treatment, with the latter table containing the much lower values, as expected.

The concentrations of the sulphidic crosslinks can now be calculated:

\[
\begin{align*}
\text{Untreated vulcanizate} & = \text{poly-} + \text{di-} + \text{mono-sulphidic crosslinks} \quad (a) \\
\text{Propane-2-thiol treated vulcanizates} & = \text{di-} + \text{mono-sulphidic crosslinks} \quad (b) \\
\text{Hexane-1-thiol treated vulcanizates} & = \text{monosulphidic crosslinks} \quad (c)
\end{align*}
\]

\[
\begin{align*}
\text{Monosulphidic crosslinks} & = (c) \\
\text{Disulphidic crosslinks} & = (b) - (c) \\
\text{Polysulphidic crosslinks} & = (a) - (b)
\end{align*}
\]

Using sample 8935 (Breon/TMTD) as an example (Table 6.2a):

\[
\begin{align*}
\text{Untreated vulcanizate} & = 62.6 \text{ mol/m}^3 \\
\text{Propane-2-thiol treated vulcanizate} & = 38.5 \text{ mol/m}^3
\end{align*}
\]
Hexane-1-thiol treated vulcanizate = 28.5 mol/m³

Monosulphidic crosslinks = 28.5 mol/m³ = 46%
Disulphidic crosslinks = 10.0 mol/m³ = 16%
Polysulphidic crosslinks = 24.1 mol/m³ = 38%

The percentage of sulphidic crosslink types are shown in Table 6.2b for the single polymer vulcanizates, and in Table 6.3b for the blends.

For the single polymers (Table 6.2b), the NR vulcanizates contain mainly polysulphidic crosslinks with either extremely low monosulphide levels or none at all. The TMTD accelerated NR vulcanizate contains about a third crosslinks which are disulphidic, while the ODIP accelerated NR has only about a fifth disulphidic crosslinks.

Perbunan vulcanizates contain predominantly polysulphidic crosslinks but no disulphidic crosslinks. For the TMTD accelerated Perbunan vulcanizate, the crosslinks consist of less than two-thirds polysulphides while the rest are monosulphides. For the ODIP accelerated vulcanizates the crosslinks consist of less than three-quarters polysulphides and just over a quarter monosulphides. The lack of disulphides is puzzling because maturation should produce them from the polysulphides. In butadiene-based rubbers the presence of vinyl side groups can lead to carbon-carbon crosslinks. Skinner has shown that polybutadienes produce very few monosulphide crosslinks, and thus it could be possible that for the NBR vulcanizates the crosslink recorded after hexane-1-thiol treatment are due mainly to carbon-carbon crosslinks. Therefore the crosslinks in the Perbunan vulcanizates could be almost entirely polysulphidic in nature.

The Breon vulcanizate containing the TMTD accelerator contains two-fifths polysulphidic crosslinks, a sixth disulphidic crosslinks and less than a half monosulphidic crosslinks. The ODIP accelerated Breon vulcanizate consists of about a third each of poly- and monosulphidic crosslinks and about two-fifths disulphidic crosslinks. If in fact there are only a few monosulphides in the Breon vulcanizates then the disulphides will be the dominant crosslinks.
The percentages of the crosslink types for the 50:50 NR:NBR blends are shown in Table 6.3b. The NBR phases are shown to be mainly monosulphidic, but if this also includes the carbon-carbon crosslinks then the NBR phases are mainly di- and monosulphidic, which still represents efficient vulcanization. The NR phase in the blends is completely polysulphidic in nature, which means inefficient vulcanization, much worse than in the parent single polymer vulcanizate of NR. The exception is the NR phase in the higher acrylonitrile blend that is accelerated with the ODIP accelerator, which shows better vulcanization efficiency than in its parent single polymer, with only a fifth polysulphidic crosslinks and the remainder being disulphidic crosslinks. The Breon phase of this blend also contains a quarter of polysulphidic crosslinks but the remainder are all monosulphidic, which is much more efficient than its single polymer counterpart, but the level of crosslinking is very much lower. Even if the level of monosulphidic crosslinks does contain a large number of carbon-carbon crosslinks the difference between the blend and single polymer is still significant. The Breon phase in the other blend containing the TMTD accelerator is predominantly monosulphidic like its parent single polymer vulcanizate, but the blend has more disulphidic and less polysulphidic crosslinks which shows more efficient vulcanization. The Perbunan phase has greater efficiency in vulcanization in the TMTD accelerated blend, which is shown by its greater predominance of mono- and disulphidic crosslinks compared to polysulphidic crosslinks. The ODIP accelerated Perbunan phase also shows greater efficiency in vulcanization compared with its parent vulcanizate, with greater predominance in di- and monosulphidic crosslinking.

The overall result is that the NBR phases in the blends have more efficient vulcanization, while the reverse is true for NR. The exception is the NR phase in the NR:Breon blend accelerated with ODIP, which has more efficient vulcanization than its parent single polymer vulcanizate (see Chapter 7 for further discussion on partitioning of accelerators and accelerator derived species).

The roles of phase morphology and crosslinking at the interface are discussed in Chapter 7.
Chapter 7

General Discussion

7.1 Introduction

The results from four main areas of this work are correlated together. These are the tensile strength, NMR, probe treatment and phase morphology analyses. Thus the processing/structure/property relationships can be dealt with.

7.2 Discussion of Factors Influencing Vulcanization and Crosslink Determination

The NMR technique has provided the means to investigate accurately the crosslink density distribution between the phases of blends. Prior to discussion of the results it is necessary to explain a number of phenomena which may be occurring in blend materials.

7.2.1 Solubility Parameters and Diffusion

Preferential location of accelerators within a blend occurs very rapidly at vulcanization temperatures, and curatives distribute themselves according to solubility parameters even before vulcanization is initiated. During the curing process the production of vulcanization intermediates\textsuperscript{10} occurs, and these also move between the phases of the blend. As vulcanization proceeds the curatives and their reaction intermediates have the opportunity to diffuse between the phases and each will do so to maintain their preferred distribution.

Furthermore, diffusion is a dynamic process which continues until all curatives are depleted.
Diffusion is not an instantaneous process and thus diffusion over-large distances may take some time to occur. Hence in blend systems, the phase sizes play an important role in the crosslink density distribution.

Table 7.1 represents solubility parameters adapted from Antal and Gardiner. Polymers with solubility parameters that are close to each other will give small phase sizes when mixed sufficiently.

<table>
<thead>
<tr>
<th>Material</th>
<th>Solubility parameter (MPa)$^{0.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber</td>
<td>16.8</td>
</tr>
<tr>
<td>Perbunan N1807</td>
<td>19.0</td>
</tr>
<tr>
<td>Breon N41</td>
<td>20.1</td>
</tr>
<tr>
<td>TMTD</td>
<td>24.0</td>
</tr>
<tr>
<td>Sulphur</td>
<td>29.8</td>
</tr>
</tbody>
</table>

Table 7.1. Solubility parameters of the rubbers and curatives.

The solubility parameter of ODIP is not to be found in the literature, but an estimate of its value is made later on in this chapter (see section 7.5). The values in Table 7.1 imply that NR/Perbunan blends should have smaller phase sizes than those of NR/Breon and this is in fact the case as determined by phase contrast microscopy (Chapter 4). The micrographs of the 50/50 NR/NBR blends show that the phase sizes for NR/Perbunan blends are less than 1μm, while those for NR/Breon blends are of the order of 20μm, for either accelerator system. Calculations were carried out by Gardiner, who used Einstein’s equation for Brownian motion, which he modified for diffusion in only one direction:

\[ X = (Dt)^{1/2} \]

\[ X = \text{width of the diffusion zone, m} \]
\( t = \text{time, s} \)

\( D = \text{diffusion coefficient, m}^2\text{s}^{-1} \)

Diffusion coefficients are in the range of \(10^{-11}\) to \(10^{-12}\) m\(^2\)s\(^{-1}\) for many rubbers and curatives\(^9\). Based on this, the time for the curatives to diffuse 1\(\mu\)m would be between 0.1 and 1 second, while to diffuse 20\(\mu\)m would take from 40 seconds to almost 7 minutes. Obviously the distances are related to the location within the phase, and only curatives travelling from the centre of one phase to the centre of the other phase would have to traverse the full distance. Thus for the NR/Breon blends the large phase sizes will have a major influence on the level of curative diffusion.

### 7.2.2 Determination of Crosslinking by Rheometry

All the blends in this work were cured to \(t_{\text{max}}\) as determined by rheometry. Rheometry of single polymers is straightforward in that maximum torque values relate to maximum crosslink densities. In blends however, the rheometer torque is mainly influenced by the continuous phase, the disperse phase having a lesser influence. A 70:30 NR:NBR blend, in which the NBR forms a disperse phase in an NR matrix, is likely to show maximum rheometer torque values close to the time when the NR is highly crosslinked. The NBR phase may have already become fully cured but may not have influenced the overall torque to a great extent because it is enveloped in a soft matrix.

Figures 7.1 - 7.2 and 7.6 - 7.7 show respectively a summary of the crosslink densities \((n_{\text{phy}})\) for the 50/50 NR/Perbunan and 50/50 NR/Breon blends and their single polymer vulcanizates, and the percentage of the poly-, di- and monosulphide crosslinks within each phase.
7.3 NR/Perbunan Blends

7.3.1 NR/Perbunan - TMTD

Figure 7.1 illustrates that the overall crosslink density, based on polymer ratio, observed for the 50/50 NR/Perbunan blend is very similar to the combined crosslink density of the single polymer vulcanizates. However, the crosslink densities of the individual components are quite dissimilar. In the blend, the crosslink density of NR is greatly reduced, while the crosslink density of Perbunan is greatly increased, compared to their respective single polymer values. The NR single vulcanizate contains only poly- and disulphidic crosslinks, whilst in the blend the NR network is purely polysulphidic in nature, indicating that the vulcanization efficiency is less than in its single polymer.

The single polymer vulcanizate of Perbunan appears to contain only poly- and monosulphidic crosslinks. This lack of disulphidic crosslinks is unusual as maturation processes would be expected to produce disulphides from the polysulphides. The discrepancy could be due to carbon-carbon crosslinks in the vulcanizate (see Chapter 6), which the probe treatment analysis would erroneously identify as monosulphidic. Thus the sulphur network of the single polymer vulcanizate of Perbunan could consist entirely of polysulphidic crosslinks.

As a component of the blend, the Perbunan phase contains all three types of crosslinks. The level of monosulphidic-crosslinks may be lower than that given by the probe treatment result, due to the presence of carbon-carbon crosslinks, but a large proportion of the crosslinks in this phase are disulphidic. Therefore, the Perbunan phase in the blend has a higher vulcanization efficiency than that which occurs in the single polymer.

The less efficient vulcanization in the NR phase of the blend could be due to a lower accelerator to sulphur ratio. This would lead to the sulphur chains not being broken down into smaller constituents, due to insufficient accelerator being present to carry out the procedure. Conversely, the more efficient vulcanization system of the Perbunan phase could be due to a higher accelerator to sulphur ratio. Combining these two factors, it would appear
Polysulphides (%): 100, 15
Disulphides (%): 0, 40
Monosulphides (%): 0, 45
Cure time (min): 4.75

Single Polymers

Polysulphides (%): 64, 60
Disulphides (%): 36, 0
Monosulphides (%): 0, 40
Cure time (min): 3.5, 16

Figure 7.1. Comparison of a 50/50 NR/Perbunan blend and the respective single polymers, with TMTD as the accelerator.
that accelerator or vulcanization intermediates have diffused into the Perbunan phase from the NR phase. This would also help explain the change in crosslink densities between the single polymers and the components in the blend.

The phases of the NR/Perbunan blends are both co-continuous, and thus, on morphological grounds, neither phase should dominate the rheometer torque. The cure time for the blend is slightly longer than that for the NR single polymer value but significantly shorter than that for the single polymer Perbunan. Again this would also suggest that there is less accelerator present in the NR phase than the Perbunan phase, which would support the observed vulcanization efficiency.

7.3.2 NR/Perbunan - ODIP

With the ODIP accelerator (Figure 7.2) the overall crosslink densities, based on polymer ratio, observed for the single polymers and the blends are very similar. The crosslink density of NR in the blend is lower than observed for its single polymer vulcanizate, while the reverse is seen with Perbunan. This was also seen in the TMTD accelerated system, but the difference in crosslink densities between the two phases, is smaller for the ODIP accelerated system.

The sulphidic crosslinks in the NR single polymer are only poly- and disulphidic, but when NR is blended with Perbunan, only polysulphidic crosslinks are detected. This follows the trend seen with the TMTD accelerated system but the change is not as large because the ODIP accelerated NR single polymer is much more polysulphidic in nature than the TMTD accelerated NR single polymer.

The Perbunan phase changes from mainly polysulphidic in nature in the single polymer, to a more evenly balanced distribution of crosslink lengths in the blend. The existence of monosulphides in the single polymer and the level in the blend is again in doubt, but the conclusion that in the blend the vulcanization efficiency is increased, compared to the single polymer, is still justified by the level of disulphides, and suggests that more accelerator or
**Figure 7.2.** Comparison of a 50/50 NR/Perbunan blend and the respective single polymers, with ODIP as the accelerator.
vulcanization intermediates exist in the Perbunan phase than the NR phase. However, as the level of change in both the vulcanization efficiency and crosslink densities between the single polymers and the blend is less than that seen in the TMTD accelerated system, it would suggest that not as much of the ODIP accelerator or its vulcanization intermediate exists in the Perbunan phase.

Due to the co-continuous phase morphology, neither phase should have a greater influence over the rheometer torque. The cure time for the blend is slightly closer to the cure time for the single polymer vulcanize of Perbunan than that of the single polymer vulcanize of NR. This would seem to suggest that the curatives favour the Perbunan phase, but not to the same degree as in the TMTD accelerated system. This again supports the conclusion that in the blend the vulcanization efficiency is increased.

7.3.3 Factors Affecting the Vulcanization Behaviour of NR/Perbunan Blends

The solubility parameters of sulphur and TMTD are much closer to the value of Perbunan than NR (Table 7.1), and so, when the two rubbers are mixed, the curatives are expected to be preferentially located in the former rubber. The crosslink density distribution in the blends would also seem to indicate that the curatives are preferentially distributed in the Perbunan phase during vulcanization. By comparison of the TMTD accelerated system with the ODIP accelerated system, the smaller difference in crosslink density distribution between the rubber phases of the latter system would suggest that ODIP might have a solubility parameter that is closer to the NR polymer than that for TMTD.

Based on solubility parameters, the Perbunan phase should contain a larger amount of accelerator, therefore a large amount of reaction intermediates could be formed quickly, resulting in maximum crosslinking being achieved much more rapidly i.e. the time to maximum cure could be very small.

Conversely, the smaller amount of accelerator in the NR phase of the blend, could mean that the production of the intermediates takes longer, as would the time to achieve maximum crosslinking i.e. maximum cure will only be reached after a longer time.
Due to the small phase sizes in the NR/Perbunan blends, the curatives and the reaction intermediates can redistribute themselves rapidly between the phases to overcome any depletion in the levels. Thus the lesser amount of accelerator in the NR phase could mean that all the accelerator in this phase is consumed very quickly, and the crosslinking reaction effectively halts. Any accelerator not consumed by reaction in the Perbunan phase will be diffusing, and if it crosses over into the NR phase, it could then be consumed to form crosslinks there.

This dynamic process continues until the final result is that the cures for both phases achieve maximum crosslinking. The total crosslink density in the blends and the single polymers is therefore similar.

The tensile strengths of the single polymer vulcanizates (Figure 7.3) demonstrates the higher values of the NR vulcanizates compared to those of the Perbunan vulcanizates, which is not surprising, given that NR is a strain-crystallizing polymer. It also shows that the Perbunan vulcanizates have very poor tensile strengths.

![Graph showing tensile strength in MPa for NR/TMTD, NR/ODIP, PERBUNAN/TMTD, PERBUNAN/ODIP](image_url)

**Figure 7.3.** Tensile strengths for single polymer vulcanizates.
It has been proven that physical properties are dependent on the nature of the crosslinks\textsuperscript{98}, and that polysulphidic crosslinks per se are more effective than other types of crosslinks in providing networks of high strength\textsuperscript{99}. At low crosslink densities though the strength is essentially independent of the crosslinking structure\textsuperscript{98}.

Figure 7.4 shows the tensile strengths of the NR:Perbunan blends and the overall trend would seem to be a decrease in tensile strength as the NBR content increases, which is to be expected due to the lower tensile strength of the NBR single polymers compared to that of the NR single polymers. Also the ODIP accelerated blends have slightly greater tensile strengths than the TMTD accelerated blends.

![Tensile strength vs NBR content graph](image)

**Figure 7.4. Plot of tensile strength against NBR content of the NR:Perbunan blends.**

By comparing the average tensile strengths that would be expected in the blends if no other physical property changed, with the tensile strengths that were obtained from measurement, differences in values are seen (Table 7.2).
<table>
<thead>
<tr>
<th>NBR content (%)</th>
<th></th>
<th>Tensile strength (MPa)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NR/Perbunan TMTD</td>
<td></td>
<td>NR/Perbunan ODIP</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Expected</td>
<td>Actual</td>
<td>Expected</td>
<td>Actual</td>
</tr>
<tr>
<td>25</td>
<td>21.2</td>
<td>25.2</td>
<td>19.4</td>
<td>25.1</td>
</tr>
<tr>
<td>35</td>
<td>18.8</td>
<td>19.3</td>
<td>17.3</td>
<td>25.8</td>
</tr>
<tr>
<td>50</td>
<td>15.2</td>
<td>18.3</td>
<td>14.0</td>
<td>20.8</td>
</tr>
<tr>
<td>65</td>
<td>11.6</td>
<td>17.7</td>
<td>10.8</td>
<td>19.2</td>
</tr>
<tr>
<td>75</td>
<td>9.20</td>
<td>15.8</td>
<td>8.70</td>
<td>16.2</td>
</tr>
</tbody>
</table>

Table 7.2. Expected and actual tensile strengths for NR/NBR blends.

For the NR/Perbunan blends the actual values are higher than those of the expected values, especially so at the high NBR contents. The difference is more notable for the ODIP accelerated blends, where some of the actual tensile strengths are almost twice the expected values.

A closer examination of the 50:50 NR:Perbunan blends and the relationship between tensile strength and crosslink density is shown in Figure 7.5.
In the NR/Perbunan blends, the tensile strength increases when changing the accelerator from TMTD to ODIP. There is also a rise in the crosslink density of the NR phase and a fall in the crosslink density of the NBR phase. The NR phase has a lower crosslink density value than the Perbunan phase, which should result in a low tensile strength for the blend, if the tensile strengths for the parent single polymer vulcanizates are compared. However, the
crosslink densities of the two rubber phases are much closer to an even distribution, and therefore will have better tensile strength.

With the Perbunan phase having very little polysulphidic crosslinks, even less than its parent polymer, the strength of the blends should suffer. The NR phase is completely polysulphidic in nature and while this is a weak crosslink, it results in a stronger material. To add to this, the crosslink density of the NR phase is much higher in the ODIP accelerated blend, than in the TMTD accelerated blend.

**7.4 NR/Breon Blends**

**7.4.1 NR/Breon - TMTD**

Figure 7.6 illustrates that when cured with the accelerator TMTD, the NR/Breon blend and the single polymer vulcanizates are very similar to their Perbunan counterparts. The main difference is that the NR phase in the NR/Breon blend has a much lower crosslink density, when compared to the NR phase in the NR/Perbunan blend. Results for the percentage of crosslink types show that the NR phase of the blend undergoes a less efficient vulcanization than the NR parent polymer. For Breon, whilst the amount of monosulphidic crosslinks may be incorrect for the reasons stated earlier in the discussion of NR/Perbunan blends, the Breon phase appears to have a more efficient vulcanization system than the Breon single polymer.

In the NR/Breon blends the total crosslink density is much lower in the blends than in the single polymers. Based on solubility parameters, almost all the curatives should be in the Breon phase, and this is shown by the greater crosslink density for Breon and the very low crosslink density for NR. The phase morphology of the blend is of a disperse NBR phase in an NR matrix. This should mean that the rheometer torque is mainly influenced by the NR, but due to the very low crosslink density of NR, compared to NBR, this is not the case. The low level of crosslinking in the NR phase will mean that the cure rate is lower, therefore the time to maximum cure for the blend will be closer to the maximum cure time for the NBR.
Figure 7.6. Comparison of a 50/50 NR/Breon blend and the respective single polymers, with TMTD as the accelerator.

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7.4.2 NR/Breon - ODIP

The NR/Breon blends vulcanized with the ODIP accelerator (Figure 7.7) appear to follow a different pattern from the other blends discussed. For the NR phase of the blend the efficiency of vulcanization has increased compared to the parent single polymer, while for the NBR phase of the blend the efficiency of vulcanization has decreased compared to the parent single polymer. This latter statement on the NBR phase is based on the fact that the lack of disulphides should also indicate a lack of monosulphides. As mentioned previously, the large percentage of monosulphidic crosslinks indicated by the probe treatment might be carbon-carbon crosslinks (formed by a radical process) and thus the sulphidic crosslinks in the Breon phase are purely polysulphidic.

The large phase sizes in the blends of these two rubbers (Chapter 4, Figure 4.3) means that diffusion distances are large and thus during vulcanization, diffusion between phases will mainly occur close to the interface. Since there is little crosslinking in NBR, and NBR is the disperse phase in the blend, the effect on the rheometer trace will be very minimal. Thus the time to maximum cure for the blend will be closer to the maximum cure time for the NR phase.

7.4.3 Factors Affecting the Vulcanization Behaviour of NR/Breon Blends

The low level of curative diffusion expected to occur between the phases of the NR/Breon blends could result in one phase consuming all its available curatives, while the other phase continues curing. In the TMTD accelerated blend the curative level in the NR phase is very low before vulcanization proceeds, and thus, even though the curing will be slow the curatives could be depleted in the NR phase before the NBR phase.

This could result in reversion in the cure of the NR, but as the crosslink density in this phase
Figure 7.7. Comparison of a 50/50 NR/Breon blend and the respective single polymers, with ODIP as the accelerator.
is very low it will not affect the cure curve of the blend very much. When the crosslinking in the NBR phase has reached a maximum, or possibly just before reaching a maximum if the NR cure has an effect, the cure curve for the blend should then plateau, in which case the curing is stopped. The result is an NR phase that has a crosslink density below the maximum achievable under the circumstances, while the NBR phase has a crosslink density equal to the maximum, or slightly below it. This could explain why the overall crosslink density for the blend is lower than that of the single polymer vulcanizates where maximum crosslinking is achieved.

Alternatively, the rate of crosslinking in the NBR phase could be very fast, so that the maximum crosslinking in the NBR phase is reached while the NR is still slowly curing. The cure curve for the blend will soon begin to plateau, since the low level of crosslinking in the NR phase will mean that the cure for the NBR phase will dominate. Again, the result is an NBR phase that is at, or very close to, maximum crosslinking and an NR phase that is below the maximum achievable crosslinking.

For the ODIP accelerated blend a similar situation to the TMTD accelerated blend exists, except that the NBR is the low crosslink density phase. This is accentuated by the sulphur and accelerator being preferentially located in different phases i.e. sulphur in the Breon phase, and accelerator in the NR phase. Thus, the cure rate in the Breon phase is extremely slow, and given enough time the Breon would cure to a reasonable level. Unfortunately, the Breon phase is not given the time to do this, and the result is a poorly crosslinked phase. The NR phase has very little sulphur, but due to the large phase sizes, will not be able to obtain any more sulphur, and so uses its supply very quickly.

The tensile strengths of the single polymer vulcanizates (Figure 7.8) show that the Breon vulcanizates have very good tensile strengths, indeed, much better than those exhibited by the Perbunan vulcanizates (Figure 7.3). The NR vulcanizates though still have the higher tensile strengths.
Figure 7.8. Tensile strengths for single polymer vulcanizates.

Figure 7.9. Plot of tensile strength against NBR content of the NR:Breon blends.
Figure 7.9 shows the tensile strengths of the NR/Breon blends and the trend of decreasing tensile strength with increasing NBR content is similar to that of the NR/Perbunan blends. The actual values for NR/Breon blends, though, are lower than those for NR/Perbunan blends, which would not be expected, due to the higher tensile strengths of the single polymer Breon vulcanizates compared with the Perbunan vulcanizates.

Comparison of the expected average tensile strengths in the blends (if no other physical property changed) with the tensile strengths that were obtained from measurement are shown in Table 7.3.

<table>
<thead>
<tr>
<th>NBR content (%)</th>
<th>Tensile strength (MPa)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NR/Breon TMTD</td>
<td>NR/Breon ODIP</td>
<td>Expected</td>
<td>Actual</td>
<td>Expected</td>
</tr>
<tr>
<td>25</td>
<td>24.8</td>
<td>15.5</td>
<td>24.3</td>
<td>17.7</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>23.9</td>
<td>11.6</td>
<td>24.1</td>
<td>15.6</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>22.5</td>
<td>9.78</td>
<td>23.8</td>
<td>12.9</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>21.0</td>
<td>10.2</td>
<td>23.5</td>
<td>9.65</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>20.1</td>
<td>8.71</td>
<td>23.3</td>
<td>9.00</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.3. Expected and actual tensile strengths for NR/Breon blends.

For the NR/Breon blends the measured values are much lower than the averaging of the tensile strengths would predict. At high NBR content the differences are very large. For the ODIP accelerated blends, the expected tensile strengths would differ by 1MPa between the lowest and highest NBR content blends, while over the same range the actual tensile strengths differed by 8.7MPa. Obviously the blending of the two rubbers does not occur with
arithmetic combination of their properties into the correct proportions with respect to polymer ratio of the blends. Many factors change and these affect the properties of the blends.

A closer examination of the 50:50 NR:NBR blends and the relationship between tensile strength and crosslink density is shown in Figure 7.10.

<table>
<thead>
<tr>
<th>Blend system</th>
<th>Tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR/Breon</td>
<td>9.78</td>
</tr>
<tr>
<td>TMTD</td>
<td></td>
</tr>
<tr>
<td>NR/Breon</td>
<td>12.9</td>
</tr>
<tr>
<td>ODIP</td>
<td></td>
</tr>
</tbody>
</table>

Figure 7.10. Comparison of tensile strength and crosslink density for 50:50 NR:Breon blends.
For the TMTD accelerated blend the crosslink density of the NR phase is very low and the crosslink density of the NBR phase is very high. This could produce a weak interface between the two rubber phases and thus result in a very low tensile strength. Also, due to the low crosslink density of the NR phase, the NR cannot contribute its high strength to the blend.

For the ODIP accelerated NR/Breon blend, the situation exists where the curatives are not both preferentially located in the same phase, as they are in the other NR/NBR blends, but instead are located in separate phases. Thus, the highly efficient vulcanization in the NR phase is based on a low level of sulphur, while the low efficiency of vulcanization in the Breon phase is based on a high level of sulphur. Infact there may be insufficient time for all the sulphur to react in the Breon phase. As the crosslink density of the Breon phase is very low and that of the NR phase is fairly good, there could be a weak interface. However, as the NR phase has a superior crosslink density value, it is the NR phase which dominates and, the tensile strength of the blend is, thus, greater than that of the TMTD accelerated NR/Breon blend when NR is the continuous phase.

7.5 Solubility Parameter of ODIP

There is no literature value for the solubility parameter of ODIP, but from the values of the rubbers and curatives quoted in Table 7.1, and the behaviour of the crosslink distribution, it is possible to form an educated guess as to its value. The solubility parameter for sulphur and TMTD would dictate that they are more soluble in both the NBR polymers compared to the NR polymer. This has been seen in the blends of NR and Perbunan from the biasing of the crosslinking in favour of the NBR phases. When compared to the TMTD accelerator, the solubility parameter for ODIP would seem to be closer to the NR polymer, due to the more even distribution of crosslinking between the phases of the blend. As the maldistribution of crosslinks still favours the Perbunan phase, the solubility parameter for ODIP must still be closer to Perbunan than NR.

From the analysis of the ODIP accelerated NR/Breon blends, where the maldistribution of
crosslinks heavily favours the NR phase, it would appear that the solubility parameter of ODIP is closer to the NR polymer than the Breon polymer. Based on all this data and the values shown in Table 7.1, the ODIP accelerator would seem to have a solubility parameter of about 18(MPa)$^{0.5}$.

7.6 Conclusions

An NR/Perbunan blend vulcanized with the TMTD accelerator gave much more crosslinking in the NBR phase, compared to the NR phase. One of the aims of this project was to reduce this imbalance. Initially a less polar analogue of the accelerator, ODIP, was used, and this resulted in a more even distribution of crosslinks, but still with a bias towards the NBR phase.

To test the influence of polymer polarity upon curative distribution and, hence, crosslink distribution, a higher acrylonitrile rubber, Breon N41, was used. Its greater polarity increased the bias towards crosslinking in the NBR phase, in blends cured with TMTD. However, with the less polar ODIP, the maldistribution was reversed, with the bias now in favour of the NR phase.

Chemical probe analysis showed that for the NR/Perbunan blends, the ODIP accelerator resulted in crosslinks containing longer sulphur chains. This more polysulphidic nature together with the more even distribution of crosslinks, produced better tensile properties. For the NR/Breon blends the ODIP accelerator produced a network comprising mainly of short sulphur crosslinks. This less polysulphidic network would be expected to give lower strength properties, but for the concomitant change in crosslink distribution. As the crosslink density in the NR phase was raised to a reasonable level, and the crosslink density in the NBR phase reduced, the properties of NR dominate in 50/50 blends and a higher tensile strength results.
8.1 Conclusions

It was found that for a standard injection moulding cure system for NR/Perbunan (18wt% acrylonitrile) blends, using the accelerator TMTD, a higher level of crosslinking was observed in the NBR phase, due to the relatively polar accelerator preferentially locating in the more polar NBR phase.

The use of the lower polarity accelerator, ODIP, in the NR/Perbunan blends resulted in a more even distribution of crosslinks, but still with a bias towards NBR.

The small phase sizes of the NR/Perbunan blends allowed diffusion of curatives and reaction intermediates to take place during vulcanization. This meant that an equilibrium could be set up between the two phases, so that both phases could cure to optimum crosslinking. This would result in maximum crosslinking being achieved in both of the rubber phases at the same time.

When a higher acrylonitrile rubber, Breon N41 (41wt% acrylonitrile), was used with the TMTD accelerator, its greater polarity resulted in a higher level of crosslinking in the NBR phase. When the less polar accelerator, ODIP, was used, the distribution of crosslinks was completely reversed with the bias towards the NR phase.

The large phase sizes of the NR/Breon blends meant that diffusion across the interface during vulcanization was only possible for the curatives close to the interface. Hence the initial location of the curatives, based on solubility parameters, was virtually permanent. This could possibly result in neither phase being cured to optimum crosslinking, and so maximum
crosslink density was not achieved.

For the NR/NBR blends the less polar accelerator gave a better balance of crosslinks between the phases, and consequently the tensile properties of the blends improved.

Examination of crosslink types showed that for the NR/Perbunan blends the less polar accelerator resulted in crosslinks containing longer sulphur chains, and this more polysulphidic nature together with the more even distribution of crosslinks, gave better tensile properties.

For the NR/Breon blends the lower polarity accelerator produced a network comprising mainly of short sulphur crosslinks. This less polysulphidic network would be expected to have given lower strength properties, but for the concomitant change in crosslink distribution. Because the crosslink density in the NR phase was raised to a reasonable level, and the crosslink density in the NBR phase reduced, the properties of NR dominate in 50/50 blends and a higher tensile strength results.

The dramatic effect of the reversal in crosslink density distribution in the NR/Breon blends due to a change in accelerator, means that there is the possibility to alter crosslink density distribution in any blend system where there is a difference in polarity between the elastomers. The best tensile strengths were found in the blends that contained a more even distribution of crosslinking between the phases and also had an adequate crosslink density in the NR phase. Thus with the use of the correct accelerator, the uneven distribution can be reduced or totally eliminated so that blends with the best tensile properties can be produced.

8.2 Further Work

For the ODIP accelerated blends, the crosslinking in the NR/Perbunan N1807 blends is biased in favour of the Perbunan phase, whilst in the NR/Breon N41 blends the crosslinking is biased in favour of the NR phase. Thus an intermediate acrylonitrile content NBR would need to be blended with NR to see if the crosslink density was evenly distributed.
NR and NBR have quite different solubility parameters and this results in limited degree of mixing at the interface of a blend. As the crosslinking between the two phases occurs within this mixed interphase, then this can cause insufficient linking between the phases, and this weakness would lead to premature failure. Differential swelling should be carried out on the blends to investigate the interfacial adhesion. From the analysis it could be discovered which blends are to be avoided, and possibly what needs to be done to improve interfacial adhesion.

In NR/Breon blends the phase sizes are very large, and although good tensile strengths can be obtained, other properties would not be as satisfactory. Work undertaken by Tinker on NR/Breon blends has shown that part substitution of one or both polymers with chlorinated rubbers, chlorosulphonated polyethylene (Hypalon) or polychloroprene (CR), can be very effective in reducing phase sizes substantially. The chlorinated polymers act by locating at the interface between NR and NBR, thereby reducing overall interfacial tension.

Block and graft copolymers are known to be extremely effective in reducing interfacial tension and hence phase size. The general view is that a properly chosen block or graft copolymer can preferentially locate at the interface between the two phases. Ideally this component should be a block or graft with different segments that are chemically identical to those in the respective places. However, the desired effect may still result if one polymer of the graft were to be miscible with or adhered to one of the phases. Graft copolymers of NR and PMMA have been available commercially for a few decades, and the potential of one of these to act as a compatibilizer in NR/NBR blends could be investigated.
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Appendix 1

Work carried out by Tinker (personal communication) shows that for materials with equivalent crosslink density, a change in the efficiency of vulcanization, alters the glass-transition temperature (Figure A).

![Graph showing glass-transition temperature versus physical crosslink density for various cure systems.]

For cure systems of the same efficiency, the correlation between crosslink density and glass-transition temperature is very good, but between the cure systems the difference is large. For example, materials with a glass-transition temperature of -69°C have a difference of over 70 mol/m³ in the crosslink density between the conventional (S:CBS 5:1) and efficient vulcanization (S:CBS 1:5) cure systems. This explains the large discrepancy seen between
crosslink densities obtained from the DSC technique, and those obtained from the NMR technique where the efficiency of vulcanization does not affect the crosslink density.