Development and evaluation of dispersing agents for carbon black filled natural rubber compounds

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DEVELOPMENT AND EVALUATION OF DISPERSING AGENTS FOR CARBON BLACK FILLED NATURAL RUBBER COMPOUNDS

by

J. Anoma G. S. G. Gunewardena

A Doctoral Thesis submitted in partial fulfilment of the requirement for the award of Doctor of Philosophy of Loughborough University

July, 1999

Supervisor: Philip K. Freakley, PhD, FPRI

Institute of Polymer Technology and Materials Engineering

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To,

NIPUNIKA
ACKNOWLEDGEMENTS

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Finally, I am thankful to my husband, Earny Silva, whose patience, sacrifices and unwavering support inspired me to overcome the drawbacks encountered during this study and to complete it.
ABSTRACT

Various additions are used in rubber compounds to accelerate mixing with particulate fillers and to improve behaviour in subsequent processing operations. Cationic surfactants of general structure \([\text{RNH}_2(\text{CH}_2)_3\text{NH}_3]^2+ \cdot 2[\text{R}^'\text{COO}]^-\) can be used in rubber processing as multifunctional additives (MFA) which act as processing aids, accelerators and mould releasing agents. However, with all these beneficial properties an adverse effect of decreased scorch time was observed when N-Tallow - 1,3 diaminopropane dioleate (EN444) was used in the filled natural rubber compound.

The aim of this research is to retain the beneficial effects of cationic surfactants while reducing or eliminating the undesirable effect on scorch time. The following were investigated:

1. Addition of retarders (CTP: N-Cyclohexylthio-phthalimide, Aspirin and Benzoic acid)
2. Synthesis of a new fatty amine (OAS; Octyl amine salt of benzylmalonic acid)
3. An alternative type of processing additive (low molecular weight polystyrene)
4. The capability of fatty amines to allow reduction of natural rubber mastication and mixing of high carbon black loadings

The additions were explored at different levels and both crosslinking and physical properties measured in order to determine optimum levels and gain insight into modes of action. CTP and Aspirin were found to be effective at 1phr loading. OAS was found to be effective at a lower level than EN444, approximately 50% less and to have a reduced effect on scorch time – 30% reduction as compared with 50% with EN444. Low molecular weight polystyrene can be used as an effective filler dispersing agent at low concentrations, without any effect on the cure characteristics. It is shown that low molecular weight polystyrene has the capability to decrease the thermodynamic work of adhesion \(W_{ad}\) between carbon black and rubber. At higher concentrations it has a tendency to reduce the reinforcement efficiency.

In previous work, it was proposed that the optimum level of fatty amine occurred when complete monolayer coverage of the filler surface is achieved. In this work calculations show optimum performance of OAS is achieved at a level well below complete monolayer coverage indicating that the available filler surface area during mixing may be more important than the total area.
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Even though processing aids generally improve processability, they are known to affect the other properties of a rubber compound to varying degrees. To solve these problems researchers have tried to find new chemicals which have multifunctional abilities. In 1983, Hepburn and Mahdi discovered a single compound ingredient which possesses several functions and the term Surfactant - Accelerator Processing Aid (SAPA) was used to describe this concept. This SAPA was categorised as a cationic surfactant whose general structure is,

\[ \text{[R}-\text{NH}_2^+(\text{CH}_2)_3\text{NH}_3]^{2+} 2[\text{R'C}O\text{O}]^- \]

It is suggested that this molecule, which was later renamed as MFA - Multifunctional Additive, remains intact at normal processing temperatures and functions as a roll mill release agent and filler aggregate dispersant. At temperatures
above 135°C, the MFA decomposes into a primary amine and a fatty acid, whose functions are an accelerator and a mould releasing agent respectively.

The mode of action of one specific MFA – EN444 has been studied by several researchers and it was found to give excellent mechanical properties to a rubber vulcanisate at an optimum amount of 2 phr (parts per hundred rubber) of EN444. The improvement in physical properties was attributed to the improved dispersion of carbon black in the rubber matrix by accelerating the incorporation and disagglomeration phases of mixing. The 2phr of EN444 was estimated to give a complete monolayer coverage on 50phr of N330 carbon black surface. Even though these surfactants, based on fatty amines, can accelerate the incorporation and dispersion of fillers in rubber by a very substantial amount, they do however have a problematic effect on rubber compounds by reducing scorch time or safe processing time.

1.2 Objectives of the project

There is still a need for further investigation into multifunctional additives. Firstly, the problematic effect of low scorch time has to be investigated and solved, hopefully by adding other chemicals or using alternative surfactants. The abilities of surfactants to enable the incorporating and mixing of high levels of fillers and the minimisation of mastication by using surfactants have to be studied. Furthermore, the effect of surfactants on product longevity indicators has to be determined.

The specific objectives are given below,
1. Modification or additions to the fatty amines, to reduce or remove the problematic effect on safe processing time.
2. Investigation of alternative surfactants.
3. Determination of the effect of selected surfactant(s) on stress relaxation
4. Determination of the ability of surfactants to enable the mixing of natural rubber
compounds with very high levels of reinforcing fillers.

5. Exploration of minimisation or elimination of the need for mastication by using surfactants - if a surfactant is mixed with natural rubber prior to filler dispersion, it may be possible to get the following results,

[a] a reduction of amount of mastication needed before filler incorporation,
[b] increase in the rates of incorporation and disagglomeration,
[c] improved mechanical properties.
CHAPTER 2
Literature Review

2.1 Introduction

Rubber is found in many of the things used in everyday life and it is of great commercial importance globally. However, the raw material is difficult to use on its own. There are many other materials that can be added to rubber and it has to undergo many processes before it is made into a useful final product. The mixture of rubber and other additives used in rubber manufacturing is known as a rubber compound and the process of making this compound is known as compounding.

A basic rubber compound is made up from the following constituents;
1. Basic polymer or a blend of polymers
2. Crosslinking agent / curing agent
3. Accelerator for the crosslinking reaction
4. Accelerator modifiers (activators and retarders)
5. Antidegrants
6. Reinforcing fillers
7. Processing aids
8. Diluents
9. Miscellaneous/ special additives

Work described in this report is mainly related to the mixing of the above constituents to get the best properties for the vulcanisate with the least cost. First of all, a brief review will be given on natural rubber which is the basic polymer to be used throughout this project. Then the process and mechanism of vulcanisation is discussed briefly. This will be followed by filler reinforcement and mixing, i.e. incorporation and disagglomeration of fillers. Processing aids and surfactants are discussed before coming on to the current understanding of multifunctional additives, which help the processing of rubber in several ways.
2.2 Natural Rubber - Its Formation and Properties

Natural rubber (NR) used for this study is a naturally occurring polymer which is obtained from the tree Hevea brasiliensis. It is a linear long chain polymer with repeating monomer units of isoprene. The structure of the monomer of natural rubber is,

\[
\begin{align*}
\text{CH}_3 \\
\text{CH}_2 - \text{C} - \text{CH} = \text{CH}_2 \\
\text{Isoprene, i.e. 2 methyl 1,4 butadiene}
\end{align*}
\]

Chemically NR is Cis 1,4 Polyisoprene which is made up of about 3000 to 50000 isoprene units and has an average molecular weight of \(3.5 \times 10^5\) to \(10^6\).

Biochemically, the polymerisation of natural rubber occurs via many steps, and many enzymes are involved in this process. Fig. 2.1(1) shows schematically the formation of rubber hydrocarbon.

\[
\begin{align*}
\text{CO}_2 & \quad + \quad \text{H}_2\text{O} \quad \overset{\text{sunlight}}{\longrightarrow} \quad \text{Carbohydrates} \quad \overset{\text{enzymes}}{\longrightarrow} \quad \text{Derivation of Acetic Acid} \\
\text{Isopentenyl} & \quad \overset{\text{enzymes}}{\longrightarrow} \quad \text{Mevalonic acid} \quad \overset{\text{enzymes}}{\longrightarrow} \\
\text{Pyrophosphates} & \quad \overset{(\text{many steps})}{\longrightarrow} \quad \text{Rubber Hydrocarbon}
\end{align*}
\]

Fig. 2.1: Biosynthesis path of rubber hydrocarbon(1)
Natural rubber is accompanied by a small amount of non-rubber substance in addition to hydrocarbon. Even though those substances are present in small amounts, they have a considerable affect upon Vulcanisation and the physical properties of the resulting vulcanisate.

Table 2.1\(^{(2)}\) gives a summary of various materials that are present in NR, although individual samples vary quite widely. The moisture content of rubber depends on temperature and atmospheric humidity. The content of nitrogen containing substances also affects the absorption of water. Nitrogen containing compounds are also effective as activators of vulcanisation. Naturally occurring antioxidants protect NR against oxidation and softening on storage. They are found in the acetone extract which contains various sterols, esters and fatty acids. Sterols are believed to be some of the main natural antioxidants.

**Table 2.1**: Typical results of analysis of materials present in NR\(^{(2)}\)

<table>
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<tr>
<th>Composition</th>
<th>Ribbed Smoked Sheets (RSS)</th>
<th>Pale Crepe</th>
</tr>
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<tbody>
<tr>
<td>Moisture, %</td>
<td>0.61</td>
<td>0.42</td>
</tr>
<tr>
<td>Acetone extract, %</td>
<td>2.89</td>
<td>2.88</td>
</tr>
<tr>
<td>(soap, sugar, sterols, etc.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Proteins, %</td>
<td>2.82</td>
<td>2.82</td>
</tr>
<tr>
<td>Ash (mineral salts), %</td>
<td>0.38</td>
<td>0.30</td>
</tr>
<tr>
<td>Rubber hydrocarbon, %</td>
<td>93.30</td>
<td>93.38</td>
</tr>
</tbody>
</table>

NR is still the preferred commercial rubber where strength, tack and easy processing are required. The feature which has a dominant effect on the strength of NR is its tendency to crystallise on stretching. Crystallisation prevents molecular chains sliding past each other and results in a large increase in hysteresis and strength. Owing to the weak interchain forces in the polymer network, when the molecular chains are straightened by stretching, they do not have sufficient attraction for each other to maintain the oriented state and retract once the force is released. In contrast to extension, compression causes direct straining of the molecular bonds, this leads to
the possibility of designing items with different moduli or stiffness in different directions.

2.3 Vulcanisation/ Crosslinking of NR

2.3.1 Introduction

Vulcanisation is a process of chemically producing network junctures by the insertion of crosslinks between polymer chains. The crosslink may be a group of sulphur atoms in a short chain, a single sulphur atom, a carbon to carbon bond, a polyvalent organic radical, an ionic cluster or a polyvalent metal ion. The process is usually carried out by heating the rubber (mixed with vulcanising agents).

The term vulcanisation is generally applied to rubbery or elastomeric materials. These materials forcibly retract approximately to their original shape after a large mechanically imposed deformation. Vulcanisation can be defined as a process that increases the retractive force and reduces the amount of permanent deformation remaining after removal of the deforming force. Thus, vulcanisation increases elasticity while it decreases plasticity.

2.3.2 The Process of Vulcanisation

Important characteristics related to the vulcanisation process are, the time elapsed before crosslinking starts (scorch time), the rate of crosslink formation and extent of crosslinking (cure) at the end of the process.

Scorch resistance is usually measured by the time at a given temperature required for the onset of crosslink formation as indicated by an abrupt increase in viscosity, which prevents further flow or shaping process. The instrument usually employed for the measurement of scorch time is the Mooney viscometer.

The rate of cure and extent of crosslinks are usually measured by curemeters. There are a wide variety of cure-meters and the most widely used are oscillating disc rheometers. Vulcanisation is measured by the increase in the torque required to maintain a given amplitude (e.g. degree of arc) of oscillation at a given temperature. The torque is proportional to a low strain modulus of elasticity. Because this torque is
measured at the elevated temperature of vulcanisation the portion of it due to viscous effects is minimal. Thus, it has been assumed that the increase in torque during vulcanisation is proportional to the number of crosslinks formed per unit volume of rubber. The torque is automatically plotted against time to give the rheometer chart, rheograph or cure curve.

2.3.3 The Chemistry of Vulcanisation

The chemistry of NR vulcanisation is so complex that it is difficult to have a comprehensive understanding of the cure reaction. Nevertheless, in the past decades, rubber scientists have unravelled some of the major reactions occurring during cure.

As it has been known, elastomer vulcanisation by sulphur with no accelerator is no longer of commercial significance, because of the long cure time. Different types of accelerators give different scorch times (premature cure) and cure rates during crosslinking. The crosslink types and chain modifications of sulphur vulcanisation in natural rubber may be present in monosulphide, disulphide, polysulphide, pendent sulphides, cyclic monosulphides and cyclic disulphides.

The formation\(^4\) of a crosslinking structure leads to the conclusion that if desulphuration proceeds rapidly, the final network will be highly crosslinked with mainly monosulphidic bonds. Such a network is termed “efficiently crosslinked”. On the other hand, if desulphuration proceeds slowly, there will be opportunities for thermal decomposition. These networks are “inefficiently crosslinked”. For the vulcanisation of natural rubber, if temperature rises above 160°C, reversion or inefficiently crosslinked networks might occur.

Accelerated sulphur vulcanisation is thought to proceed by the following steps:\(^2,5\)

(i) The accelerator reacts with the sulphur to give monomeric polysulphides of the type Ac - Sx - Ac, where Ac is an organic radical derived from the accelerator.
(ii) The polysulphides can interact with rubber to give polymeric polysulphides of the type Rubber - Sx - Ac.
(iii) The rubber polysulphides then react, either directly or through a reactive intermediate, to give crosslinks or rubber polysulphides of the type Rubber-Sx-Rubber.
A flow diagram of the overall course of accelerated sulphur vulcanisation is given in Fig. 2.2.

Fig 2.2: Overall Course of Accelerated Sulphur Vulcanisation (6)

Vulcanising ingredients
- sulphur, accelerator, activators
  or
- sulphur donor, activators

Active Sulphurating Agent

Rubber Bound Intermediate
R-Sy-X

Initial Polysulphidic Crosslinks
R-Sx-R

Network Maturing Reactions

(i) crosslink shortening with additional crosslinking
(ii) crosslink destruction with main chain modification (dehydrogenation and cyclic sulphidic formation)
(iii) S-S bond interchange

Final Vulcanisate Network

Aged Vulcanisate Network
During a study of kinetic models\(^{(7)}\) of cure reactions Hsich has shown that scorch time reduces with an increase in filler loading, as shown in Table 2.2

**Table 2.2 : Decrease in scorch time with increased loading of N330 carbon black\(^{(7)}\)**

<table>
<thead>
<tr>
<th>Filler Loading, phr</th>
<th>Temperature, °C</th>
<th>Scorch time, min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>130</td>
<td>18.25</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>6.09</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>2.40</td>
</tr>
<tr>
<td>10</td>
<td>130</td>
<td>12.79</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>4.13</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>1.75</td>
</tr>
<tr>
<td>20</td>
<td>130</td>
<td>9.70</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>3.19</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>1.58</td>
</tr>
<tr>
<td>30</td>
<td>130</td>
<td>8.83</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>2.96</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>1.43</td>
</tr>
<tr>
<td>40</td>
<td>130</td>
<td>8.05</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>2.76</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>1.39</td>
</tr>
<tr>
<td>50</td>
<td>130</td>
<td>7.34</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>2.58</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>1.30</td>
</tr>
<tr>
<td>60</td>
<td>130</td>
<td>7.15</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>2.53</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>1.18</td>
</tr>
</tbody>
</table>
2.4 Scorch Control and Its Exploitation

2.4.1 Introduction

A most important criterion in the design of a rubber compound is to ensure that it has adequate scorch safety. The amount of scorch delay required will be determined by the nature of the compound itself and also by the severity of the processing operations. By increasing scorch safety it is possible in many cases to increase processing speeds and temperatures, and thus to increase productivity.

There are several ways by which scorch safety can be controlled: choosing the right accelerator and its level, using a combination of accelerators, replacing some of the sulphur in the vulcanisation system by a sulphur donor such as dithiodimorpholine or using a retarder.

2.4.2 Cure with Accelerators

An accelerator\(^{(8)}\) is defined as a chemical which will accelerate the vulcanisation process, when it is added to a rubber compound containing sulphur. Kempermann\(^{(9)}\) describes accelerators as products which increase the rapidity with which rubber compounds are crosslinked by sulphur and/or which increase the resulting number of crosslinks.

The origin of accelerators can be traced back to 1906 with the discovery by Oenslager, of the accelerating action of aniline, and since then there has been a continuing increase in number of accelerators with properties developed to meet the industry's requirements in terms of technical desirability.

The properties of different types of accelerators vary widely and can be classified according to different aspects.

Classification according to rate of vulcanisation is given below\(^{(8)}\)
i) **Fast Curing Delayed Action Accelerators**

This class of accelerators is the most widely used in the rubber industry today. These accelerators combine delayed action with fast cure rate and confer excellent physical properties. Sulphenamide accelerators fall into this category, including the N-cyclohexylbenzthiazyl sulphenamide which is used in this study.

ii) **General Purpose Accelerators**

This class of accelerators lacks the delayed action property but, other than that, they give good all-round properties. eg. Thiazoles

iii) **Slow Curing Delayed Action Accelerators**

This class has a long delayed action and gives a good plateau effect but with very slow cure. Guanidines fall into this category.

iv) **Ultra Fast Accelerators**

This class provides rapid cure at low temperatures. These are generally used in prevulcanization of latex. But when used for dry rubber compounds the rapid curing behaviour can be reduced by using in combination with retarders. Dithiocarbamates fall into this category.

The classification procedure based on chemical composition\(^9\) is as follows;

Dithiocarbamate accelerators,
Thiuram accelerators,
Thiazole accelerators (including sulphenamides),
Amine accelerators (including guanidines) and
Accelerators for special rubbers.

According to Kempermann\(^9\), this method of classification is unsatisfactory because the functional groups mainly responsible for the accelerating effect are not always indicated. The majority of the accelerator chemistry occurs during the scorch delay or induction period. The length of the scorch delay varies widely between accelerators. During this scorch delay, various accelerator complexes are formed. The
literature on accelerator chemistry suggests that the key accelerator species are of the nature,

\[
\text{Ligand} \quad \xrightarrow{X} \quad \text{S} \quad \xrightarrow{Zn} \quad \text{Sy} \quad \xrightarrow{X} \quad \text{Ligand}
\]

where, Ligand, such as amines and X is the accelerator moiety such as:

![Chemical structures](image)

In this study, 0.5 phr of CBS is used as the vulcanisation accelerator. CBS is preferred as it combines scorch delay with fast cure rate and good modulus development.

As can be seen from the above there are a wide variety of accelerators, ranging from the low scorch time dithiocarbamates to the delayed action sulphenamides. The first step in obtaining the requisite scorch delay (Figure 2.3\(^{(10)}\)) is therefore to select the most suitable basic accelerator.
Fig. 2.3: Range of scorch times with conventional cure systems - NR compound with 50phr of N330 carbon black - measured by Mooney viscometer\(^\text{(10)}\)

An examination of rheographs at a typical cure temperature, shown in Figure 2.4\(^\text{(10)}\), confirms the Mooney data in Figure 2.3 and also demonstrates the influence of accelerator on the rate of cure.

It can be seen that, whilst CBS gives longer processing safety than MBTS, the overall cure times are similar and a lower level of CBS is required to develop the same modulus as that given by MBTS. Thus it would appear that unless there are sound technical or economic reasons against its use, CBS will give the best compromise in terms of safe processing, fast cure and low cost.
2.4.3 Role of Amine Compounds in Vulcanisation

Amine type accelerators are important in this research work because the existing multifunctional additive has amine groups, which are assumed to be the cause of its fast curing and poor scorch behaviour.

The effect of amine on vulcanisation has been studied by several scientists. Hydrofuramide which was the most studied amine, was found to increase the percent cure, decrease the scorch time and increase the vulcanisation rate. Furthermore, it was found that amine increases the role of metal - accelerator - carboxylate complexes in network formation, usually in conjunction with stearic acid or similar fatty acids. Kerbs studied the reaction of sulphur with amines and sulphide ions. He suggested that amine accelerated the vulcanisation reaction through the ring opening of sulphur, and noted that the accelerating action increased with the base strength of the amine. In addition to homolytic thermal cleavage at relatively high
temperatures, the sulphur (S$_8$ ring) underwent rapid ionic cleavage at lower temperatures in the presence of amine or sulphide ion.

\[
S_8 \xrightarrow{heat} S - S_6 - S
\]

\[
S_8 + NR_3 \xrightarrow{room\ temperature} R_3N^+ \rightarrow S_7 - - - S^-
\]

\[
S_8 + S^- \xrightarrow{room\ temperature} S^- - S - S_5 - S - S^-
\]

More recent studies\textsuperscript{14} suggest that amines do not react directly with sulphur but instead with traces of $H_2S$ or sulphur dioxide. This results in the formation of highly thiophilic species such as HS$^-$ which subsequently give ionic cleavage of the sulphur ring.

\[
R_3N + H_2S \rightleftharpoons R_3NH^+ + HS^-
\]

\[
HS^- + S_8 \rightleftharpoons HS_9^-
\]

A binary accelerator system refers to the use of two (or more) accelerators in a given formulation. Usually, binary accelerator systems are used when they show favourable synergistic behaviour\textsuperscript{14}, eg. on cure rate.

### 2.4.4 Retarders

Retarders\textsuperscript{(15,16)} are substances which reduce the activity of accelerators or combinations of accelerators, at compound processing and storage temperatures but become substantially exhausted or decompose at higher temperatures, so that the rate of cure is either unaffected or only slightly reduced. Therefore, in this way their function is to control scorch tendencies on the mill, calendar and extruder without prolonging production cycles or affecting ultimate physical properties.

The conventional retarders traditionally used have been nitrosodiphenylamine (NDPA) and organic acids such as salicylic acid, benzoic acid or phthalic anhydride.
The exact mechanism of acid retarders is uncertain. There are several suggested mechanisms.
1. By delaying the interaction of sulphur with rubber by neutralising basic substances in the polymer.
2. By causing ionic scissions of rubber cross-links early in vulcanisation.
3. By interacting with degradation products of the accelerators to reduce vulcanisation.
4. By interfering with the zinc complex and reacting with amine fragments, which delay the cross-linking step.

The activity of phthalic anhydride is equally complex. Some transformations include,
* direct reactions with rubber,
* hindrance of the MBT-ZnO-stearic acid complex,
* formation of a phthalic anhydride-ZnO-MBT complex,
* direct reaction with sulphenamides.

NDPA, although more active than acid retarders, causes severe staining and often porosity due to its gaseous decomposition products. Its activity is also very dependent on mixing temperature, low mixing temperatures giving the greatest activity but also a greater risk of porosity occurring during processing, which can carry through to the final vulcanisate. NDPA was withdrawn from use many years ago for health reasons.

2.4.5 The New Class of Prevulcanisation Inhibitor

More recently a new class of prevulcanisation inhibitors was developed to overcome the disadvantages of traditional retarders. This includes a widely used prevulcanising inhibitor\(^\text{10,17}\), N-cyclohexylthio-phthalimide (CTP or Santogard PVI) which offers several advantages over conventional retarders. With a number of vulcanising systems it can extend scorch safety without adversely affecting cure rate and can give an almost linear increase in scorch time with concentration. (Figure 2.5)\(^{10}\) Its effect on cure rate and state of cure is minimal as shown in Figure 2.6.\(^{10}\)
Fig. 2.5: CTP, pre-vulcanising inhibitor activity in NR\textsuperscript{10}

![Graph showing pre-vulcanising inhibitor activity](image)

Fig. 2.6: Effect of CTP activity on cure characteristics\textsuperscript{10}

![Graph showing cure characteristics](image)
Mechanisms of Scorch delay by CTP

(a) in the presence of sulphenamide accelerator

The commonly used sulphenamides are the oxidative coupling products of MBT (mercaptobenzothiazole) and an organic amine. In the case of CBS, MBT is reacted with cyclohexamine.

The simplest set of general reactions consistent with several experimental results is as follows for a benzothiazylsulphenamide accelerator.

\[
\begin{align*}
\text{BtSNR}_2 + S_8 & \quad \text{slow} \quad \rightarrow \quad \text{BtS}_x\text{NR}_2 \\
\text{BtSNR}_2 + \text{BtSH} & \quad \text{fast} \quad \rightarrow \quad \text{BtS}_x\text{S} \text{Bt} + \text{HNR}_2 \\
\text{R}_2\text{NH} + S_8 + \text{BtSNR}_2 & \quad \text{fast} \quad \rightarrow \quad \text{BtS}_x\text{NR}_2 \\
\text{BtS}_x\text{S} \text{Bt} + S_8 & \quad \text{fast} \quad \rightarrow \quad \text{BtS}_x\text{NR}_2 \\
\left[ \text{BtS}_x\text{Bt} \right] + \text{Rubber} & \quad \rightarrow \quad \left[ \text{BtS}_x\text{Rubber} \right] + \left[ \text{Bt SH} \right] \\
\left[ \text{BtS}_x\text{NR}_2 \right] + \text{Rubber} & \quad \rightarrow \quad \text{Rubber S}_x\text{Rubber} + \left[ \text{Bt SH} \right] \\
\left[ \text{BtS}_x\text{Rubber} \right] + \text{Rubber} & \quad \rightarrow \quad \text{Rubber S}_x\text{Rubber} + \left[ \text{Bt SH} \right] \\
\left[ \text{R}_2\text{N S}_x\text{Rubber} \right] & \\
\end{align*}
\]

The delayed action in delayed action sulphur crosslinking is largely based on the auto-catalytic disappearance of the accelerator. When a benzothiazole derived
accelerator is used, MBT (also represented as BtSH, where Bt is the 2-benzothiazolyl group) is formed simultaneously with the crosslink intermediate, Ac -Sx -rubber. Thus, benzothiazole sulphenamide type accelerators deplete, in an autocatalytic fashion, with the formation of MBT. The rate of the depletion is approximately inversely proportional to the amount of MBT present. If MBT could be taken out of the system as fast as it forms, substantial increase in processing safety would result. This is what happens when CTP is present. CTP traps MBT and amine thus slowing the rate of formation of intermediate polysulphides.

A complex radical quenching reaction scheme was proposed for the reaction of MBT with CTP. First, CTP\textsuperscript{19} reacts rapidly with MBT to form cyclohexyl dithiobenzothiazole (CDB) and phthalimide.

Since CDB\textsuperscript{20} is a fairly good accelerator, it is reasonable to assume that CDB (in the presence of sulphur) would form bis(2-benzothiazolyl)polysulphide (BPS) and cyclohexylpolysulphide (CPS). This assumption was indirectly supported by examination of an aged sample of NS-50 which is a 50:50 mixture of N-t-butyl-2-benzothiazolesulphenamide and N-(cyclohexylthio)phthalimide. It contained among other things, cyclohexyl disulphide. BPS would react with rubber to form crosslinks as usual while CPS would influence the scorch time.
Both mechanisms\textsuperscript{21} for delayed action (radical quenching and MBT removal) could coexist. In addition, a compound such as CTP can react in the system to give polysulphides such as; CDB (cyclohexyldithiobenzothiazole) or CPS (cyclohexylpolysulphide) which would quench crosslink precursor thiy radicals.

\textbf{(b) in the presence of amine accelerators}

CTP's effectiveness is not limited to thiazole accelerators. It seems reasonable to postulate that other accelerated sulphur cure systems follow similar reaction paths. Boustan\textsuperscript{22} found that amines react with CTP to produce organothio amines which also function as prevulcanising inhibitors. Cyclohexylthio amine formed by CTP reacts faster with MBT and acts as a scavenger of MBT.
The formation of further cross-links is stopped if CTP is added to a partially
cured (marginally scorched) rubber. This procedure indicates that it may be possible to
intercept intermediates of vulcanisation such as rubber-Sx-MBT.
After vulcanisation is complete, CTP cannot devulcanise a cured stock.

2.5 Theories of Filler Reinforcement

2.5.1 Introduction

The use of filler to reinforce elastomers is one the most important aspects of
rubber technology. Reinforcement\textsuperscript{23,24} is defined as the ability of fillers to increase
the stiffness of vulcanised compounds and to improve a variety of vulcanisate
properties. According to Dannenberg\textsuperscript{25} filler reinforcement is defined by the
improvement in the service life of a rubber article. However, different fillers will not
enhance all the properties to the same degree. Harwood\textsuperscript{26} and Dannenberg\textsuperscript{25} have
reported that the reinforcing effect of an active filler as well as the dosage required
can be quite different from one elastomer to another. Carbon black and silica are used
widely as reinforcing fillers. Silicates, clays, whittings and other mineral fillers are also
used, where a high degree of reinforcement is not required.
2.5.2 Mechanisms of Reinforcement

A number of hydrodynamic and molecular network mechanisms\(^{(24)}\) have been proposed to account for the phenomenon of filler reinforcement. These are summarised in an excellent review paper by Dannenberg.\(^{(25)}\) Many different interfacial interactions and network processes have been suggested by scientists over the past years.

(i) Hydrodynamic theories of Smallwood and Guth

Early theoretical studies of reinforcement attempted to establish a relationship between the volume concentration of filler and the observed increase in stiffness. Smallwood\(^{27}\) showed that modulus properties of several large particle fillers at low concentration fitted the relationship,

\[
E = E_0 (1 + 2.5\phi) \tag{1}
\]

where \(E\) is Young’s modulus of the mixture measured at low extension in the linear region, \(E_0\) is the value for unfilled gum vulcanizate, and \(\phi\) is the volume fraction of filler.

Guth\(^{28}\) modified this equation to account for particle interactions at higher concentrations by adding a squared term,

\[
E = E_0 (1 + 2.5\phi + 14.1\phi^2) \tag{2}
\]

This equation fitted the data for a fine thermal black up to a volume fraction 0.3. More reinforcing carbon blacks departed significantly from this relationship, and Guth suggested that this was due to the asymmetric nature of carbon aggregates. He therefore modified the equation to include a shape factor, \(f\), the ratio of the length to the width of the aggregates,
\[ E = E_0 \left( 1 + 0.67f\phi + 1.62f^2\phi^2 \right) \] (3)

With proper choice for the value for \( f \), this equation gives fair agreement with the modulus - concentration data for many systems. Recent electron microscope studies of carbon blacks before mixing in rubber have given shape factors in the range of \( 2 \) - 3 for reinforcing blacks. The Guth equation is useful for expressing the concentration dependence of mechanical properties at low extensions, such as hardness, compression modulus, Young’s modulus and dynamic elastic modulus.

Instead of employing shape factors to obtain reasonable correlation, the use of a modified or effective, rather than the true volume concentration of the dispersed phase has been suggested. Medalia added “occluded rubber” volume to the actual filler volume to obtain the effective volume of the rigid phase, a procedure which improved the agreement between theory and fact. Occluded volume was estimated from aggregate morphology and void volume measurements.

(ii) Strain - amplification theory of Mullins

The statistical theory of rubber elasticity predicts that the modulus of elasticity of an ideal elastomeric network is directly related to absolute temperature. Stress \( \sigma \) as a function of elongation ratio \( \lambda \) follows the relation

\[ \sigma = v k T \left( \lambda - 1/\lambda^2 \right) \] (4)

where \( v \) is the concentration of elastically effective chains. Since experimental agreement with this equation is not satisfactory, the well known empirical modification was introduced by Mooney and Rivlin.
the C2 term represents the departure from ideal network behaviour. When these factors are minimised, as for highly solvent-swollen gum vulcanisates, the C2 term is nearly zero, and 2C1 is thus equal to \( v_k T \). Equation (5) should apply to a filled vulcanizate if it can be assumed that the major function of the dispersed phase is to increase the effective strain of the rubber phase. Since the filler is rigid, the local strain of the rubber matrix must be larger than the measured overall strain. Various strain amplification functions have been suggested. Mullins and Tobin\(^{32}\) have recommended the use of the volume concentration factor of the Guth equation to estimate the effective strain, \( \lambda' \), in the rubber matrix,

\[
\lambda' = \lambda (1 + 2.5\phi + 14.1\phi^2)
\]  

(6)

This factor agrees only for large particle size thermal blacks and at moderate extensions.

Mullins and Tobin\(^{32}\) have attributed the well-known stress softening effect of filled vulcanizates to the same source as that in gum vulcanisates, except that the strain in the rubber network is amplified by the presence of filler in the filled vulcanize. This condition causes increased hysteresis due to a more pronounced departure from ideal network behaviour. Stress-softening was attributed to non-affine deformation of network junction points and the incomplete subsequent recovery to their original positions. The strain amplification factor can also be increased to agree better by introducing the effect of aggregate anisometry or shape factor or by the use of an adjusted volume concentration based on the addition of "occluded" rubber volume to the true filler volume, as mentioned previously for the Guth equation. This latter adjustment assumes that a portion of the rubber phase is closely associated with the filler surface and essentially immobilised, thus acting as an additional rigid filler volume.
(iii) Blanchard and Parkinson Mechanism

Blanchard and Parkinson\textsuperscript{33} suggested that reinforcing fillers cause important changes in the nature of the rubber network. These changes involve the formation of weak and strong linkages between network segments and particle surface sites. They attributed the stress softening or the "Mullins effect" to breakage of weak linkages. The strength of the weak linkages was estimated from the energy consumed to varying degrees of softening up to the point of rupture. Strength and reinforcement were attributed to the relatively few strong linkages, which survive to rupture. The relative unimportance of the weak linkages was demonstrated by the small effect of prestressing on abrasion, tear, and tensile properties.

Blanchard\textsuperscript{34} has added another contribution to stress, called strain hardening. Strain hardening in highly deformed rubbers is due to (1) tightening of short rubber chains between particles, (2) strain alignment of molecular segments between particles, and (3) slip arrangements giving greatly increased alignment and stress sharing by lightly stretched chains. The significance of oriented rubber structures may be that they stop or divert tearing and by this means increase reinforcement. This concept of Blanchard has a number of points common with the molecular - slippage mechanism of reinforcement\textsuperscript{25}.

(iv) Bueche's Interparticle Chain Breakage Mechanism

Bueche\textsuperscript{24} has proposed a mechanism of stress softening and reinforcement based on the simple concept of the breakage of network chains, or their attachment to adjacent filler particles, during extension. These interparticle chains have a distribution of lengths, and the shorter chains will rupture first, at small elongations. Since the stress on a chain before rupture is large, it contributes greatly to the stiffness or modulus. Chains broken on the first stretch will not be able to affect stiffness on the second stretch and softening will occur. Bueche attributes stress recovery to the return to a random distribution of interparticle chains by the replacement of the original broken chains by other similar chains. Their original statistical distribution is lost.
during the first stretch, and stress recovery occurs by return to a random distribution. Bueche doesn’t explain exactly how this chain-replacement phenomenon occurs, but a similar process has been suggested for the molecular-slippage mechanism of reinforcement.

(v) Molecular Slippage Mechanism

Dannenberg and others\(^{25,35}\) have proposed a mechanism of reinforcement which attempts to explain the complex mechanical properties of reinforced vulcanizates. This mechanism assumes that, under stress, the surface adsorbed network segments move relative to the surface, accommodating the imposed stress and preventing molecular rupture. As a consequence of this movement or slippage process, the stress is redistributed to neighbouring molecules. Stress redistribution results in molecular alignment and increased strength. This process first absorbs strain energy, and then dissipates it by slippage as frictional heat and, in this manner acts as a major source of hysteresis. Energy requirements for the rupture process are thus increased by dissipation of a portion of the strain energy as heat. On relaxation of stress, the system tends to regain a more random equilibrium configuration as a result of surface molecular rearrangements resulting from the dynamic nature of physical adsorption processes. A schematic diagram illustrating this reinforcement mechanism is shown in Figure 2.7\(^ {25}\)
Further extension causes either desorption, chain breakage, or chain slippage.

Figure 2.7: Molecular slippage mechanism of reinforcement\(^{(36)}\)

(vi) Restricted Mobility of Surface Layer of Rubber

The restricted mobility of the molecular segments resulting from strong surface adsorption forces should change the physical properties of the rubber near the particle surfaces, producing an encapsulating shell of higher rigidity and having a higher Tg than the matrix rubber phase.

Attempts at demonstrating the existence of such a quasi-glassy surface phase have been made by dynamic testing and NMR methods. Kraus and co-workers\(^ {36,37} \) found 'no significant layer of immobilised rubber' in both dynamic and NMR spin-lattice relaxation studies. Baccaredda and Butta\(^ {38} \) found that short-range mobility of chain segments was not affected by filler. In contradiction to these results, Smit
measured the dynamic modulus behaviour of SBR in forced shear vibration at 2.4% amplitude, 8.5 Hz and -40°C and estimated an immobilised surface layer thickness of 20Å and an increase in Tg of 30°C. NMR studies by Fujiwara and Fujimoto\textsuperscript{39} with natural rubber at 60 MHz indicated a layer thickness of 50 Å. Kaufman and Slichter\textsuperscript{40} showed that the thickness of the tightly absorbed layer was dependent on the difference between the Tg of the elastomer and the temperature of measurement. These workers used samples of the dried carbon black-rubber gel, obtained from normal bound rubber determinations, in order to obtain a high concentration of constrained or absorbed rubber.

The evidence now appears quite convincing that the carbon black surface layer of rubber is more constrained than the matrix, but is definitely not rigid at normal temperatures. This layer is a source of higher hysteresis than the matrix and contributes to gradual stress gradients and uniform stress distribution across the solid - elastomer interface.

(vii) Immobilised Rubber Theory of Clarke and Freakley

Clarke and Freakley\textsuperscript{41} proposed that the reduction in viscosity of a compound during mixing is due to mastication of the elastomer and disagglomeration of carbon black. The effect of mastication could be removed by calculating values of relative viscosity, using the viscosity of the gum treated in a similar way to the compound and with an allowance being made for strain and strain rate amplification.

They suggested that the mechanism by which the relative viscosity of the compound decreases with increased mixing is as follows; agglomerates in a compound contain immobilised rubber, which behaves as a part of the solid agglomerate and hence contributes to the effective fraction of filler in the compound. As agglomerates are broken down during mixing, immobilised rubber is released, causing a reduction in effective volume fraction of filler and a consequent decrease in relative viscosity.
Using the addition of a further term to the Einstein equation proposed by Guth and Gold as shown below:

\[
\eta / \eta_0 = 1 + 2.5\phi + k_1 \phi^2 \\
\]

where

\( \eta \) = viscosity of the suspension
\( \eta_0 \) = viscosity of the suspending medium
\( \phi \) = volume fraction of suspended particles
\( k_1 \) = constant

A theoretical value of 7.35 was determined for \( k_1 \) by Vand while Guth-Gold calculated a value of 14.1. Clarke and Freakley's results indicate that the carbon black in both primary aggregate and agglomerate forms, is behaving as non-attracting spherical particles, despite irregularity in shape. They found \( k_1 \) values of 15.13 for the well mixed compound and 9.69 for the badly mixed compounds. This result suggests that although the spherical particles are fused together into aggregates, the rubber flows freely and closely around them. There is no occluded rubber associated with primary aggregates, either within the structure or as an adsorbed layer on the carbon black surface, during steady state flow at a shear rate of 1.0 s\(^{-1}\).

Clarke and Freakley also explained why their results are contrary to the findings of other researchers, who have attributed differences in rheological behaviour of various carbon blacks to the amount of occluded rubber associated with primary aggregates. They suggest that some of the compounds in the previous researchers' experiments were not completely mixed. If some agglomerates remained, then the rubber immobilised within the agglomerates would be assumed to be associated with primary aggregates.

Although the immobilised rubber theory of Clarke and Freakley was only applied to viscosity, this and preceding theories are equally valid for viscosity and modulus.
2.6 Rubber Mixing

2.6.1 Mixing Mechanisms

The principal task of the mixing operation is to incorporate additives in to the base material. Palmgren\textsuperscript{42} describes the mixing as the process whereby particulates of bulk fillers and minor components, are dispersed into polymer matrix to give a uniform and homogeneously mixed compound. This is an energy intensive process and involves a number of stages.

The complete process\textsuperscript{43} of mixing rubber with filler and other additives involves different physical operations. This is divided into four basic operations.

(i) Viscosity reduction
(ii) Incorporation
(iii) Distributive mixing
(iv) Dispersive mixing

According to Palmgren there is another step; subdivision before the incorporation step. However, as subdivision is the preparatory step for incorporation, it can be treated as a part of the incorporation step. According to Nakajima’s\textsuperscript{44} mixing model subdivision is necessary, not only for incorporation but also for dispersion.

These stages can occur at the same time and each can be the main rate determining process, which will control the mixing time. The stages of mixing are shown in Fig. 2.8\textsuperscript{44}. 

32
Raw rubber, especially natural rubber, is stiff, elastic and has a high viscosity. Because of this nature it will not take up other ingredients such as particulate additives. Therefore, it is necessary to convert the rubber to a state which will accept the additives. This stage is called viscosity reduction and is achieved by three mechanisms, which are interdependent.

(a) temperature rise
(b) chain extension and freeing of untrapped chain entanglements
(c) mastication
The initial deformation of rubber during mixing requires high mechanical energy, some of which is converted to heat causing rapid temperature rise and viscosity reduction. The shear during mixing also reduces viscosity because of extension, disentanglements and orientation of polymer chains. Mastication, or mechano-chemical breakage of bonds during shearing, also causes viscosity reduction.

(ii) Incorporation

When viscosity is reduced the rubber can flow around additives, including fillers, to form a coherent mass. Further incorporation occurs when the rubber penetrates into the voids of agglomerates and wets the surface of the filler particles.

According to Nakajima\textsuperscript{44} the incorporation step may be modelled in two different ways. Mechanism (a) involves a large deformation and subsequent relaxation of rubber domains, a sandwiching of the carbon black agglomerates with rubber. Mechanism (b) involves comminution of rubber domains and subsequent mixing with carbon black. (Figure 2.9)

In reality, mechanisms (a) and (b) are not separate, both take place simultaneously.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig2.9}
\caption{Schematic illustration of mechanism of carbon black incorporation}
\end{figure}

(a) lamination \quad (b) comminution\textsuperscript{44}
(iii) Distributive Mixing

Distributive mixing\textsuperscript{43} is reduction of the scale of segregation between the components of the rubber compound. Incorporation and distributive mixing proceed simultaneously, the distribution commencing as soon as incorporation additives are available. There are two mechanisms for distributive mixing.

(a) Random Bulk Convective Mixing

This is also known as exponential mixing and is the more efficient mechanism of distributive mixing. Incorporation, subdivision and distribution are largely due to exponential mixing mechanisms. Folding flows provide exponential mixing, as does the separation and recombination of flow streams in different patterns. It is also necessary for the absorption of liquid additives.

(b) Laminar Shear Convective Mixing

This is an inefficient mechanism compared to random bulk convective mixing. This mechanism applies to the mixing which occurs between the nog and chamber wall and between rotors of intermesh type rotor mixers. During laminar mixing “domain” thickness decreases and interfacial area increases.

Comparison of efficiencies of exponential mixing and laminar mixing is shown in Fig. 2.10\textsuperscript{43}.
(iv) Dispersive Mixing (Dispersion)

During dispersive mixing solid particles or agglomerates are broken into smaller fragments. Fracture of solid particles or agglomerates occurs during mixing when external stresses are higher than the forces holding agglomerates together. Dispersive mixing is stress dependent and therefore occurs most effectively in high stress regions of the mixer.

In other words, the dispersion process involves a large deformation of rubber domains in order to create a stress high enough to break up the carbon black agglomerates. The rubber domains themselves are also broken up/ decreased in size in the process of improving microscopic homogeneity.
Shiga and Furuta\textsuperscript{45} showed a different interpretation of mixing. They have proposed a model named “the onion model” to explain carbon black dispersion. The morphological changes of rubber matrix is not shown in this model. Rather it is used to illustrate the process in which carbon black is progressively dispersed from pellets to aggregates and then into final particles. Here the aggregates are either individually or collectively scraped out from the surface of agglomerates. It is also shown that a mathematical expression of the model can semi-quantitatively describe the changes in distribution of agglomerate diameter with mixing time. The attractive force between the scraped aggregates and the agglomerate surface is thought to result from interparticle tie molecules. The schematic diagram shown in Figure 2.11 explains the above model.

![Diagram of Shiga and Furuta's model for carbon black dispersion](image)

**Fig. 2.11:** Shiga and Furuta’s model for carbon black dispersion “the onion model”\textsuperscript{45}
2.6.2 Mastication

Mastication is the term used to describe molecular weight reduction during processing. As explained earlier in 2.6.1 the viscosity of natural rubber is reduced by mastication before the incorporation by mixing of fillers and other ingredients. Despite the introduction of viscosity-stabilised CV grades of rubber, mastication as a separate step (pre-mastication) or as an integral part of the mixing cycle is still extensively practised for non-viscosity-stabilised grades.

The effect of mastication on rubber has been extensively studied\(^{46}\) and it is very well established that the breakdown of rubber on a mill or in an internal mixer occurs more rapidly at either high (above 120°C) or moderately low temperatures (below 80°C) than it does at temperatures around 100°C.

A typical example of the effect of mastication i.e. mechanical breakdown on natural rubber is shown in Fig.2.12,\(^{46}\) in which the whole curve is a composite one and reflects the occurrence of two independent reactions which would give curves A and B respectively.

![Fig.2.12: Breakdown of natural rubber after 30 minutes mastication at different temperatures.\(^{46}\)](image-url)
2.6.3 The Batch Internal Mixer and Operating Variables

The working part of an internal mixer consists of a two-lobed chamber holding two rotors. The rotors are driven by a motor and gears. Although the details of the flow pattern depend upon the rotor and chamber geometries, the same principles apply to all internal mixers. The moving rotors cause drag flow between the tip of the blade and chamber wall as well as between the shaft body and the wall. Francis Shaw K1 Intermix shown in Fig. 2.13, can be taken as a sample of an internal mixer which was used in this study.

Fig. 2.13: Francis Shaw K1 Intermix\(^55\)
The efficiency of mixing in an internal mixer is affected by the following factors\(^{43,47,48}\). Uniformity of the batch is also depend on these factors.

1. Rotor speed
2. Fill factor
3. Ram pressure
4. Circulating water temperature
5. Mixing sequence and criteria for batch discharge

1. Rotor Speed

The rate of distributive mixing is a function of rotor speed, proceeding rapidly as speed is increased; however to retain a high viscosity in the rubber for dispersive mixing it is desirable to run the mixer slowly, to minimise the rise in batch temperature. The restriction on batch temperature is also necessary when mixing temperature sensitive additives, such as curing agents, placing a practical limit on the rotor speed for distributive mixing.

2. Fill Factor

The fill factor is defined as the fraction of free volume of mixer which is occupied by polymer and additives at the final stage of mixing.

\[
\text{Fill factor} = \frac{M}{F \times \rho}
\]

Where,
- \(M\) = mass of the batch
- \(F\) = free volume of the mixer
- \(\rho\) = density of the batch
Freakley and Wan Idris\textsuperscript{49} found that the flow patterns depend upon the fill factor used. They have reported that optimum fill factor ranges from 0.65 - 0.85 depending on the type of mix, in a tangential rotor mixer.

Under-filling of the mixer results in voids forming in the rubber mass behind the rotor wings and nogs, providing effective mechanisms for exponential distributive mixing, by free folding flows and by flow stream division. Even though under-filling of the mixing chamber is essential for efficient mixing, too much under-filling also makes the mixing process less efficient.

Over-filling undermines the mix uniformity and produces bad dispersion, high energy consumption, increase in dump temperature, high power level, longer mixing time and also closed streamline flow. This is because the material remains in the "throat" of the mixer and does not take part in the mixing.

Dizen\textsuperscript{49} has also shown that there is a maximum fill factor for effective dispersion which depends upon the type of carbon black.

3. Ram Pressure

The force applied to the ram, should ensure that materials charge into the mixer engage rapidly with the rotors and be sufficient to prevent the subsequent upthrust of the batch by the upward displacement, producing a stagnant region similar to that resulting from an extremely high fill factor.

Increase in ram pressure will increase the efficiency of the mix. This is due to the increase in contact force between rubber and rotor or chamber wall, and the reduction in wall slippage. Increase in ram pressure also reduces the mixing time due to more rapid incorporation and improves filler dispersion.

Comes\textsuperscript{50} examined the effect of ram pressure in Banbury mixers. The mixing time could be decreased from 9 to 2 minutes for the same dispersion as the ram
pressure increased from 12 to 90 psi. Because of the reduction in mixing times, high ram pressures, typically 60 psi, have become the norm for modern internal mixers.

Whitaker\textsuperscript{51} examined the combined effects of increased ram pressure and increased rotor speed on the mixing time, power and work with a Francis Shaw Intermix K2A internal mixer and standard SBR recipe. He found that mixer time could be greatly reduced by increasing ram pressure to 60 psi with little further change at higher pressures.

4. Circulating Water Temperature

The temperature of the mixer exerts a strong influence on the characteristics of mixing. During start up of the mixer heat transfer from the batch is extremely efficient, due to the considerable mass of the metal in the rotors and chamber, delaying the rise in batch temperature. The first batch effect and subsequent variations in the properties of mixed batches are reduced by controlling the temperature of the water circulated through the chamber, rotors and drop door for cooling.

Raising the circulating water temperature has the effect of slightly decreasing the mixing time but causing a small deterioration in mixed-material properties. It has been shown, for most mixers, that the best results are obtained with water temperature set in the region of $30^\circ C$\textsuperscript{52,53}.

5. Mixing Sequence and Criteria for Batch Discharge

Mixing sequence is concerned with the operations which have to be performed in order to achieve a mixed batch having the properties required for down stream processing and production performance. The choice of sequence depends on the compound type and desired properties. The properties partly depend on relative contributions of three mixing processes.
For example, a compound of natural rubber has to be masticated first, to reduce the viscosity before addition of other ingredients. In a general rubber compound, all the ingredients should be mixed together to allow maximum distributive mixing and reduce the subsequent scorch risk. Highly reinforced compound is mixed totally different from the above two types; that is by adding and mixing black and rubber together to give a dispersive mixing and to add curatives later to reduce the risk of scorching.

There are three main criteria used to determine when an additive or filler should be charged into an internal mixer or when mixing should be terminated. These are mixing time, batch temperature and mixing energy. The mixing time depends on the type of the compound being mixed and the mixing conditions. Batch temperature is related both to the amount of energy expended in mixing and the rate at which it is extracted. Despite being influenced strongly by variations in mixer temperature, it is sensitive to mixing performance and provides a good indication of state of mix. Mixing energy, which is invariably taken to be the electrical energy delivered to the motor, minus that required to run the mixer in an empty condition, is measured by a power integrator.

Mixing time and energy are often used to determine when materials should be charged into the mixer during conventional or sequential addition mixing, whereas temperature is normally used only as a dump or discharge criterion. Additionally, the electrical-power requirement of the mixer motor is often used as a criterion for material additions and particularly for oil additions, usually immediately after the power peak due to dispersive mixing is reached. For constant speed mixing this point is usually in the region where the power required by the mixer motor is decreasing rapidly after the dispersive mixing peak or plateau, as shown in Figure 2.14.
2.6.4 Ancillary Rubber Mixing Equipment

i. Two-roll Mill

Although two-roll mills have been dispossessed of their primary mixing role by the internal mixer, (due to the problem of dust), mill mixing still retains a crucial role in many factories for speciality rubber mixing, for laboratory sample preparation and for the addition of curatives and accelerators and sheeting batches from internal mixers. This is due to the three valuable assets present with two-roll mills: low temperature running characteristics, versatility and self-purging. They can operate
successfully with temperature sensitive compounds and change operation from one compound to another in a rapid and efficient manner, without incurring significant waste.

The same fundamental physical processes control mixing in both internal mixers and mills. The primary differences are the kinematics of flow governed by the differences in geometry and the stress levels achieved in practice.

ii Dump or Batch Extruder

Continuous mixers or extruders used as mixers have made relatively little impact on the rubber industry. The required geometry of the feed material means that they can only replace the second of a two-stage process for bale rubber. Usually particle incorporation and black mixing are poor in a continuous mixer so that an internal mixer is more efficient in the first stage.

However, hot feed extruders have been used by the rubber industry, where the feed stock is pre-warmed in a prior operation. The dump or batch extruder designed to accept the mix discharged from an internal mixer possesses features which differentiate it from the normal hot-feed machine. In order to accept and feed successfully, the mass of material from the internal mixer, the screw is of large diameter in the hopper section, tapering to the discharge diameter just forward of the hopper. An inclined pneumatically operated pusher in the hopper section forces the rubber down into the flights of the screw. A plain slit die may be fitted to produce slab or alternatively, a roller die may be used to produce dimensionally accurate and flaw-free thick sheet.
2.6.5 Mixing Systems and Methods

(i) System layout

There are three basic steps in rubber processing: mixing the compound, shaping the compound into a desired form and setting or curing the shaped form. Each of these steps consists of several processing operations as shown in Fig. 2.15.

Fig: 2.15 : Flow diagram for a processing operations
(ii) Mixing Systems

There are various types of mixing processes available currently; single stage, two stage or multi-stage mixing.

In the single stage technique all the mixing is carried out to completion in a single mixer. Variable speed mixing is sometime used so that the temperature rise can be checked by the reduction of speed. Cycle time for this process is similar to the total cycle time on a two or multi-stage process. The dump could be on a two-roll mill or extruder. This system is such that the unit can also be used as a master batch unit and final mix unit; and any special compound needing two or more stages can be mixed in this way.

Out of these systems, two or multi-stage mixing is widely used. A multi-stage system is used for compounds with large amounts of reinforcing filler. This system can be divided into three stages as shown in Fig. 2.16.

* Master batch
In this stage filler and rubber are subjected to high speed in an internal mixer resulting in distributive and dispersive mixing.

* Remill
This is a high speed mixing operation causing further dispersive mixing.

* Curative Addition
This is usually done at low speed, in order to keep a low temperature in the batch to reduce the scorch of the compound. This is a distributive type mixing. Alternatively, remilling and curative addition can be done on a two-roll mill.
Fig: 2.16: Flow diagram for a multiple stage mixing system
Fig: 2.16 : Flow diagram for a multiple stage mixing system 51
(iii) Conventional and Upside down Mixing

The basis for all the techniques employed in the mixing process lies on the assumption that a high level of shear stress is an important prerequisite for efficient dispersion of additives. Viscosity of rubber is known to increase with the addition of dry additives. Therefore most of the powdery ingredients are added at the beginning of the mixing cycle when rubber is still cool. Compounding ingredients such as plasticizers and processing oils, that tend to reduce the viscosity of the mixing stock are added towards the end of the mixing period when most of the additives are already incorporated and dispersed. Furthermore process oil tends to cool the hot compound slightly. This method is commonly known as conventional mixing technique.

The opposite of the conventional method is the upside down mixing technique. It is the procedure by which all the ingredients of a batch are introduced into the mixer at the same time, and the ram is immediately applied, thus developing high energy input to the batch at the start of the mixing cycle. Improved dispersion of additives is the result of the high power input required by the stiff consistency of the batch.

When all the ingredients of the batch are thrown together in the mixer at one time the rubber is 'broken up' and is heavily coated with the pigments which are then quickly incorporated. The rapidly formed stiff stock demands the maximum work and hence maximum power is required. A high level of dispersion of additives is obtained by this technique though it is accompanied by higher power consumption and the mixer is subjected to higher strain.
2.7 Reinforcement of Elastomers with Carbon Black

2.7.1 Introduction

The importance of carbon black as a reinforcing filler for all types of elastomers has been established for many decades. For a long time it has been simply accepted that the addition of carbon black gives improved properties to rubber vulcanizates, but an understanding of how this reinforcement comes about was developed more slowly. Initially many detailed studies of the effects of many different grades of channel and furnace blacks on the physical properties of elastomers were made.

From there onwards, many theories were proposed and developed to explain the reinforcing action of carbon black. Reinforcement of elastomers with carbon black can be divided into five main sections for easy understanding.

1. Nature of carbon black
2. Effect of incorporating carbon black in elastomers
3. Effect of state of mix on reinforcement
4. Interaction between carbon black and polymer
5. Surface interactions and reinforcement

2.7.2 Nature of Carbon Black

Reinforcement by fillers especially carbon black, is one of the most important aspects of rubber technology. The principal relevant properties of carbon black include,

(1) Particle size, surface area and porosity
(2) Aggregate structure (bulkiness)
(3) Amount of carbon black per aggregate
(4) Surface activity
(5) Surface chemistry
The smallest unit of carbon black under well dispersed conditions is called a primary aggregate; it is composed of a number of spheroidal particles which are formed in the flame and fused together in a single paracrystalline entity in which the graphitic carbon layers are arranged parallel to the surface. The particle and aggregate sizes are controlled by furnace conditions, especially feed stock concentration, temperature history and traces of alkali metals. Carbon black can be characterised by electron microscopy coupled with image analysis, which show a 60-fold difference in the average amount of carbon per aggregate between two extreme grades (N110 and N765). The technique has revealed considerable information about the shape and the complexity of aggregates.

Surface area (per gram) is measured by adsorption of nitrogen or cetyltrimethyl-ammonium bromide (CTAB). Iodine adsorption is a common technical procedure which gives results within 10% - 20% of the surface area, but it is also affected by various other factors.

The bulkiness of individual aggregates, referred to as 'structure', is measured by adsorption of dibutylphthalate. Optical and other methods can be used for measuring the average amount of carbon per aggregate, while distributional information can be obtained from electron microscopy or centrifugal sedimentation. Surface activity is measured by adsorption of gases or by rubber itself (bound rubber), while surface chemistry is conventionally tested by slurry pH and by weight loss on heating.

Carbon formation, and particle growth and aggregate formation are shown in figures 2.17 and 2.18.57
Fig. 2.17: Carbon black formation reactions.\textsuperscript{57}

Fig. 2.18: Schematic representation of particle growth and structure formation.\textsuperscript{57}
2.7.3 Effect of Incorporating Carbon Black in Elastomers

The incorporation process as explained earlier in 2.6.1, refers to the wetting of carbon black with rubber and squeezing out entrapped air. According to Cotton\textsuperscript{58}, during the first stage of incorporation, carbon black agglomerates become encapsulated by polymer. At this stage, the interstices within these agglomerates are still filled with air, giving a very weak crumbly composite. The rubber is forced into these interstices during the second stage of incorporation. As the rubber is being forced through the narrow channels between the aggregates, bound rubber is being formed. The immobilised layer of polymer tends to reduce the effective cross section of the channels through which more rubber must pass before reaching the inner agglomerates. Thus, as the activity of carbon black increases, the higher amount of bound rubber increases the incorporation time.

At a given carbon black activity, the effective thickness of the immobilised polymer layer tends to increase with increasing molecular weight of the polymer, while oil loading has no effect other than that associated with the lowering of bound rubber content.

The primary aggregate size and shape properties of carbon blacks are system dependent\textsuperscript{59} and often vary as a function of polymer type, compound viscosity and mixing procedure. Electron microscope image analysis techniques provide a direct measure of black morphology in specific rubber systems. ‘High structure’ carbon blacks generally undergo greater aggregate breakdown during rubber compounding in comparison to ‘low structure’ types. Elastomers of high viscosity such as natural rubber also cause greater breakdown of the black than low viscosity polymers. Vulcanizate failure properties are dependent on the size and shape of the black aggregate and their degree of dispersion. Tensile strength and abrasion resistance increase with diminishing aggregate size (higher surface area) and higher dispersion level. Abrasion resistance is also improved by greater black-polymer interaction, i.e. higher bound rubber.
2.7.4 Effect of State of Mix on Reinforcement\textsuperscript{57}

In order to reinforce, carbon black must be adequately dispersed. In the early stages of incorporation into rubber, the pellets are broken-down into rubber-filled fragments. As explained earlier in section 2.6.1 continued shear stretches out the inclusions and brings about colloidal dispersion of the ultimate units - the aggregates which form a network. Increasing dispersion reduces the Mooney viscosity, by reduction in the amount of rubber immobilised between aggregates and by decreasing the molecular weight of unbound rubber.\textsuperscript{60} (Fig. 2.19)

As shown in Fig. 2.20, the tensile strength reaches a maximum in 3 min. and then levels off. Elongation and laboratory abrasion (not shown in Fig. 2.20) behave similarly. In a vulcanised compound, with well dispersed black, the static modulus depends mainly on the volume fraction of carbon black plus the rubber occluded within the aggregates; this is controlled by the aggregate bulkiness. Carbon black contributes to high hysteresis at low amplitudes, by breaking and reformation of interaggregate bonds; and at high strains (stress softening) by various mechanisms including molecular slippage.
Fig. 2.19: Rheological properties of uncured compound vs. mixing time.
(numbers refer to percentage of carbon black dispersed)⁶⁰

Fig. 2.20: Stress-strain properties vs. mixing time (numbers refer to percentage of 
carbon black dispersed)⁶⁰
2.7.5 Interaction between Carbon Black and Polymer

In the presence of carbon blacks or other active fillers, polymers which originally are completely soluble in a given solvent, become partially insoluble. The insoluble rubber, often referred to as bound rubber, results from the presence of strong associations between polymer and carbon black, and from the three dimensional rubber-black network which is formed through these associations (Figs.2.21 and 2.22). Bound rubber, ideally, is measured by means of a polymer - filler masterbatch in which the curing agents have not been added. Fig 2.21 shows a dimensional schematic of a bound rubber model.

Fig.2.21: Dimensional schematic of bound rubber model
Carbon black concentration - 54 phr
Carbon particle diameter - 300 Å
Distance between particle centres - 452 Å
Distance between particle edges - 152 Å
Length of polymer chain, MW = 350,000, 19250 Å
2.7.6 Surface Interactions and Reinforcement

Studies on reinforcement generally agree that the surface interaction between fillers and rubber molecules or network segments involve ranges of bond energies from relatively weak to very strong. In all cases, physical adsorption undoubtedly occurs to varying degrees depending on the particular surface and molecular segments.

Evidence for chemical bonding at the interface is also conclusive for some systems, but the importance and the necessity for this type of interaction are far from evident. When physical interaction is high, such as for carbon black in hydrocarbon rubbers, there may be little added contribution to reinforcement from the chemical bonding which normally occurs, although this may contribute to other desirable properties. It is also probable that chemical interaction improves interfacial wetting and adhesion, improves dispersion and prevents reflocculation of dispersed particulates. Chemical interaction may provide a dispersing surface layer, analogous to the surface layer obtained from the use of dispersing agents in liquid systems.
In addition to the simple dispersing effect of chemical interaction, there may also occur an actual bridging or coupling of the particle surface to the elastomeric network.\textsuperscript{64,65} This acts to stabilise the special arrangement of particles in the elastomeric network, a desirable feature for good dynamic performance. However, it was shown that attempts to increase or decrease chemical interaction\textsuperscript{25} have led only to secondary effects on the degree of reinforcement by carbon black and that chemical bonding is not a necessary requirement for reinforcement.

### 2.8 Processing Additives

#### 2.8.1 Introduction

In his review of processing aids, Crowther\textsuperscript{66} referred to a definition given by Kirchoff and Trowman\textsuperscript{67} as being: ‘materials which when added to a rubber compound at relatively low loadings, will improve processability without adversely affecting physical properties’. This definition is limiting because some products currently available can adversely influence building tack, scorch, cure rate and bloom; properties which are critical for a number of key operations.

In any case, use of processing aids in rubber compounding\textsuperscript{68} can play a significant role in assisting the industry’s needs to reduce costs and improve output and quality. Efficient processing depends on the equipment and its mode of use, rheological properties of the compound and the quality of the surfaces in contact with it. Output is governed by factors such as flow rate, shearing forces, die design and the sensitivity of the compound viscosity to temperature.

The functions of processing aids can be summarised as follows:

* Improve plasticisation
* Improve filler dispersion
* Reduce mixing time and mixing energy
* Better mill handling
* Faster extrusion and lower heat build up on extrusion
* Reduce die swell
* Better calendering
* Shorter injection moulding time
* Improve mould release
* Easier fabrication
* Improved product appearance

2.8.2. Types of Plasticizing Processing Aids

In view of the increasing number and range of products available, classifying processing aids can take different paths. Processing aids which are mostly mixtures can be divided into a number of chemical classes. 69

1. Fatty acid derivatives

These are mixtures derived from naturally occurring long chain saturated or unsaturated carboxylic acids such as stearic, palmitic, oleic or linoleic acids. The derivatives may be methyl or ethyl esters; sodium, potassium, zinc or calcium salts or metal soaps; amides; bis-amides or alcohols.

2. Natural synthetic resins

Mostly ill-defined polymeric products, often originating from thermal polymerisation of side products or residues of the petroleum or coal industries. These include aliphatic/ naphthenic/ aromatic resins, coumarone-indene resins and blends of poly (coumarone-indene) with polystyrene, polychloropentadiene or polyolefins. O'Connor and Slinger 70 have divided this group of processing aids into three main categories. They are,

- hydrocarbon resins,
- petroleum resins and
- phenolic resins.
3. Polar surfactants

These are from a varied group, mostly comprising mixtures, for example, barium salt of tall oil bound to inorganic fillers, polar surfactants on high activity silica or processing lubricants with surfactant activity.

4. Low molecular weight polymers

This class includes the saturated polyethylenes, polypropylenes and polybutenes, and unsaturated natural rubber, polyisoprene, polybutadiene, epoxidised polybutadiene and trans-polyoctenamer. Nearly all synthetic polymers are available in low molecular weight fractions, either as by-products of the high molecular weight polymerisation process or as specific low molecular weight polymerisation products.

5. Fluorinated products

Comprise two commercialised products: a 'fluorochemical' and a modified PTFE.

6. Miscellaneous

Products which do not readily fall into the previous categories and include zinc methacrylate, paraffin oil/ sulphonic acid blends and sodium alkylsulphates.

7. Rubber process oils

Crowther\textsuperscript{71} has reported three main classes of rubber process oils. They are, paraffinic, $C_nH_{2n+2}$

These oils are generally recognised as acting less effectively as process aids but have little effect upon ageing characteristics or colour stability. The low temperature flexibility of compounds containing these oils are good and generally little effect on cure characteristics is noticed.
Naphthenic, \( \text{C}_n\text{H}_{2n} \)

These are intermediate between paraffinics and aromatics in their effects on natural rubber, giving a good balance between colour stability and processing characteristics.

Aromatic, \( \text{C}_n\text{H}_{2n-6} \)

This class of oils is claimed to give the best processing characteristics but colour is generally poor and thus compound colour stability is usually affected. Cure characteristics can also be adversely changed.

Despite these classifications, rubber processing oils are usually mixtures of all three types, and are classified according to the nature of the predominating oil.

2.8.3 Methods of Achieving Plasticization

(a) By Mechanical breakdown\(^{69}\)

One of the methods to achieve plasticization of natural rubber is by mechanical breakdown. As explained earlier in section 2.6.2 in mastication, natural rubber shows a significant decrease in Mooney viscosity under shear forces such as those encountered during internal mixing or mill mixing. However, in other rubbers such as butyl and SBR, the reduction in viscosity is less than that of natural rubber, as shown in Fig. 2.23\(^{69}\)
Fig. 2.23: Effect of milling on viscosity of natural, isobutene-isoprene, polychloroprene and styrene-butadiene rubbers

(b) By Chemical Plasticisers (peptisers)

Mastication aided by the use of peptisers is an established alternative to mechanical shear alone as a means of reducing viscosity to a level appropriate for mixing and subsequent processing. Peptisation has a number of attractions, since mechanical breakdown is time consuming and requires a large energy input. This has increased use of peptisers, particularly for mixes intended for injection moulding.

Peptisers rapidly reduce molecular weight (by chain cleavage) and Mooney viscosity. This treatment does not adversely affect the vulcanisation rate or the physical properties of cured rubber. Several aromatic disulphides and mercaptans are used as peptisers.
Peptisation can occur under high shear mixing or milling, resulting in chain rupture due to homolytic carbon - carbon bond cleavage and the production of polymeric radicals. Peptisers assist in this breakdown by initiating radical sites that cleave or by neutralising radicals that have formed on cleavage products by supplying hydrogen atoms or intercepting the polymer radical by thyl radical. Since many radicals are forming during mastication, the peptiser promotes oxidation.

The effect of chemical peptiser on the Mooney viscosity and mixing time is shown in Fig. 2.24 and some commercially available peptisers are shown in Table 2.3 together with their minimum operative temperatures.

![Graph showing the effect of chemical plasticiser on Mooney viscosity](image)

**Fig. 2.24:** Effect of chemical plasticiser: pentachlorothiophenol, on the Mooney viscosity of SBR rubber during mastication.
Table 2.3: Commercially available peptisers and their minimum operative temperatures.55

<table>
<thead>
<tr>
<th>Producer</th>
<th>Trade Name</th>
<th>Chemical Name</th>
<th>Minimum Operative Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anchor Chemicals</td>
<td>Peptone 22</td>
<td>Di(o-benzamidophenyl) disulphide</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>Peptone 44</td>
<td>Activated Di(o-benzamidophenyl) disulphide</td>
<td>70</td>
</tr>
<tr>
<td>Bayer</td>
<td>Renacit IV</td>
<td>Zinc salt of Pentachlorothiophenol</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>Renacit VII</td>
<td>Pentachlorothiophenol with activating and dispersing additives</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>Renacit VIII</td>
<td>Metal complex on an organic carrier</td>
<td>70</td>
</tr>
</tbody>
</table>

Crowther72 reports that an appropriate level of peptizer for a natural rubber compound lies between 0.05 and 1.15 phr. Recommended levels of proprietary blends of peptizers and process aids usually contain levels of chemical peptizers below 0.15 phr, which lead to good flow properties.

Noakes73 has shown that the use of a higher than normal levels of peptiser (more than 0.6 phr) and process aids, to achieve very low mix viscosity, can lead to inferior physical properties in natural rubber vulcanisates.
(c) By Physical Plasticizers

Chemical plasticizers have limited use due to certain parameters, such as temperature of mixing, type of rubber, cost, etc. Hence, physical plasticizers are often used in practice. Physical plasticizers weaken the intermolecular forces between rubber molecules and make it easier for the chains to slip past each other and for the whole mass to flow. Most of the processing aids work as physical plasticizers.

2.8.4 Modes of Action of Plasticizing Processing Aids

Three modes of action of rheochemicals have been proposed, depending on the compatibility of the material with the rubber compound.74

Model 1 - The product has limited or low compatibility. This product will bloom to the surface of the rubber where it acts as an external lubricant at the rubber-metal interface producing slippage in the processing equipment.

Model 2 - The product has medium-low compatibility. Providing its concentration is kept below a certain limit, the material will act as an internal lubricant, favouring slippage between flow units of the compound. If the limit of concentration is exceeded, then an external lubricant action is added which may become dominant.

Model 3 - The product has high compatibility. Such materials will modify rheological properties of rubber compound in a completely different manner. As no blooming will occur, they essentially behave as bulk viscosity modifiers and two situations are proposed:
(a) through intermacromolecular action, to produce a reduction in the magnitude of enlargements between polymer molecules.

(b) through intramolecular action, diffusing into the polymer molecule and consequently softening it by swelling.

Most commercially available processing aids fall into the first two categories. Depending on the rubber compound, the chemical considered and its concentration, the actual mechanism lies somewhere in between acting as an external lubricant and as a bulk viscosity modifier.\textsuperscript{75}

Fig 2.25: Modes of action of rheological chemicals/processing aids.\textsuperscript{74}
2.9 Surfactants

2.9.1 Introduction

Surfactants are a special group of chemicals which include many of the plasticizing processing aids described in section 2.8.2.

Surfactants or surface active agents are substances that, when present at low concentration, have the property of adsorbing on to the surfaces or interfaces of the system and of altering, to a marked degree, the surface or interfacial free energies of those surfaces. In a definition given by Ottewill\textsuperscript{76,77} surfactants are compounds which are able to lower the surface tension of the air-water and water-oil interfaces and also, in general, to adsorb strongly at solid-liquid interfaces.

The surface activity of a surfactant depends on the presence of a hydrophobic (non-polar, water-insoluble) hydrocarbon chain and a hydrophilic (polar, water soluble) group. If surfactant molecules become located at an air-water or oil-water interface, they are able to locate their hydrophilic group in the aqueous phase and allow the hydrophobic hydrocarbon chains to escape into the organic vapour or oil phase.

Fig 2.26: Activity of surfactants\textsuperscript{76}
Surface active agents are characterised by their linear structure. One end of this linear structure is composed of radicals which are compatible with the solvent, and the opposite end of incompatible radicals. For example, fatty amines are composed of a hydrophobic (non-polar, water insoluble) hydrocarbon chain, characterised by weak residual valence forces in one end and a hydrophilic (polar, water soluble) cationic nitrogen group which has strong residual valence forces on the other end as shown below.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{NH}_3^+ \\
\text{Hydrophobic hydrocarbon chain} & \quad \text{Hydrophilic ammonium group}
\end{align*}
\]

2.9.2 Classification of Surfactants\textsuperscript{78,79,80}

The most common system used to classify surfactants is one which depends on the distribution of electrical charge on the molecules, and this will be described below.

2.9.2a Anionic Surface Active Agents

This class of surfactant is characterised by the inclusion of a low affinity hydrocarbon chain adjacent to the anion and is usually soluble in aqueous solutions. Sodium stearate (C\textsubscript{17}H\textsubscript{35}COONa) is a typical anionic surfactant since it ionises in solution to form Na\textsuperscript{+} and the long chain stearate ion C\textsubscript{17}H\textsubscript{35}COO\textsuperscript{-}, which is considered to be responsible for its surface activity. In this class some of the most important end groups are carboxy (-COOH), sulphonic acid (-SO\textsubscript{3}H) and sulphuric ester (-OSO\textsubscript{3}H).
2.9.2b Non-ionic Surface Active Agents

The non-ionic class has non-ionisable high-affinity end group i.e. no residual electrical charge as for example, dodecylalcohol ethoxylate:

\[ \text{CH}_3(\text{CH}_2)_{10}\text{CH}_2(\text{OCH}_2\text{CH}_2)_n\text{OH} \]

Usually the non-ionic surfactants contain a number of oxygen, nitrogen or sulphur atoms in non-ionising configurations. Also falling into this group are,

Monoglyceride of a long chain fatty acid,

\[ \text{RCOOCH}_2\text{CHOHCH}_2\text{OH} \]

Polyoxyethylenated alkyl phenol,

\[ \text{RC}_6\text{H}_4(\text{OC}_2\text{H}_4)_x\text{OH} \]

2.9.2c Amphoteric (Zwitterionic) Surface Active Agents

This class is characterised by the presence of both positive and negative centres in one molecule. Depending on the pH of the medium, cationic, anionic or non-ionic type properties may be exhibited. Examples include;

\[ \text{RN}^+\text{H}_2\text{CH}_2\text{COO}^- \quad \text{long chain amino acid} \]

\[ \text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{SO}_3^- \quad \text{sulphobetaine} \]
2.9.2d Cationic Surface Active Agents

In this group the surface active portion bears a positive charge. Cetyltrimethyl ammonium bromide is an example of this class. In aqueous solution it ionises according to,

\[
\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{N}+\text{Br}^- \rightleftharpoons \text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{N}^+ + \text{Br}^-
\]

In this class the most important end groups are primary, secondary and tertiary amino groups and the quaternary ammonium groups.\(^81\)

The hydrophobic, hydrocarbon chain portion (R) is usually derived from either fatty acids or from petrochemical sources. Fatty acids are usually derived from natural sources such as coconut oil or tallow. Therefore R will vary in both the chain length as well as in the degree of saturation.\(^82\)

When R is derived from petrochemical sources, many components have been traced due to variation in molecular weight, degree of branching, the presence of cyclic impurities or different ring substituents in aromatic system. Variation in the long chain hydrocarbon R', that is in its nature and composition, can significantly affect different characteristics. Some commercially available cationic surfactants are shown in Table 2.4.\(^82\)
### Table 2.4

**Some commercially available cationic surfactants**

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Trade Name</th>
<th>Code</th>
<th>Description</th>
<th>App. % Active</th>
<th>Physical Form</th>
<th>Properties and/or Uses</th>
<th>Examples of Fields of Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Akzo Chemie UK Ltd</td>
<td>General Formula: $RNH(CH_2)_3NH_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Form strongly bonded films on the surfaces of metal, textiles, plastics, etc.</td>
<td>Metal working emulsion for car underseals, carbon papers and typewriter ribbons</td>
</tr>
<tr>
<td>Duomeen</td>
<td>T</td>
<td>R = Tallow</td>
<td>89</td>
<td>Heavy paste</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Duomeen</td>
<td>C</td>
<td>R = Coconut</td>
<td>89</td>
<td>Liquid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Duomeen</td>
<td>CD</td>
<td>R = Coconut</td>
<td>89</td>
<td>Paste</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Duomeen</td>
<td>S</td>
<td>R = Soya bean</td>
<td>89</td>
<td>Pasty liquid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Duomeen</td>
<td>O</td>
<td>R = Oleic</td>
<td>89</td>
<td>Liquid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Croda Chemicals Ltd</td>
<td>Fatty Alkyl Propylene Diamines ($RNH \text{C}_2\text{H}_2\text{C}_2\text{NH}_2$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Strongly cationic and substantive to negatively charged surfaces</td>
<td>Dispersants for pigments, corrosion inhibitors, drawing aids for copper wire and tubing etc.</td>
</tr>
<tr>
<td>Dicrodamine</td>
<td>1.C</td>
<td>R = Coconut</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dicrodamine</td>
<td>1.T</td>
<td>R = Tallow</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dicrodamine</td>
<td>1.HT</td>
<td>R = Hydrogenated tallow</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dicrodamine</td>
<td>1.0</td>
<td>R = Oleic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KenoGard UK Ltd</td>
<td>Diamine</td>
<td>HBG</td>
<td>R = Hydrogenated tallow</td>
<td></td>
<td></td>
<td>Same as above</td>
<td>Same as above</td>
</tr>
<tr>
<td>Diamine</td>
<td>B11</td>
<td>R = alkyl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Cationic surfactants can be divided into five different categories. They are,

i) Straight chain alkyl ammonium compounds.

ii) Polymeric cationic surfactants.

iii) Cyclic alkylammonium compounds.

iv) Petroleum derived cationics.

v) Miscellaneous non-nitrogen containing cationic surfactants.

The majority of cationic surfactants used currently fall into the first two categories.

i) **Straight chain alkyl ammonium compounds.**

Until recent developments in the petrochemical industry, the main raw materials for the preparation of cationic surfactants were animal fats and vegetable oils. Fatty amines and their derivatives which may have one, two or three long chains connected directly or indirectly to the nitrogen atom may represent all this class of cationic surfactants.

(a) **Alkyl Diamine Cationic Surfactants**

An alkyl diamine cationic surface active agent such as R-NH(CH₂)₃NH₂, where R is an alkyl group derived from any fatty acid, is prepared by reacting a primary amine with acrylonitrile as shown in equations 2.1 and 2.2 below.

\[
\begin{align*}
\text{RNH₂} + \text{CH₂ = CHCN} & \rightarrow \text{RNHCH₂CH₂CN} \quad \text{(Eq.2.1)} \\
\text{Primary fatty amine} & \quad \text{Acrylonitrile} & \quad \text{Aminonitrile} \\
\text{RNHCH₂CH₂CN} + \text{H₂} & \rightarrow \text{RNHCH₂CH₂CH₂NH₂} \quad \text{(Eq.2.2)} \\
& \quad \text{N-alkyl 1-3 diaminopropane}
\end{align*}
\]
The reaction represented by equation 2.1 will take place at 70 to 80°C in the presence of water. The diamine produced (see equation 2.2) is often called an amino-bridged amine. This is because the alkyl group (R) is connected by an amino group to the active amino group at the end of the chain. Diamines undergo most of the reactions of primary fatty amines. The principal one is its reaction with oleic acid. When two molecules of oleic acid\(^3\) react with one molecule of diamine, the di-oleate is produced.

\[
\text{R-NH(CH}_2\text{)}_3\text{NH}_2 + 2\text{ C}_17\text{H}_33\text{COOH} \rightarrow \text{(RNH}_2\text{(CH}_2\text{)}_3\text{NH}_3)_2\text{(C}_17\text{H}_33\text{COO}^-)} 
\]

The dioleate salts produced by the above equation are considered highly surface active materials and among the important surfactants which are commonly used in various applications such as pigments, wetting agents, corrosion inhibitors for epoxy coatings, etc. This was the starting material used in Hepburn and Mahdi's research work, which led to the discovery of multifunctional additives. Commercially available diamides and their uses are given in Table 2.5.

(b) Amide-bridged Amines (ABA)

Amide-bridged amines have been synthesised, where a long aliphatic chain (R) is separated from the amino group by an amide, which is another functional group. These cationic surfactants are among the most versatile surface active agents. A great variety of linked amines have been synthesised. Each particular type has its own raw materials and reaction conditions; for example unsymmetrical fatty acyl ethylenediamine is prepared\(^4\) by the action of fatty acid ester in an excess of ethylenediamine as shown in the equation below:
It was found\textsuperscript{85} that some of the diacyl compounds; \( \text{RCONH(CH}_2\text{)}_2\text{NHCOR} \) are formed at the same time as \( \text{RCONH(CH}_2\text{)}_2\text{NH}_2 \). This does not behave as a surface active agent, but as a hydrophobic, water-repellent substance.

ii) Polymeric cationic surfactants.

The general structure of the polymeric surface active agents can be divided into two parts: one is that of a high molecular weight polymer and the other part is that of basic groups, usually either a weak amine or quaternary ammonium ion, distributed along the chain.

The other three groups of cationic surfactants identified in page 71, do not have any applications in the rubber or polymer industry.

Surface active agents are evaluated and utilised for what is called their gross effect.\textsuperscript{86} These gross effects can be grouped into five classes:

i) Wetting
   ii) Foaming
   iii) Detergency
   iv) Dispersion
   v) Emulsification
<table>
<thead>
<tr>
<th>Supplier</th>
<th>Code</th>
<th>Description</th>
<th>Use and Field of Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Croda Chemicals</td>
<td>EBS</td>
<td>RCO = stearyl = CH₃(CH₂)₁₆CO</td>
<td>Plastic industry: mould release agents for PVC and other plastics</td>
</tr>
<tr>
<td>Ltd.</td>
<td>EBO</td>
<td>RCO = oleyl = CH₃(CH₂)₇CH=CH(CH₂)₇CO</td>
<td>Paper industry: water repellent for cardboard and other paper products</td>
</tr>
<tr>
<td></td>
<td>EBL</td>
<td>RCO = lauroyl = CH₃(CH₂)₁₀CO</td>
<td>Print and inks: in-house stability of pigment dispersion. As corrosion inhibitor for paints and surface coatings.</td>
</tr>
<tr>
<td></td>
<td>EBE</td>
<td>RCO = erucyl = CH₃(CH₂)₇CH=CH(CH₂)₁₀CO</td>
<td>Antifoam agents: recommended as an antifoam in steam generators and sugar beet liquor evaporators</td>
</tr>
<tr>
<td></td>
<td>EBB</td>
<td>RCO = behenyl = CH₃(CH₂)₂₀CO</td>
<td>Metal drawing: they have the advantage of producing products without surface erosion or residual surface films</td>
</tr>
<tr>
<td></td>
<td>EBM</td>
<td>RCO = myristyl = CH₃(CH₂)₁₄CO</td>
<td></td>
</tr>
</tbody>
</table>
2.10 Cationic Surfactants as Multi-Purpose Rubber Compounding Ingredients

2.10.1 Introduction

In 1983 Hepburn and Mahdi\(^{88,89,90}\), during their research on 'the effect of cationic surfactants on NR/SBR truck tyre side wall compounds', found a certain cationic surfactant which functioned in four successive ways during production, first - as a mill roll release agent, second - as a filler dispersant, third - as an accelerator for sulphur vulcanisation, fourth - as a mould releasing agent.

This chemical was called a Surfactant Accelerator Processing Aid (SAPA), because of the above mentioned capabilities.

The general structure of this chemical is,

\[
[RNH_2(CH_2)_3NH_3]^2+ 2[R’COO]^- 
\]

Since this discovery, the term Multifunctional Additive (MFA) has replaced the original name which better describes the wider properties of these materials. According to Hepburn and Mahdi\(^{88}\), MFA or SAPA affects all cure characteristics; scorch and \(t_{90}\) cure times were reduced to about 50% of their original values. Tensile, modulus and resilience properties were all greater than those of the control. Furthermore, it was observed that mixes containing MFA(SAPA) possessed excellent flow properties. They were released both from the mill rolls and, when vulcanised, from the moulds more readily than in the cases of using other process oils and aids.

It is suggested that MFA (SAPA) functions in rubber by two different routes. At processing temperatures (50 to 100\(^{\circ}\)C) it remains essentially intact as the original chemical entity, thereby functioning as a roll mill release agent and filler aggregate dispersant. However, at vulcanisation temperatures, commencing at about 135\(^{\circ}\)C, MFA dissociates into two primary components, a primary amine, \(RNH_2(CH_2)_3NH_2\)
and a fatty acid R'COOH. Simultaneously the amine acts as an accelerator and the fatty acid functions as an excellent mould release agent.

The following flow chart gives a summary of MFA’s functions.

\[
[RN\text{H}_2(\text{CH}_2)_n\text{NH}_3]^2^+ \quad 2[R_1\text{COO}]^- \\
\text{(where } R \text{ and } R_1 \text{ are long chain alkyl groups derived from fatty acids)}
\]

**Before dissociation**

1. An internal processing aid
2. A filler-rubber surfactant (enabling wetting to take place between the rubber/filler interfaces)
3. A vulcanisation accelerator activator
4. Internal flow additive
5. Mould release agent
Asore’s PhD research work on “fatty-diamine cationic surfactants in rubber compounds: synthesis, mixing and properties”, also demonstrated the above properties of MFA. Apart from commercially available cationic surfactants - EN444 and Duomeen TDO, six new fatty diamine cationic surfactants have been synthesised and investigated. These surfactants, based on oleic acid, linoleic acid, rubber seed oil, 1,2-ethane diamine and 1,6-hexane diamine, have exhibited a high activation energy of vulcanisation and have functioned effectively as activators and accelerators in SBR mixes. However, a decrease in scorch time was also observed.

Even though EN444, Duomeen TDO and one of the new salts EDDO (1,2-ethane diamine dioleate) show properties like cure acceleration, reduction in mixing time and energy and enhancement of mechanical properties, they also show a decrease in scorch time which is a disadvantage in rubber processing.

2.10.2 MFA/SAPA as an Activator and Accelerator of Cure

Hepburn and Mahdi investigated the ability of SAPA(MFA) to function as a cure activator and accelerator in its own right. They compared a mix containing an accelerator system consisting of MFA/S with a normal mix containing ZnO/Stearic acid/CBS/S.

The examination of data revealed the following:
(i) SAPA can function in its own right as an accelerator of sulphur vulcanisation.
(ii) It is not necessary to have present in the formulation any zinc oxide and stearic acid to function as activators of vulcanisation.
(iii) Good strength, modulus, rebound resilience and hardness properties were obtained using the simple SAPA/S cure system.
(iv) These properties increased a little as the proportion of SAPA was increased from 1 to 3 phr; the level of 7 phr of SAPA was obviously too much for optimum properties and at this proportion it exhibited a diluting and plasticising effect.
(v) The rate and state of cure was dependent upon the proportions of SAPA used, as can be seen from figure 2.27.
(vi) The scorch time of the SAPA mixes was much less than that of an equivalent
delayed action sulphenamide system.

Fig. 2.27: Curemeter traces of NR/SBR compound containing various levels of SAPA 1/1 as a combined cure activator/accelerator system. Cure conditions: $160^\circ C \pm 3$

Hepburn and Mahdi showed that SAPA can also act as a crosslinking agent
for halogen containing elastomers such as polychloroprene. They found that a
divalent metal oxide, such as ZnO or MgO, was not necessary to obtain a good state
of cure. Furthermore, they found that the chloroprene vulcanisate crosslinked by
SAPA showed long scorch times and had good physical properties, in particularly
low compression set. In the case of polychloroprene, SAPA was classed as amine
bridged amides of a cationic surfactant (ABA).
Ismail and others\textsuperscript{93} also showed that all cure characteristics, including the rate and state of cure were dependent on the level of MFA. Compared to the control, scorch time for the filled compounds was reduced about 50\% and $t_{95}$ cure time was reduced by about 30\%. They also noted a similar effect for gum compounds, scorch time being reduced by 75\% and $t_{95}$ by 40\%.

2.10.3 Modes of Action of MFA in Carbon Black filled NR Compounds

Freakley and Ismail\textsuperscript{94,95} have studied the modes of action of a specific MFA - EN444, in natural rubber compounds filled with carbon black and silica. The EN444 incorporated compounds showed an enhancement in mechanical properties. Fig. 2.28 shows effect of EN444 loading on tensile strength and 300\% modulus of N330 filled vulcanised rubber.

The addition of EN444 to a natural rubber compound with 50phr N330 carbon black is shown to increase certain physical properties up to a level of 2phr, but at higher loadings there is a gradual deterioration of properties. The optimum level found was correspond approximately to the amount needed for a monolayer coverage of the carbon black surface.
Fig. 2.28: Effects of EN444 loading on tensile strength and 300% modulus of a natural rubber compound filled with 50phr of N330.94

A theoretical calculation was made by Ismail to determine the amount of EN444 needed for a monolayer coverage, supposing that the EN444 molecules were closely packed and laid flat with the EN444 molecule axes parallel to the carbon black surface.

The total number of carbon atoms in a EN444 molecule was estimated to be around 60 from X-ray photoelectron spectroscopy (XPS) and elemental analysis results. The area covered by one EN444 molecule was calculated as approximately 326Å. Therefore the amount of EN444 needed to cover the surface of 50g of N330 carbon black (surface area 78m²/g) was:

\[
\frac{50 \times 78 \times 10^{20} \text{ M}}{326 \text{ N}_A} = 1.9 \text{ (g)}
\]
where, $N_A$ was the Avogadro constant ($6.02 \times 10^{23}$)

$M$ was the molar mass of the EN444 which is estimated to be about 940.

The EN444 exerts its greatest effect at the elastomer - carbon black interface while gum compounds show minimal changes in physical properties with EN444 concentration. Figs.2.29 and 2.30 show the effect of EN444 loading on tensile strength and tear strength for gum and filled natural rubber compounds. In this investigation swelling test results showed very little change in the solvent uptake with increasing EN444, indicating that the effect on crosslink density was small. Therefore, the improvement in physical properties with increasing amount of EN444 cannot be attributed to the crosslink density. However, the carbon black dispersion measurement, carried out by computer - aided image analysis and scanning electron microscopy (SEM) showed a substantial improvement with increasing EN444 concentration, hence the improvements in physical properties were attributed to the improved dispersion of the carbon black.

Fig. 2.29 : Effect of MFA loading on tensile strength for gum and filled NR compounds

94
Furthermore, bound rubber (Fig. 2.31) was found to decrease with the addition of EN444 and a limiting bound rubber value was obtained at the EN444 loading which corresponded to the monolayer coverage of the carbon black. This is thought to be due to the reduction of the amount of rubber immobilised in carbon black agglomerates due to the improved carbon black dispersion. Therefore, it is believed that EN444 acts as a carbon black surface wetting agent, by reducing the interaction between the carbon black and the rubber and thus aiding the breakdown of carbon black agglomerates at the mixing stage.

The carbon black agglomerate is composed of loosely bound aggregates of fused carbon black primary particles. A schematic representation of immobilised rubber within a carbon black agglomerate is shown in Figure 2.32. The mechanism of adsorption by multifunctional addition is shown Fig. 2.33.
Fig. 2.31: Effects of EN444 level on bound rubber of N330 determined with o-xylene extraction at room temperature\textsuperscript{96}

Fig. 2.32: Schematic representation of immobilised rubber within a carbon black agglomerate\textsuperscript{95}
a) At less than monolayer coverage: partial coverage of carbon black surfaces by MFA molecules

b) At monolayer coverage: complete coverage of carbon black surfaces by MFA molecules

c) At more than monolayer coverage: formation of second MFA layer. Poor MFA - MFA interaction results in deterioration of properties

Fig. 2.33: Mechanism of adsorption by multifunctional additive (MFA) ⁹⁴.
Sheng et al\textsuperscript{96} have studied the interfacial effects of EN444 on carbon black filled rubber. During their study, several normal cure rate carbon blacks were characterised by XPS (X-ray photoelectron spectroscopy) and vapour - phase chemical derivatization: carbon blacks were found to have very few functional groups on their surfaces. Hence, it was concluded that the interaction between carbon black and EN444 was probably due to dispersion interactions as the surface of carbon black is chemically inert.

The studies on silica filled natural rubber showed much higher optimum EN444 level than for carbon black filled compounds, which was attributed to a different orientation of the EN444 molecule at the silica - rubber interface. The EN444 molecules were thought to stand on the filler surface with their polar sites attached to its surface, giving rise to a much higher monolayer value at 7.5phr.

2.10.5 Thermal Stability of EN444

Sheng et al\textsuperscript{96} have also studied the thermal behaviour of EN444 using fourier transform infra red spectroscopy with a temperature cell. FTIR spectra at different temperatures in the region between 1000 and 1900 cm\textsuperscript{-1} are shown in Fig.2.33.

They have shown that EN444 is a typical amine salt of a carboxylic acid and it is thermally stable up to \textasciitilde 120°C, proving Hepburn and Mahdi's theory. Striking changes in peak intensity occurred as temperature was raised above 120°C, including the decrease of peaks at 1558 cm\textsuperscript{-1} (-NH\textsubscript{3}\textsuperscript{+}/-NH\textsubscript{2}\textsuperscript{+}) and 1400 cm\textsuperscript{-1} (-COO\textsuperscript{-}), and an increase in the peak at 1714 cm\textsuperscript{-1} (-COOH).
According to Fig. 2.34, they concluded that EN444 decomposition starts at \(-120^\circ C\) and is completed at \(-170^\circ C\). The decomposition of the EN444 can be written as,

\[
[RNH_2^+(CH_2)_3NH_3^+] (R'COO)_2
\rightarrow RNH(CH_2)_3NH_2 + 2 R'COOH
\]

where diamine acts as an activator and accelerator for vulcanisation and carboxylic acid acts as an internal flow additive and also as a mould releasing agent.
CHAPTER 3

Experimental

3.1 Experimental Plan

The research reported in this thesis was undertaken in four stages.

1. Exploration of additives for reducing the undesirable effect of fatty amine (N-Tallow-1-3, diaminopropane dioleate) on scorch and cure behaviour of the rubber compound.

2. Synthesis and evaluating of an alternative fatty amine, designed to have a lesser influence on scorch and cure time. (Octyl amine salt of benzylmalonic acid)

3. Investigation of low molecular weight polystyrene, as a representative of a different class of dispersing agent.

4. Exploration of the use of multifunctional additives for reduction of mastication time and increase of the maximum filler loading of a rubber compound.
3.2 Materials

Materials and chemicals used in this investigation are given in Table 3.1.

Table 3.1: Materials and chemicals

<table>
<thead>
<tr>
<th>Name</th>
<th>Physical form</th>
<th>Manufacturer/Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber (SMR 10)</td>
<td></td>
<td>MRPRA</td>
</tr>
<tr>
<td>Carbon black, HAF(N330)</td>
<td></td>
<td>Cabot (UK)</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>Solid</td>
<td>Anchor Chemicals Ltd. (UK)</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>Solid</td>
<td>Anchor Chemicals Ltd. (UK)</td>
</tr>
<tr>
<td>Sulphur</td>
<td>Solid</td>
<td>Anchor Chemicals Ltd. (UK)</td>
</tr>
<tr>
<td>Flectol H</td>
<td>Solid</td>
<td>Monsanto Chemicals</td>
</tr>
<tr>
<td>EN444</td>
<td>Viscous liquid</td>
<td>Akzo Chemicals</td>
</tr>
<tr>
<td>N-Tallow-1,3-propane-diaminedistearate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CTP</td>
<td>Solid</td>
<td>Monsanto Chemicals</td>
</tr>
<tr>
<td>N-Cyclohexylthio-phthalimide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aspirin</td>
<td>Solid</td>
<td>Aldrich Chemicals</td>
</tr>
<tr>
<td>Acetyl salicylic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>Solid</td>
<td>Fisons Chemicals</td>
</tr>
<tr>
<td>Octyl amine</td>
<td>Liquid</td>
<td>Aldrich Chemicals</td>
</tr>
<tr>
<td>Benzylmalonic acid</td>
<td>Solid</td>
<td>Aldrich Chemicals</td>
</tr>
<tr>
<td>Polystyrene (molecular weight - 800)</td>
<td>Viscous liquid</td>
<td>Aldrich Chemicals</td>
</tr>
</tbody>
</table>
3.3 Mixing

3.3.1 Haake Rheocord 90 Internal Mixer

The Haake Rheocord 90 internal mixer is a computer controlled, Banbury type internal mixer with variable speed drive and a chamber capacity of 78 ml. The computer controls the machine temperatures and rotor speeds, and the torque and melt temperature. The Haake Rheocord was used for experiments in Chapters 4 and 6.

Mixing Conditions:

Fill factor 0.6
Rotor speed 60 rpm
Initial temperature 90 °C

Mixing Procedure:

The mixing cycle shown in Table 3.2 was selected by changing the mixing time after addition of the filler and selecting the best mixed sample visually. It was applied to all subsequent work.

Table 3.2: Mixing cycle used in Haake Rheocord 90

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Additions</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>SMR 10 + ZnO + St.Acid + Flectol H</td>
</tr>
<tr>
<td>2</td>
<td>N330 + Surfactants/ other chemicals</td>
</tr>
<tr>
<td>6</td>
<td>CBS</td>
</tr>
<tr>
<td>7</td>
<td>Sulphur</td>
</tr>
<tr>
<td>9</td>
<td>Dump</td>
</tr>
</tbody>
</table>
3.3.2 Francis Shaw K1 Intermix

Francis Shaw K1 Intermix is a fully automated computer controlled internal mixer which has conveyer feed of rubber and minor additives, hopper feed of filler and oil injector into the mixing chamber, for good batch-to-batch repeatability. The mixer has a chamber volume of 5.5 litres.

Mixing Conditions:

<table>
<thead>
<tr>
<th>Fill factor</th>
<th>0.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotor speed</td>
<td>35 rpm</td>
</tr>
<tr>
<td>Circulating water temperature</td>
<td>35 °C</td>
</tr>
</tbody>
</table>

The circulating water temperature was increased to 40°C for the mastication experiments described in Chapter 7.

Mixing Procedure:

The basic mixing cycle, which was used during this study, is given in Table 3.3. This was chosen with reference to previous research work done on multifunctional additives. However, this cycle in Table 3.3 was altered in some experiments and the particular cycles are given in the respective chapters.

**Table 3.3**: Mixing cycle used for mixes in Francis Shaw K1 Intermix.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Additions</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>SMR 10 + ZnO + St. Acid + Flectol H</td>
</tr>
<tr>
<td>120</td>
<td>N330 + Surfactants/other chemicals</td>
</tr>
<tr>
<td>180</td>
<td>CBS</td>
</tr>
<tr>
<td>240</td>
<td>Sulphur</td>
</tr>
<tr>
<td>320</td>
<td>Dump</td>
</tr>
</tbody>
</table>
3.4 Tests on Uncured Compounds

3.4.1 Determination of Curing Characteristics

The curing characteristics were determined by Wallace Precision Cure Analyser (Wallace PCA). This machine has been jointly developed by the Rubber and Plastics Research Association of Great Britain and H.W. Wallace Co. Limited. A small amount of the compound, approximately 2.5g, was used for this test. The test piece volume has been kept to less than 1.5 cm$^3$ and the sample thickness 1mm. Thus it produces rapid heating with nearly isothermal data, enabling the presenting of torque - time plots, from which cure times at different cure levels can be obtained.

The testing conditions are given in Table 3.4.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (kPa)</td>
<td>600</td>
</tr>
<tr>
<td>Frequency (Hz)</td>
<td>1.7</td>
</tr>
<tr>
<td>Strain</td>
<td>0.25</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>160</td>
</tr>
</tbody>
</table>

A typical cure curve obtained from the Wallace PCA is shown below.
**Torque**

**ML** - Minimum torque

**M_{HP}** - Maximum torque for a plateau curve

**t_2** - Scorch time (time taken to reach 2% of torque rise above ML)

**t_{95}** - 95% Cure time (time taken to reach 95% of the maximum torque)

**Scorch rate** = \[
\frac{\text{Torque at } t_2 - ML}{t_2 - \text{time to reach } ML}
\]

**Cure rate** = \[
\frac{\text{Maximum torque} - \text{torque at } t_2}{\text{Time to reach maximum torque} - t_2}
\]
3.4.2 Determination of Compound Viscosity

(i) Mooney Viscometer

The Mooney viscometer\textsuperscript{98} consists of two dies, which together form a cylindrical cavity, a cylindrical rotor, a temperature control device and a pressure control device. The surfaces of dies and rotor are grooved to prevent slippage of material. (Figure 3.1)

As its name suggests the viscosity measured by this machine is known as Mooney viscosity. The measuring was done in accordance to the British Standard, BS 903: Part A58 1990. The torque required to rotate a metal disc or rotor in the shallow cylindrical chamber or cavity filled with a rubber compound is measured as the Mooney viscosity. This torque is displayed on a digital monitor.

The samples were tested at 100°C using a pre heat time of 1 minute and test running time of 4 minutes. The viscosity of the compound was displayed on the digital monitor during the test running time and the end of 4 minute test time the final reading (the Mooney viscosity) was retained. Three samples were tested from each rubber compound and the results averaged.

(ii) Negretti TMS Biconical Rotor Rheometer

This variable speed biconical rotor rheometer\textsuperscript{99} was produced by Negretti Automation Limited (Aylesbury, UK) and is named the TMS rheometer (a schematic diagram is shown in Figure 3.2) after those responsible for the initial design, Turner, Moore and Smith. Unlike the single speed Mooney viscometer this instrument is capable of shear rates at which sample temperature rise resulting from viscous dissipation is a significant effect. The existence of sample temperature rise due to shear heating in the TMS rheometer is made manifest by a distortion of the flow curve towards the shear rate axis.
In the measurement of the viscous flow behaviour of the rubber compounds, 25 g of sample was pre-heated in the transfer chamber for 240 seconds at 100 °C, after which the sample was transferred to the test chamber. The rotor speed was increased in a series of steps and the torque on the rotor at each speed recorded. The TMS rheometer operates in the shear rate region of 0.1 to 100 per second. Three samples were tested from each rubber compound and the results averaged.

![Diagram of Mooney viscometer](image)

**Fig.3.1** : Schematic diagram of the Mooney viscometer.
3.5 Determination of Physical Properties

3.5.1 Tensile Properties

The test was carried out in accordance with BS 903: Part A2\textsuperscript{100}, using a 'Hounsfield 500L' testing machine at room temperature. The set up of the machine was:

- Rate of separation of grips: 500 mm/min
- Load cell: 500 N

The test specimens were moulded into sheets of 2.5 mm thickness and vulcanised at 160°C, based on 95% cure times calculated from cure curves obtained from the
Wallace PCA. These sheets were cut into dumb-bell shaped test samples. Figure 3.3 shows the shape of dumb-bell test piece. Eight samples were tested from each rubber compound and the results were averaged.

![Dumb-bell test piece diagram]

Fig. 3.3: Shape of dumb-bell test pieces

(i) Tensile Strength
   This value is calculated as follows:

   \[
   \text{Tensile strength} = \frac{\text{Force at break}}{\text{Initial cross-sectional area}}
   \]

(ii) Modulus at a given tensile strain
   This is actually a tensile stress at a given strain, usually measured at 100% and 300% elongations. The calculation is given by:

   \[
   \text{Modulus (at 100% or 300%) = \frac{\text{Force (at 100% or 300%)}}{\text{Initial cross-sectional area}}}\]

(iii) Elongation at break (EB)
   This was calculated as follows:
Elongation at break, EB (%) = \frac{100(1 - \frac{1}{l})}{lo}

where, 
'lo' - initial test length 
'l' - test length at break

Initial distance is usually 2.5 cm. When using the 'Hounsfield 500L' machine the elongation at break is measured automatically with the use of a laser light beam.

3.5.2 Tear Strength

In this investigation tear strength was measured using the crescent test piece according to Method C of BS 903: Part A3\textsuperscript{101}. The sample sheets were moulded similarly as for stress-strain properties and a 'Hounsfield 500L' was used to measure the tear strength. A 500 N load cell was used with an extension rate of 500 mm/min. The shape of the crescent test piece is shown in Figure 3.4.

Fig.3.4: Crescent test pieces for tear strength test
The following equation was used to calculate the tear strength;

\[
\text{Tear Strength (kN/m)} = \frac{\text{Maximum force (kN)}}{\text{Thickness of the test piece (m)}}
\]

3.5.3 Hardness

Hardness measurement was carried out by using a Wallace Croydon IRHD Instrument according to BS 903: Part 26\textsuperscript{102}, at room temperature. Hardness is a simple way of obtaining a measure of the elastic modulus (modulus at a very small deformation) of a rubber by determining its resistance to a rigid indentor.

3.5.4 Abrasion Resistance

During this investigation, the abrasion resistance was measured according to Method A of BS903; Part A9\textsuperscript{103}, using an Abrasion Debris DIN abrader. (Fig.3.5) The flat end of a cylindrical test piece was abraded against the surface of a rotating drum covered with an abrasive cloth, while the test piece was traversed from one end of the drum to the other to reduce the contamination of the cloth.

Abrasion resistance was measured in term of volume loss which is the mean value calculated by three test runs on three different test pieces from each rubber compound. Volume loss is expressed as milligrams volume loss of the test piece after an abrasion run of 40m.
3.6 Determination of Dynamic Properties

The dynamic properties measured in this investigation are storage shear modulus (in-phase modulus) $G'$ and tan loss angle $\tan \delta$ at different double strain amplitudes.

These properties were measured using the Dartec servo-hydraulic testing machine. The settings were programmed using Dartec software, on an MS-DOS computer interfaced to the 9500 controller for the Dartec machine.

The circular cross section test pieces with a diameter of 32mm were made by bonding rubber to metal. First, the surfaces of the metal discs were cleaned with fine steel wool and 1,1,1 trichloromethane, to remove rust and dirt, and to degrease the
surfaces. Thereafter, a bonding system, comprising Chemlok 205 primer and Chemlok 220 overcoat was applied to the prepared metal surfaces, with a drying period of 12 hours in between each application.

After the surface preparation, the rubber compounds were bonded to the metal discs in a transfer mould at 160°C for their 95% cure time. A diagram of the moulded test piece is shown in Figure 3.6.

Subsequently, cyclic tests were performed on each test piece at a total of seven double strain amplitudes of 0.001, 0.003, 0.01, 0.03, 0.1, 0.3 and 1.0. The frequency was kept constant at 1 Hz throughout the whole range of amplitudes and 30 cycles were done at each amplitude, capturing data at the 28th cycle of amplitude to avoid any transient effects of the amplitude change. Three test pieces were tested from each compound and the values were averaged for the final result. (See Appendix C)

![Diagram of the moulded test piece for the Dartec machine](image)

Fig.3.6: Diagram of the moulded test piece for the Dartec machine

### 3.7 Filler Dispersion Measurements

#### 3.7.1 Volume Fraction of Agglomerates (Thin Section)\(^41\)

Small flat sheets were pressed at 160 °C for the 95% cure times of each compound. Thin sections 1 to 2 μm thickness, were cut using a sledge microtome with a carbon dioxide cold stage. These thin sections were then swollen in xylene, spread out on a microscope slide and allowed to dry. The thin sections were viewed by using a video camera and monitor attached to a light microscope used in the transmission (i.e. through - illumination) mode. The overall magnification factor was approximately 1000. An image analysis package (VIDS V) was used to determine
area fractions of agglomerates by drawing around the images using a graphic tablet. Only agglomerates greater than 4 \( \mu \text{m} \) in diameter were included in the analysis. Ten fields of the same thin section were analysed for each sample, with about 5 to 50 agglomerates being measured for each field. In addition, photomicrographs of some of the samples were taken using a 35 mm camera attached to the microscope.

3.7.2 Computer Aided - Dark Field Image Analysis\textsuperscript{104}

For this test equipment comprising a microscope, video camera and PC MS-DOS computer, plus visual analysis hardware and VIDs image analysis software supplied by AMS Ltd of Cambridge was used. A schematic layout of the equipment is shown in figure 3.7.

![Fig. 3.7: A schematic layout of the 'Dark - Field' image analysis equipment\textsuperscript{104}](image-url)
The 'Dark Field Image Analysis' method of carbon black dispersion is based on the principle of dark field reflected light microscopy. In this method the dispersion of fillers in rubber compounds are characterised by using the intensity of light reflected from a freshly cut surface of a sample. The cut surface of carbon black filled rubber will have localised roughness, partly due to altered deflection near the blade of the more rigid regions and partly due to the less even cutting of carbon black agglomerates.

The scattered light is sensed by selecting regions from the raster of a video camera. The signals was used to construct an image of the cut surface. The scanned image is effectively divided into 100 zones per field and the reflected light intensity for each of them can be measured. Once the values have been collected they are exported to a spread sheet where they are processed to give estimates of the uniformity of the specimen, such as maximum, minimum, mean and standard deviation.

Procedure:

Test samples were cut from moulded flat sheets of thickness between 2.5mm and 3mm with a new degreased razor blade. Toluene was used as the degreasing solvent. The sheet was placed on a firm rubber base under a vertical sliding post. Then the cutting edge of the blade pressed down through the specimen. The sample was held in a sample holder with the freshly cut surface facing downwards and loaded onto the microscope stage. The focusing of the specimen was done by viewing the image shown on the monitor (with a linear magnification of x260), taken from the video camera mounted permanently on top of the microscope. The monitor also has 100 collection zones outlined on the image. Data were collected using image analysis software and stored on the hard disc of the MS-DOS computer. Normally data were collected for nine fields from each sample.
Calibration:

Before testing each batch of specimens, the instrument was calibrated using a zero illumination and a standard illumination. For each zone the correction was in the form:

\[
\frac{100 \times (\text{signal} - \text{zero})}{(\text{standard} - \text{zero})}
\]

3.8 Compression Stress Relaxation

This test was carried out using a computer controlled machine, known as the Relaxometer which has been developed at IPTME in collaboration with Hounsfield Technical Equipment Limited. This equipment (as shown in figure 3.8), consists of a plunger which is driven pneumatically, and a platform which houses the load cell and can traverse up and down mechanically. In operating mode the mechanical drive can bring the plunger and platform together at rates from 0.01 mm/min to 250 mm/min. The pneumatic drive, with 5 - 10 bar air pressure, provides a plunger speed of 2 ms\(^{-1}\) for a rapid loading process.

The relaxometer\(^{105}\) is controlled by software via information received from the load cell which acts as a pressure measuring device giving a predetermined compression adjustable to 10 microns. When the loading is completed the load cell sends a string of numeric values every 1 second for 15 minutes, to a store from where they may be retrieved to the computer where they are corrected to zero and converted into force values. Data analysis is done on a spread sheet and presented as a graph of residual force versus log time. The compression applied can be varied. (see Appendix D)
Fig. 3.8: The Hounsfield relaxometer

Sheets of 15 x 10 cm with the approximate thickness of 6 mm were moulded using T95 as the cure time. Small cylindrical buttons drilled out from these sheets were used for the actual test. Nine test pieces taken from different areas of the sheets were tested and the average was taken as the final value.

% Compressive strain: 25
Loading rate (ms⁻¹): 2
Test duration (min): 15
A typical short-term compression stress-relaxation curve\textsuperscript{105} (obtained from Hounsfield Stress Relaxometer) showing the relationship between residual force and logarithmic (time) is shown in Fig. 3.9. It was observed that from $10^{-4}$ to $10^{-2}$ seconds there was a 'surging' of the specimen. The force increased from the start of data capture $10^{-4}$ seconds after the impact of the plunger. The force is then seen to drop and be followed by a subsequent increase in force to a maximum at $10^{-2}$ s. The actual mechanism of stress relaxation is therefore considered to take place from $10^{-2}$ seconds and it is at this point that the initial force measurement are taken.

The ability to measure stress relaxation by this curve is assumed to commence from $10^{-2}$ seconds with the measurement below this time being meaningless as the force in this time is due to impact of the plunger on the specimen. The linear relationship between force and log(time) which occurs from about 10 seconds onwards is physical relaxation.
Fig. 3.9: Typical curve between residual force and logarithmic (time) obtained from Compression Relaxometer
CHAPTER 4

Modification of the Undesirable Effect of EN444 (N-Tallow-1-3, diaminopropane dioleate) on Crosslinking by Addition of Retarders and Pre-vulcanising Inhibitors

4.1 Addition of retarders/ pre-vulcanising inhibitors

As described earlier in Chapter 2, the MFA\textsuperscript{88} molecule remains intact at normal processing temperatures functioning as a roll mill release agent and filler aggregate dispersant. Above 135°C, it decomposes into a primary amine, RNH\textsubscript{2}(CH\textsubscript{2})\textsubscript{3}NH\textsubscript{2} and a fatty acid R'COOH. Simultaneously the fatty acid released then functions as a mould release agent. It has been concluded that 2 phr of EN444 is the optimum amount needed to give enhanced properties in a rubber vulcanisate when 50 phr of N330 carbon black is used.

However, all the research work carried out shows that with increasing EN444 content, the scorch time\textsuperscript{93,95} or the time rubber is capable of flowing, decreases by almost 50\% at 2phr of EN444. This presents a major problem for safe processing. Therefore, referring to the objectives stated in Chapter 1, modifications or additions to the existing MFA were explored to remove this problematic effect on safe processing.

Retarders\textsuperscript{106} are substances which reduce the activity of accelerators at compound processing and storage temperatures but become substantially exhausted with time at room temperature or more rapidly decompose at higher temperatures, so that the rate of cure is either unaffected or only slightly reduced. Therefore, in this way, they function to control scorch tendencies during mixing, calendering and extrusion without prolonging production cycles or affecting ultimate physical properties. Organic acids or nitroso compounds are commercially available as retarders. Conventional retarders include benzoic acid, salicylic acid, phthalic anhydride and nitrosodiphenylamine (NDPA).
4.2 Experimental:

(a) Retarders used in the study:

i) CTP : N-Cyclohexylthio-phthalimide

\[
\begin{align*}
\text{Density} & \quad 1.25/1.35 \\
\text{Supplier} & \quad \text{Monsanto}
\end{align*}
\]

This is the most frequently used retarder in the rubber industry and is commonly known by its Monsanto trade name Santogard PVI prevulcanising inhibitor.

ii) Acetyl salicylic acid

\[
\begin{align*}
\text{Commonly known as Aspirin} \\
\text{Density} & \quad 1.00 \\
\text{Supplier} & \quad \text{Fisons}
\end{align*}
\]
iii) Benzoic acid

![Chemical structure of Benzoic acid]

- Density: 1.08
- Supplier: Fison

(b) Mixing:

The batches were compounded according to the formulations in Table 4.1. Apart from the 12 batches with increasing amounts of retarders, 2 more batches were compounded, i.e. the control - without any retarders and another without retarders or EN444. Altogether 14 batches were tested. Mixing of all 14 batches was done according to the mixing cycle in Table 3.2, using the Haake Rheocord 90 under the conditions given in section 3.3.1.

**Table 4.1:** Different amounts of cure retarders in carbon black filled natural rubber compounds, with 2 phr of EN444.

<table>
<thead>
<tr>
<th>Material</th>
<th>Amount, phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber</td>
<td>100</td>
</tr>
<tr>
<td>ZnO</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>3</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>1</td>
</tr>
<tr>
<td>Carbon black</td>
<td>50</td>
</tr>
<tr>
<td>EN444</td>
<td>2</td>
</tr>
<tr>
<td>Retarder&lt;sup&gt;1,2,3&lt;/sup&gt;</td>
<td>0.5, 1.0, 1.5, 2.0</td>
</tr>
<tr>
<td>CBS</td>
<td>0.5</td>
</tr>
<tr>
<td>Sulphur</td>
<td>2.5</td>
</tr>
</tbody>
</table>

1. CTP
2. Aspirin
3. Benzoic acid
(c) Testing:

Testing of cure characteristics was done with the Wallace PCA, at 160°C, 140°C and 120°C. As the scorch time was very short at 160°C, the other temperatures were used to extend scorch time in order to make accurate measurements in the scorch region. Tensile properties were measured with a Hounsfield 500L tensile machine to determine if the retarders had any effect on mechanical properties. The tensile properties are, perhaps, the best overall indicators of mechanical properties.

4.3 Results and Discussion:

4.3.1 The process of crosslinking in a rubber compound

Before starting to discuss the results obtained from this experiment, it will be useful to review the process of crosslinking in a rubber compound in relation to a cure curve. A cure curve\textsuperscript{106} gives a complete picture of the overall kinetics of crosslink formation for a given rubber mix.

With respect to the time, vulcanisation occurs in three different stages, (i) an induction period, (ii) a curing or cross linking stage and (iii) a reversion or over - cure stage.

The induction period or scorch time represents the time interval at the curing temperature, during which no measurable crosslinking can be observed. It is of practical importance in that its duration determines the safety of the stock against "scorching" during various processing steps, which precede final cure. Although processing operations are carried out below the vulcanisation temperature, the induction period at the curing temperature is related to the time required to scorch at some lower temperature by some definable temperature dependence. Following the
induction period, crosslinking occurs at a rate, which is dependent on temperature and nature of the composition. In cure system design the drive is to attain the highest possible cure rate in association with adequate protection against scorching.

The control compound used for this study has the cure behaviour of a fairly good rubber compound by the preceding criteria. It has a scorch time of 45 seconds, a cure rate of 0.1188 Nms$^{-1}$ and a 95% cure time of 483 seconds at 160$^\circ$C.

When 2 phr of EN444 was added the cure curve showed some drastic changes. The cure time was reduced to 348s and the cure rate was increased to 0.2535 Nms$^{-1}$. However, the addition of 2 phr of EN444 also reduced the scorch time by almost 50%, from 45 seconds to 22 seconds thus reducing scorch safety. (Table 4.2) Not only did the scorch time decrease but there was also an increase in torque during this time, which indicate some formation of crosslinks. The formation of a small number of crosslinks during storage or processing is a major problem, as this causes an increased elasticity and viscosity in the compound, which leads to increased swell and melt fracture in extrudates and distortion and an introduction of stresses in mouldings. Thus the changes in scorch behaviour caused by the addition of EN444 are a serious problem for processing.

4.3.2 Effect of retarders on the cure behaviour of a compound with 2phr of EN444

As shown in Fig. 4.1 the scorch time of the compound with 2 phr of EN444 increased with increasing amount of retarder at 160$^\circ$C. It was also found that at 140$^\circ$C and 120$^\circ$C the retarders showed the same trend. However, the efficiency in increasing scorch time is different between the three retarders. The differences in efficiencies are also shown in Fig. 4.2.
Fig. 4.1: Change in scorch time with different amounts of retarder - at 160°C in compounds with 2phr of EN444

Fig. 4.2: Change in the cure curve obtain on Wallace PCA in the compound with 2phr of EN444 and with 1phr of different retarders - at 160°C
The scorch time achieved by addition of 1phr of CTP was similar to that of the compound without EN444, but the increase in scorch time was insignificant when 1phr of benzoic acid is added. At 1phr acetyl salicylic acid shows an increase in scorch time which was similar to that of 1phr of CTP (Table 4.2). However, at higher loadings, CTP was shown to be the most effective retarder. Even though retarders increased the scorch time, they did not change the cure time substantially, especially with CTP and benzoic acid. When 0.5 phr of CTP was added to the compound with 2phr of EN444 the 95% cure time remained the same, at 348 s.

The increased scorch rate (the formation of cross-links which occurred during scorch time) with the addition of EN444, was also decreased by adding CTP and acetyl salicylic acid. (Table 4.3) At 1 phr both CTP and acetyl salicylic acid decrease the scorch rate approximately by 60%. Further when compared with the compound without EN444, the addition of 1phr of CTP or acetyl salicylic acid decreases the scorch rate by 38%. The increased cure rate also remains the same as for 2phr of EN444 for both CTP and benzoic acid, although there was a 20% decrease in cure rate when 1.5 phr of acetyl salicylic acid was added. (Tables 4.3 and 4.4) According to literature, acidic retarders such as salicylic acid, acetyl salicylic acid, phthalic anhydride and benzoic acid increase scorch time but reduce the crosslink formation rate after the delay period. This could have happened due to the fact that as these acidic retarders neutralise the amine accelerators during scorch time, there was no enough accelerators to increase the rate of cure. In this study, this phenomenon was observed by the addition of acetyl salicylic acid to the compound with EN444, although the increased acceleration of cure remains similar with the addition of benzoic acid.
Table 4.2: Curing properties at 160°C measured by Wallace PCA.

<table>
<thead>
<tr>
<th>Amount of retarder</th>
<th>Min. Torque, Nm</th>
<th>Max. Torque, Nm</th>
<th>(Max-Min) Torque, Nm</th>
<th>$t_{72}$, s.</th>
<th>$t_{95}$, s.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 2phr EN444</td>
<td>0.0</td>
<td>0.76</td>
<td>2.94</td>
<td>2.18</td>
<td>22</td>
</tr>
<tr>
<td>CTP</td>
<td>0.5</td>
<td>0.79</td>
<td>3.22</td>
<td>2.43</td>
<td>38</td>
</tr>
<tr>
<td>CTP</td>
<td>1.0</td>
<td>0.83</td>
<td>3.25</td>
<td>2.42</td>
<td>50</td>
</tr>
<tr>
<td>CTP</td>
<td>1.5</td>
<td>0.84</td>
<td>3.24</td>
<td>2.40</td>
<td>92</td>
</tr>
<tr>
<td>CTP</td>
<td>2.0</td>
<td>0.86</td>
<td>3.10</td>
<td>2.24</td>
<td>107</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>0.5</td>
<td>0.73</td>
<td>3.17</td>
<td>2.41</td>
<td>26</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>1.0</td>
<td>0.71</td>
<td>3.17</td>
<td>2.46</td>
<td>30</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>1.5</td>
<td>0.72</td>
<td>3.28</td>
<td>2.56</td>
<td>32</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>2.0</td>
<td>0.69</td>
<td>3.28</td>
<td>2.59</td>
<td>36</td>
</tr>
<tr>
<td>Acetyl salicylic</td>
<td>0.5</td>
<td>0.78</td>
<td>3.17</td>
<td>2.39</td>
<td>40</td>
</tr>
<tr>
<td>Acetyl salicylic</td>
<td>1.0</td>
<td>0.75</td>
<td>3.17</td>
<td>2.42</td>
<td>48</td>
</tr>
<tr>
<td>Acetyl salicylic</td>
<td>1.5</td>
<td>0.76</td>
<td>3.23</td>
<td>2.47</td>
<td>52</td>
</tr>
<tr>
<td>Acetyl salicylic</td>
<td>2.0</td>
<td>0.79</td>
<td>3.24</td>
<td>2.45</td>
<td>61</td>
</tr>
<tr>
<td>Without EN444</td>
<td>0.0</td>
<td>0.64</td>
<td>2.45</td>
<td>1.81</td>
<td>45</td>
</tr>
</tbody>
</table>
Table 4.3: Scorch rate and Cure rate (increase in torque for a unit time) at 140°C.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Scorch rate (Nms⁻¹)</th>
<th>Cure rate (Nms⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control - 2phr EN444</td>
<td>0.0928</td>
<td>0.0858</td>
</tr>
<tr>
<td>CTP - 0.5</td>
<td>0.0633</td>
<td>0.0795</td>
</tr>
<tr>
<td>CTP - 1.0</td>
<td>0.0387</td>
<td>0.0638</td>
</tr>
<tr>
<td>CTP - 1.5</td>
<td>0.0280</td>
<td>0.0689</td>
</tr>
<tr>
<td>CTP - 2.0</td>
<td>0.0181</td>
<td>0.0845</td>
</tr>
<tr>
<td>Benzoic acid - 0.5</td>
<td>0.0877</td>
<td>0.1069</td>
</tr>
<tr>
<td>Benzoic acid - 1.0</td>
<td>0.0608</td>
<td>0.0869</td>
</tr>
<tr>
<td>Benzoic acid - 1.5</td>
<td>0.0871</td>
<td>0.0918</td>
</tr>
<tr>
<td>Benzoic acid - 2.0</td>
<td>0.0705</td>
<td>0.0672</td>
</tr>
<tr>
<td>Acetyl salicylic acid- 0.5</td>
<td>0.0475</td>
<td>0.0983</td>
</tr>
<tr>
<td>Acetyl salicylic acid- 1.0</td>
<td>0.0392</td>
<td>0.0742</td>
</tr>
<tr>
<td>Acetyl salicylic acid- 1.5</td>
<td>0.0458</td>
<td>0.0545</td>
</tr>
<tr>
<td>Acetyl salicylic acid- 2.0</td>
<td>0.0458</td>
<td>0.0647</td>
</tr>
<tr>
<td>Without EN444 or retarder</td>
<td>0.0637</td>
<td>0.0311</td>
</tr>
</tbody>
</table>

Table 4.4: Cure rate (increase in torque for a unit time) at 160°C.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Cure rate (Nms⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control- 2phr EN444</td>
<td>0.2535</td>
</tr>
<tr>
<td>CTP - 0.5</td>
<td>0.3279</td>
</tr>
<tr>
<td>CTP - 1.0</td>
<td>0.2818</td>
</tr>
<tr>
<td>CTP - 1.5</td>
<td>0.2962</td>
</tr>
<tr>
<td>CTP - 2.0</td>
<td>0.2444</td>
</tr>
<tr>
<td>Benzoic acid - 0.5</td>
<td>0.2828</td>
</tr>
<tr>
<td>Benzoic acid - 1.0</td>
<td>0.2812</td>
</tr>
<tr>
<td>Benzoic acid - 1.5</td>
<td>0.2936</td>
</tr>
<tr>
<td>Benzoic acid - 2.0</td>
<td>0.2804</td>
</tr>
<tr>
<td>Acetyl salicylic acid- 0.5</td>
<td>0.2767</td>
</tr>
<tr>
<td>Acetyl salicylic acid- 1.0</td>
<td>0.2309</td>
</tr>
<tr>
<td>Acetyl salicylic acid- 1.5</td>
<td>0.2023</td>
</tr>
<tr>
<td>Acetyl salicylic acid- 2.0</td>
<td>0.1671</td>
</tr>
<tr>
<td>Without EN444 or retarder</td>
<td>0.1188</td>
</tr>
</tbody>
</table>
There is a slight increase in minimum torque, maximum torque and (maximum - minimum) torque when 2phr of EN444 is added to the control compound with CBS and sulphur. Minimum torque is proportional to dynamic shear modulus $G'$ which is a function of molecular weight, crosslink density and filler dispersion. In the two compounds; the control without EN444 and with EN444 the increase in $G'$ could only be attributed to the increased crosslink density as the improvement in other properties will decrease the $G'$. Sheng et al\textsuperscript{106} have shown that EN444 starts to decompose at around $120^\circ$C, and it was observed that the temperatures of the compounds at the end of the mixing were $115^\circ$C. Therefore, this increase in above properties could be due to some chemical reaction between decomposed EN444 and the curatives in the system, which would cause a change in crosslink type during mixing.

The addition of CTP or acetyl salicylic acid to the compound with 2 phr of EN444, does not have any significant effect on either minimum torque or (maximum - minimum) torque values (a useful indication of crosslink density) as would be expected from lack of effect on tensile properties. (Table 4.5, page 121) When CTP was first synthesised one of the properties expected of it was not to affect the rate or the degree of crosslinking after the increased scorch time. Therefore, the results obtained are consistent with respect to CTP.

Further, it has been noted in literature\textsuperscript{107} that benzoic acid, apart from retarding the onset of vulcanisation, softens unvulcanised compounds and hardens the vulcanisates especially when they contain a large proportion of reinforcing filler. However, the decrease in minimum torque when 0.5 phr of benzoic acid is added to the compound with 2phr of EN444, is 4%. At the level of 2phr of benzoic acid the decrease in minimum torque is 9%. Therefore, the reduction in minimum torque is insignificant compared with the effect reported in literature, which could be due to the accelerating of vulcanisation by the dissociation products of EN444.
Experiment and theory agree in that the reactions involved in vulcanisation proceed at a rate which is a function of the reciprocal of the absolute temperature, which can be represented by the Arrhenius equation,

\[ k = S e^{-E/RT} \]

where, \( k \) - the reaction rate constant
\( S \) - a constant
\( E \) - the activation energy
\( R \) - the gas constant
\( T \) - the absolute temperature

By manipulating the above equation and substituting scorch time (ST) for the reaction rate constant, an empirical equation is obtained. (\( K \) and \( b \), as constants)

\[ ST = K e^{-bT} \]

The linear logarithmic correlation between scorch time and temperature is utilised in figure 4.3. To estimate how long a compound with 2phr of EN444 and with 1phr of CTP can be stored at room temperature (for example at 24°C) the lines drawn through the scorch times at 160, 140 and 120°C were extrapolated to a temperature of 24°C. It was found that a compound with 2phr of EN444 can be stored for three weeks without scorching. By adding 1phr of CTP to this compound the storage time increases to 3 months. Similarly, the addition of acetyl salicylic acid and benzoic acid at the same amount, 1phr, was found to increase the scorch time by six weeks. These are storage times before scorch - production storage times would have to leave sufficient process safety and would be shorter.
4.3.3 Effect of retarders on the tensile properties of a compound with 2phr of EN444

As can be seen from Table 4.5 increasing the level of retarder does not cause a significant difference in the physical properties. Therefore the results indicate that retarders do not have an detrimental affect on the tensile strength, modulus or elongation at break. Action of a retarder is to increase the scorch time or delay the action of vulcanisation. When all the retarder has been consumed by scavenging the accelerator intermediate the normal vulcanisation reactions are expected to proceed.\textsuperscript{19,112} Even though the reaction kinetics are affected by the vulcanisation chemistry which occurs in the inhibition time, the final degree of crosslinking is not affected. Therefore, the physical properties achieved by the addition of EN444 should not be affected by the addition of retarders.
### Table 4.5: Tensile properties

<table>
<thead>
<tr>
<th></th>
<th>Amount of retarder</th>
<th>Tensile strength, MPa</th>
<th>Modulus at 300%, MPa</th>
<th>Elongation at break, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control, 2phr EN444</td>
<td>0</td>
<td>28.2</td>
<td>21.3</td>
<td>397</td>
</tr>
<tr>
<td>CTP</td>
<td>0.5</td>
<td>25.6</td>
<td>19.5</td>
<td>385</td>
</tr>
<tr>
<td>CTP</td>
<td>1.0</td>
<td>27.6</td>
<td>16.6</td>
<td>456</td>
</tr>
<tr>
<td>CTP</td>
<td>1.5</td>
<td>29.4</td>
<td>19.2</td>
<td>436</td>
</tr>
<tr>
<td>CTP</td>
<td>2.0</td>
<td>26.2</td>
<td>17.1</td>
<td>431</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>0.5</td>
<td>25.7</td>
<td>21.2</td>
<td>332</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>1.0</td>
<td>26.3</td>
<td>19.5</td>
<td>343</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>1.5</td>
<td>26.9</td>
<td>21.6</td>
<td>368</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>2.0</td>
<td>26.9</td>
<td>20.4</td>
<td>396</td>
</tr>
<tr>
<td>Acetyl salicylic</td>
<td>0.5</td>
<td>25.2</td>
<td>20</td>
<td>369</td>
</tr>
<tr>
<td>Acetyl salicylic</td>
<td>1.0</td>
<td>26.4</td>
<td>19.7</td>
<td>384</td>
</tr>
<tr>
<td>Acetyl salicylic</td>
<td>1.5</td>
<td>26.5</td>
<td>21.4</td>
<td>363</td>
</tr>
<tr>
<td>Acetyl salicylic</td>
<td>2.0</td>
<td>24.8</td>
<td>19.9</td>
<td>367</td>
</tr>
</tbody>
</table>

#### 4.3.4 Mechanisms of scorch delay by Retarders

(a) For CTP

As mentioned earlier in section 2.4.3, CTP has the capability to act as an efficient retarder or a pre-vulcanising inhibitor for vulcanisation in the presence of different types of accelerators. The results show that even in the presence of EN444, CTP increases scorch time effectively. According to the mechanisms of scorch delay by CTP, it can be assumed that CTP interferes with the sulphur vulcanisation,
accelerated by CBS and also with the acceleration by the amine released by dissociation of EN444.

It has been suggested\textsuperscript{108,109} that an accelerator such as CBS must be converted by reaction with sulphur to a polythiobenzthiazole, a crosslink intermediate, before crosslinking can take place. This reaction is catalysed by mercaptans such as MBT, formed by thermal dissociation of the sulphenamide. CTP’s capability for trapping the MBT formed during these reactions, is responsible for slowing the rate of formation of intermediate polysulphides, which leads to the increase in the processing safety. The competitive reaction of CTP with MBT to form 2-cyclohexyldithiobenzthiazole (CDB), disrupts and delays the formation of pendant modified rubber, which ultimately leads to cross-links. Further, according to Boustan\textsuperscript{22}, CTP also reacts with amines to produce organothio amines, which also function as pre-vulcanising inhibitors. Cyclohexylthio amine formed by CTP reacts faster with MBT and acts as a scavenger of MBT. It can be assumed that the amine produced during the decomposition of EN444 at high temperatures reacts similarly with CTP and traps the MBT formed during vulcanisation.

From the results obtained, it is suggested that either of the above mechanisms or both have taken place to increase the scorch time by CTP.

(b) For Aspirin and Benzoic acid

There are several suggested mechanisms of how acidic retarders delay the scorch time. One possible mechanism\textsuperscript{106} is by neutralising the basic substances in the rubber and thereby delaying the interaction of sulphur with rubber. Acidic retarders may interfere with the zinc complex and react with amine fragments. Therefore, when EN444 is decomposed to fatty acid and an amine, the acidic retarders could either neutralise or interfere with the amine part, which is known to accelerate the cure.

However, from the work carried out by Son\textsuperscript{110}, it is clear that among acidic retarders, only phthalic anhydride is capable of interfering with the Zn complex. The acidic retarders used in this study do not have this ability as they need two adjoining
carboxylic groups to form this PA-Zn-MBT complex (PA = phthalic anhydride). Therefore, it can be concluded that the current two acidic retarders only neutralise the amine fragments present in the vulcanisation system.

Usually, irrespective of the polar type, nearly all ortho – substituted benzoic acids are stronger than benzoic acid. Thus, any substituent group that reduces the electron density at the carbon atom attached to the carboxyl group will cause a withdrawal of electrons from the oxygen atom of the OH group and consequently facilitate the proton release, thereby increasing the strength of the acid. Consequently, acetyl salicylic acid which is an ortho substituted compound of benzoic acid and is usually stronger than benzoic acid\textsuperscript{111}, could thus neutralise the amine compounds released from EN444 and consequently increase the scorch time.

4.4 Conclusion

The difference in efficiencies shown by the three retarders could be attributed to their different mechanisms of increasing the scorch time. According to the reaction mechanisms, CTP is directly affecting the vulcanisation reactions whereas, according to the literature acidic retarders used in this work have the capability of neutralising the amine groups.

It is possible to reverse the reduction in scorch delay caused by EN444 by adding conventional retarders. The addition of CTP, (N- cyclohexylthio-phthalimide), at a concentration of 1phr, restores the scorch delay of a compound with 2phr of EN444, to that of a compound without EN444, without affecting the cure time or tensile properties.

Out of the acidic retarders; at 1phr acetyl salicylic acid also restores the scorch delay in a manner similar to that of 1phr of CTP. However, unlike CTP, acetyl
salicylic acid has the tendency to increase the cure time, although this increase is lower than that of the compound without EN444. Even at 2phr, the other acidic retarder, benzoic acid has not been able to increase the scorch time of that compound without EN444.

Therefore, it can be concluded that either CTP or acetyl salicylic acid can be used as a retarder to eliminate the scorch problem of EN444. Although, while the addition of acetyl salicylic acid slightly increases the cure time, it does not cause health hazards and is less expensive than CTP.
CHAPTER 5

Synthesis and Evaluation of a New Fatty Amine - Octyl Amine of Benzylmalonic Acid

5.1 Introduction

The general chemical structure of the existing MFA is represented as:

\[ [\text{RNH}_2(\text{CH}_2)_3\text{NH}_3]^2+ \quad 2[\text{R'COO}]^- \]

N-tallow-1,3-propane diaminedioleate was used originally by Mahdi[^84] for his Ph.D. research in 1983, but the full chemical structure of Akzo EN444, used in the present work, is unknown except that R and R' are long chain alkyl groups. However, the chemical structures of both are similar in that each has positively charged nitrogen atom at one end of the molecule, attached to the hydrophobic fatty acids. Hepburn and Mahdi[^88] found that the predominating influence on the cure behaviour of the compound is the free availability of the positively charged amine group which can act as an accelerator for cure. A substantial reduction of scorch time is also attributed to this free availability of amine groups. The need for a chemical which would act as an effective dispersing agent without having a big effect on cure properties, was thus identified.

Octyl amine and benzylmalonic acid were used in the synthesis of octyl amine salt of benzylmalonic acid (OAS). Octyl amine, a primary amine, was selected in the expectation that it would exert a reduced influence on scorch time because it contains only one nitrogen atom, instead of the two present in the existing MFA. Benzylmalonic acid was used instead of a common fatty acid, as it is believed to have more affinity for carbon black because of its benzene ring. It also has two -COOH groups, which are expected to have retarding effects on scorch by neutralising the basic nature of the amine groups present in the system[^106,^113]. Therefore, we hoped to
find improved action as a dispersing agent for carbon black as well as a lesser effect on scorch time.

5.2 Experimental

5.2.1 Methodology:

The mixing experiments reported in this chapter were undertaken in two parts. Firstly, OAS was synthesised and mixed in increasing amounts into the rubber compounds using the Haake Rheocord, to determine the optimum amount to be used in a rubber compound filled with 50phr of N330.

Following the above experiment, a natural rubber compound with 50phr of N330 and the optimum amount of OAS, was mixed in the Francis Shaw K1 Intermix, which delivers more material for testing and has a mixing characteristic closer to those of an industrial system. The objective of this experiment was to determine how the OAS functions in the rubber - filler system compared to 2phr of EN444. Further to determine whether OAS has an effect on polymer - filler interaction and crosslink density, the mixing was extended to completely disagglomerate the carbon black and thus minimise the effect of state of mix on measured properties.

5.2.2 Synthesis of octyl amine salt of benzyImalonic acid

(a) Chemicals used:

* Octylamine

\[ CH_3(CH_2)_7NH_2 \]

This is a primary amine.
Mol.wt. 129.25
Boiling point 175 -177°C
Supplier - Aldrich Chemicals
* Benzylmalonic acid

\[
\text{CH(COOH)₂} \quad \text{Dicarboxylic acid}
\]

\[
\text{CH}_2
\]

Mol. weight 194.19
Melting point 120–122°C
Supplier - Aldrich chemicals

(b) Procedure

The amine was added to the diacid and heated up to 120°C in a normal atmosphere for 5 min. and mixed well. The chemicals were added in a molecular weight ratio of 1:1, expecting the amine to react only with one acid group.

\[
\begin{align*}
\text{Weight of the amine} &= 3.550 \text{g} \\
\text{Weight of the diacid} &= 5.033 \text{g}
\end{align*}
\]

The newly synthesised chemical; octyl amine salt of benzylmalonic acid was analysed using FTIR spectroscopy, to determine the outcome of the reaction.

5.2.3 Mixing

(a) Mixing Experiments with the Haake Rheocord 90

The formulation given below in Table 5.1 was used for compounds with 0.3, 1.0, 2.0, 3.0 and 5.0 phr of OAS. A control compound without any OAS and a compound with 2 phr of EN444 were also mixed for comparison purposes. The mixing cycle and conditions used are as in section 3.3.1.
**Table 5.1:** Different amounts of OAS in carbon black filled natural rubber compounds.

<table>
<thead>
<tr>
<th>Material</th>
<th>Amount, phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber</td>
<td>100</td>
</tr>
<tr>
<td>ZnO</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>3</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>1</td>
</tr>
<tr>
<td>Carbon black</td>
<td>50</td>
</tr>
<tr>
<td>Octyl amine salt of benzylmalonic acid</td>
<td>0.3, 1.0, 2.0, 3.0, 5.0</td>
</tr>
<tr>
<td>CBS</td>
<td>0.5</td>
</tr>
<tr>
<td>Sulphur</td>
<td>2.5</td>
</tr>
</tbody>
</table>

(b) Mixing Experiments with the Francis Shaw K1 Intermix

Six batches were mixed with the Francis Shaw K1 Internal mixer, using the conditions given in section 3.3.2. and the formulations given in Table 5.2.

A set of three compounds; C₁, E₁ and O₁ were mixed for comparison purposes according to the mixing cycle in Table 3.3 (320 s) where the state of mix may not be similar due to improved dispersion by the fatty amines. A second set of compounds; C₂, E₂ and O₂ were mixed for a longer time using the addition cycle in Table 5.3 (750 s). In this second set of batches, the mixing time was extended to produce a similar state of mix in all three batches.
### Table 5.2: Carbon black filled natural rubber compounds with surfactants

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>E</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>ZnO</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Carbon black</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>EN444</td>
<td>-</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>Octyl amine salt</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>CBS</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Sulphur</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>

### Table 5.3: Mixing cycle used for extended mixing of compounds

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Addition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Part I</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>SMR 10 + ZnO + Stearic acid + Flectol H</td>
</tr>
<tr>
<td>120</td>
<td>N330 + Surfactant</td>
</tr>
<tr>
<td>600</td>
<td>Dump</td>
</tr>
<tr>
<td>Part II</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>Masterbatch from Part I</td>
</tr>
<tr>
<td>60</td>
<td>CBS + Sulphur</td>
</tr>
<tr>
<td>150</td>
<td>Dump</td>
</tr>
</tbody>
</table>
5.2.4 Testing:

All the batches were tested for cure characteristics with the Wallace Shawbury
Precision Cure Analyser at 160°C, to determine effect of OAS on the scorch and cure
behaviour. Three samples were tested from each batch.

To determine the state of mix, the volume fraction of remaining agglomerates
was measured by quantitative microscopy on thin sections cut with the sledge
microtome, freezing with a carbon dioxide in cold stage. Mixer power traces were
obtained from the data recorded from the Francis Shaw K1 Intermix to determine how
the OAS affects the compound mixing.

The test samples were moulded using a cure time of 95 plus 5 min at 160°C.
The tensile properties of the batches were measured with a Hounsfield 5001 testing
machine at room temperature, according to BS 903: Part A2. A cross head rate of
500mm/min used. Other vulcanisate properties: hardness, tear strength, compression
set and abrasion resistance, were also measured according to BS 903.

Dynamic properties of elastic (in-phase) shear modulus, loss (out-of-phase)
shear modulus and loss angle tan δ were measured with a DARTEC servo-hydraulic
testing equipment, at double strain amplitudes of 0.001, 0.01, 0.1 and 1 and frequency
of 1Hz, at room temperature. Stress relaxation measurements were carried out on the
Hounsfield compression relaxometer. These tests were carried out to determine how
the OAS affects the rubber-filler system and the effect of OAS on the properties.
5.3 Results and Discussion:

5.3.1 Octyl Amine salt of Benzylmalonic acid (OAS):

The FTIR spectrum of the new octyl amine salt of benzylmalonic acid (OAS) is shown in Appendix B (in page 203). It shows an absorption peak at 2900 cm\(^{-1}\) which is attributed to \(-\text{CH}_2/\text{CH}_3\) groups. The peak at 1700 cm\(^{-1}\) indicates that there is an unreacted carboxylic group present in OAS. When an amine and a carboxylic acid are reacted there can be two different products, RCOO\(^-\) + NH\(_3\)R or RCONHR. According to the FTIR spectrum the chemical made during the synthesis is the RCOO\(^-\) + NH\(_3\)R type as the spectrum shows a prominent peak at 1550 cm\(^{-1}\) which is attributed to the NH\(_3\)++OC group. (The spectrum is shown in Appendix B) Therefore, these absorption peaks of FTIR spectrum show evidence of reaction between the amine and the carboxylic group, as well as showing a free carboxylic group present in the OAS salt. As FTIR indicates only the functional groups present in a mixture, even though there are different numbers of chemicals present and there may be small amounts of impurities present in the salt. However, Asore\(^9\) who synthesised several cationic surfactants using conditions similar to those employed in this study, found that there is little or no impurity present in the salts by comparison of salts before and after the isolation and purification. Therefore, in the current work, purification was not considered to be necessary.

5.3.2 The Effect of OAS level on Physical Properties

The cure characteristics of the newly synthesised OAS show a similar trend to those of EN444. Even though carboxylic groups present in OAS were expected to act as a conventional acidic retarder and to neutralise the basic fragments present in the system, OAS reduced the scorch time. Both scorch time (Fig.5.1) and 95% cure time (Fig.5.2) decreased with increasing amount of OAS and at 2phr gives similar results as those of 2phr EN444.
Fig. 5.1: Change in scorch time (●) and tensile strength (▲) with increasing amount of OAS; scorch time of 2phr of EN444 (■).

Fig. 5.2: Change in 95% cure time with increasing amount of OAS.
It can be assumed that OAS decomposes into its original fatty acid and amine, and these amine fragments accelerate the cure. Therefore, it appears that OAS has a similar decomposition characteristic to that of EN444, although the temperature of decomposition is unknown. Although the effect of OAS on scorch time was disappointing, it was decided to continue experiments to determine its efficiency as a dispersing agent.

There is a small decrease in minimum curemeter torque, (which corresponds to the elastic shear modulus of the uncured compound), with increasing amount of OAS which is attributed to improved dispersion of carbon black (Fig. 5.3). The substantial decrease between 3 and 5phr of OAS may be due to internal lubrication by the OAS. The difference between maximum and minimum curemeter torque (Fig. 5.5), which corresponds to crosslink density, shows OAS has a small effect. However, there is a decrease above 2phr of OAS, probably due to internal lubrication.

\[ \text{Fig. 5.3: Change in minimum torque with increasing amount of octyl amine salt of benzylmalonic acid} \]
Tensile strength (Table 5.4) shows a maximum between 0.3 and 1phr of OAS. Tensile strength, together with the difference between maximum and minimum torque results, shows that there is an increase in crosslink density compared to that of the control, with the addition of 1phr of OAS but the increase in tensile strength over that of the control is small when compared with EN444. The tensile strength of compounds with OAS is below that of the compound with 2phr of EN444. (Table 5.4) With EN444, it was proposed that levels higher than 2phr, (which is the optimum), result in a second EN444 layer forming, with a weak EN444 to EN444 interlayer, thus reducing the physical properties. When calculations were made (refer to 5.3.8), it was found out that 3.5 phr of OAS was needed to form monolayer coverage over 50phr of N330 carbon black.

Although tensile strength is decreased above 1phr of OAS, there still is still probably an increase in crosslink density. From the literature it is evident that a decrease in tensile strength alone does not indicate a decrease in crosslink density. Tensile strength goes through a maximum with increasing crosslink density. (Fig. 5.4) Further, according to the decrease in minimum curemeter torque values, as the dispersion of the compound improves with the addition of OAS, there should be a decrease in modulus. Instead, the 100% modulus (which corresponds the elastic modulus of the cured compound) of compounds with OAS increases and reaches a plateau (Table 5.4). Therefore, the increase in 100% modulus is attributed to an increase in crosslink density with the addition of OAS.
**Table 5.4:** Curing and tensile properties of batches with OAS.

<table>
<thead>
<tr>
<th>Amount of OAS used, phr</th>
<th>0</th>
<th>0.3</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>5</th>
<th>2phr EN444</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cure characteristics</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Minimum torque, Nm</td>
<td>0.53</td>
<td>0.53</td>
<td>0.51</td>
<td>0.47</td>
<td>0.47</td>
<td>0.22</td>
<td>0.76</td>
</tr>
<tr>
<td>Maximum torque, Nm</td>
<td>2.04</td>
<td>2.19</td>
<td>2.08</td>
<td>2.07</td>
<td>1.82</td>
<td>1.49</td>
<td>2.94</td>
</tr>
<tr>
<td>(Max.-min.)torque, Nm</td>
<td>1.51</td>
<td>1.66</td>
<td>1.57</td>
<td>1.60</td>
<td>1.35</td>
<td>1.27</td>
<td>2.18</td>
</tr>
<tr>
<td>Scorch time, s</td>
<td>45</td>
<td>38</td>
<td>31</td>
<td>27</td>
<td>21</td>
<td>12</td>
<td>22</td>
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<tr>
<td>T95, s</td>
<td>483</td>
<td>416</td>
<td>377</td>
<td>343</td>
<td>279</td>
<td>211</td>
<td>348</td>
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</tbody>
</table>

**Tensile properties**

<table>
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<tr>
<th></th>
<th>0</th>
<th>0.3</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>5</th>
<th>2phr EN444</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus at 100%, MPa</td>
<td>3.8</td>
<td>3.9</td>
<td>4.4</td>
<td>4.3</td>
<td>4.6</td>
<td>4.3</td>
<td>5.76</td>
</tr>
<tr>
<td>Modulus at 300%, MPa</td>
<td>16.8</td>
<td>16.6</td>
<td>18.1</td>
<td>17.3</td>
<td>18.1</td>
<td>—</td>
<td>21.53</td>
</tr>
<tr>
<td>Tensile strength, MPa</td>
<td>22.9</td>
<td>23.8</td>
<td>23.9</td>
<td>21.1</td>
<td>21.1</td>
<td>11.6</td>
<td>28.2</td>
</tr>
<tr>
<td>Elongation at break, %</td>
<td>391</td>
<td>410</td>
<td>396</td>
<td>366</td>
<td>348</td>
<td>186</td>
<td>392</td>
</tr>
</tbody>
</table>

© Wallace Precision Cure Analyser, at 160°C
Fig. 5.4: Dependence of tensile strength on crosslink density for natural rubber vulcanised by sulphur system

Fig. 5.5: Change in (max. - min.) torque with increasing amount of OAS
Finally, it was decided to use 1phr of OAS, to study further and determine the effects of OAS on the properties of carbon black filled natural rubber compound. This decision was taken by considering the results shown in Fig. 5.1. From this figure it is clear that tensile strength decreases with the additions of OAS higher than 1phr. Further, the scorch time obtained with 1phr of OAS is longer than that of 2 phr of EN444.

5.3.3 The Effect of 1phr of OAS on Filler Dispersion

(i) Volume Fraction of Agglomerates

Measurement of carbon black dispersion reveals that OAS is an effective dispersing agent. The volume fraction of agglomerates remaining in the OAS compound mixed for 320 s with the Francis Shaw K1 Intermix was 14.5%. In comparison, the control compound yielded a value of 34.5% and the compound with 2phr of EN444 gave 18.4%. Therefore, it is clear that 1phr of OAS acts as effectively as 2phr of EN444 in improving the dispersion of carbon black in natural rubber.

Further, the decrease in minimum torque with 1phr of OAS (which is proportional to viscosity of the compound) from that of the control is attributed to the improved dispersion of carbon black and is similar to the minimum torque of the compound with 2phr of EN444. (Table 5.5 given in page 144)

(ii) Mixer Power Traces

The mixer power traces also show evidence that at 1phr OAS accelerates the incorporation of carbon black. Generally, insight into mixing rubber and a filler in an efficient mixer is gained from the mixer power trace. A power trace obtained from the Francis Shaw K1 intermix for the control compound is shown in Figure 5.6 and can be used as an example for explanation of typical features. The major changes of power
are due to raising and lowering the ram, at the addition of filler and different chemicals at points A, B, C and D. Following A the mixer power is used mainly to masticate the rubber and also to incorporate zinc oxide, stearic acid and antioxidant. The carbon black was added at point B, (for the other batches, fatty amines were also added to the compound at this point) and the accelerator CBS and sulphur were added respectively before the ram went down at points C and D. Usually the power increases from point B onwards, after the addition of filler, until it reached the peak E, which indicated the black incorporation time (BIT)

The power traces, which illustrate the effects of adding surfactants to the rubber compound, are shown in Fig. 5.7. There is a rapid rise of power following the carbon black addition when OAS is used. It is evident from this observation that OAS has accelerated the incorporation of carbon black in a manner similar to that of 2phr of EN444. Further, the power at discharge for the compound with 1phr of OAS is lower than the control and similar to that of 2phr of EN444, which indicates that the compound with OAS has better state of mix than that of the control and similar to that with EN444, as can be seen from the volume fraction of agglomerate results in the previous section. The ram up points are taken out of the traces in Figure 5.8 to show the changes in power during mixing with OAS and EN444 after the addition of filler more clearly.
**Fig. 5.6:** Power trace obtained for the control compound

**Fig. 5.7:** Power traces of the three batches; control, 2phr of EN444 and 1phr of OAS in the 320s mixing cycle
5.3.4 The Effect of 1phr of OAS on Crosslinking Characteristics:

Fig. 5.8: Power traces of the three batches after the addition of filler; in 320s mixing cycle (ram up points are taken out)

There is a decrease in scorch time and 95% cure time from that of the control when 1phr of OAS is used, confirming the results obtained from Haake Rheocord experiments. These results clearly indicate that OAS has the capability of functioning as an accelerator for cure. The compounds mixed for 750s employing the two-stage mixing cycle (Table 5.3), also give evidence of OAS ability of accelerating the cure. One of the reasons for employing a two stage mixing cycle is to prevent scorching, as the mixing time after the curative addition is short and the increase in temperature is less than that of a single stage mixing cycle. In the two stage mixing cycle employed for the compounds mixed for 750s, the mixing time after the curative addition was 90s where the discharge temperatures were recorded as 112, 119 and
108°C for the control, OAS and EN444 respectively. Therefore, it was expected for the fatty amines to have a lesser effect on crosslinking, than in the compounds mixed for 320s in the single-stage cycle. (Tables 5.5 and 5.6) However, neither OAS nor EN444 show an increase in scorch time. In two-stage mixing, this is attributed to, the fatty amines were already dissociated during the first part of the mixing cycle, enabling them to act as accelerators for cure during the second half of the mixing. The temperature at the end of the mixing of each masterbatch was 137°C. As the dissociation temperature of EN444 is known to be around 115°C, it will have dissociated during the first half of the mixing cycle as given in Table 5.3. Similarly as OAS does not show any significant change in scorch time with compounds mixed for 320s or 750s, it is assumed that OAS dissociated at a temperature similar to that of EN444 and acts similarly during vulcanisation.

In compounds mixed for 320s, the difference in maximum and minimum torque value does not show an increase over that of the control when 1 phr of OAS is used. The compound with 2phr of EN444 also showed a less pronounced result for the (max. - min.) value, than that of the similar compound with 2phr EN444 mixed in Haake Rheocord. Curemeter torque is a function of the crosslink density and effective volume fraction of filler. It will be expected that torque decreases with improved dispersion and increases with increasing crosslink density. From the results of minimum torque and volume fraction of agglomerates (Table 5.5), it is clear that both EN444 and OAS improved dispersion. Therefore, it is evident from differences in maximum and minimum torque, that there was an increase in crosslink density with addition of surfactants, when mixed for 320s. Further, it is evident that OAS had less influence on crosslink density than that of EN444.

However, when mixing time was extended up to 750s, where the volume percentage of agglomerates showed that the states of mix were virtually equal, the crosslink densities of the compounds with EN444 and OAS are lower, (as indicated by the difference between the maximum and minimum torque), than that of the control.
5.3.5 The Effect of 1phr of OAS on Physical Properties:

Compounds mixed for 320s

The hardness of three compounds; (Table 5.5) the control, OAS and EN444 showed similar trends to that of the corresponding minimum torque values. Hardness, as applied to vulcanised rubber, means resistance to deformation or it serves essentially as an indirect measure of elastic modulus. Elastic modulus and viscosity have a similar dependence on mixing. Therefore, similar trends in hardness and minimum torque were expected.

Similar tensile strengths were obtained from compounds with EN444 and OAS and both were higher than the control. The tensile strength of the compound with OAS had increased more than that for the compound mixed in the Haake Rheocord. Tensile strength results obtained from EN444 and control compounds in this study were similar to the results obtained by Ismail\(^9\), who also mixed compounds in the Francis Shaw K1 internal mixer, using a similar mixing cycle (320s).

The 100% and 300% modulus were also increased with the addition of OAS, which together with increase in tensile strength, suggests that there was an increase in crosslink density. There was an increase of 8% and 14% over the control, in 300% modulus for EN444 and OAS respectively. Similarly, the increases in 100% modulus for EN444 and OAS over that of the control were 15% and 39% respectively. The compound with OAS showed higher values for both 100% and 300% modulus, even though the crosslink density indicated by the difference in curemeter torque was higher for EN444. Further, the improved dispersion of carbon black did not show any effect on the 100% or 300% modulus. Payne\(^1\) and Donnet\(^2\) who observed a similar effect, concluded that after vulcanisation the changes due to dispersion are reduced or almost diminished.
Tear strength and abrasion resistance were increased with the addition of OAS which could again be attributed to the increased crosslink density. However, tear strength and abrasion are dependent upon resistance to crack growth. Thus, improvement in these properties is also attributed to the better dispersion of carbon black. Abrasion\cite{117,118} involves principally the mechanical removal of small, possibly microscopic, particles from a rubber surface due to its frictional interaction with another surface. Patterns consisting of small tongues of rubber often develop during abrasion and the production of these tongues is attributed to crack growth. The increase in abrasion resistance is attributed to the smaller amount of carbon black agglomerates and to the shining surface of the compounds with fatty amines. The shining surface of mouldings is due to carboxylic acid released from the decomposition of fatty amides, which is expected to migrate to the moulded surface and act as a mould releasing agent. Thus, improved abrasion resistance is, in part, due to the presence of a slip layer, reducing frictional loses.

It has been reported\cite{119} that the migration to the moulded surface can be reduced by using fatty acids with high molecular weights. Although EN444 has a high molecular weight (~924), the fatty acid decomposed from it was still migrating to the surface, may be because it was very incompatible with the rubber. Further, it was observed the mouldings made of the compound with OAS have less shining surfaces which indicate the fatty acid of decomposed OAS has more difficulty in migrating to the surface than that of the EN444. This could be attributed to the benzene ring present in benzylmalonic acid.
**Table 5.5**: Physical properties of batches mixed using the 320 s mixing cycle

<table>
<thead>
<tr>
<th></th>
<th>Control (C₁)</th>
<th>EN444, 2phr (E₁)</th>
<th>OAS, 1phr (O₁)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cure Characteristics</strong>&lt;sup&gt;α&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum torque, Nm</td>
<td>1.81</td>
<td>1.92</td>
<td>1.74</td>
</tr>
<tr>
<td>Minimum torque, Nm</td>
<td>0.39</td>
<td>0.33</td>
<td>0.32</td>
</tr>
<tr>
<td>(Max - min) torque, Nm</td>
<td>1.42</td>
<td>1.59</td>
<td>1.42</td>
</tr>
<tr>
<td>Scorch time, s.</td>
<td>43</td>
<td>23</td>
<td>31</td>
</tr>
<tr>
<td>T&lt;sub&gt;95&lt;/sub&gt;, s</td>
<td>402</td>
<td>380</td>
<td>315</td>
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<tr>
<td><strong>Vulcanisate properties</strong></td>
<td></td>
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<tr>
<td>Hardness</td>
<td>76</td>
<td>72</td>
<td>74</td>
</tr>
<tr>
<td>Tensile strength, MPa</td>
<td>26.9</td>
<td>28.9</td>
<td>28.5</td>
</tr>
<tr>
<td>Modulus at 100%, MPa</td>
<td>5.4</td>
<td>6.2</td>
<td>7.5</td>
</tr>
<tr>
<td>Modulus at 300%, MPa</td>
<td>22.5</td>
<td>24.3</td>
<td>25.6</td>
</tr>
<tr>
<td>Elongation at break, %</td>
<td>343</td>
<td>324</td>
<td>321</td>
</tr>
<tr>
<td>Tear strength, kN.m⁻¹</td>
<td>91</td>
<td>89</td>
<td>117</td>
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<tr>
<td>Abrasion resistance, DIN (volume loss/mm³)</td>
<td>152</td>
<td>141</td>
<td>144</td>
</tr>
<tr>
<td>Compression set, %</td>
<td>7.6</td>
<td>6.8</td>
<td>10.1</td>
</tr>
<tr>
<td>18°C, 72 hrs.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Volume of agglomerates</td>
<td>34.8</td>
<td>18.4</td>
<td>14.5</td>
</tr>
<tr>
<td>Rate of relaxation (Reduction in force/decade of time, %)</td>
<td>4.29</td>
<td>3.95</td>
<td>4.05</td>
</tr>
</tbody>
</table>

*α* Wallace Precision Cure Analyser, at 160°C
Compounds mixed for 750s

The hardness values of all three batches mixed for 750s where the states of mix were equivalent, also show a trend similar to their corresponding minimum torque values. (Table 5.6) The modulii of the compounds with OAS and EN444 were lower than those of the control. Further, tensile strengths of the compounds with OAS and EN444 were higher than that of the control.

The three batches mixed for an extended time (750s) showed better dispersion and the number and the size of the carbon black agglomerates present were smaller when compared with the agglomerates of compounds mixed for 320s. (Tables 5.5 and 5.6) Consequently, surface area of the carbon black and area of the interface of rubber – filler, in compounds mixed for 750s, is larger than that of the compounds mixed for 320s. As the surfactants are believed to decrease the rubber – filler interaction, it is reasonable to assume that the effect of OAS and EN444 on crosslink density was changed in compounds mixed for 750s (Table 5.6) as indicated by their modulus results.

The tear strengths of compounds with OAS and EN444 showed an increase compared to the control. The abrasion resistance of OAS was similar to that of the control. However, the abrasion resistance had increased for the compound with EN444. The increase in abrasion resistance could also be due to the external lubrication by EN444, as mentioned earlier with compounds mixed for 320s. As mentioned earlier with compounds mixed for 320s, the tear strength test and abrasion resistance are dominated by crack initiation. The improvements in these properties of compounds mixed for 750s, were attributed to reduction in inherent flaw size due to improved dispersion, as shown by the volume fraction of agglomerate results.
Table 5.6: Physical properties of batches mixed using the 750 s mixing cycle

<table>
<thead>
<tr>
<th></th>
<th>Control</th>
<th>EN444, 2phr</th>
<th>OAS, 1phr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C₂</td>
<td>E₂</td>
<td>O₂</td>
</tr>
<tr>
<td><strong>Compound properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum torque, Nm</td>
<td>2.63</td>
<td>1.83</td>
<td>2.37</td>
</tr>
<tr>
<td>Minimum torque, Nm</td>
<td>0.54</td>
<td>0.21</td>
<td>0.51</td>
</tr>
<tr>
<td>(Max - min) torque, Nm</td>
<td>2.09</td>
<td>1.62</td>
<td>1.86</td>
</tr>
<tr>
<td>Scorch time, s</td>
<td>58</td>
<td>22</td>
<td>29</td>
</tr>
<tr>
<td>T₉₅, s</td>
<td>449</td>
<td>411</td>
<td>460</td>
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<tr>
<td><strong>Vulcanisate properties</strong></td>
<td></td>
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</tr>
<tr>
<td>Hardness</td>
<td>75</td>
<td>73</td>
<td>74</td>
</tr>
<tr>
<td>Tensile strength, MPa</td>
<td>23.9</td>
<td>25.3</td>
<td>26.7</td>
</tr>
<tr>
<td>Modulus at 100%, MPa</td>
<td>6.5</td>
<td>4.7</td>
<td>5.1</td>
</tr>
<tr>
<td>Modulus at 300%, Mpa</td>
<td>22.5</td>
<td>19.6</td>
<td>21.5</td>
</tr>
<tr>
<td>Elongation at break, %</td>
<td>319</td>
<td>385</td>
<td>375</td>
</tr>
<tr>
<td>Tear strength, kN.m⁻¹</td>
<td>116</td>
<td>127</td>
<td>127</td>
</tr>
<tr>
<td>Abrasion resistance, DIN (volume loss/mm³)</td>
<td>149</td>
<td>111</td>
<td>142</td>
</tr>
<tr>
<td>Compression set, %</td>
<td>10.8</td>
<td>8.4</td>
<td>9.6</td>
</tr>
<tr>
<td>18°C, 72 hrs.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Volume of agglomerates</td>
<td>0.91</td>
<td>0.32</td>
<td>0.42</td>
</tr>
<tr>
<td>Rate of relaxation</td>
<td>4.14</td>
<td>3.45</td>
<td>3.88</td>
</tr>
<tr>
<td>(Reduction in force/decade of time, %)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

@ Wallace Precision Cure Analyser, at 160°C
5.3.6 Effect of 1phr of OAS on Dynamic Properties

Compounds mixed for 320s

The changes in dynamic moduli $G'$ and tan $\delta$ with double strain amplitude for compounds mixed for 320s are shown in Figs. 5.10 and 5.12. The $G'$ values of compounds with OAS and EN444 were higher than that of the control at 320s mixing cycle, suggesting that both OAS and EN444 have higher crosslink density. Further, at DSA equal to 1, $G_{oo}'$ for the three compounds; control, EN444 and OAS were recorded as 1.4, 1.8 and 1.7 MPa respectively.

![Fig. 5.9: Qualitative interpretation of strain amplitude dependence of $G'$](image)

The elastic modulus curves are represented in idealised form in Fig. 5.9. The idealised curve is shown as levelling off at a value $G_{oo}'$ at high amplitude and $G_0'$ at
low amplitude. Donnet\textsuperscript{120}, explaining the concept of reinforcement by Payne\textsuperscript{121}, stated that the effect of carbon black at high amplitude is attributed to a combination of a hydrodynamic effect and additional effective crosslinks due to rubber – filler bonds. The hydrodynamic effect is described by the Guth-Gold equation,

\[ G_{cpd} = G_{gum} \left( 1 + 2.5\phi + 14.1\phi^2 \right) \]

where, \( G_{cpd} \) = in-phase dynamic shear modulus of filled compounds, \( G_{gum} \) = in-phase dynamic shear modulus of gum compounds, \( \phi \) = effective volume fraction of filler

The volume percentage of agglomerates of the three compounds; control, compounds with 2phr of EN444 and 1phr of OAS are 34.8, 18.4 and 14.5 respectively (Table 5.5). Therefore, when this equation was applied to the three batches, it was anticipated that \( G' \) should be higher for the control as the dispersion of other two compounds was better than that of the control. Although for a proper calculation to determine whether the results obtained in this study fit the Guth-Gold equation, some investigation on the effect of OAS and EN444 on the gum compound was needed. Ismail\textsuperscript{94} and Abidin\textsuperscript{122} who have worked on EN444, have shown that the effect of EN444 on the gum compound was insignificant. A similar study to determine the effect of OAS on the gum compound was essential.

However, \( G_{oo}' \) values of OAS and EN444 (1.7 and 1.8 MPa) which were higher than that of the control (1.4 MPa), indicated that there was some other effect which overshadows the hydrodynamic effect on \( G_{oo}' \). From the physical properties, as well as from the difference in maximum and minimum curemeter torque, there is evidence that 2phr of EN444 had increased crosslink density. At 1phr, OAS also had an effect on crosslink density even though it was not as prominent as 2phr of EN444. Therefore, this increase in crosslink density by the addition of fatty amide surfactants could be the reason for the higher \( G_{oo}' \). A higher \( G' \) at DSA equal to 1 was also
observed with 2phr of EN444 than that of the control, in the work done by Ismail\textsuperscript{94}. Further, the change of elastic shear modulus $G'_0 - G'_\infty$ ($\Delta G'$) with increasing strain amplitude which was attributed to the interaggregate interaction or to the carbon black structure (as Payne first proposed it) did not show a significant difference between the control and the compounds with OAS and EN444, as shown in the Fig.5.10 below.

![Graph showing change in elastic shear modulus with double strain amplitude](image)

**Fig. 5.10**: Change in elastic shear modulus with double strain amplitude; compounds mixed for 320s

Other researchers have experienced results similar to this and their explanations are as follows. Payne and Whittaker\textsuperscript{123} who have worked on the effect on crosslinking of the vulcanisates on the structure breakdown curve observed very similar changes in $G'_0 - G'_\infty$ for all vulcanisates, even though $G'_\infty$ varies two or three fold. According to them the mechanism responsible for the modulus change with strain work of oscillation must be substantially independent of curative level of the rubber matrix. Further, Coran and Donnet\textsuperscript{116} found that after the samples were
vulcanised, many effects due to changes in carbon black dispersion quality became greatly reduced, modified or even disappeared. They have interpreted this as a reduction in bonding between agglomerates occurring during vulcanisation.

**Fig.5.11:** Schematic diagram by Meng-jiao Wang to explain the change in $\Delta G'$ with dispersion $^{125}$

Further, according to more recent work by Meng-jiao Wang$^{124,125}$ on dynamic properties, $\Delta G'$ (the Payne effect) increases with improving macro-dispersion and decreases with improving micro-dispersion or decreasing flocculation, as shown by his schematic diagram in Fig.5.11. According to this theory, in the early stage of mixing, the Payne effect increases with increasing mixing time due to more undispersed filler masses being dispersed in the polymer matrix, forming filler network or agglomerates which are the main origin of the Payne effect. If the filler is not dispersed, the strain would only take place in the polymer phase and no Payne effect would be observed, even though the strain amplitude in the polymer matrix is higher than that of the gum, due to hydrodynamic effect of the filler. With increasing
mixing time or intensity, more filler is dispersed in the polymer matrix, and more developed filler network can be formed. Therefore, due to more rubber being trapped in the filler agglomerates, the effective filler volume fraction increases very rapidly with increasing mixing time (in this study by adding OAS and EN444) and improvement of macro dispersion.

The values obtained for the $\Delta G'$ for the control and compounds with OAS and EN444 are 3.68, 4.86 and 4.81 respectively. Therefore, according to Wang's interpretation the compounds with fatty amides has improved macro-dispersion and $\Delta G'$ increased.

![Graph](image)

**Fig. 5.12**: Change in $\tan \delta$ with double strain amplitude; compounds mixed for 320s

The change in $\tan \delta$ with double strain amplitude (Fig. 5.12) for compounds mixed for 320s shows that of the compound with EN444 has decreased more than that of the other two compounds. $\tan \delta$ which is a measure of the ratio of energy lost to energy stored in a cyclic deformation $G''/G'$ is proportional to hysteresis.
The low tan δ indicates low hysteresis or low energy dissipation. Reduction in tan δ in EN444 can be attributed to improved dispersion.

It was reported that the phase angle at intermediate and high amplitudes reduced with improved dispersion, especially during initial stages of mixing (up to 4 min). Beyond 4 min there is little change in phase angle. According to Dannenburger, the reduction in hysteresis can be attributed to reduction in carbon - carbon frictional losses as the dispersion is improved. Boonstra and Medalia also found that improved dispersion gives a decrease in torsional hysteresis as well as lower heat build up. These reasons also could be true for the compound with EN444.

However, the improved dispersion cannot be the only reason for the decrease in tan δ with EN444, because OAS also improved the dispersion, similar to EN444. According to Ismail, the presence of EN444 at the interface weakens the interfacial interaction (∼30%) between carbon black and rubber. In Ismail’s interpretation, the detachment of rubber molecules from the EN444 layer and re-attachment or slippage of rubber molecules from EN444, is easier than with a simple natural rubber – carbon black interface. This leads to a decrease in tan δ. According to recent work done by Wang, when molecular motion is increased, it is easy to follow the dynamic strain and thus decreases tan δ. However, at 1phr OAS, it is calculated that only 28% of the surface of N330 carbon black is covered. Therefore, OAS may not decrease the rubber - filler interaction at 1phr even though it improves the dispersion. Therefore, the difference in surfactant concentration used could be the reason for the difference in tan δ between the compounds with OAS and EN444.
Compounds mixed for 750s

The changes in G', G'' and tan δ with double strain amplitude for the rubber compounds mixed for 750s are shown in figures 5.13, 5.14 and 5.15.

The dynamic elastic shear modulus G' and loss (viscous) shear modulus G'' are decreased when the surfactants OAS and EN444 are added to the compounds mixed for 750s (Figs. 5.13 and 5.14). Elastic modulii G', of the compounds show similar trends to their static modulii measured at 100% and 300% elongations.

Fig. 5.13: Change in elastic shear modulus with double strain amplitude; compounds mixed for 750s
The change in $G'_\infty - G'_\infty (\Delta G')$ decreased with the addition of OAS and EN444, more than the control. It has been reported\textsuperscript{37} that increase in $\Delta G'$ with little effect on $G'_\infty$ shows poorer micro – dispersion (in nm level) of blacks. Even though it is assumed that the dispersion of the three batches were almost equivalent with extended mixing, (for 750s) the micro – dispersion, which was invisible through optical microscopy or TEM was improved with the addition of OAS and EN444. As explained earlier and shown by Fig 5.11, better micro – dispersion will lead to less filler networking or flocculation during vulcanisation, which decreases $\Delta G$. The change in the ratio of $\Delta G'$ of the three compounds were similar to their volume percentage of agglomerates measured by thin sections (0.99, 0.32 and 0.42 for the control, compounds with 2phr of EN444 and 1phr of OAS respectively).

The tan $\delta$ values of the compounds with OAS and EN444 were lower than that of the control. The decrease in $\Delta G$ with low tan $\delta$ indicates better network carbon – carbon dispersion. The reduction in hysteresis is associated with reduction of $\Delta G$, both symptomatic of improved dispersion at submicron level. This can be due to two
causes; (i) more successful separation of carbon black aggregates from each other during mixing and (ii) prevention of reagglomeration after mixing. It is also reported\textsuperscript{124} that the reduced scorch times and increased cure rates prevent the flocculation or filler networking of carbon black agglomerates during vulcanisation. It is clear that compounds with OAS and EN444 have this ability as they increase the cure time. All these factors obtained with surfactants lead to lower tan δ than that of the control.

![Graph](image_url)

**Fig. 5.15**: Change in tan δ with double strain amplitude; compounds mixed for 750s

5.3.7 The Effect of 1phr of OAS on Stress Relaxation

The compounds with surfactants showed decreases in rate of relaxation, in comparison with the control. When mixed for 320s, when the dispersions were different, compounds with OAS and EN444 showed 6% and 8% decrease in rate of relaxation. Further, when mixed longer for 750s and the states of mix were similar,
rate of relaxation of compounds with OAS and EN444 is 6% and 17% lower than that of the control.

Stress relaxation in a gum rubber, is a cumulative effect of number of separate physical and chemical processes. Physical stress relaxation is due to the viscoelasticity of the rubber, and is considered to involve rearrangement of molecular network, movement of the molecular chain and its entanglements, breakdown of secondary bonds by the application of stress, and the reorganisation of "microzones".

Physical relaxation has been found to be an approximately linear function of log(time) for a wide variety of materials. According to Ore, rupture of secondary bonds is the main reason for physical relaxation.

Chemical relaxation mechanisms include chain scission of the rubber network through thermal and oxidative effects. Both types of process occur simultaneously but because of their different natures the times and temperatures at which one or the other dominates may be different. The stress relaxation measured here, was measured for a time duration of 15min at room temperature, was most probably due to physical relaxation.

Other factors that may influence the stress relaxation behaviour of the control and the compounds with OAS and EN444 include the nature of crosslinks and crosslink density.

The generally increased stress relaxation of rubber containing carbon black is explained by the theory of "strain amplification". According to strain amplification, due to the inextensibility and/or incompressibility of the filler, the rubber matrix is prevented from deforming uniformly by adhesion of the rubber to the surface of filler particles and thus the strain occurring locally in the rubber phase is greater than that overall apparent strain. As such the ratio of stress to strain is increased by a certain factor (strain amplification factor) which takes into account both the disturbance of strain distribution and absence of deformation in the filler. Further, according to
Derham\textsuperscript{133}, high relaxation rates may be associated with filler-filler or filler-polymer failure.

This strain amplification\textsuperscript{131} could be the reason for the higher rate of stress relaxation in the control than that observed with the compounds with OAS and EN444, where the dispersions are improved and effective volume fractions of fillers are smaller. Thus in the compounds containing OAS and EN444, the strain amplification on the gum rubber is smaller than that of the control. Therefore, rates of relaxation were decreased in the compounds with OAS and EN444, compared to that of the control. The higher straining on gum rubber probably allows lesser opportunity for the bond and crosslinks to reorientate or bring gradual disentanglement, leaving the only alternative of bond rupture especially at the weaker bonds of polymer -- filler interface such that greater effect is observed with increased effective volume fracture of filler.

Further, the increased crosslink density, with the addition of OAS and EN444, could also be a factor to decrease the rate of relaxation in the compounds mixed for 320s.

Compression set (\%) of the three compounds mixed for 320s (Table 5.5) which could be taken as an indication of recovery are 7.6, 6.8 and 10.1 for the control, EN444 and OAS respectively. EN444 shows better compression set over that of the control. This could be attributed to the increased crosslink density in EN444 compound (of the control). OAS shows an apparently abnormal value which may be due to some experimental error, probably an under cure in the vulcanisation press.

However, when mixed for 750s, compounds with OAS and EN444 still showed a lower rate of stress relaxation (at the control). It is surprising to find the rate of stress relaxation decreasing with the addition of OAS and EN444, as the effective volume fraction of filler of the three batches was almost similar. In fact, as the development of filler networking was less with the addition of surfactants, there should have been an increase in the rate of relaxation. Further, as indicated by the difference in curemeter torque, the crosslink density of the control compound was
higher than the other two with surfactants. However, crosslinks measured in compounds mixed for 750s are chemical crosslinks, which were least active in the stress relaxation measured here.

The compression set values of the three compounds mixed for 750s (Table 5.6) were 10.8, 8.4 and 9.6 for the control, EN444 and OAS respectively. They have a similar trend as the rates of relaxation which were 4.14, 3.45 and 3.88 for the control, EN444 and OAS respectively. More extensive work on stress relaxation of surfactant compounds is needed to explain the above results.

**5.3.8 Monolayer Coverage of Carbon Black by OAS**

According to Ismail\textsuperscript{94}, the amount of the fatty amine EN444 for monolayer coverage of carbon black surface corresponds to the optimum level needed for dispersion of carbon black and for maxima or minima of the mechanical properties. In a compound with 50phr of N330 carbon black, the optimum level of EN444 is 2phr. In contrast, a value of 3.5phr was obtained when a similar calculation was done for OAS.

\[
\frac{W \times \text{CTAB} \times 10^{20} \times M}{A \times 6.02 \times 10^{23}} = m
\]

\[
\frac{50 \times 83 \times 10^{20} \times 323}{63.82 \times 6.02 \times 10^{23}} = 3.5 \text{ g}
\]

where,
- \(W\) = weight of N330 carbon black used, 50g
- \(M\) = molecular weight of OAS
- \(A\) = area covered by one molecule of OAS
- \(m\) = weight of OAS required for a monolayer coverage
- \(\text{CTAB}\) = CTAB no of N330 which corresponds to the area
of N330 in m²g⁻¹

6.02 x 10²³ = Avogadro number

However, as is clear from the results, the dispersion of carbon black can be improved effectively with 1phr of OAS and amounts of OAS greater than 1phr lead to poor physical properties; (Table 5.4 and Fig.5.1). Therefore, it can be concluded either that the mode of action of OAS is different to that of EN444 or that the hypothesis of monolayer coverage for EN444 is not true. When the theoretical calculations were made to determine the amount of EN444 needed to form a monolayer coverage on N330 carbon black, it was assumed that EN444 molecules are closely packed and that they lie flat with EN444 axes parallel to carbon black surface. The monolayer structure formation of OAS could be different from that of the EN444. For the same EN444, a different orientation in packing on the surface of silica filler is proposed. It was assumed that the EN444 molecule may stand on the silica surface with their polar sites attached to the silica surface. Similarly, the adsorption of OAS on the surface of carbon black could be different.

According to Ismail's conclusions, at 2phr of EN444 the crosslink density is at the maximum level and he refers to the work done by Grishin et al. on a surfactant; poly (ethylene glycol) ethers of n - alcohols, to explain the increase in crosslink density. Grishin and his team found that the adsorption of a surfactant on carbon black and the accelerated formation of polysulphide fragment of accelerator (ie. the crosslink pre-cursor), increased the degree of crosslinking in the interface layer and the intensity of interface interaction in filled rubber. However, where OAS is concerned, it is difficult to predict a similar influence on crosslink density.

Although, in theory there is not enough OAS to form a continuous monolayer on 50phr of carbon black at 1phr, OAS has an effect similar to that of 2phr of EN444 during mixing. However, at the optimum, 1phr OAS was calculated to be only covering 28% of the total carbon black present. According to Asore, the fatty amines facilitate the dispersion of filler by improving the wettability of the filler particles by rubber. The results obtained in this study suggest that OAS can improve wettability in a manner similar to that of EN444, but it is obvious that more work is
needed to determine the exact mode of action of fatty amines. In early stages of mixing the carbon black surface area available to rubber and OAS is small compared with the CTAB value on which the monolayer calculation is based.

The difference in improving wettability of filler between OAS and other diamine fatty acids could be due to difference in their structure. The original fatty amine surfactant used by Mahdi\textsuperscript{54}, N-tallow-1,3-propane diaminedioleate and thereafter Akzo EN444 (even though the structure is unknown in this chemical) have long chains in their fatty acids. In the case of EN444, there are around 60 carbon atoms present as determined by X-ray photoelectron spectroscopy and elemental analysis results. However, the structure of OAS is different from the above fatty amines and has a comparatively small molecular weight, 324 as compared to 936 for EN444. The OAS molecule does not have a long chain alkyl group, but a benzene ring. Further, OAS has an unreacted -COOH group present in the salt, which in the presence of water can be ionised to -COO\textsuperscript{-}. From these chemical features of OAS, it may act differently in wetting the carbon black and thus improve the dispersion.

5.4 Conclusions and Recommendations for Further Work

1. The filler dispersion can be improved by the addition of OAS. At 1phr OAS can accelerate the incorporation and disagglomeration of carbon black and increase the dispersion of 50phr of N330 carbon black in rubber to a level achieved with 2phr of EN444.

2. The octyl amine salt of benzylnomalonic acid also decreases the scorch time and cure time of a carbon black filled natural rubber compound containing the accelerator system CBS and sulphur. However, at its optimum level of 1phr, the scorch time reduction is 30\%, in comparison with 50\% for EN444 at its optimum level of 2phr (on 50phr of N330 carbon black).
3. The action on vulcanisation of natural rubber compounds, by both EN444 and OAS can be assumed as similar to each other. The acceleration of the sulphur vulcanisation by the amine dissociated at elevated curing temperature proposed for EN444 agrees with OAS, even though the dissociation temperature of OAS is still unknown. At optimum levels, OAS has less influence on crosslink density than EN444.

4. Dynamic properties, together with other physical properties, show that when mixed for a longer period, there is a change of effect by the fatty amines' on crosslink density. Thus, EN444 and OAS have a tendency to decrease the reinforcing effect of the carbon black. The decrease in reinforcement could be attributed to the improvement in micro-dispersion which indicates that EN444 and OAS may have decreased the interfacial interaction or $W_{ad}$ (thermodynamic work of adhesion) between rubber and carbon black.

5. As for further work, OAS should be mixed in a gum compound to provide a better knowledge of comparative behaviour in gum and filled systems. OAS should also be analysed further to determine its molecular configuration and dissociation temperature. It would also be useful to be able to calculate $W_{ad}$ between rubber and carbon black with the addition of OAS and EN444, by determining the surface free energies of OAS and EN444.
CHAPTER 6

Investigation of Low Molecular Weight Polystyrene as a Dispersing Agent

6.1 Use of polystyrene as a dispersing agent/surfactant

The use of low molecular weight polystyrene as a dispersing agent for carbon black in natural rubber was studied. Polystyrene\textsuperscript{134} is a linear, thermoplastic polymer of styrene. The polymerisation is initiated by a peroxide,

\[
\begin{align*}
\text{CH} = \text{CH}_2 & \overset{\text{peroxide}}{\rightarrow} [\text{CH}_2 \cdots \text{CH} \cdots \text{CH} \cdots \text{CH}_2]_n \\
\text{C}_6\text{H}_5 & \quad \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5
\end{align*}
\]

Although much attention has focused on the morphology of various types of carbon black (particle size and structure) and their effect on rubber properties, it has been recognised the main feature of blacks that distinguishing them from other fillers, is their high surface activity, which has an essential effect on the nature of the interaction able to take place between filler surface and polymer matrix. According to Wolff and Wang\textsuperscript{135} carbon black possesses a high dispersive component of surface energy, which is responsible for the strong interaction between filler and hydrocarbon rubber and exerts a profound influence on the properties of the rubber compound.

However, the high level of interaction between carbon black and rubber may lead to large amounts of occluded rubber and a poor dispersion. When the interaction is high, more mechanical energy is required to break down the carbon black agglomerates and release the rubber within the agglomerates. In this study, polystyrene was used as the dispersing agent, for its expected capability of decreasing the thermodynamic work of adhesion\textsuperscript{136} between carbon black and rubber. The thermodynamic work of adhesion ($W_{ad}$) is the reversible work done in the separation of unit area of two interfaces. A high $W_{ad}$ for two surfaces means that the attraction
between the two phases is strong. The thermodynamic adhesion of unit area ($W_{ad}$) can be calculated from the dispersion component of surface energy ($G^d$).

Dupre$^{137}$ suggested the following equation to calculate the thermodynamic adhesion of unit area,

$$W_{ad} = G_S^S + G_L^S - G_{SL}^S$$  \hspace{1cm} (Eq 6.1)

where, $W_{ad}$ - thermodynamic work of adhesion on unit area
- $G_S^S$ - surface free energy of the solid in the absence of vapour from the liquid
- $G_L^S$ - surface free energy of the liquid
- $G_{SL}^S$ - the excess free energy of the solid - liquid interface

Modifying Dupre's equation, Good and Girafalcod$^{138,139,140}$ obtained the following equation for interfaces involving one non-polar material, where interactions contributing to the thermodynamic work of adhesion, $W_{ad}$, consisted principally of dispersion forces.

$$W_{ad} = 2(G_S^d . G_L^d)^{0.5}$$ \hspace{1cm} (Eq 6.2)

where, $G_S^d$ - dispersion component of surface free energy of the solid
- $G_L^d$ - dispersion component of surface free energy of the liquid

From the equation 6.2, the thermodynamic work of adhesion for interfaces between carbon black - rubber was calculated to be 77.5 mJm$^{-2}$. (The $G^d$ of rubber, polystyrene and carbon black are 30, 40 and 50 mJm$^{-2}$ respectively.)$^{141,142}$ From the interfacial energies, the thermodynamic work of adhesion between low molecular weight polystyrene and carbon black is 89.4 mJm$^{-2}$. As the $W_{ad}$ between the carbon black and polystyrene interface is higher than between carbon black and rubber, polystyrene has the capability of wetting the carbon black completely, reducing the interaction between carbon black particles and thereby theoretically improving the dispersion of carbon black in rubber. Even though the cohesive energy of carbon black is larger than that of energy of adhesion between carbon black and polystyrene, the breakdown of carbon black particles by mechanical shear in the internal mixer will
facilitate the spreading of low molecular weight polystyrene on to the carbon black surface.

Apart from the interfacial attractions, polystyrene is an inert chemical. Therefore, it was expected that polystyrene would not have any effect on crosslinking. Further, low molecular weight polystyrene is expected to have a plasticization effect on the rubber compound.

6.2 Experimental:

(a) Raw material:

The low molecular weight polystyrene which was used in this study was supplied by the Aldrich Chemicals Co. Limited.
Product name : Polystyrene standard
Formula weight : 800
Appearance : Very viscous colourless liquid
Molecular weight determination by gel permeation chromatography

: \( M_w = 794 \)
: \( M_n = 700 \)
: \( M_p = 761 \)
: \( M_v = 687 \) (intrinsic viscosity)

(b) Formulation:

The batches were compounded according to the formulation in Table 5.1 (see page 127) which was used for the mixing of rubber compound with OAS. The low molecular weight polystyrene was used in increasing amounts of 0, 0.3, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 and 5.0phr. Two series of batches were mixed, with two different fillers; one with 50 phr of carbon black N330 and the other with 30 phr of clay, to have a better understanding of the plasticizing and lubricating effect of polystyrene. Clay is a
relatively non-reinforcing filler, and was chosen as a particulate carrier for polystyrene when it was found that polystyrene could not be mixed directly into a gum elastomer. Clay is a semi-reinforcing filler with a much lower specific interaction with rubber than carbon black.

(c) Mixing:

The mixing was done according to the mixing cycle in Table 3.2, using the Haake Rheocord 90 under the conditions given in section 3.3.1. Polystyrene was added with the filler. As it was very viscous, the polystyrene was first dissolved in toluene, then added to the filler. This mixture was kept at room temperature for one day, to allow the toluene to evaporate fully before the mixing was carried out. To compensate for any effect of toluene on mixing and dispersion of the rubber compounds with polystyrene, the amount of toluene used to dissolve 5 phr of low molecular weight polystyrene was added to the carbon black of the control batch.

(d) Testing:

The batches with carbon black filler were evaluated for curing characteristics, using the Wallace Precision Cure Analyser, at the temperature of 160°C, and the tensile properties were determined with the Hounsfield 500L tensile machine. Volume percentages of agglomerates were determined by light microscopy at a magnification of 250 on thin sections cut using a sledge microtome. The test procedures are given in section 3.6.1. The repeatability of results for the control were determined from several repeated experiments. Volume fraction of agglomerates for the control were 10.54, 10.23 and 11.42.

The batches with clay filler were only tested for Mooney viscosity at a temperature of 100°C, to evaluate the plasticization/lubrication effect of polystyrene.
6.3 Results and Discussion:

6.3.1 Effect of polystyrene on the dispersion of carbon black in rubber and compound viscosity

The change in volume percentage of agglomerates, the most fundamental measurement of dispersion, with increasing amount of polystyrene is shown in figure 6.1. The volume percentage of agglomerates passes through a minimum at approximately from 0.5phr to 3phr of polystyrene, which is shown to be as effective a dispersing agent as EN444. The low molecular weight polystyrene was anticipated to act as a surfactant as explained earlier, possibly by wetting the carbon black by forming a monolayer on the carbon black surface and thereby preventing the carbon – carbon attraction, which facilitates the dispersion of carbon black in the system.

Fig. 6.1: Change in %volume fraction of agglomerates with increasing amount of polystyrene
The subsequent increase in % agglomerate is attributed to the plasticizing effect of the low molecular weight polystyrene. As excess polystyrene acts as a plasticizer, it reduces the viscosity of rubber. The reduction of the compound viscosity is shown by the decreasing minimum curemeter torque with the increasing amount of polystyrene (Fig. 6.2) assuming minimum torque is proportional to the viscosity of the compound. The reduction in viscosity with increasing amount of polystyrene in compound with clay filler is shown in figure 6.3. Because of this lowering of viscosity, stresses during mixing were relatively low and resulted in less efficient dispersive mixing and hence, vulcanised samples showed higher volume percentage of agglomerates when higher concentrations of polystyrene were present.

Fig. 6.2 : Change in minimum torque with increasing amount of polystyrene; with 50phr of N330 carbon black
Fig. 6.3: Change in Mooney viscosity with increasing amount of polystyrene; with clay as the filler

6.3.2 Effect of polystyrene on the curing characteristics

Figure 6.4 and Table 6.1 show the changes in scorch times and cure times with increasing amount of low molecular polystyrene. There is no significant difference in scorch times from the control with the addition of polystyrene as expected. Therefore, by using polystyrene, the problem of short scorch time (as observed in the EN444 system) can be eliminated. The 95% cure times are longer with the addition of polystyrene which confirms that it does not act as an accelerator, as does EN444. Figure 6.4 demonstrates the scorchy nature of EN444 when compared with the polystyrene–based batches.
Table 6.1: Cure properties at 160°C

<table>
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<tr>
<th></th>
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<th>Control</th>
<th>0.3phr PS</th>
<th>1phr PS</th>
<th>2phr PS</th>
<th>3phr PS</th>
<th>5phr PS</th>
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<td>Max Torque, Nm</td>
<td>1.96</td>
<td>2.16</td>
<td>2.00</td>
<td>1.86</td>
<td>1.95</td>
<td>1.74</td>
<td>1.69</td>
</tr>
<tr>
<td>Torque, Nm</td>
<td>0.32</td>
<td>0.33</td>
<td>0.36</td>
<td>0.32</td>
<td>0.31</td>
<td>0.32</td>
<td>0.29</td>
</tr>
<tr>
<td>(Max-min) torque, Nm</td>
<td>1.64</td>
<td>1.82</td>
<td>1.65</td>
<td>1.64</td>
<td>1.64</td>
<td>1.42</td>
<td>1.39</td>
</tr>
</tbody>
</table>

Fig. 6.4: Cure curves obtained by Wallace Precision Cure Analyser for compounds with different amounts of polystyrene
6.3.3 Effect of polystyrene on the vulcanisate properties

Figures 6.5, 6.6 and 6.7 show tensile properties of samples with 0.3 to 5 parts of polystyrene. From Figure 6.5 it can be seen that the modulus values decreased with the increasing amount of polystyrene. The initial decrease in modulus is attributed to the reduction of immobilised rubber in the system. However, the sample with 5 phr of polystyrene has a higher %volume fraction of agglomerates (Figure 6.1), which would be expected to give high modulus values, due to an increased effective filler loading caused by rubber immobilised in the carbon black agglomerates. The plasticisation effect of low molecular weight polystyrene is confirmed by the fact that minimum torque and modulus decrease monotonically, until % agglomerates goes through a minimum and then increases.

Tensile strength decreases significantly as could be expected if the polystyrene forms an interlayer between the rubber and filler and reduces the energy of the interaction. The reduction of tensile strength and increase in elongation at break may be correlated with the reduced crosslinking density at high levels of polystyrene as shown by the decrease in (maximum - minimum) torque.

Fig. 6.5 : Change in 300% modulus with increasing amount of polystyrene
Fig. 6.6: Change in tensile strength with increasing amount of polystyrene

Fig. 6.7: Change in elongation at break with increasing amount of polystyrene
6.3.4 Monolayer coverage of low molecular weight polystyrene

The free energy of adhesion\textsuperscript{136} between two phases can be determined using equation 6.1 and follows from the fact that the act of separation involves the disappearance of the interface 1-2 (for e.g. solid and liquid) with formation of equal areas of surfaces for rubber and carbon black. These processes are shown schematically in Fig. 6.8.

Fig. 6.8: (a) Work of adhesion and (b) cohesion

The free energy of cohesion of the rubber phase, \( G_c \) is given by,

\[
G_c = 2G_S \quad \text{(Eq. 6.3)}
\]

Subtracting equation 6.3 from equation 6.1,

\[
W_{ad} - G_c = G_L - G_S - G_{SL} \quad \text{(Eq. 6.4)}
\]

It may be reasonable to expect reinforcement only when the energy of adhesion is larger than the energy of cohesion of rubber, that is when,
$G_{SL} + G_L - G_S < 0$

This inequality is also the well known condition in surface chemistry for the spreading of phase 1 on the surface of 2, to form a “duplex” film\textsuperscript{135}, ie. a layer thick enough to exhibit the normal tension at the surface opposite the interface 1-2. It is thus noted that the usual condition for wetting of a surface is equivalent to the postulated thermodynamic condition necessary for reinforcement.

The calculation\textsuperscript{94} used for EN444 and OAS, showed that to cover the surface of 50g of N330 carbon black with a monolayer, 2.4g of polystyrene was needed; assuming polystyrene molecules are closely packed and lie flat on the carbon black surface. The area of one polystyrene molecule was calculated to be approximately 0.2798nm$^2$ (27.98Å$^2$). As the low molecular weight polystyrene used in this experiment has a formula weight of 800, there could be 7 to 8 repeating units of styrene. From these values the area covered by one low molecular weight polystyrene molecule is calculated as 223.8 Å$^2$ (ie. 27.98 x 8).

Therefore, the amount of low molecular weight polystyrene needed to cover the surface of 50g of N330 carbon black is:

$$\frac{W \times \text{CATB} \times 10^{20} \times \text{M}}{A \times 6.02 \times 10^{23}} = m$$

$$\frac{50 \times 83 \times 10^{20} \times 800}{223.8 \times 6.02 \times 10^{23}} = 2.4 \text{ g}$$

where, $W$ = weight of N330 carbon black used, (50g)

$M$ = molecular weight of low molecular weight polystyrene

$A$ = area covered by one molecule of low molecular weight polystyrene (in Å$^2$)

$m$ = weight of low molecular weight polystyrene needed for a monolayer coverage

$\text{CATB} = \text{CATB no of N330 which corresponds to the specific surface area of N330 (in m}^2\text{g}^{-1})$

$6.02 \times 10^{23} = \text{Avagadro number}$
The calculation showed a value of 2.4g was needed for a monolayer coverage of 50g of carbon black. However, in this study as the volume fraction agglomerates passed through a minimum, from 1 to 3phr for low molecular weight polystyrene, it was assumed the monolayer coverage of the 50phr of N330 carbon black surface by polystyrene, would be from 1 to 3phr. This could be due to the branched benzene rings of the polystyrene leading to a steric hindrance and thereby showing a monolayer around carbon black surface, with less dense packing at low levels of polystyrene.

6.4 Conclusion and recommendations

When used in low concentrations, low molecular weight polystyrene can be used as an effective dispersing agent for carbon black filled rubber compounds. At high concentrations, it acts as a lubricant. Even though it acts as a good dispersing agent, it has tendency to decrease the reinforcing effect of carbon black.

Further work is now needed under conditions which more closely simulate large scale mixing. As a precursor, an efficient and economical method of producing low molecular weight polystyrene is required. Further work is also needed to determine the mechanism for the observed effect of polystyrene on crosslink density.
CHAPTER 7

Exploration of the use of Fatty amines for Reduction of Mixing Time and Increase in Maximum Filler Loading

7.1 Introduction

In the work described in Chapter 5, it was concluded that the fatty amines investigated have the ability to decrease the mixing time. Surfactants were believed to coat the internal surfaces of filler agglomerates and lubricate the entry of rubber molecules into the internal void volume, hence accelerating the filler incorporation. Thus, the decrease in mixing time was attributed to the ability of fatty amines to accelerate the incorporation of fillers in the rubber, which allowed more time for disagglomeration of the filler.

In this Chapter the utilisation of the ability of fatty amines to accelerate the incorporation of filler, was investigated with respect to two aspects of rubber mixing:
• ability to minimise mastication time
• ability to increase the maximum filler loading.

(i) Exploration of minimisation or elimination of the need for mastication using surfactants

Mastication is an important step in the manufacture of rubber compounds. It decreases the viscosity of rubber, promotes good dispersion of fillers and chemicals, and increases compound plasticity. This facilitates improved processing, calendering or extruding, by reducing the nerve or elasticity of the rubber. The rheological properties such as die swell, calendar shrinkage and building tack are improved. Historically the first methods of mastication employed were purely mechanical processes, later chemicals were discovered capable of catalysing the mastication of rubbers, thus improving the efficiency of the process considerably. During
mastication, under shear in the internal mixer or on the two-roll mill, natural rubber molecules undergo scission reducing the molecular weight. However, with over reduction of molecular weight undesirable properties result in the final product, which may affect strength and service life. Therefore, it would be beneficial if surfactants could be used to reduce the amount of mastication needed, without adversely affecting incorporation during mixing.

In this section a study is reported, which was done to determine whether it may be possible to:
(i) reduce the amount of mastication needed before filler incorporation,
(ii) improve mechanical properties.

(ii) **Determination of the ability of surfactants to increase the maximum filler loading**

For some rubber articles, like rubber rollers and conveyor belts, where high toughness and abrasion resistance are important, a high loading of carbon black is normally used. However, incorporating high amounts of carbon black is difficult and requires high amounts of energy and power in the mixer. Even then, large agglomerates may remain at the end of mixing, resulting in a poor final product.

To determine the maximum amount of carbon black that can be incorporated into the rubber in a single addition, the Dibutyl phthalate adsorption (DBPA) value of the carbon black was considered. It has been suggested that during the initial stages of carbon black incorporation, the carbon black is enclosed in discrete masses by the rubber. During this time, the black is being crushed by the shearing and compressive forces, so that the void volume will correspond roughly to the DBPA value. Subsequently rubber is forced into those voids and air expelled. Therefore, the amount of immobilised rubber present in agglomerates is related to the structure of the particular carbon black, as given by its DBPA value. If it is assumed that the amount of immobilised rubber in an agglomerate is equivalent to the DBPA value of that
particular carbon black, then the volume fraction of immobilised rubber\textsuperscript{41} in an agglomerate is given by the equation:

\[
\alpha = \frac{\text{DBPA}}{\text{DBPA} + \left(\frac{100}{\rho_{cb}}\right)} \\
\text{Eq. 7.1}
\]

where, \(\alpha\) = volume fraction of immobilised rubber in an agglomerate

\[
\text{DBPA} = \text{DBPA value (cm}^3/100\text{g)} = 102 \text{ for N330}
\]

\[
\rho_{cb} = \text{density of carbon black (g/cm}^3) = 1.8
\]

The calculated value of 0.647 is obtained when equation 7.1 is used to calculate the volume fraction of immobilised rubber in an agglomerate of N330 carbon black.

Therefore,

\[
\text{Volume fraction of rubber} = 0.65 \\
\text{Volume fraction of carbon black} = 0.35
\]

Converting volume fractions to mass ratios in an natural rubber compound \((\rho_{NR} = 0.93)\), we have:

\[
\begin{align*}
0.6\text{g of rubber immobilised in} & \quad 0.64 \text{ g of carbon black} \\
100\text{g of rubber immobilised in} & \quad (0.64/0.6) \times 100 \\
& \quad 107 \text{ g of carbon black}
\end{align*}
\]

At a loading of 107phr, all the rubber will be immobilised within the carbon black at the end of the incorporation period, if all the voids in the agglomerates were to be filled with rubber. However, more rubber is needed outside the agglomerates to bind the carbon black together to prevent crumbling of the rubber compound.
In the case of a rubber compound, where 50phr by weight of carbon black is incorporated in 100phr of rubber, there is only 47phr of immobilised rubber at the end of incorporation and the other 53phr of rubber is available for holding together the carbon black/rubber matrix. For this study, approximately half of this amount (50%) of extra rubber was assumed to be adequate to prevent crumbling of the batch, and from the above calculations it was found 70phr of carbon black satisfied this criterion. A mastication time of 120s was chosen, as it was shown from work on the effect of mastication time on incorporation 7.1 (ii), that some mastication is needed for surfactants to be most effective.

7.2 Experimental:

7.2.1 Mixing

(a) Reduction of mastication time

Batches were compounded according to the formulations in Table 5.2. The mixing was done in a Francis Shaw K1 intermix at a rotor speed of 35 rev/min according to Table 7.1, keeping the body temperature of the mixer at 40°C at the start of the mixing. The time of mastication of rubber before adding the carbon black was varied between 45, 90, 120 and 180 seconds.

Table 7.1: Mixing cycle used for batches for mastication experiment.

<table>
<thead>
<tr>
<th>Addition</th>
<th>Time between each addition (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
</tr>
<tr>
<td>SMR10 + ZnO + St.acid +</td>
<td>0</td>
</tr>
<tr>
<td>Flectol H</td>
<td>45</td>
</tr>
<tr>
<td>N330 (+surfactant)</td>
<td>120</td>
</tr>
<tr>
<td>CBS +Sulphur</td>
<td>80</td>
</tr>
</tbody>
</table>
Three batches were mixed at each mastication time. A control compound with no additives, one with 2phr of EN444 and one with 1phr of octyl amine salt of benzylmalonic acid were mixed. Altogether 12 rubber compounds were produced.

(b) Increase in maximum filler loading

Three batches were mixed according to the formulation given in Table 5.2., except that 70phr of N330 was used instead of 50phr. To prevent scorching of the batches due to increased batch temperature during mixing, due to the increased filler loading, 1.5phr of pre-vulcanising inhibitor CTP was also added at the time of carbon black addition. A mastication time of 120 s was chosen, as it was shown from work on the effect of mastication time on incorporation, that some mastication was needed for the surfactants to be most effective. The amount of surfactant added was adjusted for the loading of 70phr of N330. The batches were mixed under the conditions given in section 3.2.2 in the Francis Shaw K1 intermix but a new two stage mixing cycle was employed to overcome the problem of scorching when high loadings of carbon black were used.

Table 7.2: Mixing cycle used for batches for increased filler loading

<table>
<thead>
<tr>
<th>Time</th>
<th>Addition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>SMR 10 + ZnO + Stearic acid + Flectol H</td>
</tr>
<tr>
<td>120</td>
<td>N330 + Surfactant + CTP</td>
</tr>
<tr>
<td>320</td>
<td>Dump</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Part II</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>Masterbatch</td>
</tr>
<tr>
<td>30</td>
<td>CBS + S</td>
</tr>
<tr>
<td>100</td>
<td>Dump</td>
</tr>
</tbody>
</table>

178
7.2.2 Testing:

Data obtained during mixing in the Francis Shaw K1 internal mixer were analysed with a spreadsheet and mixing power traces were plotted for each batch, from which the black incorporation times were calculated.

The batches were tested for Mooney viscosity at 100°C for the mastication experiment 7.2.1(a) and Negretti TMS biconical rotor rheometer was used for the increased filler loading batches. The tensile properties were measured with a Hounsfield 500L tensile machine.

Thin sections of 1 to 2μm thickness, cut by using a sledge microtome with a carbon dioxide cold stage, swollen in xylene and spread out on a microscope slide, were used to calculate volume fraction of filler values of the samples obtained from the mastication experiment 7.2.1(a). The dispersion of batches with 70phr of carbon black was measured by dark field, reflected light image analysis equipment on specimens cut with degreased razor blades.

7.3 Results and Discussion:

7.3.1 Exploration of minimisation or elimination of the need for mastication by using fatty amines

7.3.1.1 Effect of fatty amines on the rate of carbon black incorporation

The power traces obtained from the Francis Shaw K1 intermix are shown in Fig. 7.1a, 7.1b, 7.1c and 7.1d where the mastication times are 45, 90, 120 and 180 s respectively. In figure 7.1a it can be seen up to 100 s of dispersive mixing time, the incorporation was dominated by the viscoelastic behaviour of the natural rubber and the effect of the surfactant/ dispersing agent was not yet apparent. It only became
significant when mastication had proceeded to a critical point. This can be seen in figure 7.1b where the mastication prior to carbon black addition (90 s) has proceeded enough to enable the dispersing agents to exert a significant influence on incorporation. The batch with 1phr of OAS showed a greater reduction of incorporation time than the control or that with 2phr of EN444 when mastication time was 90s. However, when mastication time was increased to 120s, OAS and EN444 show similar rates of incorporation, both of which are better than that of the control. The effect of the surfactants was more pronounced at the highest degree of mastication (figure 7.1d).

Fig. 7.1a : Change in power with mixing time after the addition of filler, mastication time = 45 s.
**Fig. 7.1b**: Change in power with mixing time after the addition of filler, mastication time = 90 s.

**Fig. 7.1c**: Change in power with mixing time after the addition of filler, mastication time = 120 s.
Fig. 7.1d: Change in power with mixing time after the addition of filler, mastication time = 180 s.

In Fig. 7.2, it can be seen that the rubber compounds with surfactants have reached the incorporation peak earlier than the control for all four mastication times. By looking at the Fig. 7.2 it is clear that the same incorporation time can be reached by masticating the rubber for shorter time (90s) than that needed for the control when either 2phr of EN444 or 1phr of OAS are added to the compound. In fact, the mastication time can be reduced from 180s to 110s by addition of 1phr of OAS, and to 115s by the addition of 2phr of EN444 can reduce the mastication time to 115s. However, from figures 7.1a to 7.1d it is clear there is an optimum amount of mastication needed to obtain the best effects of surfactants. As surfactants are thought to act on the rubber – filler interface, some mastication is needed to decrease the molecular weight/chain lengths of rubber molecules, and for surfactants to have a reasonable area of interface to act upon.
Fig. 7.2: Change in time to reach the incorporation peak with increasing mastication time

7.3.1.2. Effect of surfactants on the disagglomeration of carbon black

(Reduction of volume percentage of agglomerates)

Fig. 7.3 shows the change in volume percentage of agglomerates with increasing mastication time, and it can be seen that adding 2phr of EN444 gave the best dispersion of carbon black in rubber. As shown in an earlier section (7.3.1.1), the compounds with OAS and EN444 reach the incorporation peak earlier, therefore these compounds generally have more time for dispersion of carbon black than the control compound. Further, masticating the EN444 batch for only 90 s had reduced the volume percentage of agglomerates, almost to the point the control had reached when it is masticated for 120s. or longer.
Times needed to obtain equivalent states of mix (volume percentage of agglomerates) in the three compounds are shown in Table 7.3 in section 7.3.1.4.

Fig. 7.3: Change in volume percentage of agglomerates with increasing mastication time

7.3.1.3. Effect of surfactants on the reduction of viscosity

Fig. 7.4 shows that there is a reduction in Mooney viscosity when mastication time was increased and the viscosities of compounds with 2phr of EN444 are generally lower. When the batch with 2phr of EN444 was masticated for 90 seconds, the Mooney viscosity of this batch had been reduced even below the level of the control batch, with the longest mastication time of 180 seconds. The further decrease in Mooney viscosity was small in each of the compounds, when the mastication time was greater than 120s. Times needed to obtain a similar Mooney viscosity in the three compounds are shown in Table 7.4 in section 7.3.1.4.
Viscosity can be reduced by increasing temperature as well as by an increase in mastication time. However, when comparisons are made between the control, compounds with OAS and EN444, the similarity of batch temperatures indicate that the results will not be effected by differences in batch temperature at the point of addition of carbon black. (Fig. 7.5) Therefore, the similarities of batch temperatures at the end of dispersive mixing indicate that fatty amines did not have significant influence on batch temperature. (Fig. 7.5)
Fig. 7.5: Change in the batch temperature in the control compound, compounds with 2phr of EN444 and 1phr of OAS at the mastication time 90s

Effect of lubrication ability of fatty amines on compound viscosity

The Guth-Gold equation gives a good prediction of the effect of volume percentage of agglomerates on viscosity, provided that the immobilised rubber is taken into account. However, as shown by Fig. 7.6 there was another effect of surfactants on the compound viscosity.

Fig. 7.6 shows the co-relationship between Mooney viscosity and volume percentage of agglomerates during different mastication times. This figure shows the combination of the effects of mastication and of surfactants, both of which tended to reduce viscosity. For the control batch, both Mooney viscosity and volume fraction of agglomerate stopped decreasing after the mastication time of 120 seconds. When the surfactants were used, this relationship dropped lower than the control, especially with 2phr of EN444: this is attributed to further release of occluded rubber. However, at similar volume percentage of agglomerates the three compounds showed different viscosities.
Therefore, apart from the accelerating the rate of incorporation, the two surfactants showed an ability to act as lubricants, especially EN444. A lubricant can act in different ways to reduce the viscosity of a rubber compound. It may act as a bulk viscosity modifier\(^{22}\) in the rubber molecules. This may be due to intermacromolecular effects by lowering the level of polymer entanglements, or intramacromolecular effects by entering between the polymer molecules, or it can act as a simple internal lubricant, reducing the friction between rubber and carbon black agglomerates and increasing the slippage between them. Further, as indicated by the dynamic properties reported in Chapter 5, EN444 and OAS have the ability to improve micro – dispersion. It has been reported that prevention\(^{124}\) of filler networking is one of the methods for lowering the compound viscosity by surfactants.
The level of EN444 used, (ie. 2phr), corresponded to the amount needed for the monolayer coverage of 50phr of carbon black, could be the reason for the greater influence of EN444 on the filler networking, and decreasing the interfacial interaction between carbon black and rubber, compared to OAS. The amount of OAS used in this series of experiments, (ie. 1phr), is calculated to only cover 28% of the total surface area of 50phr of carbon black, (as mentioned earlier in Chapter 5).

7.3.1.4 The effect of selection of mastication time on incorporation time and overall mixing time to reveal a constant property level

Table 7.3 shows how the overall mixing time can be reduced by the addition of surfactants, to achieve an equivalent state of mix. A value of 3.5% agglomerates was obtained when a mastication time of 180s was used for the control. The time to obtain a similar amount of agglomerates with surfactants, as calculated from Fig. 7.3, is shown in Table 7.3.

Table 7.3: Times needed to obtain an equivalent state of mix (volume percentage of agglomerates – 3.5) in all three compounds

<table>
<thead>
<tr>
<th></th>
<th>Mastication time, s</th>
<th>Incorporation time, s</th>
<th>Time for dispersion, s</th>
<th>Overall mixing time, s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>180</td>
<td>110</td>
<td>90</td>
<td>380</td>
</tr>
<tr>
<td>EN444, 2phr</td>
<td>82</td>
<td>135</td>
<td>65</td>
<td>282</td>
</tr>
<tr>
<td>OAS, 1phr</td>
<td>105</td>
<td>105</td>
<td>95</td>
<td>305</td>
</tr>
</tbody>
</table>

Similarly, the time to obtain a similar Mooney viscosity with surfactants, as calculated from Fig. 7.4, is shown in Table 7.4.
Table 7.4: Times needed to obtain a similar Mooney viscosity (86) in all three compounds

<table>
<thead>
<tr>
<th></th>
<th>Mastication time, s</th>
<th>Incorporation time, s</th>
<th>Time for dispersion, s</th>
<th>Overall mixing time, s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>180</td>
<td>110</td>
<td>90</td>
<td>380</td>
</tr>
<tr>
<td>EN444, 2phr</td>
<td>55</td>
<td>160</td>
<td>40</td>
<td>255</td>
</tr>
<tr>
<td>OAS, 1phr</td>
<td>100</td>
<td>105</td>
<td>95</td>
<td>300</td>
</tr>
</tbody>
</table>

Table 7.5: Reduction of mastication time at constant time for incorporation by addition of surfactants.

<table>
<thead>
<tr>
<th></th>
<th>Incorporation time, s</th>
<th>Mastication time needed, s</th>
<th>Overall mixing time, s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>110</td>
<td>180</td>
<td>380</td>
</tr>
<tr>
<td>EN444, 2phr</td>
<td>110</td>
<td>115</td>
<td>315</td>
</tr>
<tr>
<td>OAS, 1phr</td>
<td>110</td>
<td>110</td>
<td>310</td>
</tr>
</tbody>
</table>

It is clear from Table 7.5, that carbon black incorporation peak can be reached at the same time, with less time for mastication, when surfactants are added. However Tables 7.3 and 7.4, show that to obtain the similar compound properties achieved with 180s of mastication time for the control compound, can be achieved with far lower mastication time by the addition of EN444 or OAS. Therefore, where Mooney viscosity is concerned, overall mixing time was decreased by 125s or 80s by adding 2phr of EN444 or 1phr of OAS respectively.

It is clear that the overall mixing time can be reduced by reducing the mastication time rather than decreasing the time after the addition of carbon black.
In the rubber industry, it is an advantage to have lower mastication time with adequate behaviour for further processing, considering the end product will have better mechanical properties attributed to higher molecular weight of the rubber.

7.3.1.5 Effect of surfactants on the tensile properties

The effect of mastication time on properties does not seem to be significant. Mastication time can be reduced by adding surfactants without adverse effects on properties. As shown in Table 7.6, there was no significant change in 200% modulus with increasing mastication time. The change in tensile strength between three batches was small, but there was a general increase in tensile strength with increasing mastication time, which could be attributed to the improved dispersion of carbon black and a subsequent decrease could be due to longer mastication. However, there was no trend in the change in elongation at break with increasing mastication time.

Table 7.6: Change in tensile properties with increasing mastication time

<table>
<thead>
<tr>
<th></th>
<th>Mastication time, s</th>
<th>Tensile strength, MPa</th>
<th>Modulus at 200%, MPa</th>
<th>Elongation at break, %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Control</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>20.9</td>
<td>18.1</td>
<td>342</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>21.8</td>
<td>17.9</td>
<td>365</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>21.9</td>
<td>19.1</td>
<td>348</td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>21.1</td>
<td>19.1</td>
<td>332</td>
<td></td>
</tr>
<tr>
<td><strong>EN444, 2phr</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>19.7</td>
<td>18.5</td>
<td>318</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>19.9</td>
<td>18.9</td>
<td>300</td>
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</tr>
<tr>
<td>120</td>
<td>21.1</td>
<td>19.8</td>
<td>311</td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>20.4</td>
<td>18.8</td>
<td>313</td>
<td></td>
</tr>
<tr>
<td><strong>OAS, 1phr</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>18.6</td>
<td>18.6</td>
<td>290</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>20.8</td>
<td>18.9</td>
<td>322</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>19.8</td>
<td>18.8</td>
<td>305</td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>21.1</td>
<td>19.7</td>
<td>319</td>
<td></td>
</tr>
</tbody>
</table>
7.3.2 Determination the ability of surfactants to increase the maximum filler loading

Figure 7.7 shows the mixer power traces for the first part of the mixing cycle. From these traces it can be seen that the dispersing agents/surfactants had a significant influence during incorporation of carbon black, even at high loading. Both surfactants showed similar effects, with an increase in the rate of incorporation.

![Power traces for the first part of the mixing cycle](image)

**Fig. 7.7:** Mixer power trace of master batch of SMR 10 and 70phr of N330 carbon black

The difficulty in incorporating 70phr of N330 in the control compound was confirmed when the batch was dumped from the mixer. Some loose carbon black was observed and the batch looked dull. The compounds which contained surfactants, looked smooth and glossy, which could be attributed to the better dispersion as well as the external lubricating effect of the two chemicals. Further, DFCS measurements confirmed that the carbon black in both compounds with surfactants, was better dispersed than that of the control. (Table 7.7)
The improved dispersion of carbon black achieved by the addition of surfactants was also confirmed by the decrease in viscosity and the minimum torque values. (Table 7.7) The low viscosity achieved by the addition of surfactants is important during the processing of a compound with high loading of filler. The viscosities measured in this study were on the final mix. If the viscosity has been measured on the masterbatch, it was expected that a larger difference between the three compounds would have been recorded, as indicated by Fig. 7.9.

It was observed that the reduction of scorch time due to addition of both OAS and EN444, in comparison with that of the control, was similar to that found in the earlier work, reported in Chapter 5 (section 5.3.2). The difference between maximum and minimum curemeter torque values, taken as an indication of crosslink density, showed an increase with the addition of EN444 and OAS.

Tensile properties of the compounds with 70phr of carbon black are shown in Table 7.7. The physical properties of a carbon black filled rubber compound varied with the carbon black content, as can be seen from Fig. 7.8. In contrast to the continuous increase in stiffness, which occurred with increasing concentration of carbon black in the rubber, tensile strength passed through a maximum. Consequently, the tensile strength values recorded in Table 7.7 were lower than those for compounds with 50phr of carbon black.
Lack of difference between tensile properties was unexpected, in view of differences in crosslink density and dispersion. Although EN444 and OAS showed better dispersion, similar to each other and better than the control, (as shown by DFCS and minimum torque results), only the compound with 2phr of EN444 showed lower modulus than that of the control. This was attributed to better dispersion. However, at 100% elongation, the compound with 1phr of OAS did also show a decrease in modulus, compared to the control.
Table 7.7: Properties of three different batches with 70phr of N330 carbon black

<table>
<thead>
<tr>
<th>Compound properties @</th>
<th>Control</th>
<th>EN444 2phr</th>
<th>OAS 1phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum torque, Nm</td>
<td>3.35</td>
<td>3.55</td>
<td>3.39</td>
</tr>
<tr>
<td>Minimum torque, Nm</td>
<td>0.99</td>
<td>0.81</td>
<td>0.80</td>
</tr>
<tr>
<td>(Max. – min) torque, Nm</td>
<td>2.36</td>
<td>2.74</td>
<td>2.59</td>
</tr>
<tr>
<td>Scorch time, s.</td>
<td>130</td>
<td>40</td>
<td>89</td>
</tr>
<tr>
<td>T&lt;sub&gt;95&lt;/sub&gt;, s.</td>
<td>549</td>
<td>350</td>
<td>425</td>
</tr>
<tr>
<td>Viscosity*, Nm&lt;sup&gt;2&lt;/sup&gt;s</td>
<td>108</td>
<td>88</td>
<td>100</td>
</tr>
</tbody>
</table>

Tensile properties

| Tensile strength, MPa | 19.31 | 19.02  | 19.86  |
| Elongation at break, % | 264   | 266    | 260    |
| 100% Modulus, MPa     | 7.65  | 6.90   | 7.49   |
| 200% Modulus, MPa     | 15.01 | 14.98  | 15.97  |

Carbon black dispersion, DFCS

| Maximum       | 71.1 | 60.1 | 51.9 |
| Minimum       | 44.5 | 37.6 | 25.3 |
| Average       | 50.7 | 45.3 | 30.7 |

@ Wallace Precision Cure Analyser, at 160°C
* From Negretti TMS rheometer at 1s<sup>-1</sup>
From Fig. 7.9, it can be seen that the mixing power demanded by compounds with surfactants was less than the control after 40s of mixing; after this time the decrease in mixer power was almost insignificant. Therefore, by adding surfactants a well dispersed compound with high filler load can be obtained at 40s of mixing. Consequently, the overall mixing time can be reduced by about 80s for the compounds with EN444 and OAS.

![Graph](image)

Fig. 7.9: Mixer power trace of second part of the mixing cycle of compound containing 70phr of N330 carbon black (ram up for curative addition is eliminated)

Considering all the results reported above, it is reasonable to conclude that the addition of surfactants improved compound properties, which will be beneficial for the processability of a rubber compound with high loading of filler. Further, OAS also enhanced the mechanical properties.
7.4 Conclusions

1. It is possible to minimise mastication by adding a fatty amine to a rubber compound. However, an optimum amount of mastication is clearly needed, to obtain the best effect from the surfactants. Compound properties adequate for processability can be achieved with far less mastication by adding surfactants.

2. Decreasing mastication time does not have a detrimental effect on the vulcanisate properties. In fact, tensile strength is improved by decreasing the mastication time.

3. There is an increase in the rate of incorporation by the addition of fatty amines, especially with the addition of OAS. There is also an increase in the amount of disagglomeration by addition of fatty amines /surfactants in comparison with a control.

4. EN444 and OAS have facilitated the mixing of high levels of carbon black in natural rubber. The addition of surfactants has improved the dispersion of carbon black and EN444 has decreased the compound viscosity, which will be beneficial for the processability of highly filled compounds.
8.1 Conclusions

Based on results obtained from various investigations carried out in the course of this research project, the following conclusions are drawn:

1. It is possible to reverse the reduction in scorch delay caused by the fatty amine EN444 (Akzo) by adding conventional retarders. The addition of CTP; N-cyclohexylthio-phthalimide at a concentration of 1phr returns the scorch delay of a compound with 2phr of EN444 to that of a compound without EN444, without affecting the cure time or tensile properties.

From the acidic retarders investigated, 1phr acetyl salicylic acid has a similar effect to that of 1phr of CTP. However, unlike CTP, acetyl salicylic acid has the tendency to increase the cure time, but to a value less than that of the compound without EN444. Even at 2phr, benzoic acid, (the other acidic retarder investigated), was not able to increase the scorch time to that of the compound without EN444.

Therefore, it can be concluded that either CTP or acetyl salicylic acid (ie.Aspirin) can be used as a retarder to eliminate the scorch problem of EN444. Although, addition of Aspirin slightly increases the cure time over that of the compound with EN444, it does not cause health hazards and is less expensive than CTP.

2. A new experimental cationic surfactant, octyl amine salt of benzylmalonic acid (OAS) was successfully synthesised, to improve the dispersion of filler similar to that of EN444, but without the problematic effect of short scorch time.

The filler dispersion can be improved by the addition of OAS. At 1phr OAS can accelerate the incorporation and disagglomeration of carbon black and increase the dispersion of 50phr of N 330 carbon black in rubber to a level approaching that achieved with 2phr of EN444. Consequently, the mixing time of carbon black filled
natural rubber compound can be reduced by addition of 1phr of OAS, to be similar to that of 2phr of EN444.

The actions of EN444 and OAS on the vulcanisation of natural rubber compounds are similar. The acceleration of the sulphur vulcanisation by the amine dissociated during curing proposed for EN444, appears to be valid for OAS, even though the dissociation temperature of OAS is still unknown. At optimum level, OAS has less influence on crosslink density than EN444.

OAS was found to decrease the cure time of a carbon black filled natural rubber compound containing a conventional sulphur accelerator system, showing that it has the ability to act as an accelerator for cure comparable to EN444. However, OAS is found to have a similar undesirable effect on scorch time or safe processing time, as EN444 but the reduction of scorch time at optimum loading is approximately 20% less than EN444.

Dynamic properties, together with other physical properties, show that the effect of fatty amines on crosslink density changes as mixing time is increased from 320s to 750s. Both EN444 and OAS have a tendency to decrease the reinforcing effect, in comparison with the control compound, when mixing time is increased to 750s, compared with the compounds mixed for 320s. The decrease in reinforcement is attributed to the improvement in micro-dispersion, which suggests that EN444 and OAS decrease the interfacial interaction or $W_{ad}$ (thermodynamic work of adhesion) between rubber and carbon black.

Even though the results obtained in this study suggest that OAS can improve wettability, in a manner similar to that of EN444, it is obvious that the mode of action of OAS is different to that proposed for EN444, when monolayer coverage theory is applied. Calculations show that only 28% of the filler surface is covered at optimum level for filler dispersion. However, during early stages of mixing the carbon black surface area available to rubber and OAS is relatively small, compared with the CTAB value on which the monolayer calculation is based.
3. When used in low concentrations, between 1 phr to 3 phr, low molecular weight polystyrene can be used as an effective dispersing agent for carbon black filled rubber compounds. At high concentrations, above 3 phr, this polystyrene acts as a lubricant. It is shown that this polystyrene has the capability to decrease the thermodynamic work of adhesion ($W_{ad}$) between carbon black and rubber. Even though it acts as a good dispersing agent, it has a tendency to decrease the reinforcing effect of carbon black.

4. There is a possibility of minimising the mastication by adding a fatty amine to the rubber compound. However, some degree of mastication is clearly needed and there is an optimum amount of mastication to obtain the best effect from the surfactants. Compound behaviour adequate for processability can be achieved with far less mastication by adding surfactants. Decreasing mastication time does not have a detrimental effect on the vulcanisate properties. In fact, tensile strength is improved by decreasing the mastication time. There is a possibility of reducing the overall mixing time by decreasing mastication time with the addition of fatty amines. Overall mixing time can be decreased by approximately 100s and 80s (24% and 19%) when EN444 and OAS are added respectively.

EN444 and OAS facilitate the mixing of high levels of carbon black in natural rubber. The addition of surfactants improved the dispersion of carbon black and decreased the compound viscosity (19% for EN444 and 7% for OAS), which will be beneficial for the processability of a highly filled compound.
8.2 Further work

The field of investigation regarding multifunctional additives and dispersing agents and their effects in rubber compounds is extensive. The following recommendations for further work in this area, are based mainly on the outcome of investigations in this project.

Even though 1 phr OAS produced filler dispersion as good as that of 2phr of EN444, calculation showed that monolayer coverage of OAS at 50phr N330 needs 2.94phr of OAS. This result for OAS casts doubt on the requirement for monolayer coverage of the filler for optimum fatty amine effect, as was proposed for Akzo EN444. Firstly, it would be useful to carry out mixing experiments with carbon black with different surface area to determine the changes in the amount of OAS required for optimum effect, which would lead to better understanding of the monolayer coverage with OAS. Further, apart from OAS, the fatty amines investigated by earlier researchers\textsuperscript{91,93,94} were consisted mainly with long chain fatty acids. Therefore, further work is needed with a range of fatty amines synthesised from fatty acids of different chain lengths and configurations to study their effect on filler dispersion at different concentration in the rubber compound.

It was also suggested that EN444\textsuperscript{93} has a different orientation on the surface of silica, than on the surface of carbon black, which led to a higher amount being required for efficient dispersion of silica. It would also be useful to explore the effect of OAS concentration in silica filled rubber compounds and to extend this to other types of fatty amines.

It is believed that multifunctional additives\textsuperscript{94} increase the in-phase shear modulus of the gum compound due to an increase in crosslink density. However, in this work the increase is attributed to the increased macro-dispersion of the compound with the addition of EN444 and OAS. Therefore, OAS should be mixed in a gum compound to improve the knowledge of how OAS works in a carbon black - rubber
system. This work would show whether OAS has an effect on the rubber matrix directly or whether it acts only at the rubber – filler interface.

It would also be useful to determine the changing $W_{ad}$ between rubber and carbon black with the addition of OAS and EN444, by determining the surface free energies of OAS and EN444.

Further work for low molecular weight polystyrene is needed under conditions which more closely simulate large scale mixing. An efficient and economical method of producing low molecular weight polystyrene is required. Further, direct injection of the low molecular weight polymer into mixer would be an advantage, to avoid the continued polymerisation which occurs on exposure to atmosphere. Further work is also needed to determine the mechanism for the observed effect of polystyrene on crosslink density.
Appendix A

List of abbreviation

À - Angstrom
ABA - Amide-bridged amines
Bt - 2-benzothiazoyl group
CBS - N-Cyclohexyl-2-benzothiazoyl sulphenamide
CDB - 2-Cyclohexyldithiobenzothiazole
CTP - N-Cyclohexylthio-phthalimade
CTAB - Cetyltrimethyl-ammonium bromide
DBPA - Dibutyl phthalate absorption number
EN444 - N-tallow-1-3, diaminopropane dioleate
FTIR - Fourier transform infra red
HAF - High abrasion furnace
MBT - Mercaptobenz-thiazole
MBTS - Dibenzthiazyl disulphide
MFA - Multifunctional additive
M_n - Number average molecular weight
M_v - Intrinsic viscosity
M_w - Weight average molecular weight
NDPA - Nitrosodiphenyl amine
NR - Natural rubber
OAS - Octyl amine salt of benzylmalonic acid
phr - parts per hundred rubber
SAPA - Surfactant- accelerator processing aid
SBR - Styrene butadiene rubber
SMR - Standard Malaysian rubber
Appendix B

FTIR spectrum of synthesised Octyl amine salt of benzylmalonic acid.

<table>
<thead>
<tr>
<th>Absorption</th>
<th>Functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>2900 cm(^{-1})</td>
<td>-CH(_2)/CH(_3)</td>
</tr>
<tr>
<td>1700 cm(^{-1})</td>
<td>-COOH</td>
</tr>
<tr>
<td>1550 cm(^{-1})</td>
<td>RCOO(^+)NH(_3)R</td>
</tr>
</tbody>
</table>
Appendix C

Definitions for parameters in the dynamic testing. (see appendix Ci)

(a) Elastic Shear Modulus (in-phase shear modulus), \( G' \)

\[ G' = \frac{\text{component of applied shear stress in-phase with shear strain}}{\text{shear strain}} \]

(b) Loss Shear Modulus (out-of-phase modulus), \( G'' \)

\[ G'' = \frac{\text{component of applied shear stress 90° out-of-phase with shear strain}}{\text{shear strain}} \]

(c) Complex Shear Modulus, \( G^* \)

\[ G^* = \frac{\text{resultant shear stress}}{\text{resultant shear strain}} \]

where each is a vector which may be represented by a complex number.

(d) Loss Tangent (loss angle), tan \( \delta \)

\[ \tan \delta = \frac{G''}{G'} \]

where \( \delta \) is the phase angle between the sinusoidal force and deformation.

(e) Shear Strain Amplitude (dimensionless)

The ratio of maximum deformation, measured from mean deformation, to the free thickness of the unstrained test piece (zero to peak in one direction only).
Sinusoidal stress-strain time cycles
DARTEC software programs used for dynamic testing

(a) The ‘Complex’ program

Through the ‘Complex’ program, the type of dynamic operations to be performed would be specified. What was being created in this program was essentially a set of stages, linked together to give the dynamic operations required. Each stage could set up the machine to operate dynamically with a set of stage parameters, i.e., waveform, mode, frequency, amplitude and number of cycles.

In dynamic testing, the test specimens were subjected to oscillations at the following double strain amplitude range: 1E -3, 3.16E -3, 1E -2, 3.16E -2, 1E -1, 3.16E -1, 1E0. This range was equivalent to the following extensions of the driving member of the machine, respectively: ±0.004 mm, ±0.0126 mm, ±0.04 mm, ±0.1264 mm, ±0.4 mm, ±1.264 mm, ±4 mm. The first stage was programmed to perform the smallest amplitude in the range, and the subsequent amplitudes were programmed in alternate stages. The stages in between were used to produce a delay to allow recorded data to be dumped to a disc. For all the effective stages, frequency was set at 1 Hz, while the number of cycles for each amplitude was 30; and the data was captured at the 28th cycle of each amplitude. This program was stored in a file and transferred to 9500 controller for testing operations.

(b) The ‘Data Capture’ program

With this program multiple captures of test data could be done. In this program, information about what channels to capture, the size of the capture, and how long to capture for, were specified. The cycle count of the function generator at which the capture is to start was also specified.
(c) The Viscoelastic Analysis program

The Viscoelastic Analysis program analyses data recorded by the ‘Complex’ and ‘Data Capture’ programs.

This program calculated the dynamic properties of the rubber compounds using forced sinusoidal oscillations. The program calculated the following dynamic properties as defined in BS: 903 Part A24: 1976: Elastic, Loss and Complex Modulus; Elastic, Loss and Complex Compliance Modulus; Loss tangent; Stress and Strain.
Performing Test

Switch on Computer [@] and Relaxometer [#]

@ Choose Set up Relaxometer from menu

While menu is changing, the computer issues the command...

MODE COM 1:9600,n,8,1

This could also have been issued in long form of...

MODE COM 1: Baud = 9600  Parity = n  Data = 8  Stop = 1

The purpose is to “tune in to” the Relaxometer when it gets to the stage of downloading data to the computer.

Measure sample height by vernier and place the sample on the Relaxometer platform.

# Press Enter and Select keys simultaneously to get a menu from which a selection can be made by the Select key and activated by pressing the Enter key.

# Choose Set Pen. Dpt and press Enter.

Set the penetration depth to the required compressive strain by adjusting the LCD to the appropriate value in mm, using the knurled metal wheel labelled Inch/Set. Then press Enter.

# Press both keys to get the menu.

# Choose Impact Mode and press Enter.

# Place sample on platform and bring the platform up almost to touch it.

This is done by using the three unlabelled square buttons on the right.

These are effectively Up/Stop/Down.

# Put safety guard in position.

# Press both buttons for menu.
Select Impact mode and press Enter. Then Enter again to confirm details. Use select button to choose confirm and then press Enter.

*The platform will first lower then the plunger will drop on to the specimen with a loud bang. It is gauging the distance to the specimen at zero force. After that it will rise again.

*At the second descent of the plunger the test will be starting and the specimen will compressed by the amount requested.

*The test will take 15 minutes to complete.

*On completion the plunger will rise.

Storing data

# Select Send data, but do not press Enter on Relaxometer yet
@ If the Norton Commander menu is present, press Esc to remove it
@ Type COPY COM1 FILENAME.PRN and press Enter

FILENAME is a name of your choice for the test data (up to 8 digits long)
The extension .PRN is convenient for spreadsheet importing

# Press Enter key on Relaxometer

The Relaxometer will then send a copy of the test data to the computer, which has been waiting for it.

Plotting Graph

@ If no menu showing, press F2.

Rapid Plot

@ VP Planner is loaded with an autoexec file
Choose the data file to plot by using the cursor and then press Enter
@ F10 to plot
@ Esc to return to table format
@ To save file press /FS and then type a filename of length less than 8 digits and press Enter

Do NOT accept the default filename of D1; this will overwrite your blank starter file!

To finish
Press Esc often enough to get to basic menu
Press /QY

**High quality plot**

@ Quattro Pro 4 is loaded with an autoexec file

@ Similar to above, but print via print menu, setting printer to "Graphics Printer" before pressing "Go".

@ Full titles, manual labelling and even arrowed labels may be added. These facilities are under the Graph menu. You can save the new graph as a named graph within the file, or save the file with a different name by printing /FA and then typing- in a filename of your choice.
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