Truck tyre tread rubber: compounding and abrasion resistance

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TRUCK TYRE TREAD RUBBER: 
COMPOUNDING AND ABRASION RESISTANCE

by

MAHDI HASSAN HALIM, B.Sc.

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

Supervisor: Dr. Claude Hepburn
DSc MSc PhD ANCRT
FRSC CChem F PRI

APRIL, 1990
To my wife and three sons
I would like to express my gratitude to my supervisor Dr. C. Hepburn for his guidance throughout the work.

My thanks to the State Enterprise for Rubber Industries, Diwanlya, Iraq for financial support.

I would like to thank Mr. Nabil A. Jajawi ex-Director General of the above Enterprise for his support.

Many thanks to Professor A.G. Thomas and Mr. P.J. Corish for their notes on tearing energy and rubber wear.

Thanks are also due to the technical staff at IPTME.
Attempts to study the complicated phenomenon of truck tyre tread abrasion and its improvement for severe service conditions are described. The common source of the complication comes from an incompatibility dilemma and a lack of correlation of abrasion with other physical properties used to assess wear in the laboratory.

A major problem with rubber vulcanisates for tyres is that improvement of abrasion resistance can only be generally achieved by a sacrifice of some other essential properties such as wet grip and heat build-up. The importance of the latter in tyre performance means that assessment of wear is, at present, always evaluated by costly and lengthy roadwear trials.

In this research work a step-by-step experimental approach was followed to isolate and examine the individual fundamental rubber properties, that constitute the phenomenon of abrasion resistance. Also, another objective was to improve some of the key durability properties of typical tread rubbers by developing a better reinforcing system, an improved polymer blend and superior heat stability. Therefore, every step was followed by an assessment of abrasion resistance and its related properties. It was found that when a bonded silica is used in conjunction with a conventional carbon black as the reinforcing system then better wear properties resulted. An essential condition was that the rubber mixing cycle had to be optimised to enhance dispersion. Abrasion resistance was evaluated by both the standard and a specially developed miniature pneumatic tyre abrasion tester which gave both frictional rubbing and abrasion fatigue; with this equipment it was found possible to produce a range of abrasive modes from mild to severe abrasion typical of the conditions that exist during road wear. Utilising this information together with measurements of crack growth and frictional resistance and some other properties a unified theoretical approach to the phenomenon of abrasion is postulated as follows:
Abrasion on abrasive paper

\[ A_1 = \frac{k_1 \mu \alpha t}{TH \tan s} \]  \hspace{1cm} (1)

where \( k_1 \) = constant; \( \mu = \) coefficient of friction; \( t = \) temperature;
\( \alpha = \) temperature coefficient of abrasion; \( T = \) tearing energy;
\( H = \) hardness; \( t = \) temperature and \( \tan s \) is the loss factor.

Abrasion of the miniature tyre

\[ A_2 = \frac{k_2 \mu s^2 \alpha t}{T \tan s} \]  \hspace{1cm} (2)

where \( k_2 \) = constant, \( s = \) slip angle (1 - 4°)

When the other factors in the equations are kept unchanged, these expressions show that abrasion is governed by friction, hysteresis and tearing energy. Application of the above approach established that the specially developed rubbers were superior in their abrasion characteristics to typical controls. Other advantages gained were improvement in the cutting and chipping resistance of these rubbers coupled with desirable low heat build-up properties.

These improvements are ascribed to enhancement of tearing energy by silica and also to better dynamic properties (e.g. resilience), fatigue and reversion resistance. The inclusion of polybutadiene with natural rubber was found to be advantageous in achieving these objectives.

Finally, a wear mechanism is proposed and wear products resulting from abrasion analysed.
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CHAPTER 1

Introduction

1.1 DEFINITION OF ABRASION AND WEAR OF RUBBER

Wear and abrasion are used so loosely that sometimes confusion results. Brown has identified wear as a general term covering the loss of materials by virtually any means. Moore defined wear as the extent of surface deterioration following exposure to friction. In fact, a comprehensive explanation may require a combination of both the above definitions. Wear involves removal of surface material which for tyres includes such diverse mechanisms as removal of chunks of rubber by cutting, high speed tearing, grooving, thermoxidative degradation (molecular rupture of polymeric chains).

The term abrasion is commonly used to refer to a process of wear in which there is displacement of material from a surface during relative motion against sharp projections or protuberances. The word abrasion is sometimes used in this way as a general term to mean wear.

Bulgin and Walters defined abrasion as removal of materials by tensile failure or tear process due to interaction of an applied shear stress at the surface.

1.2 IMPORTANCE OF RUBBER WEAR

Wear of rubber is one of the serious problems that the industry has been facing for a number of decades. This is because tyres have to catch up with the increase in vehicle performance in terms of load and speed. This imposes another task on tyre designers to search for improved models and tyre compounders to develop high wear resistant formulations. In one instance an analysis of reasons
why tyres wear out, from the data of tests on hundreds of thousands of series production tyres, shows that 60 - 90% of these tyres go out of use because of wear in the tread. Therefore, it is not surprising that there exists a persistent economic driving force to improve the life of tyres, especially since legislation by many countries has limited the minimum tread depth to more than 1 mm.

Tread pattern depth lower than this is insufficient to hold a vehicle safely on wet roads. Moreover, at one extreme are circumstances in which excessive wear of the tread can jeopardise the viability of a complete tyre.

1.3 DIFFICULTIES OF WEAR STUDIES

Wear studies and developments have always been confronted by incompatibility problems between this and other related properties that are also essential for tyre performance. The main well known dilemma is between abrasion resistance on one hand and road traction and heat build-up on the other. High wear resistant tread rubbers which are based on conventional ingredients normally run with either higher heat build-up or lower traction than their equivalents of lower wear resistance. Reduced road traction means that the tyre has detrimental lower road holding and driving safety while excessive heat build-up means that a severe treadlift is more likely. Nevertheless, tyre performance has been enhanced enormously through step-by-step compounding and design developments over a period of nearly 100 years. Of these developments, the introduction of carbon black as a reinforcing filler and the radial tyre design remain landmarks. Additionally, progressive improvements in polymer blends, curing systems and stabilizations are other examples of improvements achieved in the compound field, resulting in improved overall tyre performance. It must be noted, however, that this overall performance is no more than a balanced compromise between the performance deciding properties. The selection of a predominant property for a certain environment becomes a matter of preference. A hot, dry
environment, for instance, may emphasise the need for less heat build-up at the cost of certain sacrifice in other properties. A wet, cold environment may demand an emphasis on higher wet traction.

Another problem in wear studies of tyres is to find an easy means to quantify wear. This will be discussed in more detail in Chapter 2.

1.4 TYRE TREAD WEAR UNDER AGGRESSIVE ENVIRONMENTS

The environment in the Middle East can be considered as one of the most aggressive for tyres for the following reasons:

A. The severity of the climatic conditions

The temperature fluctuation ranges from a few degrees below 0°C during winter in parts of the area to more than 45°C during the long summer. The temperature on a paved road can rise to more than 70°C during the hot season causing the temperature of a running truck tyre to rise to more than 150°C.

The effect of excessive ambient temperature has been shown in a number of studies as drastic. Amongst many workers Amon and Dannenberg\textsuperscript{110} showed that NR treads have higher rates of wear at temperature above 20°C and lower rates below 10°C. Another study\textsuperscript{104} showed an interesting chart (given as Figure 1.1) of the effect of ambient air temperature on tyre wear. This chart, representing a composite of data from many sizes of tyres, shows that an average tyre will wear twice as fast on an 2°C day as on a 30°C day.

Grosch\textsuperscript{11} has stated that relative tyre wear depends only on the temperature at the surface of the tyre no matter what the severity of use might be (Figure 1.2).
Figure 1.2: Effect of ambient temperature on expected tyre mileage

Figure 1.2: Effect of tyre surface temperature on tyre wear ratings
B. Road conditions

Although much attention has been paid to improving the transportation network in recent years, this is limited to highways and city centres. Countrysides are expected to stay with poor roads for decades. Even some city roads are damaged as a result of overloading or poor maintenance. This means that an on-road designed truck tyre can face a large proportion of driving time travelling on roads in these conditions. It is therefore essential that this situation should be taken into consideration in the design and compounding of tyres. In the author's knowledge, most tyres presently used in Iraq are designed to serve either on or off the road conditions.

C. Operating conditions

Most transport activity is managed by the private sector which does not usually use scientific transport management techniques. Vehicles carrying commodities such as petroleum derivatives, steel, cement etc. are overloaded over very long distances most of the time under high temperature ranges. Therefore, they wear rapidly as wear is directly related to the load being carried. Other common practices are, tyre upgrading (in order to increase vehicle load by up to 50%), improper tyre inflation and misalignment, with these factors directly affecting wear although irrelevant to the present study.

1.5 LOCAL WEAR STUDIES

Local production of tyres is very limited and tyres are imported from different manufacturers in the world each of whom uses his own technology.
Local tyre wear trials, if they are made at all are meant to serve quality control or rating purposes. The simpler laboratory tests are perhaps more frequently employed to check uniformity of production batches.

These studies are not expected to explain the direct effect of the environmental and operating conditions on a specific tread formulation unless the main elements of the compound factors contributing to treadwear are broken down and investigated more scientifically. Achievement of such a goal may ease the task of proposing certain formulations to suit the service conditions. Therefore a decision has been made to undertake the present work as a step in this direction.

1.6 PRESENT WORK PROPOSALS

The final aim is to achieve through step-by-step compounding developments, truck tyre tread rubbers that acquire high wear and cut-chip resistance without undermining heat build-up properties. Achievement of such a goal demands awareness of the predominant wear mechanisms, the rôle of each of the main commercial compound ingredients and methods of preparation on the process of wear.

In any multivariable study such as this, several requirements are necessary in order to have a comprehensive yet manageable programme. These requirements are difficult to find at any single research centre or Institute. Therefore, the project was planned to be conducted in two stages. The first was to be experimental in a pilot plant using commonly available or modified equipment necessary to give a prediction of service performance. The second part was to undertake a roadwear test. Unfortunately, difficult circumstances have made it impossible for the second part to be achieved within the time span of the research. However, an attempt is being made to test some of the experimentally developed formulations on a medium scale Cabot chip-cut tester but the results cannot appear in this thesis. The layout of the experimental programme can be seen in Figures 1 and 2 of the Appendix.
CHAPTER 2

A REVIEW ON ROAD WEAR AND LABORATORY ABRASION OF TREAD RUBBER

2.1 INTRODUCTION

The problem of rubber wear and its determination was not acute in the early stages of the tyre industry as tyres during those days went out of use usually for reasons other than tread wear. This situation however did not last long and the advent of introducing new reinforcing materials for the tyre casing made it outlast treadlife. Tread wear since then has become one of the major concerns for rubber technologists in their efforts to improve mileage.

It is therefore understandable that scientists and rubber technologists have repeatedly attempted to determine abrasion properties of rubbers in laboratories to predict service life. Additionally, laboratory assessment of wear properties has been adopted to evaluate the general performance of new rubber ingredients and to improve the quality of the used ones. Unfortunately, however, a detailed scientific understanding of abrasion has not yet been achieved\textsuperscript{1,2,3,4}.

Consequently, tyre rubbers have been developed on an empirical basis. Although this procedure has been remarkably successful, there is no way of knowing which direction will prove valuable for future improvements or on what basis one should choose new polymers, fillers and crosslinking systems\textsuperscript{1}. Thus there has been a clear need for understanding the mechanism or mechanisms of abrasive wear in order to be able to specify relevant test methods and to design rubber formulations in a rational way. Moreover, it seems rather peculiar that after nearly one hundred years of tyre production, the wear properties are still determined by protracted and expensive road tests. Having said that it should also be noted that the conditions of abrasion with laboratory devices can not be
expected to duplicate satisfactorily a lengthy procedure like a tyre wear test unless certain measures are taken to simulate as much as possible the true service conditions. Some workers have gone as far as acknowledging that the reproducibility of the road test itself under the most carefully controlled conditions is questionable. In general, in performing laboratory tests it is necessary to obtain a significant amount of abrasion in a short time in order to have a measurable weight loss. This has led to tests based on the use of sharp abrasive surfaces and high slip velocities although these conditions are not representative of service. These conditions exert a great surface cutting, tearing and chunking over very short periods which result in severe damage. On the other hand wear of tyre treads under conditions of normal use are also largely influenced by the high temperature reached with steady high speed driving on smooth roads and also to the fatigue of the rubber due to repeated deformation cycles. The occurrence of tear as a failure mechanism may only happen occasionally for tyres such as during strong braking or cornering. Also there are some reports which note that laboratory tests can give meaningful correlation between extensive roadwear tests and laboratory measurements in these particular techniques, rapidity, economy and accuracy of prediction were achieved.

Due to its complexity, the rubber abrasion phenomenon generally needs to be studied by adopting certain approaches. These must combine both direct and indirect evidence on the way by which rubber is removed and break down the various mechanisms of the process. This has led to the 'development' of certain trends in the study of tyre wear.

2.2 TRENDS IN STUDIES OF RUBBER WEAR

Tread wear and abrasion of rubber in general has been extensively studied over the last fifty years or so, but the literature dealing with the subject is rather scattered. It was therefore thought that a brief review of the present trends and methods of wear studies would be beneficial.
2.2.1 Road wear

Fleet test of tyres to assess their wear properties quantitatively is extremely time consuming and requires a lot of data to be collected. Yet, it is considered by the rubber industry as the most reliable one presently available\textsuperscript{8,9}. For this reason the major tyre producers have constructed costly test tracks, usually specially designed to simulate various road conditions of service. The common procedure followed is to mount the test tyre on a vehicle or a towed trailer and to run it under certain controlled conditions for a certain time. If a comparative test with a standard tyre is required then more than one vehicle may be used. The test could last for several months but under certain circumstances its severity (tonnage x speed) can be increased to save time. Several factors contribute to the test results, to mention just a few, the topography of the road surface, tyre and ambient temperature, tread compound and driver's practice must be taken into consideration during the course of the test\textsuperscript{31}. Moreover the validity of the results critically depends on the equality of the test condition of the tyres even when they are mounted on the same vehicle. At the end of the test, wear is assessed either by measuring the weight loss (from which volume loss is worked out) or by measuring the reduction in tread depth. It is significant to note that the road test method has its own many handicaps such as the difficulty in controlling many of the operating conditions. For instance, it is difficult to predict and obtain reproducible weather conditions and thus maintain the same road effect and driving practices etc. on wear. Therefore, it should be borne in mind that road tests are not straightforward and the usual assumption that a particular road test gives an absolute measure of a particular abrasive wear is questionable. For instance Veith\textsuperscript{4} conducted an extensive roadwear test to explore the effect of track topography on wear rating of two tread compounds; his findings indicate that a reversal in rating can be obtained according to the road surface (Table 2.1).
Table 2.1 Effect of pavement type on wear rating of two tread compounds in an accelerated test

<table>
<thead>
<tr>
<th>Tread compound</th>
<th>Texture of pavement</th>
<th>Wear rating or index</th>
<th>Absolute wear rate controla</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Blunt</td>
<td>100</td>
<td>35</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>Harsh</td>
<td>100</td>
<td>250</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>73</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>Harsh</td>
<td>100</td>
<td>60</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>Blunt</td>
<td>110</td>
<td>55</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>114</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>Blunt</td>
<td>100</td>
<td>190</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>Texas fleet testing</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>B</td>
<td>Texas roads</td>
<td>69</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>Harsh</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is interesting to note that to save cost and time, attempts were made to simulate a full scale road test by a semi-service type laboratory testing device. In these tests a small two wheeled trailer was towed behind a vehicle on the open highway. To obtain the required severity, the solid wheels were adjusted at a certain slip angle and run under specific loads. The first reported use of such a device was by Schallamach. Although the conditions of abrasion with this device cannot be expected to reflect in all ways the conditions encountered during wear of tyres, the one thing that was constant in both cases was that of the abraded surface.
Generally, it can be said that the prime task of roadwear tests is for relative rating purposes rather than to obtain a scientific understanding of the way by which rubber is removed. Therefore, for a highly competitive industry like the tyre industry, reports of wear studies in the literature are not easily found. Nonetheless there has been a considerable amount of literature published on the subject by RAPRA\textsuperscript{11} and MRPRA\textsuperscript{102}. A major contribution has also come from the carbon black industry. Of interest are the studies of Scott and Chirico\textsuperscript{99}, Veith\textsuperscript{50} and Brenner and Kondo\textsuperscript{31}. Moreover, fruitful studies exist of correlation between abrasion resistance as measured by various techniques and extensive roadwear tests with these being conducted by Westlinning\textsuperscript{70}, Satake et al\textsuperscript{100} and Bassi\textsuperscript{13}.

2.2.2 Correlation between abrasion resistance and some other selected strength properties

Some rubber technologists have tried in the past and indeed more recently to use traditional strength properties, normally utilised as an indication of rubber quality, to draw conclusions about its potential abrasion resistance. The correlation of abrasion resistance with some of these typical laboratory properties is discussed below.

2.2.2.1 Correlation with tensile strength

Among the early workers Bulst and Davis\textsuperscript{17} have revealed a significant correlation between the increase in tensile strength and hardness on the one hand and an increase in abrasion resistance on the other. Later Thronley\textsuperscript{16} was able similarly to show a correlation between tyre wear with both tensile product and hardness. Zapp\textsuperscript{22} gave the relationship shown below (2.1) to describe results for the abrasion of a butyl rubber in which a small rotary, slipping wheel was used as the test specimen.

\[
\text{abrasion loss} \sim \text{dynamic modulus} \times \text{friction} \quad \text{.....2.1}
\]
However, it was anticipated later that attempts to find a simple and direct relationship between abrasion and tensile strength as measured by conventional methods would be unsuccessful in producing convincing results\textsuperscript{14,19}. Consequently, scientists have done an extensive amount of work to find a solution to this problem. Ratner\textsuperscript{20}, basing his conclusions on extensive laboratory measurements using abrasive papers, has introduced additional factors. He concluded that the wear of rubber (V) is linked with strength (σ) and resilience (D) by the simple equation

\[
V = \text{const.} \cdot \frac{(1-D)\mu}{\sigma} \quad \ldots \quad 2.2
\]

where (μ) is the coefficient of friction. According to this equation any increase in resilience is expected to produce lower abrasion. This was in contrast at the time to the ideas of Ecker\textsuperscript{14} who held the widely accepted opinion that an increase in hysteresis reduces wear. Kragelj\textsuperscript{21} and co-workers\textsuperscript{21} suggested that the wear and strength are related to each other as shown in Figure 2.1. Reznikovskii\textsuperscript{85} proposed that wear conforms to the Whöler curve of fatigue.

![Figure 2.1](image)

**Figure 2.1** Relationship between wear of rubber and its strength
More recently Uchlyama\textsuperscript{2,3} has suggested that the wear of rubber on abrasive paper (S) can be calculated according to the equation

\[ S = k_4 \frac{\mu P}{\rho \sigma_B} \]  \( \ldots \ldots 2.3 \)

where (P) is the load, (\( \rho \)) is the fractional rebound resilience and (\( \sigma_B \)) is stress at break.

It should be noted however that these additional approaches to obtain correlation with tensile strength only gained limited success. One of the reasons given for this, is based on the argument that the conventional tensile test is usually carried out at room temperature and at a strain velocity of about 10\% per second, whereas an estimated deformation velocity of 10\(^4\) to 10\(^6\) percent per second has been suggested to occur during abrasion\textsuperscript{4,14,19}. Another important factor which must also be taken into consideration is the temperature of the test. While the usual tensile strength measurements are done at room temperature, some sources have predicted that very high temperature will be obtained in the area of contact between the rubber surface and the abradant\textsuperscript{14,24}. These temperatures, if reached, could decompose tread rubbers on a microscale\textsuperscript{25,46}. Evidence that this occurs may be seen as the smoke which is evolved in certain cases i.e. from a tyre tread during an aircraft's landing or during the sudden braking of a car under certain extreme conditions. To account for these effects Schallamach\textsuperscript{19} and Ecker\textsuperscript{14} have designed special experiments which allowed them to measure tensile strengths at strain rates as high as 10\(^4\) per cent per second and over a wide range of temperatures. The outcomes of such attempts have shown better correlations between abrasion resistance, as measured by silicone carbide paper, and tensile rupture energy.
2.2.2.2 Correlation with tear strength

The questionable correlation between abrasion and tensile strength led investigators to search for a better criterion. Tear strength has long been considered as a basic property to measure rubber reinforcement\textsuperscript{24,25}. Therefore its role on the mechanism of abrasion has been extensively investigated by many workers, most of whom have shown that tear strength is in fact an important factor for abrasive wear\textsuperscript{4,51}.

To simulate the interaction between abrasive asperities of the road and the surface of the rubber Schallamach\textsuperscript{16} used the well known experiment of the gramophone needle. Examination of the damaged surface led him to suggest that abrasion of rubber on sharp pointed asperities is produced by the removal of rubber from the bulk due to stress concentration produced by impinging of these asperities on the surface followed by catastrophic tearing of the area behind the moving track asperities. This means that stress magnification in certain weak regions tends to make the strength properties of the surface layer fall beyond a certain critical level and the small flaw start to grow as a crack.

However, Schallamach's model of simulation of the elementary abrasion process by such a fast and exaggerated and straightforward tearing was later described as a simplistic type of failure mechanism which is unlikely to occur in service\textsuperscript{25}.

Another attempt to explain the role of tear on rubber abrasion has been sought using the characteristic appearance of abrasion patterns. These normally appear when a rubber specimen is continuously abraded in one direction against a rough surface i.e. the abrasive wheel of an Akron abrader. They are usually seen by the naked eye as equi-distanced arrays perpendicular to the direction of abrasion\textsuperscript{9}, and were later called Schallamach patterns. They look like saw blades with their teeth pointing in the sliding direction of rubber as shown in Figure 2.2.
It has been suggested that their presence increases the rate of abrasion as they must be bent backward when meeting track asperities, so their underside is gradually abraded while their roots propagate deep in the rubber before they eventually weaken and tear off. Their loss was thought to make a relatively large contribution to the abrasion. If rubber toughness is high enough to resist their propagation, then it would be expected that the rubber would show a higher resistance to abrasion. It is considered useful to point out that the importance of abrasion patterns has been disputed by Gehman, who suggested that most of the treadwear on roads produces an absence of abrasion patterns on the worn rubber surface. He based his remarks on the observation of the low wear rates for tyre treads (1 mm/100 mile) as a reason for his thinking that abrasion patterns do not contribute much to wear under low severities.

To sum up, it must be said that although various theories consider rubber abrasion as a strong function of tear strength, the experimental evidence remains scanty. A complete analogy cannot be drawn between laboratory abrasive wear and tear strength as
measured by the usually fast and catastrophic tear tests. Also, the former process occurs in the thin surface layer and not throughout the material and is governed by a large number of variables. To add to the problem, the measurement of tear strength itself is difficult and known to involve a good deal of uncertainty.

2.2.2.3 Correlation with tearing energy (Fracture Mechanics)

The continuous quest for a valid correlation between abrasion and an independently measured fundamental property has led Champ, Southern and Thomas to propose a quantitative theory. The theory was based on scraping rubber under accelerated conditions using a single asperity i.e. by the passing of a blade over the surface of rubber. This approach has been called fracture mechanics. The theory assumes that if a sufficiently sharp metal blade under load comes repeatedly into contact with a rubber surface in one direction, then it causes the abrasion patterns to be pulled back and then released as the blade passes on. The stress produced in this process is assumed to cause crack growth in re-entrant corners (P) and (Q) at the root of the cracks as shown in Figure 2.3.

Figure 2.3 Schematic diagram of deformation of abrasion patterns
When a steady state is reached, the presumably idealised patterns are postulated to show crack growth as illustrated in Figure 2.4. If a rubber disk of thickness \( h \) is used then the tearing energy \( T \) (the amount of energy released per a unit area of the new surface) was shown to follow the equation

\[
T = \frac{1}{h} \cdot \frac{dU}{dc} \quad \ldots \ldots 2.4
\]

where \( dU \) is the amount of energy consumed and \( dc \) is the resultant crack growth.

On the other hand the tearing energy for a trouser tear specimen was equated as

\[
T = \frac{F}{h} \left( 1 + \cos \theta \right) \quad \ldots \ldots 2.5
\]

Using these independent mathematical equations, Champ, Southern and Thomas have shown experimentally that \( T \) values of gum rubbers as measured using a trouser tear specimen and the corresponding ones as measured according to the fracture mechanics were almost identical (see Figure 2.5). Only one exception was reported which was the crystallizable gum natural rubber vulcanisate. The anomaly of this rubber was seen in its low \( T \) value as obtained by Equation 2.4 compared to the one obtained from Equation 2.5.

A great advantage can emerge from the use of fracture mechanics if it can hold a valid relation between abrasion and a fundamental property like tearing energy for filled rubbers.

Such a promising relationship had attracted other scientists to search for an improved model experiment in order to widen the range of application of industrial rubbers.\(^{1,94}\)
Figure 2.4: Sketch of two stages in the abrasion of a rubber surface by a blade.

Figure 2.5: Rate of crack growth as a function of the tearing energy as derived from direct measurements (full lines) and from abrasion results.
Gent and Pulford\textsuperscript{1} used a modified version of the aforementioned apparatus but the technique remained basically the same. The modified version allowed them to carry out their experiments under a wider range of temperatures and tests were performed usually at 25\textdegree C and 100\textdegree C. The apparatus was also designed to allow experiments to be conducted under an inert gas atmosphere. The other advantage claimed was the ability of being able to measure both the frictional forces and the coefficient of friction with acceptable fluctuations. After an extensive study on various types of filled and unfilled elastomers they have concluded that abrasion of rubber, whether filled or unfilled, strain crystallizable or amorphous, involves two mechanisms. One is the removal of microscopic particles of rubber by fracture processes and the other is chemical deterioration of the rubber surface initiated by mechanical stress and prompted by oxygen in the atmosphere. They have also proposed that wear rates of elastomeric materials are proportional to the power \( n \) of the applied frictional force. The value of \( n \) was shown to depend upon the composition of the elastomer and ranged from 1.5 for carbon black filled SBR to 3 for unfilled BR. Moreover, they have concluded that only a general parallelism was evident between the observed rates of wear and crack growth under repeatedly applied stress. For filled materials in particular the abrasion rates were not found to be a smooth function of mechanical fatigue. Surprisingly, they have also suggested that the temperature has a relatively small effect upon the rate of wear which was in clear contrast to its effect on crack growth.

It is worthwhile to note here that beside the application of the questionable energetic approach in the theory of fracture mechanics there are some expected difficulties which include:

a. Not being fully successful in giving a conclusive explanation for the effect of crystallization on both crack growth and abrasion.
b. No consideration was given to the part of energy dissipated other than crack propagation such as hysteretic losses and elongation.

c. The theory does not appear to have taken into consideration the usual temperature rise in the rubber specimen which is expected to affect the measurements of $T$ value.

d. The theory is based on a single asperity whose sharpness may cause some cutting rather than fatigue.

2.2.3 CORRELATION WITH VISCOELASTIC PROPERTIES

Time plays a very important role in the properties of polymers over a very wide range of temperatures. For some materials the principle of time-temperature superposition has been a convenient and a useful concept\textsuperscript{27}. It implies that increasing the temperature is equivalent in its effect on properties to increasing time. This if valid can be very useful in bringing several curves from their position at the experimental temperature to the reference temperature by means of a master curve proposed by Williams-Landel-Ferry and called WLF transform. The principle of time-temperature superposition derives from an equation of the form\textsuperscript{28}:

$$\log A_T = \frac{C_1(T-T_g)}{C_2+T-T_g} \quad \ldots \ldots 2.6$$

where $A_T$ is the shift factor

$C_1$ and $C_2$ are constants

$T_g$ is the glass transition temperature of the polymer

$T$ is the reference temperature
The elastic modulus is perhaps the property that has enjoyed the most popularity in the time-temperature shift factors. Schallamach\textsuperscript{9} applied the shift to investigate the dependence of abrasion of unfilled rubbers, as measured on a silicone carbide paper, of both velocity and temperature to save time and to ease interpretation. He has finally concluded that the transform is only strictly applicable to unfilled amorphous compounds.

Ecker\textsuperscript{14} studied the effect of viscoelastic properties on the entire process of abrasion. He particularly emphasized in that the energy transformation is set off by a mechanical process. Hence dynamic properties like rebound \( R_d \), loss modulus \( E^\prime \), and dynamic modulus \( E^\prime\prime \) were evaluated and related to the abrasion process as measured by a DIN abrader. Owing to the temperature dependence of their values the temperature trend was taken into consideration. Consequently the values of the dynamic properties were taken at room temperature and at \( 100^\circ \text{C} \). By purely empirical means he equated

\[
W = \frac{\mu AR_d (\Delta E^\prime / \Delta E^\prime\prime)}{\sigma_{\beta_2} / \sigma_{\beta_1}} \quad \ldots \ldots 2.7
\]

where \( W \) = volume loss
\( R_d, \Delta E^\prime, \Delta E^\prime\prime \) are the difference between their values at room temperature and at \( 100^\circ \text{C} \).
\( \sigma_{\beta_1} \) is the tensile strength at room temperature and an extension ratio of 10\% per sec.
\( \sigma_{\beta_2} \) is the tensile strength of the rubber at \( 100^\circ \text{C} \) and an extension ratio of 10\% per sec.

Medalla and coworkers\textsuperscript{79} gave another example of a simple relationship between roadwear test and rebound resilience. They showed roadwear indices as decreasing with the increase in rebound as demonstrated in Figure 2.6.
The inverse correlation between these two properties is in conflict with earlier equations (2.2 and 2.3) suggested by Kragelski and Uchlyama.

![Graph showing inverse correlation of treadwear index and rebound](image)

**Figure 2.6** Inverse correlation of treadwear index and rebound showing higher wear resistance corresponding with higher hysteresis\(^7\).\(^9\).

Friction, as another viscoelastic property\(^3\).\(^9\), is expected to exert a major influence on abrasion. Empirical expressions constructed to describe the results of laboratory abrasion tests, within the limitations of the testing procedures and the compound tested, have usually shown the rate of abrasion to be proportional to the coefficient of friction as determined by some standard way\(^2\).\(^5\).
2.2.4 LABORATORY MEASUREMENT OF ABRASION

2.2.4.1 Background

The previous sections have postulated how difficult is the approach of deducing a satisfactory correlation between abrasion resistance and other properties. Thus many investigators have continuously attempted to simulate the wear process itself in the laboratory using a wide range of abrasion machines.

Early experiments to evaluate abrasion resistance empirically started during the late 1920's and early 1930's. Since then various types of machines started to appear or disappear and various types are still in use. No attempt will be made to list them all in the present work as most of them are well documented elsewhere. However, there is one thing they all have in common, that is, they give a substantial amount of abrasion in short times. The accelerated test which is deliberately designed to reduce time and cost, demands the use of sharp abrasives, high loads and sometimes high slip angles.

However, abrasion machines fall into two categories according to the type of abradant they use; these are:

A. Machines that use loose abradants, such as powder shotblasting or water jets. They are generally used on a limited scale to avoid smearing.

B. Machines that use solid abradants:
   These can be subdivided into the following:

a. Machines that use abrasive paper such as the Du Pont and the DIN abrader (see Fig.4 in the Appendix for the DIN abrader).

b. Those which use abrasive wheels i.e. the Akron and the Dunlop abraders. (Fig.5 in the Appendix for the Akron)
c. Metal knives, such as the Pico abrader.

From the technical point of view, the more popular machines with solid abradants are designed to abrade rubber by two distinct mechanisms. Accordingly, they are grouped into two categories.

The machines of the first category apply a constant load and speed upon the usually flat specimen throughout the experiment. The machines of the second category use solid wheels that roll against a suitable abrasive at constant speed and adjustable slip angle. The slip controls the difference between the travelling and circumferential velocity. The relevant difference between a simple sliding apparatus and a slipping wheel arrangement is that each circumferential element of the wheel is stress-free for the best part of a revolution but undergoes a complete stress-strain cycle each time it passes through the contact area.

2.2.4.2 Laboratory abrasion, achievements and difficulties

Despite research difficulties with laboratory abrasion machines there have been many reports about excellent correlation achieved between the results of carefully selected experimental conditions and comprehensive roadwear tests under various conditions. A good example is seen in the work of Geesink and Prats who conducted a comprehensive roadwear test and suggested that laboratory and road wear may be compared directly, providing that the comparison is made at the same abrasion loss of the reference compound. Davison and collaborators trying to apply equal severity criterion, had modified the Lambourn machine into an abrader with a unique automatic control of constant transmitted power. This allowed them to extend laboratory tests down to severity levels comparable to, or less than those experienced on the highway. Their results show (Table 2.2) that if severity is controlled good correlation between roadwear and laboratory can be obtained.
Table 2.2 Comparison between laboratory abrasion indices and road wear of different severities.

<table>
<thead>
<tr>
<th>Tread</th>
<th>Laboratory index</th>
<th>Road index</th>
<th>Severity</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>100</td>
<td>100</td>
<td>lowest</td>
</tr>
<tr>
<td>BR</td>
<td>65</td>
<td>54</td>
<td>middle</td>
</tr>
<tr>
<td>NR</td>
<td>91</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>SBR</td>
<td>100</td>
<td>100</td>
<td>middle</td>
</tr>
<tr>
<td>BR</td>
<td>88</td>
<td>83</td>
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</tr>
<tr>
<td>NR</td>
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</tbody>
</table>

Good correlations have also been reported by Bassi\textsuperscript{13}, Satake et al\textsuperscript{100} and WestlInning\textsuperscript{70}. However there has also been a considerable number of reports on a lack of correlations\textsuperscript{2,9}. The poor correlation is generally believed to be due to one or more of the following factors:

a. The tyre tread rubber usually undergoes a different manufacturing and curing process from the ones applied on abrasion specimens. This will lead to a difference in the degree of filler dispersion, the rate of elastomer breakdown and state of cure\textsuperscript{4}.

b. Duration of the test: Evaluation of abrasion properties in the laboratory normally takes a few minutes whereas a road wear test may take months during which rubber properties may be affected by environmental test conditions.

c. Severity: The high severity of the laboratory test may result in introducing further mechanisms which are dissimilar to those encountered during a normal or a mild road test. The severity of some tests results in a high degree of wear not only to the rubber specimen but also to the abradant. Therefore, care must be taken to avoid any errors due to this effect.
d. Weather conditions: Weather conditions are impossible to control in a road test and are difficult to simulate in a laboratory. The temperature, for instance, is known to be a crucial factor yet it is extremely difficult to control.

e. Smearing of the rubber surface: Smearing or clogging of the laboratory abrasion specimen is one of the most peculiar problems which is as old as the abrasion experiments themselves. The source of smearing has not been clearly identified but it has been speculated that its occurrence is connected with the decomposition of the rubber by heat and excessive friction and/or due to migration of certain components of the rubber formula\(^9\). To counteract this problem investigators have used dusting powders although the dusting process itself may cause further problems\(^2,2^9\).

2.2.4.3 Reproducibility of abrasion measurements

Expression of laboratory abrasion results with reference to a standard rubber tested at the same time on the same abradant is a common practice in the abrasion experiments. This has been adopted for two reasons, firstly because of the change in the abrasive power of the abradant with use and secondly to reproduce the results in various parts of the world.

Such a practice is considered to be vital to avoid variability between identical machines and abradant as well as to obtain good reproducibility. It should be borne in mind, however, that the coefficient of variation of abrasion results as measured by different batches of a standard rubber would not be less than 8%\(^2^6\). This variation seems to be inevitably acceptable probably due to the difficulty in reproducing not only the test conditions but also the rubber properties.
2.2.4.4 Methods of wear measurements

Commonly, there are three methods in the determination of wear rates; these are⁴:

a. Linear rate of wear: This is calculated as follows:

\[ \Delta V = \frac{\text{Thickness of rubber removed}}{\text{Sliding distance}} \]  \hspace{1cm} ......2.13

This method is widespread for measuring the roadwear of tyres but can be used on a laboratory scale³.

b. Volumetric rate of wear: This method is widely used for expressing laboratory measurements. According to this method the volume loss is calculated from

\[ \Delta V = \frac{\text{Volume of rubber removed}}{\text{Sliding distance} \times \text{Apparent area}} \]  \hspace{1cm} ......2.14

c. Energy index of wear: The energetic rate of wear is calculated according to the equation

\[ \Delta V = \frac{\text{Volume of rubber removed}}{\text{Work of friction}} \]  \hspace{1cm} ......2.15

2.2.4.5 Standard tests

The latest revision of BS 903 Part A9 was issued in 1988. The standard specifies four methods of testing as no single method has been found adequately to simulate the various conditions to which rubber products may be subjected in service. All of these express the result obtained with respect to a standard rubber tested under identical conditions. Four standard rubbers are selected based on natural rubber and SBR filled with different types of reinforcing systems. However, some earlier reports favoured the DIN abrader²⁶ as the most convenient test for quality routine use. Moreover, major research centres use this abrader as a standard experimental technique¹⁰². The Akron abrader is distinctive for its ability to vary slip angle in a simple manner.
Burgess and Scott\textsuperscript{46,105} confirmed the ability of the machine results (with low carbon black loaded SBR compounds) to forecast actual treadwear. Over the wide range of treadwear rating from 54 to 120, they forecasted actual data with an error of 5 units or less in 91 of 100 cases.

2.2.6 MECHANISMS OF RUBBER WEAR

Despite the complexity of rubber wear there seems to be a plausible agreement that it occurs by one or more of the following mechanisms:

2.2.6.1 Abrasive wear

This type of abrasion mechanism is known to be the most damaging. It is commonly agreed that its occurrence is related to interaction between sharp projections of the abradant and rubber under high loads\textsuperscript{21,32}. This interlocking is accompanied by adhesion and when rubber slides, frictional forces cause an extensive stress concentration between the sharp asperities and rubber. This results in the removal of rubber particles mainly by cutting as shown in Figure 2.7 below\textsuperscript{16}. It has been suggested that the resistance to this mechanism is favoured by high tensile and tear strength, higher elongation and hardness. This type of mechanism is expected to take place during sharp cornering on normal roads and on stony surfaces in off the road driving. It has been suggested for instance that wear on British roads is generally favoured by this mechanism\textsuperscript{2}. 

28
2.2.6.2 Fatigue wear

When the asperities of the surface are rough rather than sharp failure occurs because of fatigue mechanism following repeated compression, expansion and reversed shearing within the surface layer of the rubber. As a result of the repeated cyclic deformation in the area of contact the fatigue mechanism produces a relatively mild form of wear which can be classified as bulk rather than surface effect. This type of wear becomes more significant when the cyclic stresses are present for long periods when the friction is relatively small and the surface temperature is high. The number of deformation cycles which the rubber will withstand before failing depends on the nature of the abrading surface. Although the process of the removal of material from the rubber surface is less understood, there have been several hypotheses, one of which is fracture mechanics. Moreover, there has also been some evidence to support the various effects of chemical attack on wear. Although commonly accepted that the appearance of smearing or oily wear is considered as an indication of a chemical effect. The lack of a clear cut difference between the various types of mechanisms and because this subject is the least studied and documented, ambiguity is expected as to where to classify the chemical effect. In fact, the rôle of the chemical
effect was known as early as 1951 when Stlehler\textsuperscript{34} suggested that oxidative mechanisms were important in abrasion. He ascribed differences in the relative rates of wear of NR and SBR treads at different ambient temperatures to differences in their oxidation resistance. Boonstra and coworkers\textsuperscript{35} have noticed the formation of surface stickiness and the removal of very small particles due to wear from the rubber surface. They attributed that to formation of highly reactive free polymer radicals which lead to decomposition when the rubber is left for a sufficient time. More recently Gent\textsuperscript{36} reviewed this phenomenon and has suggested that oily wear can suppress or stop tearing with a resultant reduction in the wear rate. He ascribed the mechanism of such a deterioration to rubber decomposition which may occur by the following mechanisms.

A. Mechanical rupture of polymeric network

According to Gent this mechanism is the main source of molecular decomposition during sliding of tough and wear resistant rubbers when the molecular network is activated by input energy. Another confirmation of the prominence of mechanical rupture among other mechanisms in rubber smearing came from investigations by Muhr and Thomas\textsuperscript{37}. They conducted abrasion experiments in the absence of large scale mechanical abrasion and suggested that the stress activated oxidation is the dominant mechanism. Their claim is based on the observation that under normal laboratory experiments, temperature rise would not be enough to enhance thermal decomposition, yet smearing occurs. On the other hand, there have been many other reports suggesting that removal of oxygen from the test piece surroundings will stop smearing even in the presence of mechanical rupture\textsuperscript{4}. On the contrary, butadiene rubber is heavily conjugated, yet it is known to show no evidence of smearing in the presence of both oxygen and mechanical rupture. It could be possible that smearing, in certain cases, might be related to migration to the surface of the less compatible ingredient of the formula under excessive stress and heat\textsuperscript{8}. 

30
B. Oxidative degradation

The effect of oxidative degradation was investigated thoroughly by Brodskii et al.\textsuperscript{38} and by Schallamach\textsuperscript{39}. They examined the abrasion resistance of protected and unprotected rubbers on laboratory machines under air and nitrogen for comparison. They showed that the unprotected vulcanisates gave higher volume losses relative to nitrogen. The protected ones, however, showed a lesser difference in their volume losses under both conditions as can be seen in Figure 2.8.

The positive effect of antioxidants on improving the fatigue abrasion resistance of rubbers has also been confirmed by Pulford\textsuperscript{40}.

![Figure 2.8](image-url)  
**Figure 2.8** Reduction of abrasion loss (Akron angle abrader) with antioxidant (A.O.) NR tread compounds.
It should be pointed out, however, that Ilina et al. have also carried out experimental work to assess the effect of antioxidants by studying the supposedly oxidised product gravimetrically. They concluded that antioxidants have no effect on abrasion.

C. Thermal decomposition

Dannenberg, Ecker and Gehman have suggested that thermal decomposition of rubber has an important role on its abrasion resistance. They noted that during the running of tyres on roads, the temperature of the surface of the rubber can reach up to $240^\circ C$. This range of temperature is surely enough to degrade NR and SBR as the former starts to decompose at $200^\circ C$ and the latter at $240^\circ C$. Grosch carried out wear tests over a wide range of severities and weather conditions and has later concluded that all severity effects disguise temperature effects if temperature is measured at the tread surface. Temperature exerts another indirect effect on abrasion by enhancing cure reversion. Reversion is a term used to describe the loss of network structure by an anaerobic ageing within the rubber. Temperature also enhances surface degradation. It has been suggested that this is the cause of the poor performance of NR tread under low severity wear. It has been acknowledged that one of the possible reasons for the poor correlation between roadwear and common laboratory experiments may lie in the neglect of the temperature effect.

2.2.6.3 Other mechanisms

Reznikovskii and Brodskii had discovered a roll formation type of wear mechanism in the early 1960's. Later Moore and Blythe emphasised its importance. It is described as an intermediate between abrasion pattern formation and thermooxidative degradation. It has been suggested that such a type of mechanism favours relatively high coefficient of frictions, smooth surfaces and perhaps low hardness. Caution must be taken to avoid confusion between this mechanism with the fatigue type as discussed earlier.
Another proposed mechanism has been called three body abrasion\textsuperscript{43}. According to this mechanism rubber does not abrade directly by the track but through a third probably rolling abradant in the interface. This mechanism is believed to take place to some extent when a tyre rolls on a dusty road. The use of powders in the laboratory between rubber specimens and tracks causes abrasion by this mechanism. However, these mechanisms may not be predominantly characteristic of tyre wear where tear strength and hardness is high except perhaps for certain extreme cases.

2.7 TREAD COMPOUND FACTORS AFFECTING ABRASION

Most recently Velth\textsuperscript{50} published a comprehensive theory on the effect of compound characteristics on its wear properties. Based on his own work and that of Lancaster\textsuperscript{12} he was able to characterise two distinct mechanisms each of which favours certain tread properties. The first mechanism was called elastic deformation (E. wear) in which loss of material occurs by means of tensile tear rupture induced by high surface shear. Resistance to this mechanism is favoured by a flexible elastic response (lower glass transition temperature Tg) and a higher degree of reinforcement, high structure and surface area of the reinforcing agent. The second mechanism was called plastic wear (P. wear) in which the loss of material is due to a plastic (deformation) rupture more aptly described as cutting-abrasive action. This mechanism is seen to be favoured by a high Tg and by a low reinforcement concentration. An increase in hardness produces an increase in P. wear provided everything else is equal. Figure 2.9 demonstrates the combined effect of these factors on various tread rubbers tested on a convoy at various temperatures on high and low pavement microtexture (mT\textsubscript{x}). Some of Velth's hypotheses run in line with earlier reports by Kragelski and Nepomnyashchii\textsuperscript{21}. Moore and Day\textsuperscript{108} have also emphasised the favourable effect of the reduced Tg of the polymer on abrasion resistance.
Figure 2.9 "Average" Rate of Wear vs Tg; for low and high reinforcement level, mTxC and temperature.
3.1 INTRODUCTION

It has been shown in the preceding chapter that the theories of rubber wear although they offer diversification in detail also demonstrate a reasonable general consensus in that an increase in tear strength and crack growth resistance is considered to enhance the resistance towards abrasive wear. Improvement of tear properties of rubbers are generally brought about by incorporating active fillers among which the carbon blacks are predominant. Although originally intended for dilution and price reduction, their incorporation in rubber showed increase in toughness and other physical properties although this is often achieved at the cost of increasing their heat build-up properties. Carbon black has since become one of the invaluable ingredients of any tyre compound formula.

This effect of reinforcing fillers on rubber strength properties is extensively discussed by different theories though as yet it is not fully understood in a theoretical sense. Medalla, Dannenberg and others have noted that the effect of carbon black on modulus and hysteresis is reasonably understood, whereas the effect on ultimate properties remains unclear, despite the voluminous literature on this subject. In part this is due to the difficulty of understanding the nature of the filler-rubber interface.

Several plausible theories suggest that an understanding of this interface will enable explanation of the reinforcing effect. Beyond a general agreement concerning reinforcement of rubbers there remains much confusion and controversy surrounding its details. Much of the past work has focussed on certain aspects of reinforcing fillers such as bound rubber and polymer-filler interactions. Nevertheless, it has been difficult to trace definite
connections between these effects and the conventionally measured strength properties of rubber vulcanisates such as tear and abrasion. These introductory remarks are intended to set the scene for some of the observations to be discussed later on reinforcement and abrasion in this and the next chapter.

3.2 REINFORCEMENT; DEFINITION AND METHODS OF EVALUATION

Like abrasion, the phenomenon of reinforcement remains vague and poorly defined. Increased reinforcement has been defined as increased modulus, rupture energy, tear strength, tensile strength and abrasion resistance. A practical definition of reinforcement is the improvement of service life of the rubber article. Abrasion as a main tyre failure phenomenon can well be considered as an important example for measuring reinforcement. However, Juve and Velth have reported that accomplishment of such a suggestion requires a standard pneumatic tyre, a standard design and a standard test, all of which are difficult to achieve. Dannenberg has concluded that the actual wear is difficult to simulate on a laboratory scale but at the same time suggested that laboratory tests give useful correlations to roadwear performance and provide means for guiding the general direction of compounding research and development. In the laboratory, reinforcement can be best judged by measuring and cross-examining a combination of properties. Some of the main methods usually applied in the laboratory are as follows:

A. Determination of mechanical properties:

Over the years rubber reinforcement has been assessed by indirect measurement of failure properties such as tensile and tear strength, cut growth and abrasion resistance, especially for quality control purposes.

B. Evaluation of rubber-filler interactions using one or more of the following three techniques.
b. Measuring die swell of unvulcanised rubber.
c. Measuring relative structure forming ability of filler-powder forms by determining the increase in torque per specific amount of filler before and after the addition of a suitable liquid (e.g. dibutyl phthlate) in an absorptometer.

c. By measuring dynamic properties: the effect of reinforcing fillers can be determined by measuring the mechanical behaviour of filled vulcanisates at low and moderate strain amplitudes.  

D. By measuring the resistance of reinforced rubbers to swelling by appropriate organic solvents with reference to their unfilled state.

3.3 SILICA IN RUBBER; PROSPECT AND DIFFICULTIES

By its unique properties, carbon black has dominated rubber reinforcement since it was made commercially available in the 1920's although attempts have also been made to use alternative reinforcing agents. Precipitated silica entered the field of fine particle reinforcing agents roughly 40 years ago. Tyre applications most often associated with silica are based on improving tear resistance. Tear strength has been frequently suggested as a critical factor especially for severe service conditions such as those encountered in mining and off-road conditions. This is because the highest possible resistance to cutting and chunking of tread is required. There have also been claims based on experimental studies and field surveys suggesting that replacement of carbon black with silica results in a lower rolling resistance without sacrificing abrasion resistance, lower heat build-up and improvement of ice friction. Details of the grades of commercially available silicas can be found elsewhere. They generally comprise approximately 16% of total carbon black production. In recent years the use of silica has
been motivated by the continuous increase in the carbon black’s price, specifically after the oil crisis and when coupling agents have been made available.

An example of a commercially available precipitated silica is Ultrasil VN3 of a surface area of 175cm²/g (produced by Degussa). It is significant to stress that the use of silica has never been easy as it is known to create peculiar processing properties such as hardening of unvulcanised rubber, increased viscosity and stickiness to the equipment. Most of these difficulties are not known to rubber compounders accustomed to using the carbon blacks. Moreover, silica retards vulcanisation while carbon black promotes it. Therefore, a silica mix requires a much higher level of curatives (sulphur and accelerators) to give the same modulus as a carbon black equivalent. Consequently, silicas are not considered as an attractive alternative for carbon blacks in terms of cost versus properties; at least at present. Most of the silica problems are attributed chemically to its surface properties. Although the gross morphology of reinforcing silica is similar to that of carbon black the fusion between the particles seems to be more extensive with some aggregates resembling coiled rods.

Studies of precipitated (hydrated) silicas also show that their problems in rubber compounding are related to their structure. They are produced by precipitation from water soluble silicates and have approximately 5% of each adsorbed and bound water. The latter are volatiles removed respectively at 105°C and 1000°C.

Amorphous silicas consist of silicon and oxygen tetrahydraulically bound into an imperfect three-dimensional structure. Their surface contains uncondensed silanols whose number and distribution depend on the synthetic method and are important to the interaction with rubber and the ultimate properties of its vulcanisates. Several studies have shown that the ideal level of silanol groups is 4.6 OH/nm² of silica. However, commercial
precipitated silicas contain more than twice this ideal level. The accessive groups present the aforementioned problems of silica compounding due to their polarity and hydrophobic tendency (see the scheme below).

![Silica Structure Diagram](image_url)

To minimise the effect of silanol groups, formulations containing silica usually include polar components such as glycerine or glycols to block some of them off. On the other hand, the use of coupling agents has become increasingly popular in recent years and is known to be effective not only in decreasing agglomeration but also in achieving better overall properties.

3.4 COUPLING AGENTS

Coupling agents are used successfully with non-black filler to couple a filler to rubber chains. Some of the principal coupling agents used are based on organic siloxanes which possess functionally active end groups, their general formula being \((RO)_3Si\_R^\prime\_Si(OR)_3\) or \(R^\prime\_Si(OR)_3\). The \(R^\prime\) denotes a common reactive site such as amino, mercaptol or vinyl group usually bonded via a short alkyl chain to the silicone atom. The \(OR\) generally represents the hydrolyzable alkoxy group attached to silicon. Some examples of these coupling agents are featured in Table 3.1. Studies of silica compounding have shown that the efficient method of using coupling agents is by premixing them...
with the filler before addition to the elastomer but the high price and the short shelf life of such products, due to this pretreatment, as well as the inhibition of the freedom to vary the coupling agent level are known deterrents. Alternatively, they can be added during the mixing of the rubber along with the silica. The use of coupling agents has been claimed to result in rubber compounds with improved filler dispersion and acceptable viscosity. Other reported advantages involve reduction of hardness and heat build-up, improvements of compression set, modulus and tear strength \(^{48,53,47,51,56}\).

### Table 3.1 Some of the commonly used coupling agents

1. \( \text{CH}_3 \text{Si} (\text{OCH}_2 \text{CH}_3)_3 \)  
   - Methyltriethoxysilane

2. \( \text{CH}_3(\text{CH}_2)_4 \text{Si}(\text{OCH}_2\text{CH}_3)_3 \)  
   - Amyltriethoxysilane

3. \( \text{CH}_2 = \text{CH} \text{Si} (\text{OCH}_2\text{CH}_3)_3 \)  
   - Vinyltriethoxysilane

4. \( \text{HSCH}_2 \text{CH}_2\text{CH}_2\text{Si} (\text{OCH}_3)_3 \)  
   - Gamma-Mercaptopropyltrimethoxysilane

5. \( \text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2 \text{Si} (\text{OC}_2\text{H}_5)_3 \)  
   - Gamma-Aminopropyltriethoxysilane

6. \( (\text{C}_2\text{H}_5)_3 \text{Si} (\text{CH}_2)_3 \text{S}_2 \)  
   - triethoxysilylpropyltetrasulphide
3.5 OBJECTIVES OF THIS RESEARCH

1. The aim was to select a reinforcing system for an on-off the road truck tyre tread compound that gives improved resistance to abrasion and cutting under severe environments.

2. Other essential properties of tyres like heat build-up and skid properties should be either improved or not adversely affected.

3.6 EXPERIMENTAL

3.6.1 Control recipe

A truck tyre tread formulation based on NR-ISAF which was well established in service was chosen as the control for its good overall properties especially with consideration of heat build-up (a key point) besides resistance to abrasion. The full recipe of the compound is seen in Table 3.2.

3.6.2 Compounding ingredients selected for experimental work

A. Reinforcing system

A precipitated silica type Ultrasil VN3 was selected to replace a typical carbon black type ISAF (ASTM N220), either partially or totally. Both of these two reinforcing fillers have a particle size of approximately 20 nm. The total level of the fillers was kept at a moderate 48 phr.

B. Coupling agent

A coupling agent type Bis-triethoxysilyl propyl tetrasulphide was selected. This coupling agent, which hereafter will be denoted as TESPT, is made by Degussa under the commercial
name of Si69. It has a reputation of showing little or no interference with the compound scorch safety\textsuperscript{49,54,57}. Its chemical structure is shown below.

\[
\begin{align*}
(C_2H_5O)_3 & \quad \text{Si}(CH_2)_3 S_2 \\
\quad & \quad \text{Si}(CH_2)_3 S_2 \\
(C_2H_5O)_3 &
\end{align*}
\]

C. Elastomer

It was decided to use NR grade SMR20 in the preparation of the experimental rubbers. This elastomer has a unique balance of properties such as superior building tack and green strength, high tear and tensile strength and is also known to confer low heat build-up to its vulcanisates. Moreover, this elastomer has also been reported to respond better to a Silica-Silane system\textsuperscript{51}.

D. Curing system

A sulphur-MBS system was selected to provide a typical higher scorch safety and to minimise reversion at an extended cure time. For the control sulphur and MBS were combined in a molar ratio of 1:1 to give a stable equilibrium cure. However, the levels of these two ingredients had inevitably to be increased to suit the silica requirements and to attain a satisfactory state of cure as will be seen later in the formulations used.
E. Miscellaneous Ingredients

The emphasis has been directed towards choosing a compound of practical interest and hence other essential ingredients were selected from commercial sources. These included zinc oxide, stearic acid, a highly aromatic oil, antioxidants (IPPD, Flectol H and a paraffinic wax).

3.6.3 Compound preparations

Rubber mixing is a very well established process and the industry would accept more elaborate methods only for special needs or if they were cost effective. Therefore, it was anticipated that silica based mixes would have a chance of acceptance, only if the present conventional and efficient techniques used for carbon black mixing are adhered to. For this reason pre-studies to experience silica mixing difficulties were considered as a valuable preliminary to this research. With this in mind, five mixes were prepared whose formulations are shown in Table 3.2, with mix 1 as the control. All the mixes were prepared in a Banbury mixer, type BR size 1.5 litre, in two stages. After each mixing cycle, each mix was homogenised for three minutes on a laboratory type two roll mill size (18 x 9") and sheeted off to a 3mm thickness. A fixed mixing time was the criterion followed to allow comparison of the rheological properties. The mixing cycle, sequence and other conditions encountered are shown in Table 3.3.
Table 3.2  Formulation of truck tread compounds
(numbers in the body of the table refer to the parts by weight)

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Trade name</th>
<th>Supplier</th>
<th>Mix no.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1 2 3 4 5</td>
</tr>
<tr>
<td>ISAF (N220)</td>
<td>Vulcan 6</td>
<td>Cabot</td>
<td>48 48 24 - -</td>
</tr>
<tr>
<td>Silica</td>
<td>Ultrasil I.D.</td>
<td>Chemicals</td>
<td>- - 24 48 48</td>
</tr>
<tr>
<td>TESPT</td>
<td>Si69</td>
<td>Degussa</td>
<td>2.5 1.75 3.5 -</td>
</tr>
<tr>
<td>Sulphur</td>
<td>-</td>
<td>-</td>
<td>1.5 1.5 1.5 2.0 2.0</td>
</tr>
<tr>
<td>MBS</td>
<td>Vulcafor</td>
<td>Vulnax</td>
<td>1.5 1.5 1.75 2.5 2.5</td>
</tr>
</tbody>
</table>

Base Ingredients: SMR20, ZnO, Stearic acid 2, IPPD 1.5
Flectoil H 1, Paraffinic wax 2, Aromatic oil 7

Table 3.3  Master-batch and final batch preparation

A  Master batch preparation

<table>
<thead>
<tr>
<th>time (min)</th>
<th>Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Added SMR20, ram down (r.d.)</td>
</tr>
<tr>
<td>1</td>
<td>Silica and TESPT (if any)</td>
</tr>
<tr>
<td>2</td>
<td>ISAF (if any) and oil</td>
</tr>
<tr>
<td>4</td>
<td>Chemicals</td>
</tr>
<tr>
<td>5</td>
<td>Sweeping</td>
</tr>
<tr>
<td>6</td>
<td>Dump</td>
</tr>
</tbody>
</table>

Conditions, ram pressure 40 psi, rotor speed 60 r.p.m., cooling water temperature 20°C, fill factor 0.8, dump temperatures 105 - 130°C. All mixes were stored for 24 hours before final mixing.

B  Final mixing

<table>
<thead>
<tr>
<th>time (min)</th>
<th>Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Rubber master-batch (ram down)</td>
</tr>
<tr>
<td>0.5</td>
<td>Sulphur + MBS</td>
</tr>
<tr>
<td>2.0</td>
<td>Dump</td>
</tr>
</tbody>
</table>

All other mixing conditions were the same except for rotor speed which was changed to 40 r.p.m. Dump temperatures ranged from 90 - 100°C.
3.6.4 Testing

All of the tread mixes in Table 3.2 underwent the same preparation and testing conditions so that practical correlation could be obtained. The test procedures used conformed to the following standards: Mooney viscosity ASTM D. 1646.81, curing characteristics (Curemeter Monsanto ODR) ASTM D. 2084.81. Cured rubber specimens were prepared according to BS 1674: 1976 at 160°C±3. Evaluation of mechanical properties was done as follows:

- Tensile strength BS903 A2:1971
- Tear strength BS 903 A3:1982
- Hardness BS903 A26:1969
- Abrasion resistance DIN. 51536 (now BS903 A9:1988).

3.7 RESULTS AND DISCUSSION

3.7.1 Processing properties

Data and observations concerning processing properties can be seen in Table 3.4. The control mix (1) was known from past experience to show satisfactory processing properties such as good mill banding of the rubber and release and acceptable viscosity values. When TESPT was included in mix (2) along with the ISAF the mill banding and release properties were further enhanced but a two unit increase in the Mooney viscosity observed. The use of the substantial quantity of Silica with ISAF black in mix (3) resulted in a deterioration of mill banding and release properties together with a 4 units' increase in Mooney viscosity. However, such a viscosity remained within the commonly acceptable range found satisfactory in the rubber processing field.

On the other hand, mix no. 4 showed, besides a visually poor dispersion of the silica filler, a tendency to stiffen and it was noticeably less smooth for banding and cohered to the mill rolls. The worst mixing and milling properties were obtained with mix no. 5 as this mix was obviously less homogeneous and contained some undispersed filler. Moreover, the stiffness of mix no. 5 was very high and the milling behaviour was generally poor. The Mooney viscosity was 30 units above that of ISAF control.
<table>
<thead>
<tr>
<th>Properties</th>
<th>Mix No. 1</th>
<th>Mix No. 2</th>
<th>Mix No. 3</th>
<th>Mix No. 4</th>
<th>Mix No. 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISAF 48</td>
<td>ISAF 48</td>
<td>ISAF 24</td>
<td>Silica 48</td>
<td>Silica 48</td>
<td>TESPT 2.5</td>
</tr>
<tr>
<td>TESPT 2.5</td>
<td>Silica 24</td>
<td>TESPT 3.5</td>
<td>TESPT 1.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total mixing time(^+) (mins)</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Dump temperature(^+) °C</td>
<td>110</td>
<td>105</td>
<td>118</td>
<td>120</td>
<td>128</td>
</tr>
<tr>
<td>Filler dispersion(^*) (first stage)</td>
<td>Good</td>
<td>V. good</td>
<td>Fair</td>
<td>Poor</td>
<td>V. poor</td>
</tr>
<tr>
<td>Mill banding</td>
<td>Good</td>
<td>V. good</td>
<td>Fair</td>
<td>Fair</td>
<td>Stiff, difficult to cut and homogenise</td>
</tr>
<tr>
<td>Mill release</td>
<td>V. good</td>
<td>Excellent</td>
<td>Fair</td>
<td>Fair</td>
<td>Adheres badly to the rolls</td>
</tr>
<tr>
<td>ML (1 + 4) 100°C</td>
<td>58</td>
<td>60</td>
<td>62</td>
<td>65</td>
<td>88</td>
</tr>
</tbody>
</table>

\(^+\) First stage
\(^*\) Visual assessment
Vulcanisate properties as determined by oscillating disc rheometer ODR

The ODR properties of any rubber vulcanisate are mainly dependent upon two parameters, filler loading and crosslink density. In the present investigation the former was kept constant so that the interpretation of the filler-rubber interaction would become less difficult. Inclusion of TESPT at a level of 2.5 phr in mix no. 2 showed no pronounced effect on scorch properties as illustrated in Figure 3.1. This confirmed what had already been reported concerning the advantage of using this particular coupling agent. Mix no. 3, however, showed a longer scorch time and $t_{95}$ coupled with a distinctive reduction in maximum torque ($T_{\text{max}}$) compared to the NR/ISAF control (see also Table 3.3). This indicated a slower rate of vulcanisation and a lower state of cure both of which are undesirable. On the other hand, the presence of TESPT in mix no. 4, shows it to possess a distinct advantage over its non S169 counterpart (mix no. 5) in its ODR properties. However, this improvement could not match the ODR properties of either NR/ISAF mixes (no. 1 and 2).

Perhaps a better understanding of the sole effect of TESPT on the ODR properties can be obtained by comparing the properties of the tread vulcanisates in pairs according to the similarity in their formulations. Mixes no. 1 and 2 are identical in composition except for the addition of TESPT to mix no. 2. A close examination of Figure 3.1 and Table 3.5 shows that TESPT results in a distinct increase in $T_{\text{max}}$. Again, mixes no. 3 and 4, are of identical formulations except for the presence of TESPT; if their ODR properties are compared, the positive role of TESPT becomes even more obvious than in the first case by increasing $T_{\text{max}}$ with an additional advantage of a decreasing $T_{\text{min}}$. This increase in the ODR torque suggests that a better rubber-filler interaction takes place when TESPT is present. Such an interaction may be attributed to the formation of stable bridging bonds which increase the coherence of the rubber-filler matrix and require a relatively higher shear force for deformation. A plausible mechanism for
Fig. 3.1 : Vulcanisation Characteristics of the rubber mixes in Table 3.2. ODR monograms showing the effect of Silica-TESPT and/or ISAF on the NR tread mixes. (curing temperature 160°C)
such coupling bonds has been reported to occur in two steps. The first is suggested to occur when the TESPT comes in contact with silica under mixing conditions (e.g. master batch mixing) and involves a condensation reaction between the OH active silica and the TESPT through the latter's functionality (i.e. Alkoxy groups). The second step is believed to occur during vulcanisation (possibly promoted by accelerators) through the cleavage of the sulphidic end of TESPT and its reaction with the polymer unsaturated groups\textsuperscript{48}. Figure 3.3 illustrates a silica-TESPT-polymer interaction mechanism.

According to this reaction scheme, a single molecule of TESPT can couple with one olefinic unit of the elastomer molecule and also with one\textsuperscript{65} or two\textsuperscript{46} silanol groups. Whilst the achievement of reaction between rubber-TESPT-silica has been considered a success\textsuperscript{65,67}, the influence of TESPT on carbon black filled rubber is less effective and less studied. It is reported in the literature that carbon black contains active groups such as phenols, carbonyl and carboxyl groups\textsuperscript{52,53} (see Figure 3.2). If these groups would react chemically with the functionally active TESPT and form bonds in a similar way as had been proposed for silica, then one would expect a similar contribution to reinforcement to occur. Such a proposal is difficult to implement but if practical could give a distinct increase in the tensile strength and modulus which would be useful.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{functional_groups.png}
\caption{The functional groups on the surface of active carbon blacks from Hepburn\textsuperscript{52}.}
\end{figure}
A Step 1: Silica-TESPT interaction during the first stage of mixing (monofunctional and difunctional reactions)

\[
\begin{align*}
\text{Si-OH} & \quad \text{Si-OH} \\
\text{Si-OH} & \quad \text{Si-OH} \\
\text{Si-OH} \quad (C_2H_5O)_3-Si(CH_2)_3-S & \quad \text{Si-OH} \quad OC_2H_5 \\
\text{Si-OH} & \quad \text{Si-OH} \\
\text{Si-OH} & \quad \text{Si-OH} \\
\text{Si-OH} & \quad \text{Si-OH} \\
\text{Silica} & \quad \text{TESPT} \\
\text{Silica-TESPT} & \quad \text{Silica-TESPT reaction product complex A}
\end{align*}
\]

B Step 2: During vulcanisation interaction occurs between the complex A and rubber

\[
\begin{align*}
\text{Si-OH} \quad OC_2H_5 & \quad \text{Si-OH} \quad OC_2H_5 \\
\text{Si-OH} \quad OC_2H_5 & \quad \text{Si-OH} \quad OC_2H_5 \\
\text{Si-OH} & \quad \text{Si-OH} \\
\text{Si-OH} \quad (CH_2)_3-S & \quad \text{Si-OH} \quad OC_2H_5 \\
\text{Si-OH} & \quad \text{Si-OH} \\
\text{Si-OH} & \quad \text{Si-OH} \\
\text{Complex A} & \quad \text{polymer} \\
\text{Rubber-filler network}
\end{align*}
\]

Figure 3.3 Silica-rubber interaction through the presence of the TESPT
3.7.3 Curing properties

Table 3.3 also summarises the physical properties of the five vulcanisates. The control mix (no. 1) shows, as expected, good tensile and tear strength, good hardness and elongation at break with a conventional moderate modulus value. Inclusion of TESPT with the ISAF as in mix no. 2 causes these properties to improve especially the tear strength and this is accompanied by a small increase of 2 degrees in the hardness. On the other hand, a comparison of all the silica mixes (nos. 4 and 5) show a lower modulus and tensile strength to result when TESPT is added. Most interesting, however, is the decrease in the crescent tear strength of the silica mix (no. 4) with the addition of TESPT. Also, both of the silica mixes (nos. 4 and 5) showed a high tendency towards rupture through a knotty tear mechanism. Silica is well known to confer relatively high tear strength to rubber vulcanisates though this is of little usefulness for truck tyre tread compounding application unless other curing properties and, in particular, abrasion resistance are also improved. Figure 3.4 shows that the DIN abrasion indices* of the silica reinforced rubber are much lower than that of the carbon black control. This reduction in abrasion index was in the reverse direction to the higher tear strength of these vulcanisates and exemplifies one of the problems of using tear strength as a sole criterion for predicting rubber abrasion. Studebaker has noted, however, that poor dispersion sometimes results in unusually high resistance to cut growth and attributed that to the interference when large filler agglomerates meet the growth of the tear pathway. On the other hand Hess has suggested that relatively dry agglomerates of filler can weaken a rubber product in two ways. Firstly, they form structural flaws and also, in effect, remove the pigment from the surrounding area, starving them from reinforcing filler and increasing the filler-filler structure at the cost of the essential polymer-filler interaction.

Hess has also shown a strong relationship between the extent of dispersion and roadwear (see Figure 3.5).

* Abrasion Index = \( \frac{\text{volume loss of standard rubber}}{\text{volume loss of test rubber}} \) x 100
Table 3.5  Curing characteristics of the vulcanisates

<table>
<thead>
<tr>
<th>Mix no.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISAF</td>
<td>48</td>
<td>48</td>
<td>24</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SiO₂</td>
<td>-</td>
<td>-</td>
<td>24</td>
<td>48</td>
<td>48</td>
</tr>
<tr>
<td>TESPT</td>
<td>-</td>
<td>2.5</td>
<td>1.75</td>
<td>3.5</td>
<td>-</td>
</tr>
</tbody>
</table>

ODR properties 160°C:

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Torque dN.m</td>
<td>65</td>
<td>68</td>
<td>54</td>
<td>63</td>
<td>54</td>
</tr>
<tr>
<td>Minimum Torque dN.m</td>
<td>13.5</td>
<td>14</td>
<td>18</td>
<td>16</td>
<td>22</td>
</tr>
<tr>
<td>Scorch time t₂(min)</td>
<td>3</td>
<td>3.1</td>
<td>3.8</td>
<td>3.7</td>
<td>3.2</td>
</tr>
<tr>
<td>t₉₅(min)</td>
<td>6.3</td>
<td>6.5</td>
<td>7.7</td>
<td>7.3</td>
<td>8.9</td>
</tr>
</tbody>
</table>

Curing characteristics:
167±3°C

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>300% Modulus MPa</td>
<td>9.3</td>
<td>10.5</td>
<td>7.8</td>
<td>8.2</td>
<td>6.2</td>
</tr>
<tr>
<td>Tensile strength MPa</td>
<td>25</td>
<td>25.4</td>
<td>23</td>
<td>20.7</td>
<td>18</td>
</tr>
<tr>
<td>Ultimate elongation %</td>
<td>615</td>
<td>607</td>
<td>724</td>
<td>778</td>
<td>739</td>
</tr>
<tr>
<td>Crescent tear strength</td>
<td>121</td>
<td>127</td>
<td>116</td>
<td>137</td>
<td>145</td>
</tr>
<tr>
<td>Hardness IRHD</td>
<td>60</td>
<td>62</td>
<td>54</td>
<td>68</td>
<td>72</td>
</tr>
</tbody>
</table>
Fig. 3.4: DIN Abrasion Indices of the tread vulcanisates of Table 3.2.

Fig. 3.5: Relative roadwear vs. carbon dispersion, ISAF. (99)
As a result of these observations, it was decided to investigate the effect of silica on dispersion as a possible factor for the poor performance of these vulcanisates.

3.8 POSSIBLE CAUSES FOR THE POOR PERFORMANCE OF SILICA MIXES

3.8.1 Dispersion efficiency

By definition ideal dispersion implies total separation of a material into its smallest units. The importance of good dispersion of fillers and vulcanising ingredients in a rubber phase has long been recognised and its relationship with strength properties proven. The mixing of fillers into rubber encompasses about four stages (1) Incorporation (2) dispersion (3) distribution (4) plasticisation. During incorporation encapsulation and wetting take place and the polymer breaks into small pieces and seals in the carbon black\textsuperscript{141}. In the dispersion phase agglomerations of filler are broken down and separated into primary particles. Homogenisation of the mix takes place during the distributional phase. During plasticization rheological properties are modified to suit subsequent processing requirements. For the purpose of the comparison between silica and ISAF in the present series of vulcanisates, measurement of filler dispersion efficiency in the vulcanised state was thought convenient. Most of the methods for analysing filler dispersion are directed at measuring the number and the size of the agglomerates that range in size from a few $\mu$m to over 100 $\mu$m in size and have the most damage on rubber strength properties. Several procedures are available to assess carbon black dispersion. ASTM D2663.82 describes two methods (qualitative and quantitative) based on using a low magnification light microscope.

Some of the other methods used are based on measuring the effect on the electrical resistivity and surface roughness with the latter being expected to be proportional to the level of agglomeration\textsuperscript{69}. Among other surface roughness analysing techniques Scanning
Electron Microscopy SEM has become increasingly popular in recent years for permitting details of the surface to be scanned and pictured with high resolution. Although the theory behind the technique is beyond the scope of the present work and can be found in detail in the literature, the principle of the SEM is to illuminate the object, collect the radiation, form an image and scan through it so as to pick up separately the response from each part with high resolution. Therefore the SEM technique was utilised to examine the silica dispersion difficulties. This was made on a comparative basis by analysing freeze-fractured as well as torn surfaces of specimens obtained from the NR/ISAF control (mix no. 1 of Table 3.2), NR/VN3/ISAF (mix no. 4) and NR/VN3 (mix no. 5). These surfaces were gold coated to prevent static charge build-up and compared by scanning under high, intermediate and low magnifications.

Figure 3.6 shows comparative SEM scans of the fractured surfaces of the three vulcanisates under (10K) magnification. This high magnification would be expected to show a tiny area of the surface, hence only particles and particle distribution and smaller aggregates are observed. The scan of the NR/ISAF control (photo A in the Figure) shows well distributed small particles with only a few coarser aggregates, suggesting that the dispersion process is completed and the mix is homogeneous on this scale. In contrast, the NR/silica mix shows (photo B) a large number of coarser aggregates and hence implies poor filler distribution. Inclusion of TESPT with silica, in mix no. 3, had apparently improved filler dispersion but is seen not to match that of the control as coarser aggregates are still visible (see photo C).

Under low and moderate magnification (x60 - 1800) (see Figure 3.7) the torn surfaces of mixes nos. 1 and 5 reveal agglomerates rather than particles or smaller aggregates. These agglomerates, as has already been noted, have a big influence on physical properties (everything else being equal) and, if not broken down can have the most damaging effects on properties. Comparison between the torn surface of mix no. 5 (photo A in the Figure) with mix no. 1
Figure 3.6: SEM micrographs of freeze fractured vulcanised specimens obtained from mixes 1, 4, 5 of Table 3.2 (magnification x10k)

(A) SEM scan of the freeze fractured surface of a vulcanised specimen from mix 1 (NR/ISAF) of Table 3.2

(B) SEM scan of NR/silica. Notice the large unwetted aggregates which are nearly 10 times the size of the above ISAF particles.

(C) SEM scan of NR/silica/ISAF where the presence of TESPT helps dispersion by breaking the larger aggregates into smaller ones.
Figure 3.7: SEM micrographs of torn vulcanisates obtained from mixes 1 and 5 of Table 3.2. (Notice the relatively larger and less wetted aggregates of the silica mix on both magnifications).
(photo B) reveals that the number of agglomerates is much higher and their size is larger in the case of the silica mix. It is considered that the silica filler is less wetted by the rubber and more poorly distributed compared with the ISAF black control. Also the torn surface of the silica mix is rough in appearance and some of the area of the micrograph shows it to be less pigmented both of which are signs of poor filler dispersion. Examination of the two torn surfaces under low magnification (photos C and D) clearly shows there to be significantly poor dispersion in the silica case where the sizes of some of the agglomerates are in the range 30 \( \mu m \). In contrast, the torn surface of the ISAF mix is seen as smooth with fewer and smaller agglomerates visible.

Since mixing time and mix temperature are almost identical for both these two mixes, the interaction forces between the silica particles, due to their polarity, is proposed as the reason for this filler agglomeration tendency. This makes it more difficult for the shear forces of mixing to break up the silica's agglomerated structure. In the case of carbon blacks, the agglomerates are considered to be weaker and therefore less difficult to break-up into their primary structure. Also, carbon blacks have a lower tendency for re-agglomeration after mixing when compared on volume to volume basis with the precipitated silica.

3.8.2 Silica-Zinc Interaction

The other consequence of using silica lies in the tendency of its silanol groups to adsorp the curatives and to absorb and reset with the vulcanisation activators (ZnO and stearic acid). A proposed mechanism for the adsorption of the activators has been suggested to occur as shown in Figure 3.856,66.

The interference reaction of zinc stearate with silica can result in undesirable consequences in two ways; first, because it reduces the amount of zinc salt available for the activation process and second, because it competes with the TESPT for the available hydroxyl groups of the silica. Hence, although mix no. 4 had higher levels of curatives compared with, for instance, mix no. 2 to start with, it may end with its vulcanisate possessing a final lower sulphidic crosslink density due to these zinc salt interference reactions.
3.9 EFFECT OF TESPT ON EQUILIBRIUM SWELLING OF THE RUBBER VULCANISATES

Rubber swelling is a function of the interpretation of various factors such as crosslink type and density, amount and type of filler and the type of elastomer. Swelling has long been used as a criterion to give a true measure of adhesion between filler particles and rubber. This technique was therefore chosen to account for the effect of the TESPT coupling bonds on silica-rubber reinforcement.

It was noticed, however, that the effectiveness of such bonds could not be studied scientifically if the tread mixes of Table 3.2 were chosen as they contain various levels of curatives and different filler systems. The solution for this problem was sought in preparing silica mixes in which the only variable was the TESPT level. Therefore three batches were prepared based on NR each of which contained 48 phr of silica. The TESPT levels ranged from 0, 7.5, 12.5% of the silica weight. All the three mixes were equally
cured with respect to time and temperature and later appropriate samples of their vulcanisates immersed in toluene at 40°C for 24 hours. Then the weight of toluene up-take per gm of the rubber hydrocarbon (Q) was measured according to an equation derived by Parks and Brown as shown below.

\[
Q = \frac{\text{Swollen wt.} - \text{De-swollen wt.}}{\text{Dry wt.} \times \frac{100}{\text{formula wt.}}}
\]

The results obtained were plotted versus the level of TESPT as shown in Figure 3.9. A large reduction (50%) in the toluene up-take was obtained when TESPT was used at the proportion of 7.5% of silica compared with the unbonded mix. A further 16% reduction was obtained when the level of TESPT was then doubled. The reduction of swelling is a clear indication that the TESPT bonds, presumed formed between rubber and silica, become a part of the curing and reinforcing system.

![Figure 3.9: The effect of TESPT/Silica interactions on restricting swelling by toluene.](image-url)
3.10 CONCLUSIONS

As evident from the foregoing sections the incorporation of silica results in reduction of the state of cure, increased viscosity, lower modulus, tensile strength and hardness. The DIN abrasion is much lower compared to the ISAF control. Nevertheless, crescent tear is seen as excellent. However, this increase in tear strength is not reflected by an increase in the abrasion resistance. This latter observation is in conflict with the generally accepted opinion that the increased tear strength will give increased abrasion resistance. The following reasons are seen as responsible for the poor performance of the silica mixes.

A. The poorer dispersion of the silica and its higher tendency for re-agglomeration during mixing.

B. Interference of the coupling reaction between the TESPT and silica by the zinc stearate.

C. Adsorption of a certain proportion of the curative by the excessive silanol groups present on the surface of the silica.

Optimisation of the silica properties probably requires the decrease or removal of adsorbed water and the promotion of the silica-TESPT reaction.

Moreover, existing procedures of mixing and testing which are mainly designed for carbon black compounding may fall short of satisfying silica needs. It was therefore concluded that the mixing cycle and sequence, evaluation of tear and abrasion properties may require further investigations.
CHAPTER 4

EFFECT OF OPTIMISING SILICA-RUBBER INTERACTIONS ON ABRASION RESISTANCE AND RELATED PROPERTIES

4.1 INTRODUCTION

At the end of the preceding chapter it was concluded that the poor performance of the silica mixes was attributed to poor filler dispersion, adsorption of curatives and lack of effective filler-rubber interactions with the mixing conditions used. However, the relatively high tear strength at low modulus conferred by the silica to the rubber vulcanisate was seen as an attractive property for the truck tread rubber if other essential properties could be enhanced. Among the three silica mixes of Table 3.2, mix no. 3 was thought to be the most promising. This conclusion was based on the observation that its processing properties, such as the mill banding and release and Mooney viscosity, were closer to those of the carbon black control. Also, it showed relatively better tensile strength at low hardness than the rest of the silica mixes. Moreover, the reduced curative and TESPT levels with which these properties were obtained could justify the choice of this particular mix as a candidate for further silica compounding developments.

4.2 OBJECTIVES

a. To maximise the silica-rubber interactions at the lowest possible level of TESPT (for practical cost considerations).

b. To improve the filler dispersion and other processing properties and measure the resultant effect on the vulcanisate properties with emphasis on abrasion resistance.

c. To widen the range of the property evaluation by developing in part methods to suit the specific requirements of silica and to offer a better representation of service conditions.
4.3 FACTORS AFFECTING SILICA-TESPT INTERACTIONS

If it is assumed that every hydroxyl group of the bound water (which consists of 5% of the total weight of the precipitated silica) would couple to one of the six alkoxy groups available on the TESPT molecule then one would expect the ideal amount of the latter (to cover all these hydroxyl groups) to be less than 1% of the total silica by weight. However, the quantitative swelling measurement of the rubber vulcanisates (section 3.9) showed that a quantity of more than 12 times the theoretical level mentioned above was actually needed before a further increase in TESPT had no appreciable effect on swelling resistance. Several reasons are believed to contribute to the lower efficiency of the coupling effect, such as the inevitable presence of other ingredients in the rubber formulation that could adsorb, react or prevent the interaction between the alkoxy groups of the coupling agent with the silanol groups. Moreover, other factors like stearic hindrance, coupling agent dimerisation and shielding of some hydroxyl groups inside the aggregates could also be contributing factors. Wolff in a recent review of the silica applications in tyre compounding suggested that under optimised mixing only 70% of the TESPT could be involved in the formation of filler-rubber coupling bonds. It was anticipated by the present researcher as essential to investigate whether the mixing sequence and condition normally applied for carbon black mixes were suitable for the efficient mixing of silica in rubber.

A conventional method of studying the optimum time-temperature combination on silica-TESPT interactions would be possible by preparing a series of mixes at different mixing times and temperatures with everything else being equal and the effect of these variables on the vulcanisate properties measured. However, this approach was not attempted as it was thought that other factors would affect these properties, such as the extent of the filler dispersion, polymer breakdown etc. Therefore, a different method was tried to study the conditions that optimised the silica-TESPT interactions, as will be seen next.
4.3.1 Experimental

A DuPont model 990 differential scanning calorimeter DSC was used for the present investigation. Firstly, a VN3 specimen was scanned at a rate of heating of 10°C/min over the range 25-200°C to account for the effect of moisture. TESPT was also scanned under the above conditions. In both cases an empty aluminium pan similar to the one that contained the specimen was used as a reference. Secondly, a mixture of 2:8 TESPT: VN3 was scanned as before but a reference pan containing the same amount of VN3 was used so that an equal amount of energy would be absorbed on the dehydration of the silica on both sides of the cell. In this way overlapping between the silica’s dehydration curve and that of the silica-TESPT reaction can be avoided.

4.3.2 Results and discussions

Figure 4.1 features the scans of the three tests plus one for dried silica. The curve of the undried silica showed, as expected, an endothermic depression due to the amount of energy absorbed for evaporation of the water. This was indicated by the substantial removal of this depression when the same specimen was rescanned. However, silica’s adsorption of moisture is a reversible process whose rate is expected to depend on the time the silica is subjected to humidity in the atmosphere. The TESPT showed no indication of any depression but rather slight and steady absorption of energy due perhaps to slight volatility or thermal expansion. However, a significant endothermic depression over the temperature range of 125-225°C is seen in the curve indicating that strong interaction between the two materials has occurred. This depression peaked at 170°C and it took the base line nearly 10 minutes to return to its original level. This shows that the reaction between the silica and the TESPT demands a relatively high temperature. Also the dependence of the reaction rate on time indicates that it is a relatively slow reaction. From a practical point of view the conditions made available for the
Fig. 4.1: DSC Scans of Silica-TESPT Reaction.
present experiment could not usually be duplicated during factory scale mixing where only 2-3 minutes are normally available for the filler to be incorporated into the rubber matrix.

A practical solution for the optimisation of silica-TESPT interaction may be achieved by applying hot mixing techniques for rubber and dumping the masterbatch at 150-170°C if the conventional carbon black mixing cycle is to be adhered to. In fact, the effect of hot mixing in general has been extensively studied and its advantages and disadvantages\textsuperscript{70,100} reported. Those in its favour suggest that the temperature of the mix should not be allowed to rise beyond certain limits otherwise physical properties of the vulcanisate can be adversely affected due to excessive polymer degradation.

4.4 EFFECT OF ZINC OXIDE

The adverse interference of the zinc oxide with the reaction between silica and the TESPT was discussed in 3.8.2. In fact, problems created by this zinc oxide interference effect have long been noticed such that producers of certain types of silica have suggested that total elimination of zinc oxide gives better properties\textsuperscript{69}. Others\textsuperscript{70}, suggest that its omission is beneficial only in certain instances but not in general and depends on the type of the elastomer and the accelerator used. It was believed that the advantages conferred by ZnO, such as the positive effect on mix processability and increasing rate and state of cure, may be lost by its omission. Therefore, the inclusion of this material in the second stage of mixing may be an acceptable compromise for its expected problematic interference with the TESPT-silica reaction and the avoidance of the formation of coarse particles of zinc silicate.

4.5 CURE RETARDATION BY SILICA

The essentially high curative level required for silica mixes is detrimental both economically and technically. Present day practical compounding demands good overall properties at the lowest possible
curative levels. Achievement of a certain acceptable compromise for silica curing was thought to be highly significant. Such a compromise may be difficult to achieve with present commercial accelerators mainly designed for carbon black mixing. The search for a convenient curing system had led to the development of an interesting cationic surfactant that has been recently reported by Hepburn and Mahdi. The surfactant has been called SAPA (Surfactant Processing Aid Accelerator) as it was observed to function in situ as a processing aid to enhance flow, mill banding and release and also as a filler dispersion agent at temperatures below 130°C; next it dissociates at higher temperatures (>130°C) to give fatty acid and amine. The amine acts as a curing promoter while the fatty acid acts, in conjunction with ZnO, as a curing activator. Another reported advantage of SAPA is that there is no need for any fatty acid such as stearic acid to be added to the rubber recipe, as is the usual practice. It must be noted, however, that the disadvantage of having SAPA in carbon black mixes is seen in the reduction of scorch time to intolerable limits. A typical example of a cationic surfactant is N-tallow, 1, 3 propane diamine distearate, whose structure and dissociation mechanism is given in Figure 4.2. The positive role of surfactants on processing and vulcanisate properties was also investigated by Ognevsky and coworkers. They have reported their use as most effective in improving dispersion, fatigue resistance, elasticity and dynamic properties.

4.6 MODIFIED SILICA RECIPES

Sections 4.3, 4.4 and 4.5 have, if optimum results are to be obtained, emphasised the need for a modification in silica mixing techniques. Therefore, it was decided to prepare a new series of mixes with due consideration for the special requirements of silica fillers.
Chemical State

\[ [RNH(CH_2)_3NH_3]^2+ 2[C_{17}H_{35}0001^-] \]

Processing Function

At normal rubber processing temperatures of 50-90°C the SAPA molecule remains intact functioning:

i) as a mill roll release additive due to the presence of the fatty acid end groups

ii) as a filler dispersant, especially effective in compatibilising hydrophilic fillers (e.g. silicas) with hydrophobic rubber

iii) as an internal processing aid and lubricant

The primary amine functions as an acceleration of sulphur vulcanisation (in a similar manner to the release of aniline by the thermal decomposition of thiazole and sulphenamide accelerators)

Mould release agent

Figure 4.2 A scheme to explain the multiplicity of functions of a SAPA multifunctional compounding ingredient.  

68
4.6.1 Experimental

Table 4.1 details the recipes of the new tread mixes. The ISAF black control has remained unchanged due to its good overall properties. Mixes no. 2 and 3 are also NR based formulations but they contain silica in equal proportions to the ISAF and a modified curing system. Mix no. 3 contains 1.5 phr of SAPA to replace both the DPG and stearic acid.

The selected levels of curatives were chosen on the basis of several preliminary trials which had included a separate series of mixes, among which was selected the one that had given the closest modulus to the control rubber. This proximity in modulus was hoped to be later employed to judge and compare the physical properties of the vulcanisates. Table 4.2 shows the specially designed mixing cycles used. All mixes were prepared in the Banbury mixer as before but the shear rates were altered by increasing the rotor speed to 80 r.p.m. and by raising the circulating water temperature to 60°C. The latter was aimed to produce masterbatches whose dump temperatures range from 140-150°C so that TESPT-silica reaction might be enhanced. Zinc oxide and SAPA were added in the second stage of mixing to avoid any interference with the above reaction. Other conditions are shown in the Table.
Table 4.1 Formulations of truck tyre tread compounds based on carbon black/silica combinations with SAPA

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Mix No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carbon Black</td>
<td>Carbon Black</td>
<td>Carbon Black</td>
<td>Silica Control</td>
</tr>
<tr>
<td></td>
<td>Control</td>
<td>Silica</td>
<td>Silica/</td>
<td>SAPA</td>
</tr>
<tr>
<td>SMR20 (raw)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>ISAF</td>
<td>48</td>
<td>24</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>SiO₂ (Ultrasil VN3)</td>
<td>-</td>
<td>24</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>TESPT</td>
<td>-</td>
<td>3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>IPPD</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>Flectol H</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>4</td>
<td>4</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>2</td>
<td>2</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Aromatic Oil</td>
<td>7</td>
<td>7</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Paraffinic Wax</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Sulphur</td>
<td>1.5</td>
<td>2.5</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>SAPA</td>
<td>-</td>
<td>-</td>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td>MBS</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>DPG</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
Table 4.2 Special conditions for the hot mixing of silica-TESPT-SAPA/NR rubber mixes

Mixing conditions: All mixes were prepared in the Banbury as before. Mixing sequences and conditions were as follows:

First Stage:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Time (minutes)</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mix 1</td>
<td>mix 2</td>
</tr>
<tr>
<td>SMR20 (raw)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SiO₂, TESPT</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>ISAF/Oil</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Chemicals (excluding the ZnO for mixes 7 and 8)*</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Dump</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Dump temperature °C</td>
<td>150</td>
<td>155</td>
</tr>
</tbody>
</table>

All mixes were homogenized on a twin roll mill for three minutes and for mixes 2 and 3 the ZnO was added in the second stage, i.e. the special ZnO mixing cycle. To complete the mixing the rubber was sheeted off 3 mm thick and stored for 24 hours before the next stage of mixing.

Second Stage:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Time (minutes)</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mix 1</td>
<td>mix 2*</td>
</tr>
<tr>
<td>MB addition, SAPA, ZnO</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sulphur, accelerators</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Dump time</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Dump temperature °C</td>
<td>100</td>
<td>115</td>
</tr>
</tbody>
</table>

* ZnO was added at the same time with the masterbatch.
4.7 RESULTS AND DISCUSSIONS

4.7.1 Effect on processing properties

Table 4.3 features the processing properties of the modified mixes of Table 4.1. The effect of the modification on some of these properties is discussed below.

4.7.1.1 Influence on Mooney viscosity ML (1+4) 100°C

A comparison of the Mooney viscosity numbers of the mixes in this series shows that they are generally lower than their counterparts in Table 3.2 where colder mixing and lower mixing shear rates were used. It is interesting to see that the silica mixes give a distinctly more favourable response to the modified mixing cycle than the ISAF control. This is in contrast to what was obtained in the earlier mixes of Table 3.2. The improvement of the viscosity can be ascribed to the effect of a higher filler breakdown most probably due to the increased shear forces, the hot mixing and the consequent inhibition of the tendency of silica towards re-agglomeration. Moreover, the presence of TESPT must be an additional factor contributing to the improvement. The combined effect of these factors resulted in the reduction of the Mooney viscosity of mix no. 2 by 6 units compared to the control. The replacement of stearic acid and DPG by SAPA in mix no. 3, however, resulted in a viscosity equal to that of the control. Achievement of equal viscosity to that of carbon black control is a significant advantage in silica mixing which could not have been achieved by conventional methods. In addition, the viscosities of all three mixes are within the range of practical compoundings where Mooney viscosities as high as 60 units are considered acceptable.
Table 4.3  Basic compound and vulcanisate properties of the optimised mixes

<table>
<thead>
<tr>
<th>Properties</th>
<th>Mix no.</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>a) Compound properties</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mooney viscosity ML(1+4)100°C</td>
<td>52</td>
<td>46</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>Wallace Shawbury precision cure analysis</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_5$ min. at 130°C</td>
<td>13</td>
<td>10.8</td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td>$t_5$ min. at 145°C</td>
<td>4.2</td>
<td>3.6</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>ODR compound properties at 160°C and 3° Arc</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scorch time $t_2$ (min)</td>
<td>2.7</td>
<td>2.6</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>Maximum torque dN.m</td>
<td>62</td>
<td>70</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>$t_{95}$ min.</td>
<td>5.6</td>
<td>5.4</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>Reversion*% (2 hrs at 160°C)</td>
<td>22</td>
<td>19</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>b) Vulcanisate properties</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hardness IRHD</td>
<td>60</td>
<td>64</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Tensile strength, MPa</td>
<td>25</td>
<td>30.2</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>100% Modulus, MPa</td>
<td>1.6</td>
<td>2.5</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>300% Modulus, MPa</td>
<td>9.2</td>
<td>11.6</td>
<td>9.6</td>
<td></td>
</tr>
<tr>
<td>Elongation at break %</td>
<td>600</td>
<td>580</td>
<td>620</td>
<td></td>
</tr>
<tr>
<td>Tear strength kNm$^{-1}$(crescent)</td>
<td>127</td>
<td>145</td>
<td>138</td>
<td></td>
</tr>
<tr>
<td>Rebound resilience %</td>
<td>52</td>
<td>58</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>Compression set at 25% strain (24 hrs at 100°C)</td>
<td>51</td>
<td>51</td>
<td>54</td>
<td></td>
</tr>
</tbody>
</table>

* Reversion% = \( \frac{\text{Max. ODR torque - Torque at the time shown}}{\text{Max. ODR torque}} \times 100 \)
4.7.1.2 Extrusion processability of the tread mixes

Despite its popularity, the Mooney viscometer would not be expected adequately to characterise the performance of a rubber mix under high shear rates, such as those encountered in all practical processing stages. It was, therefore, decided to use a Davenport type extrusion rheometer for this purpose. This instrument, which provides shear rates similar to those encountered during tread extrusion\textsuperscript{103}, was utilised to extrude a certain amount of the tread mixes at a constant barrel temperature of 110\textdegree C. The choice of this temperature was made to simulate the average temperature reached during factory processing. A slit type die of dimensions 20 x 1 x 10 mm \([l \times h \times w]\) was used for the extrusion. Various shear rates \(\dot{\gamma}\) were applied and the corresponding shear stress \(\tau_w\) was estimated from the voltage as monitored on a chart recorder. Because the flow rates of the rubber mixes are not Newtonian, the following equation is used to calculate the apparent shear rate when the slit die is used

\[
\dot{\gamma}_{\text{app.}} = \frac{6Q}{\pi R^2 h w^2} \quad \ldots \ldots 4.1
\]

where \((Q) = \text{output rate} = \pi R^2 V\)

where \((R) = \text{radius of the ram}\)

\((W)\) and \((h)\) are die width and height respectively

\((V) = \text{velocity of the ram}\)

The shear stress was calculated from the equation

\[
\tau_w = \frac{\Delta P h}{2L} \quad \ldots \ldots 4.2
\]

where \((\Delta P) = \text{pressure in the barrel}, \ (L) = \text{die length}\).
Table 4.4 Extrusion characteristics of the tread mixes as measured by a Davenport capillary rheometer

<table>
<thead>
<tr>
<th>Mix no.</th>
<th>Formulation</th>
<th>Flow Rate g/min</th>
<th>Die Swell Ratio</th>
<th>Shear Stress Tw kPa</th>
<th>Surface Finish</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NR/ISAF (control)</td>
<td>32.5</td>
<td>1.52</td>
<td>226</td>
<td>good</td>
</tr>
<tr>
<td>2</td>
<td>NR/silica/ISAF</td>
<td>31.3</td>
<td>1.49</td>
<td>237</td>
<td>good</td>
</tr>
<tr>
<td>3</td>
<td>Ditto + SAPA</td>
<td>29.5</td>
<td>1.45</td>
<td>262</td>
<td>v.good</td>
</tr>
</tbody>
</table>

* The test was conducted at a constant value of $290 \text{ sec}^{-1}$

Table 4.4 shows the results obtained. The ISAF filled control (mix no. 1) is seen as slightly superior to both the silica mixes in terms of the flow rate and the shear stress. However, the latter mixes are seen as having a superior die swell and in the case of mix no. 3 the surface finish was much better than the control.

While the Mooney viscosity figures of Table 4.3 show no appreciable differences between mixes no. 1 and 3, Figure 4.3 shows that the silica mixes exhibit relatively higher $\tau_w$ at all $\dot{\gamma}$ values. This effect has no bearing on silica up to certain practical processing limits as VN₃ has a higher surface area than the ISAF and the same effect would have been exerted by carbon blacks if they were to have the same particle size as that of the precipitated silica used.
4.7.1.3 Energy consumption

If other parameters are kept unchanged energy consumed during mixing can give a good indication of filler dispersion. In the present investigations different filler systems are used and the aforementioned example does not apply. Nevertheless, a comparison of the power consumed for each mix was sought as advantageous for its own importance and practicality. Table 4.5 shows the power consumed during the two stage mixing cycle in the Banbury mixer at the same cycle time. The silica mixes show, as expected, a higher power consumption compared with the ISAF control. This is in accord with the result of the capillary rheometer as discussed in the previous section. It can be seen, however, that the SAPA containing mix no. 3, shows a higher energy consumption than the other silica counterpart (mix no. 2). This effect is believed to be due to the inclusion of SAPA in the second stage of the mixing cycle of the former whereas stearic acid was included in the first stage of the mixing cycle of the latter. Thus, mix no. 2 had a longer stearic acid lubricated mixing with a consequent lower power consumption.

Table 4.5 Amount of energy consumption per litre of each of the tread mixes

<table>
<thead>
<tr>
<th></th>
<th>NR/ISAF (mix no.1)</th>
<th>NR/silica/ISAF (mix no.2)</th>
<th>NR/silica/ISAF/SAPA (mix no.3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power Consumption</td>
<td>1542</td>
<td>1656</td>
<td>1708</td>
</tr>
<tr>
<td>KJ/litre</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.7.1.4 Scorch time and vulcanisate characteristics as determined by Monsanto ODR

The critical parameters in the process of vulcanisation are the time that elapses before it starts and the rate at which it occurs. There must be a sufficient delay or scorch time before the onset of vulcanisation to allow processing to be completed and then afterwards the formation of crosslinks must be rapid. Different types of equipment are used to assess scorch time. For the purpose of the present research a recently developed Wallace type precision cure analyser was used together with the Monsanto Rheometer ODR.

Data concerning curing properties of the three mixes can be seen in Table 4.3 and their ODR traces in Figure 4.4. These reflect the effectiveness of the optimised mixing cycle on both the rate and the state of cure of the silica mixes compared to the present ISAF control. Also a greater enhancement over the previous silica mixes is seen with no adverse effect on the processing safety. The silica-TESPT system showed an additional advantage in reducing the overcure reversion, a typical phenomenon of NR-carbon black vulcanisates.

4.7.1.5 Dispersion

The experimental work in the previous chapter has established that the degree of reinforcement provided by a filler depends on a number of variables. One of the most important is dispersion efficiency. A filler may apparently behave as non-reinforcing not merely because of a lack of filler-rubber interaction but due perhaps to poor dispersibility\(^2\). The hot mixing and the increased rotor speed of the Banbury mixer showed a profound effect on processability, as was seen in the preceding section. Consequently, their milling behaviour was improved. SAPA, which was incorporated in the second stage of mixing, (to avoid any interference with the silica-TESPT reaction and also to avoid
Fig. 4. ODR traces of the tread vulcanisates (160°C), 3° Arc.
scorch) showed a distinctly favourable effect on dispersion with no detrimental effect on scorch safety. This can easily be recognised in microscale from the SEM micrograph of mix no. 1 (NR/ISAF) and that of mix no. 3 (NR/silica-TESPT-SAPA-ISAF) as shown in Figure 4.5. The modified mixing technique had changed the silica dispersion (earlier described as very poor, see Figure 3.7) into one very similar to that of the ISAF control in terms of microscale dispersion of filler particles. The efficient mixing cycle has apparently resulted in an extensive breakdown of the relatively large silica agglomerates into primary particles.

4.7.1.6 Mechanism of the silica-rubber interactions

The effectiveness of the optimised mixing cycle on improving the silica dispersion and the consequent increase in the processing and vulcanisate properties is believed to be due to some physical and chemical processes as discussed below.

A. Hydrophoblation of silica

Fast elimination of adsorbed water from the silica surface in the first stage of mixing is expected to free more silanol groups early in the mixing cycle, and to provide more efficient interactions with the coupling agent. The preheated mixing chamber is believed to provide the essential heat required for an effective evaporation of a substantial amount of the adsorbed water, so that each of the six ethoxy groups of the coupling agent will have a better chance to be involved in the coupling reaction with the silica. Earlier reports have suggested that two or, at the best, four of these ethoxy groups would be involved in the reaction with the silanol groups of silica, perhaps due to encirclement of some of the latter by water. The effect of heat on the expulsion of water occurs as shown in the scheme below.

\[
\begin{array}{c}
\text{Si} - \text{O} - \text{H} \\
\text{O} \\
\end{array} \quad \overset{\Delta}{\underset{100-150^\circ C}{\text{Si} - \text{O} - \text{H} + \text{H}_2\text{O}}} \quad \begin{array}{c}
\text{Si} - \text{O} - \text{H} \\
\end{array}
\]

80
Figure 4.5  SEM micrographs of two torn vulcanisates (mixes no. 1 and 3 of Table 4.1) showing good state of dispersion achieved in both mixes.
B. Efficient silica-TESPT Interactions

The relatively high mixing temperature is expected to enhance the interactions between the freed silane group and a higher proportion of the TESPT, so that the amount of unreacted TESPT will be minimal. Such a reaction has already been seen as temperature and time sensitive (Figure 4.1). In consequence coupling bonds contribute to the filler-rubber interactions and strength as shown in step (1) of Figure 4.6. The delayed incorporation of zinc oxide must be another factor in avoiding the side interference hence providing the right environment for the maximisation of the coupling efficiency.

C. The action of SAPA

A certain proportion of the silanol groups is expected to escape the silica-TESPT coupling reactions due perhaps to steric hindrance or the expected TESPT/silica disproportionality especially at lower TESPT concentration. These unreacted silanol groups can still cause limited problems such as re-agglomeration and adsorption of some of the curative. They are believed to be the reason behind the need for the inclusion of DPG in the formulation of mix no. 2. It must be borne in mind that it is significant that the accelerator dosage should be decreased in tread compounding. Thus, the inclusion of SAPA in mix no. 3 appears to have satisfied this condition and the amount of MBS remained equal to that of the control rubber without any need for a co-accelerator. The mechanism of the SAPA action is believed to occur in two steps. These are:

a. SAPA dissociation

This has already been discussed in section 4.5.
b. Silica-amine interaction

There have been several reports to suggest that silica, by virtue of its acidity, has a preference to adsorb amines. The release of strongly alkaline amine from the SAPA dissociation during the vulcanisation process is expected to neutralise the acidity of silica related to the presence of unreacted silanol groups left from the TESPT reaction. This would allow the normally base catalysed sulphur vulcanisation reaction to proceed unhindered. A proposed mechanism for the action of the released amine is demonstrated in steps 2, 3 and 4 of Figure 4.6. Experimental evidence to support the suggested interaction between silica and the released amine and hence to substantiate the proposed mechanism was provided experimentally by infrared spectroscopy. A specimen of silica was dried at 110°C and then scanned. Then a mixture of the dried silica and a primary amine (1,2-diamino propane) at a proportion of 9:1 was preheated for five minutes at 60°C, left to cool and also scanned. The aim behind the drying of silica is to expel adsorbed water which normally gives an IR band that interferes with the spectra of silanol groups.

Figure 4.7 shows that for the dried silica a broad band appears at 3500 cm\(^{-1}\) indicating the presence of silanol groups, probably hydrogen bonded. For the mixture, this band is much smaller and flatter, suggesting that some irreversible interactions have taken place between the silanol groups and the amine. It is believed that the same interaction mechanism occurs between the amine released from SAPA dissociation and the excessive silanol groups left from the silica-TESPT reaction in the present silica mixes.

4.7.2 Effect on vulcanisate properties

4.7.2.1 Modulus

Among other variables, rubber modulus is known to be dependent on crosslink density and filler dispersion. In the previous series
Figure 4.6 Outline of the coupling mechanism between hydroxyl active silica and TESPT and rubber using a two stage internal mixing cycle

First stage of mixing
Hydroxy active silica and TESPT are mixed together at 130 - 160°C in an internal mixer (in the absence of zinc oxide).

Step 1
Silica-TESPT interaction occurs in the absence of ZnO, accelerated by heat:

\[
\begin{align*}
\text{Si-OH} & \quad \text{TESPT} \\
\text{Si-OH} & \quad (\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\cdot\text{S} \\
\text{Si-OH} & \quad (\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\cdot\text{S} \\
\text{Si-OH} & \quad \text{Si-} \quad \text{OH} + \text{C}_2\text{H}_5\text{OH}
\end{align*}
\]

Second stage of mixing
This second stage of the mixing cycle during which the SAPA is added is carried out at a lower temperature, not exceeding 120°C, to enable the SAPA to function, at this stage, only as a surfactant.

Vulcanisation stage
On heating the compounded rubber to >135°C, for the purpose of vulcanisation, then steps 2, 3 and 4 are considered to occur to complete the reaction mechanism as follows:

Step 2
During vulcanisation SAPA dissociation by heating occurs during the vulcanisation stage
Figure 4.6 (continued)

**Step 3:**
During vulcanisation interaction then occurs between the amine and the unreacted hydroxyl groups of the silica filler to give Complex B.

![Silica-Amine Complex B](image)

**Step 4:**
Finally, later during vulcanisation crosslinking occurs between the TESPT-Silica Complex B and the unsaturated diene backbone of the rubber thus giving a 'silica-rubber-chemically-coupled-complex' in which the originally hydrophilic rubber incompatible silica filler has been changed into a hydrophobic rubber compatible silica.

![Hydrophobic Silica-Rubber Compatibilising Group](image)
Fig. 4.7: IR spectra of dried precipitated Silica and a dried Silica - Amine complex
of mixes (Table 3.2) the silica/ISAF vulcanisate did not match the ISAF control in modulus. This was attributed to the inefficient silica-TESPT interaction with the consequent poor dispersion and the adsorption of a part of the curatives by the large number of silanol groups available in the mix. In the present series of mixes this relatively low modulus value changed to values higher than the carbon black equivalent (cf. mixes no. 2 and 3 in Table 4.3).

This high modulus can be considered as further evidence of a greater coupling efficiency.

It is significant, however, that one of the established desirable objectives in compounding development for tyre treads is that any increased abrasion resistance should be obtained without an increase in modulus and hardness values; otherwise, properties such as grip, wet slip etc. are adversely affected. This objective was achieved by the incorporation of SAPA in mix. no. 3. This reduced the increase in modulus in mix no. 2 where DPG is present as a secondary accelerator.

4.7.2.2 Tensile strength

Examination of Table 4.3 reveals a significant increase (20%) in the tensile strength of the silica/ISAF mixes over the ISAF control. Several factors are believed to have contributed to this beneficial increase such as the formation of coupling bonds, the improved dispersion and perhaps the type of polysulphidic crosslinks. These cross relationships complicate the task of interpretation. It must be remembered that mixes no. 2 and 3 inevitably contained a higher sulphur/accelerator ratio compared to the control. Hence, one would expect a more polysulphidic/dianol monosulphidic ratio in their composition relative to the control. If this argument is valid, then the predominance of polysulphidic crosslinks at relatively similar moduli would contribute to the increased tensile strength. They have always been known to allow a greater chain orientation and flexibility, hence higher loads would be tolerated; but their disadvantage lies in their reduced resistance to heat.
To account for the individual effect of coupling bonds PAL and DE74 have reported a method in which the tensile strength was measured before and after the cleavage of these bonds. Their findings showed that the contribution of coupling bonds was substantial. It should be noted that the technique they used for the cleavage (i.e. by immersing tensile specimens in benzene under ammonia atmosphere) remains questionable. The uncertainty is ascribed to the view that some of the rubber-rubber sulphidic crosslinks will also be affected. Therefore, the technique was not applied. Instead an attempt was made to simplify the rather complicated task of interpreting the effect of some of the main elements that were believed to have contributed to the tensile strength of the vulcanisates. Formulations of four silica mixes were chosen such that minimal variations existed between their ingredients. Therefore, rubber parameters contributing to the reinforcement could be isolated and studied. The compounds selected for the study are seen in Table 4.6 in which mix A is similar to mix B, except for the presence of TESPT in the latter. Also, both of these mixes were prepared similarly in an unoptimised mixing cycle. Examination of the tensile strength shows that mix B is superior to that of A. This increase is due to the coupling between silica and rubber, as sulphur and accelerator levels are equal. Similarly, mixes C and D were identical in their formulation and were prepared by an optimised mixing cycle and the only difference was the presence of SAPA in mix D instead of the DPG and stearic acid in mix C. Here, no noticeable difference in tensile strength of the two vulcanisates can be seen. It is interesting, however, to notice that the tensile strengths of mixes (C + D) is 50% more than those of mixes (A + B). This dramatic increase cannot be justified on the basis of the presence or absence of TESPT and for the level of sulphur-accelerators only, as these showed only limited effect in the case of mixes A and B.
Table 4.6 The role of optimised mixing cycle on the tensile strength of silica vulcanisates

<table>
<thead>
<tr>
<th>Identification</th>
<th>Type and loading of filler</th>
<th>Type of mixing</th>
<th>Sulphur phr</th>
<th>MBS phr</th>
<th>DPG phr</th>
<th>TESPT phr</th>
<th>Addition of ZnO</th>
<th>Tensile strength MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Ultrasil VN3 48 phr</td>
<td>Cold chamber</td>
<td>2.5</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>1st stage</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60 r.p.m.</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>B</td>
<td>Ultrasil VN3 48</td>
<td>Cold chamber</td>
<td>2.5</td>
<td>2</td>
<td>-</td>
<td>3.5</td>
<td>1st stage</td>
<td>20.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60 r.p.m.</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>C</td>
<td>Ultrasil VN3 24</td>
<td>Hot chamber</td>
<td>2.5</td>
<td>1.5</td>
<td>0.5</td>
<td>3</td>
<td>2nd stage</td>
<td>30.2</td>
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<tr>
<td></td>
<td>ISAF</td>
<td>80 r.p.m.</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>Ultrasil VN3 24</td>
<td>Hot chamber</td>
<td>2.5</td>
<td>1.5</td>
<td>-</td>
<td>3</td>
<td>2nd stage</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>ISAF</td>
<td>80 r.p.m.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(SAPA system)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>
It could be suggested that it was the optimised mixing cycle that allowed good dispersion together with efficient coupling and reduced tendency towards curative adsorption; these caused the improvement in the tensile strength. Also, the analysis of swelling and ageing characteristics (sections 4.10 and 4.14), which normally give a crude indication of the type of sulphidic crosslinks, offer little or no support for the argument concerning the prominence of polysulphidic over dianol monophidic crosslinks in the silica mixes (nos. 2 and 3) relative to the ISAF control (mix no. 1). Hence, the assumption concerning the contribution to the tensile strength from the assumed polysulphidic crosslinks is unlikely.

This contribution of the coupling bonds to reinforcement may be explained in accordance with Bueche's theories of rubber reinforcement, i.e. the more stable chemical bonds between silica and rubber would be expected to contribute to resistance to strain by distributing and sharing any applied load more evenly, with perhaps a better flexibility towards orientation due to their extended length. Such flexibility keeps the mobility of the whole network less affected by the strain. On the other hand, a comprehensive study of the effect of the degree of carbon black dispersion on some vulcanisates was made by Scott and Chirico. They have confirmed a well-recognised fact in rubber technology that there are relationships between carbon black dispersion and ultimate rubber properties. A profound effect for instance was found for dispersion on tensile strength and strain energy as shown in Figure 4.8.

4.7.2.3 Tear strength

Table 4.1 features an advantageous increase in the crescent tear strength of the silica/ISAF mixes over the ISAF control. The values obtained confirm the effectiveness of silica on this crucial property. Also it was noticed during the course of the experiment that the silica mixes show a greater tendency towards knotty tear mechanism compared with the control. The higher extent of tear pull deviation of a well dispersed reinforcing system may lead to
Fig. 4.8: The effect of Carbon Black Dispersion on Tensile Strength and Strain Energy.

Fig. 4.9: Modes of tear (reinforced rubber specimens.)
the assumption that the silica-TESPT-NR molecular structure could result in a higher degree of orientation at right angles to the tip of the growing tear. The contribution of the coupling bonds in the reinforcing structure ahead of the tear path necessitates extra force for the progress of the crack due to the need to break the molecular bonds of the rubber and also the relatively large number of silica-NR bonds with the latter blunting and deflecting the tear path from its original route to one close but parallel to the direction of stretching as seen in the Figure 4.9.

4.8 EFFECT ON ABRASION RESISTANCE

Although the preceding section has emphasised the favourable effect of the optimised silica-rubber interactions on the tear and the tensile strength, some judgement on the reinforcement of the vulcanisates by determining their abrasion properties was considered as essential and relevant in serving the general purpose of the work.

To obtain a useful measure of the rather complicated relationship between the reinforcing system used and the abrasion characteristics a multi-step approach was followed.

4.8.1 Methods adopted to assess the abrasion characteristics

A. By direct measurements of volume or weight loss using three different machines each of which corresponded to a particular mode of abrasion.

B. By examining the possible correlations between the volume or weight loss from the methods of A and some other reinforcement criteria such as hot tearing energy (using specially reinforced specimens) and the resistance of the vulcanisates to swelling with the latter technique being used to measure filler-rubber interaction.

C. By studying the abrasion mechanisms of A, as illustrated on the abraded surface topography, and wear product morphology and drawing conclusions about the extent of wear.
4.8.2 EXPERIMENTAL EVALUATION OF ABRASION

4.8.2.1 Determination of abrasion on the DIN abrader (DIN 53516)

Rubber sheets were prepared from the three mixes of Table 4.1 by compression moulding at 160°C to a thickness of 10 mm. Test specimens were later cut and tested according to this DIN procedure and tested at room temperature. The average volume loss (mm³) of three determinations was plotted versus the type of the vulcanisate and the results shown in Figure 4.10. Mixes no. 2 and 3 are seen to possess significantly improved abrasion indices; respectively, 11 and 22 points higher than the control. Bearing in mind that the type of abrasion mechanism on this machine is predominantly a mixture of tensile-tearing and cutting (due to the use of abrasive paper), then the improvement in the tensile and tear strength imparted by the silica must be a factor contributing

![Figure 4.10: Relative abrasion indices of the experimental tread vulcanisates on the DIN abrader.](image-url)
to the superiority of its vulcanisates in this particular mode of abrasion. It was thought interesting to compare the abrasion properties of the present silica mixes with that of an ordinary mixed silica containing rubber. Therefore, mix no. 5 of Table 3.2 was selected for the required comparison. This mix, whose number remained unchanged in Figure 4.10, was seen to possess only half the DIN abrasion Index of the present optimised silica mixes. The latter observation shows how important it is to obtain efficient rubber-silica interaction for optimum abrasion resistance.

4.8.2.2 Measurement of abrasion by the Akron machine (BS 903.A9-1988)

The main difference between the DIN abrader and the Akron machine is that in the former the test piece is continuously and totally in contact with the abradant, consequently there is a much greater possibility of heat build-up in the specimen, whereas the test piece for the latter is a solid disc rolling over an abrasive wheel at a predetermined slip angle. Using a slip angle means that the rubber sample moves with a speed different from that of the circumferential velocity of the abradant. The specimens for the Akron abrader were prepared by moulding at 160°C for 20 mins and tested at room temperature under a standard load of 10 lbs and a slip angle of 15°. Test pieces were run for 4000 revolutions then measurements were taken after every 1000 revolutions. The average of three measurements was used for the results which are plotted in Figure 4.11. The Akron abrader, whose dominant mechanism is believed to be a mixture of microscale tearing and fatigue (as opposed to the DIN tester, where rubbing abrasion predominates) clearly shows the superiority of both the silica-ISAF filled vulcanisates over that of the ISAF filled mix. It was very interesting to see that the use of a combined filler of silica-ISAF and TESPT has resulted in obtaining an Akron abrasion resistance Index of a value as high as 160 which is 60 points higher than the ISAF filled rubber used as a control when the two rubber specimens were prepared and tested under the same conditions. No further significant improvement over the silica-ISAF-TESPT was gained by using SAPA in mix no. 3.

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The role of the silica bonded system on the mechanism of wear by this technique may be better understood by examining the SEM micrographs in Figure 4.12A of the worn surfaces of the three vulcanisates. The NR/ISAF control (mix no. 1) shows coarse high patterns which are nearly 1 mm apart from each other. Also, they are seen as twisted around themselves suggesting that the large sticky debris obtained during the abrasion might have been a result of a failure of these patterns by a mechanism of roll formation. On the other hand mix no. 2 (Figure 4.12B) shows a lower height, smoother ridged pattern perhaps due to the increased resistance of the vulcanisate to the penetration of their tips deep into the rubber. This was indicated by the fine debris obtained during the abrasion. In contrast to both mixes no. 1 and 2, mix no.3 shows (Figure 4.12C) no uniform abrasion patterns and fine wear debris. From this experiment it was clear that the finer the patterns the lower the abrasion loss.
A. Control mix. ISAF filled vulcanisate. Notice the approximately parallel coarse ridges on the surface of the abraded rubber.

B. SiO₂/ISAF/TESPT reinforced rubber
Note the lower height, smoother ridged pattern. Has better abrasion resistance than A (x19 magnification)

C. SiO₂ + ISAF + TESPT + SAPA reinforced rubber
Note that absence of a uniform abrasion wear pattern, i.e. no ridged surface. Has better abrasion resistance than A & B (x19 magnification)

Figure 4.12 SEM MICROGRAPHS (x19 MAGNIFICATION) OF WORN SURFACES ON THE AKRON ABRADER
4.8.2.3 Miniature tyre test

4.8.2.3.1 Principles of the technique

The technique was specifically developed to provide different test conditions from the normally severe ones encountered during both foregoing abrasion tests and its development provided a test with sufficient discrimination to distinguish between the wear properties of the various vulcanisates being investigated. The technique allowed a miniature pneumatic tyre to be tested under controlled conditions i.e. speed, pressure and slip angle. Additionally, it offered the advantage of using different types of abradants.

4.8.2.3.2 Description of the machine

Figure 4.13 shows by means of a photograph the main parts of this abrasion machine whose individual components can be summarised as follows:

a. Rotary drum: This is an AC-driven steel drum of 34 cm diameter and 13 cm wide. Its outer surface can be covered by any suitable abradant either by gluing or clamping. The drum drives the miniature tyre at 360 revs/min which corresponds to a linear velocity of 7.5 kilometers per hour.

b. Adjustable carriage: This is located beneath the drum to support the mechanism that holds the tyre. The position of the carriage can be adjusted in four directions relative to the drum by means of two feed screws.

c. Support shelf: This is a hollow steel shaft which holds the tyre at one end, while the other is connected to a counter. This shaft is firmly fixed to a steel base which in turn is bolted to the mobile carriage at one end, while the other runs along a curved slot in the carriage itself. The slot is designed to give the shaft, and subsequently, the tyre a certain slip angle against the rotary drum. The tyre is
clamped on the shaft and can be inflated to the required level by means of a pressurised air stream conducted through a plastic hose that runs through the shaft. Each miniature tyre can be deflected against the rotary drum by moving the carriage through the front feed screw which is supplied with a small rotary wheel for this purpose. The extent of deflection is indicated by markings on the handle that control the screw movement. The tyre can also be subjected to a certain torque by applying a load on the middle of the freely moving shaft.

d. Miniature tyre: This was made of a 100% rubber and produced by compression moulding using a three piece mould. The weight of the tyre ranged between 60 and 65 gm. Its main dimensions and geometry are shown in Figure 4.14.

e. Wire gauze: Any type of gauze can be used as the abradant but a steel wire gauze of 1 mm diameter round wire with a square grid of 1.2 cm side was found convenient for the following reasons:

I) It removes most of the degraded rubber, which would adversely effect the results by smearing, by trapping it within the wire grids. The adverse effect of smearing on the reproducibility of other abrasion machines was discussed in Section 2.2.4.2.

II) It contains no sharp projections therefore it offers a better correlation with the type of fatigue abrasion than that of a tyre running over a relatively smooth surface e.g. tarmac or concrete.

III) The wire gauze was less affected by the abrasion process than the abrasive paper of the DIN abrader.
Figure 4.13: Developed miniature tyre testing facility
Fig. 4.14: A Cross-Section of a miniature tyre mounted on the shaft.
4.8.2.3.3 Experimental

Miniature tyres were obtained from the modified tread mixes of Table 4.1 by vulcanisation to $t_{95} + 4$ minutes at 160°C. These were trimmed and accurately weighed to the nearest 0.1 mg. Each tyre was then loaded onto the machine and underwent a deflection of 15% under 1 kg/cm² air pressure and a slip angle of 5°. A hot air gun was adjusted (see Figure 4.13) to give an equilibrium temperature range of 70-80°C as measured by a thermocouple which was in continuous contact with the sidewall of the tyre.

It should be noted, however, that a more precise temperature measurement was not possible with a running tyre as such a process is commonly known to be difficult to control. Every tested tyre was allowed to run for a total of 75000 revs under the above conditions. This took 3.47 hours and was estimated to be the equivalent to a linear distance of 25.4 km. However, the test was stopped for weight measurements at three intervals each of 25000 revs. The weight of the tested tyre was taken when the tyre had cooled to room temperature. This took not less than 20 minutes and aimed to estimate tyre weights when they were cold to avoid variation due to humidity.

4.8.2.3.4 Results and discussion of the miniature tyre test

Figure 4.15 is a comparative histogram of the wear indices of the three vulcanisates tested. The NR/ISAF control was selected as the control, as was done in the preceding abrasion tests.

The optimised silica/ISAF mix no. 2 showed an index of 22 points more than the control. Inclusion of SAPA in mix no. 3 reduced the gain in the wear index to 15 points. Such a performance of the SAPA containing mix was seen as lower than that of the same mix when the DIN and the Akron abraders were used. This may be explained by considering the basis of the mechanism of abrasion on these three abrasion machines. For instance, the use of the round wire gauze as the abradant for the miniature tyre test enhances
Fig. 4.15. : Wear indices of the tread vulcanisates as found by testing on the miniature tyre machine.
the thermal degradation of the surface rather than the predominant
tensile-tear and cutting mechanisms of the DIN and Akron tests.
The superiority of the silica mixes over the ISAF control resisting
the cut-tear mechanism could be higher than that of thermal
degradation. The use of high test temperature for the pneumatic
miniature tyre experiment added another difference to those already
in existence between the DIN and the Akron abraders. This high
temperature, however, was meant to represent better the moderate
and low temperature ranges to which a truck tyre tread is
normally subjected during service\textsuperscript{104}.

It was interesting to see that, when the weight loss of the three
vulcanisates was measured at specific intervals, the control mix
showed lower loss for the first 25000 revs than that of the
silica/ISAF/SAPA mix. However, this situation reversed in the
second round of the test and continued in the same fashion with
the gap widening in favour of the silica mixes as shown in Figure
4.16. This indicates that the superiority of the silica containing
mixes is maintained for longer test intervals under hot
environments where thermal degradation is predominant.

4.8.2.3.5 Wear products and surface observations

An examination of wear products is often useful to help explain the
mechanism by which the rubber is removed. Therefore, care was
taken during the course of the miniature tyre testing to collect the
wear products and to study the worn surface topography. The
wear debris was collected in a container located beneath the
running tyre and the tread surface was examined by using a low
magnification light microscope. All three vulcanisates gave debris
mainly irregular in shape. Their post-extraction sizes (dry) range
from 3 - 100\mu . (See Figures 4.16A and 4.16B). Also, some
sausage shaped debris was noticed. The total weight of the debris
collected at the end of the examination was 60-65\% of the total
weight loss. This difference is believed to be either lost as a
gaseous emission or heavily degraded and stuck in between the
grids of the gauze.
Fig. 4.16: Weight Loss of the Miniature Tyres (test conducted at 70 - 80°C)
<table>
<thead>
<tr>
<th>Size (microns) under</th>
<th>% Size (in band) microns: under</th>
<th>Size (microns) under 100.0</th>
<th>% Size (in band)</th>
</tr>
</thead>
<tbody>
<tr>
<td>188.0</td>
<td>100.0</td>
<td>0.1:</td>
<td>17.7:</td>
</tr>
<tr>
<td>162.0</td>
<td>99.9</td>
<td>0.2:</td>
<td>15.3:</td>
</tr>
<tr>
<td>140.0</td>
<td>99.7</td>
<td>0.3:</td>
<td>13.2:</td>
</tr>
<tr>
<td>121.0</td>
<td>99.5</td>
<td>0.3:</td>
<td>11.4:</td>
</tr>
<tr>
<td>104.0</td>
<td>99.2</td>
<td>0.2:</td>
<td>9.8:</td>
</tr>
<tr>
<td>89.9</td>
<td>99.0</td>
<td>0.4:</td>
<td>8.5:</td>
</tr>
<tr>
<td>77.5</td>
<td>90.5</td>
<td>1.1:</td>
<td>7.3:</td>
</tr>
<tr>
<td>66.9</td>
<td>97.5</td>
<td>1.7:</td>
<td>6.3:</td>
</tr>
<tr>
<td>57.7</td>
<td>95.8</td>
<td>2.2:</td>
<td>5.4:</td>
</tr>
<tr>
<td>49.8</td>
<td>93.6</td>
<td>3.1:</td>
<td>4.7:</td>
</tr>
<tr>
<td>42.9</td>
<td>90.5</td>
<td>4.3:</td>
<td>4.1:</td>
</tr>
<tr>
<td>37.1</td>
<td>86.2</td>
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<td>32.0</td>
<td>80.2</td>
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<td>73.3</td>
<td>7.0:</td>
<td>2.6:</td>
</tr>
<tr>
<td>23.8</td>
<td>66.3</td>
<td>6.6:</td>
<td>2.2:</td>
</tr>
<tr>
<td>20.5</td>
<td>59.7</td>
<td>6.0:</td>
<td>1.9:</td>
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</table>

Fig. 4.16A: Particle size of the debris after post-extraction by toluene; NR / ISAF control.
<table>
<thead>
<tr>
<th>Size (μm)</th>
<th>%</th>
<th>Size (μm)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>188.0</td>
<td>100.0</td>
<td>17.7</td>
<td>87.3</td>
</tr>
<tr>
<td>162.0</td>
<td>100.0</td>
<td>15.3</td>
<td>83.9</td>
</tr>
<tr>
<td>140.0</td>
<td>100.0</td>
<td>13.2</td>
<td>80.4</td>
</tr>
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<td>121.0</td>
<td>100.0</td>
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<td>75.5</td>
</tr>
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<td>104.0</td>
<td>100.0</td>
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<td>69.6</td>
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<td>99.3</td>
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</tr>
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<td>32.0</td>
<td>98.1</td>
<td>3.0</td>
<td>17.9</td>
</tr>
<tr>
<td>27.6</td>
<td>97.2</td>
<td>2.6</td>
<td>13.3</td>
</tr>
<tr>
<td>23.8</td>
<td>94.8</td>
<td>2.2</td>
<td>9.7</td>
</tr>
<tr>
<td>20.5</td>
<td>91.1</td>
<td>1.9</td>
<td>6.8</td>
</tr>
</tbody>
</table>

Fig. 4.16B: Particle size of the debris after post-extraction by toluene; NR / Silica-ISAF
It was observed that the tread surface and the debris collected from the silica vulcanisates were less sticky than those of the ISAF control. A close examination of these surfaces revealed very fine ridges visible to the naked eye. However, a microscopic examination of these ridges did not reveal a predominant tearing mechanism. The main mechanism in the absence of large scale tearing might be a failure due to fatigue delamination on a monolayer scale. This could be a result of adhesive friction possibly promoted by thermo-chemical degradation.

4.9 CUTTING AND CHIPPING

4.9.1 Background

OTR and OOR tyres used in the construction industry and similar services are subject to tread damage commonly referred to as cutting and often chipping, both of which are a major problem for such tyres\(^9\). Cutting takes place when the tyre strikes a sharp object with such force that the surface is penetrated or cut. Chipping is the fragmentation of the damaged part of the tread usually after tearing\(^5\). It has been noted that properties important in cutting and chipping are tear, tensile strength and elongation modulus\(^9\). Moreover, energy absorption and abrasion resistance have also been seen as important factors. Cutting and chipping resistance is normally assessed by lengthy and costly field tests and the author is not aware of any standard laboratory test for these properties despite their importance for the tyre industry.

Beatty and Mikesch\(^9\) have recently developed a device for measuring cutting and chipping which has been claimed to be reproducible and correlates well with field tests. The device consists of a single asperity and a solid rubber disc. For the present work, a different device was developed based on a pneumatic miniature tyre and triasperity. The goal was to measure cutting and chipping resistance of the experimental tread vulcanisates and the effect, in particular, of the silica on such properties.
4.9.2 Developed test for cutting and chipping

The device was made using the concept of the miniature tyre machine. Figure 4.17 demonstrates the main parts of the simple device which consists of three metal asperities firmly clipped on the drum of the machine in an equidistant arrangement. Each asperity comprises a metal tongue with a wide, sharp end pointing in the direction of the drum rotation so that maximum cutting and surface damage are inflicted upon the running miniature tyre. The sharpness of each asperity, although it was arbitrarily chosen, was found to be adequate especially for comparative purposes. It must be noted, however, that several trials using miniature tyres obtained from the NR/ISAF control (mix no. 1 of Table 4.1) showed that the sharpness of the asperities was not affected by a short term test.

4.9.3 Experimental

The speed of the drum of the miniature tyre machine was set as in the case of the previous wear test. This allowed each tyre tested to make 360 contacts per minute with all three asperities. Miniature tyres were prepared from the three mixes of Table 4.1 by compression moulding to a cure state of $t_{95} + 5$ minutes. Every tyre tested was subjected to the same inflation pressure (1 kg/cm²), slip angle and position with regard to the rotary drum. Each miniature tyre was allowed to run for 20,000 revs under a temperature range of 90 - 100°C which was obtained as in section 4.8.2.3.3. This high temperature range was meant to represent a severe service condition. Later the weight loss and visual examination of the surface damage were taken as criteria for assessing the responses of each vulcanisate.

4.9.4 Results and discussion of the chipping and cutting test

Table 4.7 summarises the results obtained at the end of the test and Figure 17A shows the damage to the contacting part of the tread.
Fig. 4.17.: Schematic diagram of the developed cutting and chipping device.
Figure 4.17A: Extent of damage inflicted by the cut-chip device
The silica containing mixes showed a clear improvement (lower weight loss) of 20 - 27% over that of the ISAF control. The surface of the silica tread was less severely damaged with small-moderate resultant chips in the case of the mixes no. 2 and 3 compared to that of mix no. 1. The percentage improvement of the three vulcanisates correlated well with their tensile strength and the DIN abrasion index of the corresponding vulcanisates. Tear strength and elongation at break unexpectedly show no easily defined correlation, although the outstanding ability of silica in diverting the tear path must be a factor contributing to its superior cutting and chipping resistance. The deterioration of the tread surface and the appearance of tackiness on the tread of the NR/ISAF vulcanisate suggest some sort of fatigue to have taken place during the test in addition to cutting. On the other hand, the silica vulcanisates showed a dry surface with less sticky debris and chips which were finer in size.

Table 4.7 Cutting and chipping: characteristics and weight loss of the miniature tyres of the three vulcanisates of Table 4.1

<table>
<thead>
<tr>
<th>Mix no.</th>
<th>Tread surface and chips characteristics</th>
<th>Weight loss mg</th>
<th>% Improvement</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR/ISAF (mix no. 1)</td>
<td>Severely cut, shiny and sticky surface and large chips.</td>
<td>891</td>
<td>-</td>
</tr>
<tr>
<td>NR/silica/ISAF (mix no. 2)</td>
<td>Dry surface, shallow cuts through the tread with moderate chip size.</td>
<td>743</td>
<td>20</td>
</tr>
<tr>
<td>NR/silica/ISAF/SAPA (mix no. 3)</td>
<td>Dry surface partial tread damage, moderate and fine chips.</td>
<td>651</td>
<td>27</td>
</tr>
</tbody>
</table>
4.10 EQUILIBRIUM SWELLING: CRITERION FOR FILLER-RUBBER INTERACTION

4.10.1 Background

Kinetic theory predicts that the equilibrium stress in unfilled vulcanisates will be proportional to the number of network chains supporting the load\textsuperscript{77}. Therefore, the number of crosslinks, initial molecular weight and the number of entanglements are expected to decide the extent of the load. Incorporation of an active filler, however, decreases the number of load-bearing chains per unit volume of the polymer (due to volumetric effects), and it increases the equilibrium stress many fold. No conclusive opinion has been given to explain this effect\textsuperscript{78}, but there have been several theories proposed. Kraus\textsuperscript{80} has suggested that additional fixed points in the network contributed by the filler-rubber attachments may simply be regarded as additional crosslinks. The plausibility of this suggestion is strengthened by the nature and chemistry of a number of functional groups on the surface of carbon black. These groups are believed to interact and graft on the polymeric chains by primary valence bonds. However, a truly rigorous examination of this concept is not available. Many workers have applied the equilibrium swelling equation or some modifications of it for filled vulcanisates to estimate the filler-rubber interactions\textsuperscript{83}. Wolff et al\textsuperscript{49} have produced a series of rubber vulcanisates of a given formulation and of fixed filler quantity and which all had similar modulus values; if these are immersed in benzene, then those that show less swelling have higher crosslink densities. Such a situation does not really apply to the tread vulcanisates of Table 4.1 as, although they have the same filler loading, they require different curative levels and possess slightly different modull. Nevertheless, it was thought that swelling measurements could be utilised to cross-examine the validity of the assumption concerning the effectiveness of the coupling bonds of the silica on the physical properties of the present vulcanisates.
4.10.2 Experimental

Three specimens of each of the three mixes of Table 4.1 were obtained from vulcanised sheets cured to their $t_{95} + 5$ min. These were immersed in an excess of toluene at $40^\circ C$ for 24 hours and their weight change accurately measured. To account for the effect on swelling due to the differences in the level of sulphur in the control mix and that of the silica mixes (1.5 phr used in the former and 2.5 phr for the latter) and the coupling bonds two additional controls were selected for the study. These controls were,

A. NR/ISAF whose formulation is exactly the same as in mix no. 1 but contained 2.5 phr of sulphur.

B. NR/silica which is mix no. 5 in Table 3.3. This control was prepared by unoptimised mixing and contained 48 phr of VN₃ (with no TESPT and ISAF). Its use was meant to give a value for the effect of the optimised mixing cycle on the swelling of the bonded silica mixes.

These controls were similarly swollen by toluene as in the case of the previous three mixes of the present experiment.

4.10.3 Results and discussion of swelling

Figure 4.18 is a plot of the ratio of toluene/rubber versus the type of the vulcanisate tested. The figure clearly reveals that the optimised silica system produced a significantly reduced swelling compared to the ISAF controls. This reduction could not be explained on the basis of the slight variation in the modulus value of the tread vulcanisates. If the density of the sulphidic crosslinks of the five vulcanisates are closer to each other then the only possible explanation for the reduced swelling ratio of the TESPT-bonded silica vulcanisates is enhanced rubber-silica interactions. Evidence to strengthen this suggestion may emerge from two observations. Firstly, the unbonded silica (mix no. 5 in
LEGEND

Mix No. 1   NR / ISAF (control)
Mix No. 2   NR / Silica-TESPT-ISAF
Mix No. 3   NR / Silica-TESPT-SAPA ISAF
Mix No. 4   NR / ISAF (2.5 phr sulphur)
Mix No. 5   NR / Silica (unbonded)

Fig. 4.18: Comparative toluene swelling of the tread vulcanisates.
Figure 4.18) gave the highest swelling of all the five vulcanisates. Secondly, when the level of sulphur in the NR/ISAF control (mix no. 4 in the figure) was 25 phr, the swelling ratio of the vulcanisate remained higher than those of mixes no. 2 and 3 despite the fact that the former vulcanisate had a modulus of 12 MPa which was the highest among the five vulcanisates.

It is interesting to note that Rhener had attempted to correlate the physical properties on the one hand and crosslink density of the polysulphidic crosslinks and the number of rubber-filler attachments using a mathematical model. Good correlation was obtained with vulcanisate properties including abrasion resistance. In the present investigation swelling ratios are also plotted versus abrasion (weight loss) in Figure 4.19. A good correlation is also seen between the resistance to swelling and abrasion. This can be another support for the argument concerning the positive role of the coupling bond on abrasion resistance and other strength properties.

4.11 TEARING ENERGY T: CRITERION OF REINFORCEMENT AND ABRASION

4.11.1 Background

It has been generally accepted that the eventual failure of a rubber article normally starts with the development of a tear. For this reason, the strength of rubber is conventionally assessed by measuring its resistance to tearing. Tearing and abrasion are sometimes associated with each other in the literature. A valid correlation between a basic property like tear strength has always been considered to be advantageous to assess a complex process such as rubber abrasion. Unfortunately, however, the simple laboratory tear test does not always offer the required correlation. This lack of correlation may be attributed to the dependence of tear strength upon the detail of the force distribution at the tip of the tear and the diversion of its path (as was seen in section 3.7.3) and perhaps the mechanism of the abrasion process.
Fig. 4.19: Laboratory weight-loss vs toluene swelling of the tread vulcanisates of Table 4.1.
Champ et al\textsuperscript{81} tried to utilise the tearing energy concept rather than tear strength to correlate abrasion (as discussed in section 2.2.2.3). It must be remembered, however, that expression of tearing energies in terms of forces has been difficult and could be less certain, especially for reinforced vulcanisates\textsuperscript{85,86}. This is ascribed, in part, to the variation of the results obtained by the commonly used tear specimens and the difficulty in preparing some geometries. On the other hand, the complexity of forces at the tip of the growing tear and the inevitable deformation of the specimen during the process make it difficult to differentiate between the true work of tearing and that of deformation\textsuperscript{44,87}. Therefore, a rational evaluation of tearing energy itself as an intrinsic property regardless of the specimen must first be vindicated. Then this property could be utilised to assess the effect of a particular filler on reinforcement and abrasion. In this part of the chapter specially developed reinforced tear specimens were employed for this purpose; the subject is discussed at length because of its relevance and importance.

4.11.2 Theory

Rivlin and Thomas\textsuperscript{66} in order to circumvent the distribution of forces, adopted an approach used by Griffith\textsuperscript{69} to express tearing in terms of energies rather than forces. The Griffith theory, which was originally proposed for glass, suggests that if a crack was to grow in a material then the elastic energy released must exceed the surface energy, thus

$$- \frac{dw}{dc} > T \frac{dA}{dc} \quad \ldots \ldots \text{4.3}$$

where $w$ is the stored energy, $c$ is the crack length, $T$ is the tearing energy and $A$ is the area of the new surface.

According to this theory, then, a quasi-static propagation of a crack is a reversible process and the tearing energy can be defined as the amount of energy required to advance a crack by unit area. One of the problems encountered during the application of this theory for polymeric materials is that it is obeyed only by
certain of them whilst, for the majority of elastic vulcanised rubbers, the minimum energy requirement to create a tear is substantially higher than the surface energy. Rivlin and Thomas suggested that the reduction in the elastically stored energy due to crack propagation may be balanced by changes in energies other than those due to an increase in the surface energy. This has been assumed to be due to hysteretic losses in the area around the tip of the crack.

In formal mathematical terms this means that $T$ can be expressed as follows:

$$T = \left( \frac{\partial U}{\partial A} \right)_l \quad \ldots 4.4$$

where $U$ is the total energy stored in a specimen that contains the crack and $A$ is the fractured surface area of the crack. The partial derivative indicates that the specimen is held at a constant length $l$ and the external forces do no work. There should also be no interference due to chemical effects.

The theory of rupture of rubber suggests that for a sheet of vulcanised rubber of a uniform thickness $t$ containing a cut of length $c$ to be deformed by applying a displacement $t$ over part of its boundary, then for the crack to spread by an amount $dc$ a work of an amount $Tt$ must be done, hence

$$-(\frac{\partial W}{\partial c})_l = Tt \quad \ldots 4.5$$

Application of this theory was originally made on unfilled rubber vulcanisates by using different tear geometries, amongst which a reasonable agreement was found. Thus, tearing energy was claimed to be a fundamental property regardless of the shape of the geometry used for its evaluation. However, two geometries have become widely accepted. These are the trouser and pure shear. For the former the following equation has been proposed to calculate $T$ value

$$T = \frac{2F \lambda}{t} - wW \quad \ldots 4.6$$
where $F$ is the stretching force, $\lambda$ is the extension ratio, $w$ is the test piece width and $W_1$ is the strain energy density in the legs.

For the pure shear specimen, $T$ is calculated from the equation

$$T = W_2 h_0$$

where $h_0$ is the unstrained height of the specimen (see Figure 4.20(b) and $W_2$ is the strain energy per unit volume at the instant of tearing. It is significant to note that there has been a mixed reaction in the published literature regarding the applicability of the tear criterion for rubbers. While some workers applied the criterion without accounting for the viscous effect, (i.e. $T$ was considered to be equal to $2F/t$ for trouser tear); others have raised the limitations and peculiarities such as the shape of the tear, anisotropy at the tip and energy release\(^2\). Bartnev et al\(^7\) have gone as far as suggesting that the theory is inapplicable due to the part of the energy that is inevitably lost during tearing. For reinforced rubber, in particular, a substantial part of energy is usually lost due to hysteritic effect during deformation, especially at normal temperature. This adds to the difficulties that already exist. Moreover, reinforcing fillers encourage tear deviation to occur\(^2\). The occurrence of a knotty tear is contingent upon formation of aligned or oriented molecular structures at right angles to the tip of the tear. This complicates the situation and makes it difficult to know where to measure tearing energy.

Major deviation of the tear path has been previously halted by using thick rubber sheets scored by partially cutting them along the desired path or by using specially moulded test pieces with a central thin region through which the tear is propagated\(^3\). Some workers used rubber sheets bonded along their edges to parallel strips of steel foil\(^6\). These were considered not to be suitable for the present investigations. Accordingly, a reinforced version of the trouser and pure shear specimens was designed. It is believed that this version will give a greater degree of control in the estimation of tearing energies.
4.11.3 Modified tear specimens

Estimation of tearing energies from a standard tear test is invalid due to the dependence of breaking loads on both tearing energy and stiffness at the instant of tearing. The latter is known to be difficult to estimate. Moreover, trouser and pure shear specimens (reinforced and unreinforced) used in the past were seen as inconvenient as they either dissipated some of the applied energy or they were difficult to grip without slippage. The latter effect was experienced with highly tough rubbers. For this reason it was considered essential to develop suitable reproducible tear specimens for which the amount of energy dissipated other than crack propagation is minimal. These specimens will be used to serve two purposes which are

A. Examination of tearing energy as a fundamental property of rubber independent of the geometry of the specimen used for its evaluation.

B. Using the tearing energy criterion to measure the effect of the bonded silica relative to that of the ISAF and also to investigate the concept of the fracture mechanics which relates the abrasion properties of rubber to its tearing energy.

4.11.3.1 Method of specimen preparation

Two fabric reinforced specimens were designed to serve the aforementioned objectives. These are shown in Figure 4.20. They were prepared in two stages as follows:

A. Preparation of reinforcing structure:

This was made by impregnating a square woven cotton sheet of 0.5 mm thickness with the compound whose tearing energy was to be measured. The thickness of each sheet after impregnation was approximately 1 mm.
Fig. 4.20: Schematic diagrams of test pieces used during the experiment.
Fig. 4.21: Reinforced rubber sheets from which tear specimens were stamped
B. Preparation of the test composite:

Uncured rubber sheets about 1 mm thick were prepared from mixes no. 1 and 3 of Table 4.1, using a laboratory rubber mill. These sheets were cut to mould size (7x15 cm). The prepared rubberised fabric was sandwiched between two of these rubber sheets of the corresponding formulation in bi-layers as shown in Figure 4.21. Uniform rubber gaps (rubber zones free from reinforcement) were left between the reinforcing zones in the sheet composites as shown in the Figure. The laminated sheets were later compression moulded at 150°C for 15 mins. Trouser and pure shear specimens were then stamped from the relevant vulcanised laminated sheets. The height of the rubber gaps in these specimens is shown in Table 4.8. Each gap was used as a path for crack propagation. Notching of the test specimen was made with a very sharp vertical razor blade to the length (Co) shown in the table. Both the length and the direction of each notch were observed and measured using a low magnification light microscope.

4.11.3.2 Test procedure

All specimens were tested using a J.J. type tensile testing machine supplied with a heating box and temperature control. Each specimen was stretched under a constant rate of extension of 10 mm/min. Two temperatures, 20 and 100°C (inside temperature) were applied to evaluate the tearing energy.

The hot test was meant to discourage stress induced crystallization of NR and subsequent tear deviation and spontaneous tearing. Measurements of forces were taken when the crack had advanced by about 1 mm (following Gent and Kim) to avoid any catastrophic tearing; hence the load-over-all deformation curve could be measured for each specimen well beyond this point. Tearing energies were calculated from the relevant equation as will be shown later.
Table 4.8 Dimensions of the tear geometries used to measure tearing energy of the tread vulcanisates of Table 4.1

<table>
<thead>
<tr>
<th>Specimen geometry</th>
<th>Overall specimen dimensions (mm)</th>
<th>Unreinforced rubber gap dimensions (mm)</th>
<th>Precrack Length</th>
<th>Vulcanisate tested</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Length</td>
<td>Width</td>
<td>Thickness</td>
<td>Gap</td>
</tr>
<tr>
<td></td>
<td>l</td>
<td>w</td>
<td>t</td>
<td></td>
</tr>
<tr>
<td>Pure shear</td>
<td>55</td>
<td>28</td>
<td>2 - 3</td>
<td>3,4,5,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.5</td>
</tr>
<tr>
<td>Trouser tear</td>
<td>55</td>
<td>20</td>
<td>2 - 3</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Mixes nos. 1 and 3 of Table 4.1
Other dimensions of the test specimen were accurately measured (up to 0.01 mm). The pre-cracks were coated with silver ink from the inside to help observe their propagation which was observed by a travelling microscope.

4.11.3.3 Results and discussion

4.11.3.3.1 Effect of the height of the unreinforced rubber gap $ho$ on $T$ values of the pure shear specimen

Of relevance to the present objectives is to check if there is any dependence of the tearing energy values on the physical shape and detail of the rubber specimen used for its evaluation. Reinforced pure shear specimens obtained from mix. no 1 of Table 4.1 were selected. All these specimens had equal $C_0$ values of 2 mm but four different values of $ho$ which were 2, 3, 5, 7.5 mm. The values of $T$ are plotted versus $ho$ in Figure 4.22. The figure clearly demonstrates that $T$ values increase non-linearly with the increase in $ho$. This shows a clear difference from earlier reports as well as recently published data, suggesting that the specimen dimensions exert only slight effect on its fracture characteristics.

It is obvious that the higher $ho$ (5 mm) caused the share of energy dissipated as hysteresis during the specimen stretching to increase; while the lower value made the stress easily reach the crack boundaries and eventually the crack tip. This was indicated by the decrease in strain value (on the stress-strain curve) with decrease in $ho$. It is interesting to note that an attempt was made earlier to extrapolate the curve of the tearing energy versus specimen length (e.g. $ho$ in the present investigation) to a hypothetical zero value to avoid hysteresis in unreinforced specimens. Such an attempt, however, was less successful apparently due to the non-linearity of the curve. In conclusion, it was found that application of equation 4.7 gave different values for $T$ when $ho$ was variable. Therefore, comparison of the tearing energies of the present vulcanisates must be made at a constant $ho$ value if the pure shear specimen is to be used in its evaluation.
Fig. 4.22: Tearing energy vs $h_o$ at constant $c_o$ (2mm), NR/ISAF control

Fig. 4.23: Tearing energy vs $c_o$ at constant $h_o$ of (4mm), NR/ISAF control
4.11.3.3.2 Effect of the crack length Co on tearing energy of the vulcanisate

Figure 4.23 is a plot of the tearing energy at 100°C of mix no. 1 of Table 4.1 (pure shear specimen) versus Co at constant ho height of 4 mm. The curve of the tearing obtained is reminiscent of the preceding one between T and ho. The only difference is that T seemed to be less sensitive to the change in Co compared with that of ho. This suggestion was indicated by the finding that a double increase in Co caused the T value to rise by approximately 45% whereas a similar increase in ho caused a 65% increase. This decrease in T value due to the increase in Co was three times higher than what was considered by Rivlin and Thomas as an acceptable tolerance. Thus, it can be concluded that a valid estimation of tearing energy requires constant Co in all pure shear specimens tested. This conclusion agrees with a recent report by Lee112.

4.11.3.3.3 Characteristics of the reinforced trouser tear specimen

In contrast to the pure shear specimen, the trouser geometry develops a tear running in the direction of stretching, thus the reinforced specimen was assumed to be less problematic. The reinforced legs, in particular, were expected to absorb no or insignificant energy during the test. Therefore it was considered possible that T = 2F/t. However, little irreversible energy might still be wasted in stretching the reduced unreinforced gap (see Figure 4.20). For strictly comparable specimens this irreversible energy could be ignored. Thus, the height (ho) of this region was always kept constant (3 mm). This selection offered the advantage of comparing T values with the relevant ones obtained earlier by using the pure shear specimen that had the same gap height.

4.11.4 Comparison of T values of the tread vulcanisates

Having established the various limitations encountered during the evaluation of T it may now be possible to set out a comparison of
the effect of the VN3-rubber coupling bonds on tearing energy, with reference to the ISAF black, in the absence of substantial variations due to hysteresis effects. Mixes no. 1 and 3 of Table 4.1 were chosen for the test which was done at first by using the reinforced pure shear geometry. The test was conducted as before at both room temperature and 100°C. Measurement of tearing energy at room temperature was not possible due to the tendency of the test specimens towards spontaneous tearing, most likely because of the crystallization of NR which enhances the resistance of the pure shear specimen to cracking. However, the measurements at 100°C showed that the silica bonded vulcanisate (mix no. 3) had a T value 13% higher than that of the ISAF control (mix no. 1) (see Table 4.9). When the trouser tear specimens were used, the values of T for both the vulcanisates were very close at room temperature (see Table 4.10). Nevertheless, the silica bonded system showed an 11% improvement over the control when the test was conducted at 100°C.

The higher T values from the pure shear test suggest that the structural barrier becomes more effective in halting the advance of the tear tip in this particular geometry for both the vulcanisates. Two factors are believed to contribute to the effectiveness of such a barrier. The first is the expected orientation of the chain supporting the load in the direction of stretching; the second is the substantial energy dissipation that is expected to be absorbed due to the stress softening throughout the unreinforced gap. These two factors are not expected to be available to the trouser specimen to the same extent due to the lack of normal stretching of the area ahead of the tear as shown in Figure 4.24. Support for this argument would come from the fact that, unlike the trouser, the pure shear specimen gave spontaneous tearing at room temperature which required higher force. The contribution of the silica-rubber chemical bonds to the anisotropy ahead of the crack would make it more difficult to break-up the bonded network ahead compared with the generally more heat sensitive interaction of ISAF-rubber regime. It was also observed that the fractured surface of the silica vulcanisate had relatively rougher texture than
### Table 4.9 Tearing energy of the bonded (silica/ISAF) vulcanisate vs. the ISAF control—pure shear specimens

<table>
<thead>
<tr>
<th>Vulcanisate</th>
<th>Co</th>
<th>ho</th>
<th>Temp. °C</th>
<th>T(kJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR/ISAF</td>
<td>2</td>
<td>3</td>
<td>100</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3</td>
<td>20</td>
<td>Spontaneous tear</td>
</tr>
<tr>
<td>NR/silica-ISAF</td>
<td>2</td>
<td>3</td>
<td>100</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3</td>
<td>20</td>
<td>Spontaneous tear</td>
</tr>
</tbody>
</table>

### Table 4.10 Tearing energy of the bonded system versus the control (trouser)

<table>
<thead>
<tr>
<th>Vulcanisate</th>
<th>gap width at 20°C (mm)</th>
<th>T(kJm⁻²) at 20°C</th>
<th>T(kJm⁻²) at 100°C</th>
<th>threefold pre-stretched to 300% elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR/ISAF</td>
<td>3</td>
<td>40</td>
<td>22</td>
<td>36</td>
</tr>
<tr>
<td>NR/silica-ISAF</td>
<td>3</td>
<td>41</td>
<td>24</td>
<td>40</td>
</tr>
</tbody>
</table>
the ISAF control. This may indicate a small scale tear deviation (knotty tearing) which also could contribute to the increased T value.

Another advantage conferred by the coupling bonds was the higher resistance of the silica bonded vulcanisate to tearing after repeated extension.

This was observed when trouser tear specimens prepared from the ISAF and VN3/ISAF vulcanisates, with reinforcement in the leg region only, were tested. The elimination of the reinforcement from the rubber zone ahead of the crack was deliberately made to allow this zone to be pre-stretched in the direction of crack growth. Tearing energies were later measured at room temperature after threefold prestretching to 300% elongation. On limited crack growth these pre-stretched specimens were considered not to be much different from the fully reinforced trouser specimen as far as the hysteretic energy dissipation in the leg region was concerned. As Table 4.7 shows, the NR/ISAF control loses a noticeable part of its T value whereas the VN3/ISAF system is only slightly affected. This indicates that the latter system could be superior during substantial stretching such as the one encountered during abrasion.

4.12 CORRELATION BETWEEN TEARING ENERGY AND ABRASION RESISTANCE

Mixes no. 1 and 3 of Table 4.1 were selected to investigate any possible correlation between the hot tearing energy and the abrasion resistance indices as measured by the three abrasion experiments discussed in section 4.8. Table 4.11 features such a correlation. Although each of the vulcanisates had different abrasion indices depending on the type of abrasion test, it can be seen that the improvement in the hot tearing energy of the silica/ISAF bonded system coincides reasonably with the improvement in its abrasion indices. The closest relationship is seen in the case of the miniature tyre possibly due to the fact that this test was conducted at a temperature nearer to the one at which the tearing energy was measured. This was thought not to be a fully conclusive correlation but indicates the effect of tearing as one of the main factors that influence abrasion.
ENERGY LOSS:
i) Fracture
ii) Extension
iii) Hysteresis
iv) Anisotropy

Fig. 4.24: Effect of the mode of stretching on energy dissipation
Table 4.11 Correlation between the hot tearing energy and abrasion resistance indices of mixes no. 1 and 3 of Table 4.1

<table>
<thead>
<tr>
<th>Property</th>
<th>NR/ISAF control mix no.1</th>
<th>NR silica/ISAF mix no.3</th>
<th>% improvement</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIN abrasion index</td>
<td>100</td>
<td>122</td>
<td>22</td>
</tr>
<tr>
<td>Akron abrasion index</td>
<td>100</td>
<td>161</td>
<td>61</td>
</tr>
<tr>
<td>Miniature tyre weight loss mg</td>
<td>100</td>
<td>115</td>
<td>15</td>
</tr>
<tr>
<td>T(kJm⁻² at 100°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- pure shear</td>
<td>30</td>
<td>34</td>
<td>11</td>
</tr>
<tr>
<td>- trouser</td>
<td>22</td>
<td>24</td>
<td>9</td>
</tr>
</tbody>
</table>

4.13 AGEING CHARACTERISTICS

Heat resistance of any tread rubber acquires a vital role especially for truck tyre treads where severe service conditions for prolonged periods are commonplace. Subjection to excessive heat promotes, among other things, rubber oxidation. Therefore, any compounding development study should pay this point careful consideration. While NR is commonly used as the major polymer for the truck tyre industry, its ageing characteristics are known to be lower than synthetic counterparts. These characteristics are not normally recognised during heavy duty services, but rather during mild wear perhaps similar to the one encountered during the miniature tyre test, where fatigue is the dominant mechanism. To alleviate elastomers’ ageing difficulties a variety of methods are employed, such as the use of higher quantities of some powerful antioxidants, a more ageing resistant curing system and polymer blends. However, the effect of reinforcing fillers on ageing
properties has led to conflicting conclusions\textsuperscript{61}. Several factors have been reported to contribute to this conflict between describing carbon black as an antioxidant on the one hand, and as an oxidation accelerator on the other\textsuperscript{97,98}.

Less controversial is the role of silica on oxidation and heat resistance of its vulcanisates and there has been sufficient evidence in the literature to support the positive effect of this material\textsuperscript{56}. Some workers attribute this to the reduction of the polymer conjugation by the coupling bonds, while others suggest that silica adsorbs oxygen on its surface\textsuperscript{51}. It should be noted here that a direct comparison between silica and ISAF is not possible in the present tread vulcanisates (Table 4.1), as the latter was used in conjunction with the former. Nevertheless, an investigation of the ageing properties of the three tread vulcanisates was thought complementary to other properties. It may also serve to establish the effect on the ageing properties by SAPA.

Therefore, specimens obtained from the three vulcanisates of Table 4.1 were heat aged in a hot oven for 3 days at 100\textdegree C (BS 903:A19) and the results are given in Table 4.12. All three vulcanisates underwent a significant reduction in properties. This is exemplified by up to 30\% reduction in tensile strength and elongation. The Table also clearly shows that the gain obtained by the silica system in tear, abrasion resistance and elongation at break, is nearly lost after the ageing. One of the possible reasons for that may lie in the presence of a higher level of sulphur in the silica vulcanisates. This raised the after-ageing modulus to an unfavourable level. It is worthwhile to suggest, however, that the retention of the properties of all three vulcanisates can still be considered as high for NR vulcanisates.
Table 4.12 Hot air ageing properties of the tread vulcanisate (3 days at 100°C)

<table>
<thead>
<tr>
<th>Properties</th>
<th>ISAF (48) mix no. 1</th>
<th>Silica/ISAF 24 phr each mix no. 2</th>
<th>Silica 24, ISAF 24, SAPA 1.5 mix no. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>3 days</td>
<td>0</td>
</tr>
<tr>
<td>100% Modulus MPa</td>
<td>1.6</td>
<td>2.4</td>
<td>2.5</td>
</tr>
<tr>
<td>% from original</td>
<td>-</td>
<td>150</td>
<td>-</td>
</tr>
<tr>
<td>300% Modulus MPa</td>
<td>9.2</td>
<td>12.4</td>
<td>11.6</td>
</tr>
<tr>
<td>% from original</td>
<td>-</td>
<td>135</td>
<td>-</td>
</tr>
<tr>
<td>Tensile strength MPa</td>
<td>25</td>
<td>18.4</td>
<td>30.2</td>
</tr>
<tr>
<td>% from original</td>
<td>-</td>
<td>74</td>
<td>-</td>
</tr>
<tr>
<td>Ultimate elongation %</td>
<td>600</td>
<td>468</td>
<td>580</td>
</tr>
<tr>
<td>% from original</td>
<td>-</td>
<td>78</td>
<td>-</td>
</tr>
<tr>
<td>Crescent tear strength KNm</td>
<td>127</td>
<td>94</td>
<td>145</td>
</tr>
<tr>
<td>% from original</td>
<td>-</td>
<td>74</td>
<td>-</td>
</tr>
<tr>
<td>Hardness IRHD</td>
<td>60</td>
<td>72</td>
<td>64</td>
</tr>
<tr>
<td>% from original</td>
<td>-</td>
<td>120</td>
<td>-</td>
</tr>
<tr>
<td>DIN volume loss (\text{mm}^3)</td>
<td>161</td>
<td>225</td>
<td>144</td>
</tr>
<tr>
<td>% from original</td>
<td>-</td>
<td>140</td>
<td>-</td>
</tr>
</tbody>
</table>
4.14 CONCLUSIONS

The following can be concluded from the results obtained in this chapter.

A. The optimal mixing cycle (hot mixing, delayed addition of ZnO, inclusion of SAPA) has shown a profound effect on the processing properties of the silica mixes making them almost similar to those of the typical NR/ISAF control. This is evidenced by the improvement of dispersion and enhancement of the state of cure at curative levels much lower than the conventional silica needs, with no sacrifice in processing properties or processing safety.

B. The normally inferior physical properties of silica (compared with carbon blacks of identical particle size) have become superior when the optimised mixing cycle, TESPT and the moderate level of curative, are used. The effectiveness of the coupling bonds on reinforcement has been evidenced by the higher resistance to swelling, higher tear and tensile strength and abrasion resistance of the silica mixes compared with the ISAF control.

C. The developed miniature tyre technique has given a promising model for assessment of fatigue abrasion under conditions that could be closer to those of on-road driving of a full scale tyre. Also, the effect of temperature and hysteresis could be better represented as compared to the other standard tests. The development of the chipping test and the good correlation with the other physical properties is seen as encouraging in giving a useful and consistent correlation with some of the physical properties.
D. In attempting to find a valid correlation between tearing energy and abrasion, the two developed reinforced specimens (pure shear and trouser) have shown large variations in their T values in favour of the pure shear specimen. This is in dispute with the prediction of the hypothesis of the theory of the tear criterion. However, a comparison of the improvement in the T values of the silica/ISAF filled rubber (tested at 100°C) has shown reasonable consistency with the improvement in the wear index as predicted by the theory of fracture mechanics when tear specimens are identical.

E. The gain in strength properties by the incorporation of silica over the whole ISAF control reduces or diminishes after the hot air ageing suggesting that a further study of the ageing characteristics may be beneficial.
CHAPTER 5

EFFECT OF CIS-POLYBUTADIENE ON THE ABRASION RESISTANCE OF THE SILICA/ISAF REINFORCED TREAD VULCANISATES

5.1 INTRODUCTION

In the preceding chapter cumulative evidence emerged to support the superiority of the silica bonded system over the ISAF control, in terms of the principal properties that are commonly regarded as prerequisites for severe tread service. NR, however, is known to lose ground to its synthetic counterparts when severity becomes moderate and the tensile/tear mechanism changes into a predominantly fatigue one. This has been attributed to the reversion characteristics of the NR vulcanisates, particularly in the early stages of tyre life where the tread surface has been subjected to the greatest degree of overcure and to thermal-oxidative degradation of the crosslinked network. Polybutadiene (BR-cis) rubber is known to have excellent wear and reversion resistance. It has, therefore, become widely used in the tyre industry, mainly as a second polymer with both SBR and NR, and is known to confer a synergistic effect upon some of the properties of the blend. These properties are exemplified by the unique resistance to abrasion and fatigue and crack growth. Moreover, its excellent influence on dynamic properties and rolling resistance has also been reported. BR, on the other hand, confers undesirable processing properties when used at high loadings, such as poor milling, reduced green strength and rough extrusion appearance compared to an NR mix of the same viscosity. Other reported disadvantages are lower strength properties and poor road holding compared to NR and SBR equivalents.
5.2 OBJECTIVES

Present objectives are two-fold. Firstly, to examine the effect of the optimised silica system on abrasion resistance and other properties when high cis BR incrementally replaces NR. Secondly, to investigate the possible mechanisms by which these rubbers abrade when this polymer is present in the formulation, compared to the NR control.

5.3 EXPERIMENTAL

Five mixes were prepared in which the level of BR was gradually increased at the cost of NR, keeping the silica-TESPT-ISAF system and the other compounding ingredients unchanged. The formulae can be seen in Table 5.1 and the mixing cycle and conditions in Table 5.2. Equal mixing time was also used to judge the rheological properties. The test procedures (unless otherwise stated) were similar to those used in Chapter 4.

5.4 RESULTS AND DISCUSSION

Table 5.3 features some of the results obtained. These reveal that the increased level of BR shows the following effects on processing and curing properties.

5.4.1 Influence on processing properties

5.4.1.1 Effect on viscosity

NR-BR blends produced, as expected, higher Mooney viscosity than the control. Figure 5.1 shows that such an increase is low at lower BR levels but increases significantly at relatively higher levels. This may be ascribed to the increased resistance of this polymer to breakdown under mixing and milling, even over relatively prolonged times\(^1\). However, a level of 70 NR/30BR produced a viscosity which nevertheless would be considered quite acceptable for practical processing.
<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Type</th>
<th>Proportion phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>SMR20</td>
<td>90, 80, 70, 60, 50</td>
</tr>
<tr>
<td>BR*</td>
<td>Euro Cls</td>
<td>10, 20, 30, 40, 50</td>
</tr>
<tr>
<td>N220</td>
<td>Vulcan 6</td>
<td>24</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Ultrasil VN3</td>
<td>24</td>
</tr>
<tr>
<td>TESPT</td>
<td>Si69</td>
<td>3</td>
</tr>
<tr>
<td>Santoflex IP</td>
<td>IPPD</td>
<td>1.5</td>
</tr>
<tr>
<td>Flectol H</td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>Paraffinic wax</td>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td>Stearic acid</td>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td>Highly aromatic oil</td>
<td></td>
<td>7.0</td>
</tr>
<tr>
<td>M.B.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td></td>
<td>4.0</td>
</tr>
<tr>
<td>Sulphur</td>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td>MBS</td>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td>DPG</td>
<td></td>
<td>0.5</td>
</tr>
</tbody>
</table>

* Cls content 92-93%
Table 5.2 Banbury mixing cycle found to be optimum for NR-BR blends

**A. Mixing cycle for the first stage**

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>SMR20 (raw) BR ram down</td>
</tr>
<tr>
<td>2.0</td>
<td>SiO$_2$, Si69 r.d.-*</td>
</tr>
<tr>
<td>3.0</td>
<td>ISAF, oil r.d.</td>
</tr>
<tr>
<td>4.0</td>
<td>Chemicals (excluding ZnO) r.d.</td>
</tr>
<tr>
<td>5.0</td>
<td>Clean down</td>
</tr>
<tr>
<td>6.5 - 7.0</td>
<td>Dump</td>
</tr>
</tbody>
</table>

Mixing conditions: rotor speed 80 rpm; ram pressure 40 psi; fill factor 0.8; cooling water temperature 60°C, dump temperature 140-150°C. Masterbatches sheeted off the mill about 3 mm thick and stored for 24 hours for the next step.

**B. Mixing cycle for the second stage**

<table>
<thead>
<tr>
<th>Time</th>
<th>Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>MB, ZnO</td>
</tr>
<tr>
<td>0.5</td>
<td>Sulphur, MBS, DPG</td>
</tr>
<tr>
<td>2.0</td>
<td>Dump</td>
</tr>
</tbody>
</table>

Mixing conditions: rotor speed 40 rpm; cooling water temperature 40°C; dump temperature 110-120°C. All rubbers were milled for 3 minutes and sheeted off 3 mm thick.

* r.d. = ram down
5.4.1.2 Mill banding and release

BR, when used in a blend with NR, is known to decrease the green tack of the latter, consequently the mill banding becomes poorer as the level is increased. In the present work this effect was less significant even at a level of 50/50 and a BR level of 30 phr did not really worsen mill banding. This result may be attributed to the presence of the silica-TESPT system that may compensate for poor mill adhesion and the tendency of the silica mix towards sticking.

5.4.2 Influence on Monsanto ODR properties

The increased level of BR gave a small increase in the time to scorch over that of the control (as shown in Table 5.3). It also showed a more pronounced effect on increasing $t_{95}$ values. Moreover, the increased resistance to degradation conferred by BR is distinct and interesting. This is illustrated in Figure 5.2, which shows that a level as low as 10 phr of BR has reduced the reversion rate to half that of the control, when the Monsanto rheometric curing was extended to 60 mins at 160°C. Reversion, (a term applied to the loss of network structure by non-oxidative thermal ageing), is usually associated with sulphur cured NR vulcanisates. The enhancement of reversion resistance has been reported as showing a remarkable effect on abrasion resistance especially under fatigue conditions. This is because degradation causes a drastic effect on wear at the top layer level, where local mechanical fracture process dominates the rubber surface$^{33,102}$. In this chapter this effect will be discussed in more detail.
Fig. 5.1: Mooney viscosity ML (1 + 4) $100^\circ$C of the tread vulcaization.

Fig. 5.2: Effect of BR level on reversion rate under anaerobic conditions (Rheometer Monsanto 1hr at $160^\circ$C)
Table 5.3 Compound and vulcanisate properties of truck tyre tread rubbers

<table>
<thead>
<tr>
<th>Properties</th>
<th>Control Mix 100 phr NR</th>
<th>NR90</th>
<th>NR80</th>
<th>NR70</th>
<th>NR60</th>
<th>NR50</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compound Properties:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ML (1+4) 100°C</td>
<td>46</td>
<td>47</td>
<td>51</td>
<td>55</td>
<td>62</td>
<td>66</td>
</tr>
<tr>
<td>ODR Properties 160°C:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scorch time $t_2$ (min)</td>
<td>2.7</td>
<td>2.7</td>
<td>2.7</td>
<td>2.8</td>
<td>2.8</td>
<td>3</td>
</tr>
<tr>
<td>$T_95$ (min)</td>
<td>5.4</td>
<td>7.7</td>
<td>7.4</td>
<td>7.5</td>
<td>7.5</td>
<td>8.1</td>
</tr>
<tr>
<td>Reversion rate % (60min)</td>
<td>17</td>
<td>8.7</td>
<td>8.7</td>
<td>7.5</td>
<td>7.4</td>
<td>6</td>
</tr>
<tr>
<td><strong>Curing Properties 160°C:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300% Modulus MPa</td>
<td>11.6</td>
<td>10.1</td>
<td>10.3</td>
<td>10.4</td>
<td>10.7</td>
<td>10.7</td>
</tr>
<tr>
<td>Tensile strength MPa</td>
<td>30.2</td>
<td>25</td>
<td>21</td>
<td>20.7</td>
<td>19.6</td>
<td>18.5</td>
</tr>
<tr>
<td>Ultimate elongation %</td>
<td>580</td>
<td>525</td>
<td>505</td>
<td>500</td>
<td>490</td>
<td>460</td>
</tr>
<tr>
<td>Hardness IRHD</td>
<td>64</td>
<td>64</td>
<td>65</td>
<td>66</td>
<td>67</td>
<td>67</td>
</tr>
<tr>
<td>Crescent tear kN m$^{-1}$</td>
<td>145</td>
<td>133</td>
<td>115</td>
<td>109</td>
<td>98</td>
<td>85</td>
</tr>
<tr>
<td>Rebound resilience %</td>
<td>58</td>
<td>62</td>
<td>62.5</td>
<td>62</td>
<td>63</td>
<td>62</td>
</tr>
<tr>
<td>Compression set at 25% strain and 20°C</td>
<td>13.6</td>
<td>9.2</td>
<td>8.5</td>
<td>7.8</td>
<td>5.6</td>
<td>5.1</td>
</tr>
<tr>
<td>De Mattia flex cracking* 100 KC</td>
<td>-</td>
<td>5</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>DIN abrader index</td>
<td>100</td>
<td>119</td>
<td>138</td>
<td>147</td>
<td>145</td>
<td>141</td>
</tr>
<tr>
<td>Akron abrasion index</td>
<td>-</td>
<td>100</td>
<td>108</td>
<td>120</td>
<td>150</td>
<td>157</td>
</tr>
</tbody>
</table>

* Graduated from 1-9 the higher the grade the higher the crack length.
5.4.3 Influence on mechanical properties

The increased substitution of NR caused a clear decline in tensile and tear strength of the vulcanisates (as illustrated in Figure 5.3). This expected trend is ascribed to the lower molecular weight of BR and its non-crystallinity which results in a reduction in the resistance of the polymeric network to the applied stress. The inclusion of BIR also shows an increase in hardness of the blended vulcanisates and a reduction in elongation at break. In contrast to these disadvantages, Table 5.3 shows a distinct and steady increase in the DIN and Akron abrasion indices up to an NR/BR level of 70/30 before they start to level off. It is difficult to explain this paradoxical effect in terms of the widely accepted correlation between abrasion and strength. It was concluded that there might have been some hidden causes that contributed to this discrepancy. Surprisingly, while the industry has enjoyed the advantages of the rather cheap BR, little has been published as to why this polymer confers high abrasion resistance. It was therefore decided to investigate the role of other factors such as viscoelasticity and fatigue and their relationship with wear.

5.5 EFFECT OF VISCOELASTIC PROPERTIES

5.5.1 Background

Zapp\textsuperscript{22}, Ecker\textsuperscript{14} and others\textsuperscript{12} proved with their theoretical and experimental tests the importance of viscoelastic behaviour as a characteristic property of abrasion. From their results a series of relationships was established between abrasion and friction and other viscoelastic properties. Most of these relationships have been reviewed in Chapter 2. On the other hand, Schallamach's theoretical deduction and practical tests led him to conclude that abrasion is a function of resilience (Rd), slip, stiffness E and real contact surface S, therefore

\[ W = F(Rd, \mu, E, S) \]

.....5.1
Fig. 5.3: Relation between the NR/BR blend proportions and some selected physical properties of the tread vulcanizates.
However, such generalised ideas are difficult to interpret unless they are broken down and studied individually. It was decided to verify the effect of some of these components with reference to abrasion resistance by using the standard and especially developed techniques to simplify some of the concepts.

5.5.2 Relationship between rubber friction and its abrasion resistance

Friction can be defined as the tangential force resisting motion when one surface is displaced relative to another under the influence of an external force. It is generally known that no rubber abrasion can take place without friction although the opposite on certain very smooth surfaces might be true. Therefore, the relationship between rubber friction and its abrasion resistance has long been studied but the detailed effect of friction mechanisms as they are operative in abrasion is not well documented.

Early descriptions of rubber sliding on rough tracks assumed that friction originates from adhesion in the true area of contact. This neglects, however, the elastic deformation losses occurring periodically on the rubber surface as rubber asperities plough over it.

A much better understanding of its role was achieved in the 1940's as the decrease in the coefficient of friction (μ) with speed, surface smoothness and the increase with surface roughness was well recognised. Later it was shown in the 1960's that μ is a property related to viscoelastic properties of rubber as friction itself. Hence on a dry rough track, both adhesion and deformation process can contribute to grip. Rubber abrasion has been reported to be a consequence of sliding friction and not the adhesive type with the latter is responsible for moving a vehicle forward.
It is significant to note that the magnitude of $\mu$ for a rubber vulcanisate is mainly determined by the elastomer itself, despite its sensitivity to the presence of various ingredients in the formulation.

Therefore, the elastomer must be selected to give sufficiently high $\mu$ values to control driving and braking forces safely with an inevitable sacrifice in abrasion properties. Hence, for abrasion studies the investigation of frictional properties is of vital importance.

5.5.2.1 Rubber friction measurements

Although many special instruments have been described in the literature, very few reliable friction tests have been standardised. Perhaps the most common rubber friction apparatus is the British Skid Tester (ASTM E303-74). This tester, which was originally developed by the Road Research Laboratory as a pavement tester, is known to correlate well with tyre traction giving a simple but useful quantitative measurement. This could be because it allows both the friction components (adhesive and hysteritic) to contribute compared, for instance, to the simple sliding measurement as evaluated by using tensile testing machines.

The specimen normally used for the tester is a block of rubber of carefully controlled composition, attached to the base of the pendulum arm which contacts the opposing surface (demonstrated in Figure 5.4). If the pendulum is made to swing, then its weighted head is free to move longitudinally so that the swing amplitude is determined by the friction against the pavement surface. This provides a skid resistance number that increases with the increase in the friction between the rubber under test and the track surface.

Giles and Sabey and later Brown have reported that the skid number can be approximately related to $\mu$ by

$$\text{Skid resistance} = \frac{330 \mu}{3 + \mu} \quad \ldots \ldots 5.2$$
Fig. 5.4: British skid tester with the slider\textsuperscript{121}
It is significant that measurements obtained with the skid tester have been shown, in several extensive works, to afford sufficient success to correlate with the performance of a vehicle with patterned tyres braking with locked wheel on a wet road at a speed of 50 km/hr\textsuperscript{121}. It was made clear, however, that such a correlation was sensitive to test temperature, rubber hardness and resilience. For the purposes of the present work a modified version of the skid tester was considered to be more suitable for the investigation of the relationship between friction and abrasion.

5.5.2.2 Skid tester modification

It was thought advantageous to reverse the mechanism by which the tester works. In the unmodified version, the flat rubber block can be used to slide over a curved or a flat surface to simulate certain conditions on the road (mainly the effect of stone polishing on skid characteristics of vehicles). In the modified version, this mechanism was altered. The slider that withholds the rubber block was replaced by a chrome plated rectangular steel block heavier in weight but similar in dimensions (3.2 x 2.5 x 1 cm). The curved stone surface was replaced by a smooth rubber surface of similar geometry (see Figure 5.5). The smooth surfaces of both the slider and the rubber block were intended to provide a high degree of friction under dry conditions, without significant interference from abrasion. This idea is based on the fact that a smooth rubber provides the maximum traction under dry conditions due to the increased area of contact. To simulate rough friction sliding under severe conditions (i.e. when a car brakes on a harsh road) a piece of abrasive paper (taken from a standard DIN abrasive) was used to strike the rubber block. This was done by clipping the paper firmly to the bottom of the slider, as shown in Figure 5.5. The main object behind these modifications was to provide comparative conditions to investigate the role of the increased level of BR on frictional forces and other viscoelastic properties and to examine the relation between these and abrasion resistance.
(a) Smooth metal slider

(b) Modified metal slider with a piece of DIN abrasive paper clipped to its contacting surface.

(c) Modified rubber specimen.

Fig. 5.5: Schematic diagrams of the slider and the rubber specimen used for evaluating friction.
5.5.2.3 Experimental

Rubber blocks required for the test were obtained from the five mixes of Table 5.1 and the control by vulcanisation to \( t_{95} + 10 \) mins using a special mould. The thickness of each block was 13.0 mm \( \pm 2 \), i.e. approximately twice that used in the standard test. The increased block thickness offers the advantage of being closer to the average thickness of a car tyre tread rubber. The test was conducted at room temperature under dry conditions. The average of five consistent readings was taken omitting the first three.

5.5.2.4 Verification of experimental results

Several reports\(^{124,129}\) have noted the sensitivity of the skid number to temperature, rubber hardness and resilience. It was, therefore, borne in mind that the less the variables the better the result. Fortunately, the hardness of the vulcanisates was similar, but there was some variation in the resilience values especially for the first three mixes. Figure 5.6 plots the tread composition, dry skid resistance (D.S.R.) and rebound resilience. The low (\( \mu \)) conferring polymer (BR) is seen as causing a steady decrease in the initially high skid resistance, as measured by the energy loss due to the dynamic pendulum impact over the rubber surface. The effect of the blend, however, was more distinct when the rough slider was used. The rough skidding of the slider differs from the smooth one as the former creates tearing and abrasion as well as friction on the surface of the rubber block. This means that the total\(^{124}\) friction force, \( F_t = F_{\text{adhesion}} + F_{\text{hysteresis}} + F_{\text{tearing}} + F_{\text{abrasion}} \) whereas \( F_{\text{abrasion}} + F_{\text{tearing}} \) might be low when the smooth slider is used. As energy dissipation is essential for frictional forces to develop, highly resilient materials are expected to show lower frictional forces. However, the rôle of BR on the skid resistance and rebound resilience was not fully conclusive: while the increase of the BR level in the vulcanisates is concurrent with a steady decrease in DSR, the rebound resilience curve also increases but then levels off at NR/BR proportion.
of 70/30. It is obvious from Figure 5.6 that higher BR levels cause a steady decrease in value at constant rebound resilience. The latter observation is not consistent with an observation by Ecker\textsuperscript{14}, who showed a linear inverse relationship between $\mu$ and resilience. It was concluded that there might be other factors involved in the relationship existed between BR level and skid resistance properties and these will be the subject of investigation in section 5.6.

5.5.2.5 Relationship between frictional properties and abrasion

The preceding section has shown that the enhancement of dynamic properties with the increased level of BR is the main reason behind the reduced frictional characteristics of the tread vulcanisates. Now examination of possible links between these properties and abrasion resistance is timely. Two abrasion techniques were chosen for this purpose. These were the DIN abrader which confers severe frictional forces and the Akron abrader which confers moderate frictional ones.

5.5.2.6 Correlation with the DIN index

Figure 5.7 demonstrates the effect of BR on both D.S.R. (rough slider) and the DIN abrasion index. Here the steady reduction in D.S.R. is concurrent with a steady increase in the DIN index up to a level of NR/BR of 70/30 before the latter starts to level off. A possible explanation for such behaviour may be the way by which rubber is removed on this machine. Two mechanisms are believed to be predominant. These are tensile tearing and frictional rubbing. At lower BR proportions the abrasion resistance of the tread vulcanisates gains from the reduction in frictional force without much sacrifice in the tensile tearing resistance. However, when the reduction in the frictional forces becomes insufficient to balance the reduction in strength, the DIN abrasion index decreases. The above explanation agrees with Ychiyama's\textsuperscript{23} ideas; he has recently suggested that the abrasion on abrasive papers does not only depend on frictional energy dissipation (see equation 2.3), but some other factors must be taken into consideration for its quantification.
Fig. 5.6: Rebound resilience vs D.S.R. on rough and smooth slider.

Fig. 5.7: Relation between DIN abrasion and frictional properties (D.S.R.) (rough slider)
It can be concluded that a level of NR/BR beyond 70/30 can be disadvantageous for abrasive wear as well as skid resistance. This means that a level of BR of 20-30 phr offers the best compromise between abrasion resistance and other essential properties including skid resistance.

5.5.2.7 Correlation with the Akron index

Figure 5.8 shows the correlation between the Akron index and the D.S.R. (smooth slider). A better correlation is seen compared with the one obtained from the DIN abrasion. The reason behind such an effect is believed to be primarily attributed to the coefficient of friction. To ease the task of interpretation, reference is made to an earlier work by Evstratov and co-workers. They established a relationship between the type and intensity of wear and the coefficient of friction. Their experimental findings show that there is a critical $\mu$ value which divides the low intensity fatigue wear from that of abrasive wear. Based on this, Moore later suggested that the relationship between the coefficient of friction and abrasion follows a pattern similar to the one shown in Figure 5.9. As the inclusion of high cis BR with NR causes a steady reduction of $\mu$ with the increase of the former, it can be assumed that this inclusion shifts the abrasion mechanism towards the fatigue side. Whilst this shift may not be enough to outweigh the reduction in strength on the abrasive paper when the level of BR is high (i.e. more than 30 phr) the situation on the Akron abrader differs. The smoother abradant offers substantial reduction in tensile tearing and cutting diminishes. Therefore, the role of strength recedes to that of friction.

In the fatigue abrasion region a slight decrease in the value of $\mu$ (such as the one produced by the inclusion of 10 phr of BR with NR) could be of far more consequence. In fact, earlier work shows that a 10% reduction in $\mu$ value could result in 25% increase in abrasion resistance.
Fig. 5.8: Relationship between Energy index of abrasion and D.S.R.

Low frictional forces due to adhesion + hysteresis + microscale tearing

High frictional forces due to adhesion + hysteresis + cutting

Fig. 5.9: Relationship between Energy index of abrasion and $\mu^{(9)}$. 

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5.6 EFFECT OF DYNAMIC PROPERTIES

5.6.1 Introduction

The term dynamic properties, as applied to elastomers, refers to the response to periodic transient forces which do not cause failure or appreciable fatigue. They are altered tremendously by the addition of a filler, plasticisers and crosslink density and knowledge of them is required for designing rubber compounds. When a rubber specimen is subjected to a uniform sinusoidal shear deformation, the stress can be resolved into two sinusoidal components; the elastic stress (storage modulus) $E'$, which is in phase with the strain and the viscous stress (loss modulus) $E''$ which is exactly out of phase. The loss tangent ($\tan \delta = E'' / E'$) represents the fraction of mechanical energy input converted into heat and proportional to hysteresis under constant energy condition. Therefore, the loss tangent $\tan \delta$ is directly related to resilience since both measure the loss of energy under conditions of definite energy input. Also, there have been several reports of its good correlation with skid resistance, rolling resistance and heat build-up when its values are measured at temperatures representative of service conditions of tyres (i.e. 80°C for rolling resistance and heat build-up and sub-zero for ice friction etc.). Friction and abrasion properties of tyres are expected to be substantially affected by dynamic properties of both the tyre and tread rubber. The latter is the subject of the following investigations.

5.6.2 Experimental

A Du Pont DMA machine was used for evaluation of the properties. The instrument is designed to measure dynamic properties under definite conditions of amplitude/frequency and temperature. Rubber specimens were stamped from cured sheets obtained from the five mixes of Table 5.1. The dimensions of each specimen were approximately (10 x 25 x 2.5 mm).
Grip to grip distance was kept at about 1 cm during the test. Care was taken not to subject the specimens to unnecessary deformation that might affect the results. The frequency and amplitude selected were 1 Hz and 0.4 mm respectively. This was done to avoid any damage to the reinforcing network that could complicate the interpretation of the role of the elastomer blends on dynamic properties. The temperature range selected was -80°C to 25°C at a rate of heating of 5°C/min.

Data concerning dynamic properties at particular time limits can be obtained through on line computer.

5.6.3 Results

A typical DMA graph is shown in Figure 5.10. Figure 5.11 displays the room temperature values of tan δ plotted versus the correspondent D.S.R. figures as evaluated on the portable skid tester (smooth specimens), for four tread vulcanisates. These are the control plus mixes 1, 3 and 5 of Table 5.1. The Figure shows that a replacement of a fraction of NR as low as 10 phr by BR results in a substantial decrease in the value of tan δ.

This reduction in tan δ is also concurrent with a similar reduction of the D.S.R. curve suggesting that the inclusion of BR similarly affects both properties. The same trend continues but the two curves crossover at the level of 70 NR/30 BR and clearly diverge when the levels of NR and BR are equal in the formulation. This indicates that a high level of BR, while reducing frictional forces offers no improvement on tan δ. Figure 5.12 is a plot between the tan δ values at room temperature and the abrasion indices of both the DIN and the Akron abrader obtained earlier for the tread vulcanisates. The use of a lower level of BR with NR gave an advantageous gain in the abrasion indices of both the two abraders which was unusually consistent with the reduction in tan δ. A crossover between the tan δ and the abrasion indices curves occurs at a level of 70 NR/30 BR which is reminiscent of that between D.S.R. and tan δ. The curve, however, shows that when
Fig. 5.10 A typical DMA graph
Fig. 5.11. Relationship between tan δ and D.S.R. of the tread vulcanisates.

Fig. 5.12. Relationship between tan δ and abrasion index of both DIN and Akron abraders.
the level of BR goes up to 50 phr, the abrasion index on the Akron abrader becomes much higher than that of the same vulcanisate on the DIN abrader possibly because the mechanism of wear on the latter is more dependent on the tensile and tear strength which was jeopardised by the inclusion of higher level of BR. It must be remembered that the reduction of tan $\delta$ should be concurrent with a reduction rather than an increase in the abrasion index as the reduced tan $\delta$ indicates that the share of frictional energy dissipated by the bulk of the rubber, other than on the abrasion process, would be lower. This makes the share of the energy dissipated on the abrasion process higher, with an expected higher volume loss. The gain in the abrasion index, as a result of the reduction in the coefficient of friction, however, might have covered this deficiency and left more to push the abrasion index higher.

5.7 AGEING CHARACTERISTICS

Because of their vital importance, care was taken to evaluate the ageing properties of the tread vulcanisates at every step of the compound modification. Specimens from the NR/BR vulcanisates were hot oven air aged at 100°C for 3 days (BS 903 Part A9). The results obtained at the end of the test are compared with that of the NR control which had undergone similar test conditions; these are shown in Table 5.4. They clearly indicate that the NR/BR vulcanisates have a lower retention of tensile strength and elongation at break compared with the control. In contrast to this pattern, however, the BR containing vulcanisates maintain superiority over the control in their abrasion resistance after ageing. This marked contrast between abrasion resistance and other strength properties gives additional support to the argument concerning the domination of frictional and dynamic parameters over strength properties in the abrasion of BR vulcanisates.
Table 5.4  Results obtained after hot oven air ageing at 100°C for three days

<table>
<thead>
<tr>
<th>Property</th>
<th>NR100 BR 0</th>
<th>NR90 BR10</th>
<th>NR80 BR20</th>
<th>NR70 BR30</th>
<th>NR60 BR40</th>
<th>NR50 BR50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Days</td>
<td>0 3</td>
<td>0 3</td>
<td>0 3</td>
<td>0 3</td>
<td>0 3</td>
<td>0 3</td>
</tr>
<tr>
<td>Tensile strength MPa</td>
<td>30.2</td>
<td>19.4</td>
<td>25</td>
<td>14</td>
<td>21</td>
<td>11.4</td>
</tr>
<tr>
<td>% change</td>
<td>-</td>
<td>-36</td>
<td>-56</td>
<td>-54</td>
<td>-51</td>
<td>-52</td>
</tr>
<tr>
<td>100% Modulus MPa</td>
<td>2.9</td>
<td>3.92</td>
<td>3.8</td>
<td>5.6</td>
<td>4.0</td>
<td>6.9</td>
</tr>
<tr>
<td>% change</td>
<td>-</td>
<td>+35</td>
<td>+47</td>
<td>+72</td>
<td>+63</td>
<td>+47</td>
</tr>
<tr>
<td>Elongation %</td>
<td>580</td>
<td>390</td>
<td>525</td>
<td>238</td>
<td>506</td>
<td>216</td>
</tr>
<tr>
<td>% change</td>
<td>-</td>
<td>-33</td>
<td>-55</td>
<td>-58</td>
<td>-64</td>
<td>-65</td>
</tr>
<tr>
<td>DIN volume index of the aged vulcanisate</td>
<td>- 100</td>
<td>- 139</td>
<td>- 144</td>
<td>- 162</td>
<td>- 169</td>
<td>- 203</td>
</tr>
</tbody>
</table>
5.8 CONCLUSIONS

Inclusion of various levels of BR with NR in the present series of silica/ISAF vulcanisates causes the following effects.

1. Disadvantageous - but, up to certain levels, tolerable increase in Mooney viscosity and deterioration in mill banding.

2. Desirable increase in overcure reversion with the latter positively affecting abrasion resistance.

3. Reduction in tensile strength, elongation at break and crescent tear strength but increase in hardness.

4. Improvement in flex cracking and compression set properties.

5. In contrast to the reduction in almost all strength properties, DIN and Akron Indices generally improved with the increase in BR level for aged and un-aged specimens.

6. Frictional properties, as measured by portable skid tester, show a steady reduction in value which is consistent with the abrasion indices, due to the shift of wear mechanism from damaging abrasive into less damaging fatigue wear.

7. Increasing the level of BR enhances rebound resilience and decreases tan $\delta$ and E'.

8. Retention of physical properties becomes lower when BR is added, except for abrasion resistance.

9. The main reason for the increase of abrasion resistance is believed to be the reduction of frictional properties which outweighs the deterioration of rubber toughness.

10. The best levels of NR/BR giving a good balance of overall properties were 80/20 and 70/30.
CHAPTER 6

EFFECT OF ANTIOXIDANTS ON RUBBER ABRASION

6.1 INTRODUCTION

Vulcanised rubbers containing high levels of unsaturation are expected to be susceptible to attack by oxygen and thus estimated to lose their performance 70 - 100 times earlier when they are mechanically stressed compared to their unstressed states or conditions\(^{109}\). Thus, various chemical and physical means of protection are generally needed for stabilization and to impart satisfactory ageing properties. The most common of these is the use of an adequate level of antioxidants or by employing more thermally stable curing systems. Rubber antioxidants are mainly based on secondary amines and phenols and their level is adjusted according to surface requirements. The mechanism of their action during normal rubber ageing (dynamic and static) can easily be found in the literature\(^{128}\). However, the role of antioxidant during the fatigue wear of a rubber vulcanisate does not seem to be sufficiently covered in the literature. A complicated process like tyre wear is expected to be coupled with flexing, thermal degradation of the rubber surface and cutting and tearing. Therefore, an anaerobic ageing within the rubber, and oxidation of degraded and ruptured polymeric chains can autocatalyze further reactions and cause more deterioration, especially when the temperature is high. An up-to-date thoroughly quantitative study on the thermal oxidative effect on tyre wear has not been reported, despite the fact that, as early as the fifties such an effect was speculated upon\(^{24,34}\). Dannenberg and Amon\(^{110}\) confirmed that the oxidative mechanisms were important in abrasion. They attributed the differences in the relative wear resistance of NR and SBR to their oxidation resistance at different ambient temperatures, as demonstrated in Figure 6.1.
Fig. 6.1: Improvement of wear resistance of SBR at higher ambient temperatures [Ref 110].

Comprehensive laboratory studies were carried out by Brodskil and Reznikovskii under carefully selected conditions. These conditions involved the use of nitrogen, argon and atmospheric oxygen under which various polymers were tested. Their findings indicate that the volume loss in oxygen is twice as great as in the other atmospheres for highly unsaturated polymers (NR, SBR) but no noticeable difference could be seen for butyl and polyurethane. More recent laboratory studies have emphasised the rôle of antioxidants on abrasion, but to a limited extent. In contrast, there also have been reports, based on roadwear and laboratory studies suggesting that no appreciable relationship exists between antioxidant and rubber wear.
The rôle of rubber degradation on its wear has also been pointed out frequently\textsuperscript{11,102}. Williams and Cade\textsuperscript{107} emphasised such a rôle, as they obtained benzene-extractable contents as high as 32-44\% of the total weight of the wear debris analysed compared to 1 - 3\% of the original tread compound.

However, it can be argued that these extractable materials may not necessarily be the only direct products of a thermoxidative degradation induced by mechanical rupture. Other factors like migration to the surface of rubber soluble materials (such as oil, wax and stearic acid) could contribute to this process. In view of such complexity it was thought that a study of chemical wear was timely and complementary to the previous work.

6.2 OBJECTIVES

Attempts will be made to investigate whether or not an improvement in abrasion resistance can be brought about by incorporation of various levels of antioxidants. Moreover, analysis of wear products will be undertaken to investigate possible mechanisms by which the abrasion process occurs.

6.3 MATERIALS

The base mix chosen for the experimental work consisted of a blend of NR and BR, whose full recipe can be seen in Table 6.1. Two commercial antioxidants (Vulnax International) were used. They were N-isopropyl-\textit{p}-phenylene dramine (IPPD) and 2,2,4 trimethyl-1, 2-dihydroquinoline (Flectol H). The former is known to be a powerful antioxidant-anti-ozonant, whereas the latter is of moderate antioxidant efficiency. The chemical structures of these two materials are shown in Figure 6.2.
Figure 6.2: Chemical structure of IPPD and Flectol H

6.4 EXPERIMENTAL

Five truck tyre tread mixes were prepared with a semi-efficient cure system. The levels of IPPD and Flectol H were varied. Formulae can be seen in Table 6.1.

Table 6.1 Tyre tread formulations with various antioxidant levels

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flectol H phr</td>
<td>0</td>
<td>0.5</td>
<td>1.0</td>
<td>1.5</td>
<td>2.0</td>
</tr>
<tr>
<td>IPPD phr</td>
<td>0</td>
<td>0.5</td>
<td>1.5</td>
<td>2.0</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Other Ingredients:
SMR20 70, BR(cis) 30, ISAF 48, ZnO 4, stearic acid 2, paraffinic wax 2, highly aromatic oil 7, sulphur 2, MBS 1.5.
A. 1st stage mixing

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Time (min)</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMR (raw)</td>
<td>0 r.d.</td>
<td>Rotor speed 80 r.p.m.</td>
</tr>
<tr>
<td>BR cis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical including</td>
<td>2.0 r.d.</td>
<td>Cooling water temp. 40°C</td>
</tr>
<tr>
<td>Antioxidants (if any)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISAF (one half)</td>
<td>3.0 r.d.</td>
<td>Fill factor 0.8</td>
</tr>
<tr>
<td>Remaining ISAF + oil</td>
<td>4.0 r.d.</td>
<td></td>
</tr>
<tr>
<td>Sweeping off</td>
<td>5.0 r.d.</td>
<td></td>
</tr>
<tr>
<td>Dump</td>
<td>6 - 7</td>
<td></td>
</tr>
</tbody>
</table>

Dump temperatures were between 130 - 140°C. Mixes were stored for 24 hours before final-isation of mixing.

B. 2nd stage mixing

The mixing cycle chosen for the second stage was as follows:

<table>
<thead>
<tr>
<th>Operation</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M.B.</td>
<td>0 r.d.</td>
</tr>
<tr>
<td>Sulphur + MBS</td>
<td>0.5 - 1 r.d.</td>
</tr>
<tr>
<td>Dump</td>
<td>2.0 r.d.</td>
</tr>
</tbody>
</table>

Mixing conditions for the second stage were: rotor speed 60 r.p.m., cooling water temperature 40°C. Dump temperature were between 110 - 120°C.

* r.d. = ram down

Table 6.2 Mixing condition and sequence for the tread vulcanisates

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Mixing was carried out in a Banbury mixer in two stages as before. Mixing cycle and conditions are as shown in Table 6.2. All abrasion experiments were done by using the DIN and Akron abraders as well as the miniature tyre facility. Other processing and curing properties were determined according to the standards used in Chapter 4. Some specialised techniques were also used for characterisation. These will be indicated as appropriate.

6.5 RESULTS AND DISCUSSION

6.5.1 Effect on processing properties

Inclusion of IPPD and Flectol H in different proportions has little effect on processing properties except for the Mooney viscosity (see Table 6.3). The absence of the antioxidants from mix no. 1, (which is taken hereafter as a control for this experiment) results in a reduction of three units compared with mix no. 2 which contains a total of 1 phr of the two antioxidants. A further increase of the antioxidant level to a total of 2.5 phr (mix no. 3) shows a 7 unit increase over that of mix no. 2. The reduction of viscosity at equal mixing times may be ascribed to an excessive rubber degradation during various stages of mixing. This is normally intensified by the presence of oxygen or the absence or scarcity of antioxidants$^{127}$.

6.5.2 Effect on curing properties

As Table 6.3 shows, the increased level of the antioxidants has no significant effect on the ODR properties (except for a slight decrease in $t_2$ and $t_{95}$.) The modulus and tensile strength are also not affected. The antioxidants present cause small but distinct increase in tear strength and a reduction in compression set. However, only abrasion resistance will now be discussed in more detail.
<table>
<thead>
<tr>
<th>Properties</th>
<th>Flecto H</th>
<th>0</th>
<th>0.5</th>
<th>1.0</th>
<th>1.5</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPPD</td>
<td></td>
<td>0</td>
<td>0.5</td>
<td>1.5</td>
<td>2.0</td>
<td>2.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound properties:</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>ML(1 + 4) 100°C</td>
<td>37</td>
<td>40</td>
<td>44</td>
<td>44</td>
<td>52</td>
</tr>
<tr>
<td>ODR properties 160°C, 3°Arc</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T max (dN.m)</td>
<td>71</td>
<td>75</td>
<td>69</td>
<td>75</td>
<td>70</td>
</tr>
<tr>
<td>t₂ (min)</td>
<td>3.2</td>
<td>3.1</td>
<td>3.1</td>
<td>3.0</td>
<td>2.8</td>
</tr>
<tr>
<td>t₉₅ (min)</td>
<td>7.4</td>
<td>7</td>
<td>7.5</td>
<td>6.6</td>
<td>6.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Curing properties:</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Modulus MPa</td>
<td>1.9</td>
<td>2.2</td>
<td>2.3</td>
<td>2.2</td>
<td>2.6</td>
</tr>
<tr>
<td>300% Modulus MPa</td>
<td>9.0</td>
<td>9.5</td>
<td>9.3</td>
<td>9.1</td>
<td>8.9</td>
</tr>
<tr>
<td>Tensile strength MPa</td>
<td>22.5</td>
<td>22</td>
<td>23</td>
<td>22.2</td>
<td>22</td>
</tr>
<tr>
<td>Breaking elongation %</td>
<td>610</td>
<td>575</td>
<td>600</td>
<td>603</td>
<td>640</td>
</tr>
<tr>
<td>Crescent tear strength KNm⁻¹</td>
<td>109</td>
<td>115</td>
<td>122</td>
<td>123</td>
<td>121</td>
</tr>
<tr>
<td>Hardness IRHD</td>
<td>69</td>
<td>70</td>
<td>70</td>
<td>72.5</td>
<td>69</td>
</tr>
<tr>
<td>Rebound resilience %</td>
<td>55</td>
<td>54.5</td>
<td>53</td>
<td>51.5</td>
<td>53.5</td>
</tr>
<tr>
<td>Compression set at 25% strain (48 hrs at 20°C)</td>
<td>10.4</td>
<td>9.9</td>
<td>9.7</td>
<td>9.5</td>
<td>8.2</td>
</tr>
<tr>
<td>DIN volume loss mm³</td>
<td>98</td>
<td>39</td>
<td>77</td>
<td>82</td>
<td>33</td>
</tr>
<tr>
<td>Akron abrasion loss mm³</td>
<td>159</td>
<td>115</td>
<td>70</td>
<td>48</td>
<td>45</td>
</tr>
</tbody>
</table>

Table 6.3 Processing and curing properties of the vulcanisates of Table 6.1.
6.6 ABRASION RESISTANCE

6.6.1 Abrasion resistance on the DIN abrader

The antioxidant-containing mixes generally showed a lower volume loss compared to the unprotected one (see Table 6.3).

This loss seemed to be independent of the level of antioxidant. This might lead to the suggestion that the antioxidants would not substantially affect the process of abrasion under severe cutting and tearing conditions, due perhaps to the shortness of the test, which allows little chance for them to bloom to the surface at the instance of abrasion. The slight improvement in the abrasion resistance (reduced volume loss) that was associated with the antioxidants' presence is likely to be due to their desirable effect in reducing the excessive degradation that usually occurs during mixing. This was reflected in terms of increased tear strength for the antioxidant containing vulcanisates. The increase in tear strength has been seen as advantageous for enhanced abrasive wear resistance.

6.6.2 Abrasion resistance on the Akron machine

The abrasive wheel of the Akron abrader used for the present experiment has been in service for many years. Therefore, it may contain many more round rather than sharp asperities.

Specimens were obtained from these five tread mixes by compression moulding and curing at 150°C for 30 minutes. Then they were tested at a slip angle of 15° in a similar way as before. Each specimen was run-in and therefore its surface conditioned using a pre-run of 6000 revs so a steady state could obtained. Each specimen was then removed, cleaned and accurately weighed within a controlled time period before being remounted. Table 6.3 displays the results obtained which show a steady decrease in volume loss with increase in level of the antioxidant. This trend is exactly similar to that reported by Schallamach⁴⁹ and Brodskii⁴⁸.
It must be noted, however, that it seems improbable that a double increase in antioxidant quantity would simply impart this dramatic reduction in volume loss over the relatively short time of a typical test interval. Therefore, it was decided to search for other possible hidden causes for such an effect, especially when a distinctly positive or improving effect on the DIN abrasion has not been achieved (see Figure 6.3). Notwithstanding the positive rôle of the antioxidants in improving the fatigue properties of rubber, especially under flex and stressing, it could be possible that they, themselves, may also increase surface lubrication and reduce abrasion. This conclusion is based on the fact that antioxidants are compatible with rubber only on a limited scale i.e. 0.5 - 1 phr. Their incompatibility may increase with the increase in temperature which in turn is produced as a consequence of abrasion. Also, their relatively low melting points (usually between 80 - 90°C) easily allow their blooming to the surface under repeated stressing. Such blooming is expected to show a major effect on the Akron abrader where both the abrasive wheel and the specimen are circular with the asperities of the former being round and not sharp and the consequent volume loss per unit time being far lower than the case with the DIN abrader. Therefore, the substantial difference between the abrasion indices of the protected and unprotected vulcanisates is possibly due to a combination of lubrication and real increase in the fatigue resistance. This combination is not expected to be available to the same extent for the DIN abrasion.

6.6.3 Wear measurements on the miniature tyre facility

The test on the miniature tyre machine under hot conditions for prolonged times was thought to provide a good opportunity for fatigue wear to materialise. Thus, the effect of antioxidants on abrasion might be better judged by this technique rather than by either of the DIN and Akron abraders. Consequently, miniature tyres were prepared from the five vulcanisates of Table 6.1 as before under strictly comparable conditions and tested for $50 \times 10^3$ revs at a temperature range of 80 - 90°C. The weight loss of the
Fig. 6.3: Volume loss vs level of antioxidants

△ DIN abrader; ○ Akron abrader
Fig. 6.4: Weight loss on the miniature tyre testing machine vs antioxidant level
vulcanisates is plotted against the level of antioxidants in Figure 6.4. The figure clearly shows that the steady increase in the antioxidant level results in a distinct reduction in the volume of rubber removed from the surface. However, the reduction seems to be far less (and perhaps more realistic) than that of the Akron abrader. It is believed that the ability of the wire gauze to remove possibly the major part of the smear formed on the surface is the main advantage in showing of this method. Nevertheless, it must be stressed that a better judgement on the effect of antioxidant on wear was thought as demanding no interference from any migration of any ingredient to the surface of rubber no matter how small, as friction between the rubber and the abrader is generally very sensitive to such lubrication. This pattern may not be the case when a tyre runs on the road.

6.7 LUBRICATION-FREE WEAR

The possibly misleading effect of smearing on abrasion results necessitate taking certain measures for its avoidance. It was anticipated that a better understanding of the rôle of antioxidants might be achieved if this effect was somehow eliminated or substantially reduced. Achievement of such an objective requires the preparation of mixes in which low molecular weight ingredients that could bloom to the surface (i.e. stearic acid, oil and wax) should be absent. Also, omission of oxygen-containing ingredients (such as ZnO, MBS and carbon black) was thought to be advantageous in easing the generally difficult task of analysing wear products. However, as most of the above materials are essential for obtaining an acceptable state of cure, the intended vulcanisates will in practice be different from those of typical tread rubbers. Yet they might offer a better chance for realistic studies of chemical wear.
6.7.1 Model gum mixes

The ingredients of the three vulcanisates of Table 6.4 were carefully selected to contain no oxygen in their composition, as this would complicate possible tests like infrared and electron spectroscopy for chemical analysis ESCA. Even fatty acid and antioxidants, usually added during BR synthesis, were substantially removed by solvent extraction with heptane before the polymer was dried and used.

These mixes were thought suitable to investigate some unanswered questions such as the dryness of the tread surface and the debris of the NR/BR blends with reference to NR and whether there are some additional reasons behind their superiority in abrasion resistance other than the reduced $\mu$ and improvement of dynamic properties. Moreover, the investigation could also clarify better the effect of IPPD on degradation and fatigue abrasion on the Akron and the miniature tyre tester.

### Table 6.4 Model gum rubber formulations (bloom free vulcanisates)

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Mix No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6</td>
</tr>
<tr>
<td>SMR20 (raw)</td>
<td>100</td>
</tr>
<tr>
<td>BR cis (European)</td>
<td>-</td>
</tr>
<tr>
<td>IPPD</td>
<td>-</td>
</tr>
<tr>
<td>Sulphur</td>
<td>2.5</td>
</tr>
<tr>
<td>CBS</td>
<td>1.5</td>
</tr>
<tr>
<td>ZEDC</td>
<td>0.5</td>
</tr>
</tbody>
</table>
6.7.2 Abrasion test

Miniature tyres were prepared from the three mixes of Table 6.4 whose vulcanisates had almost the same 300% modulus. These were tested under hot and cold conditions for 25000 revs in each case. Debris was collected in a container for chemical analysis. Wear results and observations are summarised as follows:

A. The unprotected NR (mix no. 6)

When the test was conducted at room temperature the unprotected vulcanisate showed little sign of smearing on the tread surface. The collected debris was irregular in shape and dry. This pattern changed when a fresh tyre was tested (at a temperature range of 70 - 80°C). The tread surface and the debris became very sticky after only 4000 revs. The tyre looked more shiny and the debris was sausage shaped. Here, away from any interference from soluble ingredients, the only possibility available for such an effect would be a surface degradation promoted by oxidative scission. Some of the collected debris was saved in order to search for more evidence and clues for the effect of degradation on wear.

B. The NR/BR (mix no. 7)

When a miniature tyre made of this mix was tested as in A, it showed no sign of stickiness under cold conditions and the debris was absolutely dry and powdery in nature. Even under heat the surface of the tread and debris were slightly sticky with the texture of the debris remaining irregular. This supports the argument concerning the ability of BR to produce both a dry tread surface and dry abrasion debris.

To explain this effect let us assume that the rupture of the cross-linked chains during abrasion would occur in the relatively weak - CH₂ - CH₂ - bonds as shown in Figure 6.5. Then one would expect BR to form highly reactive free...
Figure 6.5 Proposed mechanisms for the effect of IPPD and BR on the decomposition of NR during the mechanically activated thermoxidative degradation (fatigue wear)
radicals due to the inherently reduced stability of these radicals compared to those of NR. The butadiene radicals are expected to recombine with each other or to trap down the NR based free radicals present in the immediate vicinity. The fast combination of the radicals would not allow oxygen an opportunity to attack them and further autocatalytes the reaction leading to reduced molecular weight chains that are normally responsible for the tackiness. If this suggestion is valid then it can be imagined that the presence of butadiene radicals also shows the same effect under the anaerobic condition deep in the rubber, where flexing can cause a large scale molecular rupture that may result in polymeric network destruction. This argument runs in line with the reported favourable effect of BR on fatigue properties and flexing. It is worthwhile noting that the suggested mechanism of BR action may not necessarily show the same effect on static ageing.

C. The protected NR (mix no. 8)

The test of the IPPD protected vulcanisate surprisingly showed a greater development of stickiness under both cold and hot conditions although it became more extensive in the latter. Moreover, the debris was sausage shaped, dark and sticky. The stickiness of the miniature tyre was not confined to the abraded area but to the whole tyre especially under hot conditions. This observation would cast doubt on the commonly accepted opinion that smearing is the only consequence of a thermo-oxidative degradation in the area of real contact where compression, shear and heat are high. More quantitative evidence will emerge from the chemical analysis of the wear product in the next section.
It should be noted, however, that the excessive smearing of the NR/IPPD mix during abrasion should not be taken as evidence of degradation in this case. It is believed that what had happened was due to blooming of IPPD itself to the rubber surface because of hot flexing. Yet its rôle in the antioxidation of rubber may not necessarily be affected.

6.8 CHARACTERISATION OF WEAR PRODUCTS

6.8.1 Determination of extent of degradation

6.8.1.1 Toluene extraction (TE)

Equal amounts of debris from that obtained during the hot wear test of the three vulcanisates of Section 6.6 were individually dissolved in an excess of toluene for 1 hour at 20°C; the unextractable residues which consist mainly of crosslinked crumbs were dried at 30°C for 24 hours to estimate their de-swollen weight. The ratio of the dried weight to the original is plotted against the type of vulcanisate in Figure 6.6. The debris of the unprotected NR vulcanisate (mix no. 6) shows significant weight loss (65%) while that of the NR/BR (mix no. 2) shows only 20%.

Surprisingly, the NR/IPPD shows an unexpected weight loss of 45%. This indicates that the presence of both IPPD and BR had resulted in a favourable reduction in the weight loss, possibly due to their favourable rôle in degradation and oxidation. It must be noted that the 45% loss of the debris of mix no. 8 could contain a high concentration of IPPD.

6.8.1.2 Thermogravimetric analysis TGA

TGA is a technique by which materials are detected according to their volatility under continuous heating at a constant rate. As degradation of rubber normally results in producing lower molecular weight components, the detection of the latter can be followed through loss of weight with temperature and comparison can be
Fig. 6.6: Weight loss of rubber debris (hot test) after toluene extraction

Fig. 6.7: TGA graphs of the hot wear debris of mix No. 1 and a fresh specimen of the same mix
made with undegraded specimens from the same rubber. This principle was applied by Williams and Cade\textsuperscript{107} to detect the extent of degradation of the polymer in debris obtained from tyres tested on an internal drum. Their findings showed that there was a slight reduction in the volatility range of the polymer in the debris with reference to the tread. However, their estimation of the extent of degradation would be more accurate if the normal blooming of low molecular weight materials from the bulk of the rubber to its surface due to heat, flexing and abrasion is avoided.

During the application of the TGA technique for the analysis of the debris in this research this difficulty was virtually absent as the unfilled and unextended vulcanisates of Table 6.4 contain no migrating ingredients and thus interference was avoided. Only mix no. 1 of Table 6.4 was selected as it was the most degraded. Debris was obtained from the hot miniature tyres and bottled. Later it was analysed by TGA under an argon atmosphere; the result was compared with a virgin specimen of equivalent weight taken from an unworn part of the tyre in Figure 6.7. The curve of the debris shows that a slight but distinct weight loss of the debris occurs at a temperature where the virgin specimen has shown hardly any sign of degradation. It should be noted, however, that the large temperature range over which the polymer degraded indicates a large variation in the molecular weight of the wear products, thus an overlap in their volatility curves is inevitable.

6.8.2 Extent of molecular rupture and wear product analysis

6.8.2.1 Introduction

It was pointed out on several occasions in chapter 2 that there is a close connection between fatigue abrasion and chemical and thermal degradation of the polymer. In view of this it was thought that analysis of wear products may help to determine the mechanism by which a tread rubber wears.
6.8.2.2 Instrument

Gel permeation chromatography (GPC) is one of the most powerful techniques for polymer characterisation. Therefore, it was selected for the present investigation and a Polymer Laboratories type GPC equipped with an on-line computer was used. In this instrument separation takes place in a chromatographic column filled with beads of rigid porous gel, highly crosslinked porous styrene and porous glass. These pores are of the same size as the dimensions of polymeric molecules\textsuperscript{111}. As the dissolved polymer molecules flow past the porous beads, they diffuse into the internal pore structure of the gel to an extent depending on their size. Larger molecules are eluted faster than smaller ones and less time is spent inside the gel.

6.8.2.3 Experimental

The debris obtained from the miniature tyre tests of the three vulcanisates of Table 6.4 was extracted with Tetrahydrofuran THF, diluted and eluted by the same solvent. Figures 6.8, 6.9, 6.10 are computer graphs of the three extracts. Comparison of Mw values of the extracts obtained from the debris of the three vulcanisates revealed that the effect of IPPD and BR was remarkable. For instance, Mw\textsuperscript{*} of the degraded polymer obtained from mix no. 1 of Table 6.4 fell to a value as low as 10.9 x 10\textsuperscript{3} gm/mol. A 20 minutes mastication of raw NR in a normal Banbury mixer gives 20 times higher molecular weight than the above\textsuperscript{127}. The presence of BR with NR in mix no. 7, however, resulted in a Mw value of 30.6 x 10\textsuperscript{3} g/mol.

\textsuperscript{*} estimated according to Mark-Houwink equation which is,

\[ n = k M^a \]

where \( n \) is viscosity, \( k \) and \( a \) are constants whose values were respectively taken as 1.25 x 10\textsuperscript{-4}, 7.17 x 10\textsuperscript{-1} for the standard polystyrene and 1.77 x 10\textsuperscript{-4}, 7.35 x 10\textsuperscript{-1} for the degraded polymers.
Fig. 6.8: GPC graph of the extract of debris obtained from the miniature tyre of mix 6 of table 6.4 (Unprotected gum NR)

NR/UNPROTECTED/HOT TESTED

Mw = 10900
Mz = 30600
Mn = 2490
Mw/Mn = 4.39

Fig. 6.9: GPC graph of the extract of debris obtained from the miniature tyre of mix 7 of table 6.4 (Unprotected NR/BR)

NR/BR/UNPROTECTED/HOT TESTED

Mw = 31900
Mz = 55400
Mn = 16900
Mw/Mn = 1.88
Fig. 6.10: GPC graph of the extract of debris obtained from the miniature tyre of mix 8 of table 6.4 (IPPD containing NR vulcanisate)

Fig. 6.11: GPC graph of the extract of debris obtained from the miniature tyre of mix 6 of table 6.4 (Cold Test)
More interesting is the value obtained for the IPPD protected NR which was $40 \times 10^3$. The higher value of the Mw of mix no. 8 can be taken as further evidence that the stickiness obtained during the process of hot wear of the miniature tyre made from this mix (see Section 6.6.1 - C) was not an indication of an extensive degradation but simply due to misleading blooming of the IPPD to the surface. Moreover, the rôle of IPPD in increasing the Mw may also explain the rôle of this material in conferring high fatigue abrasion resistance on both the Akron and miniature tyre tests.

It must be pointed out, however, that when a miniature tyre made from the unprotected NR (mix no. 6) was tested under room temperature, analysis of the extracts obtained from the wear debris showed a value of Mw as high as $30.6 \times 10^3$ (see Figure 6.11).

This may indicate that heat has a staganistic effect added to that of frictional forces. Also, the effect of both IPPD and BR may become less significant when the test temperature is low.

6.8.3 Infrared spectroscopy (IR)

IR spectroscopy is another standard technique used mainly as a qualitative means of diagnosing, in the elastomer fields, functional groups according to their absorption spectra. Therefore, it was also utilised to identify the nature of the extractable part of the rubber debris obtained from the hot abrasion. The debris of the hot test of a miniature tyre made from mix no. 6 was selected. The procedure followed was to extract the benzene extractable components and to concentrate the solution by evaporating virtually all benzene under vacuum. The thick gel was transferred onto a KBR crystal and the latter left under an IR lamp to remove any traces of benzene that could interfere with the rubber. This process left a very thin film which was later scanned. Figure 6.12 illustrates the spectra obtained for the extracts as well as that of a raw natural rubber and a thin cured sheet of mix no. 6. A close examination of these spectra reveals no resemblance at all between that of the extract and the vulcanised sheet, obviously
Fig. 6.12: IR spectra of extracts obtained from hot wire gauze abrasion of Mix No.6 (Table 6.4.) [Trace 3] versus those of raw natural rubber [Trace 2] and a fresh vulcanised of the same mix [Trace 1.]
due to the effect of curing. A comparison of the spectrum of the rubber extract with that of the raw natural rubber shows that the two spectra are almost identical except for the presence of some additional bands in the spectrum of the extract and, in certain regions, an increase in the band size. Analysis of these bands indicates the presence of some carbonyl and hydroxyl groups most likely formed due to rubber oxidation. This shows that the thermal degradation concurrent with the gauze abrasion results in the destruction of the sulphidic bonds (devulcanisation) and also degrades the originally high molecular weight chains into lower molecular weight. These processes are coupled with oxidation.

6.9 A proposed mechanism for fatigue wear (wire gauze)

The previous section has shown the extent of polymer degradation during fatigue wear of gum vulcanised rubbers. Fatigue abrasion of reinforced vulcanisates is also expected to cause the destruction of the polymeric network in a similar style but this may be concurrent with the destruction of the filler-rubber interface.

A proposed mechanism for the fatigue abrasion of the miniature tyre is postulated in Figure 6.13. The frictional force exerted during the interaction with the abrading surface mechanically activates the surface layer making it more ready for thermal degradation, especially in the presence of heat and continuous flexing. As a result, various chemical and physical processes take place, such as cleavage of polysulphidic and C-C bonds. Additionally, rubber-filler and filler-filler linkages deteriorate resulting in a loss of the network structure. If oxygen is present and antioxidants are absent or scarce, then the polymeric free radicals will be vulnerable to oxidation especially when they are relatively stable, as shown in Figure 6.13.

The attack by oxygen and the reduction in the molecular weight results in the appearance of a thin layer of smearing. The degraded layers are expected to twist into strands. Each strand is an aggregate of various wear products which in turn are composed
Fig. 6.13: A proposed mechanism for the fatigue abrasion of the reinforced tread vulcanisates on the miniature tyre testing machine.
of various lower molecular weight products. These aggregates are held together by strong cohesive forces arising from their stickiness. When this cohesion is removed by an organic solvent the residue is seen as fine vulcanised crumbs and filler aggregates. Measurement of the dimensions of these particles are shown in Figure 4.16A. This shows that their size distribution falls in the range 10 - 50\(\mu\) which indicates that their failure has taken place on a microscopic scale. The effect of fatigue is not expected to be confined to the surface layer but also within the rubber where the polymeric network and the rubber-filler interaction undergo structural breakdown. However, the anaerobic conditions there may alleviate this breakdown and the antidegradant could play an important rôle in resisting the autocatalyzed degradation by stabilising the broken chains.

6.10 Electron spectroscopy for chemical analysis (ESCA)

This is a very effective technique for diagnosing elements quantitatively according to the intensity of their reflection. Its limitation, however, is that it is effective on a very thin surface layer. This technique was thought advantageous in measuring the increase in oxygen content before and after abrasion under circumstances where there is no migration from within the rubber of oxygen containing materials as these have already been omitted from the formulations.

Therefore, a miniature tyre from mix no. 6 was hot tested and the percentage of oxygen on the tread was determined with reference to a piece of rubber taken from the sidewall. The result showed that the amount of oxygen increased by 2%. The reason behind such a low difference is believed to be the continuous removal of lower molecular weight products that contain oxygen from the tread surface by the abradant.

6.11 AGEING CHARACTERISTICS

Antioxidants were originally used in rubber because of their vital effect on surface durability of rubber items under both dynamic
<table>
<thead>
<tr>
<th>Property</th>
<th>time hrs</th>
<th>IPPD 0</th>
<th>0.5</th>
<th>1.5</th>
<th>2.0</th>
<th>2.5</th>
<th>Flectol 0</th>
<th>0.5</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Modulus MPa % from original</td>
<td></td>
<td>2.0</td>
<td>3.2</td>
<td>2.2</td>
<td>4.7</td>
<td>2.3</td>
<td>4.0</td>
<td>2.2</td>
<td>5.3</td>
<td>2.6</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>Tensile strength MPa % from original</td>
<td></td>
<td>22.5</td>
<td>8.3</td>
<td>22</td>
<td>10.6</td>
<td>23</td>
<td>12</td>
<td>22.2</td>
<td>14.8</td>
<td>22</td>
<td>16.3</td>
<td></td>
</tr>
<tr>
<td>Elongation at break % % from original</td>
<td></td>
<td>610</td>
<td>242</td>
<td>575</td>
<td>230</td>
<td>600</td>
<td>260</td>
<td>603</td>
<td>323</td>
<td>640</td>
<td>430</td>
<td></td>
</tr>
<tr>
<td>Hardness IRHD % from original</td>
<td></td>
<td>69</td>
<td>62</td>
<td>70</td>
<td>70</td>
<td>69.5</td>
<td>65</td>
<td>72.5</td>
<td>68</td>
<td>68</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>DIN abrasion loss mm³ % from original</td>
<td></td>
<td>98</td>
<td>144</td>
<td>89</td>
<td>125</td>
<td>77</td>
<td>105</td>
<td>82</td>
<td>126</td>
<td>83</td>
<td>133</td>
<td></td>
</tr>
<tr>
<td>Akron abrasion loss mm³ % from original</td>
<td></td>
<td>159</td>
<td>268</td>
<td>115</td>
<td>246</td>
<td>70</td>
<td>198</td>
<td>48</td>
<td>248</td>
<td>45</td>
<td>245</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.5 Ageing characteristics of the tread vulcanisates at 100°C
and static conditions. Therefore, much effort has been expended over the years to assess their influence under accelerated conditions which are specially designed to predict behaviour in service.

To determine the effect of variable levels of the antioxidants used in the present series of the tread vulcanisates hot air ageing was used.

Table 6.5 displays the results obtained. They show that the retention of tensile strength and elongation at break improves with increase in the level of the antioxidants. Moreover, the ageing causes a significant reduction in the hardness of the unprotected vulcanisates at a time when the rest is less affected. It also causes a drastic effect on the volume loss of all the five vulcanisates on both the DIN and Akron abraders. This can be clearly seen in Figure 6.14, which also shows the favourable effect of protection on the abrasion. It is worthwhile, however, to note the relatively reduced volume loss obtained with mix no. 3 on both the DIN and Akron abrader. The reason for such an effect is not yet known.

6.12 CONCLUSIONS

The following conclusions can be drawn from the experimental results.

1. The antioxidants used have shown no pronounced effect on the abrasive wear where quick tearing and tensile mechanisms are predominant; e.g. as in the DIN abrader.

2. Their use, however, has caused a consistent reduction in the fatigue abrasion (i.e. Akron and miniature tyre) with the increase of their levels up to certain limits, after which no more reduction in abrasion can be obtained.
Fig. 6.14: Volume loss after ageing (3 days at 100°C) on the DIN and Akron abraders of the tread vulcanisates of Table 6.1.
3. The reduction in fatigue wear has been seen as due to two distinct effects:

a. the favourable enhancement of fatigue properties of the vulcanisates.

b. lubrication of the surface by the leaching of the antioxidants to the surface. The extent of leaching increases with temperature and the increase of antioxidant level.

4. The unprotected NR vulcanisate has given the highest abrasion with the most degraded types of abrasion debris compared to the protected one and also that of NR/BR blend.

5. Smearing, which has been seen as a major source of experimental error, cannot always be taken as an indication of polymer degradation only, but a combination of this and leaching of lower molecular weight ingredients.

6. The conditions encountered during fatigue abrasion result in polymer devulcanisation accompanied by oxidation.

7. The retention of physical properties after hot air ageing increases with the increase in the level of antioxidants but the curves of the volume loss on both the DIN and Akron abrader show a minima at 2.5 phr of the antioxidants.

8. BR-clis when used with NR in the vulcanisate is seen to enhance fatigue type abrasion resistance. This is believed to be due to the relative instability of its free radicle formed during abrasion; its use is therefore advantageous for tread vulcanisates undergoing such abrasion.

9. The process of contact fatigue wear is not necessarily similar to normal fatigue as the former may involve mechanical activation by the abrasion process itself occurring with large scale filler-rubber breakdown.
CHAPTER 7

THE ROLE OF STEARIC ACID ON FATIGUE ABRASION

7.1 INTRODUCTION

The rôle of the major ingredients of the truck tyre tread formulation on its abrasion resistance has been discussed in the previous chapters. Other minor ingredients, however, are expected to play their specific rôles in the process of treadwear.

Conventionally, stearic acid is used with ZnO as a vulcanisation co-activator and a processing aid. Its usual level in tread compounds ranges from 1.5 - 2.5 phr. The rôle of stearic acid in conferring a beneficial reduction in the viscosity has also been established. The theory behind this effect suggests that, if this material is present in a rubber mix, then free radicals formed during the rubber macromolecule rupture will have a lower tendency to recombine and, instead, attack the fatty acid molecule.

More interesting, is the recent discovery by MRPRA that thermal stability of both conventional sulphur and semi-efficient vulcanisates could be improved by introducing higher than normal levels of stearic acid in NR/BR tread compounds. Additionally, it was also shown that a level of stearic acid as high as 6 phr, while reducing the tear strength by one third compared with a similar formulation containing only 2 phr, exhibited (in one instance) better wear performance. The judgement on the wear properties was made against conventionally-cured NR, semi EV cured NR/BR and SBR/BR controls. Laboratory and roadwear tests showed that the high stearic acid-containing formulation was superior to those of the NR control; under one specific condition this being when the modified compound was used as a truck tyre tread for the third axle (relatively low severity). It was inferior when used for the fourth axle (high severity due to the predominance of tensile-tear wear mechanism) where the use of a high level of stearic acid
causes a reduction in the vulcanisate strength. It was later concluded that the wear mechanism on the third axle is predominantly thermal degradation where the presence of stearic acid conferred the best overcure reversion resistance. Apparently, this improvement in overcure reversion resistance outweighed the loss in tear strength.

On the basis of the above information it was decided to investigate the rôle of higher levels of stearic acid on the abrasion resistance of NR and NR/BR vulcanisates, under the mild conditions of the wire gauze abrasion.

7.2 EXPERIMENTAL

Formulations of model gum mixes were selected for the experimental work can be seen in Table 7.1. These were chosen to avoid the usually excessive toughness of reinforced tread vulcanisates where the rôle of the minor ingredient might be difficult to isolate and study.

From the three mixes of the Table, mix no. 1 was chosen as control and was given a good level of anti-oxidant protection and a semi EV system. The other two mixes were deliberately left without protection so that the possible rôle of stearic acid on overcure reversion and thermal degradation could be investigated. All mixes were prepared on a twin-roll mill pre-heated to 40°C and mixed using a single stage cycle. Specimens for evaluation of physical properties were prepared by compression moulding at 150°C for 90 + 5 mins. Miniature tyres were prepared by compression moulding at the same temperature and time of cure. Each of these miniature tyres was inflated to 0.1 Kg/cm² and tested at a temperature range of 70 - 80°C and at a slip angle of 5° for 60 x 10³ revolutions.
7.3 RESULTS AND DISCUSSION

Table 7.2 displays the Monsanto ODR and some selected physical properties. All mixes underwent significant over-cure reversion due perhaps to the absence of filler reinforcement and other conventional ingredients. This is in contrast to the trend that has been reported by MRPRA. The excessive level of stearic acid showed only a little influence on the over-cure reversion of the vulcanisates. An approximately 30% reduction in the crescent tear strength and tensile strength was also concurrent with the high stearic acid level in mixes no. 2 and 3. When the miniature tyres were tested using a wire gauze, the high stearic acid vulcanisate (mix no. 2) showed a similar weight loss to the lower stearic acid containing counterpart (mix no. 1) but higher than that of the NR/BR vulcanisate (mix no. 3). This indicates that, for the hot wire gauze abrasion, the tear and tensile strength values are not
critical factors. Whilst the high quantity (6 phr) of stearic acid reduces the strength properties of its vulcanisates (mixes nos. 2 and 3); it shows almost equal but not improved wear resistance to the control (mix no. 1) which contains 2 phr of the acid most likely due to exudation to the surface of excessive acid and the consequent effect on surface lubrication. This is indicated by the relatively higher bloom to the surface of the excessive acid (see Figure 7.1). It must be noted, however, that the higher wear resistance of mix no. 3 would not be expected to be ascribed to the presence of the acid only but to the BR cis.

<table>
<thead>
<tr>
<th>Property</th>
<th>mix no. 1</th>
<th>mix no. 2</th>
<th>mix no. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>ODR reversion % (150°C for 24 mins)</td>
<td>39</td>
<td>35</td>
<td>34</td>
</tr>
<tr>
<td>300% Modulus MPa</td>
<td>1</td>
<td>0.88</td>
<td>0.8</td>
</tr>
<tr>
<td>Tensile strength MPa</td>
<td>17</td>
<td>12.5</td>
<td>9.5</td>
</tr>
<tr>
<td>Elongation at break %</td>
<td>775</td>
<td>900</td>
<td>910</td>
</tr>
<tr>
<td>Crescent tear strength kNm⁻¹</td>
<td>42</td>
<td>28</td>
<td>22</td>
</tr>
<tr>
<td>Miniature tyre loss (gm) (70 - 80°C for 60,000 revs)</td>
<td>0.379</td>
<td>0.373</td>
<td>0.340</td>
</tr>
</tbody>
</table>

Table 7.2 Some selected properties of the gum vulcanisates

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7.4 CONCLUSIONS

The comparison between the performances of low and high levels of stearic acid in the gum vulcanisates has shown that the increased level of the acid has little advantageous effect on over-cure reversion which has frequently been reported as one of the main drawbacks of NR. The higher level of the acid has reduced the tear and tensile strength of the vulcanisates by one third compared with the lower acid containing equivalent. One of the advantages of the acid is seen in maintaining the hot fatigue wear resistance despite the reduction in the tensile and tear strength. This additional advantage (to the excellent effect of stearic acid on processing) cannot simply be ascribed to the minor gain in over-cure reversion but possibly to lubrication. For abrasive wear where the strength of the rubber is critical, stearic acid would not be recommended.
CHAPTER 8

THE COMBINED EFFECT OF THE BONDED SILICA AND CIS-BR ON
THE WEAR AND OTHER PROPERTIES OF THE DEVELOPED TRUCK
TYRE TREAD RUBBER

8.1 INTRODUCTION

Five consecutive attempts have so far been made to enhance the abrasion resistance and other essential properties of the truck tyre tread formulation developed earlier. Each attempt dealt with one or more of the key ingredients in the formulation. Thus, various tread rubbers have emerged with different abrasion properties. Here, a sixth and final attempt is made to investigate whether or not a synergistic effect can be achieved with regard to abrasion resistance and other essential properties when cis-BR and the bonded silica system are brought together into a single formulation using the SARA optimised mixing cycle with moderate sulphur level i.e. (2 phr).

8.2 CONTROL RUBBERS

The judgement on vulcanisate properties of a given experimental rubber would be more acceptable if it included rigorous comparison with a wider range of tread rubber controls. Consequently, the emphasis was directed to include, in addition to the best of the experimentally developed rubbers, some industrial tread mixes. It is significant that, from a technical point of view, some of these mixes were deliberately chosen to contain different polymers or polymer blends, variable levels of curatives and some other ingredients to widen further the range of the comparison. These mixes were used to compare various relevant properties.
8.3 PREPARATION OF TREAD MIXES

The formulations of the new and some of the old mixes are shown in Table 8.1. Amongst these, mix I is the one that contains the optimised polymer blend, the optimised reinforcing system and the moderate (1.5 phr IPPD and 1 phr of Rectol H) anti-oxidant level. Also, it contains typical sulphur level of 2 phr. The new mixes were prepared as follows:

8.3.1 Mixing

The optimised two-stage Banbury hot mixing cycle was used as before. The mixing cycle, start temperature and sequence of the material addition, especially when silica system was included, were done as in Section 4.6. Dump temperature of the masterbatches ranged from 140 - 150°C.

8.3.2 New Instrument for analysing processing properties

As well as the typical Mooney viscometer, a rheometer type TMS (Negretti Automation) was used\textsuperscript{116}. A schematic diagram of the recently developed machine is shown in Figure 8.1. Its choice offered several advantages over the Mooney viscometer. One of these advantages is the ability to vary rotor speed from 0.1 - 100 cpm. This results in a wide range of shear rates which could be closer to those encountered during factory processing. Another advantage is that the rubber mix feeds into the test cavity by transfer moulding giving more uniform distribution. Moreover, the use of a biconical rotor gives better distribution of shear forces.
<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Polymer(s)</th>
<th>Reinforcing system</th>
<th>Anti-oxidants</th>
<th>Curing system</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMR20</td>
<td>SBR1500</td>
<td>SBR1712</td>
<td>BR cis</td>
<td>ISAF</td>
<td>VN3</td>
</tr>
<tr>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td>IPPD</td>
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<td>Fletol N</td>
</tr>
<tr>
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<td>Paraffinic wax</td>
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<tr>
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<td></td>
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<td>MBS</td>
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<td>SAFPA</td>
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<td>ZnO</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>Stearic acid</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td>Highly aromatic oil</td>
</tr>
<tr>
<td>Mix Identification</td>
<td>Factory tread mixes</td>
<td>Developed mixes (previous work)</td>
<td>New experimental mixes</td>
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<tr>
<td></td>
<td>NR control mix 1 of Table 4.1</td>
<td>SBR/BR new control Mix 3 of Table 4.1</td>
<td>Mix 2 of Table 4.1</td>
<td>Mix 3 of Table 4.1</td>
<td>Mix 3 of Table 5.1</td>
</tr>
<tr>
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<td>B</td>
<td>C</td>
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</tr>
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<td>BR cis</td>
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<td>35</td>
<td>-</td>
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</tr>
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<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
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<tr>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Paraffinic wax</td>
<td>2</td>
<td>1.5</td>
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<td>2</td>
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<tr>
<td>Sulphur</td>
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<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>MBS</td>
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<td>-</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>CBS</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DPG</td>
<td>-</td>
<td>0.1</td>
<td>0.5</td>
<td>-</td>
<td>0.5</td>
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<tr>
<td>SAFPA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3</td>
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<tr>
<td>ZnO</td>
<td>4</td>
<td>2.5</td>
<td>4</td>
<td>2.5</td>
<td>4</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>Highly aromatic oil</td>
<td>7</td>
<td>10</td>
<td>7</td>
<td>7</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 8.1 Tyre tread formulations (controls and experiments) chosen for performance comparison
Fig. 8.1: Schematic diagram of the TMS Rheometer
Finally, the machine is supplied with a stepper motor drive giving a programmable speed control and data can be processed through an on-line computer to ease calculation. The shear rate on this machine is related to the rotor speed through the following equation

\[ \dot{\gamma} = \frac{W}{\alpha} \]  ... 8.1

where \( w \) is the rotor speed in rad/sec. and \( \alpha \) is the rotor's angle in rad.

8.4 COMPARISON OF PROCESSING AND VULCANISATE PROPERTIES

8.4.1 Comparison of processing and ODR properties

8.4.1.1 Processing properties

Table 8.2 shows the viscosity values of the controls (mixes A and B) plus four other developed mixes expressed in terms of Mooney viscosity readings. Generally, all viscosities fall in the acceptable range of 44 - 55 Mooney. However, as viscosity of a filled rubber varies dramatically with the change in shear rates, the rheological properties cannot be adequately defined by measuring viscosity at one stage\textsuperscript{113}. Hence, for an industrial investigator, attempts to express these properties by as high a shear rate as possible is desirable in order to be consistent with the trends towards higher efficiency in processing\textsuperscript{114}. The TMS machine, which became available at a later stage of the research, was seen as more suitable to fulfill such a demand. Therefore, its use made it possible to characterise on a comparative basis the rheological properties of the experimental mix I with the NR/ISAF control mix H. Both mixes H and I were also compared with a gum mix that contained all the ingredients of mix H except for the reinforcing system. This gum mix was meant to serve as a base to judge the effect of the different reinforcing systems on the rheological properties. Shear rates selected were 0.1, 1, 10, 20 s\(^{-1}\) and the test was conducted at 100\(^0\)C. The shear stresses obtained are plotted against the increased shear rates in Figure 8.2.
The gum mix shows, as expected, the lowest $T$ at all values followed by the NR/ISAF control (mix H). The presence of both the silica and the cis-BR caused the value of $T$ for (mix I) to increase. This high but tolerable increase is believed to be due to the known resistance of BR to break-down (see Section 5.4.2) and also to the presence of silica. A peculiar observation is seen at a shear rate of 20 s$^{-1}$ where the steadily marching curve of the NR/ISAF control tends to decline whereas both the silica containing mix and the gum control remain unaffected. This phenomenon has been observed earlier for some carbon black mixes and attributed to the sensitivity of these mixes to temperature. In other words this means that high shear rates tend to increase the temperature of the specimen beyond the experimental due perhaps to the internal friction within the mix system. This results in a reduction in the shear stress in the observed trend. The above explanation however does not adequately characterise the case with the silica and the gum mixes.

8.4.1.2 Monsanto ODR properties

Tread mixes A, C and D gave typical shorter scorch times compared to the SBR/BR mix regardless of the reinforcing system used. However, all the scorch times of the tread mixes fall within the technically desirable limits normally designed for this property. Also, the inclusion of BR with the NR gave a beneficial increase in the extended over-cure reversion. The reduced reversion offers (besides the advantages that have already been discussed in Section 5.4.2) the ability to conduct curing at higher temperature.

8.4.2 Curing properties

Comparison of the basic physical properties, as shown in Table 8.2, reveals that mix I acquires good modulus and hardness both of which are believed to be favourable for skid resistance. However, the presence of BR caused an expected decrease in tensile and tear strength. Elongation at break was moderately affected.
Fig. 8.2: Rheological properties of two selected tread mixes of Table 8.1 and a base gum mix
<table>
<thead>
<tr>
<th>Property</th>
<th>Mix Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td># Processing properties</td>
<td></td>
</tr>
<tr>
<td>ML(1+4)100°C</td>
<td>50</td>
</tr>
<tr>
<td>ODR properties 160°C.</td>
<td></td>
</tr>
<tr>
<td>(Mixes H and I at 150°C)</td>
<td></td>
</tr>
<tr>
<td>t₂(min)</td>
<td>2.7</td>
</tr>
<tr>
<td>t₉₅(min)</td>
<td>5.6</td>
</tr>
<tr>
<td>Maximum torque dN.m</td>
<td>62</td>
</tr>
<tr>
<td>Overcure reversion % (2 hrs)</td>
<td>22</td>
</tr>
<tr>
<td>Curing properties 160°C</td>
<td></td>
</tr>
<tr>
<td>300% Modulus MPa</td>
<td>9.2</td>
</tr>
<tr>
<td>Tensile strength MPa</td>
<td>25</td>
</tr>
<tr>
<td>Ultimate elongation %</td>
<td>600</td>
</tr>
<tr>
<td>Crescent tear strength kNm⁻¹</td>
<td>127</td>
</tr>
<tr>
<td>Zwick rebound resilience %</td>
<td>52</td>
</tr>
<tr>
<td>Hardness IRHD</td>
<td>62</td>
</tr>
</tbody>
</table>

Table 8.2 Processing and curing properties of the selected tread mixes
Nevertheless, these moderate values remain much superior to those of the SBR/BR control (mix B). Also, the use of silica and BR in mix I caused a distinctive increase (about 20%) in resilience. In fact, such an effect was noticed earlier when these two ingredients were used individually (Table 4.1 and 5.3). It is known that vulcanisates acquiring high resilience normally show favourable heat build-up properties. The heat build-up and some other selected properties that are usually considered critical for tread life will be discussed in detail in the next sections.

8.4.2.1 Tearing Energy T

The experience gained from the previous experimental work (Chapter 4) has shown, within the limitations of the test, that the tearing energy can be utilised as a good criterion for measuring the effect of reinforcing fillers on rubber strength. Thus, this criterion was also used to judge the strength properties of four selected tread vulcanisates of Table 8.1. The experimental procedure was conducted as in Section 4.10 using the trouser tear geometry; the test was carried out at 20 and 100°C. The results obtained are displayed in Table 8.3. As the Table shows, the NR-silica-ISAF/SAPA (mix D) gave the highest T value while the SBR/BR/ISAF (mix B) showed the lowest. The experimental rubber (mix I) had a T value at 20°C which is 33% lower than the NR/ISAF control (mix A) but 48% higher than the SBR/BR vulcanisate (mix B). A more drastic reduction in T value of mix I is seen when the test was conducted at 100°C. However, this value remained higher than that of mix B. The reason behind such a reduction may be ascribed to the presence of BR, whose molecular structure and weight do not allow higher resistance to the applied forces compared with the NR based vulcanisates. It is interesting to note the ability of the whole NR vulcanisates to retain more than 50% of their T values when the test was conducted at 100°C whilst those of SBR/BR and NR/BR retained slightly more than one third.
Table 8.3  Tearing energies (reinforced trouser) of four of the tread vulcanisates

<table>
<thead>
<tr>
<th>Mix</th>
<th>Identification</th>
<th>Tearing Energy kJ/m² at 20°C</th>
<th>Tearing Energy kJ/m² at 100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix A</td>
<td>40</td>
<td></td>
<td>22</td>
</tr>
<tr>
<td>Mix D</td>
<td>41</td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>Mix B</td>
<td>18.3</td>
<td></td>
<td>6.2</td>
</tr>
<tr>
<td>Mix I</td>
<td>27</td>
<td></td>
<td>9.3</td>
</tr>
</tbody>
</table>

8.4.2.2 Dynamic crack growth resistance

Higher crack growth resistance is one of the essential properties that a tread vulcanisate must acquire. Therefore, it was decided to judge the dynamic crack growth resistance of selected tread vulcanisates of Table 8.1 [mixes B, H and I] according to BS 903 Part A11 : 1976.

Each moulded specimen was pre-cracked, using a piercing tool, in the bottom of the groove at a point equidistant from the edges of the groove, as recommended by the standard. Each crack was made by a single insertion with the blade of the piercing tool moistened with water. Only specimens that had a perpendicular crack to the flexing direction were counted. The length of each crack was then measured with a low magnification light microscope. The tests were conducted on the specimens at 20 and 100°C.
Crack propagation due to cyclic flexure was later deduced from the increase in the length of the crack per a given number of cycles. The results are expressed in terms of rate of crack propagation in Table 8.4.

The SBR/BR based vulcanisate (mix B) gave 4 - 5 times higher propagation rate than the other NR vulcanisates at room temperature. This is hardly surprising as SBR vulcanisates are known to have lower resistance to crack growth compared with NR. However, the presence of BR-silica combination in the experimental rubber mix I improved the crack growth resistance compared with the NR/ISAF control mix A. This is believed to be the result of a combination of greater resistance to flexural failure conferred by the cis.BR and a higher tendency towards microscale diversion of the crack growth path conferred by the silica. When the test was conducted at 100°C the specimen of mix B ruptured completely before one kilocycle was completed, while the NR vulcanisates mixes H and I showed much lower response to the hot flexure. This is not merely related to the filler system but perhaps to the presence of NR which has a proven hot crack resistance.

<table>
<thead>
<tr>
<th>Mix Identification</th>
<th>Cold Crack Growth mm/kc</th>
<th>Hot Crack Growth mm/kc</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR/BR (mix B)</td>
<td>1.665</td>
<td>ruptured</td>
</tr>
<tr>
<td>NR/ISAF (mix H)</td>
<td>0.453</td>
<td>2.24</td>
</tr>
<tr>
<td>NR-BR/silica-ISAF (mix I)</td>
<td>0.306</td>
<td>2.02</td>
</tr>
</tbody>
</table>

Table 8.4 Crack growth of selected tread vulcanisates on De Mattia machine
8.4.2.3 Stress relaxation

Stress relaxation is the measurement of change in stress with time under constant strain. It is therefore used as a guide to ageing (chemical relaxation) as well as physical relaxation. The former is generally ascribed to attack by oxygen or ozone which is usually intensified under stretching, whereas the latter is attributed to weakening or failure of polysulphidic or rubber-filler chemosorptive forces (i.e. when carbon black is used as a reinforcing filler) or weak polymeric chains.

Both of these modes of failure are relevant to tread rubber where repeated flexing and compression against the road at elevated temperature is commonplace. Stress relaxation is sometimes utilised as a criterion for assessment of the effect of fillers on reinforcement, as has already been noted in Section 3.2. Therefore, it was decided to assess the effect of BR, silica and the moderate level of sulphur on the rate of relaxation of the experimental rubber (mix I) compared to the NR/ISAF control mix H which has an identical amount of sulphur. Both extension and compression modes of relaxation were selected.

8.4.2.3.1 Stress relaxation in extension

This test was conducted to BS 903 Part A52 : 1986 by using a Wallace type age-tester. Test specimens from both the vulcanisates (mixes H and I) were prepared by moulding to t95 to a thickness of approximately 0.4 mm and cut to size using a sharp cutter (10 mm wide). They were later extended to 100% of their clamped length and the test was conducted in a hot air oven at 100°C for 7 days during which stress decay was monitored continuously. The results obtained are expressed in terms of stress relaxation

\[
\frac{F_o - F_t}{F_o} \times 100
\]
Fig. 8.3: Stress relaxation in 100% extension at 100°C of 0.4mm thick vulcanised strips obtained from mixes H and I of Table 8.1.
and are plotted versus time in Figure 8.3. The Figure clearly mirrors the superiority of the experimental rubber over the whole period of the test. At the end of the experiment the NR-BR/silica-ISAF rubber (mix I) had retained 20% of its initial stress versus 7% for the NR/ISAF control.

This finding may support the earlier argument concerning the effectiveness of the silica-rubber interaction at high temperature and extension in withstanding chemical and physical decays. This superiority was disguised in the static ageing of the silica vulcanisates (discussed in Section 4.14) by the presence of a higher level of sulphur (2.5 phr) compared to the lower level used in the present series of mixes.

8.3.4.3.2 Stress relaxation in compression

An extensive research programme carried out by a team at Loughborough University has shown that none of the equipment used to evaluate this property was entirely satisfactory. Therefore a new instrument has been developed. Reports\textsuperscript{133} were published later claiming that the developed instrument has eliminated many of the technical shortcomings.

This machine was therefore chosen to evaluate the relaxation properties of mixes H and I. Cylindrical specimens 6.3 mm in height and 12.70 mm in diameter were prepared by compression moulding to \( t_{95} + 5 \) mins at 150\(^\circ\)C. The specimens were then clamped at 25% strain and the test was conducted at 20\(^\circ\)C and 100\(^\circ\)C for a week with measurements of force taken frequently. The results of stress relaxation at room temperature are plotted against time in Figure 8.4. The Figure again shows the NR/silica rubber mix I as giving lower stress relaxation compared with the NR/ISAF control at this temperature.
Fig. 8.4: Stress relaxation under 25% compression at room temperature (20°C) of vulcanised specimens obtained from mixes H and I of Table 8.1.
Fig. 8.5: Stress relaxation under 25% compression at 100°C of vulcanised specimens obtained from mixes H and I of Table 8.1.
However, this superiority is not maintained as a different pattern is seen in Figure 8.5 where the hot compression resulted in a lower retention (higher rate of relaxation) for the experimental rubber compared to the control. At the end of the test the experimental rubber had retained 32% of its original stress compared to 43% of the control. It is believed that the prolonged compressive loads under heat leads to failure by shear. The relatively long coupling bonds between rubber and silica may be less resistant to the shear compression under heat than under normal temperature. This tendency was in contrast to the case of stress relaxation under extension in which failure is believed to be due to network rupture.

8.4.2.4 Heat build-up HBU

HBU properties must be taken into consideration in abrasion development studies because these properties are known to be incompatible with increase in abrasion resistance of carbon black vulcanisates. Therefore, HBU was studied by two different methods. The first was by utilising damping properties at moderate strain and low frequency. Such a method has been widely reported to give a good correlation with heat build-up and rolling resistance especially when tan δ, for instance, is measured at temperatures representative of the surface i.e. 80°C for a tread rubber47,49. The second method was selected to determine the HBU properties under more severe conditions, by utilising the Goodrich flexometer to BS 903 Part A50 : 1984. This test gives a measure of heat generated under dynamic compression (destructive test).

8.4.2.4.1 HBU under moderate strain and low frequency

It has been noted in Section 5.6 that dynamic properties are dependent on several factors such as filler type and loading, crosslink density and structure and the type of elastomer. These factors are not all identical in the present series of mixes. Therefore, the comparison is made on the basis of equality in the filler loadings and proximity of the moduli.
A recent study\textsuperscript{130} has established that rubber components that are subjected to sinusoidal dynamic stress will generate heat according to the following equation

\[
\text{Ed} = \frac{W}{2} (S_o)^2 \mathcal{J}^\prime (W) \quad \ldots \quad 8.2
\]

where

- \text{Ed} = \text{energy dissipated per second}
- \text{W} = \text{frequency of the applied stress (radian/sec)}
- \text{So} = \text{amplitude of the stress}
- \mathcal{J}^\prime (W) = \text{loss compliance}

The maximum stored energy in the same part is described by

\[
\text{Es} = \frac{W}{4} (S_o)^2 \mathcal{J}^\prime (W) \quad \ldots \quad 8.3
\]

where

- \text{Es} = \text{energy stored per second}
- \mathcal{J}^\prime (W) = \text{storage compliance}

Equation 8.2 can be restated as

\[
\text{Ed} = \frac{W}{2} (S_o)^2 \tan \delta \mathcal{J}^\prime (W) \ldots \quad 8.4
\]

with \( \tan \delta = \mathcal{J}^\prime (W)/\mathcal{J}^\prime (W) \)

Evaluation of damping properties was made by the DMA machine at a moderate amplitude (0.4 mm) and a low frequency (1Hz) using cured rectangular specimens of dimensions 30 x 10 x 2 mm with the clamped length of the specimen kept to about 10 mm. Earlier work has shown that the selected frequency gives a good correlation between \( \tan \delta \) and actual heat build-up of the rubber\textsuperscript{131}.

The values of \( \tan \delta \) and \( E \) at various test temperatures of six selected mixes from Table 8.1 are shown in Table 8.5 which shows that the SBR/BR vulcanisate (mix B) exhibits the highest value for both \( \tan \delta \) and \( E \) at both 0 and 20\degree C. This observation is consistent with the known fact that, everything being equal, SBR is more hysteretic than NR. Inclusion of silica/TESPT system with both NR and NR/blends further reduces \( \tan \delta \) and \( E \) values.
<table>
<thead>
<tr>
<th>Mix identification</th>
<th>tan $\delta$</th>
<th>$E^*$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at tg</td>
<td>at 0°C</td>
</tr>
<tr>
<td>Mix A</td>
<td>0.8777</td>
<td>0.1606</td>
</tr>
<tr>
<td>Mix B</td>
<td>0.4952</td>
<td>0.2</td>
</tr>
<tr>
<td>Mix C</td>
<td>0.9674</td>
<td>0.1843</td>
</tr>
<tr>
<td>Mix D</td>
<td>0.9816</td>
<td>0.2332</td>
</tr>
<tr>
<td>Mix F</td>
<td>0.7374</td>
<td>0.1561</td>
</tr>
<tr>
<td>Mix I</td>
<td>0.7462</td>
<td>0.1328</td>
</tr>
</tbody>
</table>

Table 8.5 DMA values of tan $\delta$ and $E^*$ of selected tread vulcanisates of Table 8.1
Reduction of tan δ and E is considered highly desirable as they are indicative of a reduced heat build-up, provided that the expected adverse effect on skid and abrasion resistance is tolerable.

8.4.2.4.2 HBU measurements by the Goodrich flexometer

This apparatus is widely used to determine the internal heat generation of rubber under flexing compression. Although the standard has pointed out that no simple correlation can be found between the accelerated test and service performance, several reports have revealed that a good prediction is possible. The apparatus offers the advantage of providing a wide range of compressive loads, high frequency of compression (30 Hz) and stroke (double amplitude) of 17.5%. Such severity usually causes the destruction of the polymeric network and possibly the filler-rubber interface. The technique also offers the advantage of not only measuring heat build-up but also compression set, dynamic compression and hardness. The specimen required for the test is a rubber cylinder 17.8 mm in diameter and 25 mm high. This is normally subjected to a standard load throughout the test and temperature is measured at the rubber surface. Therefore, this technique was also chosen to assess experimentally the heat build properties of two selected tread vulcanisates. Due to the local unavailability of the apparatus, the test was conducted at RAPRA Laboratories.

Specimens were prepared from three of the tread vulcanisates of Table 8.1; these were the NR/ISAF (mix H), the bonded silica experimental (mix I) and the SBR/BR/ISAF mix B. There were three reasons for this choice.

A. All three vulcanisates contained equal moduli which are considered as critical factors in the determination of HBU.
<table>
<thead>
<tr>
<th>Property</th>
<th>NR/BR- Silica/ISAF Mix I</th>
<th>NR/ISAF Control Mix H</th>
<th>SBR/BR/ ISAF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static load Kg</td>
<td>11</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>Indentation hardness IRHD</td>
<td>63</td>
<td>67</td>
<td>62</td>
</tr>
<tr>
<td>Initial height mm</td>
<td>24.52</td>
<td>24.71</td>
<td>24.65</td>
</tr>
<tr>
<td>Final height mm</td>
<td>24.37</td>
<td>24.39</td>
<td>24.15</td>
</tr>
<tr>
<td>Compression set %</td>
<td>0.61</td>
<td>1.30</td>
<td>2.03</td>
</tr>
<tr>
<td>Static compression %</td>
<td>52.56</td>
<td>49.01</td>
<td>-</td>
</tr>
<tr>
<td>Total dynamic compression</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- initial %</td>
<td>43.85</td>
<td>40.69</td>
<td>-</td>
</tr>
<tr>
<td>- final %</td>
<td>44.06</td>
<td>42.13</td>
<td>-</td>
</tr>
<tr>
<td>Applied stroke mm</td>
<td>4.45</td>
<td>4.45</td>
<td>4.45</td>
</tr>
<tr>
<td>Peak to peak displacement °C</td>
<td>4.267</td>
<td>4.115</td>
<td>-</td>
</tr>
<tr>
<td>Ambient temperature °C</td>
<td>21</td>
<td>21</td>
<td>21</td>
</tr>
<tr>
<td>Thermocouple base temperature °C</td>
<td>19.9</td>
<td>20.6</td>
<td>23</td>
</tr>
<tr>
<td>Running time min</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Temperature rise T</td>
<td>20.9</td>
<td>27.7</td>
<td>54</td>
</tr>
<tr>
<td>% increase</td>
<td>-</td>
<td>32</td>
<td>158</td>
</tr>
</tbody>
</table>

Table 8.6 · Heat build-up as measured by Goodrich flexometer BS903 Part 50:1984 of two of the tread vulcanisates
B. The value of tan $\delta$ of mix H was already seen as the lowest of the non-silica containing vulcanisates predicting good dynamic properties for it as a control. On the other hand mix B showed the highest tan $\delta$ indicating the generally high heat build-up of the SBR and justifies its selection as an opposite extreme to the NR/ISAF control.

C. It was hoped that the selected vulcanisates would give a comparison between the effect of ISAF versus the optimised silica/ISAF system of mix I.

Table 8.6 shows the results obtained under the test conditions indicated. Although both the NR vulcanisates show excellent HBU properties, the superiority of the silica bonded experimental mix I is obvious. This may be attributed to the presence of coupling bonds which, due to their length, offer a better distribution of the impact. They also improve resilience and elasticity leading to better overall dynamic properties and consequent unique reduction in heat build-up under repeated compression. The SBR vulcanisate shows a $\Delta T$ value twice as high as those of the NR vulcanisates.

8.4.2.5 Abrasion resistance

Specimens for the DIN and Akron abraders, as well as miniature tyres of some of the nine tread vulcanisates of Table 8.1, were tested under similar conditions so that a comparison of the performance of these vulcanisates could be made. The DIN and Akron specimens were tested according to the standard as before while the miniature tyres were tested hot as in Section 4.8.2.3.3. Table 8.7 displays the values of the abrasion loss on the three machines. These indicate, as has been noted earlier, that the presence of the bonded silica as a filler with the ISAF in mixes C, D, E and I causes the abrasion resistance of these vulcanisates to improve with reference to NR/ISAF controls (Mixes A and H) on all the abrasion machines used. The presence of BR with both NR and SBR also shows a positive effect on the abrasion resistance of the vulcanisates containing it for each of the reinforcing systems used.
<table>
<thead>
<tr>
<th>Mix identification</th>
<th>Volume loss DIN abrader $\text{mm}^3$</th>
<th>Volume loss Akron abrader $\text{mm}^3$</th>
<th>Miniature tyre loss mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix A : NR/ISAF (control)</td>
<td>162</td>
<td>86</td>
<td>400</td>
</tr>
<tr>
<td>Mix B : SBR/BR/ISAF (control)</td>
<td>128</td>
<td>48</td>
<td>283</td>
</tr>
<tr>
<td>Mix C : NR/Silica/ISAF</td>
<td>144</td>
<td>61</td>
<td>322</td>
</tr>
<tr>
<td>Mix D : NR/Silica/ISAF /SAPA</td>
<td>132</td>
<td>50</td>
<td>344</td>
</tr>
<tr>
<td>Mix E : NR/BR/Silica /ISAF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mix F : NR/BR/ISAF</td>
<td>128</td>
<td>70</td>
<td>301</td>
</tr>
<tr>
<td>Mix H : NR/ISAF (medium sulphur)</td>
<td>164</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mix I : Nr/BR/Silica /ISAF/SAPA</td>
<td>122</td>
<td>59</td>
<td>317</td>
</tr>
</tbody>
</table>

Table 8.7 Comparative abrasion loss of tread vulcanisates of Table 8.1 on three abrasion machines
The positive effect of the bonded silica has already been ascribed to its enhancement of the tearing energy and the improvement of dynamic properties of its vulcanisates. The effect of BR has been attributed to the reduction of the frictional forces between the rubber and the abrading surface.

8.4.2.6 Wet skid resistance WSR

8.4.2.6.1 Background

This property is considered one of the most critical factors in the determination of tyre performance. Published data show that accidents involving wet skidding in Britain are more than twice as frequent as on dry roads\textsuperscript{138}. However, the frequency increases to as high as 6 times in parts of the United States and Germany\textsuperscript{119}. Therefore, it is understandable that much emphasis has been placed on the optimisation of WSR to decrease accidents. Skid resistance in tyres can be classified as being either vehicle or trailer tested. The typical measurements made in a vehicle test are either the stopping distance from some given speed or measurement of lateral spinout speed. However, these measurements depend on specific road, vehicle and tyre characteristics. As far as the tyre is concerned the type and depth of tread patterns and tyre construction are the main factors in the determination of its skid properties. Nevertheless, the composition of the tread compound plays a minor but vital part in the determination of the overall skidding resistance. Reports by Grosch\textsuperscript{120}, Giles and Tabor\textsuperscript{121} and others\textsuperscript{124} have shown, after extensive road and laboratory tests, that it was possible to predict the relative WSR by using a British skid tester which was preferred for its cheapness, reproducibility and ease of handling. A modified version of this instrument is discussed in Section 5.5.2.2. An attempt is made here to try the modified skid tester to evaluate the relative WSR of the tread vulcanisates of Table 8.1.
Test specimens were prepared from the tread mixes by curing to $t_{95} + 10$ minutes at $150^\circ$C. These were tested in a procedure similar to that of Section 5.5.2.2 except for the wetting of the surface by water. The latter was achieved by a spray gun supplied with a head with very small nozzles so that very small water drops can settle on the surface. This model was seen, after several trials and errors, as a satisfactory way of achieving a uniform water film on the curved specimen. To ensure that enough water was present, the spraying was also done at the instant of the test. It must be recognised, however, that absolute measurements of the thickness and homogeneity of the water film (whose values are important for the end results) was not possible. The average of five readings of each of the tread vulcanisates tested was taken omitting the first three. Before discussing the results, it must be recalled that, during the investigation of the DSR, the adhesive properties of the individual polymer predominantly decide its skidding properties. The resilience at constant hardness was seen as a minor factor. However, the effect of sliding friction becomes very low or entirely diminished when a water film is present and hence the rôle of factors like resilience and hardness may become more critical. As the values of resilience and hardness of the present series of mixes were not equal, some effect on the corresponding values of WSR is expected.

This effect was not seen as having a bearing on the present investigations as the real objective was to check where the relative WSR of the optimised tread rubbers stood regardless of the individual ingredients and other details. The achievement of such a demand necessitated defining the vulcanisates as a control. Experience as well as some field surveys, have shown that SBR are the best skid resistant treads among tyre polymers when the hardness is equal. This was ascribed to their higher hysteretic losses. However, SBR is rarely compounded on its own for tread rubbers and BR is the usual supplementary polymer. Therefore, mix B (SBR/BR) was chosen as a prime control for the present purpose.
Table 8.8 shows the values of WSR of the tread vulcanisates. The first observation is that the skid numbers have values about one quarter of those obtained when the DSR was measured. Also, it is difficult to find striking differences in the values except perhaps for the SBR/BR vulcanisate. Its reported superior skid resistance however is not as high as expected possibly due to the presence of BR.

The wetting of the surface is generally responsible for the drastic fall in traction. Nevertheless, it can be seen from Table 8.8 that the combined and individual effect of both BR and silica cause a slight reduction in WSR compared with the NR/ISAF control.

<table>
<thead>
<tr>
<th>Vulcanisate identification</th>
<th>Wet skid number</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR/ISAF control mix A</td>
<td>14</td>
</tr>
<tr>
<td>SBR/BR control mix B</td>
<td>18</td>
</tr>
<tr>
<td>NR/silica/ISAF/TESPT mix C</td>
<td>13</td>
</tr>
<tr>
<td>NR/silica/ISAF/TESPT/SAPA</td>
<td>13</td>
</tr>
<tr>
<td>NR/BR/silica/ISAF mix E</td>
<td>14</td>
</tr>
<tr>
<td>NR/BR/ISAF mix F</td>
<td>14</td>
</tr>
<tr>
<td>NR/ISAF/mod. sulphur mix H</td>
<td>14</td>
</tr>
<tr>
<td>NR/BR/silica/ISAF/SAPA mix I</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 8.8 Wet skid numbers for selected tread vulcanisates of Table 8.1 as measured by the modified British skid tester

Table 8.8 also indicates that when the adhesion between the metal slider and the rubber block is slight, $\tan \delta$ of the tread vulcanisates correlates reasonably with their WSR values indicating the importance of rubber hysteresis on skidding characteristics.
8.4.2.7 Ice skid resistance ISR

Polymers that show high wet skid resistance on the whole show poor ice friction. It has been proposed that softness and resilience are far more important for better traction on ice\textsuperscript{134}. Because of this, the use of blends of BR with NR have become increasingly popular in winter tyres to cope with the emphasis that has been given to ice friction in the last few decades. More recently, Roberts et al\textsuperscript{2,3} have reported that the use of silica in truck tyres improved ice traction. Therefore, it was decided to obtain data to assess the response of the silica and cis-BR containing polymers of the present series compared to the other carbon black containing controls of various polymer systems. The icy conditions required were simulated by a modified method of one used by Ahagon et al\textsuperscript{134}.

8.4.2.7.1 Method

Cured rubber blocks were obtained from the vulcanisates of Table 8.1 (except for mixes D, E and F) and these were enveloped in polyethylene bags and kept in a deep freezer to cool down to a temperature as low as \(-20^\circ\text{C}\). The smooth metal striker was also cooled down by immersion in liquid nitrogen, as was the metal clamp that holds the rubber block. Ice on the part of the striker that comes into contact with the rubber specimen was obtained by wiping the bottom of the frozen striker with a water-wetted cloth. The surface of the resultant ice layer was then levelled off on a piece of glass. Each rubber block was fitted firmly on the frozen clamp at approximately equal times (10 seconds). The temperature inside the rubber specimen was controlled by using a thermocouple inserted in the centre. Then the temperature was left to rise to \(-2^\circ\text{C}\) for the rubber block and to \(-10^\circ\text{C}\) for the ice on the bottom of the striker. These temperatures were randomly selected as simulating icy conditions. Immediately before the commencement of the test the surfaces of both the striker and the specimen were wiped with a dry clean cloth to remove any frost which otherwise causes misleading results and perhaps the lowest ever traction. This procedure was repeated for each specimen tested\textsuperscript{134}. The first reading was recorded.
8.4.2.7.2 Results

The results obtained are displayed in Table 8.9.

<table>
<thead>
<tr>
<th>Vulcanisate identification</th>
<th>Ice skid number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix A</td>
<td>13</td>
</tr>
<tr>
<td>Mix B</td>
<td>7</td>
</tr>
<tr>
<td>Mix C</td>
<td>11</td>
</tr>
<tr>
<td>Mix D</td>
<td>14</td>
</tr>
<tr>
<td>Mix F</td>
<td>14</td>
</tr>
<tr>
<td>Mix I</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 8.9 Ice skid resistance number of selected tread vulcanisates of Table 8.1 as measured by the modified British skid tester

It is obvious from the Table that mix B (SBR/BR) gives the lowest number while mix I (NR/BR/silica/ISAF) shows the highest. Other vulcanisates fall between these two values. Mix B behaved in this experiment in an opposite manner to its behaviour in the wet skid experiment where the highest wet skid number was obtained by this vulcanisate. This might be associated with the relatively high Tg of this polymer which makes it less flexible (harder) at the temperature of the test. On the other hand the NR and NR/BR containing vulcanisates showed a higher ice skid number, although the difference between them remained low because the reduced Tgs of these two polymers make them more resilient at the test temperature. Therefore, more frictional forces are created during the contact as some energy is dissipated by the rubber.
8.4.2.8 Dry skid resistance DSR

Five selected tread vulcanisates of Table 8.1 were comparatively dry tested by the modified skid tester following the procedure of Section 5.5.2.3. The results obtained are displayed in Table 8.10.

<table>
<thead>
<tr>
<th>Mix identification</th>
<th>DSR number</th>
<th>μ*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix A (NR/ISAF)</td>
<td>53</td>
<td>0.58</td>
</tr>
<tr>
<td>Mix B (SBR/BR/ISAF)</td>
<td>47.5</td>
<td>0.50</td>
</tr>
<tr>
<td>Mix C (NR/silica/ISAF/TESPT)</td>
<td>49.5</td>
<td>0.51</td>
</tr>
<tr>
<td>Mix D (NR/silica/ISAF/TESPT/SAPA)</td>
<td>51</td>
<td>0.53</td>
</tr>
<tr>
<td>Mix I (NR/BR/silica/ISAF/TESPT/SAPA)</td>
<td>46</td>
<td>0.485</td>
</tr>
</tbody>
</table>

* estimated from the equation:

\[
\text{skid number} = \frac{330 \mu}{3 + \mu}
\]

Table 8.10 DSR number (smooth slider) of five selected tread vulcanisates of Table 8.1

The data in the Table clearly shows the NR/ISAF control as having the highest DSR number with subsequent highest μ. Inclusion of silica, however, seems to reduce these values. The combined effect of both the silica and BR-clis causes a further reduction in the values of both DSR and μ. These values remain closer to those of the SBR/BR control than the NR/ISAF.
8.5 Unaged vs. aged properties

The ageing properties studied on three previous occasions were aimed to investigate the effect of certain isolated factors on these properties such as the reinforcing system, the polymer blend and the anti-oxidants. It was seen that a better opportunity was offered to investigate the cumulative effect of these variables at this stage as they are available in a single formulation (mix I). Also, the presence of good quality controls and in certain cases, the advantageous resemblance in the ingredient range, were seen as helpful in comparing the ageing properties with a broad range of tread vulcanisates.

Table 8.11 displays the difference between some of the unaged properties of the vulcanisates and those obtained after ageing in a hot air oven for 3 days at 100°C. All the vulcanisates retained between 50 - 74% of their tensile strength values which can be considered as adequate for the temperature of the test. The retention of tear strength was even better than that of tensile strength. Examination of the individual values, which perhaps gives a more meaningful picture than the retention, showed the NR vulcanisates had higher aged values when the silica/ISAF system is used compared to those reinforced with ISAF, indicating more heat stability conferred by the silica. However, the crescent tear values do not reflect such a trend.

A further examination of the figures in the Table shows that the presence of ISAF alone in the NR/BR blend (mix E) gives better properties than when a mixture of silica/ISAF/TESPT is used (mix F). This is in contrast to what would have been expected, as it has been speculated that the presence of BR with NR tends to attract the carbon black fillers to the BR proportion starving NR of its shear. On the other hand, NR has been reported to have a higher tendency towards silica and the presence of silica and ISAF in a single formulation was thought to give a better overall filler distribution. When SAPA was used with the silica/ISAF reinforced NR/BR vulcanisate (mix I) the physical properties enhanced to almost match those of the NR/BR-ISAF vulcanisate (mix F) especially in the aged properties.
<table>
<thead>
<tr>
<th>Mix Identification</th>
<th>NR ISAF</th>
<th>SBR/BR ISAF</th>
<th>NR/ISAF Silica/SAPA</th>
<th>NR/ISAF Silica</th>
<th>NR/BR ISAF/Silica</th>
<th>NR/BR ISAF</th>
<th>NR/BR High Sulphur Silica/ISAF/SAPA</th>
<th>Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>time (hrs)</td>
<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
<td>E</td>
<td>F</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>0 72</td>
<td>0 72</td>
<td>0 72</td>
<td>0 72</td>
<td>0 72</td>
<td>0 72</td>
<td>0 72</td>
<td>0 72</td>
<td>0 72</td>
</tr>
<tr>
<td>100% Modulus MPa</td>
<td>1.6 2.4</td>
<td>1.8 2.5</td>
<td>2.0 2.8</td>
<td>2.5 3.4</td>
<td>2.3 3.8</td>
<td>4.1 6.7</td>
<td>1.8 3.4</td>
<td>1.7 2.7</td>
</tr>
<tr>
<td>% Increase</td>
<td>- 50</td>
<td>- 39</td>
<td>- 40</td>
<td>- 36</td>
<td>- 65</td>
<td>- 63</td>
<td>- 89</td>
<td>- 59</td>
</tr>
<tr>
<td>Tensile strength MPa</td>
<td>25 18.4</td>
<td>18 12.7</td>
<td>30 20.5</td>
<td>30.2 19.4</td>
<td>23 14</td>
<td>20.7 10.5</td>
<td>27 16</td>
<td>21 14</td>
</tr>
<tr>
<td>% Retention</td>
<td>- 74</td>
<td>- 71</td>
<td>- 68</td>
<td>- 64</td>
<td>- 62</td>
<td>- 51</td>
<td>- 59</td>
<td>- 67</td>
</tr>
<tr>
<td>Elongation at break %</td>
<td>600 468</td>
<td>500 325</td>
<td>620 425</td>
<td>580 372</td>
<td>610 341</td>
<td>500 180</td>
<td>630 350</td>
<td>560 315</td>
</tr>
<tr>
<td>% Retention</td>
<td>- 78</td>
<td>- 65</td>
<td>- 69</td>
<td>- 78</td>
<td>- 56</td>
<td>- 36</td>
<td>- 55</td>
<td>- 54</td>
</tr>
<tr>
<td>Tear strength Crescent KNm(^{-1})</td>
<td>127 94</td>
<td>42 33</td>
<td>138 93</td>
<td>145 103</td>
<td>122</td>
<td>- 109</td>
<td>- 124</td>
<td>98 100 60</td>
</tr>
<tr>
<td>% Retention</td>
<td>- 74</td>
<td>- 78</td>
<td>- 73</td>
<td>- 71</td>
<td>-</td>
<td>-</td>
<td>- 79</td>
<td>- 60</td>
</tr>
<tr>
<td>Hardness IRHD</td>
<td>60 72</td>
<td>62 -</td>
<td>60 67</td>
<td>64 73</td>
<td>69.5</td>
<td>65 -</td>
<td>68 67</td>
<td>63 63</td>
</tr>
</tbody>
</table>

Table 8.11 Comparison of unaged and aged properties (72 hours at 100\(^\circ\)C) of the tread vulcanisates of Table 8.1
8.6 CONCLUSIONS

The combined use of UltraSil VN₃ and BR-cis with the moderate level of sulphur and accelerator together with the optimised mixing cycle (which in turn included SAPA) has shown the following effects on the processing and curing properties of the tread vulcanisates.

1. The processing properties as measured over a wide range of shear rates are slightly inferior to those of the carbon black equivalent (control) due to the combined effect of both silica and BR-cis. Yet these properties remain within the technically acceptable range. The state of filler dispersion is excellent when the optimised mixing cycle is applied.

2. The use of unusually equivalent amounts of curatives for the silica/ISAF and ISAF filled rubbers shows good rate and state of cure obtained for the former filler system despite the use of advantageous lower sulphur level than the silica normally demands.

3. The use of BR-cis with NR causes an expected decrease in tensile and tear strength and tearing energy compared with the 100% NR equivalent. These reduced values remain higher than those of the SBR/BR control.

4. Silica and BR-cis have an advantageous higher crack growth resistance compared with the NR and SBR/BR controls under dynamic flexing at zero extension (DeMattia m/c). This has been attributed to the resistance of BR-cis to flexing and the tendency of silica to divert crack tips.
5. The experimental rubber shows higher resistance to stress relaxation under heat and extension as well as cold compression. In contrast, hot relaxation under compression shows the NR/ISAF as superior. The latter effect has been attributed to the reduced resistance of rubber-silica network to shear.

6. The experimental rubber exhibits only a little improvement in its DIN index over those obtained from the previously optimised silica mixes of Table 8.1. The DIN Index, however, remains higher than that of all NR/ISAF controls.

7. The experimental rubber possesses lower wear index on both the Akron and the wire gauze abrasion compared with the SBR/BR/ISAF control especially when the temperature of the test is high.

8. The additional advantage of the combined effect is seen in the reduced heat build-up of the experimental rubber compared with both the NR and SBR/BR controls.

9. The use of silica and BR-cl is causes slight reduction in dry and wet frictional properties compared to the NR controls. Ice friction measurements show the opposite effect.

10. When the amount of sulphur and accelerator is identical the percentage of physical properties retention of the experimental rubber is higher than that of the NR/ISAF equivalent. In previous chapters such a superiority was not seen when higher sulphur levels for silica mixes were necessary.
CHAPTER 9

THE ROLE OF COMPOUND FACTORS IN THE PHENOMENON OF TREADWEAR AND ITS MECHANISMS

9.1 INTRODUCTION

The rôle of each of the predominant compound parameters has been discussed throughout the previous chapters. Such factors were involved directly or indirectly in the complicated process of wear depending on the type of abrasion and its mechanisms. The contribution of each factor has been difficult if not impossible to isolate and study as each is dependent on other factors. For instance the increase in the compound modulus increases the hardness and reduces friction. Therefore, it was thought essential to have a wider and more manageable relationship between these factors.

In this chapter an attempt is made to simplify the subject by dividing these factors into:

A. Primary factors

These were considered as the main factors that control the process of wear from the compound point of view. If other abrasion factors involved are constant, estimation of the values of the primary factors may provide a possible prediction of the performance of each rubber under specific abrasion conditions. This, on a laboratory scale, means that it should provide a valid compound rating against selected controls.

B. Secondary factors

These are expected to be less significant than the primary factors as they confer minor effects. Their values may not necessarily provide a good prediction of the extent of wear under given conditions. In all cases, however, A and B are expected to contribute together to the process of wear and in practical terms it could be impossible to isolate them.
9.2 FACTORS CONTROLLING THE MECHANISM OF WEAR

So far, abrasion mechanisms have been described as either abrasive or fatigue although the latter was associated with roll-formation in one instance. For a given abrasion, however, it may not be possible to find a single mechanism throughout the process but a mixture of predominant and non-predominant mechanisms. Certain compounding ingredients may directly or indirectly result in conferring certain properties to their vulcanisates making them favour certain abrasion mechanisms. For instance, it has been speculated in Section 5.5.2.8 that the inclusion of BR-cis with NR causes a steady decrease in the coefficient of friction which indirectly shifts the mechanism of wear from abrasive into less damaging fatigue on the same abradants.

9.2.1 Effect of compounding factors on abrasive wear (DIN abrasion)

As has already been noted abrasive wear results from the contact between rubber under load and sharp projections and is characterised by the appearance of rough surface with deep scratches. Therefore, this mechanism is less dependent on thermal properties of the elastomer used and more sensitive to the rubber properties that increase its resistance to cutting i.e. type and level of reinforcement. If other factors are constant resistance to abrasive wear favours the following as primary factors

A. low coefficient of friction (µ)
B. high tearing energy (T)
C. high (up to certain level) hardness (H)
D. high tan S (high hysteresis)
E. an elastomer that has, or elastomers that have, low temperature coefficients of abrasion (α).
The resistance to abrasive wear is believed to favour the following as secondary factors:

a. Increased tensile strength
b. Increased elongation at break and modulus

This relationship between abrasive wear and compound properties is expressed schematically in Figure 9.1 where primary factors are shown in the inner circle and secondary factors in the outer.

Emphasis has been placed throughout the experimental work of the previous chapters on the primary factors of the tread rubber and this has been achieved as follows.

1. Inclusion of the well dispersed bonded silica instead of part of the ISAF black resulted in enhancement of the tearing energy, tensile strength but a reduction in the dry friction coefficient, elongation at break and tan $\delta$.

2. Inclusion of BR with NR in the silica optimised system gave a further reduction in $\mu$ concurrent with a reduction in T value, tensile strength and tan $\delta$.

3. The inclusion of BR, silica and anti-degradants enhances the thermal stability of the tread rubber over a wide temperature range. The above three factors are expected to interact during the wear process in a way defined by the following unified approach:

$$AD = \frac{K_1 \mu \alpha t}{HT \tan \delta}$$  

where $AD$ is the volume of rubber removed by the abrader in mm$^3$. $K_1$ is a constant.
Fig. 9.1: Model of factors affecting abrasive wear of tread rubber.
The value of $\alpha$ was estimated as 4% per $^\circ$C for NR vulcanisates and 2% per $^\circ$C for synthetic rubbers* following Schallamach$^{1,37}$ and Veith$^{50}$.

* The value of $\alpha$ can be experimentally estimated from the following equation

$$\alpha = \frac{A_t - A_0}{A_0(t - t_0)}$$

where $A_t$ is abrasion at temperature $t$, $A_0$ is abrasion at reference temperature $t_0$ where $t > t_0$.

9.2.2 Experimental evidence for the proposed hypothesis

Evidence to substantiate the approach of equation 9.1 emerges from Figure 9.2; this is a plot of the actual volume loss of six tread vulcanisates selected from Table 8.1 and their theoretical values as estimated from the equation. These theoretical values (whose estimation necessitates recalling some data from the Tables of Chapter 8 which are regathered in Table 9.1 for convenience) show a reasonable concordance with the actual volume loss.

9.3 EFFECT OF THE TREAD COMPOUND FACTORS ON FATIGUE WEAR

9.3.1 Mechanism of fatigue wear

Fatigue wear occurs due to repeated contact between the rubber surface and rough projections (i.e. blunt asperities of a track or a wire gauze) during which failure of rubber-rubber and rubber-filler network occurs possibly on a monolayer scale. This process activates the occurrence of thermoxidative degradation which in its turn enhances the abrasion process. Fatigue wear can be distinguished from the appearance of stickiness on the abraded surface and rolled debris and occasionally ridge formation. The latter can be seen when the wear process is made in one direction.
<table>
<thead>
<tr>
<th>Mix Identification</th>
<th>Vulcanisate</th>
<th>tan δ</th>
<th>DSR*</th>
<th>µ**</th>
<th>Rebound %</th>
<th>Hardness IRHD</th>
<th>Tearing energy (N/mm)</th>
<th>Tensile product</th>
<th>DIN abrasion mm³</th>
<th>Miniature tyre loss gm</th>
<th>Akron abrasion mm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>NR/ISAF</td>
<td>0.138</td>
<td>53</td>
<td>0.58</td>
<td>52</td>
<td>60</td>
<td>40</td>
<td>150</td>
<td>162</td>
<td>0.4</td>
<td>86</td>
</tr>
<tr>
<td>B</td>
<td>SBR/BR/ISAF</td>
<td>0.215</td>
<td>47.5</td>
<td>0.5</td>
<td>49</td>
<td>62</td>
<td>18.3</td>
<td>92</td>
<td>128</td>
<td>0.283</td>
<td>48</td>
</tr>
<tr>
<td>C</td>
<td>NR/Silica/ISAF/TESPT/SAPA</td>
<td>0.130</td>
<td>51</td>
<td>0.53</td>
<td>54</td>
<td>60</td>
<td>41</td>
<td>186</td>
<td>132</td>
<td>0.322</td>
<td>50</td>
</tr>
<tr>
<td>D</td>
<td>NR/Silica/ISAF/TESPT</td>
<td>0.121</td>
<td>49.5</td>
<td>0.52</td>
<td>58</td>
<td>64</td>
<td>43</td>
<td>175</td>
<td>144</td>
<td>0.344</td>
<td>61</td>
</tr>
<tr>
<td>I</td>
<td>NR/BR</td>
<td>0.117</td>
<td>46</td>
<td>0.485</td>
<td>63</td>
<td>63</td>
<td>27</td>
<td>118</td>
<td>122</td>
<td>0.317</td>
<td>59</td>
</tr>
</tbody>
</table>

* DSR = Dry skid resistance as measured by the modified British skid tester

**µ was estimated from the equation DSR = \[
\frac{330 \mu}{3 + \mu}
\]

Table 9.1 Selected properties of the tread vulcanisates of Table 8.1
Fig. 9.2. Correlation between actual volume loss (DIN abrader) and calculated one (equ. 9.1.) for the tread vulcanisates of Table 9.1.

Fig. 9.3. Correlation between actual weight loss (hot wire gauze wear) and calculated one according to equation 9.2.
9.3.2 Resistance to fatigue wear

The extent of fatigue wear is slight compared to that of abrasive wear over a given time scale. The resistance to fatigue wear has been seen to favour the following as primary factors.

A. Low coefficient of friction

B. An elastomer or elastomers with high thermoxidative resistance and thermal stability

Secondary factors involve

a. high filler-rubber interactions (i.e. reinforcement) as measured by the hot tearing energy

b. high tan $\delta$

c. high tensile strength

d. low Tg of the elastomer used

During the course of the tread rubber compounding and test in the previous chapter it was observed that

1. The use of BR-cis with NR in some of the tread vulcanisates was the main reason behind the substantial increase in their fatigue abrasion resistance. This was due to the effect of this polymer in reducing the overall frictional forces during the abrasion process and to its beneficial effect in tackling thermoxidative degradation. These advantages outweigh the reduction in strength and tan $\delta$ compared to the 100% NR control.

2. The use of the well optimised mixing cycle and SAPA enhanced the degree of silica dispersion and bonding with the elastomer(s). Therefore the rubber-filler interaction was satisfactory.
3. The use of adequate levels of antioxidant also had a positive effect on the fatigue abrasion resistance especially of the NR tread vulcanisates. The combined effect of the above factors gave a positive effect on the fatigue abrasion resistance of the developed tread rubbers compared to the NR controls. This was evidenced experimentally during the hot wear test of the miniature tyres by wire gauze abrasion. It was found later that tread vulcanisate rating and wear on the miniature tyre over a temperature range 20 - 80°C could be predicted from the following equation

\[ A_m = \frac{K_2 \mu \alpha S^2 t}{T \tan \delta} \]  \hspace{1cm} \ldots \hspace{1cm} 9.2

where \( A_m \) is the weight loss in gm. \( S \) is the slip angle, \( t \) is the test temperature.

Evidence to support this claim emerges from Figure 9.3 which illustrates the actual and estimated wear values of some selected tread vulcanisates of Table 8.1. The Figure shows a reasonable concordance.

9.4 CONCLUSIONS

The usually complicated compound factors that decide abrasion behaviour under given abrasion conditions have been broken down into primary (predominant) and secondary (non-predominant) factors according to the share of their contribution to the process of wear and its mechanism. The preceding experimental study allows some of the main factors to be isolated and studied comparatively. Then, a unified approach has been suggested to gather these factors in a single equation for each of the abrasive and fatigue wear mechanisms. The comparison of the actual wear values and the ones estimated from the equations for six tread vulcanisates having a wide range of dynamic and strength properties shows a reasonable agreement.
10.1 CONCLUSIONS

10.1.1 On compounding developments of truck tyre tread rubbers

A. Cross-examination of several properties by various techniques has demonstrated that it is possible to obtain silica-carbon black NR tyre tread formulations of superior abrasion and cut-chip resistance and lower heat build-up than the present conventional NR/ISAF black types. This has been achieved by conventional mixing techniques, by using a combination of bonded-hydrophobic silica-ISAF black to give vulcanisates that possess high tearing energy, tensile strength and good dynamic properties.

Such vulcanisates, possessing a substantial proportion of silica, have earlier shown poor processing properties, high need for curatives and lower strength properties. The introduction of a hot mixing cycle, delayed addition of ZnO and the use of a cationic surfactant such as SAPA changed this situation by conveying a satisfactory processability to the developed formulations and an unusually low curative level. However, a deterrent to the use of developed mixes at present has been the relatively higher cost (to be discussed later) due to the increased price of the coupling agent.
B. The convention of using a rubber formulation based on 100% of NR for truck tyre treads does not offer the best abrasion resistance when the dominant mechanism of abrasion is fatigue, although heat build-up and strength properties conferred by this polymer are excellent. This is because of its tendency to devulcanise and oxidise during the process to a higher extent than its synthetic counterparts. Inclusion of Br.cis, at a proportion of 20–30% of NR, has been seen to tackle this problem and improve the thermal stability of the blend with an advantageous increase in abrasion resistance and decrease in heat build-up with only little effect on frictional characteristics.

C. Evidence has emerged during the experimental work that whilst typical antioxidants, such as IPPD and Flectol H, have no pronounced effect on abrasive wear, they exert a noticeable influence on fatigue abrasion (i.e. hot miniature tyre wear). Care must be taken however, not to confuse such an effect with the tendency of the antioxidant to bloom and lubricate the interface under repeated stress and heat. Such a blooming may give misleading results on a laboratory scale compared with the situation on the road.

D. The use of a higher than usual level of stearic acid has shown no conclusive evidence of enhancement of resistance to fatigue abrasion when its blooming to the surface is substantially cut.

E. The combined effect of the bonded silica-ISAF in an 70NR/30BR.cis truck tyre tread formulation, prepared in the SAPA optimised mixing cycle, shows a unique combination of higher resistance to both abrasive and hot fatigue wear with good heat build-up and thermal stability. These promising properties suggest that this formulation may serve well in hot service conditions where on-off road driving is more typical.
10.1.2 On methods of analysis

Unless care is taken to avoid factors that effect the process of rubber abrasion, erroneous conclusions may be drawn. One of the main factors is smearing (lubrication) of the abraded surface. High loads and sharp abraders that are not representative of the road condition give misleading conclusions and should be avoided. The use of the miniature tyre test facility has offered promising correlations with some of the fundamental properties of the vulcanisate with consistent abrasion rating of the tread vulcanisates when moderate abrasion conditions are made available but further studies are required for correlation with roadwear.

10.1.3 Correlation of rubber abrasion with other properties

The lack of consistent correlation between abrasion resistance and other typical strength properties (usually assessed in the laboratory) has led to the proposed unified approach between the volume loss of the vulcanisates and some of its key properties. Such an approach has shown a fair degree of success on a laboratory scale. If roadwear tests support the proposed formula, it will be useful in predicting the wear characteristics on road and perhaps the chance of more abrasion studies which could be conducted on a minor scale.

10.2 Cost consideration

In the short term, compounding with precipitated silica (bonded) is more costly than the carbon black of equivalent particle size. This is not because silica itself is more expensive than the black (VN3 is cheaper than ISAF) but because of the high cost of the coupling agents. Table in the appendix displays a break-down of the cost of the raw materials of three selected tread vulcanisates of the present study, one of which is the NR/ISAF typical control. This shows that the use of the coupling agent has resulted in a cost increase of 13% when the comparison is made on a volume to volume basis.
However, if the combined high wear resistance and lower heat build-up is achieved, it may be worth spending the extra money to have a better tyre to serve better in such a severe environment.

10.3 Recommendations for future work

The experimental evidence suggest that the developed truck tyre tread formulations are roadwear-test worthy. A recommended trial may involve:

a. Preparation of full-scale Banbury mixes by scaling-up the present mixing conditions. If this cannot be afforded then multi-mixes may be prepared in a small scale Internal mixer.

b. The produced batches may then be used for retreading a full scale truck tyre and roadwear tests conducted in comparison with the control, preferably under a hot environment over harsh to blunt road surfaces; then wear and chip-cut resistance can be measured.

c. The results obtained may be correlated with the proposed formula for rubber abrasion to check its validity.

d. Modification of the miniature tyre facility to provide a better control on the temperature of the test, a better filtering system to collect the debris and the use of other types of abradants i.e. precast concrete or asphaltic blocks to simulate various conditions.
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   Kautschuk Gummi Kunststoffe, in Press
APPENDIX
FIGURE 1

LAYOUT OF EXPERIMENTAL STUDY OF TRUCK TYRE TREAD COMPOUNDING AND WEAR

Role of the type of reinforcing agent on abrasion resistance and other properties

Effect of type of polymer on wear

Effect of typical commercial antioxidant on wear

Effect of high levels of stearic acid

Combined effect of A, B, C on performance of truck tyre tread rubber

Development of a unified approach to the phenomenon of rubber wear based on experimental evaluation of certain key properties of tread rubbers

1. A comparison of the performance of precipitated silica (VN₄) bonded and unbonded versus ISAF carbon black.
2. Effect of a silica optimised mixing cycle on dispersion and processing properties.
3. Effect on overall physical properties.
   - The resultant effect on abrasion resistance as measured by three different abrasion machines.
5. Assessment of cutting and chipping resistance by a modified technique.
6. Comparative heat resistance study.
7. Evaluation of filler-rubber interactions.
8. Investigation of the concepts of rupture of rubbers and fracture mechanics with reference to effect of silica and ISAF.
9. Relationship between abrasion resistance and some selected physical properties.
10. Studies of surface morphology and wear products of rubbers.

1. Effect of various levels of BR cis on processing properties of NR tread vulcanisates.
2. Influence on physical properties and abrasion resistance (abrasive wear and fatigue).
3. Ageing characteristics.
4. Viscoelastic properties and their effect on abrasion.
5. Relationship between abrasion and frictional properties of vulcanisates.

1. Investigation of effect of various levels of IPPD and flectol H on processing and vulcanisate properties of truck tyre tread rubbers.
2. Effect of antioxidants on hot fatigue abrasion using a wire gauze as an abradant and a pneumatic miniature tyre.
3. Analysis of wear products.
4. Effect of antioxidants on ageing characteristics of truck tyre tread rubbers.
5. Studies of rubber reversion, smearing and devulcanisation as a result of wear.

1. Comparative effects of high and low quantities of stearic acid on hot fatigue abrasion resistance by wire gauze.
2. Role of stearic acid on over cure reversion.
3. Influence of stearic acid on surface lubrication.
4. Effect of stearic acid on physical properties.
5. Analysis of combined effect on processing and curing properties.
6. Wear properties.
7. Heat build-up.
8. Stress relaxation.
10. Skid resistance (wet and ice).
### FIGURE 2

Test methods proposed for investigating abrasion and related properties

<table>
<thead>
<tr>
<th>Correlation with selected rubber properties</th>
<th>Direct measurements</th>
<th>Indirect methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Hot tearing energy</td>
<td>DIN abrasion (DIN 53516) for abrasive wear</td>
<td>A modified pneumatic miniature tyre testing machine for evaluation using a wire gauze as abradant at various temperatures and slip angles</td>
</tr>
<tr>
<td>2. Dynamic properties</td>
<td>Akron abrasion (variable slip abrasion)</td>
<td>A modified version of British skid tester for properties</td>
</tr>
<tr>
<td>3. Coefficient of friction</td>
<td></td>
<td>A developed cut-chip device</td>
</tr>
<tr>
<td>4. Rebound resilience</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Hardness</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. Tensile and tear strength</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Component</td>
<td>Density gm/cm³</td>
<td>Cost £/kg</td>
</tr>
<tr>
<td>---------------------</td>
<td>----------------</td>
<td>-----------</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
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<tr>
<td>MIX NO.</td>
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<tr>
<td>SMR20</td>
<td>0.92</td>
<td>0.78</td>
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<tr>
<td>BR cis</td>
<td>0.91</td>
<td>0.78</td>
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<tr>
<td>ISAF</td>
<td>1.81</td>
<td>0.75</td>
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<td>S102</td>
<td>1.95</td>
<td>0.604</td>
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<td>TESPT</td>
<td>1.074</td>
<td>8.5</td>
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<td>IPPD</td>
<td>1.28</td>
<td>3.8</td>
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<tr>
<td>TMQ</td>
<td>1.06</td>
<td>3.145</td>
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<tr>
<td>Paraffinic wax</td>
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<tr>
<td>Aromatic oil</td>
<td>1.02</td>
<td>0.25</td>
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<tr>
<td>SAPA</td>
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<td>2.0</td>
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<td>ZnO</td>
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<tr>
<td>Stearic acid</td>
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<td>Sulphur</td>
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<tr>
<td>MBS</td>
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</tr>
<tr>
<td>Total</td>
<td></td>
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</tr>
<tr>
<td>Compound density</td>
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<td></td>
</tr>
<tr>
<td>Mix cost £/kg</td>
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<td></td>
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<tr>
<td>Volume cost £/litre</td>
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</tr>
</tbody>
</table>
Figure 4. Schematic illustration of the DIN abrader

All dimensions are in millimetres.

Figure 5: Akron Abrasion machine