The influence of mixing on the morphology and properties of blends of natural and nitrile rubber

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THE INFLUENCE OF MIXING ON THE
MORPHOLOGY AND PROPERTIES OF BLENDS
OF NATURAL AND NITRILE RUBBER

by

DILHARA G. EDIRISINGHE, B.Sc., M.Sc.

A Master’s thesis submitted in partial fulfilment of
the requirements for the award of
Master of Philosophy
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Supervisor

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Institute of Polymer Technology and Materials Engineering

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ABSTRACT

The overall objective of this research is to develop natural rubber/acrylonitrile-butadiene rubber (NR/NBR) blends having physical properties superior to NBR compounds and a tolerable resistance to swelling in oils and fuels. This would increase consumption of NR by replacing NBR used in various engineering applications with less costly NR/NBR blends.

The rheology of blend components was studied in detail in order to choose mixing conditions and interpret the morphology of NR/NBR blends filled with 20 phr N660 carbon black. It was found that a high shear rate/high temperature combination results in similar apparent viscosities for the two elastomers.

Blends were prepared according to single-stage and masterbatch mixing techniques with an intermeshing rotor internal mixer. Rheological, cure and physical properties of the blends were measured and related to mixing conditions, morphology and carbon black distribution.

The filled 40/60 NR/NBR single-stage blends prepared at a high rotor speed had a finer morphology than the blends prepared at a low rotor speed. The fine textured blends showed higher tensile strength, lower abrasion resistance and improved compression set at elevated temperatures over those of coarse textured blends. Also, the fine textured blends showed a positive synergism of tensile strength. Modulus and tear strength were highest with most of the carbon black in the NBR phase, whereas ASTM oil and toluene uptake were lowest with most of the carbon black in the NR phase. However, percentage compression set was lowest with carbon black equally distributed between the phases.

It was concluded that an NBR (26.6% acrylonitrile) compound could be replaced by the single-stage blends, particularly the fine textured ones, with regard to physical properties such as moduli, hardness, tear strength and compression set in engineering applications, where 2-4 % (by mass) oil swell is tolerable. Oil swell of the NR/NBR single-stage blends is about 5 % (by mass) lower than the predicted.
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<tr>
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<td>Abrasion Resistance Index</td>
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<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
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<td>Bromobutyl Rubber</td>
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<tr>
<td>CTM</td>
<td>Cavity Transfer Mixer</td>
</tr>
<tr>
<td>CTP</td>
<td>N-(Cyclohexylthio) Phthalimide</td>
</tr>
<tr>
<td>CV</td>
<td>Conventional Vulcanising</td>
</tr>
<tr>
<td>D.R.C.</td>
<td>Dry Rubber Content</td>
</tr>
<tr>
<td>DBPA</td>
<td>Dibutyl Phthalate Absorption</td>
</tr>
<tr>
<td>DCP</td>
<td>Dicumyl Peroxide</td>
</tr>
<tr>
<td>DOP</td>
<td>Diocetyl Phthalate</td>
</tr>
<tr>
<td>DTDM</td>
<td>Dithiodimorpholine</td>
</tr>
<tr>
<td>ENR</td>
<td>Epoxidised Natural Rubber</td>
</tr>
<tr>
<td>EPDM</td>
<td>Ethylene-Propylene-Diene Terpolymer</td>
</tr>
<tr>
<td>EPM /</td>
<td>Ethylene-Propylene Rubber</td>
</tr>
<tr>
<td>EPR</td>
<td>Efficient Vulcanising</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>GPF</td>
<td>General Purpose Furnace</td>
</tr>
<tr>
<td>HAF</td>
<td>High Abrasion Furnace</td>
</tr>
<tr>
<td>IIR</td>
<td>Isobutene-Isoprene (Butyl) Rubber</td>
</tr>
<tr>
<td>IR</td>
<td>Polyisoprene Rubber</td>
</tr>
<tr>
<td>IRHD</td>
<td>International Rubber Hardness Degrees</td>
</tr>
<tr>
<td>ISAF</td>
<td>Intermediate Super Abrasion Furnace</td>
</tr>
<tr>
<td>MB</td>
<td>Masterbatch</td>
</tr>
<tr>
<td>MBT</td>
<td>2-Mercaptobenzothiazole</td>
</tr>
<tr>
<td>MBTS</td>
<td>Bis(2-benzothiazolyl) Disulphide</td>
</tr>
<tr>
<td>MC</td>
<td>Magnesium Carbonate</td>
</tr>
<tr>
<td>MRPRA</td>
<td>Malaysian Rubber Producers’ Research Association</td>
</tr>
<tr>
<td>NBR</td>
<td>Acrylonitrile-Butadiene (Nitrile) Rubber</td>
</tr>
<tr>
<td>NBRMB</td>
<td>Nitrile Rubber Masterbatch</td>
</tr>
<tr>
<td>NR</td>
<td>Natural Rubber</td>
</tr>
<tr>
<td>NRMB</td>
<td>Natural Rubber Masterbatch</td>
</tr>
<tr>
<td>OTOS</td>
<td>N-Oxydiethylene dithiocarbamyl-N’-Oxydiethylene-Sulfenamide</td>
</tr>
<tr>
<td>phr</td>
<td>Parts per hundred rubber</td>
</tr>
<tr>
<td>PPO</td>
<td>Poly(2,6-dimethylphenylene Oxide)</td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinyl Chloride</td>
</tr>
<tr>
<td>PVI</td>
<td>Prevulcanising Inhibitor</td>
</tr>
<tr>
<td>RAPRA</td>
<td>Rubber and Plastics Research Association</td>
</tr>
<tr>
<td>rpm</td>
<td>Revolutions per minute</td>
</tr>
<tr>
<td>RSS</td>
<td>Ribbed Smoked Sheet</td>
</tr>
<tr>
<td>SBR</td>
<td>Styrene-Butadiene Rubber</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SMR CV</td>
<td>Standard Malaysian Rubber- Constant Viscosity</td>
</tr>
<tr>
<td>SRF</td>
<td>Semi Reinforcing Furnace</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TBBS</td>
<td>N-tert.-Butyl-2-Benzothiazolyl Sulphenamide</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>-------------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TMS</td>
<td>Turner, Moore and Smith</td>
</tr>
<tr>
<td>TMTD</td>
<td>Tetramethylthiuram Disulphide</td>
</tr>
<tr>
<td>TMTM</td>
<td>Tetramethylthiuram Monosulphide</td>
</tr>
<tr>
<td>TSR</td>
<td>Technically Specified Rubber</td>
</tr>
<tr>
<td>$ZD_mC$</td>
<td>Zinc Dimethyl-dithiocarbamate</td>
</tr>
</tbody>
</table>
CHAPTER ONE

INTRODUCTION

1.1 GENERAL INTRODUCTION

The development of many new types of polymer blends as well as the usage of blends has increased remarkably during the past few decades. This is because, for many applications, single polymers provide inadequate performance. It is significantly cheaper to produce a new material by mixing existing polymers than it is to develop new monomers possibly requiring new polymerisation processes. Blends are often used to combine the desired properties of individual polymers to obtain an improved product. This is possible by careful selection and mixing of the component polymers.

There are two ways of forming polymer blends i.e. chemical blending and physical blending. The properties of physical blends are different from those of parent polymers and often are not simply an averaging of the properties of the two components. They can be unique. The physical properties are also determined by the physical structure of the blend. For many practical purposes, rubber products are manufactured from blends of two or more dissimilar polymers. These blends are generally classified as rubber-rubber and rubber-plastic blends.

Mixing of elastomers and compatibility began to be of scientific and technological interest with the arrival of synthetic rubbers. Natural rubber (NR) is blended with synthetic rubbers for a wide variety of purposes. These blends offer considerable potential for the development of future new materials. The use of blends of NR with general purpose synthetic rubbers mainly polybutadiene rubber (BR) and styrene-butadiene rubber (SBR) is common place in the industry, especially in tyre building. McDonel et al.\(^1\) have reviewed the usage of elastomer blends in tyre applications. Reduced compound cost, simplification or improvement in tyre building and enhanced final product performance were the three main reasons for utilising blends rather than individual elastomers. The development of the radial ply tyre is a particular case where elastomer blends have proved to be beneficial. Blends of 70/30 NR/SBR have been found to give an optimum balance between the flex cracking associated with NR and ozone cracking associated with SBR in radial tyre sidewalls\(^2\).

Most elastomer blending continues to be based on physical blending procedures and is widely carried out using internal mixers, two-roll mills and extruders. The properties
of new materials formed after blending are often determined by the exact mixing technique.

The great bulk of polymer blends possess a heterogeneous morphology by virtue of their immiscibility. The early work of Walters and Keyte\(^{(3)}\) on blends of NR with SBR was the beginning of an approach to elastomer blends from both technical and economic points of view. They demonstrated that elastomer blends are never truly homogeneous and show discrete areas of each elastomer varying from \(\sim 0.5\ \mu\text{m}\) upward, depending on methods of mixing, elastomer viscosity, crystallinity, etc. An elastomer blend need not be necessarily physically homogeneous to exhibit good physical properties. The advantages of physically inhomogeneous systems in terms of the ability to alter the phase morphology for specific performance criteria have now been recognised\(^{(4)}\). Frequently, it is possible to obtain new property combinations only in this way, and hence, blended systems have become an important and accepted field of elastomer technology. However, Bhowmick et al. reported that many physical properties of rubber blends are insensitive to the details of the two phase structure\(^{(5)}\).

Rubber product manufacturers currently using 100% special-purpose synthetic rubbers or speciality rubbers in their compounds may well find that use of blends of these rubbers with NR will enable them to achieve improvement in technical properties with reduced compound costs by substituting part of the synthetic component with NR. Blends of NR with speciality synthetics which combine the excellent qualities of NR with the special properties of the synthetic component have gained considerable importance in the field of polymer science. Nitrile rubber (NBR) which falls in this group of speciality synthetic rubbers is regarded as the engineer’s rubber, as it combines excellent resistance to oils both at normal and elevated temperatures with good physical properties and moderate cost. NBR is the basic product used by rubber manufacturers in the preparation of a wide range of engineering components. Attempts have been made in the past to blend NBR with NR, for it was thought that the use of NR would bring about improved processability and better building tack, in addition to reduced material costs. When dimensional stability is important for NBR vulcanisates, NR is often added in small amounts as a non-extractable plasticizer or process aid, so that shrinkage of the vulcanisate due to extraction of plasticizer during solvent or oil swelling is avoided. High green strength and high strength of gum vulcanisates are the other favourable properties introduced by NR into the blends with NBR.

Because of its strong polar properties, NBR is poorly compatible with NR which has a non-polar, aliphatic nature. Since the polarity of NBR increases, with increasing acrylonitrile, the compatibility of NR becomes poorer accordingly. For this reason,
NBR types with relatively low amounts of acrylonitrile are generally considered for blending with NR. But, even with NBR containing only 28% acrylonitrile, the overall picture of physical properties shows impairment with increasing amounts of NR in the blend. With up to 10 or 20% of NR in the combined weights of the rubbers, the weakening of the strength level and other physical properties is still tolerable. The very good swelling resistance of NBR compared with NR deteriorates with this amount of NR in the blend. Hence, NR/NBR blends are frequently used for economic reasons, and in applications, where there is only a moderate demand on solvent swell resistance.

With the increasing demands of the automobile industry (petrols with a higher content of aromatic substances, higher operational temperatures), the requirements for the resistance of rubbers to swelling and heat increase. Nitrile rubber with a very high content of acrylonitrile, which has been used as the major blend component throughout this study, represents a solution for these requirements.

1.2 Objectives

The main reason for carrying out this research is to assess the feasibility of increasing market opportunities for NR by development of natural rubber (NR)/speciality elastomer blends, to the benefit of NR producers.

The availability of these blends will enable NR to take up part of the markets of speciality synthetic rubbers. For example, if a manufacturer requires oil resistance in a particular product, he will be forced to use an oil resistant rubber such as nitrile rubber (NBR) because NR is deficient in this property. If the oil resistance of, say a 40/60 NR/NBR blend is adequate for that manufacturer’s need, then NR will be able to reach 40% of that market through displacement of NBR.

This research is focused on blends of NR and NBR. NBR was selected as the speciality elastomer because of its wide commercial usage in engineering applications. Although NR is deficient in the above mentioned properties, it possesses good gum stock tensile strength, tear strength, resilience, etc., which are also required for engineering applications. Hence, new property combinations suitable for specialised applications are to be expected from these NR/NBR blends. It is hoped that NR/NBR blend compounds having physical properties superior to NBR compounds and a tolerable degree of swelling in oils and fuels could be developed. This would satisfy the ultimate aim of increasing consumption of NR by replacing NBR used in various engineering applications with the NR/NBR blends.
The specific objective of this research is to study the physical properties of the developed NR/NBR blend compounds in relation to rheology and compatibility of the individual rubbers and mixing treatment, morphology and carbon black distribution in the blends.

1.3 PLAN OF THE THESIS

Chapter 1: Introduction

Chapter 2: A Review of Rubber Technology

The purpose of this chapter is to review fundamentals of rubber technology relevant to this study. Initially a general background about NR and NBR, which are the two blend components used throughout the study, is given. Details of the rubber mixing system employed in this work and the influence of mixing on properties are considered. Short summaries of factors affecting rheological properties of polymer melts; in particular, the effect on viscosity are considered. This chapter also gives a detailed account of reinforcement with carbon black, compounding and vulcanisation, all of which influence the ultimate physical properties of a rubber vulcanisate. Finally, the swelling of rubber networks and the influence of fillers on swelling are reviewed briefly.

Chapter 3: A Review of Rubber Blends

This chapter provides a literature review of relevant work on rubber blends carried out by other researchers. It includes a brief account of different techniques of blending polymers, followed by a detailed review of factors which influence the properties of polymer blends. In addition, parameters affecting carbon black distribution and transfer in rubber blends and its effect on morphology and properties are considered. A short summary of the major findings on carbon black distribution and transfer is included.

Chapter 4: Experimental

The purpose of this chapter is to provide sufficient details of experimental procedures including standard test methods employed in the preparation of rubber compounds, analysis of rheological behaviour, analysis of cure characteristics, microscopical analysis, determination of physical properties and swelling measurements, in order to
guide interpretation of methods. This chapter also gives other researchers necessary information to repeat this work, for future studies.

Chapter 5: Results and Discussion

The results of the research mainly in the form of graphs are provided in this chapter. The main purpose of this chapter is to discuss the results of the experiments conducted throughout the research project. First of all, immiscibility of NR and high nitrile (45% ACN) blends is assessed in terms of solubility parameters of the two elastomers. Subsequently, the rheology of blend components used in the preparation of both single-stage and masterbatch blends is discussed. This is followed by detailed discussion of the results of analysis of phase morphology, carbon black distribution and properties; rheology, cure characteristics and physical properties. The explanations are mainly based on the effects of mixing conditions and location of carbon black within the blend rubber phase.
REFERENCES


CHAPTER TWO
A REVIEW OF RUBBER TECHNOLOGY

2.1 GENERAL BACKGROUND OF NATURAL RUBBER

2.1.1 STRUCTURE AND PROPERTIES OF NR

Natural rubber (NR) is derived from the latex of the tropical tree, hevea brasiliensis. NR is a linear long chain molecule made up of repeating isoprene units \((\text{C}_5\text{H}_8)_n\), where ‘\(n\)’ is about 10,000, linked at the first (1) and fourth (4) carbon atoms in a head-to-tail arrangement as shown in Fig. 2.1. The molecular structure of the rubber hydrocarbon is extremely regular (> 99% of cis-1,4-polyisoprene). Because of its stereoregularity NR can crystallise when stored at low temperatures (0°C and below) or when it is strained. The rate of crystallisation varies with temperature\(^{(1)}\). As the NR latex comes from the tree, the molecular weight of the rubber hydrocarbon varies from about 750,000 to 2,500,000.

![Fig. 2.1 Structural units of cis-1,4-polyisoprene](image)

NR is available commercially as a raw material in two basic forms, latex concentrate with a dry rubber content (D.R.C.) of 60% and solid raw rubber (e.g. Ribbed Smoked Sheet rubber) (RSS), Crepe and Technically Specified Rubber (TSR)), the latter being the predominant form for engineering applications.

The specific gravity of raw NR at 20°C is 0.934, and it increases somewhat, if the rubber is either frozen or stretched. NR which is purified after extraction with acetone, has a refractive index at 20°C of 1.5215 to 1.5238\(^{(1)}\).

NR being worked in an internal mixer or on a two-roll mill undergoes mechanical degradation, the rubber becomes softer and more plastic. This is known as mastication and is due to the shearing action of the mill or mixer combined with small amounts of oxygen. Mastication facilitates the dispersion of compounding ingredients which is an important requirement for excellent physical properties.
To be practically useful, NR must be crosslinked to tie the NR molecules into a three dimensional network. The chemical reaction between NR with sulphur under heat, gives rise to the formation of crosslinks between long chain molecules. This phenomenon is known as vulcanisation and is dealt with in greater detail in Section 2.5. Besides the use of free sulphur, sulphur donors such as tetramethylthiuram disulphide (TMTD) and peroxide cures give rise to vulcanisates with good heat resistance.

Another beneficial property of NR is its high rate of cure. However, since NR has a relatively poor heat resistance, it can comparatively easily revert during cure. Therefore, curing is generally done at relatively low temperatures, and the length of cure cycles have to be strictly controlled. The higher the cure temperatures, the poorer are the mechanical properties of the vulcanisates.

NR is amorphous under most conditions. It has an outstanding combination of strength and resilience qualities, and in consequence its overall performance in engineering applications is not yet matched by any other rubber. Due to the previously mentioned strain crystallisation, which also occurs in vulcanisates, NR has, contrary to most types of synthetic rubber, a high tensile strength of 20 MPa or more, even in gum vulcanisates. By adding reinforcing fillers to compounds, the tensile strength can rise up to 30 MPa. Even at higher temperatures, NR vulcanisates have a good tensile strength\(^2\). NR also has excellent resistance to chipping, cutting and tearing, and has a high abrasion resistance. The tear resistance is also influenced by the strain crystallisation of NR\(^3,4\) and is therefore very good, and much better than that of most synthetic rubber vulcanisates. Highly reinforcing fillers in NR compounds give a much better tear resistance than non-reinforcing fillers.

At ambient and slightly elevated temperatures, the compression set of NR vulcanisates is relatively low. At lower temperatures the compression set appears to be poor due to the tendency of the rubber to crystallise, while at higher temperatures, the poor heat resistance of the NR vulcanisate has a detrimental effect on the compression set due to chemical reactions\(^5\).

Since NR is non-polar, its vulcanisates have little resistance to swelling in non-polar oils and solvents. When in contact with mineral oils, benzene and gasoline, the volume of NR vulcanisates increases several hundred percent. In alcohols, ketones and esters, the vulcanisates swell less, however.
2.1.2 USES OF NR

NR is a very versatile raw material. It is used mainly as solid rubber. NR is used in virtually all the major engineering applications, other than those involving special requirements in heat, weathering or oil resistance.

NR has always been of great importance for producing truck tyres due to its low heat build-up\(^6\).

An important application of NR in the latex form is in the production of thin-walled, soft products with a high strength, such as balloons, surgical gloves or sanitary rubber products. Due to its strain crystallisation and thus, self-reinforcing properties, NR still dominates in these applications.

Its high elasticity, combined with a low hysteresis, also makes it an important material for producing suspension elements and bumpers\(^7\).

2.1.3 THE SMR SCHEME

Standard Malaysian Rubber (SMR) was the first, and is still today the most important NR grade belonging to the group of Technically Specified Rubbers (TSR). The SMR Scheme has been developed by Malaysia and the first Scheme was introduced in 1965\(^8\). Other NR producing countries mainly Sri Lanka, Indonesia and Thailand have joined this Scheme because of the strong marketing successes of SMR grades. All rubber which has been classified according to this Scheme is generally referred to as Technically Specified Rubber (TSR). By treating NR latices with hydroxyl amine salts\(^9\) it is possible to obtain NR grades which are largely stabilised against storage hardening, e.g. SMR CV. The new SMR Scheme comprises of two new SMR CV grades namely, SMR 10CV and SMR 20CV. These are identical to field grade material SMR 10 and SMR 20, but with the constant-viscosity features obtained by treatment with hydroxyl amine neutral sulphate. The viscosity levels of the two new grades 60\(^{(10)}\) Mooney units for 10 CV and 65\(^{(10)}\) Mooney units for 20CV\(^{(10)}\) are producer limits only. The viscosity-stabilised grades facilitate the production of particularly uniform compounds.

2.2 GENERAL BACKGROUND OF ACRYLONITRILE-BUTADIENE RUBBER

2.2.1 STRUCTURE AND PROPERTIES OF NBR

Acrylonitrile-butadiene rubber, commonly known as nitrile rubber (NBR) is a copolymer of butadiene and acrylonitrile (ACN). NBR is produced by emulsion...
polymerisation and most of the synthesis processes are batch processes. Synthesis of NBR is shown below.

\[
\begin{align*}
\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 &+ \text{CH}_2 = \text{CH} \\
\text{butadiene} &\quad \text{acrylonitrile} \\
\text{polymerisation} &\quad \text{polymerisation} \\
\end{align*}
\]

\[
\begin{align*}
\text{C} = \text{N} &\quad \text{C} = \text{N} \\
\left( \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 \right)_n \left( \text{CH}_2 - \text{CH} \right)_m \\
\text{acrylonitrile-butadiene rubber} &\quad \text{acrylonitrile-butadiene rubber}
\end{align*}
\]

Butadiene is a very stable non-polar hydrocarbon due to the symmetry of its molecular structure. Acrylonitrile is a very polar molecule due to the lack of symmetry of the triple-bonded nitrogen coupled with the nitrogen lone-pair electron effect. The lone-pair effect plus a large dipole moment created by the nitrogen develops a very strong H-bonding potential. The butadiene monomer copolymerises into three distinct structures i.e. trans-1,4, cis-1,4 and 1,2. The proportion of the individual forms differ slightly with the temperature of polymerisation. The trans configuration dominates (~78%) in a typical nitrile rubber.

Commercially available NBR's differ in three major aspects:

(1) ACN content
(2) Polymerisation temperature
(3) Mooney viscosity

Classification of nitrile rubbers according to the content of acrylonitrile, together with approximate values of swelling resistance are given in Table 2.1.

<table>
<thead>
<tr>
<th>Acrylonitrile Content (%)</th>
<th>Volume Swell (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>low</td>
<td>about 20</td>
</tr>
<tr>
<td>medium low</td>
<td>25</td>
</tr>
<tr>
<td>medium</td>
<td>30</td>
</tr>
<tr>
<td>medium high</td>
<td>35</td>
</tr>
<tr>
<td>high</td>
<td>40</td>
</tr>
<tr>
<td>very high</td>
<td>above 40</td>
</tr>
</tbody>
</table>

Table: 2.1 Volume swell of nitrile vulcanizates (standard recipe) in a light petroleum-benzene mixture (3:1) after 72 hrs at 23°C

10
Many of the vulcanisate properties are directly related to the proportion of ACN in the rubber\(^{11,12}\) as shown below.

Low \[\rightarrow\] Acrylonitrile Content \[\rightarrow\] High
\[\rightarrow\] Cost increases \[\rightarrow\]
\[\rightarrow\] Resistance to petroleum-based fluids & hydrocarbon fluids increases \[\rightarrow\]
\[\rightarrow\] Solubility in ketones and esters increases (uncured) \[\rightarrow\]
\[\rightarrow\] Resistance to gas permeation increases \[\rightarrow\]
\[\rightarrow\] Compression set deteriorates \[\rightarrow\]
\[\rightarrow\] Heat & ozone resistance improves \[\rightarrow\]
\[\rightarrow\] Abrasion resistance improves \[\rightarrow\]
\[\rightarrow\] Tensile strength increases \[\rightarrow\]
\[\rightarrow\] Hardness increases \[\rightarrow\]
\[\rightarrow\] Density increases \[\rightarrow\]
\[\rightarrow\] Solubility in aromatic solvents decreases \[\rightarrow\]
\[\rightarrow\] Resilience decreases \[\rightarrow\]
\[\rightarrow\] Low-temperature flexibility decreases \[\rightarrow\]

The polarities of acrylonitrile and butadiene are very different, and the polarity of the copolymer becomes greater with increasing amounts of acrylonitrile. With increasing ACN content in the copolymer, the solubility parameter also increases, changing the solubility of NBR in solvents of various polarity. For example, acetone is a good solvent for NBR containing 34% ACN. Similar criteria are also valid for indicating the resistance of NBR's to swelling in oils and other liquids.

Specific gravity of nitrile rubber is 0.96-1.00 and that of nitrile rubber compounds is 1.00-1.80. Refractive index of high nitrile NBR is 1.596\(^{13}\).

NBR vulcanisates have good physical properties over a wide hardness range. The main property of nitrile rubber is its oil and fuel resistance. It is this property, in conjunction with its excellent physical properties, which account for much of its commercial use. The strongly polar nitrile side groups increase the total polarity of nitrile rubbers, thus decreasing the degree of swelling in substances of non-polar or slightly polar character, such as petroils and mineral oils (Fig. 2.2). Swelling is less for carbon black filled systems than for non-black fillers.
Fig. 2.2 Dependence of the swelling resistance of NBR on the content of combined acrylonitrile: ASTM Oil No.3, 70 h at 100°C(5)

In strongly polar solvents e.g. acetone, the NBR vulcanisates swell much more than non-polar vulcanisates such as NR. Figures 2.3 and 2.4 show swelling of NBR in various solvents(14). The swelling resistance depends very much on the NBR grade, the compound components, filler loading, type and amount of plasticizer, immersion temperature, nature of the liquid and the degree of vulcanisation. Polymers of high ACN content (35 to 40%) are not soluble in aromatic solvents such as toluene.

Fig. 2.3 Swelling of acrylonitrile-butadiene copolymers(14)
Only nitrile rubbers with a low content of ACN are sensitive to the degree of vulcanisation and they swell strongly at low crosslink densities. For nitrile rubber with a high content of ACN, degree of vulcanisation has a relatively small effect on the degree of swelling except in highly swelling liquids, the reason being that the origin of the resistance to swelling is mainly the attraction between the dipoles of the \(-\text{CN}\) groups of the ACN units.

Unlike NR, NBR's do not crystallise, either spontaneously or on stretching, and therefore they have a low tensile strength in the unfilled state.

Like most other rubbers, NBR is not perfectly elastic, but exhibits some plastic properties. Thus if deformed for a period, particularly at elevated temperatures it does not completely recover, but exhibits a permanent set, the extent of which depends on deformation experienced, time and temperature. In addition to retention of physical properties in air or fluids at elevated temperatures, NBR used in sealing applications must retain its ability to seal. The compression set of vulcanisates has commonly been regarded as an indicator of their ability to seal in service. The resistance of NBR to compression set is good and this enables its use in articles which are used under permanent compression such as o-rings and seals. Compression set in sulphur vulcanisates is lowest for carbon black filled compounds in optimised low sulphur/sulphur donor systems\(^{(15)}\). The compression set characteristics are generally
improved by longer curing times, higher curing temperatures and by using EV systems or peroxides.

NBR vulcanisates have a distinctly better heat resistance than NR. Vulcanisates of NBR are generally considered to be serviceable up to 120°C for continuous use\(^{(5,16)}\), while the maximum service temperature of NR is 100°C\(^{(11,17)}\). If oxygen is excluded the ageing resistance of NBR vulcanisates becomes even better\(^{(18)}\). Naturally, the heat resistance depends very much on the compound formulation. The thermal conductivity of NBR is of the same order as for NR.

NBR vulcanisates formulated with reinforcing fillers have an abrasion resistance which is about 30% greater than that of comparable NR vulcanisates\(^{(19)}\). The abrasion differences between NR and NBR are largely dependent upon the filler loading; they become smaller with increasing loading. The viscosity of the raw NBR has almost no effect on the abrasion loss\(^{(20)}\).

Properties of vulcanised NBR can be modified to a great extent by the type and quantity of the various other ingredients added to produce the final mix. Unfortunately it is not possible to have all the desirable properties developed to the maximum extent simultaneously and to achieve some desired result, sacrifice in some other property is usually necessary.

2.2.2 Compounding, Processing and Uses of NBR

(a) Compounding and Processing

NBR compounds are mixed and processed using conventional rubber machinery and follow general procedures used for NR\(^{(21)}\). Compounding of NBR is similar to NR with nearly the same ingredients used in NR compounds, but due allowance must be made for the toughness of NBR. Processing is improved by the use of 'ester' type plasticisers e.g. dioctyl phthalate (DOP). Addition of NR also facilitates processing, the slight reduction in solvent resistance is often tolerable.

Nitrile rubbers are not broken down by mastication to the same extent as NR and, therefore, the viscosity of the rubber as produced has an important effect on its processing properties, in addition to polymerisation temperature. "Cold" rubbers require little premastication, and develop less heat during mixing. Low Mooney viscosity rubbers absorb fillers and plasticisers more easily than high Mooney grades; they also cause less heat build-up during mixing and fast extrusion rates can be obtained\(^{(22)}\). The decrease in Mooney viscosity through mastication is higher in those types with a high original viscosity and very low in types with a low original viscosity\(^{(5)}\). For compounds with a low content of softeners and fillers, the NBR types
with Mooney viscosities about 45-60 ML units are suitable. More highly viscous types (70-80 ML units) are suitable for compounds with a high content of softeners and fillers.

In order to achieve good mechanical properties, reinforcing fillers must be added because the unfilled vulcanisates do not crystallise on stretching and hence lack self-reinforcing properties. Whilst all types of carbon black and non-black fillers may be used with NBR, the most common practice is to use mainly the semi-reinforcing varieties because this is a means of obtaining suitable physical properties allied to low raw material costs\(^{(22)}\).

Nitrile rubbers are vulcanised by sulphur and accelerators in the conventional manner used for NR. However, a main difficulty and a cause of reduced physical properties in NBR vulcanisates is poor dispersion of normal ground sulphur. One way of overcoming this difficulty is to use a MgCO\(_3\) coated sulphur which produces free flowing, non caking powders\(^{(23)}\). Optimum sulphur and accelerator content depends on a number of factors, include the danger of scorching due to heat development in mixing. Increasing the amount of sulphur increases hardness as is the case with NR. A sulphur content which is too high lowers tear resistance and elongation at break. For optimum heat resistance and high temperature compression set properties, the sulphur content should be kept low\(^{(12)}\). Hofmann\(^{(24)}\) recently studied the optimisation of compression set in sulphur/sulphur donor cures of NBR. He concluded that the following are required:

(a) NBR of low acrylonitrile content  
(b) N550 or N770 carbon black filler  
(c) low plasticiser content (or none)  
(d) a combination of the accelerators tetramethylthiuram disulphide (TMTD), Bis(2-benzothiazolyl) disulphide (MBTS), N-oxydiethylene dithiocarbamyl-N'-oxydiethylene sulfenamide (OTOS) and optimised sulphur and/or 4,4' dithiodimorpholine (DTDM-sulphur donor) curative levels

(b) Uses

Because of its relatively high price, NBR is used in applications where, besides good mechanical properties, there is also the requirement for good resistance to swelling in oils and gasoline, good resistance to heat ageing, abrasion resistance and low permanent set. NBR is the oil-resistant elastomer of choice for typical fluid sealing applications. In many oil seal applications, low compression set and creep characteristics are equal in importance to swelling resistance.
The main use sectors are:

(1) Automotive and aeronautical construction, which account for 65% of commercial outlets. All parts expected to be in permanent or accidental contact with fuels, oils or greases, such as o-rings, radiator hoses, and pressed cork gaskets.

(2) Hydrocarbon handling and transport, hoses for tanker loading and unloading, flexible tanks, valve and piping gaskets. Dunn and Vara (25) reported that NBR with 50% acrylonitrile appears to be good for automotive or marine engine fuel line hose tubes.

(3) Rollers and cylinder lining in the textile, paper and printing industries.

(4) Safety shoe soles

(5) Adhesives for cementing:
   (a) rubber
   (b) plasticised PVC on various supports, since the presence of the polar group renders it compatible with PVC

2.3 **REINFORCEMENT WITH CARBON BLACK**

2.3.1 **THE NATURE OF CARBON BLACK**

Carbon black is formed by thermal decomposition of hydrocarbons. The particles of carbon black are not discrete, but are fused ‘clusters’ of individual particles termed as aggregates. An aggregate is composed of a number of spheroidal particles which are formed in the flame and fused together in a single paracrystalline entity in which the graphitic carbon layers are arranged parallel to the surface. An aggregate is the smallest basic unit of carbon black under well dispersed conditions. These aggregates appear to be the working unit, as they can be seen in vulcanised rubber.

The principal relevant properties of carbon black include

(1) Particle size, surface area and polarity
(2) Aggregate structure (bulkiness)
(3) Amount of carbon per aggregate
(4) Surface activity
(5) Surface chemistry and
(6) Trace constituents

The fusing of particles into aggregates is associated with the concept of carbon black ‘structure’, where ‘structure’ is a measure of the bulkiness of the aggregates. The
aggregates flocculate to form agglomerates (larger structure), held together by van der Waals forces.\(^{26}\) Agglomeration has an important effect on the ease with which a carbon black is incorporated in rubber. As aggregates are largely unaffected by the mixing process, they exert an influence on the final reinforcement. Generally, the higher the structure, the higher is the modulus of the vulcanisate.

Carbon blacks are mainly classified as channel blacks, furnace blacks and thermal blacks according to the type of manufacturing process.

The surface of the carbon black particle, is very important for adsorption processes. A carbon black particle consists of roughly concentric layers of graphitic structures or very small crystallites with a high degree of disturbed and exposed graphitic layers and their edges, giving it high irregularity and adsorption power.\(^{27}\) Besides the geometrical factor of adsorption, the reactive groups of carbon black surface such as acid groups, phenolic groups, quinone groups and carboxylic lactone groups significantly influence adsorption.\(^{28}\)

### 2.3.2. The Phenomenon of Reinforcement

Reinforcement by fillers, especially carbon black, is one of the most important aspects of rubber technology. For a long time technologists accepted the fact that the addition of carbon black gave improved properties to rubber vulcanisates. 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 the service life of a rubber article. Kraus\(^{29}\) has reported that a precise definition of the term “reinforcement” is difficult because it depends somewhat on the experimental conditions and the intended effects of the filler addition. He regards reinforcement broadly as the modification of the viscoelastic and failure properties of a rubber by a filler to produce one or more favourable results without serious loss of reversible extensibility. Kraus from his review of the literature on carbon black-polymer interaction concluded that bonding of polymer molecules to the surface can occur by a variety of mechanisms, both physical and chemical. Moreover, he concluded that the various complex phenomena of reinforcement are governed by strength of surface bonds, a limiting state of adhesion, the particular distribution of bonding energies or by the mobility of surface attachments.\(^{30}\) Uncured elastomers which are mixed with a sufficient quantity of finely divided carbon black form a “carbon-gel network” or “bound rubber”\(^{29}\).

The degree of reinforcement provided by a filler depends mainly on the development of a large polymer-filler interface, which can only be obtained with particles of colloidal
dimensions. In non-reinforcing carbon black filled systems, the associations between polymer and carbon black are weak, primarily physical, with the dispersed particles free to move about in the matrix and through particle-to-particle associations, to flocculate and cluster\(^{(31)}\), whereas in reinforcing carbon black filled systems, strong carbon-polymer bonds are substituted for weak bonds, with the result that the filler particles, form a part of the elastomer network and are no longer free to move independently. The net result of this difference is improved modulus and failure properties such as tensile strength and abrasion resistance.

Carbon blacks and silicas are the commonly used reinforcing fillers in the rubber industry. In order to reinforce, carbon black must be adequately dispersed. In the early stages of incorporation into rubber, the pellets are broken down into rubber-filled fragments (‘inclusions’). Continued shear stretches out the inclusions and brings about colloidal dispersion of the aggregates\(^{(32)}\). Hence, good dispersion involves reduction in the size and number of highly loaded regions (inclusions), and bringing the matrix to approximately the nominal loading of carbon black, at a scale of segregation\(^{(33)}\) approaching that of the carbon black aggregates. Gessler\(^{(34)}\) found higher aggregate breakdown with increasing compound viscosity or polymer molecular weight. Moreover, he found that the breakdown was less in the low unsaturation polymers and hence suggested that interaction between carbon black and polymer may exert an influence.

Inclusions act as flaws when the rubber is stretched\(^{(35)}\) and it is these pellet fragments or inclusions which actually degrade the failure properties. The size of the inclusions affect the tensile strength\(^{(32)}\). Schallamach\(^{(36)}\) has shown that abrasion involves the rupture of a great many tendrils of microscopic size and thus the presence of a large number of small inclusions (each of which can produce premature failure of a small tendril) is as harmful as the presence of a small number of large inclusions (which may lead to breaking away of large pieces under abrasion conditions). Consequently, in abrasion, it is the total volume of inclusions that is important rather than their size\(^{(32)}\).

The choice of a grade of carbon black for a particular application depends on the properties it will impart to the rubber vulcanisate, its processability and its cost. In compounding with carbon black, the most important properties are surface area, structure and loading. Generally the cost decreases with decreasing surface area (increasing particle size). Dispersion time also decreases with decreasing surface area.

On the matter of vulcanisate properties, one of the most commonly specified properties is the hardness which is related to the modulus at fairly low deformation. Hardness is affected by carbon black loading. The same is true for the 300% tensile modulus. With
a given carbon black, tensile strength passes through a maximum as the loading is increased through the practical range. The same is true for NR compounds\(^{(37)}\). The elongation at break decreases with increasing loading, over the same range.

Byers\(^{(38)}\) reported that the surface area and loading are the most important factors for abrasion resistance. The lower surface area GPF (general-purpose furnace) carbon blacks (N650 and N660) showed a rather small improvement in abrasion resistance of NR compounds, regardless of the loading level, in comparison with the improvement in abrasion resistance shown by the NR compounds containing HAF (N339 and N356) carbon blacks. The abrasion resistance of the latter is considerably better and it is highly dependent on the carbon black loading and influenced by structure.

Tear strength of carbon black filled NR compounds is shown in Fig. 2.5\(^{(38)}\). It is apparent from this figure that the tear strength of NR compounds with finer particle size carbon blacks goes through a maximum as the carbon black loading is increased, whereas the tear strength of GPF carbon blacks (N650 and N660) increases with the carbon black loading.

Fig. 2.5 Tear strength (Source: Ashland Chemical Co., Carbon Black Div.)\(^{(38)}\)
Two important molecular network mechanisms of reinforcement are Bueche's mechanism and Dannenberg's molecular slippage model.

Bueche\(^{(39)}\), first of all, reported that reinforcing fillers e.g. various carbon blacks have two things:

1. they can be highly dispersed in rubber with particle diameters reaching as low as 10 nm
2. the surface of each is chemically active and can undergo direct molecular bonding with the rubber

He makes the point that with non-reinforcing fillers there is no molecular bonding between the filler and rubber, and that in this case the filler can be treated as particulate matter suspended in a viscoelastic material.

Reinforcing fillers increase modulus at high extensions to a greater extent than similar non-reinforcing fillers because, in addition to the viscous contribution related only to suspended particulate matter, there is an elastic contribution resulting from the strong bonding between rubber and carbon black. The strong bonding acts as additional crosslinking in the rubber vulcanisate and is associated, in Bueche's view, with the stress softening (Mullins effect) which reinforced vulcanisates exhibit when they are relaxed and then stretched for a second time.

Bueche, in his theory, deals also with the recovery from Mullins softening which occurs when a vulcanisate is heated (up to 90°C) following the second extension cycle. At elevated temperatures, network chains break and reform, and in the process the original random distribution of network chains which is destroyed by the breakage of shortest chains between filler particles (which leads to stress softening), is restored. Dannenberg\(^{(40)}\) has pointed out that at elevated temperatures, filler particles are able to move more easily in the matrix as the vulcanisate is stretched, and this movement serves to distribute the stress load more effectively to the rubber network chains than was the case before the sample was heated.

Dannenberg\(^{(30,40)}\) in contrast to Bueche, reported that the attachments between rubber and reinforcing fillers range from weak van der Waals bonds to primary chemical bonding due to the energetically heterogeneous nature of the carbon black surface. His view is that a major portion of the rubber molecules located at the filler surface can undergo slippage and other molecular rearrangements when the resulting vulcanised rubber system is stressed.
Dannenberg's molecular slippage model is shown in Fig. 2.6.

Fig. 2.6 Molecular slippage model of reinforcement mechanism

In Fig. 2.6 (top) three rubber chains attached to two filler particles are shown, (1) in the initial relaxed state
(2) when complete extension of the shortest chain occurs on continued stretching
(3) & (4) molecular slippage, which requires much less energy than chain breakage (as
in the Bueche process) or the desorption or detachment of a surface bond, takes place
(indicated by the marks on the chains)

The above mechanism for stress distribution and molecular alignment has been
proposed by Dannenberg for the increase in strength of the rubber phase in reinforced
vulcanisates. As extension increases the deforming force becomes shared by more and
more of the rubber chain segments connecting the filler particles as molecular slippage
occurs.

When the sample is relaxed after extension, retraction is produced by elastic recovery
of the crosslinked matrix network. Recovery is not complete due to the rupture and re-
formation of network chains under strain. An important point is that the chains in the
relaxed sample in contrast to the case of the initial relaxed sample ((1) in Fig. 2.6) have
chains of equal length ((5) in Fig. 2.6) produced by molecular slippage. Therefore a
second extension of the pre-stressed sample gives a lower modulus (Mullins softening).
As the system rests, random chain length is achieved ((6) in Fig. 2.6), and eventually
the system returns nearly to its initial relaxed state.
2.3.3 Fracture and Wear of Filler Loaded Rubbers

(A) Fracture

Fracture of rubber always takes place from points of weakness. These include flaws, heterogeneities of composition or structure, cuts, moulding defects, gels, unavoidable dirt particles, etc. When a rubber is deformed, the stresses concentrate in these regions of weakness, are magnified greatly and can be many times larger than the average applied stress\(^{(41)}\). Generally, there will be a single flaw at which the stress is magnified to the greatest degree and where fracture begins.

The strength of a rubber vulcanizate depends on its viscoelastic properties and such processes as crack formation and growth which again determine the life-span of a specimen. It has been shown\(^{(42, 43)}\) that failure surfaces manifest typical characteristics dependent on the nature of the test. Tensile failure is believed to be due to initiation of a crack (from a small flaw) followed by its growth or propagation. It has been found\(^{(42)}\) that in a filled NBR vulcanisate the flaw leading to tensile failure starts from one corner of the specimen. The tensile fracture surface also shows occurrence of two different tear rates in the case of the filled NBR vulcanisate (slow tear markings originate from the flaw, and at a certain loss of cross-sectional area fast tear and ultimate failure occurs). Reinforcing fillers strengthen the tear resistance of non-crystallising NBR. In a filled NBR vulcanisate, tear starts from the nick end and tear fracture is characterised by a few long flow lines. These flow lines merge, after some length, to a long tear line. In filled NBR, the character of the tearing is a discontinuous stick-slip process. A tensile ruptured NR filled specimen has shown\(^{(43)}\) formation of a deep depression at the sample edge, while tear fractured NR filled specimens have shown the enhancement of crystallinity throughout the matrix and a rough surface.

Gent\(^{(44)}\) demonstrated crack initiation from spherical inclusions of various sizes and coatings, embedded in rubber and obtained an expression for the minimum applied stress for debonding as

\[
\sigma_{\text{ic}} = 2 \left[ \pi \frac{G_{\text{ic}} E}{3 r_p} \right]^{1/2}
\]

where \(G_{\text{ic}}\) is the interfacial fracture energy, \(r_p\) is radius of the filler particle and \(E\) is the Young’s modulus of rubber.

There is always some characteristic stress and energy for a fracture to begin and the energy approach is most widely used in rubber.

Although the initiation of fracture is similar for all elastomeric materials, the propagation of the same is very much different. The propagation depends on the strain.
energy release rate $G$ which is defined as the rate at which the strain energy is converted into fracture energy with the growth of a crack. This is shown mathematically as

$$G = -2 \left( \frac{\delta W}{\delta A} \right)$$

where $W$ is the strain energy density of rubber

$A$ is the surface area of the specimen.

The crack propagation, or tearing, depends on factors such as viscoelasticity, strain crystallisation in elastomers e.g. NR, reinforcement with carbon black, etc.\(^{(45)}\). In multi-phase elastomers and interpenetrating networks, the higher strength arises from the mechanism of higher viscoelastic losses.

Reinforcing carbon blacks increase the fracture energy over a range of temperatures and rates. This is due to the following three processes:

(a) an increase in intrinsic strength

(b) higher energy dissipation in filled rubbers

(c) a change in the character of fracture from a smooth process to a stick-slip or knotty process which requires more energy.

In contrast, Mathew, Bhowmick and De\(^{(46)}\) reported that on the addition of fillers such as HAF (N330) carbon black makes the matrix brittle and there are more cracks on the fracture surface. Goldberg et al.\(^{(47)}\) made detailed studies on initiation of flaw sites of SBR filled with 15, 25 and 35 phr carbon black and reported an increase in the size of the flaw with an increase in the carbon black loading.

Also, the addition of carbon black must reduce the degree of stress magnification (and hence load on the chains) at the tips of flaws. A filled elastomer has a higher resistance to deformation than an unfilled one. This fact implies that for a given degree of macroscopic extension, the chains in a filled specimen carry an average load that is greater than for an unfilled specimen (due, in part, to strain amplification).

Flaws originally present in a sample are very small and cracks originating from them become visible only after about 90% of the life of the test specimen has elapsed. For a long strip of rubber with a small cut of length $c$, deformed in simple extension, the tearing energy is given by\(^{(48)}\)

$$T = 2KcW$$
where \( W \) is the energy stored per unit volume in the portion of the strip under simple
extension (away from the cut) or simply the strain energy density

\[ K \]

is an insensitive function of the extension ratio which may be taken as constant

\( (B) \) Wear

Wear of rubber is a complicated process which accompanies, in many cases, the
formation of ridge patterns and the detachment of small and large particles called
‘debris’. The prime interest in the abrasion of rubber is due to the wear of tyres.
Conveyor belting, printing rolls and shoe soles are the other major areas where
abrasion plays a role. Abrasion is defined as the removal of rubber from a surface in
sliding contact with another surface. Abrasion is a mechanical cut growth process
which starts from stress concentrations set up in the rubber in the vicinity of track
asperities both due to the load on them and particularly to the stresses which are set up
in the rubber because of frictional forces between rubber and track asperities.

The abrasion loss will depend on the environmental conditions such as the pressure
between the two surfaces in contact, the nature of the hard surface against which the
rubber slides and whether sliding takes place over the whole of the contact area or only
over part of it. It will also depend on the material properties of a particular rubber.

It is generally believed\(^{(49)}\) that abrasion of polymer occurs by two mechanisms:
(a) abrasive - resulting from microcutting by solid projections on the surface of
the abraded body
(b) frictional - resulting from the forces of friction created by projections which
deform the surface layers of the elastic material many times and
separate them off without tearing.

In the first type longitudinal furrows are formed on the abraded surface, and transverse
ridges in the second. The abrasive mechanism (a) of abrasion is less dependent on the
thermal properties of the elastomer used and more sensitive to the rubber (or
compound) properties that increase its resistance to cutting, i.e. type and level of
reinforcement.
Bhowmick et al.\(^{(50)}\) have reported that the frictional mechanism (b) is observed in the
filled vulcanisates.

Mahdi\(^{(51)}\) reported that compound factors which involve in the complicated process
of wear can be divided as primary and secondary factors. If other abrasion factors
are constant, the following were considered as the primary factors which favour resistance to abrasive wear.

(a) low coefficient of friction (μ)
(b) high tearing energy (T)
(c) high (up to certain level) hardness (H)
(d) high tan δ (high hysteresis)
(e) an elastomer that has, or elastomers that have, low coefficient of abrasion (α)

Secondary factors are:

(a) increased tensile strength
(b) increased elongation at break and modulus

Estimation of the values of the primary factors may provide a possible prediction of the performance of a rubber under specific abrasion conditions. Secondary factors may not necessarily provide a good prediction of the extent of wear under given conditions.

The formation of a ribbed structure on the abraded surface of a filled vulcanisate may occur through the mechanism of abrasion by roll formation. For example, Akron abrasion tests on an NBR vulcanisate generated fibrillar coils which are agglomerated in a ribbed structure on the surface. Southern and Thomas indicated that crack growth (under dynamic condition) is an important factor in ridge formation. In filled NR as the crack growth resistance is high, the small abraded particles coalesce to form a large mass before removal. Removal of the ridges depends on the deformation and strength properties of the elastomer at a range of temperatures. Abrasion appears to be a combination of crack growth processes strongly influenced by temperature and oxygen whereby the temperature is largely generated in the friction process itself.

Schallamach was the first to point out that very often in an abrasion process equally spaced ridges normal to the direction of sliding appear as a result of abrasion. These have been called abrasion, or Schallamach patterns (Fig. 2.7). Also shown in Fig. 2.7 is a cross-section of an abraded surface and the direction of abrasion. The mode of mechanical failure in pattern abrasion is thought to be intermediate between tensile break and tear propagation.

Abrasion by roll formation which is often observed with filled vulcanisates, has all the features of pattern abrasion in a more severe form. In addition to the high extensibility of the compound involved, smeary abrasion debris is also present. The edges of the pattern turn over and stick to the flap forming a roll which leads to a co-ordinated peeling action of the rubber, thereby increasing the abrasion considerably. Gent and Pulford noticed that under similar experimental conditions smearing also depends on the type of compound. Carbon black filled compounds tend to smear more than
unfilled ones, especially NR, SBR and EPR. They suggested three contributions to the abrasion process: (a) thermal degradation due to local frictional heating (b) oxidation which could be assisted by the frictional temperature rise and (c) the formation of free radicals in the rupture process which then also oxidise.

Fig. 2.7 Schallamach abrasion patterns of two carbon black filled NR tread compounds on different road surfaces and the profile of an abrasion pattern obtained from a worn tire surface

1. 2 - 25 phr HAF; 3, 4 - 45 phr HAF
1, 3 - fine tarmac; 2, 4 coarse concrete
Magnification = 14x

Bhowmick indicated that abrasion resistance of a filled compound may become high due to dissipation of some of the sliding energy on the old surface which would have otherwise been utilised to create new surfaces for crack growth. He concluded that the size and shape of the ridges depend upon the frictional force per unit length of the abrader in contact with the rubber and the nature of the rubber and the abrasive. Also he observed that the small abraded particles which occur in the first step of ridge formation due to microtearing, are not loose, and, hence, are not removed easily if the strength of the matrix is high.

Zhang investigated the abrasion of filled NBR at various stages of wear. He found that the addition of carbon black notably reduced the wear rate of NBR, especially under severe conditions, and reduced its dependence on frictional work. He stated that this could be due to the tensile strength gain of filled NBR as pointed out by Gent and Pulford. Moreover, Zhang has reported that abrasion of NBR appears as a dry
(particulate) wear. The formation of macroridges on filled NBR appeared to involve two distinct ridges one formed after the other. First, fine and tightly spaced primary ridges, followed by rough and sparsely spaced secondary ridges. As for the filled NBR, both the scale and roughness of the secondary ridges happened to be uneven, even if steady state had been reached.

The intensity of abrasion patterns increases with increasing coarseness of the track and with decreasing stiffness of the compound. The most important characteristic, is that they increase the rate of abrasion. Mahdi (51) has shown recently that the finer the abrasion pattern the lower the abrasion loss. The intensity and spacing of abrasion patterns formed with slipping wheels e.g. Akron abrasion tester, depends not only on the load, but on the length of the sliding path.

Both ridge height and ridge spacing, two characteristic features of an abrasion pattern, increase with increasing severity of wear (57). In long wearing compounds, the pattern is very shallow and absent in some regions. The spacing of the abrasion pattern increases with the load and depends on the elastic properties of the rubber. Rubbers with a high extensibility and low modulus form more pronounced patterns than hard ones of low extensibility (54).

Thavamani and Bhowmick (58) found that, abradability increases linearly with ridge spacing per unit frictional force. Further they found that abradability is inversely proportional to breaking energy and shear loss modulus and is independent of the nature of diene rubbers, their composition and the testing temperature.

2.4 **RUBBER MIXING**

2.4.1 **THE BATCH MIXING SYSTEM**

The rubber industry is dominated by batch mixing technology. While the throughput advantages of continuous mixing are well recognised, commercial rubber operations usually employ batch mixing because rubber is obtained in large solid bales, whereas a continuous mixer is supplied continuously with particulates or free flowing materials.

The objective of the batch mixing process is to produce a compound with its ingredients sufficiently thoroughly incorporated and dispersed so that it will process easily in the subsequent forming operations, cure efficiently and develop the necessary properties for end-use; all with the minimum expenditure of machine time and energy. Viscosity, dispersion, scorch stability and cure rate are the properties relevant to
subsequent operations. Thus, in order to mix efficiently and profitably, one must direct attention to raw materials, mixing procedures, mixing equipment and quality control.

Internal mixers are batch mixers which have become the workhorse of the rubber industry due to their versatility and efficiency. In contrast to the two-roll mill, more uniform compounds and larger batches can generally be prepared using the internal mixers.

Common features of internal batch mixers are:
(a) ability to exert a high localised shear stress to the material being mixed (dispersive mixing)
(b) a lower shear rate stirring (distributive mixing)

There are two basic designs of rotor in internal mixers; non-intermeshing (e.g. Farrel Banbury) (Fig. 2.8(a)(59)), and intermeshing (e.g. Francis Shaw Intermix) (Fig. 2.8(b)(59)).

Fig. 2.8(a) Cross section of a Farrel Bridge Banbury showing tangential rotors(59)
Fig. 2.8(b) Cross section of a Francis Shaw Intermix showing interlocking rotors\textsuperscript{(59)}

Intermeshing rotors provide better heat transfer and are therefore better for heat-sensitive compounds with lengthy mixing cycles. Intermeshing rotors such as used with the Shaw Intermix machines are far less susceptible than those used with Banbury to the slippage problem which occurs as the rotors try to draw the rubber into the chamber\textsuperscript{(60)}. 

29
Mixing Operation

There are four main processes, which take place during the mixing cycle.

(1) Viscosity reduction - In this stage the rubber is rapidly converted to a state in which it will accept compounding ingredients and is achieved by three interdependent mechanisms: mastication, temperature rise and chain extension\(^{(59)}\).

(2) Incorporation - This stage is when the initially free ingredients become attached to the rubber. This is also known as the wetting stage. The elastomer undergoes large scale shearing and stretching deformations increasing the surface area for accepting filler agglomerates, which are then sealed inside when masses of the elastomer are folded or recombined.

(3) Distributive mixing - This is the process by which the composition of the rubber compound is homogenised and the scale of segregation reduced. There are two sub-processes: laminar shear mixing and exponential (subdivision) mixing, of which the latter is more efficient. A fill factor of less than one is needed for effective exponential distributive mixing. Fill factor is the proportion of the mixing chamber volume occupied by the finished mix. As the fill factor is increased a transition occurs from exponential to laminar distributive mixing\(^{(59)}\).

(4) Dispersive mixing - In this stage the filler agglomerates are broken down to their constituent primary aggregates giving a fine scale of mixing. This is especially important in the case of carbon black because at this stage an intimate contact between the surface of the carbon black and the elastomer develops, resulting in strong reinforcement. High stress is required for the disruption of filler agglomerates and result from both shear and elongational deformations. Funt\(^{(60)}\) and Mason\(^{(61)}\) discovered that the rate of agglomerate size reduction is proportional to deformation rate. Furthermore, they found that for the same total strain, elongational flows give significantly higher dispersion. More recently Clarke and Freakley\(^{(62)}\) discovered that dispersive mixing occurs by a sub-divisional fracture mechanism in both shear and elongational flow regimes and under conditions of both low and high stress.

Each of the above processes can occur simultaneously.
2.4.2 **PROCESS VARIABLES AND CONTROL**

(1) **PROCESS VARIABLES**

The following are the important variables affecting quality and efficiency of internal mixing.

(a) **Shear Stress**

The general conclusion drawn from a number of theoretical analyses on the dispersive mixing of carbon black in elastomers is that high shear stresses and low particle-particle attraction increase the rate of dispersion, but that for a given particle there is a critical stress below which dispersion will not occur. The maximum shear stress is inversely proportional to the square of the gap, so this clearance is critical\(^{(63)}\). Elongational flow is also important in particle size reduction\(^{(64)}\).

(b) **Shear Strain and Rate of Shear Strain**

The total shear strain necessary for a particular degree of mixing can be imposed at any rate, the shorter time required at high rates being offset by higher power consumption and heat generation. Shear strain rates for a variety of types and sizes of mixers approximate to \(r/x\), where \(r\) is the peripheral rotor speed and \(x\) is the rotor tip clearance. Therefore, small mixers must be run at higher rotational frequencies to give the same shear strain rate as larger mixers\(^{(63)}\).

(c) **Rotor Speed**

Rotor speed directly affects shear strain rate (or deformation rate) and thus the speed of mixing. Although high rates of deformation obtained by high rotor speeds give rise to high torques in the early stages of a mixing cycle, they are rapidly reduced due to the reduction in batch viscosity associated with the rise in batch temperature and can result in a deterioration in dispersive mixing. This has been attributed to the strongly non-Newtonian behaviour of rubber\(^{(59)}\). Hence to retain a high viscosity in the rubber for dispersive mixing, a low rotor speed is desirable, to minimise the increase in batch temperature.

Low rotor speeds may enable the requirement for a second dispersive mixing operation to be avoided (due to improved filler dispersion) and, allow curatives to be added (due to the low batch temperature), considerably reducing the total cost of mixing and the associated batch handling\(^{(65)}\). As rotor speed is reduced, at the expense of extended mixing times, mixed-material properties which depend on filler dispersion are improved. The rate of
distributive mixing is a function of rotor speed, proceeding more rapidly as speed is increased.

(d) Ram Pressure

The function of the ram is to keep the compounding ingredients in the mixing area. In practice a high ram pressure, up to 0.55 MPa, has definite advantages, especially for high viscosity mixes, as it decreases voids within the mixture and increases shear stress by reducing slippage. In addition, increasing pressure increases the contact force between the rubber and the rotor surface, thus increasing the critical stress so that flow begins at a lower temperature\(^{(63)}\).

The force applied to the ram should be sufficient to prevent the upthrust of the batch from displacing it upwards. The upthrust is strongly dependent on fill factor. Often, available ram force places a practical limit on fill factor.

A substantial reduction in ram pressure causes a drop in the mixing efficiency.

(e) Temperature

Temperature control is an important factor in mixing as the temperature of the mixer exerts a strong influence on the characteristics of mixing. This is shown by the first-batch effect, where the physical properties of batches produced immediately after commencement of mixing are significantly different from those subsequently produced when the mixer has achieved its “operating temperature”. This effect and subsequent variations in the properties of batches are reduced by controlling the circulating water temperature.

Water-tempering systems usually control the circulating-water temperature in a range extending from the feed-water temperature up to approximately 80°C. Batch-batch uniformity of mixing has been improved in this way. However, only the temperature of the circulating water is controlled directly. The temperature gradients through the chamber and rotors, and the batch temperature, will also depend on other mixing variables\(^{(59)}\).

With a mixer having a variable-speed drive the batch temperature can be controlled directly. The batch temperature will remain constant if the mechanical energy input via the rotors is equal to the heat extracted from the batch.
(f) **Fill Factor**

Fill factor is the proportion of the mixing chamber volume occupied by the finished mix. It is calculated as shown below.

$$\text{Fill factor} = \frac{\text{Volume of batch}}{\text{Net volume of chamber}}$$

where $$\text{Volume of batch} = \frac{\text{Batch weight}}{\text{Specific gravity}}$$

Efficient mixing occurs when the mixing chamber is underfilled\(^{(66)}\). Freakley and Wan Idris\(^{(66)}\) found that the flow patterns depend upon the fill factor. Fill factors in the range 0.65-0.85 are generally used, depending on mix type. Highly reinforced compounds mix more successfully towards the lower end of the range, while moderately reinforced compounds can be mixed effectively at the upper end of the range\(^{(59)}\). Dizon\(^{(67)}\) has shown that there is a maximum fill factor for effective dispersion which depends upon the type of carbon black. Very low fill factors are uneconomic and very high fill factors result in some of the material not taking part in mixing. Batch temperature, measured at either a constant mixing time or energy, increases substantially as fill factor is increased, over the whole range of fill factors\(^{(65)}\).

(g) **Mixing sequence**

In an ideal mixing sequence, all the ingredients of a compound are charged into an internal mixer together and mixed in a single cycle, without danger of scorch. General-rubber goods compounds can be mixed according to this ideal sequence, by using a variable speed drive or, in the case of single speed mixers, by mixing at a sufficiently low rotor speed to avoid increase in batch temperature, which would prevent the addition of curatives.

Three-stage mixing sequences having the sequence: masterbatch, remill, and final mix, are used for compounds containing large quantities of reinforcing fillers. Each stage is carried out in an internal mixer. In the masterbatch stage, the rubber and the reinforcing filler are mixed at a high rotor speed (40-60 rpm, depending on the size of the mixer), together with any other ingredients which are insensitive to temperature. For moderately
reinforced compounds the remill stage may not be necessary or as an alternative a two-roll mill can be used for the remill stage, as the environment/health problem of loose filler does not arise.

Freakley(68) has reported that mixing time (or mixing energy), fill factor and rotor speed are the dominant variables, while ram pressure and circulating water temperature exert a lesser effect on mixing performance.

Brantley(69) evaluated the effect of rotor speed on mixing and found that

Increasing rotor speed:
(a) increases energy consumption
(b) reduces mixing time
(c) increases discharge temperature
(d) reduces Mooney viscosity

(2) PROCESS CONTROL

There are three main criteria used to determine when a compounding ingredient should be charged into an internal mixer or when to end the mixing process. These are mixing time, batch temperature and mixing energy. The aim is to guarantee the quality of the end product, avoid overmixing and reduce variation between batches. Mixing time and energy are often used to determine when materials should be added into the mixer, whereas temperature is generally used only as a discharge criterion.

Mixing time does not provide any compensatory adjustment for the influence of relatively uncontrolled variables, such as mixer temperature and feedstock properties, on mixing performance. Batch temperature is influenced strongly by variations in mixer temperature(70). It is sensitive to mixing performance and provides a good indication of state of mix. The changes in power consumption in a typical rubber mix are indicative of stages in the process, such as wetting, dispersion and plasticisation and can be related to the development of end product properties. A more precise and reproducible control of the mixing cycle can be obtained by considering the energy input at various stages in the cycle in terms of both instantaneous power and integrated power or work input. Mixing energy, which is the power consumed by an internal mixer, minus the power consumed to run the empty mixer is measured by a power integrator and this criterion provides a reasonable indication of mixing performance(59,71).
Brantley, Jr., reported that a mixing procedure based on the power profile gives more uniform mix quality than one based on temperature. Energy required for mixing can be reduced with slightly higher discharge temperature by increasing cooling water temperature\(^{(69)}\).

2.4.3 EFFECT OF MIXING ON PROPERTIES

Mechanical properties of SBR 1712 compounds and vulcanisates containing ISAF (N220) carbon black obtained from very short to more than adequate mixing procedures are given in Table 2.2\(^{(32)}\). The data show how reinforcing abilities are influenced by variations in mixing procedure. After 1.5 min. of mixing, the tensile strength attained is two-thirds of its maximum value. Other failure properties such as elongation and abrasion behave in a similar manner, i.e. reaches a maximum and then levels off. The abrasion resistance is about 40% of that of the best dispersion (two-stage). However the tear strength is quite insensitive to mixing time. 100% modulus drops from 34 kgf/cm\(^2\) for the short-time mixed vulcanisate to less than half that value for the vulcanisate from the fully mixed compound. The reduction in 100% modulus with increased mixing time, which is a reflection of the reduction in viscosity has been attributed to the breakdown of carbon black agglomerates.

The mechanism proposed by Boonstra and Medalia for the reduction in viscosity of a compound with increased mixing is given in Sub-section 2.5.3. More recently Clarke and Freakley\(^{(72)}\) attributed the reduction in viscosity of an uncured SBR/N330 carbon black compound during mixing to disagglomeration of carbon black and mastication of the elastomer. The effect of mixing time on mechanical properties of SBR compounds and vulcanisates is in line with the results of Dannenberg\(^{(73)}\).

Also, Dannenberg studied the effect of carbon black mixing time on properties of a NR tread compound and a nitrile rubber compound both containing 50 phr carbon black. Increasing the carbon black mixing time from 1.1 to 4 min. did not significantly alter the properties of the NR tread compound. Hence Dannenberg suggested that the mixing of carbon black with NR is accompanied by a concurrent process of rapid wetting and disintegration of carbon aggregates and further mixing does not significantly influence the aggregate size. The nitrile rubber compound showed a rapid increase in tensile strength with increased carbon black mixing time, as its pure gum tensile properties are in the same class as SBR. However similar to NR, in other properties NBR is rather insensitive to mixing.

35
<table>
<thead>
<tr>
<th>Property</th>
<th>Mixing Time (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td>Tensile strength (kgf/cm²)</td>
<td>173</td>
</tr>
<tr>
<td>100% Modulus (kgf/cm²)</td>
<td>34</td>
</tr>
<tr>
<td>300% Modulus (kgf/cm²)</td>
<td>130</td>
</tr>
<tr>
<td>Elongation (%)</td>
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</tr>
<tr>
<td>Hardness (IRHD)</td>
<td>65</td>
</tr>
<tr>
<td>Tear strength (kgf/cm)</td>
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</tr>
<tr>
<td>Abrasion (Akron, vol. loss,cm³/10⁶ rev.)</td>
<td>289</td>
</tr>
<tr>
<td>Permanent set, %</td>
<td>4.6</td>
</tr>
<tr>
<td>Mooney viscosity ML (1+4)100°C</td>
<td>133</td>
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<tr>
<td>Dispersion rating (%)</td>
<td>23.6</td>
</tr>
<tr>
<td>Heat build-up</td>
<td>51</td>
</tr>
</tbody>
</table>

Cure time : 60 min. @ 144°C for sheets, 70 min. @ 144°C for thicker specimens

Table: 2.2 Effect of mixing time on properties of single-stage mix of ISAF (N220) carbon black in oil-extended SBR-1712

Hess et al. reported that for SBR compounds, with increasing mixing energy, the modulus levels were slightly higher for the finer carbon blacks and lower for the coarser grades. Also he found that the 300% modulus of EPDM compounds increased slightly at higher mixing times, but the dominant variables were dibutyl phthalate absorption.
(DBPA), carbon black loading and oil loading in that order of significance. In SBR compounds the tensile strength increased by about 8-12% (across the range of carbon blacks studied) as the mixing energy was increased from 750-1400 MJ/m$^3$. Carbon black surface area was the main variable affecting the tensile strength.

Wijayarathna et al.\textsuperscript{(75)} studied the effect of mixing temperature and rotor speed on the tensile strength and elongation at break of nitrile rubber vulcanisates containing both HAF (N330) and ISAF (N219) carbon black. The stress at break ($\sigma_b$) or in other words tensile strength reaches maximum values at temperatures between 65°C and 100°C at a rotor speed of 80 rpm as shown in Fig. 2.9. When mixing is carried out at low temperatures and high speeds, the local heat generation facilitates incorporation, reducing the stiffness of the rubber matrix and the slippage between the mix and the mixing chamber. Thus the rate of improving stress at break by increasing rotor speed is higher for low temperature mixing (Figures 2.9 and 2.10). However, the stress at break is reduced when mixing is carried out at increased rotor speed and very high mixing temperatures. This was attributed to reduced shear stresses in the gap between rotor nip and chamber wall causing inferior filler dispersion. Poor mechanical properties of compounds mixed at very high temperatures and high rotor speeds also result from thermal and mechanical degradation of the rubber.

![Fig. 2.9 Tensile strength of NBR vulcanisates formulated with both HAF (N330) and ISAF (N219) carbon black as a function of mixing temperature at various rotor speeds\textsuperscript{(75)}](image-url)
Except for mixing temperatures below $50^\circ$C, strain at break ($\varepsilon_b$) decreases as the temperature is increased. Optimal values of $\varepsilon_b$ are obtained at rotor speeds between 60 and 80 rpm (Figures 2.11 and 2.12).

Fig. 2.10 Tensile strength of NBR vulcanisates formulated with both HAF (N330) and ISAF (N219) carbon black as a function of rotor speed at various temperatures$^{(75)}$

Fig. 2.11 Strain at break ($\varepsilon_b$) of NBR vulcanisates formulated with both HAF (N330) and ISAF (N219) carbon black as a function of mixing temperature at various rotor speeds$^{(75)}$
Dannenberg\(^{(73)}\) reported that high temperature mixing resulting from high speed internal mixing effects only a slight change in mechanical properties of a NBR compound containing 50 phr HAF (N330) carbon black, and this property of heat resistance makes NBR an outstanding industrial product. However high temperature mixing caused an increase in 300\% modulus, lower tensile strength, and elongation, lower hardness, lower hysteresis losses, lower permanent set, increased abrasion resistance and lower tear strength of the NR tread compound. He attributed these changes to changes in the NR matrix such as thermal breakdown, oxidative crosslinking of the rubber and the formation of a carbon black-rubber gel complex.

Lee\(^{(76)}\) established a new technique for improving the degree of mixing of the filler in an elastomer matrix and studied the effect of the same on mechanical and permeability properties. This technique includes a unique heating and cooling mixing procedure in conjunction with surface modification of the carbon black and choice of polymers. It was proposed that the cooling cycle enhanced carbon black dispersion, while the heating cycle decreased micro-void concentration. The rubber used in this study was polychloroprene.

Fig. 2.12 Strain at break (\(\varepsilon_b\)) of NBR vulcanisates formulated with both HAF (N330) and ISAF (N219) carbon black as a function of rotor speed at various mixing temperatures\(^{(75)}\)
Cyclically mixed polychloroprene showed an improvement in the degree of mixing over the conventionally mixed polychloroprene. It was noted that mechanical properties such as tensile strength, ultimate elongation, fatigue life, permanent set, hysteresis and permeability properties of the cyclically mixed polychloroprene are superior to those of the conventionally mixed polychloroprene. Lee, finally concluded that the good state of mix obtained using the new mixing technique (Table 1 of Appendix) can enhance the mechanical and permeability properties of filled elastomers.

2.5 Rheology of Polymer Melts

2.5.1 General Rheological Behaviour

Rheology in its broadest definition is the science of flow and deformation of matter. The greater part of rheology is concerned with the interrelation of stress, strain and time and their dependence upon such factors as temperature, shear rate, molecular weight, concentration of various additives and chemical constitution. Polymeric fluids exhibit viscous behaviour in steady-state flows, but transient flows invoke viscoelasticity.

Simple shear is the most important type of deformation in studies of polymeric materials. For example, steady-state laminar flow of a liquid between two parallel plates set in relative motion at constant speed is a simple shear flow with a constant strain rate (77).

The viscosity of rubber can vary substantially with deformation rate, and thus the rheological properties cannot be defined by measuring viscosity at one strain rate. Rheological properties are often presented in the form of a flow diagram which plots shear stress as a function of rate of deformation.

For Newtonian (ideal) fluids these parameters are related by

\[ \tau = \eta \dot{\gamma} \]

where \( \eta \) is the viscosity
\( \tau \) is the shear stress
\( \dot{\gamma} \) is the shear rate
For non-Newtonian fluids e.g. polymer melts,
\[ \tau = f(\dot{\gamma}) \]

For many polymers it has been found that the flow curves - shear stress against shear rate - can be described by a simple power law of the form
\[ \tau = K \dot{\gamma}^n \] (also known as the Ostwald de Waele equation) \(^{(97)}\)

where \( K \) and \( n \) are material parameters.

\( K \) is the consistency index and is a measure of the fluidity of the material, a high value of \( K \) indicates a very viscous material. \( n \) is the power law (flow) index and is a measure of the non-Newtonian behaviour of the fluid. For a Newtonian fluid \( n = 1 \) and \( K \) is the viscosity. The more \( n \) differs from unity, the more the system is non-Newtonian. For \( n < 1 \), a fluid is called 'pseudoplastic' and the viscosity decreases with increasing shear rate; for \( n > 1 \), a fluid is called 'dilatant', and the viscosity increases with increasing shear rate. For rubbers \( n \) is generally in the range 0.15-0.4 \((n < 1)\) \(^{(59)}\) and \( K \) is generally in the range 70-120 kPa.s \(^{(79)}\).

The Ostwald de Waele power equation is the most widely used empirical model for representing melt-flow behaviour because of its analytical simplicity as well as its ability to represent the viscous behaviour of the system.

In logarithmic form the power law equation may be written
\[ \log \tau = \log K + n \log \dot{\gamma} \]

Plots of \( \log \tau \) versus \( \log \dot{\gamma} \) for various polymers are often linear through substantial ranges of operation.

It is a direct consequence of the shape of a pseudoplastic flow curve (plot of \( \tau \) against \( \dot{\gamma} \)) that there is no constant of proportionality between shear stress and shear rate. Therefore instead of the coefficient of viscosity (\( \eta \)) which we use with Newtonian liquids, it is more common to refer to the 'apparent viscosity' \( \eta_a \) defined as shear stress/shear rate i.e. \( \eta_a = \tau / \dot{\gamma} \)

The apparent viscosity is the slope of the secant line from the origin to the shear stress at the given value of shear rate as shown in Fig. 2.13.
Behaviour of apparent viscosity with rate of shear for dilatant, Newtonian and pseudoplastic fluids is illustrated in Fig. 2.14, shown below.

Fig. 2.14 Apparent viscosity-shear rate curves for a dilatant, a Newtonian and a pseudoplastic fluid which have the same apparent viscosity at zero shear rate\(^{(81)}\)
The decrease in the apparent viscosity as the rate of shear increases is of great importance in the processing and fabrication of elastomers. Viscosity decreases nearly linearly with \( \dot{\gamma} \) on a log-log plot. In this linear range, the power law

\[
\tau = K \dot{\gamma}^n
\]

\( \eta_a = K \dot{\gamma}^{n+1} \) equation applies

2.5.2 **Effect of Temperature on Viscosity**

Two important aspects of rubber mixing are the dependence of viscosity on temperature and shear rate.

The viscosity of most polymers changes greatly with temperature according to the Arrhenius equation (80)

\[
\eta = A e^{E/RT}
\]

at temperatures 80°C or more above their glass transition temperatures. A is a constant at a given shear stress or rate. E is the activation energy and is generally in the range 40 - 200 kJ / mole. R is the universal gas constant and T is the absolute temperature.

Shear stress is a significant parameter in filler dispersion; it is directly dependent on viscosity. Hence, shear stress is dependent on the temperature of the mix.

In the case of polymer melts apparent viscosity, \( \eta_a \) is a function of the rate of shear characterised by either \( \tau \) or \( \dot{\gamma} \), as well as a function of temperature. The temperature coefficient of the apparent viscosity must be specified at constant shear stress (\( \partial \eta_a / \partial T \)) or constant shear rate (\( \partial \eta_a / \partial T \)) \( \dot{\gamma} \). In general the two will not be equal and two Arrhenius equations result (77).

\[
( \eta_a)_\tau = A e^{E/RT}
\]

\[
( \eta_a)_{\dot{\gamma}} = A e^{E\dot{\gamma}/RT}
\]

2.5.3 **Effect of Fillers on Viscosity and Effective Filler Volume Fraction**

The rheological curves of rubber-carbon black systems conform approximately to the Ostwald de Waele empirical equation, given in Sub-section 2.5.1.
Zakharenko and co-workers\textsuperscript{(82)} found that the non-Newtonian or power-law index ($n$) increases with the content of active filler i.e. $n$ changes linearly with the filler content. For P-20 polyisobutylene and its mixtures with carbon black

$$n = 1 + 0.012 \, c$$

where $c$ is the filler content (parts per 100 parts of polymer by weight)

However the value of $n$ is unchanged in the presence of inactive filler e.g. chalk. i.e. it is the same as for the pure rubber.

Moreover these researchers found that the viscosity-temperature relationship of carbon black filled rubbers is also governed by the exponential expression $\eta = A e^{ER/T}$, as for pure elastomers. The temperature coefficient of viscosity $\partial \eta / \partial T$ and the activation energy $E$, were found to be independent of the nature and amount of filler\textsuperscript{(82)}.

The relative influence of different types of carbon black on the viscosity does not appear to depend strongly on shear rate\textsuperscript{(83)}. Higher carbon black structure gives higher viscosity which is readily understood on the basis of the occluded rubber theory\textsuperscript{(84)}. An even stronger effect is found from surface area. At constant structure level carbon blacks of higher surface area (i.e. lower particle size) give higher viscosity\textsuperscript{(83)}, which may be due to the formation of more bound rubber, or to the stronger inter-aggregate association expected with higher area carbon blacks. Increased carbon black loading has the obvious effect of increasing the viscosity of the compound and can be counteracted by using more oil in the compound\textsuperscript{(85)}.

The greatest effect of carbon black on the viscosity relative to unfilled polymer is observed at low shear stresses or rates as illustrated in Fig. 2.15\textsuperscript{(29)} with data on HAF (N330) carbon black in a linear narrow distribution solution copolymer of butadiene and styrene (75:25) of $M_w = 260,000$. Kraus has suggested that this phenomenon involves secondary aggregation effects. At high shear rates the effects of aggregation are smaller.
When the unfilled polymer is strongly non-Newtonian, the additional shear dependence due to added carbon becomes small and the viscosity-shear stress curves become more nearly equidistant along the log $\eta$ axis. Fig. 2.15 shows the ratio $\eta(\text{filled})/\eta(\text{unfilled})$ to increase greatly as the shear stress is reduced below $10^5$ Pa.

At high shear stresses i.e. above $10^5$ Pa, the unfilled polymer becomes increasingly non-Newtonian, the viscosity ratio becomes roughly constant (at equal shear stress), as in the data reported by Smit\(^{(86)}\) for HAF (N330) carbon black in SBR 1509 (Fig. 2.16).

Smit has found that the relative viscosity

$$\eta_r = \left[ \frac{\eta(\text{filled})}{\eta(\text{unfilled})} \right]_{\tau = \text{constant}, \ c = \text{constant}}$$

where $c$ is the volume fraction of filler, varies relatively little with shear stress ($\tau > 10^5$ Pa) or temperature.
Fig. 2.16 Apparent viscosity vs. shear stress for carbon black filled conventional SBR\(^{(86)}\)

Smit assumed that the particles are covered by a rigid, immobilised adsorption layer, which effectively increases the filler concentration as no reasonable shape factor was found based on representation of the structure aggregates. The estimated thickness of this layer was between 2.5 and 7 nm. This work was superseded by the work of Clarke and Freakley\(^{(72)}\), who found that there is no immobilised rubber associated with primary aggregates either as occluded rubber or as an adsorbed layer on the carbon black surface. This is in contrast to Medalia who postulated the existence of occluded rubber within primary aggregates which, in a similar way to the immobilised rubber, contributes to the effective volume fraction of filler\(^{(87)}\). Clarke and Freakley\(^{(72)}\) attributed this finding by Medalia to incomplete mixing of the compound used in the experiments. They suggested that if some agglomerates remained due to incomplete mixing, then the rubber immobilised within the agglomerates would be assumed to be associated with primary aggregates.

The effect of fillers on the viscosity of polymer compounds has been described by theory used to model the rheological behaviour of suspensions\(^{(88)}\). Einstein derived the following
theoretical viscosity equation$^{(89)}$ to describe the behaviour of suspensions of non-attracting spherical particles:

$$\eta = \eta_0 \left(1 + 2.5 \phi\right)$$

where

- $\eta$ = viscosity of the suspension
- $\eta_0$ = viscosity of the suspending medium and
- $\phi$ = volume fraction of suspended particles

The above equation can only be applied at low particle concentrations because the particles are assumed to behave independently. As suspensions become more concentrated, particles will increasingly interact with each other. This effect has been accommodated by the addition of a further term to the Einstein equation, as shown below$^{(89)}$.

$$\eta = \eta_0 \left(1 + 2.5 \phi + k_1 \phi^2\right)$$

where $k_1$ is a constant with theoretical values which vary according to the assumed spatial arrangement or packing of spherical particles.

This expanded version of Einstein equation applies to suspensions of non-attracting spherical particles. Vand$^{(90)}$ determined a theoretical value of 7.35 for $k_1$, while Guth and Gold$^{(91)}$ found a value of 14.1. More recently, Clarke and Freakley$^{(72)}$ found $k_1$ values of 15.13 for a well mixed rubber compound and 9.69 for badly mixed rubber compounds and suggested that although the spherical particles are fused together into primary aggregates, rubber flows freely and closely around them. Moreover, their results also indicated that the carbon black in both primary aggregate and agglomerate form behaves as non-attracting spherical particles.

Volume fraction of filler can be calculated from the weight of filler and the densities of the filler and polymer. There is a general increase in relative viscosity with increase in volume fraction of filler, but the relationship depends on the characteristics of the filler and the polymer.

It has been shown that particle size has little effect on relative viscosity for relatively large particles$^{(89)}$. Boonstra and Medalia$^{(92)}$ have shown that for particles less than about 1μm diameter, relative viscosity increases with decreasing particle size.
Boonstra and Medalia\(^{(92)}\) have proposed that disagglomeration of carbon black may result in a reduction in relative viscosity by causing a decrease in the effective volume fraction of filler, which includes the carbon black itself and elastomer which is immobilised within agglomerates. They suggested that immobilised rubber behaves as part of the filler particle. Clarke and Freakley\(^{(72)}\) also suggested that reduction in relative viscosity of a compound during mixing is entirely due to disagglomeration of carbon black. The mechanism proposed by Clarke and Freakley by which the relative viscosity of the compound decreases with increasing mixing is as follows: “agglomerates in a compound contain immobilised rubber, which behaves as part of the solid agglomerate and hence, contributes to the effective volume fraction of filler in the compound. As agglomerates are broken down during mixing, immobilised rubber is released, causing a reduction in effective volume fraction of filler and a consequent decrease in the relative viscosity”. Values of relative viscosity have been used in their study instead of apparent viscosity in order to isolate the effect of mastication on the viscosity of the compound from the effect of disagglomeration.

Gessler et al.\(^{(93)}\), suggested that in thoroughly mixed compounds, carbon black aggregates make their individual contribution to viscoelastic properties, because of their own volume and that of the rubber occluded within them. Also they suggested that at shorter mixing times the highly loaded regions (inclusions) act as large filler particles. The effective volume of these inclusions is higher than that of the carbon black alone, owing to both the rubber occluded within the aggregates and the additional rubber immobilised between the aggregates. Hence these inclusions make a larger contribution to viscous properties than well dispersed carbon black. Improved dispersion of carbon black lowers the Mooney viscosity in the same way as progressive decrease in molecular weight which has been attributed in the past to mechanical breakdown of rubber molecules.

2.6 **COMPOUNDING AND VULCANISATION**

2.6.1 **INTRODUCTION**

(A) **Compounding**

Long\(^{(94)}\) has defined rubber compounding as “the art and science of selecting and combining elastomers and additives to obtain an intimate mixture that will develop the necessary physical and chemical properties for a finished product”.

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The objectives of rubber compounding are:

1. to secure certain properties in the finished product to satisfy service requirements
2. to attain processing characteristics necessary for efficient utilisation of available equipment

In other words, the most important criterion in compounding is to secure an acceptable balance between demands arising from these two criteria\(^{(94)}\).

A practical compound formulation is usually one that consists of ten or more ingredients. Each ingredient has a specific function and an impact on properties, processability and price. Compounding ingredients can be classified into ten major categories as shown below.

1. Elastomers
2. Vulcanising agents
3. Accelerators
4. Activators and retarders
5. Antidegradants (antioxidants, antiozonants, protective waxes)
6. Processing aids (peptizers, lubricants, release agents)
7. Fillers (carbon blacks, non-black materials)
8. Plasticizers, softeners and tackifiers
9. Colour pigments
10. Special purpose materials (blowing agents, deodorants, etc.)

\(B\) Vulcanisation

Gardiner\(^{(95)}\) has defined vulcanisation as "an irreversible process during which an elastomeric compound is, through chemical crosslinking in its molecular structure, converted from a thermoplastic to a thermoset having improved elastic properties". A vulcanised piece of rubber can undergo large deformation on stretching. When released, it will recoil to nearly its original dimension provided that adequate time is allowed. A vulcanised rubber does not dissolve but swells when immersed in a good solvent. Crosslinking occurs at points in the rubber molecule which are reactive to vulcanising agents and accelerators. During vulcanisation some bonds are broken and allowed to react with other materials such as sulphur bearing ingredients. These intermediates then react with adjacent polymer chains which then become attached to one another or crosslinked.

Practically all unsaturated rubbers are vulcanisable by sulphur, which is the most widely used vulcanising agent in the rubber industry. Natural rubber and nitrile rubber are two
examples of commonly used rubbers which are cured this way. These rubbers differ in
their basic structure, degree of unsaturation and location of the double bonds. Thus, they
are expected to react with sulphur in a different way.

Critical parameters related to the process of vulcanisation are the time elapsed before it
starts (called scorch time), the rate at which it occurs, and the extent. A typical cure curve
is shown in Fig. 2.17(94).

![Cure Curve](94)

2.6.2 SULPHUR VULCANISING SYSTEMS

Sulphur vulcanising systems are classified as given in Table 2.3.

<table>
<thead>
<tr>
<th>Class</th>
<th>Sulphur concentration (pphr)</th>
<th>Accelerator concentration (pphr)</th>
<th>Approximate range of E* values obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>EV (Efficient)</td>
<td>0.3 - 1.0</td>
<td>6.0 - 2.0</td>
<td>1.5 - 4</td>
</tr>
<tr>
<td>Semi-EV</td>
<td>1.0 - 2.0</td>
<td>2.5 - 1.0</td>
<td>4 - 8</td>
</tr>
<tr>
<td>CV (Conventional)</td>
<td>2.0 - 3.5</td>
<td>1.0 - 0.5</td>
<td>10 - 25</td>
</tr>
<tr>
<td>Very inefficient</td>
<td>3.5 - 10</td>
<td>0.5 - 0</td>
<td>25 - 100</td>
</tr>
</tbody>
</table>

Table 2.3 Classification of sulphur vulcanising systems(96)

* E is defined as the number of network-combined sulphur atoms present per physically-
effective chemical crosslink.
Out of the vulcanising systems listed above, semi-EV and conventional (CV) vulcanising systems are in common use. In the initial stages of vulcanisation all these systems give rather similar networks in which the crosslinks and the accelerator-terminated pendant groups are di- or polysulphidic. The difference in the final networks appears progressively as the cure time is increased: EV systems eventually form simple networks in which the crosslinks are exclusively monosulphidic. The networks from conventional and very inefficient systems become increasingly more complex, containing mixtures of mono-, di-, and polysulphidic crosslinks, and the rubber chains become more and more modified with olefinic and sulphur containing groups. These changes in structure are accompanied by corresponding changes in physical properties\(^{96}\).

Sulphur vulcanising systems for NR usually contain sulphur in amounts of 2.5-3 pphr and accelerator in amounts of 0.5-1.0 pphr (conventional system). The synthetic rubbers require a higher proportion of accelerator (1.5 pphr) with a corresponding reduction in the amount of sulphur: often equal parts of accelerator and sulphur give a useful vulcanisate. Synthetic rubbers are slower curing than NR and hence mixtures of accelerators are often used to bring curing times within the range customary for NR. The use of zinc oxide (ZnO) and stearic acid as the activator system is also usual, although the effect seems to be less marked than it is for NR\(^{97}\).

EV and semi-EV systems significantly reduce reversion and improve ageing resistance in NR vulcanisates due to the reduction of polysulphidic crosslinks and the preponderance of di- and monosulphidic crosslinks formed in the network. The latter are much more stable thermally than the polysulphidic crosslinks\(^{98}\). In general a conventional (CV) system gives rise to a vulcanisate with high tensile strength, resilience and resistance to fatigue and abrasion. An EV system shows improved heat ageing, reversion resistance and low compression set. Semi-EV systems have properties intermediate between those of CV and EV systems.

2.6.3 **THE CHEMISTRY OF ACCELERATED SULPHUR VULCANISATION**

Vulcanisation of rubber by sulphur in the presence of an accelerator or a combination of accelerators in general occurs by a mixed ionic and free radical mechanism. The relative extent of each mechanism depends on the nature of the rubber, the type of accelerators and whether ZnO and fatty acid are used.
The vulcanisation process generally proceeds in three main steps as schematically shown below (98).

**Accelerator (s), activator, sulphur, rubber**

1. **Active sulphurating agent**
   \[(\text{AS} \rightarrow \text{S}_x \rightarrow \text{SA} \text{ or } \text{AS} \rightarrow \text{S}_x \rightarrow \text{Zn} \rightarrow \text{S} \rightarrow \text{A})\]
   Where A denotes an accelerator
   \[\text{Rubber (RH)}\]

2. **Rubber bound intermediate**
   **Crosslinking precursor**
   \[(\text{R} \rightarrow \text{S}_y \rightarrow \text{A})\]
   \[\text{Rubber}\]

3. **Crosslinked rubber network**
   \[(\text{R} \rightarrow \text{S}_x \rightarrow \text{R})\]

A rubber bound intermediate consists of accelerator groups pendant to the rubber chain backbone.

Zinc oxide and stearic acid is the most widely used activating system in the rubber industry. Zinc stearate which is formed in situ is only sparingly soluble in rubber.

In terms of efficiency, the accelerated sulphur vulcanisation system in general requires only from 1-15 sulphur atoms to form a chemical crosslink in contrast to 40-55 sulphur atoms for an unaccelerated sulphur vulcanisation system. In reacting with the rubber molecule, the sulphur attacks almost exclusively at the \(\alpha\)-methylene carbon atoms (99).

Accelerators are classified as slow, medium fast, fast and ultra fast. Thiuram disulphides are regarded as ultra fast accelerators while sulphenamides fall to the class of fast accelerators. Sulphenamides are the most widely used accelerators today due to their unique combination of long scorch delay and relatively fast cure rate. The delay in onset of crosslinking is believed to be related to the disappearance of the original sulphenamides, which in turn depends on the amount of mercaptobenzothiazole (MBT) formed in situ on heating. Hence, the onset of crosslinking is expected to be delayed either by increasing the concentration of the sulphenamide or by removing the MBT as fast as it is being formed (100). A prevulcanization inhibitor (PVI), when used with a sulphenamide,
scavenges the MBT formed at the beginning of vulcanisation. This prevents, the autocatalytic depletion of sulphenamide, thus, delaying crosslinking. N-(Cyclohexylthio) phthalimide (CTP) is the widely used PVI in the rubber industry. Although CTP delays the onset of crosslinking, it has no effect on the rate of vulcanisation.

2.6.4 CURE SYSTEMS AND CURE CHARACTERISTICS OF NBR MIXES

Normally sulphur and accelerator are used for vulcanisation. Sulphur-free vulcanisations may also be carried out by addition of thiram disulphide or organic peroxides. Peroxides are only used in special cases. In usual vulcanisations, the sulphur concentration is generally lower than it is with natural rubber\(^{101}\). This is because NBR already has some crosslinks depending on its production process. The number is always generally greater than for NR. The dosage of sulphur usually does not exceed 1.5-2.0 phr. Nitrile rubbers which contain a relatively high proportion of acrylonitrile generally require less sulphur for vulcanisation than do those types which contain relatively less acrylonitrile.

In principle, practically all the accelerators which are commonly used in NR may be used in NBR but their activity in NBR is often quite different than in NR. Addition of thiram accelerators results in a longer scorch period\(^{20}\). Processing safety and outstanding vulcanize characteristics are attained also with the use of dibenzothiazyl disulphide (MBTS) and of sulphenamides, which in many cases are activated with basic accelerators or with TMTM. Vulcanisates which have been made with TMTD with little or no sulphur tend to ‘bloom’ because of the high dosage but this can be reduced or eliminated by the simultaneous use of MBT, MBTS or CBS. The torque vs. time curves are almost linear over a wide range of vulcanisation times. Therefore a low state of vulcanisation is obtained with short curing times and a high state with longer heating.

Sulphur donor and peroxide curing systems are normally used for applications requiring good high-temperature performance and low compression set. Also, semi-EV and EV systems, play a special role in NBR vulcanisates to obtain a high heat resistance and a low compression set. A particularly good heat resistance is obtained if TMTD is used without or with little (0.25 phr) sulphur or a sulphur donor (0.5 phr) such as 4,4'-dithiodimorpholine (DTDM). Cadmium oxide, which is, however, undesirable because of its toxicity, gives vulcanisates with a high heat resistance\(^{18,102}\). The compression set characteristics are also improved by longer curing times and higher curing temperatures\(^5\). More recently, the use of N-oxydiethylene dithiocarbamyl-N'-oxydiethylene sulphenamide (OTOS), or that of a new optimised accelerator blend, coded DEOVULC EG 28 (DOG...
Deutsche Oelfabrik, Hamburg), has been proposed in place of CdO-based cure systems. These new cure systems give a particularly low compression set at high temperatures and a high heat resistance.

For various applications specific vulcanisation systems are required. A scheme representing the most commonly used sulphur and sulphurless systems, with an indication of their advantages, is given in Table 2.4.

Table 2.4 Vulcanisation systems (phr) for nitrile rubber

NBR is insensitive to over-vulcanisation. NBR compounds may be cured at 200°C and higher in absence of oxygen without harm to the material. Vulcanisates with especially good resistance to hot air are obtained when compounds contain TMTD, with or without small proportions of sulphur.
2.6.5 **INFLUENCE OF FILLERS ON VULCANISATION**

Kraus\(^{104}\) has reported that reinforcement by carbon black is non-specific with regard to the chemistry of widely different crosslinking reactions. Interactions of carbon black with polymer through the vulcanisation recipe occur and can contribute to reinforcement phenomena.

Dogadkin et al.\(^{105}\) have shown that sulphur combines with carbon black during vulcanisation and the reaction is favoured by high hydrogen content of the carbon black. Rivlin et al.\(^{106}\) investigated the chemisorption of an olefin (2-methyl-2-octene), both in absence and presence of vulcanising agents. Their work showed that chemisorption takes place simply by heating the olefin with furnace black at vulcanisation temperature. Sulphur alone increases the chemisorption but accelerator (benzothiazyl disulphide) decreases it, presumably by competitive adsorption with the olefin\(^{107}\). These changes are small compared to the direct chemisorption of the olefin. The direct chemisorption also provides a more stable linkage.

Channel blacks are known to retard the cure as compared with furnace blacks. The cause of this retardation can be traced to the greater or lesser acidity of the filler which influences the kinetics of the crosslinking reaction. Channel blacks are acidic compared to furnace blacks.

Cotten\(^{108}\) has shown that the chemistry of the carbon black surface plays an important role in the initial steps preceding the actual crosslinking reaction as well as in the crosslinking rate itself. In a rheometer trace \(\Delta L_{\text{max}}\), is the maximum change in torque during vulcanisation. The effect of the loading of carbon black on this value is shown in Fig. 2.18. When this entity is plotted against the loading \(X\), a straight line is obtained, the slope of which has been called \(\alpha_F\) by Wolf\(^{109}\). This parameter \(\alpha_F\) is used to characterise the structure of fillers, in particular of carbon blacks. In principle, \(\Delta L_{\text{max}}\) is closely related to the modulus at rather low strain.
Gessler et al.\textsuperscript{(110)} have reported that the surface chemistry of carbon blacks and trace constituents are chiefly important in affecting the cure rate for general purpose rubbers, although they may have additional effects with speciality rubbers.

The determination of the concentration of chemical crosslinks in the presence of filler-rubber bonds and rubber-rubber entanglements is a difficult task. A filler may influence the degree of crosslinking. Reinforcing fillers such as carbon blacks interact strongly with unsaturated hydrocarbon rubbers during milling or mastication in an internal mixer. The amount of ‘bound rubber’ (rubber which remains associated with the rubber when the mixture is subsequently immersed in a rubber solvent) is often used as a measure of this interaction. The adsorption of rubber on the filler surface alters the stress-strain properties and reduces the extent of swelling in a solvent. Stress-strain behaviour and equilibrium swelling measurements are the principal means of assessing crosslink density, but when a reinforcing filler is present in the rubber the effects of crosslinks cannot be readily distinguished from the effects of rubber-filler interaction.

Porter\textsuperscript{(111)} noted that carbon black increases the efficiency of crosslinking of sulphur systems. The effect of the filler is to cause a reduction in polysulphide crosslinks and increases in di- and monosulphide crosslinks.

Carbon blacks are often considered to “activate the cure” of elastomeric compounds. Kraus\textsuperscript{(112)} has reported that when the number of network chains in a carbon black stock is

\[ \Delta l_{\text{max}}(\text{gum}) \]

\[ \Delta l_{\text{max}}(50) \]

\[ \text{Time (min)} \]

\[ \text{Torque, } L \]

Fig. 2.18 Effect of carbon black loading as shown on the oscillating disc rheometer trace\textsuperscript{(22)}
determined from swelling data, the result will include the contribution of all types of linkages and will represent the number of effective network chains in an equivalent network of tetrafunctional crosslinks. He concluded that the filler "contribution" depends on the degree of cure, the vulcanisation system and the filler particle or aggregate shape. It depends only slightly on the particle size or surface area of the filler.

2.6.6 EFFECT OF VULCANISATION ON VULCANISATE PROPERTIES

Major effects of vulcanisation are shown in Fig. 2.19. The increase in modulus and decrease in permanent set are due to the extra load bearing linkages holding the network chains together giving higher retractive forces. The maximum in tear strength and tensile strength is reached due to the inextensibility of the rubber network; too many crosslinks shorten the network chains and hence reduce the molecular mobility of the chains, making them more prone to rupture\textsuperscript{(98,100)}.

![Fig. 2.19 The effects of vulcanisation\textsuperscript{(100)}](image)

The properties shown in Fig. 2.19 are also affected by the type of crosslink, the nature of the rubber, the type and amount of filler, etc. Modulus and hardness depend only on degree of crosslinking. Elongation at break and solvent swelling decrease with increasing degree of crosslinking, whereas abrasion resistance increases with increasing degree of crosslinking. These properties are partly dependent on degree of crosslinking\textsuperscript{(113)}. 57
Curing curves for NR and SBR show differences. Thus the tensile strength of NR reaches a peak and then declines (i.e. reversion occurs). The modulus behaves very similarly, except that the peak is later than that for tensile strength (Fig. 2.20 (a)). SBR does not show any reduction of tensile strength on overcure: it remains approximately constant and a 'marching cure' occurs, i.e. the modulus rises gradually (Fig. 2.20 (b)). Nitrile rubbers show curing characteristics very similar to those of SBR, except that they exhibit a very pronounced improvement in compression set on prolonged cure.

![Graph showing curing characteristics of NR and SBR](image)

Fig. 2.20 Tensile strength and modulus against time of cure: (a) NR, (b) SBR\(^{(97)}\)

2.7 **Swelling of Rubber Networks**

2.7.1 **Introduction**

The phenomenon of swelling is the increase in volume of a rubber due to the absorption of a liquid. Swelling causes deterioration of physical properties. Raw rubbers are completely soluble in certain liquids, but vulcanised rubbers are virtually insoluble. Strong bonds, such as chemical crosslinks between the rubber chains, prevent rubber molecules becoming completely surrounded by the liquid and restrict the deformation of the rubber.
The swelling of rubbers by liquids occurs as the liquid diffuses from one part of the sample to another. As this process proceeds, the dimensions of the rubber increase until the concentration of the liquid is uniform and equilibrium is achieved.

The amount of a given solvent that will diffuse into the rubber until it reaches equilibrium depends on:

1. the cohesive energy densities (square of solubility parameter) of the rubber and liquid
2. the number and type of crosslinks which determine the modulus of the network
3. the amount and type of non-rubber ingredients.

The greater the number of crosslinks per unit volume, the shorter the average length of rubber chains between crosslinks and the lower the degree of swelling.

2.7.2 Degree of Swelling and Its Relationship to the Degree of Crosslinking

The degree of swelling can be expressed as the percentage increase in volume or as the volume fraction of rubber in the swollen gel ($V_r$). The degree of swelling also depends upon the compatibility of the rubber and liquid on a molecular scale and the amount and type of filler present in the rubber. The rate at which swelling proceeds also depends upon the relative molecular size of the diffusing liquid molecule.

If rubber and liquid molecules are compatible on a molecular scale, then the liquid will readily swell the rubber. In practice it is found that in the absence of a specific interaction between dissimilar molecules, and of crystallisation, a rubber and liquid will be compatible if their values of solubility parameter are within unity of each other. The degree of swelling is generally highest with chloroform ($\delta = 9.3$ (cal.cm$^{-3}$)$^{1/2}$) for all rubbers except butyl ($\delta = 7.6$ (cal.cm$^{-3}$)$^{1/2}$). Acetone ($\delta = 10$ (cal.cm$^{-3}$)$^{1/2}$) is a poor swelling agent, except in strongly polar nitrile rubber ($\delta = 9.9$ (cal.cm$^{-3}$)$^{1/2}$).

In swelling, the mixing of polymer chains with solvent is opposed by the elastic retraction of the network. At equilibrium these two effects are balanced. The equilibrium degree of swelling can therefore be treated in terms of a combination of solution theory with the theory of rubber elasticity$^{(114)}$. The equilibrium degree of swelling attained by a rubber network in a swelling agent is related to physically manifested crosslinks ($n_{\text{phys}}$) by the Flory-Rehner equation$^{(115)}$ or by the modified equation$^{(116)}$. 

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\[-\ln (1 - V_r) - V_r - \chi V_r^2 = 2 \rho V_o \eta_{phys} V_r^{1/3}\] - Flory-Rehner equation\(^{(115)}\)

\[-\ln (1 - V_r) - V_r - \chi V_r^2 = 2 \rho V_o \eta_{phys} (V_r^{1/3} - V_r/2)\] - Modified Flory-Rehner\(^{(116)}\) equation

where \(V_r\) is the volume fraction of rubber in the swollen gel at equilibrium
\(V_o\) is the molar volume of the swelling liquid
\(\chi\) is a parameter characteristic of interaction between the rubber network and the swelling liquid referred to as the rubber-solvent interaction parameter
\(\rho\) is the density of rubber

\(\eta_{phys}\) or the physical degree of crosslinking is equal to the number of gram-moles of physically manifested crosslinks per gram of rubber in the network.

### 2.7.3 Swelling of Filled Rubbers

The effect of fillers on swelling is relatively small compared with the effect of the rubber-liquid interaction. However, Boonstra and Dannenberg\(^{(117)}\) have noted a very pronounced decrease in matrix swelling with some fillers when the filler loading is increased. With carbon black, the decrease in matrix swelling is an almost linear function of the loading, particularly with channel black and when strongly swelling liquids are used.

For a filled rubber, the network chain density \(\nu = \nu_{app}\), an apparent effective network chain density. Kraus\(^{(29)}\) has stated that

\[\nu_{app} \equiv \nu_r \times f (c, \ldots)\]

where \(f (c, \ldots)\) is a function of carbon black loading and other variables relating to the particular carbon black employed, e.g. structure and particle size. For any given carbon black at any fixed loading \(c\), the apparent network chain density becomes a "relative" measure of the true \(\nu_r\) and not of filler-rubber attachments \(\nu_f\).

Unlike in gum stocks, determination of the number of effective network chains in filler-reinforced compounds by the swelling technique is advantageous over modulus data as the results are not obscured by linkages between rubber and filler\(^{(112)}\).
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CHAPTER THREE

A REVIEW OF RUBBER BLENDS

3.1 METHODS OF BLENDING RUBBERS

Rubber-rubber blends can be prepared by a variety of methods which include: latex blending, solution blending, solution and latex blending, mechanical blending and blending of powdered rubbers. Mechanical blending is the most widely practiced procedure and the method employed in the preparation of blends throughout this study. Hence, the other general blending methods are beyond the scope of this study, however, details can be found in the literature\(^{(1,2)}\). The high shearing forces required to blend high molecular weight elastomers are such that mechanical blending is confined to internal mixers, two-roll mills and extruders.

The above blending methods may be further divided into the two general categories of "preblending" (most commonly used for the mixing of elastomer blends in an internal mixer) and "phase mixing". In the former, the compounding ingredients are generally added to the premixed elastomers in a manner similar to the mixing of a single elastomer whereas in phase mixing, the specific locations of filler and/or extender oil and curing agents are controlled. This is generally done by the preparation of separate masterbatches which are then blended mechanically.

The masterbatch formulation may
(a) be the same as the compound formulation, but without curatives
(b) contain only rubber, filler and some softeners; or
(c) contain more filler than the final compound

In type (c), it is difficult to disperse the hard filler masterbatch in the relatively soft elastomers added in the second stage. The masterbatch technique has found general acceptance in mechanical blending technology\(^{(3,4)}\). Where elastomers of different cure rates are to be blended, a masterbatch process may be desirable\(^{(5)}\).

Evans and Partridge\(^{(6)}\) found that mixing compounding ingredients directly into a blend of the elastomers (preblending) have advantages over previously prepared masterbatches. They showed that a single stage preblending procedure was a more cost-effective method for preparing blends of NBR and chlorobutyl (CIIR) rubber. However, it was found that rubber properties were not significantly different for the two blending methods. Bristow\(^{(7)}\) also found no major differences in properties of
NR/BR blends prepared according to different methods namely, preblending, addition of ingredients with no preblending and the blending of masterbatches containing proportionate amounts of the compounding ingredients. However, no studies were carried out with uneven proportions of compounding ingredients added to the separate masterbatches. In contrast, Hess and Chirico\(^8\) reported that for best results, the polymer components of a blend should be mixed for a short time (\(\equiv 0.5\) min.) prior to addition of fillers and other compounding ingredients.

In addition to the general blending methods discussed above, a number of special mixing techniques have been developed to control more exactly the different aspects of the overall homogeneity, phase morphology, filler distribution and interfacial interaction of the different components of elastomer blends. This includes the use of a Cavity Transfer Mixer (CTM)\(^9\), Controlled Ingredient Distribution Mixing (CIDM) technique\(^10\), constant temperature mixing\(^11\), dynamic vulcanisation\(^12\) and compatibilisation\(^13\).

### 3.2 Major Factors Affecting Properties of Polymer Blends

#### 3.2.1 Introduction

The properties of a polymer blend depend on several factors which are themselves interdependent\(^14\).

These include

1. choice of polymers;
2. composition;
3. compatibility of the polymers;
4. phase morphology;
5. method of blend preparation

In addition to the above factors, distribution of compounding ingredients especially reinforcing fillers, also has a great effect on the properties of elastomer blends. Factors (1) and (2) are obvious.

#### 3.2.2 Effect of Composition on Vulcanisate Properties

The properties of a polymer blend do not depend in a simple manner on its composition. Baker, Hallam and Smith\(^15\) studied the trends in vulcanizate properties of filled, sulphur cured, NR/NBR (41\% acrylonitrile) blends differing in composition, over a wide hardness range by altering the carbon black loading. A steady crosslink density was achieved for the unfilled blends by varying the sulphur/accelerator concentrations proportionately to the single elastomers present in the blends (Fig. 3.1).
At high loading the blends showed a higher modulus than either NR or NBR and a marked peak in modulus was shown by the 40/60 NR/NBR blend (Fig. 3.1). The relationship of hardness to SRF (N770) carbon black loading for NR/NBR blends and single elastomers was similar to that of modulus. The maximum tensile strength decreases in the order 80/20, 20/80, 60/40, 40/60 NR/NBR and most of these blends are inferior to NR and NBR vulcanisates themselves as shown in Fig. 3.2. Poor tensile strength values were recorded at low hardness. This indicated some incompatibility between the two rubbers and has been attributed to reduced shear stresses during mixing at low filler loadings. The tear strength of the 80/20 NR/NBR blend was superior to all other blends and to the two single rubbers (Fig. 3.3). Compression set improved as the NR content was reduced. Similarly, compression set improved with increase in hardness. Hence, very low set was obtained with 20/80 and 40/60 NR/NBR blends as shown in Fig. 3.4. Swelling measurements showed that the 20/80 NR/NBR blend has the least swelling in ASTM oil No.3 at room temperature followed by the 40/60 NR/NBR blend (Fig. 3.5). Swelling decreased at high hardness.

Fig. 3.1 Variation of modulus with carbon black loading for NR/NBR blends.
Fig. 3.2 Variation of tensile strength with hardness for NR/NBR blends\(^{(15)}\)

Fig. 3.3 Variation of tear strength with hardness for NR/NBR blends\(^{(15)}\)
Fig. 3.4 Variation of compression set with hardness for NR/NBR blends \(^{(15)}\)

Fig. 3.5 Volume swelling in ASTM oil No.3 for NR/NBR blends at room temperature \(^{(15)}\)
Baker et al. concluded that replacement of NBR by a 20/80 NR/NBR blend should be acceptable in virtually all applications except where the maximum degree of oil resistance is required. Under some conditions where the NBR vulcanisate shows shrinkage, the 20/80 NR/NBR blend has a slight swell which is of advantage in sealing applications. The results also suggest that replacement of NBR by a 40/60 NR/NBR blend should be acceptable with regard to hardness and modulus. However these researchers have not assigned any reasons for these variations in vulcanizate properties with composition. The data of a SRF carbon black loaded (0-75 phr) polychloroprene (CR) compound included in all figures are not relevant to this review.

On the other hand Ahmad and Wheelans\textsuperscript{(16)} studied the variation in vulcanizate properties of unfilled NR/NBR (41% Acrylonitrile) blends with composition. Dicumyl peroxide (DCP) was chosen as the curative. In the absence of fillers tensile properties were very poor. A sharp fall in tensile strength and elongation at break was observed when 10-20% NBR was added to NR (Fig. 3.6). When the ratio changed from 70/30 to 50/50 NR/NBR both of these properties increased and fell again at higher ratios of NBR. Ahmad and Wheelans suggested that this may be due to either the blend morphology or the result of cutting through or around large particles of poorly dispersed rubber in the tensile test piece. The trend in the variation of tensile strength with composition is not similar to that of Baker et al. However modulus, hardness and volume swelling results support the work of Baker et al. Modulus and hardness rose as the percentage of NBR increased (Figures 3.6 and 3.7), but volume swelling was reduced (Fig. 3.8). The variation in tensile properties was attributed to the changes in morphology as the blend ratio was altered. The mosaic pattern created by the 70/30 and 50/50 NR/NBR blends due to the existence of co-continuous phases, was suggested as the main cause for the higher tensile strength and elongation at break of these blends in comparison to the other NR/NBR blends. The latter showed both discrete and continuous phases which accounts for the lower tensile strength.
Fig. 3.6 Dependence of tensile properties on NR/NBR (Breon 1041) ratio\textsuperscript{(16)}

Fig. 3.7 Dependence of hardness on NR/NBR (Breon 1041) ratio\textsuperscript{(16)}
3.2.3 Compatibility of Elastomer Blends

A mixture of two components is said to be compatible on a molecular scale, only if mutual solution takes place during mixing and the resultant blend constitutes a thermodynamically stable single-phase system at room temperature. In the literature the term miscibility is often used interchangeably with the word compatibility to indicate single phase behaviour. An immiscible blend exhibits a two phase morphology. The majority of elastomer blends consists of two phase systems i.e. they are not truly compatible on a molecular scale, but on a slightly larger (macroscopic) scale, and especially in cured compounds containing a high loading of carbon black, may function effectively as one phase. In a two phase system the discrete phase is dispersed in the continuous phase or the two phases exist as co-continuous. The major blend

Fig. 3.8 Dependence of volume swelling in ASTM No.1 and No.3 oils on NR/NBR (Breon 1041) ratio

\[ \text{Volume swelling, } \% \]

- ASTM No.3 oil
- ASTM No.1 oil

NR Breon 1041 0 20 40 60 80 100

Volume swelling, %

180
160
140
120
100
80
60
40
20
0

0 20 40 60 80 100

3.8 Dependence of volume swelling in ASTM No.1 and No.3 oils on NR/NBR (Breon 1041) ratio\(^{(16)}\)
component will generally tend to form the continuous phase, while the minor component the discrete phase\textsuperscript{(17,18,19,20)}.

Attention must be focused on aspects of polymer miscibility as it is one of the important factors affecting the physical properties of polymer blends. Roland and Bohm\textsuperscript{(21)} have related the adhesion of plied rubbers to their miscibility. Peel adhesion was found to increase with time as a result of interdiffusion of polymer between the plies. Miscibility was reported for blends of NR with 1,2-BR. However miscibility is not a requirement for most rubber applications. Homogeneity at a fairly fine level is necessary for optimum performance, but some degree of microheterogeneity is required to preserve the individual properties of the respective polymer components. Almost all physically blended bulk mixes of elastomer blends are microheterogeneous to varying degrees. Microheterogeneity may diminish when carbon black is added to the preblended elastomers, but may also increase when carbon black is mixed selectively into one of the polymer components.

A limited number of compatible blends are known, such as PPO i.e. poly(2,6-dimethylphenylene oxide)/polystyrene\textsuperscript{(22)} and ENR (epoxidized natural rubber)-50/PVC\textsuperscript{(23)}. In the above blends compatibility is due to specific interactions between the two components of the blend.

In general compatibility depends on the type of polymers, relative viscosities, preparation and mixing conditions.

Incompatibility between dissimilar rubbers may occur due to:

1) the difference in viscosities; which prevents or greatly delays the formation of intimate blends\textsuperscript{(24,25)}

2) thermodynamic incompatibility, which prevents mixing on the molecular scale\textsuperscript{(26,27)}

3) the difference in cure rate\textsuperscript{(27)}

   In an extreme case of cure rate incompatibility, the faster curing component polymer consumes a greater portion of the curative which is available in a composition than the other polymer.

Compatibility of a blend may be characterised by the solubility parameters of the individual polymers, thermodynamics, glass transition temperature of the blend and microscopy. These techniques will be dealt with in detail in the forthcoming sub sections.
3.2.3.1 **SOLUBILITY PARAMETER APPROACH**

The miscibility of the constituents of a polymer blend can be judged by the similarity of their solubility parameters ($\delta$) via the Flory-Huggins segmental interaction parameter $\chi$. The smaller the difference in $\delta$ between two polymers, the greater the segmental interaction, and hence, the miscibility.

The polymer/polymer interaction parameter ($\chi_{AB}$) between two non-polar or slightly polar (weakly interacting) polymers A and B is related to the Hildebrand solubility parameters\(^{(28)}\), $\delta_A$ and $\delta_B$ according to the following equation,

$$\chi_{AB} = \left( \frac{V_r}{RT} \right) (\delta_A - \delta_B)^2$$

where $V_r$ - reference volume taken as close to the molar volume of the smaller polymer repeat unit, often taken as 100 cm$^3$

$R$ - universal gas constant

$T$ - absolute temperature

The individual solubility parameter of a polymer is estimated from either the Group Contribution Method\(^{(29,30)}\) as given in the experimental section or by experiment. Experimentally, the solubility parameter of a polymer is estimated by immersing identical crosslinked samples in a range of solvents until equilibrium swelling is reached. Solubility parameter of the solvent giving the greatest swelling is taken as the solubility parameter of the polymer\(^{(31)}\).

Complete miscibility occurs only if $\chi_{AB}$ is less than a critical value ($\chi_{AB}\text{crit}$) given by \(^{(14)}\),

$$\chi_{AB}\text{crit} = 0.5 \left( \left( \frac{1}{m_A} \right)^{0.5} + \left( \frac{1}{m_B} \right)^{0.5} \right)^2$$

where $m_A$ and $m_B$ are the degree of polymerisation of A and B respectively.

Bohn\(^{(32)}\) and Corish\(^{(33)}\) compiled lists of compatible and incompatible polymer pairs, detailing the solubility parameter differences between the components. The solubility parameter difference between compatible polymers is always small (less than 0.5 (cal.cm$^{-3}$)$^{1/2}$ $\approx$ 10$^3$ (Jm$^{-3}$)$^{1/2}$). However Bohn concluded that solubility parameters do not give a precise measure of polymer interaction as there are numerous examples of incompatible blends with similar small values. According to the list compiled by Corish, the solubility parameters of NR, low nitrile NBR (20% ACN) and high nitrile...
NBR (40% ACN) are 8.25, 8.93 and 9.92 \( \text{cal.cm}^{-3} \text{mole}^{-1/2} \) respectively. The solubility parameter of NBR (45% ACN) is 10.5 \( \text{cal.cm}^{-3} \text{mole}^{-1/2} \). Consequently a blend of NR and high nitrile NBR appears to be more incompatible than a blend of NR and low nitrile NBR.

### 3.2.3.2 THERMODYNAMIC APPROACH

Criteria for a miscible rubber blend can be obtained from the Gibbs free energy of mixing \( \Delta G_{\text{mix}} \) relationship, which is defined as:

\[
\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}
\]

The basic criterion for miscibility is negative \( \Delta G_{\text{mix}} (\Delta G_{\text{mix}} < 0) \). However this is not a sufficient criterion. The state of mixing is determined by the shape of the free energy of mixing curve as a function of composition\(^{35}\). Mixtures with negative \( \Delta G_{\text{mix}} \) can be unstable relative to an intermediate composition and will lead to phase separation (partial miscibility). \( \Delta H_{\text{mix}} \) and \( \Delta S_{\text{mix}} \) are the enthalpy (or heat of mixing) and entropy of mixing respectively. The smaller the \( \Delta H_{\text{mix}} \) or the larger the \( \Delta S_{\text{mix}} \) the greater is the possibility of molecular miscibility. \( \Delta S_{\text{mix}} \) decreases as the degree of polymerisation increases. Hence in high molecular weight polymers, \( \Delta S_{\text{mix}} \) becomes negligible and the \( \Delta H_{\text{mix}} \) term determines miscibility. Therefore miscibility in most pairs of polymers results from a negative \( \Delta H_{\text{mix}} \). This has been attributed\(^{36,37}\) to the presence of specific interactions between the two components such as hydrogen bonding.

The Flory-Huggins theory of polymer solutions\(^{38,39,40}\) has been successfully applied to polymer mixtures and the Flory-Huggins equation has been used in predicting the polymer blend miscibility\(^{41,42}\).

The Flory-Huggins equation yields the Gibbs free energy of mixing \( \Delta G_{\text{mix}} \).

\[
\Delta G_{\text{mix}} = \left( RT \frac{V}{V_r} \right) \left( \phi_A X_A \ln \phi_A + \phi_B X_B \ln \phi_B + \chi_{AB} \phi_A \phi_B \right)
\]

where \( V \) - total volume of two weakly interacting polymers
\( \phi_A \) and \( \phi_B \) - volume fractions of polymers A and B respectively
\( X_A \) and \( X_B \) - degree of polymerisation of polymers A and B in terms of \( V_r \)
\( V_r, R \) and \( T \) are defined as mentioned in Section 3.2.3.1.

\( \chi_{AB} \) is the interaction parameter between the two polymers A and B as given in Section 3.2.3.1. With two polar polymers, a negative \( \chi_{AB} \) due to specific interactions
between the two polymers is not excluded. A near zero $\chi_{AB}$ (or $\Delta H_{mix}$) results if the solubility parameters of the two polymers are nearly equal.

3.2.3.3 Glass Transition Temperature

The most common method for assessing the degree of polymer blend compatibility is via the determination of glass-transition temperatures ($T_g$), but it does not provide any specific information on blend morphology. Glass transition temperatures of NR, NBR (40% ACN) and NBR (50% ACN) are -70, -20 and -15 respectively\(^{43}\).

As temperature is reduced the glass transition occurs when the segmental motions in the amorphous regions of a polymer cease. Below $T_g$, the motion in the polymer main chain is restricted to vibrational motions. $T_g$ is accompanied by changes in properties such as specific volume, heat capacity, modulus, etc.\(^{44}\).

Since most polymer blends are incompatible, they have two $T_g$ values, one characteristic of each separate component. As the polymers become compatible, the component $T_g$'s broaden until at complete miscibility they merge to a single intermediate $T_g$. However the appearance of a single $T_g$ does not necessarily imply that the blend components are compatible because if the two components have equal or close $T_g$'s, then the resolution of the technique employed may not be sufficient. In semi-compatible polymer blends, the transitions are shifted towards each other. A broadening of the width of the glass transition over a wide temperature range also suggests a semi-compatible blend and indicates microheterogeneity of a polymer blend\(^{45}\).

3.2.3.4 Characterisation of Compatibility Using Microscopy

Although glass transition studies have shown compatibility in some binary blends, two phases have been observed microscopically. Hence microscopy is the most widely used technique today, to assess the compatibility of polymer blends. At present two main microscopy techniques i.e. phase contrast microscopy and electron microscopy, are used. Transmitted light microscopy is more commonly used with polymer blends than reflected light microscopy and it is the microscopy technique used throughout this study.

Usually refractive index differences in polymer systems are small and the visibility of the features in a normal light microscope is difficult. This difficulty can be overcome by
using phase contrast light microscopy. In phase contrast microscopy the sample is illuminated with light and the differences in refractive index determine the ability to observe the heterogeneity of a polymer blend\(^{(2,24,46)}\). The microscope optics produce a phase shift between the diffracted and transmitted light, which provides phase contrast with only small differences in refractive index. The higher refractive index elastomer appears darker. Phase contrast light microscopy requires very thin specimens (1-4 \(\mu\)m) which can be prepared by cryo-sectioning. Limitations of the phase contrast method are low resolution and poor contrast with certain polymer combinations, distortion of the polymer phases from swelling and the limited applicability to carbon black filled systems. Carbon black raises the refractive index difference of polymer mixtures and eliminates the phase contrast mechanism\(^{(2)}\). Furthermore, this technique is only qualitative.

On the other hand in electron microscopy thickness differences determine the ability to observe heterogeneity. Hence phase differentiation is caused by dissimilar swelling and extension. Marsh et al.\(^{(46)}\) found that no phase difference could be observed using a non-swelling liquid and phase differences appear only in stretched sections. The elastomer having the higher degree of swelling corresponds to the lighter phase\(^{(46)}\), since it will stretch more easily than the other under equal stress reducing its thickness.

Since the presence of carbon black reduces the swelling of a vulcanisate, electron micrographs of sections of filled elastomer blends are not as simply interpreted as those of pure elastomers\(^{(47)}\). A filled elastomer will stretch much less under a given load than the unfilled elastomer and these differences are emphasised after swelling. e.g. in unfilled elastomer blends of IR and BR, IR is always the lighter phase and BR the darker, since swollen unfilled IR stretches more than swollen unfilled BR. The presence of carbon black in the IR will reverse this phenomenon. Transmission electron microscopy (TEM) is an ideal method because of its high resolution and applicability to both filled and unfilled elastomers. Thin microtome sectioning (0.1 \(\mu\)m or less) is a requirement for TEM. However, for most elastomer blends there is no contrast between polymer phases in a TEM. Osmium tetroxide (OsO\(_4\)) staining is a commonly used method for developing contrast in polymer blends\(^{(48)}\) containing elastomers of widely different unsaturation levels. However, achieving contrast for TEM analysis of blends of high unsaturation rubbers is a problem. Plasma etching technique\(^{(49)}\) is another method which can be used to achieve contrast between the phases in a highly filled blend.

Phase contrast microscopic method was first applied by Walters and Keyte\(^{(17)}\) to the analysis of binary blends. They examined a variety of binary blends using phase contrast and electron microscopy. In the case of SBR/BR blends heterogeneity was
observed and the domain size ranged from 0.2 µm to several microns. The blends were also incompatible when blended in solution. In contrary, the work of Marsh et al.\textsuperscript{(46)} using phase and electron microscopy showed that SBR/BR blends are completely compatible after two minutes of mixing. Kiyek and Schoon\textsuperscript{(50)} also examined a range of rubber blends, excluding SBR/BR but never found them to be completely compatible. The work of Callan, Topcik and Ford\textsuperscript{(18)} on ethylene-propylene-diene terpolymer (EPDM)/butyl rubber (IIR) blends using phase contrast microscopy showed that there is a tendency for low molecular weight EPDM to be compatible with IIR.

3.2.4 BLEND MORPHOLOGY

3.2.4.1 INTRODUCTION

For incompatible rubber blends the basic factors that govern blend morphology are:

1) Composition of the components
2) Relative mixing viscosities of the components
3) Mixing conditions or the method employed to produce the blend

These are sometimes interrelated. The major blend component in a binary blend will tend to form the continuous phase, while the other the discrete phase. This behaviour has been supported by many workers\textsuperscript{(17,18,19,20)}. The general aim is to achieve as fine a dispersion of the minor component as possible, which generally means the use of compounding equipment generating high shear stresses and long mixing times. The degree of shear stress determines the size of the discrete phase. The basic parameters used to characterise blend morphology are phase continuity and width and shape of the domains.

3.2.4.2 EFFECT OF COMPOSITION ON MORPHOLOGY

As previously mentioned (Section 3.2.2), composition (or blend ratio) significantly influences the physical properties, mainly the tensile properties, via changes in the morphology of a blend. Although the work of Ahmad and Wheelans\textsuperscript{(16)} on unfilled blends of NR/NBR (41% ACN) showed the existence of co-continuous phases in 50/50 NR/NBR blends, in contrary, Scott et al.\textsuperscript{(51)} reported that the NBR is the
dispersed phase in 50/50 NR/NBR blends (unfilled) and exhibits very large domains. All the other unfilled 50/50 blends of NR with cis-BR, SBR-1500, CR, Chlorobutyl and EPDM were co-continuous and the domains were very much smaller than the NR/NBR blends. The relatively large domains exhibited by the unfilled NR/NBR as well as the unfilled SBR/NBR blends were attributed to the very high viscosity (or molecular weight) of NBR\(^{(20)}\). Also these researchers reported a significant change in the morphology of the unfilled NR/NBR blends with composition. Quantimet phase contrast micrographs of 25/75, 50/50 and 75/25 NR/NBR blends are shown in Fig. 3.9.

![Micrographs of 25/75, 50/50, and 75/25 NR/NBR blends](image)

Fig. 3.9 Pure gum blends of NBR with NR as imaged by the quantimet\(^{(20)}\)

The NR phase appears to be the lighter phase in this blend system. NR is the discrete phase in the 25/75 NR/NBR blend, whereas NBR is the discrete phase in the 75/25 NR/NBR blend. This means a phase reversal takes place when the composition of the blend is changed from 25/75 to 75/25 NR/NBR.

### 3.2.4.3 Effect of Relative Mixing Viscosity of the Components and Mixing Conditions on Morphology

In incompatible blends such as NR/NBR, it is primarily the rheological factors which control the morphology. Hence, knowledge of the rheology of the component polymers is useful. The early work of Walters and Keyte\(^{(17)}\) on NR/SBR and NR/BR blends showed that, in the case of mechanical blending, the dimensions of the domains are influenced by the relative viscosities of the component elastomers. They concluded that smaller domains are obtained at a 50:50 blend ratio when the Mooney viscosities of the components are similar. The above phenomenon was also supported by Avgeropoulos et al.\(^{(25)}\) and they concluded that, at equal component ratio, the continuous phase is invariably found in rubber of lower viscosity. Their work was based on EPDM/BR blends and the relative viscosities were varied by changing the shear rate and/or mixing temperature. It was also possible to shift the disperse phase from one polymer to another even though that polymer was the minor component. In

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this instance, the low viscosity phase encapsulates the high viscosity component and then becomes continuous.

Avgeropoulos et al. explained the dependence of blend morphology on the relative viscosities of the components in terms of a tearing or fracture mechanism. They proposed that for 50/50 blends of unequal viscosity, this tearing or fracture would occur first in the high-viscosity material, which would thus become the discrete phase. For equal mixing viscosities and hence equal mixing torques, tearing would be equally likely in both phases, and a co-continuous system would be obtained.

The shape of the domains is more nearly spherical when the high viscosity component is the disperse phase. A softer disperse phase gives elongated domains\(^{(25)}\). Kiyek and Scoon\(^{(50)}\) also found that in polymer blends the harder component is embedded in the softer in the form of spheres. Supportive results have been obtained by Hess and Chirico\(^{(8)}\), when separate masterbatches were blended. In contrast, Tokita\(^{(52)}\) found that the domains of EPM in a NR/EPM blend are clearly spherical in shape when the Mooney viscosity of the EPM is lowest. The highest-Mooney EPM domains were irregular in shape and showed a wide range of sizes at short mixing times, but with increasing mixing time, the shape of the particles became spherical.

Tokita developed a theoretical expression for blending based on the assumption that an equilibrium domain size of dispersed phase will be reached when the break down rate and the coalescence rate are balanced.

\[
R^* = \dot{\gamma} \left( \frac{12}{\pi} \right) \rho \sigma \phi_D / \left( \eta \dot{\gamma} - \left( \frac{4}{\pi} \right) \rho \phi_D E_{DK} \right)
\]

where

- \(R^*\) - equilibrium domain size
- \(\rho\) - probability that a collision will result in a coalescence
- \(E_{DK}\) - macroscopic breaking energy
- \(\dot{\gamma}\) - shear rate
- \(\eta\) - apparent viscosity of the matrix phase
- \(\sigma\) - interfacial tension
- \(\phi_D\) - volume fraction of the dispersed phase

In order for breakdown to occur, the apparent shear stress, \(\eta \dot{\gamma}\) must exceed the macroscopic breaking energy density of the dispersed phase. The above equation then can be expressed as

\[
R^* \approx \left( 12 \rho \sigma \phi_D / (\pi \eta \dot{\gamma}) \right) \left( 1 + 4 \rho \phi_D E_{DK} / (\pi \eta \dot{\gamma}) \right)
\]
The above equations indicate that the equilibrium domain size becomes smaller when,

(i) the apparent stress field (which is mainly due to the matrix viscosity) is increased

(ii) the macroscopic breaking energy becomes smaller under the same stress field

(iii) the interfacial tension becomes smaller

and (iv) the concentration of dispersed phase decreases

An unfilled NR/EPM blend was used to verify this theory. The changes in the domain size of EPM were studied with regard to the above four factors. Mooney viscosity of the EPM samples was taken as a measure of $E_{OK}$, since an appropriate method to measure $E_{OK}$ at high rotor speed (60 rpm) was not known. $E_{OK}$ was postulated as proportional to Mooney viscosity of the EPM samples since all of them had the same microstructure and narrow molecular weight distribution.

Quantitatively, the experimental results were found to be consistent with the theoretical prediction. Experimental results also indicated that viscosity matching between matrix and dispersed phases is desirable to obtain small dispersed domains in a short time, or in other words, to increase the blending efficiency. Tokita concluded that on changing from an internal mixer to a two-roll mill, temperature becomes one of the most influential factors that control the domain size. Higher mixing temperature appeared to reduce domain size by diminishing the interfacial tension. Since the temperature normally goes up during mixing, high shear stress blending of polymers with similar viscosities will give the most homogeneous mixtures.

Ahmad and Wheelans\textsuperscript{[16]} studied the effect of mixing time and mixer rotor speed on the morphology of unfilled 80/20 NR/NBR (41\% ACN) blends. Only a small reduction in domain size was reported with increasing the Banbury mixing time from 3 to 6 minutes at 77 rpm and there was no further reduction in domain size after 10 or 20 minutes of mixing. This is possibly associated with the viscosity of NBR, which is the dispersed phase as the work of Tokita\textsuperscript{[52]} has shown that the rate of break down is slower in a higher-Mooney dispersed phase than in a lower-Mooney one. No improvement in vulcanisate properties was reported with increased mixing time, as a consequence of there being no change in blend morphology. Increases in Banbury rotor speed to 116, 155 and 230 rev./min. caused a significant increase in work done and dump temperatures at constant Banbury mixing time, but there was no reduction in the domain size of the NBR. The highest rotor speed caused the worst tensile properties due to the larger domain size, while modulus remained unchanged. The batches discharged were 'crumbly' at all mixing speeds.
In addition to the previously mentioned factors, addition of homogenising agents, variations in polarity and the amount and type of filler also affect the domain size.

There was evidence from the work of Ahmad and Wheelans\textsuperscript{(16)} that reduction of interfacial tension by addition of homogenising resins such as Strucktol 60 NS and Strucktol TH10 (Schill and Seilacher, Hamburg), 5 phr to 80/20 NR/NBR (41% ACN) blends (unfilled) helped to reduce domain size giving better adhesion between NR and NBR. There was no further advantage in using 10 phr Strucktol 60 NS instead of 5 phr. Addition of SBR to NR and NBR to the ratio 35/35/30 NR/NBR/SBR also helped to reduce the domain size of NBR to 10-15 μm. Addition of Strucktol 60 NS gave no further reduction of domain size in this ternary blend. Strucktol 60 NS weakens the adhesion between NBR and other rubbers (NR and SBR).

Further studies on unfilled NR/NBR (41% ACN) showed that the acrylonitrile content of NBR also has an influence on the domain size. These researchers concluded that 80/20 NR/NBR blends have a coarse domain structure if the ACN content of the NBR is greater than 34%, while if the ACN% is 28% or less, 80/20 blends have a fine domain size with domains too small to be resolved by the optical microscope. Holes in xylene-swollen microtomed sections of NR/NBR blends suggested poor adhesion between NBR domains and the continuous NR phase. Low peel strength values also confirmed poor bonding between NR and NBR. Moreover, they concluded that if the swelling resistance is not too critical for an application, blends of NR/NBR would have better mechanical properties based on NBR's with an ACN content of 28% or less.

Gessler et al.\textsuperscript{(53)} reported that the addition of fillers reduces the size of the separate polymer domains. In 50/50 NR/BR blends where the loading of ISAF carbon black was varied from 10-40 phr, the darker BR phase becomes finer and more continuous with increased carbon black. The improvement in blend uniformity is attributable to the carbon black, which raises viscosity and hence increases stress during the mixing cycle.

3.2.4.4 EFFECT OF MORPHOLOGY ON PROPERTIES

Phase morphology does not appear to have a major effect on modulus\textsuperscript{(54,55)}. In EPDM/BR blends, at comparable polymer concentrations modulus did not change significantly when the BR was changed from the continuous to disperse phase. Supportive results have been obtained by Walters and Keyte\textsuperscript{(17)}, who studied the effect of domain size on gum stock physical properties of NR/SBR and NR/BR blends. They reported that modulus as well as hardness, tear strength and tensile strength are not greatly affected by the size of the domains. The work of Ahmad and Wheelans\textsuperscript{(16)} on unfilled NR/NBR blends has also shown that modulus does not change with domain size. However the blend with the largest domain size showed the worst tensile...
properties. The work of Hamed\textsuperscript{(56)} on unfilled 75/25 EPDM/BR blends has shown that the energy at break ($E_b$) increases significantly when the disperse phase (BR) changes from large and fibrous to small and spherical. The polymer of highest strength as the continuous phase is a criterion for maximising tear resistance\textsuperscript{(8)}.

3.3 **CARBON BLACK DISTRIBUTION AND TRANSFER**

3.3.1 **INTRODUCTION**

The physical properties of vulcanised rubber blend compounds are also greatly influenced by the distribution of compounding ingredients (especially reinforcing fillers like carbon black) in addition to the heterogeneity of the blend. In general, the properties are more significantly affected by filler distribution than they are by morphology\textsuperscript{(2)}. Therefore, knowledge about the distribution of carbon black between the phases in a blend will be of use to explain the variations in physical properties. Transmission electron microscopy (TEM) in conjunction with cryosectioning and staining techniques, has proved to be the best means of resolving filler distribution.

The work of many researchers indicates that carbon black distribution in elastomer blends is determined by a combination of complex factors including the ability of an elastomer to wet and form strong attachments to the filler surface, relative polymer viscosities, and mixing technique, the effect of which is discussed herein.

3.3.2 **EFFECT OF TYPE OF POLYMER**

Displacement of carbon black from one elastomer to another was noted by Callan, Topcik and Ford\textsuperscript{(18)} for EPDM/butyl rubber (IIR) and by Craig and Fowler\textsuperscript{(57)} for NR/NBR blends. The work of Callan and co-workers showed that EPDM has a higher affinity for carbon black than IIR, since carbon black transferred from IIR to EPDM during blending. This was attributed to the chain entanglement of the long, supple molecules of EPDM, which readily occlude or "entrap" large volumes of fillers. The studies of Craig and Fowler involved the addition by milling of NBR to a NR and carbon black masterbatch. The carbon black was assumed to be displaced from NR by the more polar NBR, due to the higher affinity for carbon black of NBR than NR. In both the works mentioned above, studies on stocks with higher carbon black loading ($> 20$ phr) were hampered because of poor inter-zone contrast and inability to cut
suitably thin specimens. Similar variations in the relative affinity of polymers for carbon black were reported by Hess, Marsh and Eckert \(^{(58)}\).

The work of Callan, Hess and Scott \(^{(20)}\) also showed that NBR has a appreciably higher affinity for carbon black than NR. Further studies on 50/50 blends of several other commercially important rubbers indicated that carbon black transfers from butyl to BR, NR and SBR. Also transfer occurred from NR/carbon black (N330) masterbatch mixed in the two-roll mill (with low heat history) to BR, but carbon black did not transfer from NR/carbon black (N330) masterbatch mixed in the internal mixer (with high heat history) to BR or SBR. They suggested that transfer of carbon black from one phase to another can occur when the adsorptive capacity of the carbon black has not been fully utilised and this situation can exist if the masterbatch has minimum heat or mechanical history, or involves low molecular weight or low unsaturation elastomers such as butyl rubber.

On the contrary, carbon black distribution studies done by Marsh and co-workers \(^{(59)}\) on mill mixed blends of NR with SBR and BR using electron microscopy did not indicate large scale phase transfer of carbon black during mixing. The lack of carbon black transfer from the NR to the BR phase was attributed to the low modulus level of such blends. Polychloroprene exhibited a strong affinity for carbon black in blends with NR. In this system, with the carbon black predispersed in the NR, the carbon black particles were observed at the polychloroprene interface, but had not entered that phase.

3.3.3 Effect of Relative Mixing Viscosities of the Components

There was evidence from the early work of Walters and Keyte \(^{(17)}\) on NR/SBR and NR/BR blends that carbon black is not always evenly distributed between the components of a blend, and this may affect physical properties. They predicted that carbon black mixes initially into the least viscous elastomer, since it is here that most of the shear strain is taking place. Thus the viscosity of this elastomer would be raised, and when it approaches that of the more viscous elastomer, the carbon black would be taken up by both elastomers. This would result in the softer elastomer being more highly loaded than the stiffer elastomer.

Supportive evidence for the viscosity dependence of carbon black affinity has been obtained from the work of Hess and co-workers \(^{(19)}\). They reported that carbon black locates preferentially in the polybutadiene (BR) in a 50/50 preblend with NR and this affinity depends on the viscosity and can be varied. However they suggested that polarity factors can supersede viscosity considerations and determine filler locations in the blend. Gessler et al. \(^{(53)}\) also found that the lower initial viscosity of the BR,
compared to NR in the NR/BR blends studied would tend to favour the acceptance of carbon black. Experiments in which the BR viscosity was increased significantly produced a reversal of this distribution pattern, i.e. a higher percentage of the carbon black was then located in the NR phase. It is to be noted that the lower viscosity NR, which results due to the breakdown of NR during mixing (mastication), has more of an affinity for carbon black than does the original NR of higher viscosity\(^{49}\). The work of Hess and Chirico\(^{8}\) also indicated preferential BR location in NR/BR preblends. It was not as great as that observed for SBR in NR/SBR preblends, or as that found in previous studies of NR/BR blends\(^{19}\) due to lower viscosity of the NR employed in this work.

3.3.4 EFFECT OF TYPE OF CARBON BLACK

The affinity of a rubber for the carbon black varies depending on polymer used, mixing technique and especially the carbon black type. Inert (partially graphitized) carbon blacks tend to distribute more evenly between the blend components regardless of which polymer contained them initially\(^{60}\). Cotton and Murphy\(^{60}\) showed that N650 carbon black (partially graphitized) distributed in both elastomers NR and EPDM in a blend of NR/EPDM with some preference for the EPDM whereas, the untreated N650 sample located almost entirely in the NR phase when added to the preblend (premixed elastomers). With the untreated (standard) carbon black, the unsaturation of the NR is the factor governing carbon black distribution. Differences in polymer molecular weight probably play a much greater role with the graphitized carbon black. However no significant difference has been observed in the NR/SBR distribution of a partially graphitized carbon black relative to its untreated (standard) sample.

In the case of phase mixed EPDM/NR blends, the untreated carbon black did not transfer significantly from either masterbatch into the other rubber (some carbon black migrated from EPDM to NR), whereas the partially graphitized N650 sample transferred between the phases, resulting in a more uniform carbon black distribution. However when butyl rubber-N650 masterbatches were blended with NR, the untreated as well as the partially graphitized carbon black transferred into the NR phase. In the case of the latter, some carbon black particles were seen remaining in the IIR domains or at the phase boundaries.

Furthermore, Cotton and Murphy\(^{60}\) showed that carbon black is located preferentially in the SBR phase in 50/50 NR/SBR blends and this preference increased in the direction of higher carbon black surface area (or lower particle size). The lesser amounts of carbon black in the NR phase of NR/SBR blends were attributed by these
authors to a lower degree of carbon black-polymer interaction in comparison to SBR and related this to steric hindrances caused by the NR microstructure, i.e. the inability for two adjacent double bonds to be in contact with the carbon black surface simultaneously.

3.3.5 EFFECT OF DIFFERENT MIXING TECHNIQUES

Massie et al.\textsuperscript{49} evaluated the distribution of an N550 carbon black in blends of 50/50 NR/BR prepared in a Haake System 40 Brabender. They prepared these blends according to three different mixing schemes and concluded that N550 has no preference for either phase. When mixed simultaneously with both polymers, the carbon black distributed itself evenly between the phases. Analysis of phase-mixed (rubber-carbon black masterbatch technique) samples showed that majority of carbon black remains in the polymer phase to which it is originally added. No significant carbon black transfer occurred even after ten minutes of mixing. An even distribution of carbon black between the phases has also been observed in SBR/NBR blends prepared according to the preblending technique (addition of carbon black to premixed elastomers)\textsuperscript{59}. The above studies indicate that distribution of carbon black in NR/BR blends differs according to the mixing technique employed.

3.3.6 SUMMARY OF MAJOR FINDINGS

Summary of findings on carbon black distribution and transfer reported by many researchers is as follows:

(1) Affinity of carbon black for elastomers decreases in the order

\begin{itemize}
  \item BR, SBR, CR, NBR, NR, EPDM, IIR\textsuperscript{20}
\end{itemize}

(2) Transfer of carbon black from one rubber-carbon black masterbatch to the other rubber phase can occur if the rubber-carbon black masterbatch has a minimum thermal or mechanical history (e.g. solution masterbatch) or involves low molecular weight or low unsaturation elastomers (e.g. butyl) in which bound rubber formation is minimised\textsuperscript{20,61,62}. The bulk of the carbon black is always found in the more highly unsaturated elastomer.

(3) When carbon black is added to the pre-blended elastomers, it does not redistribute if both elastomers have equally high interaction with the carbon black and a high degree of compatibility with each other\textsuperscript{62}.
(4) Surface polarity of the carbon black influences its distribution. Inorganic fillers like silica tend to accumulate in the NR phase. For example in cis BR/NR blends, silica tends to accumulate in the NR phase\(^{(19,51)}\).

(5) Point of addition of carbon black, viscosities of the elastomers and the method of blending also influence carbon black distribution\(^{(19,51)}\).

(6) No significant amount of carbon black migrates from one rubber phase to the other upon Brabender mixing of a masterbatch with a second rubber\(^{(20,62,63,64,65)}\).

Based on the above findings Lee proposed the Controlled Ingredient Distribution Mixing (CIDM) theory\(^{(66)}\) and an alternate stage addition mixing process\(^{(67)}\). According to the former, the major and minor rubber components are individually preblended with the appropriate amounts of the compounding ingredients including carbon black and the curing agents. Finally they are cross-blended. This gives rise to a compound that has heterogeneous ingredients distribution in the individual phases. Lee, finally studied the heterodistribution of fillers on properties such as flow properties, green strength, crack-growth resistance, heat build-up, oil swelling resistance, covulcanisation, air permeability and electrical properties\(^{(63,64,68,69)}\).

3.3.7 EFFECT OF VARIED CARBON BLACK DISTRIBUTION ON BLEND MORPHOLOGY

There is evidence from the work of several researchers that the morphology of an elastomer blend is significantly affected by the distribution of carbon black between the phases. The work of Lee\(^{(64)}\) showed that the morphology of SBR/BR blends prepared by free carbon black (20 phr N330) mixing of the three components, SBR, BR and carbon black is similar to that of blends prepared by mixing SBR-carbon black masterbatch with BR (at constant mixing time). However this morphological feature was significantly different from that of blends prepared by mixing BR-carbon black masterbatch with SBR.

On the other hand Hess et al.\(^{(70)}\) reported that the sizes of the BR domains in an 80/20 NR/BR blend compounds were fairly similar for the preblend (addition of carbon black into premixed elastomers) and the blends containing 30 and 60 phr of carbon black (N299) in the BR. The BR domains were about the same size as those in the unfilled 80/20 blend. Overall, the blended carbon black masterbatches tend to produce larger polymer domain sizes in comparison to the polymer preblends. The 80/20 NR/BR blend containing the 90 phr carbon black loading in the BR showed considerably larger BR domains (0.5 - > 50 \(\mu\)m). This morphology was represented by all the blends.
containing a relatively high carbon black loading in the BR masterbatch, except when
the BR content was 80% of the blend. At a 50/50 NR/BR blend ratio, BR appeared to
be the more continuous phase in the blended masterbatches of equivalent carbon black
loading, but NR was more continuous with a 90 phr carbon black loading in the BR
phase. At 30 phr in the BR, both polymers exhibited elongated domains with the NR
phase being somewhat more continuous. Hess et al.\(^{70}\) suggested that this appears to
be an important consideration in maximising tear strength and fatigue life.

3.3.8 EFFECT OF VARIED CARBON BLACK DISTRIBUTION ON PROPERTIES

Carbon black phase distributional variations can cause significant changes in physical
properties of an elastomer blend. Hess and co-workers\(^{19}\) reported that road wear
resistance and tensile strength of 50/50 NR/BR blends were highest with most of the
carbon black (N220) in the polybutadiene (BR) phase (based on solution-mixed
masterbatches). The increase in tensile strength with increasing percentage of carbon
black in the BR phase is in agreement with the recognised need for carbon black
reinforcement to develop optimum mechanical properties of polybutadiene and the
ability of NR to exhibit an alternate mechanism of reinforcement by crystallisation
under stress. Tear strength was optimised with about 60% of the carbon black in the
BR phase. However the above authors have not given any explanation for the observed
changes in tear strength and road wear resistance with variation in carbon black
distribution.

Sircar et al.\(^{65}\) also reported low tensile strength for NR/BR and NR/SBR blends with
a lower carbon black loading in the synthetic elastomer. Krakowski and Tinker\(^{71}\) have
also shown that preferential placement of the carbon black (N330) in the BR phase of
NR/BR blends significantly improves the resistance to abrasion. However the studies
of Hess and Chirico\(^{8}\) on the rubber properties for a N220 carbon black with different
phase distributions in 50:50 blends of NR/SBR, NR/BR and SBR/BR showed only
slight variations in modulus and tensile strength. Tread wear results also showed only
a minimal dependence in carbon black location (based on masterbatches mixed in the
internal mixer).

As in the case of the previous work of Hess et al.\(^{19}\), tear strength results of Hess and
Chirico\(^{8}\) showed significant variations in NR/SBR and NR/BR as a function of carbon
black location. In NR/SBR, the highest tear strength was achieved with most of the
carbon black in the SBR. The tear strength of the preblend was quite similar to that of
the 75% carbon black-SBR compound. The NR/BR, showed a reverse pattern, i.e. tear
strength was highest with 75% of the carbon black in the NR due to the co-continuous

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nature of the NR phase, even with a high carbon black content and lowest with high carbon black in the BR phase. High tear strength is apparently related to a high carbon black loading in the continuous polymer phase. This is the case in NR/SBR when the carbon black is added either to the preblend or preferentially to an SBR masterbatch (Fig. 3.10).

Addition of carbon black preferentially to NR produces large NR-carbon black domains surrounded by SBR with a relatively low carbon black loading. It has been suggested that the rupture path in this configuration can move freely through the weaker SBR domains, thus lowering the tearing energy. In contrast the high-carbon black-SBR three-dimensional mesh configurations, which also impart higher hysteresis, are able to divert the rupture path and dissipate energy along the domain boundaries.

In the case of NR/BR blends, the most continuous carbon black-elastomer three-dimensional mesh configuration was formed when the carbon black was added preferentially to the NR. The NR/BR blends with a high carbon black loading in the BR phase and a low carbon black loading in the NR phase gave poor tear resistance due to a preferential failure path through the continuous phase with low carbon black
loading. In NR/BR blends, the tear resistance showed an even greater improvement over that of NR/SBR blends. Hence, it may also be desirable to have the stronger elastomer (NR) or in other words the elastomer of highest strength as the continuous phase with high carbon black loading for maximising tear resistance. Supportive results have been obtained by Hess et al.\textsuperscript{(70)}, who studied the changes in tear strength of NR/BR blends as a function of carbon black phase distribution.

Although there is evidence for some improved abrasion resistance with a preferential carbon black-BR phase distribution in blends of NR/BR and SBR/BR, there appear to be anomalies relating to mixing procedure and carbon black type/loading. For example, in the case of solution mixed masterbatches tread wear resistance increased progressively with increasing carbon black in the BR phase, whereas in the case of masterbatches mixed in the internal mixer (Farrel Banbury) no significant wear differences were observed as a function of carbon black phase distribution\textsuperscript{(8)}. Also, N220 carbon black showed some wear advantage for the BR phase distribution, whereas the differences were much smaller for the larger particle size carbon blacks and the effects of phase distribution were inconsistent\textsuperscript{(8)}.

Comparison of mixing methods (chlorobutyl/NBR blend) have shown an advantage in physical properties, for directly mixing compounding ingredients into the blend of elastomers over mixing previously prepared masterbatches\textsuperscript{(6)}. Stress-strain data on SBR/NBR blends have also shown that the best balance of tensile strength and modulus can be obtained by preblending the elastomers before adding carbon black, which gives rise to an even distribution of carbon black between the phases\textsuperscript{(59)}.

Several researchers have also studied the effect of carbon black distribution on rheological properties as discussed herein. The work of Bhowmick et al.\textsuperscript{(72)} on EPDM/bromobutyl rubber (BIIR) blends has shown that viscosity increases with more carbon black mixed into the BIIR phase.

Sircar et al.\textsuperscript{(65)} reported that the viscosity values of blends prepared by diluting masterbatches mixed in the internal mixer with unfilled elastomers are much lower than those prepared by conventional mixing techniques and than the single elastomers at the 50 phr carbon black loading due to the carbon black structure development, i.e. the second elastomer segregates the carbon black elastomer aggregates formed in the first stage, resulting in discontinuous carbon black structure units surrounded by layers of unfilled elastomer. In contrast, Hess et al.\textsuperscript{(19)} reported an unexpected phenomenon that NR/BR blends had higher viscosities than the single elastomers. Their work also indicated that, NR phase undergoes fairly excessive molecular breakdown, while BR
does not. They suggested that the free radicals formed by chain scission of the NR molecules react with the BR forming graft interpolymers, which in turn raise the viscosity of the blends due to the high molecular weight of the grafted molecules.

On the other hand Lee(64) found that the shear viscosity of SBR/BR blends containing 20 phr N303 carbon black is not affected by mixing and the location of carbon black in the individual rubber phases has little effect on the shear viscosity (Figures 3.11 and 3.12). The experimental results were in agreement with the theoretically calculated viscosity values. The model used was a blend of two different fluids (the carbon black preloaded rubber was considered as one fluid).

Fig. 3.11 Shear viscosity versus shear rate for 80 parts SBR, 20 parts BR and 20 phr carbon black (N303) model compounds. Mixing time is one minute(64)
A = free mixing,
B = mechanically mixed SBR-carbon black masterbatch approach,
C = mechanically mixed BR-carbon black masterbatch approach
Fig. 3.12 Shear viscosity vs. shear rate for 80 parts SBR, 20 parts BR and 20 phr carbon black (N303) model compounds. Mixing time is 8 minutes (64)

A = free mixing,
B = mechanically mixed SBR-carbon black masterbatch approach,
C = mechanically mixed BR-carbon black masterbatch approach
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14. Alger, M.S.M. and Dyson, R.W. "Engineering Polymers"-Thermoplastic Composites, Chap.1
18. Callan, J.E., Topcik, B. and Ford, F.P., Rubber World, 151(6) (1965) 60
34. Hofmann, W., Prog. Rubber Technol., 46 (1984) 46
CHAPTER FOUR
EXPERIMENTAL METHODS

4.1 INTRODUCTION

The main stages of this study and their purpose are described briefly here.

1. Single-Stage Mixing of Filled NR/NBR Blends

For the initial stage of experimentation, the effect of internal mixer rotor speed and initial temperature of NBR on morphology, carbon black distribution and properties was investigated.

The aim was to determine the influence of these variables on properties via domain size. Variation of mixer rotor speed was chosen to adjust the ratio of apparent viscosities of the NR and NBR, which is known to have an effect on the dimensions of the domains\(^1,2,3\). The initial temperature of the NBR (45% ACN) was also varied to affect viscosity and hence domain size. Both mixer rotor speed and initial NBR temperature were selected with reference to rheological characterisation of the two elastomers.

2. Masterbatch Mixing of Filled NR/NBR Blends

For the second stage of experimentation, the effect of distribution of carbon black on morphology and properties was investigated, since the properties of elastomer blends are known to be significantly affected by carbon black distribution\(^4,5,6,7,8,9\). Carbon black distribution in the blends was varied by varying the level of carbon black in each elastomer. Transfer of carbon black from one rubber/carbon black masterbatch to the other was also investigated.

NR exhibits self reinforcement due to strain crystallisation, whereas reinforcing fillers must be added to NBR because the unfilled vulcanisates do not strain crystallise and hence lack self-reinforcement. Hence the aim was to explore the effect of varied carbon black distribution on properties via changes in the degree of reinforcement of the two phases NR and NBR.
3. Mixing of Filled NR and NBR Compounds

For the third stage of experimentation, properties of the filled NR compound, NBR (45% ACN) compound and the filled NBR control (26.6% ACN) compound were investigated.

The aim of this investigation was to compare with the properties of the filled single-stage blends in order to determine the suitability of the latter as a replacement for NBR compounds, particularly the control NBR compound which is used in the manufacture of oil seals.

4. Mixing of the NR/NBR Single-Stage Gum Blend

For the fourth stage of experimentation the morphology of the NR/NBR single-stage gum blend was investigated.

The aim was to ascertain the influence of carbon black on the morphology via a comparison with the corresponding filled compounds.

5. Mixing of the Filled NR/NBR Single-Stage Blend with a Short Mixing Cycle

For the final stage of experimentation, a partially mixed single-stage NR/NBR blend was prepared with the idea of ascertaining the location of carbon black in the NR/NBR single-stage blends.

The aim was to obtain a very coarse textured morphology consisting of domains larger than aggregates of carbon black via a short mixing cycle, so that investigation of distribution of carbon black between the two phases NR and NBR would be easier than in the case of fine textured blends.

A schematic illustration of the sequence of experiments undertaken is shown by the flow diagram in Fig. 4.1.
Rheological characterisation of NR and NBR

Mixing, analysis of morphology, carbon black distribution and properties of filled NR/NBR single-stage blends

Mixing, analysis of morphology, carbon black transfer and properties of filled NR/NBR masterbatch blends

Mixing and analysis of properties of filled NR and NBR compounds

Mixing and analysis of morphology of the NR/NBR single-stage gum blend

Mixing and analysis of location of carbon black of the filled NR/NBR single-stage blend with a short mixing cycle

Fig. 4.1 Schematic diagram of the sequence of experiments
4.2 MATERIALS AND FORMULATIONS

4.2.1 Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Grade</th>
<th>Chemical Name</th>
<th>Trade Name</th>
<th>Supplier</th>
<th>Country of Supply</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>TSR</td>
<td>Cis-1,4-polyisoprene</td>
<td>SMR 10CV</td>
<td>MRPRA</td>
<td>Malaysia</td>
</tr>
<tr>
<td>NBR</td>
<td>45% ACN</td>
<td>Acrylonitrile-butadiene rubber</td>
<td>Nipol DN 001 W45</td>
<td>Zeon</td>
<td>UK</td>
</tr>
<tr>
<td>NBR</td>
<td>26.6% ACN</td>
<td>Acrylonitrile-butadiene rubber</td>
<td>Paracril ALT</td>
<td>Uniroyal</td>
<td>UK</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>Rubber grade</td>
<td>Rubber grade</td>
<td></td>
<td>BDTP</td>
<td>UK</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>Rubber grade</td>
<td>Rubber grade</td>
<td></td>
<td>BDTP</td>
<td>UK</td>
</tr>
<tr>
<td>Carbon black</td>
<td>GPF (N660)</td>
<td>Sterling V</td>
<td>Cabot Carbon</td>
<td></td>
<td>UK</td>
</tr>
<tr>
<td>Sulphur</td>
<td>MC</td>
<td></td>
<td></td>
<td>Schill &amp; Seilacher</td>
<td>UK</td>
</tr>
<tr>
<td>TMTD</td>
<td></td>
<td>Tetramethyl thiuram disulphide</td>
<td>Perkacit TMTD -Thiurad</td>
<td>Flexysys</td>
<td>UK</td>
</tr>
<tr>
<td>CBS</td>
<td></td>
<td>N-cyclohexyl-2-benzothiazolyl sulphenamide</td>
<td>Santocure CBS</td>
<td>Flexysys</td>
<td>UK</td>
</tr>
<tr>
<td>TBBS</td>
<td></td>
<td>N-tert-butyl-2-benzothiazolyl sulphenamide</td>
<td>Santocure TBBS</td>
<td>Flexysys</td>
<td>UK</td>
</tr>
<tr>
<td>PVI (CTP)</td>
<td></td>
<td>N-(cyclohexylthio) phthalimide</td>
<td>Santogard PVI</td>
<td>Flexysys</td>
<td>UK</td>
</tr>
</tbody>
</table>

Continued on page 103
Table 4.1 Materials

<table>
<thead>
<tr>
<th>Antioxidant TQ</th>
<th>Polymerised 1,2-dihydro-2,2,4-trimethyl quinoline</th>
<th>Flectol H</th>
<th>Flexysys</th>
<th>UK</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM oil No.2</td>
<td>RAPRA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>Fisher Scientific</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xylene</td>
<td>Fisher Scientific</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cedar wood oil</td>
<td>Raymond Lamb</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Osmium tetroxide (5%)</td>
<td>Scientific</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: The Mooney viscosities of SMR 10CV and NBR (45% ACN) are 55 and 41 Mooney units respectively.

4.2.2 FORMULATIONS

1. Filled NR/NBR Blends for Single-Stage Mixing

The compound formulation of filled single-stage blends and the standard ASTM (ASTM D 2934-89) reference formulation for oil seals\(^{(10)}\) are given in Table 4.2. A low level of N660 carbon black was used as the morphology of highly filled blends is difficult to interpret by microscopy, as evident from the literature\(^{(11)}\).
### Table 4.2 Compound formulations of the single-stage blends and the standard ASTM reference compound, phr

<table>
<thead>
<tr>
<th>Compound</th>
<th>Standard ASTM Reference Formulation</th>
<th>Single-stage Blend Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMR 10 CV</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>NBR(45% ACN)</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>NBR(Paracril BJLT)</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>ZnO</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Flectol H</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Carbon black(N660)</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>Carbon black(N539)</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td>TMTD</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>CBS</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>TBBS</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>PVI</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>DOP</td>
<td>5</td>
<td>-</td>
</tr>
</tbody>
</table>

2. Masterbatches and Filled NR/NBR Blends for Masterbatch Mixing

The formulations of NR and NBR masterbatches (Stage I) and the compound formulations of filled masterbatch blends (Stage II) are given in Tables 4.3 and 4.4 respectively.

### Table 4.3 Stage I: Masterbatch formulations, phr

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NBR</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Carbon black *</td>
<td>5</td>
<td>25</td>
<td>45</td>
<td>3.33</td>
<td>16.7</td>
<td>30</td>
</tr>
</tbody>
</table>

* N660
Table 4.4 Stage II: Masterbatch blend formulations

<table>
<thead>
<tr>
<th>Diblend components</th>
<th>NR10NBR90 Compound</th>
<th>NR50NBR50 Compound</th>
<th>NR90NBR10 Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component ratio</td>
<td>NR:NBR</td>
<td>NR:NBR</td>
<td>NR:NBR</td>
</tr>
<tr>
<td>% carbon black in NR</td>
<td>40:60</td>
<td>40:60</td>
<td>40:60</td>
</tr>
<tr>
<td>% carbon black in NBR</td>
<td>10</td>
<td>50</td>
<td>90</td>
</tr>
<tr>
<td>Carbon black loading, phr</td>
<td>90</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>Composition*</td>
<td>MB.A 42</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MB.B</td>
<td>- 50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MB.C</td>
<td>-</td>
<td>-</td>
<td>58</td>
</tr>
<tr>
<td>MB.D</td>
<td>-</td>
<td>-</td>
<td>62</td>
</tr>
<tr>
<td>MB.E</td>
<td>-</td>
<td>70</td>
<td>-</td>
</tr>
<tr>
<td>MB.F</td>
<td>78</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZnO</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Flectol H</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>TMTD</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>CBS</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>PVI</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 4.4 Stage II: Masterbatch blend formulations

* MB = Masterbatch, see Table 4.3

3. Filled NR and NBR Compounds

The formulations of the filled NR compound, NBR compound and the control NBR compound are given in Table 4.5. Formulation of the control compound was derived from the ASTM reference formulation for oil seals (see Table 4.2).
<table>
<thead>
<tr>
<th>Compounding Ingredient</th>
<th>NR Formulation</th>
<th>NBR Formulation</th>
<th>Control NBR Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NBR (45% ACN)</td>
<td>-</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>NBR (26.6% ACN)</td>
<td>-</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>ZnO</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Flectol H</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Carbon black (N660)</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>TMTD</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>CBS</td>
<td>1</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>TBBS</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>PVI</td>
<td>2</td>
<td>2</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.5 Compound formulations of filled NR and NBR compounds, phr

4. The NR/NBR Gum Blend for Single-Stage Mixing

The formulation of the NR/NBR gum blend is given in Table 4.6.

5. Filled NR/NBR Blend with a Short Mixing Cycle for Single-Stage Mixing

The partially mixed filled NR/NBR blend was prepared with the single-stage blend formulation in Table 4.2.
Table 4.6 Compound formulation of the NR/NBR gum blend, phr

<table>
<thead>
<tr>
<th>Compounding Ingredient</th>
<th>NR/NBR Gum Blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>40</td>
</tr>
<tr>
<td>NBR (45% ACN)</td>
<td>60</td>
</tr>
<tr>
<td>ZnO</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>0.5</td>
</tr>
<tr>
<td>Flectol H</td>
<td>2</td>
</tr>
<tr>
<td>TMTD</td>
<td>2</td>
</tr>
<tr>
<td>CBS</td>
<td>1</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1</td>
</tr>
<tr>
<td>PVI</td>
<td>2</td>
</tr>
</tbody>
</table>

4.3 **Mixing Equipment**

4.3.1 **Francis Shaw K1 Intermix**

A Francis Shaw K1 Intermix with intermeshing rotors (see Fig. 2.9 (b) of Section 2.4.1) and a mixing action closer to that of the two-roll mill was used throughout this work for mixing filled rubber compounds and the NR/NBR gum blend. The K1 Intermix has a chamber volume of 5.5 litres and is fitted with a variable speed drive and circulating water temperature control system. The main cycle and the feeding of ingredients are computer controlled.

4.3.2 **Two-roll Mill**

A laboratory two-roll mill (J.R.Dare Ltd.) with a friction ratio of 1.0:1.1 and a circulating water temperature of 50°C was used to sheet out each rubber mix discharged from the K1 Intermix by a single pass, while hot.
4.4 **TEST METHODS**

4.4.1 **DETERMINATION OF THE SOLUBILITY PARAMETERS OF NR AND NBR**

Solubility parameter of a polymer can be calculated as proposed by Small\(^{(12)}\) according to the following equation.

\[
\delta = \frac{\rho \sum F_i}{M} \quad \text{(i)}
\]

where, \(\rho\) is the density of the polymer at any temperature

\(M\) is the molecular weight of the repeat group in the polymer and

\(\sum F_i\) is the sum of all the molar attraction constants of the chemical groups in the polymer repeat unit.

The values of \(F_i\) have been improved and updated by Hoy\(^{(13)}\). These revised values are given in Appendix (Table 2).

The above equation can be modified\(^{(14)}\) for a random copolymer as shown below, in order to take into account the fraction of the two types of molecules (\(\phi\)).

\[
\delta = \frac{\rho \left( \sum F_{i1}\phi_1 + \sum F_{i2}\phi_2 \right)}{M_1\phi_1 + M_2\phi_2} \quad \text{(ii)}
\]

Hence, the solubility parameters of NR (\(\delta_{NR}\)) and NBR (\(\delta_{NBR}\)) were calculated using the above equation taking into account the following values and the molar attraction constants of the respective chemical groups.

- **Molecular weight of NR unit** = 68.13
- **Density of NR** = 0.934 Mgm\(^{-3}\)
- **Molecular weight of ACN unit** = 53
- **Molecular weight of butadiene unit** = 54
- **Density of NBR** = 1.00 Mgm\(^{-3}\)
4.4.2 Rheometry

Since knowledge of the rheology of the component rubbers is useful for understanding the factors controlling morphology, rheological characterisation of raw rubbers, masterbatches and rubber compounds was carried out using the Negretti TMS biconical rotor rheometer.

The Negretti TMS biconical rotor rheometer\textsuperscript{(15)} is an instrument designed to give comprehensive information on the processing characteristics of raw elastomers, unvulcanised rubber compounds and other polymers. The TMS can assess viscous flow and viscoelastic characteristics of polymeric materials. In conjunction with excellent temperature control, the conditions found in practical processes can be simulated and evaluated. This instrument involves rotary shear deformation of a sample enclosed in a heated cavity. The TMS has a biconical rotor with a cone angle of 6°, to give approximately uniform shear throughout the test specimen. Fig. 4.2 shows a cross-section of the TMS rheometer.

![Cross-section showing the biconical rotor, the cavity and the dies of the TMS rheometer](image)

The cavity filling is either by injection or compression. In this study the cavity filling was by compression. The biconical form enables a closed test cavity to be used, so that the test specimen can be effectively pressurised to eliminate edge fracture. The rotor is driven by a stepper motor giving programmable speed control. The variable rotor speed enables data acquisition over a range of shear rates. Speed profiles are possible and closed-loop control of rotor torque can be achieved.
The relationship between shear stress and shear rate under conditions of steady-state viscous flow can be obtained between shear rates of 0.1 to 100 s\(^{-1}\) at temperatures between 50°C and 200°C. However the standard test temperature is 100°C. The required number of shear rate steps is programmed into the instrument together with the run time (or duration) at each step. The shear stress at each step is then recorded at the specified programmable data acquisition (or sampling) rate.

The following are the test conditions set up for the evaluation.

| Preheating time | - 200 seconds |
| Filling time | - 10 seconds |
| Sampling rate | - 10 readings / s |
| No. of steps | - 7 |

Table 4.7 shows the shear rates applied in the ascending order and the corresponding step durations used, to achieve the steady state.

<table>
<thead>
<tr>
<th>Step No.</th>
<th>Step duration (s)</th>
<th>Shear rate (s(^{-1}))</th>
<th>Sampling mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>35</td>
<td>0.1</td>
<td>Continuous</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0.4</td>
<td>Continuous</td>
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<td>3</td>
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</tr>
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<td>4</td>
<td>10</td>
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</tr>
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<td>5</td>
<td>5</td>
<td>10</td>
<td>Continuous</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>40</td>
<td>Continuous</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>100</td>
<td>Continuous</td>
</tr>
</tbody>
</table>

Table 4.7 Testing sequence of shear rates and the corresponding step durations

The results are obtained in fundamental units and hence these can complement results from other test methods.

Shear stress values obtained directly from the microprocessor were plotted against time by the use of a spread sheet to ascertain the steady-state shear stress values corresponding to the seven shear rates employed. The results are presented mainly in the form of logarithmic plots of shear stress (τ) against shear rate (γ) and apparent viscosity (\(\eta_a = \tau/\gamma\)) against shear rate.
4.4.3 Cure Testing

Determination of Cure Characteristics with a Wallace Shawbury Precision Cure Analyser

Cure analysis of all rubber compounds was carried out using the Wallace Shawbury Precision Cure Analyser.

This Curemeter is a rotorless instrument which deforms the test sample by the oscillatory motion of the lower half of the die cavity. The test sample required for this is small and the upper and lower dies have high thermal mass, thus minimising the effect of sample heating time on the results. As cure proceeds, the torque required to shear the rubber increases and a curve of torque versus time (see Fig. 2.18 of Section 2.6.1) is generated.

Torque versus time plots together with the cure characteristics i.e. scorch time (time to achieve 2% of the cross-link density, 90% cure time (time to optimum cure), Cure Rate Index (CRI) \[\frac{100}{(90\% \text{ cure time} - \text{scorch time})}\] or cross-link insertion rate and (Max.-Min.) torque, which is an indication of cross-link density, are obtained from the Analyser. The torque value is directly related to the shear modulus of the sample and hence to crosslink density. Frequency and strain applied were 1.7 Hz and 0.25 respectively for all the mixes.

4.4.4 Analysis of Morphology and Carbon Black Distribution Using Microscopy

(A) Transmitted Light Microscopy

Phase morphology of the rubber blends was analysed using transmitted light microscopy.

Thin sections (1 micron thick) were prepared from tiny pellets of vulcanised material using a sledge type microtome fitted with a carbon dioxide cooling stage. The pellets were cooled to below the glass-transition temperature of NR which is very much lower than \(T_g\) of NBR, prior to sectioning using a glass knife mounted perpendicular to the sledge at an angle 10 degrees to the horizontal. After each stroke the rolled up sections were removed from the knife edge and stretched on glass slides using xylene. Xylene swells both NR and NBR and makes it easy to unroll the sections. It is also sufficiently volatile and dries out quickly from the section when it has been mounted. Swelling also makes the sections more transparent. Sections were mounted in a
suitable fluid and covered with a cover slip to avoid appearance of holes due to degradation of the rubbers. Glycerol with low volatility and having a refractive index of 1.46 which is close to the refractive index of NR was used as the immersion oil to fill any air space which might remain between the slide and the cover slip. This also minimises the thickness variations and other artefacts.

Sections were then examined in a transmitted light phase contrast microscope using phase contrast illumination. As the contrast between the phases was poorer with phase contrast illumination when compared to bright field transmitted light illumination (zone boundaries were more clear) sections were examined using the latter. A plano type objective lens with a magnification of 40X and a numerical aperture of 0.65 was used for this examination. The plano objective is outstanding in the visual surveying of large areas of specimens. It improves the flatness of a field when compared to the conventional objective. Plano objectives are also at their best for transmitted light when used with rather thin specimens.

The phase structures of all the blends were photographed as video prints.

Identification of the NR and NBR phases was carried out using the Becke Line method and Computer-aided Image Analysis technique as described herein.

**Becke line method**

The Becke line arises due to a phenomenon associated with a vertical contact of two substances of different indices of refraction observed on the stage of a microscope. The Becke line may not be seen when the microscope is exactly focused on a specimen. When the tube of the microscope is slightly raised, a narrow line of light which is referred to as the Becke line appears just inside or outside one of the phases of a diblend. If the Becke line moves into say phase 1 when the microscope tube is raised (or the stage is lowered), the refractive index of phase one is higher than that of phase 2 or vice versa. Lowering the tube (or raising the stage) reverses the effect. The greater the difference in the refractive indices between the two phases, the greater is the displacement of the Becke line as the microscope tube is raised or lowered\(^\text{16}\).

Cedar wood oil was added between the glass slide and the cover slip to eliminate thickness effects during the microscopical analysis\(^\text{17}\) and get a clear picture of the phase structures. A conventional objective lens with a magnification of 45X and a numerical aperture of 0.65 was used for this identification.
(B) Scanning Transmission Electron Microscopy

Carbon black distribution and transfer in the blends were analysed using scanning transmission electron microscopy, since electron microscopy has played a major role in analysing carbon black distribution and transfer in elastomer blends. The scanning transmission electron microscope (STEM) combines features of the scanning electron microscope (SEM) and the transmission electron microscope (TEM). It consists of a series of lenses which focuses a probe onto the specimen which is then scanned in the usual way. Unlike in the SEM modes of operation however, the specimen is made sufficiently thin to allow the transmission of electrons. After transmission these are detected and the signals amplified and displayed.

Differential swelling technique first utilised by Callan et al.\textsuperscript{(18)} was employed with the idea of obtaining inter-phase contrast, which is the major problem in electron microscopy. Thin sections were collected from xylene in a swollen condition. Thereafter the sections were stretched on specimen support grids and observed, after solvent evaporation in the stretched state using a TEM based JEOL JEM 100CX scanning transmission electron microscope. Contrast is further increased by degradation and removal of the highly swelling phase by electron bombardment (at an accelerating voltage of 100 kV). The phase that swells to a greater extent appears lighter and the domains are thinner\textsuperscript{(18)}. Since the presence of carbon black restricts swelling, this technique is not suitable for compounds containing a high carbon black loading\textsuperscript{(11)}. It was assumed that the low level of carbon black (20 phr) present in the blends will not have a significant effect on the amount of swelling of any of the two phases. Micrographs were obtained at different magnifications using bright field illumination.
Also the thin sections were stained with osmium tetroxide \((\text{OsO}_4)^{(19,20)}\) with the idea of getting a better contrast between the two phases. Contrasting with \(\text{OsO}_4\) is based upon the capability of this material of reacting with the carbon-carbon double bonds of the rubber. The selective reaction of the \(\text{OsO}_4\) stains with the higher unsaturation elastomer makes that phase darker in TEM due to greater opacity to electrons. Cudby and Gilbey\(^{(21)}\) have reported that \(\text{NR}\) is stained to a greater extent than \(\text{NBR}\). Hence, the \(\text{NR}\) phase would be expected to appear darker and the \(\text{NBR}\) phase lighter in \(\text{OsO}_4\) stained thin sections of these blends.

The phase structures were photographed on a polaroid film. The phase structures recorded on the polaroid film were developed and enlarged onto Kodak bromide paper.

### 4.4.5 Physical Testing

Physical testing of all filled rubber compounds was carried out after preparation of the relevant test pieces by moulding in an electrically heated platen press according to the 90% cure times. However, the compression set test pieces were prepared according to the cure times stated below. Since longer curing times give better resistance to compression set\(^{(22)}\), the test pieces used for ageing were prepared by curing beyond the 90% cure times.

<table>
<thead>
<tr>
<th>Test</th>
<th>Cure Time</th>
<th>Cure Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compression set at room temperature</td>
<td>90% cure time</td>
<td>140/150</td>
</tr>
<tr>
<td>Compression set at 70°C</td>
<td>90% cure time + (\pm) 5 min.</td>
<td>140</td>
</tr>
<tr>
<td>Compression set at 70°C</td>
<td>90% cure time + (\pm) 2.5 min.</td>
<td>150</td>
</tr>
</tbody>
</table>

The time, additional to the 90% cure time at 150°C was taken as half of that at 140°C as it was experienced from the single-stage blends that the 90% cure time at 150°C is approximately half of that at 140°C.

(1) **Tensile Properties**

The tensile properties of all the filled rubber compounds were determined at room temperature in accordance with BS 903 : Part A2 (1971), using a "Hounsfield 500L" tensile testing machine with a laser extensometer. The rate of separation of the grips
was 500 mm/min. Modulus, tensile strength and % elongation at break values calculated according to the equations given below were obtained directly from the microprocessor. For each mix six dumb-bell shaped specimens were tested and the average values of the results were calculated.

\[
\text{Tensile strength (TS)} = \frac{\text{Load at break}}{\text{Original cross-sectional area}}
\]

\[
\text{Modulus at 100\% elongation} = \frac{\text{Load at 100\% elongation}}{\text{Original cross-sectional area}}
\]

\[
\text{Modulus at 300\% elongation} = \frac{\text{Load at 300\% elongation}}{\text{Original cross-sectional area}}
\]

\[
\text{% Elongation at break} = \left(\frac{\text{Distance between bench marks at the breaking point} - \text{Original distance between bench marks}}{\text{Original distance between bench marks}}\right) \times 100
\]

(2) \textbf{Tear Strength}

The tear strength of all the filled rubber compounds was determined in accordance with Method B, Procedure (a), BS 903 : Part A3 (1982), using a “Hounsfield 500L” tensile testing machine. Angle test pieces were cut from vulcanised sheets and 10 test pieces were tested for each compound. This test is a combination of tear initiation and propagation. The stress is built up at the base of the angle until it is sufficient to initiate a tear and then further stresses propagate this tear. This method enables only to measure the overall force required to rupture the test piece. A cross-head speed of 500 mm/min. was used as given in the standard for angle test pieces.

The tear strength which is generally calculated according to the following equation was directly obtained from the microprocessor in N/mm which is equivalent to kN/m (or kJ/m²).

\[
\text{Tear strength} = \frac{\text{Maximum force (N)}}{\text{Thickness (mm)}}
\]

(3) \textbf{Hardness}

Hardness is defined as the resistance to indentation under conditions that do not puncture a rubber. It is also a measurement of the elastic modulus of a rubber by determining its resistance to a rigid indentor to which is applied a force. The
indentation is usually measured with a dial gauge with its scale calibrated in Shore A or in International Rubber Hardness Degrees (IRHD).

Hardness determination of all the filled rubber compounds was carried out using a Shore A Micro Hardness Tester (Durometer type). The Shore A scale corresponds approximately to the IRHD scale.

(4) COMPRESSION SET

Compression set is the unrecovered amount of deformation after removal of an applied stress or strain in compression. It does give some relative indication of the success achieved in producing an elastic material. Elastic properties are important in seal applications. Hence, compression set is a more important parameter when judging sealing efficiency than creep or stress relaxation. The distorted rubber exerts a pressure on the contacting surface to maintain the seal. The results of compression set measurements are sensitive to the state of cure. Therefore, it may serve as an indication of state of vulcanisation. Longer curing times give better resistance to compression set as stated earlier.

Compression set measurements of all the filled rubber compounds were conducted in accordance with Method A of BS 903 : Part A6 (1969) at room temperature (20°C) and at elevated temperature (70°C).

The compression set at constant strain (25%) was calculated according to the following equation.

\[ \text{Compression set} = \frac{t_0 - t_r}{t_e - t_s} \times 100 \]

where,  
\( t_0 \) = original thickness of test piece  
\( t_r \) = thickness of test piece after recovery  
\( t_s \) = thickness of the spacer (4.73 ± 0.01 mm)

Three sets of test pieces (three for each set) were tested for each compound and the results were averaged.

(5) ABRASION RESISTANCE

Abrasion is of major importance when considering elastomeric components for dynamic applications. Dynamic seals for example can undergo abrasion when sliding over a dry surface where friction is correspondingly high.
Initially the Akron abrader was used to measure the abrasion mass loss of the filled blends according to BS 903: Part A9 (1988) (Method B). The test piece is a moulded wheel driven by an electric motor at a constant speed and held against the abrasive wheel by a constant force of 45 N. The planes of the test piece and the abrasive wheel are inclined at an angle (called slip angle) to each other. Akron abrader is distinctive for its ability to vary slip angle in a simple manner (15° is the standard for all rubbers except those whose abrasion resistance is large). Density of the blends were determined in accordance with BS 903: Part A1 (1980) (Method B) and the abrasion volume loss per 1000 revolutions was calculated accordingly.

Subsequently, the abrasion resistance of all the filled rubber compounds was determined using the DIN abrader, since this method is very convenient, rapid and well suited to quality control. A disc test piece in a holder is traversed across a rotating drum covered with a sheet of the abradant. The degree of slip (the ratio of rate of slipping of the test piece to rate of movement of the test piece (or abradant) expressed as a percentage) is 100%. The test was conducted according to BS 903: Part A9 (1988) - Method A and the abrasion resistance index (ARI) was calculated using the equation

\[ ARI = \frac{V_t}{V_s} \times 100 \]

where \( V_t \) is the volume loss of the test rubber (mm\(^3\))

\( V_s \) is the volume loss of the standard rubber (mm\(^3\))

These volume losses were calculated from the respective mass losses and densities. Densities were determined according to BS 903: Part A1 (1980) - Method A. Abrasion resistance is the reciprocal of volume loss.

Analysis of the abraded surface of blends for the specific abrasion pattern or more commonly the Schallamach abrasion pattern was conducted using a Cambridge Instruments Stereo Scan 360, Scanning Electron Microscope (SEM) (at an accelerating voltage of 10 kV) at 10 and 18.5 times magnifications in order to interpret the results of abrasion resistance. The use of SEM generally involves much simpler specimen preparations than TEM. The abraded surfaces were examined, after coating with a thin layer of gold to avoid electrostatic charging and poor image resolution.

4.4.6 **Swelling Measurements**

Swelling measurements of all the filled rubber compounds were conducted at room temperature using toluene and ASTM oil No.2. Cured test pieces of dimensions
30 x 5 x 2 mm (length x width x thickness) were weighed to the nearest 1 mg (using an analytical balance) and each test piece was immersed in a stoppered glass vessel containing the oil/fuel for a period of 72 hours. The vessels were kept in the dark to prevent oxidation. The samples were then removed from the glass vessels and excess oil/fuel removed by lens blotting paper. Subsequently the samples were placed in closed vessels, to prevent evaporation and the masses of the swollen samples were determined. Three specimens were tested for each compound and the results were averaged. % increase in mass was calculated according to the following equation as given in ASTM : D 471-479.

\[
\text{Increase in mass, } \% = \frac{(M_2 - M_1)}{M_1} \times 100
\]

where \( M_1 \) is the initial mass of specimen (g) and \( M_2 \) is the mass of specimen (g) after immersion

### 4.5 SINGLE-STAGE MIXING OF FILLED NR/NBR BLENDS

#### 4.5.1 EXPERIMENTAL DESIGN

Mixing was carried out according to a two-level two-variable factorial mixing experiment (Table 4.8). Mixer rotor speed and initial NBR temperature were taken as the two variables because the rheological measurements showed that the apparent viscosity of NR and NBR changes significantly with shear rate and temperature respectively, and could be expected to influence the mixing behaviour.

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>Rotor speed (rpm)</th>
<th>Initial NBR temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-level</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) S20T20</td>
<td>20</td>
<td>room temperature (( \leq 20 ))</td>
</tr>
<tr>
<td>factorial</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2) S20T85</td>
<td>20</td>
<td>85</td>
</tr>
<tr>
<td>points</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3) S60T20</td>
<td>60</td>
<td>room temperature (( \leq 20 ))</td>
</tr>
<tr>
<td>4) S60T85</td>
<td>60</td>
<td>85</td>
</tr>
</tbody>
</table>

Table 4.8 Combinations of rotor speed and initial NBR temperature used for the single-stage blend formulation

\( S - \) Mixer rotor speed, \( T - \) Initial temperature of NBR
The mixing procedure employed is given in Table 4.9. Mixing was controlled by the number of rotor revolutions, from which the time of mixing at the two rotor speeds was calculated.

<table>
<thead>
<tr>
<th></th>
<th>No. of working rotor revolutions</th>
<th>Mixing time at 20 rpm (s)</th>
<th>Mixing time at 60 rpm (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR+NBR+ZnO + stearic acid + Flectol H addition</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Carbon black addition</td>
<td>90</td>
<td>270</td>
<td>90</td>
</tr>
<tr>
<td>TMTD + CBS+PVI addition</td>
<td>150</td>
<td>450</td>
<td>150</td>
</tr>
<tr>
<td>Dump</td>
<td>210</td>
<td>630</td>
<td>210</td>
</tr>
</tbody>
</table>

Table 4.9 Mixing sequence and the corresponding mixing times of the single-stage blends at 20 and 60 rpm rotor speeds

Each batch was sheeted out by a single pass through the two-roll mill while hot to obtain a sheet with the required thickness. A single pass was used to avoid uncontrolled changes to the morphology of state-of-mix.

4.5.2 **MIXING CONDITIONS**

- Mixer rotor speed = 20 and 60 rpm
- Fill factor = 0.60
- Circulating water temperature = 40°C

4.5.3 **TESTING AND CHARACTERISATION**

1) **RHEOMETRY**

Rheological characterisation of the blends was conducted at 100, 110 and 120°C using the Negretti TMS biconical rotor rheometer, as described in Section 4.4.2. Rheological characterisation of the blend components, i.e. raw NR and NBR was also conducted at 80, 90, 100, 110, 120, 130, 140, 150°C, as described in Section 4.4.2.
(2) **Cure Testing**

Cure characteristics of the blends were determined at 140 and 150°C using the Wallace Shawbury Precision Cure Analyser, as described in Section 4.4.3.

(3) **Microscopy**

Phase morphology of the blends was analysed using the transmitted light phase contrast microscope, as described in Section 4.4.4 (A). Carbon black distribution between the phases was investigated using the scanning transmission electron microscope, as described in Section 4.4.4 (B). The electron micrographs of the 1 micron thin sections were obtained at magnifications 4,000 and 10,000. Since most of the 1 micron thin sections consisted of holes, 2 micron thin sections were prepared out of the S60T20 blend and micrographs were obtained at different magnifications including 20,000 and 50,000. Staining with OsO₄ was carried out on the 2 micron thin sections of S20T20 and S60T20 blends and the micrographs were obtained at 20,000 magnification. However application of this staining technique to S20T20 and S60T20 blends was unsuccessful as it was difficult to identify carbon black as well as the two phases from the respective electron micrographs.

(4) **Physical Testing**

Physical properties; tensile, tear, hardness, compression set and abrasion of the blends were determined under standard conditions as described in Section 4.4.6.

Also the abraded surface of S20T20 and S60T20 blend test pieces was analysed for the Schallamach abrasion pattern using the scanning electron microscope, in order to interpret the results of abrasion resistance.

(5) **Swelling Measurements**

Swelling measurements of the blends were conducted in ASTM oil No.2 and toluene as described in Section 4.4.7.

4.6 **Masterbatch Mixing of Filled NR/NBR Blends**

4.6.1 **Experimental Design**

Mixing was conducted in two stages. The initial location and proportion of the carbon black in each elastomer phase of the diblend was varied by making individual
elastomer/carbon black masterbatches in the first stage of the mixing cycle. In the second stage, blending of the masterbatches followed by the addition of other compounding ingredients was carried out to produce 40/60 NR/NBR blends with either 10, 50, 90% of the carbon black located initially in each elastomer (Table 4.4).

Mixing cycle used in the preparation of masterbatches (stage I) and masterbatch blends (stage II) is given in Tables 4.10 and 4.11 respectively.

<table>
<thead>
<tr>
<th></th>
<th>No. of working rotor revolutions</th>
<th>Mixing time at 60 rpm (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR or NBR addition</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Carbon black addition</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Dump</td>
<td>210</td>
<td>210</td>
</tr>
</tbody>
</table>

Table 4.10 Stage I: Mixing sequence and the corresponding mixing times of the masterbatches at 60 rpm rotor speed

<table>
<thead>
<tr>
<th></th>
<th>No. of working rotor revolutions</th>
<th>Mixing time at 60 rpm (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NRMB+NBRMB + ZnO + stearic acid + Flectol H addition</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TMTD+CBS+sulphur+PVI addition</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Dump</td>
<td>120</td>
<td>120</td>
</tr>
</tbody>
</table>

Table 4.11 Stage II: Mixing sequence and the corresponding mixing times of the masterbatch blends at 60 rpm rotor speed

4.6.2 **Mixing Conditions**

- Mixer rotor speed = 60 rpm
- Fill factor = 0.60
- Circulating water temperature = 40°C
4.6.3 Testing and Characterisation

(1) Rheometry
Rheological analysis of the NR and NBR masterbatches containing 5, 25, 45 and 3.33, 16.7, 30 phr of carbon black respectively, as well as that of the three masterbatch blends, was carried out at the standard test temperature, i.e. 100°C, as described in Section 4.4.2.

(2) Cure Testing
Cure characteristics of the blends were determined at 150°C, as described in Section 4.4.3.

(3) Microscopy
Phase morphology of the blends was analysed, as described in Section 4.4.4 (A). Carbon black transfer between the phases was investigated, as described in Section 4.4.4 (B). The electron micrographs of the 2 micron thin sections were obtained at magnifications 5,000, 10,000 and 20,000. Staining with OsO₄ was also carried out and the micrographs were obtained at 20,000 magnification. This was unsuccessful as in the case of single-stage blends.

(4) Physical Testing
Physical properties; tensile, tear, hardness, compression set and abrasion of the blends were determined under standard conditions as described in Section 4.4.6.

(5) Swelling Measurements
Swelling measurements of the blends were conducted in ASTM oil No.2 and toluene as described in Section 4.4.7.

4.7 Mixing of Filled NR and NBR Compounds

4.7.1 Mixing Procedure
A 20 phr carbon black filled NR compound, NBR compound and a control NBR compound were prepared with the mixing cycle in Table 4.12. The number of working rotor revolutions employed in each step was similar to that of the single-stage blends.
The filled NR compound was prepared at 60 rpm rotor speed, whereas both the filled NBR compounds were prepared at 40 rpm, since the filled NBR (45% ACN) compound prepared at 60 rpm rotor speed scorched (partially crosslinked), probably due to the high heat build-up in the compound at high rotor speeds. However, the number of working rotor revolutions employed was similar in each case.

<table>
<thead>
<tr>
<th></th>
<th>No. of working rotor revolutions</th>
<th>Mixing time at 40 rpm (s)</th>
<th>Mixing time at 60 rpm (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR or NBR (45% ACN) or NBR (26.6% ACN) +ZnO + Stearic acid +Flectol H addition</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Carbon black addition</td>
<td>90</td>
<td>135</td>
<td>90</td>
</tr>
<tr>
<td>TMTD+CBS+Sulphur+PVI addition</td>
<td>150</td>
<td>225</td>
<td>150</td>
</tr>
<tr>
<td>Dump</td>
<td>210</td>
<td>315</td>
<td>210</td>
</tr>
</tbody>
</table>

Table 4.12 Mixing sequence and the corresponding mixing times of filled NR and NBR compounds at 40 and 60 rpm rotor speeds

4.7.2 MIXING CONDITIONS

Mixer rotor speed = 40 or 60 rpm
Fill factor = 0.60
Circulating water temperature = 40°C

4.7.3 TESTING AND CHARACTERISATION

(1) CURE TESTING

Cure characteristics of the filled NR compound, NBR (45% ACN) compound and the control NBR compound were determined at 150, 150 and 140°C respectively as described in Section 4.4.3.

(2) PHYSICAL TESTING

Physical properties; tensile, tear, hardness, compression set and abrasion of the three filled rubber compounds were determined under standard conditions as described in Section 4.4.6.
(3) **Swelling Measurements**

Swelling measurements of the three filled rubber compounds were conducted in ASTM oil No.2 and toluene as described in Section 4.4.7.

4.8 **Mixing of the NR/NBR Single-Stage Gum Blend**

4.8.1 **Mixing Procedure**

The mixing cycle employed in the preparation of the NR/NBR single-stage gum blend is given in Tables 4.13. It is to be noted that the mixing cycle of single-stage gum blend is similar to that of the filled NR/NBR single-stage blends, with the exception of the carbon black addition step.

| No. of working | Mixing time at |
| rotor revolutions | 60 rpm (s) |
| NR+NBR+ZnO+Stearic acid+ | 0 | 0 |
| Flectol H addition | | |
| TMTD+CBS+Sulphur+PVI addition | 150 | 150 |
| Dump | 210 | 210 |

Table 4.13 Mixing sequence and the corresponding mixing times of the NR/NBR gum blend at 60 rpm rotor speed

4.8.2 **Mixing Conditions**

**NR/NBR single-stage gum blend:**

- Mixer rotor speed = 60 rpm
- Fill factor = 0.60
- Circulating water temperature = 40°C
4.8.3 Testing and Characterisation

(1) Cure Testing

Cure characteristics of the NR/NBR single-stage gum blend were determined at 150°C as described in Section 4.4.3.

(2) Microscopy

Phase morphology of the NR/NBR single-stage gum blend was analysed as described in Section 4.4.4 (A). The thickness of the sections had to be increased to 5 microns as the 1 micron thin sections prepared initially, were difficult to stretch on glass slides without the formation of holes.

4.9 Mixing of the Filled NR/NBR Single-Stage Blend with a Short Mixing Cycle

4.9.1 Mixing Procedure

The mixing cycle employed in the preparation of this filled NR/NBR single-stage blend is given in Table 4.14.

<table>
<thead>
<tr>
<th></th>
<th>No. of working rotor revolutions</th>
<th>Mixing time at 20 rpm (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR+NBR (45% ACN)+ZnO+</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>stearic acid+Flectol H addition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon black addition</td>
<td>15</td>
<td>45</td>
</tr>
<tr>
<td>TMTD+CBS+Sulphur+PVI</td>
<td>50</td>
<td>150</td>
</tr>
<tr>
<td>addition</td>
<td>Dump</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>270</td>
</tr>
</tbody>
</table>

Table 4.14 Mixing sequence and the corresponding mixing times of the filled single-stage blend with a short mixing cycle, at 20 rpm rotor speed.
4.9.2 **Mixing Conditions**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixer rotor speed</td>
<td>20 rpm</td>
</tr>
<tr>
<td>Fill factor</td>
<td>0.60</td>
</tr>
<tr>
<td>Circulating water temperature</td>
<td>40°C</td>
</tr>
</tbody>
</table>

4.9.3 **Testing and Characterisation**

(1) **Cure Testing**

Cure characteristics of this filled NR/NBR single-stage blend were determined at 150°C as described in Section 4.4.3.

(2) **Microscopy**

Phase morphology of this filled NR/NBR single-stage blend was analysed as described in Section 4.4.4 (A), in order to ascertain the location of carbon black in filled NR/NBR single-stage blends.
REFERENCES

15. Trim, R.S., Rubber World, November (1989) p.31
18. Callan, J.E., Topcik, B. and Ford, F.P., Rubber World, 151(6) (1965) 60
CHAPTER FIVE

RESULTS AND DISCUSSION

5.1 CHEMICAL / MOLECULAR COMPATIBILITY OF NR AND NBR

It has been found\(^{(1)}\) that the miscibility of a blend can affect physical properties. Thus, it is necessary to determine whether blends of NR and high nitrile (45% ACN) NBR are miscible at molecular level.

The methods generally employed to characterise the miscibility of a diblend have been reviewed in Chapter 3. The most common method is to determine the difference between the solubility parameters of the two rubbers. Group Contribution by Small’s Method (utilising the molar attraction constants of the chemical groups) is a simple way of obtaining the solubility parameters of the rubbers. The solubility parameters of NR (\(\delta_{NR}\)) and NBR (\(\delta_{NBR}\)) were calculated using the equations given in Chapter 4, Section 4.4.1, as shown below. Since NBR is a random copolymer, equation (ii) which takes into account the fraction of the acrylonitrile and butadiene units was used in the calculation of its solubility parameter.

(i) Total molar attraction constants for NR unit:

<table>
<thead>
<tr>
<th>No. of Groups</th>
<th>Type of Group</th>
<th>Molar Attraction Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-CH(_3)</td>
<td>147.3</td>
</tr>
<tr>
<td>2</td>
<td>-CH(_2)-</td>
<td>2 x 131.5</td>
</tr>
<tr>
<td>1</td>
<td>-CH=</td>
<td>121.53</td>
</tr>
<tr>
<td>1</td>
<td>(\geq C=)</td>
<td>84.51</td>
</tr>
</tbody>
</table>

\[
\sum F_i = 616.34 \text{ (cal.cm}^3{)}^{1/2} \text{ mol}^{-1}
\]

Using the equation, \(\delta = \rho \sum F_i / M\),

\[
\delta_{NR} = (0.934 \times 616.34) / 68.13 = 8.4 \text{ (cal.cm}^3{)}^{1/2}
\]
i.e. \(\delta_{NR} = 17.19 \times 10^3 \text{ (Jm}^3{)}^{1/2}

**Note:** the conversion factor to SI is, \(1 \text{ (cal.cm}^3{)}^{1/2} = 2.046 \times 10^3 \text{ (Jm}^3{)}^{1/2}\)
(ii) Total molar attraction constants for acrylonitrile (45%) unit:

<table>
<thead>
<tr>
<th>No of Groups</th>
<th>Type of Group</th>
<th>Molar Attraction Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>- CH₂-</td>
<td>131.5</td>
</tr>
<tr>
<td>1</td>
<td>- C≡N</td>
<td>354.56</td>
</tr>
<tr>
<td>1</td>
<td>&gt;CH -</td>
<td>85.99</td>
</tr>
</tbody>
</table>

\[ \sum F_1 = 572.05 \text{ (cal.cm}^3\text{)}^{1/2} \text{ mol}^{-1} \]

Total molar attraction constants for butadiene (55%) unit:

<table>
<thead>
<tr>
<th>No of Groups</th>
<th>Type of Group</th>
<th>Molar Attraction Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>- CH₂-</td>
<td>2 \times 131.5</td>
</tr>
<tr>
<td>2</td>
<td>- CH =</td>
<td>2 \times 121.53</td>
</tr>
</tbody>
</table>

\[ \sum F_1 = 506.06 \text{ (cal.cm}^3\text{)}^{1/2} \text{ mol}^{-1} \]

Using the equation,

\[ \delta = \rho \left( \sum F_1 \varphi_1 + \sum F_2 \varphi_2 \right) \left( M_1 \varphi_1 + M_2 \varphi_2 \right) \]

\[ \delta_{\text{NBR}} = 1.00 \left( 572.05 \times 0.45 + 506.06 \times 0.55 \right) = 10 \text{ (cal.cm}^3\text{)}^{1/2} \]

\[ \left( 53 \times 0.45 + 54 \times 0.55 \right) \]

i.e. \[ \delta_{\text{NBR}} = 20.46 \times 10^3 \text{ (J.m}^3\text{)}^{1/2} \]

The calculated \( \delta_{\text{NR}} \) and \( \delta_{\text{NBR}} \) indicate that blends of NR and NBR (45% ACN) are highly immiscible at molecular level as there is a marked difference \[ 3.27 \times 10^3 \text{ (J.m}^3\text{)}^{1/2} \] between the two values which is greater than \( 10^3 \text{ (J.m}^3\text{)}^{1/2} \), the normal limit of miscibility\(^2\). However, rheological matching between the blend components would be expected to produce a blend with a very fine textured morphology.
5.2 RHEOLOGY OF BLEND COMPONENTS

5.2.1 RHEOLOGY OF RAW NR AND NBR

Many researchers\(^{(3,4,5)}\) have found that viscosity of the two components in a blend can be an important factor in determining the morphology. The smallest domains have been obtained when the mixing viscosities of the components are equal. Hence, this rheological study was carried out to find the conditions of shear rate and temperature, which give rise to similar viscosities for the two components, NR and NBR.

Fig. 5.1 shows the $\log \tau - \log \dot{\gamma}$ plots of raw NR (SMR 10CV) and NBR (45% ACN) at temperatures 80, 120, and 150°C measured in the Negretti TMS rheometer as described in Section 4.4.2. Although testing was conducted at eight temperatures, in the temperature range 80-150°C, only three temperatures which represent the range are shown here, in order to get a clear picture of the variation of shear stress with shear rate of the two elastomers at different temperatures. It was not possible to obtain accurate shear stress values for both the rubbers at 80°C when the applied shear rate was 100 s\(^{-1}\). This may be due to improper flow of the rubbers at low temperatures.

![Figure 5.1 Shear stress against shear rate plots of NR and NBR at different temperatures](image)

It is apparent from this figure that at temperatures 80°C and 120°C, the plots of $\log \tau - \log \dot{\gamma}$ for NR and NBR, at the same temperature, cross-over at shear rates between 4-100 s\(^{-1}\). At these shear rates the viscosities of the two rubbers become equal. The shear rate and the corresponding shear stress at which the viscosities of the two rubbers become equal is denoted as cross-over shear rate and cross-over shear stress respectively. At 150°C, the shear rate at which the viscosities of NR and NBR
become equal, exceeds 100 s$^{-1}$ and hence the cross-over point cannot be determined using this equipment.

Fig. 5.2 shows the variation of cross-over shear rate of raw NR and NBR with temperature. There is a marked increase in the cross-over shear rate as the temperature is increased from 80 -120°C.

Fig. 5.2 indicates that a low temperature and a low shear rate or a high temperature and a high shear rate give similar viscosities and thus might be expected to result in good blending for the NR and NBR used in this study$^{(3,4)}$. The increase in the cross-over shear stress with temperature is less significant in comparison to that of shear rate (Fig. 5.3), owing to the pseudoplastic behaviour of the two elastomers.
If cross-over conditions can be achieved in the mixer, it should be possible to produce a good blend of NR and NBR.

According to Fig. 5.2, the apparent viscosities of NR and NBR cross-over at a low shear rate when the temperature is low and at a high shear rate when the temperature is high. Hence, a low shear rate / low temperature combination or high shear rate / high temperature combination would be expected to favour the production of a single-stage blend of NR and NBR with a fine textured morphology. However, at low shear rates, the stresses which result from the imposed shear field as well as from elongational deformations are small and may not be high enough to greatly reduce the size of the domains\(^5\) in order to produce a good blend. Thus, it may be necessary to aim for a high shear rate / high temperature combination. In practice, a high shear rate achieved by using a high mixer rotor speed imparts considerable mechanical energy to the batch, which is converted to heat due to friction between molecules, causing a rapid rise in batch temperature. This phenomenon is commonly known as shear heating. Hence, at high rotor speeds, the high shear rate / high temperature combination is automatically satisfied in the mixer.

Early in the mixing operation (before a high temperature has been reached), an alternative way of achieving similar viscosities is to add rubber at different temperatures. At a low temperature, the cross-over point is situated towards lower shear rate in comparison to that at high temperature (Figure 5.2). Hence, at low temperature the apparent viscosity of NBR is higher than that of NR at most shear rates. It was reported earlier that the apparent viscosity of NBR is more sensitive to temperature than NR even at high shear rates. Thus, the cross-over point could be achieved by adding NR together with heated NBR at the commencement of mixing.

Thus, the reason for selecting mixer rotor speed (20 and 60 rpm) and initial NBR temperature (20° and 85°C) as the two variables, was to bring about the above mentioned changes in viscosity, which was expected to affect the physical properties of the blends via changes in morphology.

5.2.2 RHEOLOGY OF NR AND NBR MASTERBATCHES

This rheological study of the masterbatches (Sections 4.2.2-2, 4.6.1 and 4.6.2) was conducted in the shear rate range 0.1-100 s\(^{-1}\) at 100°C using the Negretti TMS rheometer (Section 4.4.2). Variation of apparent viscosity of the three NR masterbatches containing 5, 25 and 45 phr of carbon black, with shear rate is shown in Fig. 5.4.
It can be seen from these plots that apparent viscosity of the masterbatches decreases in the order of NRMB (45 phr C.B.), NRMB (25 phr C.B.), NRMB (5 phr C.B.) and this order is maintained throughout the shear rate range studied. Thus the data reflect a rise in the viscosity with increasing the proportion of carbon black. This is in accord with the original Einstein equation as well as with the expanded version of the Einstein equation proposed by Guth and Gold, which applies to suspensions of non-attracting spherical particles\(^\text{6}\).

As expected, the difference in apparent viscosity between the three masterbatches is somewhat greater at lower shear rates and becomes smaller as the shear rate is increased. This implies that the influence of the proportion of carbon black on the viscosity diminishes at high shear rates. Kraus\(^\text{7}\), attributed this phenomenon to secondary aggregation effects which become smaller at high shear rates. However, he reported that the additional shear stress or rate dependence of viscosity due to added carbon becomes small when the unfilled polymer is strongly non-Newtonian.

The apparent viscosity of the three NBR masterbatches containing 3.33, 16.7 and 30 phr of carbon black (Sections 4.2.2-2, 4.6.1 and 4.6.2) plotted against shear rate, obtained using the Negretti TMS rheometer (Section 4.4.2) is shown in Fig. 5.15.
Unlike in the case of NR, the proportion of carbon black does not have a significant effect on the viscosity of NBR even at very low shear rates. Although NR appears to be more non-Newtonian than NBR (Figure 5.1), the effect of the proportion of carbon black on the apparent viscosity of NR is greater than that of NBR. In the case of NR, at low shear rates, increasing the amount of carbon black increases the viscosity as the stresses available for disagglomeration are low. However, in the case of NBR, although the stresses available for disagglomeration are low, disagglomeration would occur because of strong interactions between the polar groups on the carbon black surface and the polar - C ≡ N groups in NBR. Hence the viscosity of NBR will not increase significantly with the loading of carbon black, unlike in the case of NR.

As mentioned earlier in Section 5.2.1, the difference between the mixing viscosities of the components in a blend is of primary importance in determining the phase morphology. Smaller domains would be expected with smaller differences between the viscosities of the components, be they raw elastomers or masterbatches. Thus, it is also necessary to compare the rheological behaviour of the pairs of masterbatches combined in the three masterbatch blends for interpretation of their morphology.

Apparent viscosity against shear rate plots of the pairs of masterbatches combined in the blends (Sections 4.2.2-2, 4.6.1 and 4.6.2), obtained using the Negretti TMS rheometer (Section 4.4.2) are presented in Figures 5.6, 5.7 and 5.8.
Fig. 5.6 Apparent viscosity against shear rate plots of the pair of masterbatches combined in the NR10NBR90 blend.

Fig. 5.7 Apparent viscosity against shear rate plots of the pair of masterbatches combined in the NR50NBR50 blend.
It is apparent from all the three figures that the drop in apparent viscosity of the NR masterbatch as the shear rate is increased is greater than that of the respective NBR masterbatch. Hence, the effect of shear rate on the viscosity of filled NR in relation to NBR is very much similar to that of the raw or unfilled elastomers.

It is also observed from the three figures that at high shear rates (> 40 s⁻¹), corresponding to high rotor speeds in the mixer, the difference in viscosity between the pairs of masterbatches decreases in the order Fig. 5.6, Fig. 5.7, Fig. 5.8. Thus the domain size of the blends would be expected to decrease in the order NR10NBR90, NR50NBR50, NR90NBR10. In other words the finest morphology would be expected from the NR90NBR10 blend.
5.3 **Phase Morphology of NR and NBR Blends**

The ultimate physical properties of a rubber blend compound are greatly influenced by the morphology of the blend. It was reported earlier in Section 5.1 that blends of NR and high nitrile (45% ACN) NBR are highly immiscible and thus a heterogeneous morphology is to be expected from these blends. Roland\(^8\) reported that heterogeneous polymer blends have advantages because of the ability to alter the morphology for specific end uses. As evident from the work of several researchers\(^{3,4,5}\), morphology of an incompatible blend is primarily controlled by the relative viscosities of the blend components. However, factors such as mixing conditions and mixing technique employed to produce blends may also have an influence on morphology. Hence, the aim of this study, conducted using transmitted light microscopy, is to relate blend morphology to the relative mixing viscosities of the components and mixing conditions.

5.3.1 **Morphology of Single-Stage Blends**

**(A) MORPHOLOGY OF THE SINGLE-STAGE GUM BLEND**

A video print of the transmitted light micrograph of the single-stage gum blend (Sections 4.2.2-4, 4.8.1 and 4.8.2) at a magnification of 400X (Section 4.4.4(A)) is shown in Fig. 5.9.

![Transmitted light micrograph of the single-stage gum blend at 400X magnification](image)

Fig. 5.9 Transmitted light micrograph of the single-stage gum blend at 400X magnification
It is clearly visible that the elastomers are immiscible due to the appearance of a lighter continuous phase and a darker discrete phase and hence the observation is in accord with the calculated solubility parameters of NR and high nitrile (45% ACN) NBR as reported in Section 5.1. The micrograph exhibits very large domains which indicates high immiscibility between the two elastomers. It is difficult to report the exact size of the domains as they are of different sizes. However, the mean domain size is approximately 60 µm.

Visual identification of the two phases was hampered due to the presence of nearly equal proportions of NR and NBR in the blend. Hence, identification of the phases was conducted by the Becke Line Method described in Section 4.4.4(A), using a conventional microscope. The Becke line is visible just outside the darker phase of the micrograph, as the microscope was not exactly focussed on the thin section. The test indicated that the darker phase has the lower refractive index, while the lighter phase has the higher refractive index. According to published data, high nitrile NBR has a higher refractive index (1.596) than NR (1.5215 to1.5238). Hence, the result implies that the continuous phase (lighter) is NBR and the discrete (darker) phase is NR. This means that the major blend component (NBR) has become the continuous phase. This behaviour confirms the previous findings of many researchers.

This is in agreement with the rheological curves of raw NR and NBR obtained for the high shear rate / high temperature combination corresponding to mixing condition 60 rpm rotor speed (see Fig. 5.1 of Section 5.2.1). In contrast, Scott et al. reported that in 50/50 NR/NBR blends NBR was the dispersed phase with very large domains. This was attributed to the very high viscosity of NBR.

(B) EFFECT OF MIXING CONDITIONS ON THE MORPHOLOGY OF FILLED SINGLE-STAGE BLENDS

Analysis of phase morphology of the single-stage blends using phase contrast illumination was hampered by the presence of carbon black. Carbon black is known to raise the refractive index of polymer blends and obscure the phase contrast (see Section 3.2.3.4), which is mainly associated with small differences in refractive index. Thus, the morphological analysis was based on conventional transmitted light microscopy. The mean widths of the domains (lighter phase) of all four filled NR/NBR single-stage blends were estimated using the micrographs by averaging the widths of ten selected domains (excluding very small and very large ones).

Video prints of the transmitted light micrographs of the four 40/60 NR/NBR single-stage blend compounds (Sections 4.2.2-1, 4.5.1 and 4.5.2 ) designated as S20T20,
S20T8S, S60T20 and S60T85 at a magnification of 400X (Section 4.4.4(A)) are shown in Fig. 5.10 as micrographs (A), (B), (C) and (D) respectively.

**Fig. 5.10 (A)** Transmitted light micrograph of the S20T20 single-stage NR/NBR blend at 400X magnification (mixer rotor speed - 20 rpm, initial NBR temperature - 20°C)

Average domain size = 14 μm

**Fig. 5.10 (B)** Transmitted light micrograph of the S20T8S single-stage NR/NBR blend at 400X magnification (mixer rotor speed - 20 rpm, initial NBR temperature - 85°C)

Average domain size = 9 μm
Fig. 5.10 (C) Transmitted light micrograph of the S60T20 single-stage NR/NBR blend at 400X magnification (mixer rotor speed - 60 rpm, initial NBR temperature - 20°C)

Average width of the domains = 5 μm

Fig. 5.10 (D) Transmitted light micrograph of the S60T85 single-stage NR/NBR blend at 400X magnification (mixer rotor speed - 60 rpm, initial NBR temperature - 85°C)

Average width of the domains = 3 μm
These micrographs confirm that the elastomers NR and NBR are incompatible. Incompatibility is distinctly distinguished from the appearance of a lighter and a darker phase, which supports the work of many researchers. It is difficult to identify the two phases visually as NR and NBR are present in nearly equal proportions (NR:NBR = 40:60). Presence of carbon black in the two phases renders the identification more difficult. However, according to the micrograph of the S20T20 blend (micrograph (A)), the lighter phase which is mostly in the form of large domains of varying dimensions is the discrete phase and the darker phase is the matrix or the continuous phase. Appearance of a co-continuous phase structure in some parts of the micrograph suggests that the two phases are somewhat interconnecting. The phase morphology of the S20T85 blend (micrograph (B)) is very much similar to the S20T20 blend. However, the discrete phase size of the former is somewhat smaller than the latter. I.e. the mean width of the domains (lighter phase) of S20T20 and S20T85 blends are approximately 14 and 9 μm respectively.

The lighter phase of the S60T20 and S60T85 blends consists of almost evenly dispersed fine elongated domains, and hence, the morphology is more towards co-continuous. These blends show microheterogeneity at a very fine level. The mean widths of the domains (lighter phase) of the S60T20 and S60T85 blends are approximately 5 and 3 μm respectively.

The above mentioned morphological observations suggest that a marked reduction in the domain size occurs, or in other words blending improves in filled single-stage blends as the mixer rotor speed is increased. This is mainly due to the high stresses imposed by high mixer rotor speeds, which are required to break down domains. The reduction in domain size as the rotor speed is increased was expected on the basis of the results of rheological measurements reported in Section 5.2.1. This behaviour supports the influence of the mixing viscosity of the component elastomers on the domain size of the dispersed phase as reported by several researchers\(^{(4,12,13)}\).

Another factor which may be able to account for the reduction in domain size at high shear rates is the reduction in interfacial tension between the phases due to the rise in mixing temperature as reported by Tokita\(^{(5)}\). Tokita found that the domain size is reversible with the mixing temperature, but is not controlled by the stress field (which is mainly due to the matrix viscosity) itself. The interfacial tension between the phases in S60T20 and S60T85 blends can be regarded as lower than that of S20T20 and S20T85 blends due to the greater rise in batch temperature, as observed from the corresponding plots of batch temperature against mixing time (Figures 5.11 and 5.12), obtained from the Francis Shaw K1 Intermix. Thus, the lower interfacial tension between the phases of the former blends in relation to the latter blends may have also
contributed to the reduction in domain size, in addition to the effect of difference between the apparent viscosities of the two elastomers.

Fig. 5.11 Batch temperature against mixing time of the S20T20 and S20T85 single-stage blends

Fig. 5.12 Batch temperature against mixing time of the S60T20 and S60T85 single-stage blends

The reduction in domain size with increasing mixer rotor speed is in contrast to the findings reported by Ahmad and Wheelans\(^{(15)}\) on unfilled blends of NR and NBR and
can be attributed to the viscosity equalizing\(^4\) and strain increasing effects of carbon black.

A computer-aided image analysis technique which is generally used to determine the distribution of carbon black (using VIDS V software) (Section 4.4.4 (A)), was used in the identification of the lighter and the darker phases. The results obtained for the four single-stage NR/NBR blend compounds (Sections 4.2.2-1, 4.5.1 and 4.5.2 ) are given in Table 5.1.

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>Area/Frame % of the lighter phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) S20T20</td>
<td>24.2</td>
</tr>
<tr>
<td>2) S20T85</td>
<td>24.7</td>
</tr>
<tr>
<td>3) S60T20</td>
<td>21.5</td>
</tr>
<tr>
<td>4) S60T85</td>
<td>26.2</td>
</tr>
</tbody>
</table>

Table 5.1 Average values of area/frame % of the lighter phase calculated from the results obtained from four selected fields

The above results indicate that the lighter phase is NR in all the four blends as the area / frame % is closer to 40%, which is the actual proportion of NR in the blend. The values obtained are less than the actual proportion of NR (40%) in the blends. This may be due to the presence of carbon black in relatively large amounts in some areas of the NR phase, making those areas almost similar in darkness to that of the NBR phase. The results suggest that the major blend component (NBR) has formed the continuous phase and supports the work reported by many researchers\(^4,11,12,13\).

In the case of the single-stage gum blend, the darker (discrete) phase is NR and the lighter (continuous) phase is NBR (see Section 5.5.1). The darker phase in the filled single-stage blends happens to be NBR. This may be due to the presence of sufficient carbon black in the NBR phase, which raises the refractive index of NBR making it darker than the NR phase. It was reported at the beginning of this section that the average domain size of the S60T20 blend (filled with 20 phr carbon black) (approximately 5 µm) is twelve times smaller than that of the single-stage gum blend (approximately 60 µm) prepared according to the same mixing conditions. This reduction in the size of the discrete phase domains in the former blend can be ascribed to the addition of carbon black, which tends to equalize the viscosity of the blend components as predicted by Walters and Keyte\(^4\) and also increase stresses imposed by the shear field during the mixing cycle. Thus, the morphological observations from the current work are in agreement with the work of Gessler et al.\(^16\) who also found that addition of fillers reduces the size of the domains.
In general, a high rotor speed and a high initial NBR temperature are the best mixing conditions to achieve a small domain size.

5.4 **Carbon Black Distribution in NR and NBR Blends**

The properties of elastomer blends are known to be more significantly affected by carbon black distribution than they are by morphology\(^{(17)}\). Hence the main aims of this study, conducted using mainly scanning transmission electron microscopy (STEM), is to determine the effect of mixing conditions on the carbon black distribution of single-stage blends and whether large scale transfer of carbon black occurs from one rubber-carbon black masterbatch to the other upon blending in the Francis Shaw K1 Intermix.

5.4.1 **Effect of Mixing Conditions on the Carbon Black Distribution of Single-Stage Blends**

Fig. 5.13 shows a video print of the transmitted light micrograph (Sections 4.4.4(A)) of the filled single-stage NR/NBR blend prepared according to a short mixing cycle as given in Sections 4.2.2-5, 4.9.1 and 4.9.2.

![Transmitted light micrograph of the single-stage blend with a short mixing cycle at 400X magnification](image)

Fig. 5.13 Transmitted light micrograph of the single-stage blend with a short mixing cycle at 400X magnification
The idea of employing a short mixing cycle was to produce a single-stage blend with a very coarse-textured morphology, in order to study the carbon black distribution between the phases. Although, the morphology is coarse textured, it is difficult to differentiate between the phases as the inter-zone contrast is very poor. It appears from the micrograph that carbon black is poorly dispersed. Carbon black agglomerates are visible as dark black patches and appear to be almost similar in size to that of the domains. Thus identification of the phases was more difficult, which in turn meant that the aim could not be achieved. Hence, electron microscopy had to be employed to study the carbon black distribution between the phases.

Carbon black distribution between the phases of the single-stage blends was studied initially using 1µ thin sections. Fig.5.14 (A) and (B) show the scanning transmission electron micrographs (Section 4.4.4(B)) of the S20T20 blend (Sections 4.2.2-1, 4.5.1 and 4.5.2) at magnifications 4,000 and 10,000 respectively, while Fig.5.14 (C) and (D) show the micrographs of the S60T20 blend (Sections 4.2.2-1, 4.5.1 and 4.5.2) at similar magnifications.

A dark and a light phase can be seen from these micrographs indicating heterogeneity, but carbon black agglomerates or primary aggregates are not clearly visible. Generally, rubber compound formulations contain ZnO in excess. Hence the sharp edged black objects distributed in both the phases may be either particles of ZnO, ZnS (extra-network material), zinc dimethylidithiocarbamate (ZDMC), decomposition products of cyclohexyl-dithiobenzothiazole (CDB) or a combination of any of these materials. It is evident from literature\textsuperscript{18} that in electron microscopy, the elastomer having the higher degree of swelling corresponds to the lighter phase, since it stretches more than the other under equal stress and becomes much thinner, making the passage of electrons easier. Since NR has a higher degree of swelling in xylene (swelling liquid) than NBR, the lighter phase corresponds to NR, while the darker phase corresponds to NBR.
Fig. 5.14 (A) Scanning transmission electron micrograph of the S20T20 single-stage blend (x 4000 magnification)

Fig. 5.14 (B) Scanning transmission electron micrograph of the S20T20 single-stage blend (x10000 magnification)
Fig. 5.14 (C) Scanning transmission electron micrograph of the S60T20 single-stage blend (x 4000 magnification)

Fig. 5.14 (D) Scanning transmission electron micrograph of the S60T20 single-stage blend (x 10000 magnification)
Carbon black may also influence the differential swelling technique as predicted by Marsh and co-workers\(^{(18)}\), but the effect would be very small because only 20 phr of carbon black is present in the blend.

Freshly cut 2µ thin sections of the single-stage blends were analysed for carbon black distribution as carbon black primary aggregates were not visible in the micrographs obtained from 1µ thin sections. The 2µ thin sections were more uniform in thickness and carbon black particles were visible even at a magnification of 5,000.

Fig. 5.15 shows the scanning transmission electron micrograph of a 2µ thin section of the S20T20 blend (Sections 4.2.2-1, 4.5.1 and 4.5.2) at a magnification of 5,000 (Section 4.4.4(B)).

![Fig. 5.15](image)

**Fig. 5.15** Scanning transmission electron micrograph of the S20T20 single-stage blend (x 5000 magnification)

It is apparent from the micrograph that carbon black resides in the NR (lighter) phase and in the outer regions (closer to the interface) of the NBR (darker) phase. However, presence of carbon black in the inner regions of the NBR phase is not clearly visible as this phase appears to be very dark, probably due to swelling restriction in the presence
of a greater proportion of carbon black\textsuperscript{(19)} and the presence of more carbon black itself.

The scanning transmission electron micrographs of the S60T20 blend (Sections 4.2.2-1, 4.5.1 and 4.5.2) at magnifications 1000, 5000 and 20000 (Section 4.4.4(B)) are shown in Fig. 5.16 (A), (B) and (C) respectively. It is clear from micrographs (A) and (B) that the contrast between the phases is not simply due to random microtoming effects as the shape of the domains takes an elongated form and hence similar to that of the corresponding transmitted light micrograph shown earlier in Fig. 5.10 (C). Also, the mean width of the domains is similar to that of the corresponding transmitted light micrograph. The presence of aggregates of carbon black in the NR phase can be seen more clearly from micrograph (C).

![Micrograph](image)

Fig. 5.16 (A) Scanning transmission electron micrograph of the S60T20 single-stage blend (x 1000 magnification)
Fig. 5.16 (B) Scanning transmission electron micrograph of the S60T20 single-stage blend (x 5000 magnification)

Fig. 5.16 (C) Scanning transmission electron micrograph of the S60T20 single-stage blend (x 20000 magnification)
The batch temperature of the S20T20 blend, just prior to addition of carbon black is approximately 90°C, whereas that of the S60T20 blend is approximately 120°C (Figures 5.11 and 5.12). It was observed from Fig.5.1 of Section 5.2.1, that the apparent viscosity of NBR is slightly lower than that of NR at 120°C and at high shear rates corresponding to high mixer rotor speeds such as 60 rpm. This may be expected to result in the preferential location of carbon black in the NBR phase of the S60T20 blend, since carbon black has been found to mix initially into the least viscous elastomer. However, it is difficult to say whether the viscosity of NBR is lower than that of NR at 90°C and at 20 rpm mixer rotor speed, since there will be a spectrum of strain rates in the mixer and it is not possible to identify an exact equivalent shear rate.

Carbon black distribution studies of the S20T85 and S60T85 blends were hampered due to holes in the thin sections. However, since the effect of shear rate on the viscosity of the elastomers was higher than the effect of initial temperature of NBR, the carbon black distribution in the S20T85 and S60T85 blends would be expected to be similar to that of S20T20 and S60T20 blends respectively.

Although it is difficult to see carbon black in the inner regions of the NBR (darker) phase, carbon black is located preferentially in the NBR phase of all the four NR/NBR single-stage blends. This can be explained by comparing the viscosities of NR and NBR at low strain rates. Generally, incorporation of carbon black into an elastomer occurs between the rotors of the internal mixer, where strain rates are low. Also, carbon black has been found to mix initially into the lower viscosity elastomer of a blend of elastomers. Since NBR has a lower viscosity than NR at very low strain rates (see Sub-section 5.2.1), it is reasonable to conclude that carbon black is located preferentially in the NBR phase of all the four single-stage blends.

5.4.2 Carbon Black Distribution and Transfer in Masterbatch Blends

Video prints of the transmitted light micrographs of NR10NBR90, NR50NBR50 and NR90NBR10 blends (Sections 4.2.2-2, 4.6.1 and 4.6.2) at a magnification of 400X (Sections 4.4.4(A) ) are shown in Fig.5.17.
Fig. 5.17 (A) Transmitted light micrograph of the NR10NBR90 masterbatch blend at 400X magnification

Fig. 5.17 (B) Transmitted light micrograph of the NR50NBR50 masterbatch blend at 400X magnification
Fig. 5.17 (C) Transmitted light micrograph of the NR90NBR10 masterbatch blend at 400X magnification

Micrographs 5.17(A), (B) and (C) clearly indicate that the contrast between the phases is predominantly due to the carbon black concentration as reported by Marsh et al.\(^{(18)}\). All three micrographs show a lighter and a darker phase. However, this is not so significant in the case of the NR50NBR50 blend as the domains are diffused and cloudy in appearance. This is almost certainly due to the presence of an nearly equivalent loading of carbon black in the two phases. It also appears that the contrast between the phases of this blend is similar to that of the single-stage gum blend, but significantly poorer than the other two masterbatch blends containing 90\% of carbon black in one of the phases. These observations suggests that no significant amount of carbon black migrates between the phases and is in agreement with the work of many researchers\(^{(13,20,21,22,23)}\). It is likely that the darker phase in micrograph (B) is NR and the lighter phase is NBR as the concentration of carbon black in the NR phase (25\%) is slightly higher than that of NBR (16.7\%). It is more certain that the darker phase in micrograph (C) is NR, whereas in micrograph (A), it is NBR.

It is also observed from the three micrographs that the morphology of all three masterbatch blends is towards co-continuous. The NR10NBR90 blend appears to be more heterogeneous in comparison to the other two masterbatch blends as both the phases are larger in size. The mean widths of the domains (lighter phase) of the
NR10NBR90, NR50NBR50 and NR90NBR10 blends are approximately 7.5, 5 and 4 μm respectively. The observed difference in morphology between these blends is possibly a result of the variation in the difference in viscosity between the pairs of masterbatches combined in these blends at high shear rates corresponding to high mixer rotor speeds, as previously reported in Section 3.2.4.3. The difference in apparent viscosity (log scale) of the pairs of masterbatches combined in the NR10NBR90, NR50NBR50 and NR90NBR10 blends at 40s⁻¹ shear rate corresponding to high mixer rotor speed is 0.248, 0.106 and 0.01 Pa.s respectively (see Section 5.2.2). Thus the difference in viscosity at high shear rates is greatest between the pairs of masterbatches combined in the NR10NBR90 blend, which may be able to account for its greater heterogeneity in relation to the other two masterbatch blends. The slightly greater domain size observed for the NR50NBR50 blend in relation to the NR90NBR10 blend can also be attributed to the slightly greater difference in viscosity between the pair of masterbatches combined in the former blend in comparison to that of the latter blend (see Figures 5.7 and 5.8 of Section 5.2.2).

This morphological study indicates that a greater percentage of carbon black in the NR phase produces more intimate blending at high shear rates in comparison to that containing a greater percentage of carbon black in the NBR phase, solely due to the smaller difference in viscosity between the component masterbatches.

The scanning transmission electron micrographs of NR10NBR90, NR50NBR50 and NR90NBR10 blends (Sections 4.2.2-2, 4.6.1 and 4.6.2) at a magnification of 5,000 (Section 4.4.4(B)) are shown in Fig.5.18 (a), (b) and (c) respectively. Comparison of micrographs 5.18 (a) and 5.18 (c) reveals that the lighter phase in these micrographs is NR, as the lighter phase of the latter appears to have a much greater amount of carbon black than that of the former. Thus, the above observation confirms the findings from phase identification of single-stage blends, reported earlier in Section 5.3.1(B). Also, it implies that no large scale transfer of carbon black occurs between phases. Thus, the observations on phase mixed compounds suggest that majority of carbon black remains in the elastomer phase to which it is originally added, which is in agreement with the work of Massie et al. (24).
Fig. 5.18 (a) Scanning transmission electron micrograph of the NR10NBR90 masterbatch blend (x 5000 magnification)

Fig. 5.18 (b) Scanning transmission electron micrograph of the NR50NBR50 masterbatch blend (x 5000 magnification)
The scanning transmission electron micrograph of the stained (with OsO₄) thin section (Section 4.4.4(B)) corresponding to the NR90NBR10 blend (Sections 4.2.2-2, 4.6.1 and 4.6.2) at a magnification of 20,000 is shown in Fig. 5.19. No significant difference was observed between the electron micrographs of the stained sections corresponding to the NR10NBR90 and NR50NBR50 blends and the NR90NBR10 blend. Thus the former micrographs have not been included under this section. As in the case of the electron micrographs of stained sections of single-stage blends (Sections 4.4.4(B) and 4.5.3(C)), it is difficult to identify carbon black particles. However, the cloudy appearance in the lighter regions may be due to the presence of carbon black in the NBR phase. Hence the staining technique employed on the masterbatch blends with the idea of obtaining further information on carbon black distribution and transfer was unsuccessful. However, confirmation of the morphology and identification of the phases would have been possible with electron micrographs of stained thin sections obtained at a low magnification, since NR is stained to a greater extent than NBR\(^{25}\).
Fig. 5.19 Scanning transmission electron micrograph of a stained section of the NR90NBR10 masterbatch blend (x 20000 magnification)
5.5 PROPERTIES OF BLENDS

5.5.1 RHEOLOGY OF BLENDS

(A) EFFECT OF MIXING CONDITIONS ON THE RHEOLOGY OF SINGLE-STAGE BLENDS

As mentioned previously in Section 4.5.1, the four single-stage blends are denoted as S20T20, S20T85, S60T20, and S60T85. The numeric following the letter ‘S’ denotes the mixer rotor speed in rpm, whilst the numeric following the letter ‘T’ denotes the initial temperature of NBR in centigrade degrees.

Fig. 5.20 illustrates the variation of apparent viscosity with shear rate of the S20T20 blend (Sections 4.2.2-1, 4.5.1 and 4.5.2), obtained using the Negretti TMS rheometer (Sections 4.2.2-2, 4.6.1 and 4.6.2) at temperatures 100, 110, and 120°C.

![](image)

**Fig. 5.20** Apparent viscosity vs shear rate plots of the filled (20 phr, N660) S20T20 blend at different temperatures

It is apparent from this figure that the variation of rheological behaviour of the single-stage blend with temperature is similar to that of the component elastomers (Figure 5.1 of Section 5.2.1).
Apparent viscosity against shear rate plots of the four unvulcanised single-stage blends (Sections 4.2.2-1, 4.5.1 and 4.5.2), obtained using the Negretti TMS rheometer (Sections 4.2.2-2, 4.6.1 and 4.6.2) at 120°C are shown in Fig.5.21.

The four plots coincide throughout the shear rate range studied reflecting a similar rheological behaviour. This indicates that the rotor speed and initial temperature of NBR do not exert a significant effect on the apparent viscosity of the single-stage blends. Also the apparent viscosity of single-stage blends is not significantly affected by morphology. Similar rheological behaviour of the four single-stage blends also indicates that the distribution of carbon black is the same for all four blends, or that the blend viscosity is independent of the distribution of carbon black within the blend rubber phase.

A comparison between the apparent viscosities of the four single-stage blends (Sections 4.2.2-1, 4.5.1 and 4.5.2), NR10NBR90 blend and the masterbatches combined in the latter blend (Sections 4.2.2-2, 4.6.1 and 4.6.2), obtained using the Negretti TMS rheometer (Section 4.4.2) is presented in Fig. 5.23.

Fig.5.22 clearly indicates that the apparent viscosity of the NR90NBR10 blend is much lower than the predicted value. A similar behaviour is observed in the apparent viscosities of the NR50NBR50 and NR10NBR90 blends in relation to the predicted values. Lowering of apparent viscosity of the masterbatch (two-stage) blend may be attributed to an improved carbon black dispersion due to the longer mixing time (5.5 min.), in comparison to the 3.5 min. mixing time of the masterbatches and the single-stage blends. Another factor which may be able to account for the lowering of apparent viscosity of the masterbatch blend is continued mastication with mixing time.
The results are in agreement with the work of Boonstra and Medalia\(^{(26)}\) and Sircar et al.\(^{(23)}\). Both groups of researchers prepared the two-stage blends by diluting the masterbatches with unloaded elastomers.

Boonstra and Medalia\(^{(26)}\) attributed the marked lowering of Mooney viscosity in blends prepared by a two-stage mixing process solely to an improved carbon black dispersion in each of the phases, due to increased mixing time in relation to that of a single-stage mixing process. As carbon black dispersion improves, rubber trapped within carbon black agglomerates, i.e. immobilised rubber is released, which in turn lowers the viscosity due to the mobility of these rubber molecules. Sircar and coworkers attributed the marked lowering of Mooney viscosity of two-stage blends in comparison to those prepared by conventional mixing techniques or the single elastomer compounds (with 50 phr carbon black loading), to the formation of discontinuous carbon black structure units surrounded by layers of unloaded elastomers. However, Sircar et al.'s model on carbon black structure development cannot be applied to explain the viscosity behaviour of the blends prepared according to a two-stage mixing process, as both the elastomers were initially loaded at least with 10% of carbon black prior to blending.

In contrast to the above phenomenon, Hess et al.\(^{(12)}\) reported an unexpected result that blends of NR and BR had higher viscosities than the single elastomer compounds. This was mainly attributed to the formation of graft interpolymers of NR and BR, which in turn raise the viscosity of the blends due to the high molecular weight of the grafted molecules.

It is also to be noted that the masterbatch viscosity ratios (log scale) of NR to NBR of NR10NBR90, NR50NBR50 and NR90NBR10 blends (Sections 4.2.2-2, 4.6.1 and 4.6.2), obtained using the Negretri TMS rheometer (Section 4.4.2) at 40 s\(^{-1}\) shear rate.
and 100°C are 0.936, 0.972 and 0.997 respectively. These ratios indicate that there is no significant difference in the carbon black dispersion between the three masterbatch blends at the same total mixing time. Dispersion in all the three blends can be regarded as good because the ratios are approximately 1, since a viscosity ratio (log scale) of about 1 to 3 produces a good dispersion, as found by Hess et al.\(^{(27)}\).

(B) **EFFECT OF THE LOCATION OF CARBON BLACK ON THE APPARENT VISCOSITY OF MASTERBATCH BLENDS**

The measured and predicted apparent viscosity values of the masterbatch blends (Sections 4.2.2-2, 4.6.1 and 4.6.2) obtained using the Negretti TMS rheometer at 40 s\(^{-1}\) shear rate and 100°C (Section 4.4.2) plotted against the percentage of carbon black in the NR phase is shown in Fig. 5.23.

![Fig. 5.23 Effect of location of carbon black on the apparent viscosity of filled (20 phr, N660) masterbatch blends at 40s\(^{-1}\) shear rate and 100°C](image)

It can be seen from this figure that the predicted and measured trends in the variation of apparent viscosity with percentage of carbon black in the NR phase are more or less similar. The apparent viscosity of masterbatch blends increases slightly with more carbon black premixed into the NR phase. This is probably a reflection of the greater effect of carbon black on the apparent viscosity of NR in relation to NBR, as discussed in Section 5.2.2.

It is concluded that the location of carbon black in the individual rubber phases has a little effect on the apparent viscosity of NR/NBR blends. This is in agreement with the work of Lee\(^{(21)}\), based on shear viscosity measurements of SBR/BR blends. This confirms that the distribution of carbon black is the same for all four single-stage blends (see Section 5.5.1 (A)).
5.5.2 **Cure Characteristics of NR and NBR Blends**

The ultimate properties of a cured elastomer blend compound are influenced by the state of mix of the unvulcanised compound. For a compound to process easily in the subsequent forming operations, cure efficiently and develop the required properties for end-use, it should be well mixed. Thus it is necessary to have a knowledge of the processing characteristics of NR/NBR blends in order to aim for optimum properties.

The four basic cure characteristics generally determined using a cure analyser as described in the experimental section are scorch time, 90% cure time, cure rate index and (Max.-Min.) torque. Determination of scorch time is one of the most frequently used tests for assessing the processability of rubber compounds, whilst 90% cure time, cure rate index and (Max.-Min.) torque give an indication of cure behaviour. One of the main aims is to study the effect of mixing conditions on these four parameters. The other is to determine whether location of carbon black within the rubber blend phases has any influence on the cure characteristics, since several researchers have found that presence of fillers influence the vulcanisation process\(^{(28,29,30,31,32,33)}\).

It is also necessary to study the cure efficiency of NR/NBR blends relative to that of NBR compounds, in order to determine the suitability of the former as a replacement for the latter, which would satisfy the ultimate aim of increasing consumption of NR.

It is also worthwhile to study the influence of the blending technique on cure characteristics, so that the best blending technique with regard to cure efficiency can be found.

Cure characteristics of all the rubber compounds prepared throughout this research project are tabulated in Table 5.2.

(A) **Influence of Mixing Conditions on the Cure Characteristics of Single-Stage Blends**

In contrast to the crumbly, powdery appearance observed by Ahmad and Wheelans for unfilled blends of NR/NBR (41% ACN) at discharge from the mixer, all the filled NR/NBR (45.5% ACN) blends studied in this project discharged in a smooth coherent manner (without a trace of crumbliness). This indicates that the two rubbers and the compounding ingredients are well mixed in all the single-stage blends. One of the reasons for this is the high mixing shear stress caused by the presence of carbon black which produces more intimate blending, and hence may reduce crumbliness. The powdery nature of the blends of NR/NBR observed by Ahmad and Wheelans is connected with inefficient mixing, slipping or skidding in the internal mixer.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Scorch Time (min.)</th>
<th>90% Cure Time (min.)</th>
<th>Cure Rate Index (C.R.I.)</th>
<th>(Max.-Min.) Torque (Nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filled NR</td>
<td>1.27</td>
<td>5.6</td>
<td>23.5</td>
<td>1.71</td>
</tr>
<tr>
<td>Filled NBR (45% ACN)</td>
<td>4.37</td>
<td>11.7</td>
<td>13.7</td>
<td>1.69</td>
</tr>
<tr>
<td>Filled NBR (26.6% ACN) - Control</td>
<td>1.83 *</td>
<td>14.1 *</td>
<td>8.1 *</td>
<td>1.75 *</td>
</tr>
<tr>
<td>Single-stage gum blend</td>
<td>3.65</td>
<td>10.3</td>
<td>15.2</td>
<td>1.0</td>
</tr>
<tr>
<td>S20T20 blend</td>
<td>2.83</td>
<td>7.93</td>
<td>19.7</td>
<td>1.47</td>
</tr>
<tr>
<td>S20T85 blend</td>
<td>3.28</td>
<td>7.73</td>
<td>22.7</td>
<td>1.42</td>
</tr>
<tr>
<td>S60T20 blend</td>
<td>2.23</td>
<td>6.05</td>
<td>26.2</td>
<td>1.47</td>
</tr>
<tr>
<td>S60T85 blend</td>
<td>2.48</td>
<td>6.25</td>
<td>26.5</td>
<td>1.39</td>
</tr>
<tr>
<td>NR10NBR90 blend</td>
<td>3.9</td>
<td>9.9</td>
<td>16.6</td>
<td>1.49</td>
</tr>
<tr>
<td>NR50NBR50 blend</td>
<td>3.9</td>
<td>9.6</td>
<td>17.5</td>
<td>1.50</td>
</tr>
<tr>
<td>NR90NBR10 blend</td>
<td>3.9</td>
<td>9.8</td>
<td>16.6</td>
<td>1.52</td>
</tr>
<tr>
<td>Filled single-stage blend - short mixing cycle</td>
<td>3.13</td>
<td>9.7</td>
<td>15.3</td>
<td>1.07</td>
</tr>
</tbody>
</table>

Table 5.2 Cure characteristics of all the rubber compounds obtained using the Wallace Shawbury Precision Cure Analyser (Section 4.4.3(A)) at 150°C

* Tested at 140°C

The variation in scorch time and 90% cure time of the four single-stage blends (Sections 4.2.2-1, 4.5.1 and 4.5.2), obtained using the Wallace Shawbury Precision Cure Analyser (Section 4.4.3(A)) at 150°C is shown in Figures 5.24 and 5.25 respectively. It is clearly seen that the S20T20 and S20T85 blends show higher scorch and cure times than S60T20 and S60T85 blend. The observed differences in scorch and cure times of the blends with rotor speed may be attributed to the heat history of
the compounds received during mixing. The dump temperature of S20T20 and S20T85 blends is approximately 105°C, whilst that of S60T20 and S60T85 blends is approximately 140°C as apparent from Figures 5.11 and 5.12 respectively (see Section 5.3.1 (B)). Thus, during the mixing stage, the amount of safe processing time (capable of flow) used up in the S60T20 and S60T85 blends is greater than in the S20T20 and S20T85 blends. This in turn shortens the scorch and cure times of the former blends.

Fig. 5.24 Influence of mixing conditions on the scorch time of filled (20 phr, N660) single-stage blends

Fig. 5.25 Influence of mixing conditions on the 90% cure time of filled (20 phr, N660) single-stage blends
The variation in cure rate index of the single-stage blends (Sections 4.2.2-1, 4.5.1 and 4.5.2), which gives an indication of crosslink insertion rate, obtained using the Wallace Shawbury Precision Cure Analyser (Section 4.4.3(A)), is shown in Fig. 5.26.

![Figure 5.26 Influence of mixing conditions on the cure rate index of filled (20 phr, N660) single-stage blends](image)

It is apparent from this figure that the cure rates of the S60T20 and S60T85 blends are higher than those of the S20T20 and S20T85 blends. These differences in cure rates with rotor speed may again be due to the heat history of the compounds received during mixing, since a higher cure rate generally reflects a lower cure time.

The variation in (Max.-Min.) torque (directly related to the shear modulus and hence to the crosslink density) of the four single-stage blends (Sections 4.2.2-1, 4.5.1 and 4.5.2), obtained using the Wallace Shawbury Precision Cure Analyser (Section 4.4.3(A)) is shown in Fig. 5.27. No significant difference is observed between the torque values of these blends. This implies that the overall crosslink density of all the four blends is almost the same, although there may be differences in crosslink distribution. Hence the results indicate that the overall crosslink density of single-stage blends is unaffected by both rotor speed and initial NBR temperature, despite differences in morphology.
The control NBR (26.6% ACN) compound, which is expected to have a good oil resistance, was prepared in order to determine the suitability of the NR/NBR blends as a replacement for the former especially in oil sealing applications. Unfortunately it is not possible to determine the suitability of the NR/NBR blends as a replacement for the control NBR compound with regard to cure efficiency due to the difference in the heat history of the compounds. According to the results given in Table 5.2, the estimated value of the 90% cure time of the control NBR (26.6% ACN) compound at 150°C is shorter than the 90% cure time of the NBR (45% ACN) compound at the same temperature. Thus the control NBR compound cures faster than the NBR (45% ACN) compound. This is probably due to the more efficient vulcanising system (with less sulphur) employed in the preparation of the former.

The results also indicate that the scorch and cure times of the masterbatch blends are higher than those of the single-stage blends. These differences may be related to the heat history of the compounds. Since the mixing cycle (at 60 rpm rotor speed) employed in the preparation of single-stage blends was longer than that employed in the second stage of masterbatch blends, the amount of scorch time used up is expected to be greater in the former blends. Hence resulting in shorter scorch and cure times obtained for the single-stage blends in relation to the masterbatch blends.

A comparison between cure rate index (C.R.I.) of single-stage blends (Sections 4.2.2-1, 4.5.1 and 4.5.2), masterbatch blends (Sections 4.2.2-2, 4.6.1 and 4.6.2) and single elastomer compounds (Sections 4.2.2-3, 4.7.1 and 4.7.2), obtained using the Wallace Shawbury Precision Cure Analyser (Section 4.4.3(A)) is shown in Fig. 5.28.
The results indicate that the NR compound cures much faster than the comparable NBR compound (Table 5.2). This may be attributed to the non-rubber components in NR, mainly proteins acting as accelerators for the vulcanisation process\(^{34}\). It is also interesting to note that the cure rate of most of the single-stage blends is closer to that of the NR compound than predicted. The fine textured single-stage blends show a positive synergism of cure rate.

It is clear from the above figure that the cure rate of the single-stage blends is well above the additivity line of the single elastomers, whereas the cure rate of the masterbatch blends is just below the additivity line. The higher cure rate of the single-stage blends in relation to that of the masterbatch blends is probably due to the difference in heat history received during mixing.

The (Max.-Min.) torque (an indication of degree of crosslinking) of both the types of blends (Sections 4.2.2-1, 4.5.1, 4.5.2 and Sections 4.2.2-2, 4.6.1 and 4.6.2), obtained using the Wallace Shawbury Precision Cure Analyser as mentioned earlier (Section 4.4.3(A)), is slightly below the additivity line of the single elastomer compounds (Fig. 5.29). This indicates that the overall cross-link density of the blends is lower than that of the single elastomer compounds. No significant difference is observed between the (Max.-Min.) torque of the single-stage and masterbatch blends. This indicates that the overall crosslink density is the same, whether the blending technique is single-stage or two-stage. Also the overall crosslink density is not significantly affected by morphology.
Overall, the comparisons reveal that the masterbatch blends are superior to the single-stage blends in terms of processing safety, whereas the single-stage blends are superior to the masterbatch blends in terms of cure efficiency.

(B) INFLUENCE OF LOCATION OF CARBON BLACK ON THE CURE CHARACTERISTICS OF MASTERBATCH BLENDS

The variation in scorch time, 90% cure time, cure rate index and (Max.-Min.) torque of the masterbatch blends (Sections 4.2.2-2, 4.6.1 and 4.6.2), obtained using the Wallace Shawbury Precision Cure Analyser (Section 4.4.3(A)) is shown in Figures 5.30, 5.31, 5.32 and 5.33 respectively.

Fig. 5.30 Influence of location of carbon black on the scorch time of filled (20 phr, N660) masterbatch blends
Fig. 5.31 Influence of location of carbon black on the 90% cure time of filled (20 phr, N660) masterbatch blends

Fig. 5.32 Influence of location of carbon black on the Cure Rate Index of filled (20 phr, N660) masterbatch blends
Fig. 5.33 Influence of location of carbon black on the (Max.-Min.) torque of filled (20 phr, N660) masterbatch blends

No significant difference is observed between the cure characteristics of these blends prepared by varying the proportion of carbon black in the individual rubber phases, despite the difference in morphology. This implies that the location of carbon black within the blend rubber phases does not significantly influence the cure characteristics of masterbatch blends.
5.5.3 Physical Properties of NR and NBR Blends

An elastomer blend can exhibit unique physical properties instead of an averaging of the properties of the individual elastomers in the blend. From a practical point of view, elastomer blends are studied to obtain novel property combinations from mixtures of elastomers with contrasting physical properties such as NR and NBR. The physical properties of the NR/NBR blends were therefore evaluated. The effect of mixing conditions and location of carbon black on properties of NR/NBR blends were studied.

An attempt has been made to relate the variations in physical properties of the single-stage blends as well as the masterbatch blends to the rheology, morphology and carbon black distribution.

A comparison of physical properties of single-stage blends with those of masterbatch blends was also conducted in order to determine the best blending technique with regard to each of the properties. Physical properties of both the types of blends were also compared with those of single elastomer compounds, especially NBR compounds in order to determine the suitability of NR/NBR blends as replacements for NBR compounds, which is the overall objective of this research project.

(1) Modulus

(a) Effect of Mixing Conditions on the Moduli of Single-stage Blends

Figures 5.34 and 5.35 show the variation in modulus at 100% and 300% elongation of the single-stage blends (Sections 4.2.2-1, 4.5.1 and 4.5.2) obtained using the Hounsfield tensile testing machine (Section 4.4.6(1)). It is clear from these figures that there is no significant difference between the moduli values of the four blends. In general, modulus is strongly affected by the crosslink density. Hence, the results imply that the overall crosslink density of the four blends is almost similar, since the distribution of carbon black is the same for all four blends (see Sections 5.5.1 (A) and (B)) and agrees with the results of (Max.-Min.) torque (see Section 5.5.2 (A)). In other words, the rotor speed and initial temperature of NBR do not exert a significant effect on the moduli and hence the overall crosslink density of single-stage blends. The results also imply that the moduli and hence the overall crosslink density of single-stage blends are not affected by the morphology as well. The former agrees with the work of several researchers\(^4,8,15,35\).
A comparison between moduli (100% and 300%) of the single-stage blends (Sections 4.2.2-1, 4.5.1 and 4.5.2), masterbatch blends (Sections 4.2.2-2, 4.6.1 and 4.6.2) and single elastomer compounds (Sections 4.2.2-3, 4.7.1 and 4.7.2), obtained using the Hounsfield tensile testing machine (Section 4.4.6(1)) is shown in Figures 5.36 and 5.37 respectively. It is not possible to compare the moduli or many of the other physical properties of the single-stage blends with those of masterbatch blends, since properties vary greatly with total mixing time (26). At 300% elongation, the single-stage blends, especially the fine textured blends, have a higher modulus than the control NBR (26.6% ACN) compound, whilst at 100% elongation the modulus of the fine textured single-stage blends is only slightly lower than that of the control NBR compound.
It is evident from literature\textsuperscript{(36)} that hardness, which is related to the modulus at low strain, increases with increasing the acrylonitrile content of NBR. Hence, a low modulus for the control NBR (26\% ACN) compound in comparison to that of the NBR (45\% ACN) compound is to be expected.

![Figure 5.36 Effect of blending conditions on the 100\% modulus of filled (20 phr, N660) NR/NBR blends](image)

![Figure 5.37 Effect of blending conditions on the 300\% modulus of filled (20 phr, N660) NR/NBR blends](image)
(b) Effect of Location of Carbon Black on the Moduli of Masterbatch Blends

The variation in moduli (100% and 300%) of the three masterbatch blends (Sections 4.2.2-2, 4.6.1 and 4.6.2), obtained using the Hounsfield tensile testing machine (Section 4.4.6(1)) is shown in Figures 5.38 and 5.39 respectively.

![Figure 5.38](image)

**Fig. 5.38 Influence of location of carbon black on the 100% modulus of filled (20 phr, N660) masterbatch blends**

![Figure 5.39](image)

**Fig. 5.39 Influence of location of carbon black on the 300% modulus of filled (20 phr, N660) masterbatch blends**

A significant feature from Figures 5.36 and 5.37 is that the modulus (or stiffness) of the NBR compound is higher than that of the NR compound (both filled with 20 phr carbon black as in the case of the blends) at low strain (100%). At higher strain (300%) the difference is not significant, most probably due to the ability of NR to exhibit reinforcement by crystallisation under strain (a self-reinforcing property) in addition to reinforcement caused by carbon black. Thus the results imply that NBR (45% ACN) vulcanisates formulated with carbon black have a modulus which is higher.
than that of comparable NR vulcanisates at low strain. Hence, a masterbatch blend containing 90% of carbon black in the NBR phase is expected to have a higher modulus than a blend containing 90% of carbon black in the NR phase at low strain (Fig. 5.38). It is to be noted that the modulus at 100% elongation is not influenced by strain crystallisation of NR.

It is apparent from Figure 5.39 that 300% modulus increases with increasing the amount of carbon black in the NBR phase. Unlike in the case of NR, which has the ability to exhibit reinforcement by strain crystallisation, reinforcing fillers must be added to NBR in order to achieve good mechanical properties, as reported in the literature. Hence, the results of 300% modulus are in agreement with the recognised need for carbon black reinforcement to develop optimum modulus of NBR and with the ability of NR to exhibit an alternate mechanism of reinforcement by strain crystallisation.

(2) **Tensile Strength**

(a) **Effect of Mixing Conditions on the Tensile Strength of Single-stage Blends**

The variation in tensile strength of the four single-stage blends (Sections 4.2.2-1, 4.5.1 and 4.5.2), obtained using the Hounsfield tensile testing machine (Section 4.4.6(1)) is shown in Fig. 5.40. Tensile strengths of the S60T20 and S60T85 blends are markedly higher than those of the S20T20 and S20T85 blends. Hence, the results indicate that rotor speed has a significant effect on the tensile strength of single-stage blends.
Higher tensile strengths of the S60T20 and S60T85 blends over those of the S20T20 and S20T85 blends may be ascribed to the finer morphology (see Section 5.3.1 (B)). Generally the size of the dispersed discrete phase influences strength properties. The finer the morphology, i.e. the smaller the discrete phase size, the higher the tensile strength of unfilled blends\(^{15}\). Since the distribution of carbon black between the phases is similar for all the four single-stage blends (see Section 5.5.1), it will not exert a significant effect on the strength properties.

Tensile failure is believed to be due initiation of a crack followed by its propagation. A crack is known to initiate from points of weakness as stresses concentrate in these regions. Since S20T20 and S20T85 blends are more heterogeneous than S60T20 and S60T85 blends there are regions where the stresses can concentrate easily, especially near the edges of the sample. In other words large domains will act as stress raisers and increase the applied stress thereby favouring crack initiation.

Size of the domains (or the number of domains present) can also influence crack propagation. Since the interfacial crosslinking in the single-stage blends is expected to be weak, a crack that has propagated to the interface between the continuous and the dispersed phase will be deviated without tearing through the dispersed phase as postulated by Hamed\(^{37}\). The deviated crack may propagate around the domain interface or tear through the continuous phase in a distorted direction until it meets another domain of the dispersed phase. The strength of a blend increases with increasing crack deviation, which increases with increasing interfacial area or with decreasing domain size. Since the crack travels from one domain to another, the amount of reinforcement depends on the number of domains present. For a given composition as the domain size decreases, the number of domains increases. Hence the number of domains in the S60T20 and S60T85 blends (domain size is approx. 3-5 \(\mu\)m) is greater than that of the S20T20 and S20T85 blends (domain size is approx. 9-14 \(\mu\)m). This results in a higher reinforcement and thus a higher tensile strength for the former blends.

The domain spacing of the S60T20 and S60T85 blends is smaller than that of the S20T20 and S20T85 blends (see Figures 5.10 (A)-(D) of Section 5.3.1 (B)). Thus in the case of the latter blends, a crack can propagate more easily through the blend without interference from many dispersed domains than in the case of the former blends, causing a lower value for the tensile strength as shown in Fig. 5.40.
The effect of rotor speed on tensile strength is not in agreement with the work of Ahmad and Wheelans\(^{(15)}\). In this current work on carbon black filled NR/NBR blends, higher internal mixer rotor speeds gave better tensile strength, whereas in Ahmad and Wheelans work on unfilled NR/NBR blends, the highest rotor speed caused the worst tensile strength. This discrepancy implies that the variation in tensile strength of NR/NBR blends with rotor speed is greatly influenced by the presence of carbon black.

It is interesting to note that the tensile strength of the S60T20 and S60T85 blends is about 6MPa higher than that of the comparable blend (40:60 NR/NBR, at 20 phr carbon black loading) prepared by Baker et al.\(^{(38)}\). 100\% modulus of the four NR/NBR blends is also about 1.5 MPa higher than that of the comparable blend of Baker et al. This increase in the tensile strength as well as the 100\% modulus of the single-stage blends over that of the comparable blend of Baker et al. may be associated with the finer morphology of the former blends.

A comparison between tensile strength of the single-stage blends (Sections 4.2.2-1, 4.5.1 and 4.5.2), masterbatch blends (Sections 4.2.2-2, 4.6.1 and 4.6.2) and single elastomer compounds (Sections 4.2.2-3, 4.7.1 and 4.7.2), obtained using the Hounsfield tensile testing machine (Section 4.4.6(1)) is shown in Fig. 5.41.

![Fig. 5.41 Effect of blending conditions on the tensile strength of filled (20 phr, N660) NR/NBR blends](image)

Tensile strength of the NR compound is higher than that of the NBR (45\% ACN) compound (both filled with 20 phr carbon black) and hence is in accord with the published ratings\(^{(39)}\). An interesting observation from this figure is that the tensile strength of the fine textured single-stage blends is about 5 MPa higher than the predicted. Also, the fine textured single-stage blends show a positive synergism of tensile strength.
(b) Effect of Location of Carbon Black on the Tensile Strength of Masterbatch Blends

Fig. 5.42 shows the variation in tensile strength of the masterbatch blends (Sections 4.2.2-2, 4.6.1 and 4.6.2), obtained from the Hounsfield tensile testing machine (Section 4.4.6(1)). In contrast to the results of moduli, the NR90NBR10 blend shows a higher tensile strength than the NR10NBR90 blend. However, there is no significant difference between the tensile strength values of NR90NBR10 and NR50NBR50 blends, which is in agreement with the morphological observations. The significantly lower tensile strength obtained for the NR10NBR90 blend in comparison to the other two blends can be attributed mainly to its coarse textured morphology (larger domain size) as described in Section 5.5.3 (2)-(a). Thus for tensile strength, morphology has a dominant effect over carbon black distribution.

![Graph showing tensile strength variation](image)

Fig. 5.42 Influence of location of carbon black on the tensile strength of filled (20 phr, N660) masterbatch blends

It is to be noted that the effect of mixing conditions and location of carbon black on the elongation at break of the single-stage and masterbatch blends respectively have not been discussed under Section 5.5.3, since the trend in the variation of elongation at break is generally similar to that of tensile strength. The arguments put forward to explain the variation in tensile strength are generally valid for elongation at break.
(3) Tear Strength

(a) Effect of Mixing Conditions on the Tear Strength of Single-stage Blends

Measurement of tear strength using angle test pieces is a combination of tear initiation and propagation. In this case, the overall force needed to rupture the test piece is measured and cannot be separated into the two components producing initiation and propagation (BS 903: Part A3 (1982)). It appears from Fig. 5.43 that differences in domain size produced by varying rotor speed do not exert a significant effect on the overall force needed to rupture the test piece and hence on tear strength. This is probably due to similar viscoelastic losses as all four blends exhibit high-carbon black-NBR three dimensional mesh configurations. As reported by Hess and Chirico (40) for NR/SBR blends, these high-carbon black-NBR three dimensional mesh configurations also exhibit high values for tear strength due to the ability to divert the rupture path and dissipate energy along the zone boundaries.

Fig. 5.43 Influence of mixing conditions on the tear strength of filled (20 phr, N660) single-stage blends

Fig. 5.44 shows a comparison between the tear strength of single-stage blends (Sections 4.2.2-1, 4.5.1 and 4.5.2), masterbatch blends (Sections 4.2.2-2, 4.6.1 and 4.6.2) and single elastomer compounds (Sections 4.2.2-3, 4.7.1 and 4.7.2), obtained using the HounsfieId tensile testing machine (Section 4.4.6(2)). It is clear from this figure that the single-stage blends are superior in tear strength to the masterbatch blends. Literature (26) indicates that tear strength is quite insensitive to mixing time. However the single-stage blends show markedly higher tear strengths than the NR90NBR10 masterbatch blend. This may be due to the high-carbon black-NBR three
dimensional mesh configurations exhibited by all the four blends. Also, the tear strength of the single-stage blends is closer to that of the NR10NBR90 blend than to the NR90NBR10 blend. This indicates that most of the carbon black is in the NBR phase of the single-stage blends. It is also apparent from this figure that the tear strength of these blends is lower than “predicted”, but is independent of morphology. This is attributed tentatively to weak interfacial cross-linking between the two phases NR and NBR, as a crack that has propagated to the interface would continue its propagation easily through the weak interface.

![Graph showing tear strength vs weight % NR in blend](image)

**Fig. 5.44** Effect of blending conditions on the tear strength of filled (20 phr, N660) NR/NBR blends

It is interesting to note that the tear strength of single-stage blends is almost similar to the two 100% NBR compounds.

**b) Effect of Location of Carbon Black on the Tear Strength of Masterbatch Blends**

Fig. 5.45 shows the variation in tear strength of the three masterbatch blends (Sections 4.2.2-2, 4.6.1 and 4.6.2), obtained using the Hounsfield tensile testing machine (Section 4.4.6(2)). Tear strength is highest with 90% of the carbon black in the NBR phase and lowest with 90% of the carbon black in the NR phase. However the tear strength of the NR10NBR90 blend is not significantly different from that of the NR50NBR50 blend, despite the large difference in morphology (see Section 5.3.2). This indicates that the tear strength of NR/NBR masterbatch blends is not significantly affected by morphology as in the case of single-stage blends.
Higher tear strength of the NR10NBR90 blend in comparison to the NR90NBR10 blend is in agreement with the necessity for carbon black reinforcement to develop optimum tear strength of NBR and the ability of NR to exhibit an alternate mechanism of reinforcement by strain crystallisation.

(4) **HARDNESS**

(a) *Effect of Mixing Conditions on the Hardness of Single-stage Blends*

Although there was no significant difference between the modulus values of the single-stage blends at low strain (which is related to hardness), the rotor speed has a small effect on the hardness (Shore A) of the single-stage blends (Fig. 5.46). This may not be of practical importance, even though the error bars show that it is significant.
A comparison between the hardness of the single-stage blends (Sections 4.2.2-1, 4.5.1 and 4.5.2), masterbatch blends (Sections 4.2.2-2, 4.6.1 and 4.6.2) and single elastomer compounds (Sections 4.2.2-3, 4.7.1 and 4.7.2), again obtained using the Shore A Micro Hardness Tester (Section 4.4.6(3)), is shown in Fig. 5.47. This figure shows that the NBR compound is harder than the NR compound (both filled with 20 phr carbon black), possibly due to the high ACN content of NBR which results in a high Tg. Also, increased rubber-carbon black interactions in the presence of highly polar CN groups may contribute to the higher hardness of NBR, since hardness measurement (low compression strain measurement) is rather sensitive to rubber-carbon black network effects. Hence, a high-carbon black-NBR three dimensional mesh configuration in the blends should show a high hardness due to the rigid structure, as apparent from the same figure.

Hardness of the masterbatch blends is lower than that of the single-stage blends, possibly a result of an improved carbon black dispersion in the former blends due to the longer mixing time as reported by Boonstra and Medalia\(^{(26)}\). Also, the hardness of single-stage blends is higher than predicted.

![Graph](image)

Fig. 5.47 Effect of blending conditions on the hardness (Shore A) of filled (20 phr, N660) NR/NBR blends

It is noteworthy that the hardness of the single-stage blends is slightly higher than that of the control NBR (26.6% ACN) compound. Thus the single-stage blends are suitable as replacements for the control NBR compound with regard to hardness.
(b) Effect of Location of Carbon Black on the Hardness of Masterbatch Blends

The variation in hardness (Shore A) of the masterbatch blends (Sections 4.2.2-2, 4.6.1 and 4.6.2) is shown in Fig. 5.48. This comparison shows clearly that the NR10NBR90 blend has a higher hardness than the other two masterbatch blends, in accord with the moduli values. The high hardness of the NR10NBR90 blend can be ascribed to the rigid structure inherited through the high-carbon black-NBR three dimensional mesh configuration, as in the case of the single-stage blends. However, no significant difference is observed between the hardness values of the NR90NBR10 and NR50NBR50 blends. Hence the results suggest that the hardness of masterbatch blends is affected by carbon black distribution via morphology.

Fig. 5.48 Influence of location of carbon black on the hardness (Shore A) of filled (20 phr, N660) masterbatch blends

(5) ABRASION RESISTANCE

(a) Effect of Mixing Conditions on the Abrasion Resistance of Single-stage Blends

Fig. 5.49 (a) and (b) show the variation in abrasion resistance of the four single-stage blends (Sections 4.2.2-1, 4.5.1 and 4.5.2), obtained using the Akron and DIN abraders (Section 4.4.6(5)) respectively. It appears from Fig. 5.49 (a) and (b) that the abrasion resistance of the S20T20 blend is much higher than the others. The lowest abrasion resistance is shown by the S60T20 blend. The abrasion resistance of the S20T20 and S20T85 blends can be regarded as higher than that of the S60T20 and S60T85 blends. This implies that the abrasion resistance is influenced by rotor speed via the effect of morphology. S60T20 and S60T85 blends show higher extensibilities than S20T20 and S20T85 blends (Section 5.5.3 (2) (a)). Hence abrasion by roll formation which is the
mechanism of abrasion in filled compounds\textsuperscript{(41)} would be easier in the former blends thereby increasing abrasion.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig549a.png}
\caption{(a) Influence of mixing conditions on the abrasion resistance (Akron) of filled (20 phr, N660) single-stage blends}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig549b.png}
\caption{(b) Influence of mixing conditions on the abrasion resistance (DIN) of filled (20 phr, N660) single-stage blends}
\end{figure}

The Schallamach abrasion pattern\textsuperscript{(42)} of the S20T20 and S60T20 blends (Sections 4.2.2-1, 4.5.1 and 4.5.2) obtained from the scanning electron microscope is shown in Fig. 5.50 (A) and (B) respectively. In both the blends ridges were perpendicular to the direction of abrasion, which indicates that the mechanism of abrasion is the frictional mechanism. It can be seen from these micrographs that the intensity of the abrasion pattern is greater in the S60T20 blend in comparison to the S20T20 blend. Hence, the micrographs indicate that the abrasion resistance of the former is lower than that of the latter as the abrasion pattern is generally very shallow in long wearing compounds. It is also observed that the spacing between the ridges is greater in the S60T20 blend than in the S20T20 blend. This also implies that the abradability of the former is higher than
that of the latter. Thus, the abrasion patterns corresponding to the S20T20 and S60T20 blends are in agreement with the abrasion results obtained from DIN and Akron abrasion tests.

Fig. 5.50 (A) Scanning electron micrograph showing the abrasion pattern of the filled (20 phr, N660) S20T20 single-stage blend, Magnification 18.5 times

Fig. 5.50 (B) Scanning electron micrograph showing the abrasion pattern of the filled (20 phr, N660) S60T20 single-stage blend, Magnification 18.5 times
Fig. 5.51 shows a comparison between the abrasion resistance of single-stage blends (Sections 4.2.2-1, 4.5.1 and 4.5.2), masterbatch blends (Sections 4.2.2-2, 4.6.1 and 4.6.2) and single elastomer compounds (Sections 4.2.2-3, 4.7.1 and 4.7.2), obtained using the DIN abrader (Section 4.4.6(5)). The abrasion resistance of the NR compound is slightly higher than that of the NBR (45% ACN) compound. This is in accord with the published ratings\(^{(39)}\). A significant feature is that the abrasion resistance of both the types of blends is lower than that of the single elastomer compounds. The low abrasion resistance of the blends is attributed tentatively to poor adhesion between the NR and the NBR (45% ACN) phase.

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(b) *Effect of Location of Carbon Black on the Abrasion Resistance of Masterbatch Blends*

The variation in abrasion resistance of the three masterbatch blends (Sections 4.2.2-2, 4.6.1 and 4.6.2), obtained using the DIN abrader (Section 4.4.6(5)) is shown in Fig. 5.52.
It is apparent from Fig. 5.52 that the abrasion resistance is highest with most of the carbon black in the NR phase. This is in accordance with the results of tensile strength and hence elongation at break, but not in agreement with that of hardness and tear strength which normally have a greater influence on the abrasion resistance than the tensile properties\(^{(43)}\). The tensile strength and hence the elongation at break of the NR90NBR10 blend is higher than that of the NR10NBR90 blend. This may be accounted for the higher abrasion resistance of the former blend. However, quite surprisingly, the abrasion resistance of the NR50NBR50 blend is almost similar to that of the NR10NBR90 blend, despite the markedly higher tensile strength and elongation at break of the former. Hence a proper correlation cannot be drawn between the abrasion resistance and strength properties of these masterbatch blends. This may be because abrasion is a complex property and is not expected to be related simply to the strength properties.

Since the domain size of the NR10NBR90 blend is significantly larger than that of the NR50NBR50 and NR90NBR10 blends (see Section 5.3.1 (C)), the abrasion resistance of the former blend is expected to be higher than that of the latter blends according to the results of Section 5.5.3 (5)-(a). However the abrasion resistance of the NR10NBR90 blend is markedly lower than that of the NR90NBR10 blend. This implies that the effect of location of carbon black on the abrasion resistance of masterbatch blends dominates the effect of morphology. NBR compounds containing reinforcing fillers are known to have an abrasion resistance which is about 30% greater than that of comparable NR compounds\(^{(44)}\). Hence a NR/NBR blend especially containing a low level, e.g. 10% of carbon black (because abrasion differences between the rubbers diminish with increasing the carbon black loading) in the NBR phase is
expected to have a higher abrasion resistance than a blend containing the same amount of carbon black in the NR phase, which agrees with the results.

(6) COMPRESSION SET

(a) Effect of Mixing Conditions on the Compression Set of Single-stage Blends

Elasticity is an important property for the majority of rubber products, especially in fluid sealing applications. Compression set is still the most widely used test to measure this property. In many oil seal applications, low compression set is equal in importance to swelling resistance. Compression set measures the ability of a rubber vulcanisate to accommodate the displacement of seal faces. Thus it is necessary to aim at minimising compression set of NR/NBR blend compounds, so that they can be used in the manufacture of sealing products.

Fig. 5.53 shows the variation in compression set of the four single-stage blends (Sections 4.2.2-1, 4.5.1 and 4.5.2), obtained using the compression set apparatus (Section 4.4.6(4)) at room temperature.

![Fig. 5.53 Influence of mixing conditions on the compression set of filled (20 phr, N660) single-stage blends at room temperature](image)

It is difficult to conclude from Fig. 5.53, whether the rotor speed, which significantly influences morphology (as reported in Section 5.3.1 (B)) and initial NBR temperature have any influence on the compression set. However, the results of elevated temperature (70°C) measurements clearly indicate that the rotor speed exerts a marked effect on the compression set of single-stage blends, whereas the effect due to the initial NBR temperature is negligible (Fig. 5.54). It is known that at elevated temperatures, compression set measurements can be used as an indication of the cross-link density. However, EV systems have a good resistance to heat ageing due to the presence of more monosulphide cross-links. The results of the elevated...
temperature measurements indicate that the elasticity of the S60T20 and S60T85 blends is higher than that of the S20T20 and S20T85 blends. This is probably due to the difference in morphology, since results of moduli and cure analysis showed that there is no significant difference between the overall cross-link density of the four single-stage blends.

Baker et al.\(^{(38)}\) reported that filled, sulphur cured 40/60 NR/NBR blends with low hardness give poorer compression set at 70°C than those with high hardness. The results in Fig. 5.54 are in general agreement with the hardness results in Fig. 5.46. However Baker et al. did not assign any reason for this effect.

Figures 5.55 and 5.56 show a comparison between the compression set of single-stage blends (Sections 4.2.2-1, 4.5.1 and 4.5.2), masterbatch blends (Sections 4.2.2-2, 4.6.1 and 4.6.2) and single elastomer compounds (Sections 4.2.2-3, 4.7.1 and 4.7.2), obtained using the compression set apparatus (Section 4.4.6(4)) at room temperature and 70°C respectively. Although literature indicates that the compression set of NBR vulcanisates is generally good, the results of this current work show that the compression set of the NBR (45% ACN) compound is greater than that of the NR compound. This may be associated with the presence of a greater proportion of acrylonitrile in NBR, since the compression set generally deteriorates with increasing the proportion of acrylonitrile in NBR. The improvement in compression set of the NBR (45% ACN) compound over that of the control NBR compound may be due to the higher curing temperature\(^{(46)}\) and/or higher hardness (or 100% modulus).
An interesting feature is that the compression set of both the types of blends at room temperature is significantly lower than that of the control NBR (26.6% ACN) compound. This is also apparent at 70°C, but less pronounced. The masterbatch blends show a lower compression set than the single-stage blends, at room and at elevated temperature. This is most probably a result of an improved carbon black dispersion in the former blends due to the longer mixing time, as reported by Boonstra and Medalia (26).

Overall, the results suggest that the compression set of both the types of NR/NBR blends is better than that of NBR compounds formulated specifically for applications requiring good compression set characteristics such as oil seals, at normal as well as elevated temperatures.
(b) Effect of Location of Carbon Black on the Compression Set of Masterbatch Blends

Figures 5.57 and 5.58 show the variation in compression set of masterbatch blends (Sections 4.2.2-2, 4.6.1 and 4.6.2), obtained at room temperature and 70°C respectively.

It is apparent from both these figures that the compression set of the NR10NBR90 blend is higher than that of the other two blends. At room temperature, the compression set of the NR50NBR50 blend is significantly lower than that of the NR90NBR10 blend, whereas at 70°C, this difference in compression set is not so significant. The lowest compression set shown by the NR50NBR50 blend suggests that
carbon black should be equally distributed between the phases in order to improve compression set. This supports one of the requirements for minimizing compression set in single elastomer compounds proposed by Farid\(^{(45)}\), i.e. a minimum amount of fillers.

It was reported in Section 5.3.2 that the morphological pattern of the NR50NBR50 blend is somewhat similar to that of the NR90NBR10 blend, whilst the NR10NBR90 blend shows a markedly different morphology. However, this trend cannot be clearly seen from the compression set results and hence it is difficult to determine from these results whether morphology has an effect on compression set.

5.5.4 Swelling Resistance in ASTM Oil No.2 and Toluene

(a) Effect of Mixing Conditions on the Swelling Resistance of Single-stage Blends

Figures 5.59 and 5.60 show the variation in percentage swell (Section 4.4.7) of single-stage blends (Sections 4.2.2-1, 4.5.1 and 4.5.2) in ASTM oil No.2 and toluene respectively. The former is a standard oil, whilst the latter is a standard fuel, used generally in the assessment of oil and fuel resistance of a rubber compound respectively. No significant difference is observed between the percentage oil swell of the four single-stage blends in ASTM oil No.2. This implies that the overall crosslink density of all the four single-stage blends (with similar carbon black distributions) is the same, since degree of swelling mainly depends on the crosslink density. The results also indicate that the morphology does not exert a significant effect on oil swelling.

![Chart showing swelling resistance](image)
As in the case of ASTM oil No.2, no significant difference in percentage toluene swell is observed with differences in initial NBR temperature. The percentage toluene swell of S20T20 blend is slightly lower than that of the S60T20 blend, whereas there is no significant difference between the percentage toluene swell of S20T85 and S60T85 blends. Hence it is difficult to suggest whether rotor speed via its effect on morphology exerts an effect on fuel swelling.

A comparison of ASTM oil and toluene swell (Section 4.4.7) between the single-stage blends (Sections 4.2.2-1, 4.5.1 and 4.5.2), masterbatch blends (Sections 4.2.2-2, 4.6.1 and 4.6.2) and single elastomer compounds (Sections 4.2.2-3, 4.7.1 and 4.7.2) is shown in Figures 5.61 and 5.62 respectively.
As expected both percentage oil and toluene swell of NBR is very much lower than that of NR. An interesting observation is, percentage oil swell of both the types of blends fall well below the additivity line and thus closer to that of the control NBR (26.6% ACN) compound than expected. In the case of single-stage blends, it is about 5% lower than the predicted. However the percentage toluene swell of the blends is much higher than that of the control NBR (26.6% ACN) compound. This is most probably because the NBR swells quite a lot in toluene and hence the toluene can penetrate to the NR phase easily. In the case of oil, it swells NBR only slightly and thus it takes a much longer time for the oil to penetrate to the NR phase. Hence the single-stage NR/NBR blends could be used in applications requiring oil resistance where the 2-4 mass % oil swell is tolerable. The percentage toluene swell of both the types of blends fall on the additivity line and hence the NBR compounds have a far better fuel swelling resistance than either type of blend.

(b) Effect of Location of Carbon Black on the Swelling Resistance of Masterbatch Blends

Apart from crosslinking restrictions, swelling also depends on compatibility of the rubber and solvent on a molecular scale and on the type and amount of filler present in the rubber. In the presence of carbon black, the swelling is generally reduced. The higher the concentration, the lower the swelling.

Figures 5.63 and 5.64 show the variation in percentage swell (Section 4.4.7) of masterbatch blends (Sections 4.2.2-2, 4.6.1 and 4.6.2) in ASTM oil No.2 and toluene respectively.
It is clear that the oil uptake reduces with more carbon black premixed in the NR phase and thus shows a similar behaviour to SBR/NBR blends studied by Lee$^{(47,48)}$. Published ratings$^{(36)}$ indicate that NBR is far more resistant to ASTM oil No.2 than NR. Lee$^{(49)}$ has also shown that the NBR phase of SBR/NBR masterbatch blends is almost impenetrable by ASTM oil No.2 and the penetrability is unaffected by carbon black loading. Thus the degree of swelling of NR/NBR masterbatch blends in ASTM oil No.2 should be governed by the degree of swelling of the NR phase. As expected, degree of swelling in oil decreases with increasing the amount of carbon black present in the NR phase. Thus the observed variation in oil swelling resistance between the masterbatch blends can be ascribed to the amount of carbon black present in the NR phase.
Toluene resistance of NBR is not substantially greater than that of NR\(^{(36,39)}\) and hence
the NBR phase is also penetrable by toluene. Unlike in the case of ASTM oil No.2,
there is no marked difference between the percentage toluene swell of NR50NBR 50
and NR90NBR10 blends. In toluene, the concentration of carbon black will affect the
swelling of both NR and NBR phases, since both these elastomers swell considerably.
As a consequence, the carbon black distribution will not have such a great effect as in
the case of the oil, where concentration of carbon black only affects swelling of the NR
phase.

If there is a difference in the amount of carbon black present in the NR phase of the
single-stage blends then it will alter the degree of swelling, despite the same overall
crosslink density as in the case of masterbatch blends. Thus the swelling results confirm
that there is no significant difference between the carbon black distribution of the
single-stage blends.
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CONCLUSIONS

1. RHEOLOGY OF COMPONENT ELASTOMERS

(a) NR is more strongly non-Newtonian than NBR, but its viscosity is less strongly dependent on temperature at typical processing temperatures. The strong dependence of viscosity of NBR on temperature is because it contains thermoplastic regions (78% of the butadiene units are in the trans 1,4 configuration), which are sensitive to heat.

(b) At high shear rates (> 40 s⁻¹) corresponding to high mixer rotor speeds, the difference in viscosity between the pairs of masterbatches decreases as more carbon black is mixed into the NR masterbatch, a consequence of the greater increase in viscosity of NR with increasing loading of carbon black in comparison with NBR.

(c) The shear rate at which the viscosities of NR and NBR become equal (cross-over shear rate) moves towards higher shear rates with increasing temperature.

2. EFFECT OF VISCOSITIES OF COMPONENT ELASTOMERS ON BLEND MORPHOLOGY

(a) At high mixer rotor speeds resulting in high shear rates and a rapid rise in batch temperature, the viscosities of the component elastomers NR and NBR become closer to each other and hence the domain size of the blend decreases. In the case of 40/60 NR/NBR (45% acrylonitrile) blends produced at high mixer rotor speeds, a fine morphology is obtained.

(b) Domain sizes of filled NR/NBR (45% acrylonitrile) blends are markedly smaller than those of comparable NR/NBR gum blends, since addition of carbon black into a blend of NR and NBR tends to equalise the viscosities of the two elastomers by raising the viscosity of the least viscous elastomer by preferential incorporation into this elastomer.

3. EFFECT OF BLEND MORPHOLOGY ON PROPERTIES

(a) The viscosity of NR/NBR blends is not significantly affected by morphology.

(b) Moduli of NR/NBR single-stage blends are not significantly affected by morphology

(c) Tensile strength of filled NR/NBR blends is dominated by morphology. Tensile strengths of the fine textured NR/NBR single-stage blends are higher than those of
coarse textured blends. Also, the fine textured single-stage blends show a positive synergism of tensile strength. Physical properties improve greatly with more carbon black in the NBR phase (see conclusion 4-(c)), but for tensile strength domain size has a dominant effect over carbon black distribution.

(d) Tear strength of NR/NBR single-stage blends is not significantly affected by morphology.

(e) At elevated temperatures fine textured NR/NBR single-stage blends show improved compression set over those of coarse textured blends.

(f) Percentage oil swell of NR/NBR single-stage blends is not significantly affected by morphology.

4. EFFECT OF LOCATION OF CARBON BLACK ON PROPERTIES

(a) The location of carbon black in the individual rubber phases of NR/NBR masterbatch blends has a little effect on the viscosity. Viscosity increases with more carbon black mixed into the NR phase.

(b) Cure characteristics of NR/NBR masterbatch blends are not significantly affected by the location of carbon black in the individual rubber phases.

(c) Moduli and tear strength of NR/NBR masterbatch blends is highest with most of the carbon black in the NBR phase. The increase in 300% modulus and tear strength on increasing the amount of carbon black in the NBR phase is in agreement with the recognised need for carbon black reinforcement to develop optimum modulus and tear strength of NBR and the ability of NR to exhibit an alternate mechanism of reinforcement by strain crystallisation.

(d) Abrasion resistance of NR/NBR masterbatch blends is highest with most of the carbon black in the NR phase.

(e) Percentage compression set of NR/NBR masterbatch blends at ambient as well as elevated temperature is lowest with carbon black equally distributed between the phases. This conclusion is consistent with the work of previous researchers on single elastomer compounds that increasing filler loading increases compression set.

(f) ASTM oil uptake of NR/NBR masterbatch blends decreases on increasing the amount of carbon black in the NR phase. The resistance of the NBR phase to swelling by ASTM oil No.2 is unaffected by carbon black loading and hence the degree of swelling of these blends in ASTM oil No.2 is governed by the degree of swelling of the NR phase, which decreases on increasing the carbon black loading.
Toluene (or fuel) uptake also decreases on increasing the amount of carbon black in
the NR phase, but to a lesser extent than with the oil. This is because the carbon
black loading affects both NR and NBR phases, since toluene causes substantial
swelling of both these elastomers.

5. The filled NR/NBR single-stage blends could be used as replacements for the
control NBR (26.6% acrylonitrile) compound (prepared according to the same
number of rotor revolutions) with regard to physical properties such as moduli,
hardness, tear strength and compression set in applications, where the 2-4% (by
mass) oil swell is tolerable. Oil swell of the single-stage blends is about 5% (by
mass) lower than the predicted.
RECOMMENDATIONS FOR FURTHER WORK

1. Estimation of the degree of crosslinking in the individual phases of the NR/NBR blends, using the newly developed techniques would be useful for interpretation of the properties of these blends.

2. One method to promote interfacial connectivity in two-phase rubber blends is to introduce a block or graft copolymer that contains two segments identical or miscible with each phase, which is generally known as a polymeric compatibilizer. Hence it would be interesting to investigate the effect of newly synthesised diblock copolymers of (i) isoprene and butadiene (ii) isoprene and acrylonitrile as compatibilizers in NR/NBR blends.

3. Crosslinking between the phases or in other words covulcanisation is important for good physical properties. Lack of covulcanisation generally results from diffusion of accelerators from one phase into the other. Hence it is suggested to substitute the primary accelerator TMTD with an equimolar quantity of a higher alkyl thiuram disulphide which has a solubility parameter midway between that of NR and NBR (45% ACN) and at the same time giving almost similar cure rates for the two elastomers, so that an even distribution of crosslinks between the phases (a necessity for covulcanisation) can be achieved.

4. More conclusive evidence for the preferential location of carbon black in the NBR phase of the single-stage blends would have been obtained from a comparison of the physical properties of the single-stage blends with that of the masterbatch blends, if the total mixing time employed in the preparation of these two types of blends (at equal rotor speed) was the same. Hence it is suggested to prepare the masterbatch blends with a total mixing time equivalent to that of the single-stage blends (at equal rotor speed), so that location of carbon black in the single-stage blends can be investigated via comparison of physical properties of the two types of blends.

5. It would be interesting to study the variation of internal mixer torque curves of the three masterbatch blends with mixing time to determine if it is possible to relate them to the different morphological features of these blends.
6. In electron microscopy, slight thickness differences give rise to the mechanism of contrast between phases. Hence thickness variations due to cutting action must be virtually eliminated. It is recommended to use diamond knives instead of glass knives especially for carbon black loaded vulcanisates in order to minimise thickness variations due to the cutting action and hence to produce thin, uniform ribbons of sections regardless of the number cut. It is also recommended to cut thin sections under a nitrogen atmosphere using an ultramicrotome in order to avoid formation of holes due to degradation when exposed to air, which greatly obscures phase identification.
# Appendix

<table>
<thead>
<tr>
<th>Mixing step</th>
<th>Time period (min.)</th>
<th>Temperature (°C)</th>
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<tbody>
<tr>
<td>1. Mixing of polymer</td>
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<td>30</td>
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<tr>
<td>2. First cooling cycle for mixing polymer and carbon black</td>
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<td>10</td>
</tr>
<tr>
<td>3. First heating cycle for mixing polymer and carbon black</td>
<td>4</td>
<td>100</td>
</tr>
<tr>
<td>4. Second cooling cycle for mixing polymer and carbon black</td>
<td>3</td>
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</tr>
<tr>
<td>5. Second heating cycle for mixing polymer and carbon black</td>
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<td>6. Low temperature mixing of oil and curatives with the elastomers</td>
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Table 1: The cyclic mixing procedure of Lee (Ref. 76 of Chap. 2)
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<td>-CH₂⁻</td>
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<tr>
<td>-C= aromatic</td>
<td>98.12</td>
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<tr>
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<tr>
<td>-O= (epoxide)</td>
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<tr>
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<tr>
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Table 2: Tabulated values of group molar attraction constants (cal.cm³)¹/² mol⁻¹ according to Hoy (Ref. 13 of Chap.4)
Fig. 1: Force vs % extension curve showing the tensile behaviour of the filled NR compound
Fig. 2: Force vs % extension curve showing the tensile behaviour of the filled NBR compound
Fig. 3: Force vs % extension curve showing the tensile behaviour of the S60T20 single-stage blend
Fig. 4: Force vs extension curve showing the tearing behaviour of the filled NR compound
Fig. 5: Force vs extension curve showing the tearing behaviour of the filled NBR compound.
Fig. 6: Force vs extension curve showing the tearing behaviour of the S20T20 single-stage blend