Internal mixing of rubber: the influence of process variables on mixed material properties

This item was submitted to Loughborough University's Institutional Repository by the/an author.

Additional Information:

- A Doctoral Thesis. Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University

Metadata Record: https://dspace.lboro.ac.uk/2134/13153

Publisher: © Peter Cheriton Ebell

Please cite the published version.
This item was submitted to Loughborough University as a PhD thesis by the author and is made available in the Institutional Repository (https://dspace.lboro.ac.uk/) under the following Creative Commons Licence conditions.

For the full text of this licence, please go to:
http://creativecommons.org/licenses/by-nc-nd/2.5/
INTERNAL MIXING OF RUBBER: THE INFLUENCE OF PROCESS VARIABLES ON MIXED MATERIAL PROPERTIES

by

PETER CHERITON EBELL
MSc, Grad.PRI

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

November 1981

Director of Research: Professor A.W Birley
Supervisors: Mr P K Freakley, Institute of Polymer Technology
and Mr J R Buxton, Department of Engineering Mathematics

© by PETER CHERITON EBELL (1981)
To my parents, and my wife
I certify that I am responsible for the work submitted in this thesis, that the original work is my own except as specified in acknowledgements, and that neither the thesis nor the original work contained therein has been submitted to this or any other institution for a higher degree.
ACKNOWLEDGEMENTS

It is the special privilege of authorship, that at the end of one's exertions, it is possible to pause, look back and formally thank the many people without whose active participation, the scheduled completion of a doctoral thesis would have been impossible.

Mr Phillip Freakley, in addition to being an effective and extremely conscientious supervisor, is also endowed with a gently persuasive manner. This combination was ideal in guiding me through the perilous area of rubber mixing. I thank him for all the encouragement and support he gave me through the last two or so years.

Mr Richard Buxton, without whom the mathematical and computing aspects of this study would have been nowhere as effective as presented here. It is comforting to have been associated with a practising statistician so ready to participate in experimentation as he was.

In addition to my two formal supervisors, I had the good fortune to be associated with another expert, this time in the field of polymer microscopy. I am indebted to Mr Derek Hemsley for having readily yielded so much of his time to inculcate in me an appreciation of the techniques of his specialism.

To Professor Arthur Birley, for his administrative skills; through which originally I arrived at the IPT, and later because of which I could afford to stay on.

My thanks also go out to the following individuals, groups and companies for sustained help during my research programme:

Mr Keith Shepherd who took the vast number of photographic negatives over and emerged from the darkroom with all the prints necessary to complete this visual project.
The Mixing Group, IPT, for all their long discussions which helped to crystallise several important ideas. Of the group my special thanks go to Dr Suresh Patel whose cheerful alacrity never ceased to lift me.

In Dunlop Ltd. Technology Division, I had for all intents and purposes a sponsoring company. Individually, Mr Pat Oubridge, Mr Doug Hubbard, Mr Martin Walters, Mr Bill Burdock and Mr Denis Keyte were my contacts; I could not have hoped for a more interested and aware group of industrialists anywhere.

To Dr Jean Leblanc of Monsanto, Belgium, and Dr Mike Bristow of the NRPRA, Hertfordshire; also to Farrel Bridge Ltd. and Francis Shaw Ltd., who both make excellent mixing machines.

My thanks to the newly renamed Science and Engineering Research Council (formerly SRC, now the SERC) for financial support during this period of research.

A big word of thanks to Mrs Janet Smith, the most efficient typist I know; who converted the products of a fevered mind and a scrawling hand, to the typescript in front of you.

Finally to my wife Jill, for the help during analysis and compilation of the results presented here, and for her patient proof-reading. Her tolerance throughout the years of my higher education never ceased to amaze me.
ABSTRACT

The work is divisible into three interconnected areas, the first of which is concerned with the empirical modelling of the rubber internal mixing process. Here, the mixing machine variables were changed in a statistical experimental design, and several resulting dispersion dependent material responses monitored. The values of these were next combined into a composite function which related to the goodness of mixing. A response equation in terms of this function and the process variables was obtained by regression analysis. Other response equations derived were for relating mixing time and dumped stock temperature to the input variables. These graduating functions were tested for adequacy of fit; graphical representations of the predictions of the models are shown in the form of contour graphs and isometric projections (both hard copy and colour graphics). These show visual evidence of the influence of each machine variable (and interaction) on the mixing process as a whole. Also by these means, it was possible to establish optimum conditions of mixing.

Next nominally identical carbon blacks from different manufacturing locations were mixed into rubber at defined processing conditions. From tests on these mixes the blacks were noted to have different dispersibilities. This was possibly attributable to the varying fines fractions and moisture contents in the test carbon blacks. To check this hypothesis, these factors were varied systematically in two common black types. The compounds resulting from mixing these experimental blacks were subjected to a wide range of tests to establish whether fines or moisture significantly affected dispersibility of blacks in rubbers.

During the preceding work, and also in the course of a critical review included here, it became evident that the commonly used methods for establishing dispersion (and thus mixing efficiency) were lacking, from several points of view. Therefore lastly a technique based on
the analysis of an image of a cut rubber surface viewed by dark field reflected light microscopy was developed. Specimen preparation is simple and analysis is accomplished using a standard television system and oscilloscope. This method yields results which discriminate between all levels of black dispersion and also correlate admirably with a variety of processing, mechanical and microscopical properties. In the final stages of the work the capabilities of the method were expanded (in cooperation with Dunlop Ltd, Technology Division) by interfacing a computer and peripherals with the original equipment; such that data acquisition, manipulation and parameter output was made easier, faster and thus more effective than in the initial concept.
## CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER 1: A REVIEW OF THE DISPERSION OF CARBON BLACK BY INTERNAL MIXING</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 Internal Mixing</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Carbon Black</td>
<td>13</td>
</tr>
<tr>
<td>1.3 The Mixing of Rubber Compounds - an Integrated Approach</td>
<td>17</td>
</tr>
<tr>
<td>1.4 General Objectives of this Research</td>
<td>19</td>
</tr>
<tr>
<td>Literature cited</td>
<td>20</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CHAPTER 2: THE THEORY AND PRACTICE OF CARBON BLACK DISPERSION IN RUBBER</th>
<th>22</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 The Mechanics of Mixing</td>
<td>22</td>
</tr>
<tr>
<td>2.2 The Theoretical Considerations of Dispersive Mixing</td>
<td>25</td>
</tr>
<tr>
<td>2.3 The Practicalities of Mixing</td>
<td>35</td>
</tr>
<tr>
<td>2.4 Estimating the Adequacy of Mixing</td>
<td>40</td>
</tr>
<tr>
<td>Literature cited</td>
<td>42</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CHAPTER 3: METHODS OF ASSESSING CARBON BLACK DISPERSION IN RUBBER MIXES - A CRITICAL REVIEW</th>
<th>44</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 Test Groupings</td>
<td>44</td>
</tr>
<tr>
<td>3.2 Processing Properties</td>
<td>46</td>
</tr>
<tr>
<td>3.3 Vulcanisate Properties</td>
<td>53</td>
</tr>
<tr>
<td>3.3.1 Static tests</td>
<td>53</td>
</tr>
<tr>
<td>3.3.1.1 Strength properties</td>
<td>53</td>
</tr>
<tr>
<td>3.3.1.2 Stiffness properties</td>
<td>59</td>
</tr>
<tr>
<td>3.3.2 Wear properties</td>
<td>61</td>
</tr>
<tr>
<td>3.3.3 Non-destructive dynamic properties</td>
<td>64</td>
</tr>
<tr>
<td>3.3.4 Other physical properties</td>
<td>73</td>
</tr>
<tr>
<td>3.3.5 Destructive dynamic tests - cut growth and flex fatigue</td>
<td>74</td>
</tr>
</tbody>
</table>
CHAPTER 3: MEASUREMENT OF POLYMER MODIFICATIONS

3.4 Measurement of Polymer Modifications

3.5 Measurement of Black-Rubber Interaction

3.6 Electrical Properties and Other Energy Based Tests

3.7 Measurement of Viscoelastic Properties

3.7.1 Stress relaxation

3.7.2 Creep

3.8 Surface Testing

3.9 Miscellaneous Other Methods

3.10 Microscopy

3.10.1 Light microscopy

3.10.2 Microradiography

3.10.3 Electron microscopy

3.11 Discussion

3.12 The Definition of a Further General Objective (of research)

3.13 Literature cited

Page No

77
78
81
82
85
88
92
93
100
101
102
104
105

CHAPTER 4: THE DEVELOPMENT AND PROVING OF A NEW MICROSCOPICAL TECHNIQUE FOR ASSESSING DISPERSION OF CARBON BLACK IN RUBBERS

4.1 Research Leading up to the Main Method

4.2 Proposed New Method

4.3 Description of the System Equipment

4.4 Specimen Preparation

4.5 Experimental Procedure

4.6 Analysis of Results

4.7 Mixing of the Experimental Proving Compounds

4.8 Compound Testing/Microscopy

4.9 Mechanical Surface Roughness Measurements

4.9.1 Operating procedure

4.10 Results and Discussion

4.11 Conclusions

4.12 A Case Study

4.13 Literature cited

Page No

116
117
136
138
139
140
141
144
148
155
160
163
258
268
273
<table>
<thead>
<tr>
<th>Chapter 5: The Evaluation of a Prototype Automatic Dispersion Tester</th>
<th>Page No</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1 Description of New Equipment</td>
<td>276</td>
</tr>
<tr>
<td>5.2 Experimental</td>
<td>283</td>
</tr>
<tr>
<td>5.3 Results and Discussion</td>
<td>287</td>
</tr>
<tr>
<td>5.4 Conclusions</td>
<td>314</td>
</tr>
<tr>
<td>5.5 Further Work</td>
<td>319</td>
</tr>
<tr>
<td>Literature cited</td>
<td>322</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 6: The Empirical Modelling and Optimisation of the Internal Mixing Process</th>
<th>Page No</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1 Introduction</td>
<td>323</td>
</tr>
<tr>
<td>6.2 The Variables of Internal Mixing and Their Effects on the Process</td>
<td>324</td>
</tr>
<tr>
<td>6.2.1 Ram pressure</td>
<td>324</td>
</tr>
<tr>
<td>6.2.2 Temperature of the mixer components</td>
<td>326</td>
</tr>
<tr>
<td>6.2.3 Fill factor</td>
<td>328</td>
</tr>
<tr>
<td>6.2.4 Rotor speed</td>
<td>330</td>
</tr>
<tr>
<td>6.2.5 Dump criteria</td>
<td>332</td>
</tr>
<tr>
<td>6.2.6 General comment</td>
<td>334</td>
</tr>
<tr>
<td>6.3 The Objectives for this Area of Research</td>
<td>335</td>
</tr>
<tr>
<td>6.4 Some Background on Modelling</td>
<td>336</td>
</tr>
<tr>
<td>6.5 Selection of an Experimental Design for Estimating the Parameters of a Polynomial Model</td>
<td>338</td>
</tr>
<tr>
<td>6.6 Analysis of Data</td>
<td>341</td>
</tr>
<tr>
<td>6.7 Judging the Adequacy of Estimation by an Approximating Response Function</td>
<td>343</td>
</tr>
<tr>
<td>6.8 Presentation of Results (Experimental Section A)</td>
<td>344</td>
</tr>
<tr>
<td>6.9 Results and Discussion of Experimental Section A</td>
<td>349</td>
</tr>
<tr>
<td>6.9.1 Dump criteria</td>
<td>349</td>
</tr>
<tr>
<td>6.9.2 Processing/vulcanisate properties</td>
<td>358</td>
</tr>
<tr>
<td>6.10 Conclusions on Experimental Section A</td>
<td>361</td>
</tr>
<tr>
<td>6.11 Experimental Section B</td>
<td>362</td>
</tr>
<tr>
<td>6.11.1 Introduction</td>
<td>362</td>
</tr>
<tr>
<td>6.11.2 The desirability function</td>
<td>363</td>
</tr>
</tbody>
</table>
6.11.3 The experimental strategy

6.12 Experimental Work

6.12.1 The experimental design

6.12.2 Mixing procedure and testing of the compounds

6.12.3 Assigning values of the desirability function to each of the experimental runs

6.13 Results and Discussion

6.13.1 The regression of D, mixing time and dump temperature

6.13.2 Adequacy of fit of the three models

6.13.3 The influence of the variables of mixing on the responses

6.14 Conclusions

6.15 Recommendations for Further Work

Literature cited

CHAPTER 7: THE INFLUENCE OF CERTAIN SECONDARY CARBON BLACK PROPERTIES ON RUBBER STOCKS PRODUCED BY INTERNAL MIXING

7.1 Introduction

7.2 The Background of the Problem

7.3 Objectives of this Segment of Research

7.4 Experimental Methods Used

7.5 Results and Discussion

7.6 Conclusions

7.7 Further Work

Literature cited

CHAPTER 8: SUMMARY AND CONCLUDING REMARKS

APPENDICES:

1 AUTOMATIC ANALYSIS TECHNIQUE

AI Description of Video Interface Board

AII Computer Program
<table>
<thead>
<tr>
<th>Page No</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>468</td>
<td>ANALYSIS OF EXPERIMENTAL DATA - MVRA BY LEAST SQUARES</td>
</tr>
<tr>
<td>475</td>
<td>THE GLIM PACKAGE</td>
</tr>
<tr>
<td>481</td>
<td>CONTOUR GRAPHING PROGRAMME</td>
</tr>
<tr>
<td>483</td>
<td>ISOMETRIC PROJECTION PROGRAMME</td>
</tr>
<tr>
<td>485</td>
<td>RELATIONSHIP BETWEEN AIR LINE AND SPECIFIC RAM PRESSURE IN THE OOC BANBURY</td>
</tr>
<tr>
<td>486</td>
<td>FORMULATIONS OF VARYING FILL FACTOR FOR OOC BANBURY</td>
</tr>
<tr>
<td>487</td>
<td>COMPLETE TABLE OF RESULTS FOR THE SIXTY-TWO RUN EXPERIMENTAL DESIGN</td>
</tr>
<tr>
<td>488</td>
<td>FLOW CHART FOR PROGRAMME FOR CALCULATION OF THE DESIRABILITY FUNCTION</td>
</tr>
<tr>
<td>489</td>
<td>DESIRABILITY FUNCTION PROGRAMME</td>
</tr>
<tr>
<td>490</td>
<td>PRINT-OUT OF DESIRABILITY VALUES (LOWER CASE) FOR ONE RESPONSE</td>
</tr>
<tr>
<td>491</td>
<td>DESIRABILITY FUNCTION PRINT-OUT FOR THE SIXTY-TWO POINT EXPERIMENT</td>
</tr>
<tr>
<td>492</td>
<td>COLOUR GRAPHICS PROGRAMME</td>
</tr>
</tbody>
</table>
1.1 Internal Mixing

In 1820, a London coachmaker had the germ of an idea, the consequences of which were to be remarkably far reaching.

The man was Thomas Hancock who is generally recognised as the father of the rubber industry. He visualised, manufactured and improved a machine whose basic principles and functions were much later to give rise to the workhorse of the rubber industry, the internal mixer.

At the time he manufactured novelty items from sheet rubber such as stocking and glove tops (like the garters and elasticated wrist bands of today), waistcoat backs, pickpocket proof pocket tops and so on. Hancock required a method of working waste off-cuts of sheet rubber, resulting from the manufacture of these products, back into a reuseable coherent form. Additionally, he needed to convert his imported raw material from the awkward and irregular state in which it was delivered, to a more convenient form. After several months of vexatious and futile endeavour, he designed and manufactured the first small experimental model of his "Pickle"; the first internal mixer.

![Hancock's "Pickle"](image.png)
In his experimental observations, Hancock describes the effect of continued rotation of the inner cylinder on the pieces of rubber inside the contraption. Heat generation, the beneficial effects of mastication, filling the chamber to various degrees, using different roller speeds, and the effect of heating the rubber before compaction are all meticulously detailed. Hancock writes: "During the process of mastication I sometimes introduced colouring matters: they combined perfectly with the rubber". Thus, the first shaky steps had been taken in the internal mixing of compounding ingredients into rubber. Progression from the original wooden one man powered machine, to a geared variant, constructed of metal and operated by two men took place. Finally, the inventor dispensed with the teeth on the shearing surfaces in favour of a fluted construction, the new device being driven by a horse mill. During these evolutionary improvements, the possible charge increased from about two ounces to two hundred pounds.

Hancock's masticator slowly gave way to the two roll mixing mills, and from about 1860 onwards these were used almost exclusively for mastication and mixing. This is somewhat surprising in conceptual terms, since shearing over a surface must have been more efficient than nip shear in terms of economy of time. It can only be surmised that the engineering capabilities and knowhow of the period precluded the possibility of producing a heavy duty efficient internal masticator/mixer. That Hancock was decades ahead of his time is now apparent; in fact, the stringent needs of mixing technology have recently prompted a return, almost to his original idea, in the shape of the 'Rutital Monomix'.
It is evident that the geometry of this new mixer is not identical to that of Hancock's Masticator, but the return to the mono-rotor enclosed mixer concept must be regarded as commending a design more than a century and a half old.

In the second decade of the twentieth century, the rubber industry was on the threshold of the growth that has since brought it to its present position in the world economy. The motor car was superceding the horse, and the truck was beginning its rise as the major transporter of commodities. Compounded rubber was needed, in steadily increasing volume for a myriad of vehicular applications.

The time consuming laborious operation of mill mixing was badly out of step with the times. Apart from being highly wasteful of time, and labour intensive, mills took up a great deal of space that could be used to better advantage: further the fine compounding ingredients used in mixing blew around the plant at the slightest provocation, escaping the mill and becoming highly objectionable flying dirt. Since the mill mix required considerable manual manipulation, the workers suffered from dermatitis due to the adverse
effects of the chemicals used, in addition to the respiratory complaints caused by the polluted atmosphere of a mixing shop.

Considering the above, the reader will perceive that the wide adoption of the open mill in the industry was a somewhat retrograde step, especially in the light of the prior existence of a closed mixer design. It would appear that with adequate development, a satisfactory device could have emerged, which would have solved the problems of mill mixing to a great extent.

In 1916, Fernley H Banbury, a Cornish engineer who migrated to the USA revived Hancock's idea of internal mixing. In a period of employment with Werner and Pfleiderer of Saginaw, Michigan which led to an interest and an understanding of machinery, Banbury recognised the need for an effective mixing machine for rubbers. Werner and Pfleiderer had already at this time started the development of a mixing machine at their Peterborough plant in England. Banbury (by this time having definite ideas on the subject) disagreed with the manner in which the company was handling the development work. He set himself the task of improving one of the original Werner and Pfleiderer machines sited at the American Metal Cap Co, Brooklyn, mostly in his own time, and in the cheapest and quickest way possible. He changed the rotor geometry slightly, and added a wooden floating weight that acted on the rubber in the mixing cavity. Disagreement with Werner and Pfleiderer prompted Banbury to file a patent in his own name, which was granted. Figure 1.3 indicates the original design of this mixer.
FIGURE 1.3 The Original Banbury Design

Soon after, Banbury joined the Birmingham Iron Foundry of Derby, Connecticut, (manufacturers of heavy machinery for the rubber industry), where he installed the first 'Banbury Enclosed Rubber mixer' in a testing room at the plant. It was here that Banbury spent much of his time during the next few years as an operator, learning the art of mixing, and at the same time extracting first hand information to help him with the many improvements he was to make in the period ahead. Most of these were engineering design changes which improved the reliability of the machine. Dust seal construction, rotor bearing and metal type selection, gearbox motor location and the drive coupling were some of the initial worries, and these still remain topical, even to this day. At the same time however, Banbury also initiated many process control improvements,
such as dual speed motors for variable speed mixing, identifying the need for certain stocks to be mixed at quite specific loadings if mixing was to proceed effectively and many others. The idea of water tempering units for internal mixers (recently resurrected) is not new, for Banbury found the disadvantages of a cold mixer in no uncertain terms, when a batch was unceremoniously deposited unmixed at his feet one Winter's day.

Since the birth of the original internal mixer several changes have taken place both commercially and technologically. No longer do Banbury mixers hold a monopoly (even though the use of the word as a generic term might convince a listener otherwise). Werner and Pfleiderer have recovered from their original design problems. Francis Shaw and Co. make the well known Intermix, and Baker Perkins has its share of the market. A variety of general designs and rotor shapes are presented in Figures 1.4, 1.5 and 1.6 to illustrate the diversions from the main theme.

The first workable internal mixer used by the Goodyear Tyre and Rubber Co. Akron, Ohio, paved the way for the widespread use of internal mixers throughout the industrial world. Improvements and refinements are continually being made; these include dust-seal design, comprehensive instrumentation, alterations to geometry of coolant passages, rotor geometry, hopper construction, ram configuration, mixer drives, discharge door design and considerable material loading improvements.

Apart from these vital engineering developments, increased flexibility for the mixing technologist has also been provided for by the machine manufacturers. In making these changes, it is obvious that a realisation that every rubber compound is not alike and does not mix equally well at preset machine conditions has come about. The following process control based modifications and mixing accessories have accrued from this philosophy.
Figure 1.4 Differing Mixer Types
FIGURE 1.5  Banbury Rotor Configurations
FIGURE 1.6  Other Mixer Rotor Configurations

- (c) WERNER PFLEIDERER
- (d) SHAW INTERMIX
Temperature control systems - Historically, mixers have been cooled. The advent of tempering units have provided the process controller with the facility for preselected temperatures to match the type and preference of the batch being mixed. A schematic drawing of a commercially available system is shown in Figure 1.7 below:

A further refinement is that a temperature differential between two components (for example the chamber wall and the rotors) of the mixer may be selected by either individually setting the thermostat controls, or even by varying the coolant/heating medium flow rates of several areas with respect to one another.

Rotor speed - The first size 11 Banbury sold had a fixed rotor speed of 20 rpm. Modern machines have the potential for greater than three times this, and now infinitely variable rotor speeds (scaled to a top speed of about 120 rpm in a size 11 machine) plus the option of individually driven rotors (in dual drive mixers) are available at a price. The concept of variable speed mixing
(changing peripheral rotor tip speed during a cycle) was proposed seventeen years ago, as a solution to the different shear strain rate needs of the various stages during a rubber mixing.

**Friction Ratio of Rotors** - This development directly accruing from the dual drive referred to above is another weapon in the armoury of the modern mixing technologist. In the context of open mills, this quantity is defined as the ratio of the individual revolving speeds of the front and back rolls.

Similarly, stated nominal friction ratios in Banbury mixers are about 1.15:1 and it is claimed that by changing this slightly it is possible to 'fine tune' this machine parameter to suit a particular compound. Not much more literature has emerged since the original postulation in 1973. In mixers such as the Banbury however, nominal friction ratios have little meaning, since no axial or radial symmetry exists in the rotors. Thus, different rotor speeds cause a spectrum of 'real' friction ratios, depending not only on the location of one rotor with respect to the other at a given point in time, but also the specific area of either rotor being considered. This variable obviously does not exist in mixers such as the Intermix where the rotors turn at equal speeds. (Even so, in these a 'pseudo friction ratio' is generated by virtue of differential peripheral speeds at different points of the irregular rotor geometry).

**Ram Pressure** - As originally introduced by Banbury, the ram (or floating weight) was an after thought, being added initially only to help stuff material into the mixing chamber. When its importance was realised, pneumatic operation was introduced, and later cylinder diameters increased. Controls were then added to enable the operator to vary the specific pressure on the batch, by altering the air line pressure feeding the cylinder. A range of specific pressures is used practically ranging from about 0.07 MPa to 0.5 MPa in an F620 Banbury using a 65 cm diameter cylinder. (Note: some
years ago Farrel Bridge and Co. who manufacture Banbury mixers changed the notation identifying the different sizes of machines. The old size 1, 3, 11 and so on related to the number of 60 inch mills a machine could replace. The new notation, for example F620 refers to the capacity of the mixer, in litres).

**Fill factor** - This refers to the fraction of the free volume of the mixer occupied by the batch, where

\[
\text{Fill factor} = \frac{\text{Mixed batch size (kg)}}{\text{Mixer volume (litres) } \times \text{Finished batch S.G (kg/l)}}
\]

(1.1)

The free volume of the new F series Banbury mixers is specified as a model identifier, as noted in a previous paragraph. (Thus F620, F370 and so on).

(In general the practical range of loading of internal mixers varies from about 0.6 to 0.85, depending on quality standards required, compound viscosity, filler and oil loading, ram pressure and internal mixer geometry.

**Dump Criteria** - Finally, the processor has to decide when to terminate a mixing cycle. Historically, time was used as a criterion, the mixed batch being dropped after a preset period of mixing. Dumping, when a rubber attains a predetermined temperature during mixing is an alternative, as is discontinuation of the process when a specified amount of energy has been dissipated. The most recently proposed criterion has been heat history; here, the times spent by a batch at different mixing temperatures are weighted with respect to their relative influence on curing, and these weighted functions are summed. Dumping of the batch takes place when a preset number of transformed degree-seconds is reached.
The theoretical bases for the adoption of the foregoing process variables will be discussed at length in Chapter 6.

Mention must be made here of the concept of continuous mixing; which is attractive and is gaining ground fairly rapidly. The Werner Pfleiderer EVK single screw mixing extruder, the Uniroyal Transfermix, the Farrel Continuous Mixer, the NRM Plasticscrew and the Pirelli Continmix are all commercial mixers of the continuous type. The Farrel Bridge MVX, the Stewart Bolling Mixramat, and the Baker-Perkins MPC/V, are the newer additions to the line, being pushed strongly by these manufacturers, for use in both the plastics and rubber industry. These developments however will be ignored in the course of this dissertation: the reason being that considerable capital expenditure has been made by rubber manufacturers investing in the more established internal mixer. One of the theses postulated here, is that more effective use of the older mixing equipment (in which so much capital is associated) is possible once the variables contributing to process efficiency are more completely understood. Moreover, due to cost considerations, continuous mixers do not appear to be overpoweringly popular at the present day. The extruder type continuous mixer has poor mixing ability, (even when fitted with a special purpose screw) and is not claimed as a primary mixer, as it requires premassed or mixed material. The twin screw type mixers (publicised as being primary in operation) need free flowing materials in particulate form for feeding, are very difficult to clean, and are more costly than comparable capacity internal mixers. On balance it appears conclusively that internal mixers will be in use for some time to come.

1.2 Carbon Black

It is perhaps coincidental, that just as the demand for reliable motor car tyres was expanding, another important discovery gave the industry a much needed boost. S C Mote of the India Rubber Gutta Percha and Telegraph Works at Silvertown discovered
the value of carbon black in rubbers, and showed that this material had the effect of increasing the mechanical performance of rubber (especially abrasion resistance) much beyond anything previously known.

Pneumatic tyres had been invented by J B Dunlop in 1888\textsuperscript{22}, but due to the inferior quality of both the reinforcing member and the tread, the demand for (and the mileage possible from) the article remained at a low level. Despite the fact that Mote had discovered black as a reinforcing agent in 1904, it was only after the introduction of cord construction for tyres by J F Palmer\textsuperscript{23} in 1908, that carbon black came into its own. Till 1916, mills were thought sufficient to produce the ever increasing supplies of black compounded rubber required by the tyre industry. Internal mixers were established just when an explosion in the demand for tyre rubber was taking place, and ever since then the material has been by far the major reinforcing filler used. The rubber industry consumes 95\% of all carbon black production, the chief method for incorporating it into elastomers being the process of internal mixing.

Carbon black had been used in rubber compounding by Hancock in the form of non-reinforcing lamp black as a cheapener. In 1864, Wright\textsuperscript{2} in the States commenced production on a commercial scale of the black used as a pigment in the paint and printing trades. The black used by Mote for strengthening rubber, was made by the Channel process, first worked by McNutt\textsuperscript{2} in 1892. This variety of black was produced by the deposition of soot from ventilated, illuminating gas flames on reciprocating iron channels. Due to economical and ecological constraints this method was superceded by the furnace (and to some extent the thermal) processes prevalent today.

Very early on in the exploration of this strange synergism between rubber and carbon black, it was found that the effects of reinforcement were more marked the smaller the particle size of
black used. In addition it was realised, for effective action the black had to be dispersed and distributed evenly within the major elastomeric phase. Early workers\textsuperscript{24-26} noted the changes in properties caused by increasing the surface area of filler in contact with the polymer. Twiss and Weigel\textsuperscript{2} drew attention to the importance of 'the smoke-like dispersion of black in rubber', necessary for optimum reinforcement. This refers to the desired colloidal state required of the material within the continuous phase.

A milestone in the history of carbon black was the invention by Wiegand in 1927 of a process for making carbon black into a 'dustless' form\textsuperscript{27}. This innovation contributed considerably to the cleanliness of mill rooms, already rendered neater by introduction of the internal mixer. The pelletisation stage also added to the flow properties of the carbon black (its fluidity), reduced it in volume, and made bulk storage and handling more convenient than ever before.

The next logical step in the evolution of mixing technology (given the improved black pellets and the manufactured volume demanded by industrial and domestic users of rubber products) was the streamlining of material handling systems for compounding ingredients. Previously carbon black had always been sold to customers in the bagged form, and the route from this raw form to compounded stock was highly labour-intensive (in an already highly capital intensive industry). Added to this, due to increased volumes being progressively handled, mixing shops were again returning to being the dusty and dirty places they used to be in the pre-pelletisation/internal mixer period. The insidious, spreading nature of carbon black (one kilogram of which has a coverage of about 50 acres) was again a major problem.

This emphasis on materials handling systems had one prime objective. It was to restrict filler delivered by the manufacturer
to a closed storage and conveying system which would feed the mixer directly. Manufacturers now began the bulk transport of carbon black in tankers to sites where it was transferred directly to storage bins or silos. In the early days of bulk handling, material feeding into the mixer was manual but not very long after followed automatic weighing systems (now computer controlled); these incorporate weigh hoppers below the bulk bin (often flexible with a fluidisation or agitation facility), and complex feed systems of both the continuous and the rapid fire batch type. Conveyance of the black from one point to another is done by means of closed pneumatic systems. Figure 1.8 shows one of the infinite number of combinations of handling systems possible in a mixing shop.

FIGURE 1.8 An Automated Handling System
As a result of the introduction of bulk transport, mechanised storage, automated mixing production flow lines and centralised hopper loading the pellet properties of carbon black became critical. As a consequence of this handling, the material is subjected to higher forces, more than bagged black ever used to be. The pellets suffer attrition in conveying systems, producing fines and this, in addition to nullifying the pelletising operation, causes problems of blockage in bulk handling systems due to bridging, plugging and the formation of cake (especially in moist blacks).

Black manufacturers then tended to make rather stronger and denser pellets, in an effort to inhibit breakdown in conveying systems. This caused immense problems during the incorporation and dispersion of carbon black in rubber. Hard aggregates, which persisted even after severe mixing, affected the material properties considerably for the worse.

A compromise solution was reached between the two extremes, probably by trial and error. The lack of literature on the subject of pellet properties (which was a topical problem in the 1960's) suggests that strong scientific reasoning was either lacking, or did not work in this instance. Another distinct possibility was that the carbon black manufacturers (who would be the main researchers into their own problems) took recourse to confidentiality for reasons of their own. In the search for the ideal pellet several secondary carbon black properties have become of interest; pellet hardness, fines content, attritability, moisture content, mass strength, pellet size distribution, bulk density and individual pellet strength have been studied, with few conclusions of any worth accruing.

1.3 The Mixing of Rubber Compounds - an Integrated Approach

Three technical disciplines interact in the mixing of rubbers. These are:

- Equipment design
Process engineering
and Materials science

Simply, designers are responsible for producing the most effective mixing machines to suit the industry in general. The material scientist selects the ingredients to be mixed on the basis of subsequent downstream processing and ultimate product performance required from the mixed compound. It is the job of the process engineer to take this recipe and mix it as effectively and safely as he can utilising the special features of the mixer; maximising the properties of the mixture in the process, and at the same time being cognisant of the economics of labour and energy so important in achieving commercial profitability.

Working independently, specialists in the above disciplines have realised significant improvements such as high speed mixers, energy controlled mixing, optimised black and oil loading; also the development of hard-wearing easy processing compounds made from carefully balanced polymer blends and compounding ingredient recipes. It appears that the equipment designers and material scientists/compounding technologists have achieved more than the process engineers in the rubber industry.

To maximise the flexibility and efficiency of processing these materials on the excellent equipment available to the rubber industry, an exploration and quantification of the effects the important process variables have on mixed material properties must be accomplished. Such areas as the relationship between the different engineering parameters (such as rotor speed, ram pressure) processing criteria (dump standards, fill factor) and material variables (carbon black make-up) are deserving of urgent and detailed study, if maximum gains are to ensue; also to redress the balance for process engineering.
1.4 General Objectives of this Research

With this review of carbon black and internal mixing as applied to rubbers, two wide areas deserving of further study emerge.

a) to examine the effects of the engineering and processing variables of internal mixing on practical mixed material properties.

b) to study selected carbon black pellet parameters with a view to establishing their effects in the internal mixing process.

These objectives will be expanded considerably, when the specific areas are considered. In addition, a third general objective will be proposed, regarding the adequate characterisation of rubber/black mixes, after exploring the background in the next chapter.
Literature cited


6. USP 1,200,070 (3.10.1916).


17. "EVK Single Screw Mixing Extruder", Werner and Pfleiderer, (Stuttgart).
22. BP 10607/1888.
23. BP 8859/1908.
CHAPTER 2
THE THEORY AND PRACTICE OF CARBON BLACK
DISPERSION IN RUBBER

It has been emphasised in the previous chapter, that the total surface area of carbon black exposed to the rubber matrix is the primary controller of the degree of reinforcement imparted by the filler. This is achieved by the progressive reduction of the aggregate size of the black, ideally to the limit of its ultimate particle size. In practice, the very high interparticle forces holding together the primary aggregates do not permit these extremes to be reached. In a tread mix (50 pph N330 of 28 nm particle size in SBR) the mean aggregate size at acceptable dispersion levels is about 150 nm in diameter, which equates to approximately forty particles of HAF black per aggregate. At the same concentration, interaggregate distance has been found to be about 600 nm.

2.1 The Mechanics of Mixing

Throughout this work, mixtures of rubber (the major component), and carbon black (the minor component) are considered. The creating of this special variety of mixture is accomplished by three basic modes of mixing, each participating to a greater or lesser degree, and each dependent on the other two.

Simple Mixing: The term simple mixing is used for any operation which causes the particles of a system to pass from a less probable to a more probable arrangement. Alternatively, there is an increase in the configurational entropy of the system; this reaches a maximum when the state of perfect randomness is achieved (when the samples are viewed on a scale, large compared to the size of the component particles) as shown in Figure 2.1.
FIGURE 2.1: Simple Mixing

Figure 2.2 shows the standard deviations of compositional observations at given times during a simple mixing operation.

FIGURE 2.2:
From the graph, the trend to increasing randomness is noted, decreasing again in practice at very long mixing times, due to geometrical differences that might exist between the two phases, leading to segregation. Simple mixing as referred to here, is exemplified by a powder blend in a rotary drum. Spontaneous simple mixing can also occur between gases or miscible liquids by diffusive mixing; it may be accelerated by turbulence.

**Laminar Shear Mixing** — With polymer melts however, the critical Reynolds number for turbulence is impossible to achieve, and thus, for such processes as mixing polymer blends, laminar mixing is dominant. Figure 2.3 shows a deformable disperse phase changing shape when subjected to a shear field. The deformations of particles cause a decrease in thickness, and a corresponding increase in main area. The distance between the adjacent particles (the striation thickness) also decreases, and with time, (and cumulative shear) the two cubes of Figure 2.3 become two sets of parallel planes, ultimately merging into one at the limit of resolution of the scale of viewing.

![Figure 2.3 Laminar mixing showing change in striation thickness with shear](image)
**Dispersive Mixing** - Consider now, not flexible particles, but rigid aggregates such as carbon black throughout a rubber matrix. Since for optimum reinforcement, a maximum surface area of the black must be exposed to the continuum, sufficient stress must be generated in the mixer if the original large entities of carbon black are to be broken down to the desirable smaller aggregates. Because of the invariably high matrix viscosity, this third form of mixing is a most energy intensive process, which has been subjected to much investigation in the search for a balance between economics and acceptable quality.

2.2 The Theoretical Considerations of Dispersive Mixing

Since dispersive mixing is of such critical importance to this study, a mathematical model developed by McKelvey\(^3\) (and its variants) is detailed next. Figure 2.4 illustrates the scheme.

![FIGURE 2.4 Forces operative in the dispersion of a two-particle agglomerate](image)

The assumptions of the model are as follows:

a) the minor component exists as two particle agglomerates of equal radii \(R\) whose overall concentration in the mix is low.
b) These are suspended in a simple shear field of a viscous Newtonian liquid.

c) The isothermal assumption is made, and the particle dimensions are small compared to the narrowest flow channel of the mixer.

d) The closest the particle centres can approach is \( 2R \).

e) The centre to centre separation of the particles is:

\[
    r = \sqrt{x^2 + y^2} \quad 2.1
\]

using the centre of one particle as the origin of a Cartesian coordinate system.

f) In the region \( 2R < r < r^* \) (where \( r^* \) is the critical radius of separation beyond which the attractive force between the particles is negligible) it is assumed the attractive force holding the particles together is constant \( (F_a) \).

Thus:

\[
    F = F_a \quad 2R < r < r^* \quad 2.2
\]

\[
    F = \infty \quad r < 2R \quad 2.3
\]

\[
    F = 0 \quad r > r^* \quad 2.4
\]

g) In Figure 2.4, the liquid surrounding the particles undergoes unidirectional shear flow to the right.

The fluid velocity \( u \) relative to the first streamline which follows the centre of the first particle is

\[
    u = \dot{\gamma} Y \quad 2.5
\]

where \( \dot{\gamma} \) is the shear rate, assumed constant over the range of interest.
Whenever there is a relative motion between the fluid and the particle, drag forces act at the particle surface. The drag force \( F_d \) on a solid sphere suspended in a Newtonian liquid with viscosity \( \mu \) at low Reynolds number is given by Stokes' law:

\[
F_d = 6 \pi R \mu v
\]

where \( v \) = the relative velocity between fluid and particle. This drag force \( F_d \) can be resolved into two components \( F_{dx} \) and \( F_{dy} \) (in the x and y directions), where

\[
F_{dx} = 6 \pi R \mu \left( \gamma v - \frac{dx}{dt} \right)
\]

and

\[
F_{dy} = -6 \pi R \mu \left( \frac{dy}{dt} \right)
\]

\( \frac{dx}{dt} \) and \( \frac{dy}{dt} \) represent the particle speeds in the x and y directions respectively.

The attractive force holding the particles together \( F_a \) may be resolved into its two components, and by equating to the components of drag force a pair of simultaneous force balance equations are obtained. (Assuming the masses of the particles are negligible).

\[
F_{dx} = F_a \cos \alpha = F_a \frac{x}{r}
\]

\[
F_{dy} = F_a \sin \alpha = F_a \frac{y}{r}
\]

(\( \alpha \) is the angle the line connecting the particle centres makes with the abcissa).
Combining equations 2(7) with 2(9), and 2(8) with 2(10):

\[ G \pi R \mu \left[ \dot{y} - \frac{dx}{dt} \right] = F_a \frac{x}{r} \quad 2.(11) \]

\[ -6 \pi R \mu \frac{dy}{dt} = F_a \frac{y}{r} \quad 2.(12) \]

are obtained which constitute a pair of simultaneous ordinary differential equations with time \( t \) as the independent variable and \( x \) and \( y \) as the dependent variables. Combining 2(11) and 2(12), a single equation in \( x \) and \( y \) having the form

\[ \left( \frac{dx}{dy} \right) - \frac{x}{y} = \frac{-6 \pi R \dot{y} \mu r}{F_a} \quad 2.(13) \]

results, and since \( \mu = \frac{\tau}{y} \) (where \( \tau \) is the shear stress in the liquid)

\[ \left( \frac{dx}{dy} \right) - \frac{x}{y} = \left( \frac{-6 \pi R \tau r}{F_a} \right) \quad 2.(14) \]

or alternatively,

\[ \left( \frac{dx}{dy} \right) - \frac{x}{y} = -Kr \quad 2.(15) \]

This force balance between the hydrodynamic drag force generated by the liquid, which acts against the interaggregate cohesive force is thus expressed in terms of the aggregate radius \( R \), shear stress in the liquid \( \tau \), the interaggregate cohesive force \( F_a \) and the dispersibility factor or constant in the equation \( K \).
Proceeding with the analysis further, it is noted that the right hand side of 2(14) is non-linear. If \( r \) is replaced with its approximate equivalent \((x + y)\), the equation becomes a first order linear differential one, with \( x \) as the dependent variable.

\[
\frac{dx}{dy} + x \left[ K - \left( \frac{1}{y} \right) \right] = -Ky
\]

2.(16)

The general solution is written

\[
\left( \frac{x+y}{y} \right) = Ce^{-Ky}
\]

2.(17)

where \( C \) is the constant of integration.

\( C \) could be evaluated by specifying that the particle centre passes through point \((x_o, y_o)\) and then 2(17) becomes

\[
\frac{x+y}{x_o+y_o} \left( \frac{y_o}{y} \right) = \exp \left( Ky_o \left[ 1 - \left( \frac{y}{y_o} \right) \right] \right) \quad 2R \leq r \leq r^* \quad 2.(18)
\]

This equation shows the particle path (and thus dispersion) depends on \( K \), the critical radius \( r^* \) (since this affects the cohesive interaggregate force), and the initial orientation of the aggregate.

By considering an example now it will be possible to graphically demonstrate that a high value of \( K \) is necessary for dispersive mixing. Referring to equation 2(18) and Figure 2.5 it is possible to quantify what happens to the balance of forces (defined
FIGURE 2.5  Particle paths for dispersion of two-particle agglomerate

as the ratio of the hydrodynamic drag force $R$ and the interparticle cohesive force $F_a$) when various values are assigned to $R$, $r^*$, $X_0$ and $Y_0$. Let the agglomerated pair of particles oriented as shown have the following characteristics:

$R = 0.5$
$r^* = 3$
$x_0 = 0$
$y_0 = 1$

The fluid surrounding the particles is subjected to shear stress from the right. If the values above are substituted into equation 2(18) and various values of $K$ are also introduced, values of $x$ and $y$ are obtained by which the path of the second particle might be traced.

At $K = \infty$, the particle follows the streamlines of the fluid, indicating that dispersive mixing has degenerated to simple mixing [$K = \infty$, when $r^*$ has been exceeded and $F_a = 0$].
The effect of the attractive force operative between particles becomes noticeable whenever $K$ is finite. For example, at $K = 4$ there is initially a slight rotation of the agglomerate and then the upper particle moves downwards and outwards on a curved path until it reaches critical radius at which point $F_a$ becomes zero and the particle moves on a flow streamline to the right.

When $K = 3$, the particle path begins the same as above but eventually reaches a point where the force balance becomes unfavourable, because of reduced fluid drag, and it reverses direction and reagglomerates itself with the other particle.

If $K = 2$, the attractive force relative to the viscous force is so strong that the centre to centre distance does not change. The path of the centre of the upper particle is a quarter circle and the net result is a rotation of the agglomerate such that its long axis lies on a streamline.

In this example, dispersive mixing would occur only when $K \geq 4$.

Thus, from equation

$$K = \frac{6 \pi R \tau}{F_a} \quad 2.(19)$$

a few generalisations might be made.

a) High shear stresses promote dispersion.

b) Correspondingly, high shear strain rates and/or viscosities will be favourable for dispersive mixing. Shear strain rates can be increased by either increasing mixing speeds or decreasing rotor tip clearances of the mixer. Higher viscosities are expected by decreasing temperature of the melt.

c) If the flow in the mixer is completely unidirectional, only those agglomerates having a favourable initial orientation will
be ruptured. The others will simply align with flow. However if the mixer makes a continuously changing flow pattern, the agglomerates are more likely to find themselves in positions advantageous to dispersive mixing.

d) When the particle size $R$ is large, the hydrodynamic drag force dominates and results in the breakdown and dispersion of agglomerates. This balance becomes less favourable for dispersion as $R$ diminishes. The process of agglomerate breakdown proceeds until an equilibrium is achieved between the opposing forces.

It is pertinent now to consider some of the assumptions in the McKelvey model critically. The main simplifying assumption is that interaggregate hydrodynamic attraction has been ignored even though it would be of considerable importance in carbon black/rubber dispersions, where also, incidentally, the minor phase is present at high concentration (typically 25-30 volume percent on the rubber). The assumption that the viscous medium is Newtonian is not too unrealistic since at the high shear rates generated in internal mixers the flow curve is approximately linear. What is more serious is the isothermal assumption, especially in view of the viscoelastic nature of rubber, and its capacity for heat generation under conditions of shear.

Two underestimations accruing from this simple model are also evident. Firstly, it only considers unidirectional flow, whereas, in reality multidirectional behaviour occurs in internal mixers (combined axial, radial and depthwise flow). The orientation of the original two particle aggregate would, under these circumstances, not be as critical as the model predicts. Further, if a multiparticle aggregate replaced the simpler example, orientation again becomes less critical, especially if it rotated and wobbled in the shear field. Inevitably, a multiparticle entity would have higher and more complex cohesive strength, due to its component interactions with one another. Further problems of interpretation occur if particles of unequal radius are assumed to make up the aggregate.
Thus, although in reality conditions in a rubber mixer are far more complicated than the model allows for, the essential points developed remain basically unchanged with more rigorous analysis.

One such analysis, documented by Dizon\textsuperscript{4}, considers both interparticle and interaggregate cohesive forces, and multiparticled aggregates. In addition he included a term to embrace filler-matrix interaction. This changed McKelvey's denominator from $F_a$ to $C/A$, where $C$ equalled the interparticle force and $A$ was the force ascribed to the filler-rubber adhesion. Thus, the following equation resulted:

$$K = \frac{6\pi R \tau A}{C}$$ \hspace{1cm} 2.(20)

where $R$ was a function of structure
$\tau =$ viscoelastic shear stress
$A =$ rubber/filler interaction term
and $C$ refers to the agglomeration tendency of the black.

In this theory, the filler-matrix force not only will augment the hydrodynamic drag force, but will also make dispersion irreversible (McKelvey's theory predicts that reaggregation is possible).

Tadmor\textsuperscript{6} extended the original analysis to pairs of interacting aggregates, and added yet another consideration to the mixing process. He stated that although the flow between the rotor tip/chamber wall in an internal mixer was predominantly shear flow, an extensional flow component exists due to the contraction of the flow channel at the nip entrance. Tadmor derived two equations for the maximum force acting on an aggregate (again of the two particle make-up but these not necessarily being of equal radius) in the special case of the two particles lying together, for both shear and extensional flow.
\[ F_{\text{max (shear)}} = 3 \pi \mu \dot{\gamma} r_1 r_2 \]  
\[ F_{\text{max (elongation)}} = 6 \pi \mu \varepsilon r_1 r_2 \]  

where \( \mu \) = fluid viscosity  
\( \dot{\gamma} \) and \( \varepsilon \) = deformation rates in shear and elongation respectively.

and \( r_1 \) and \( r_2 \) = the radius of the two particles.

Comparing these equations, it is seen that at equivalent rates of deformation, the force disrupting the particles in elongational (extensional) flow is twice that generated in shear flow. In practice however, large shear rates are obtainable in internal mixers, while similarly large elongational rates are difficult to generate. Kao and Mason show graphically the effects on particle breakup of PMMA beads in silicone oil, in extensional and shear fields.

**FIGURE 2.6** The effects of elongational and shear fields on particle disruption
2.3 The Practicalities of Mixing

It is now possible, in the light of the previous theoretical considerations, to detail an account of what practically takes place when rubber and carbon black are mixed together in an internal mixer. The sequence of events as presented here, is not sacrosanct, since several methods of mixing are applied in factory processing ranging from the conventional method (where rubbers are introduced into the mixer first) through side by side, and upside-down mixing where all the ingredients are loaded before the addition of the polymer. What is important is that all these interdependent operations do take place at any mixing cycle which is taken to completion.

Thus, when the highly elastic rubber is fed into the mixer, extension of the polymer chains occurs due to the passage of the rubber into high shear areas of the mixing cavity. An initial lowering of viscosity purely by virtue of chain extension takes place, resulting from the freeing of untrapped chain entanglements.

![Figure 2.7: Schematic chain extension](image)
The elastomer at this point is stiff, and resists the imposed deformation, so continued shearing may cause breakup of the coherent material, as predicted by Tokita and White for rubber milling. This shredding is a very highly energy intensive stage (see Figure 2.8) and may be made less so by the use of large particled granulated rubber.

Due to the temperature rise resulting from frictional and shearing energy dissipation within the mixer, a coalescence of these particles now occurs; the elasticity of the polymer begins to fall, and the viscous component starts to dominate. Sustained shearing causes continuous elastic and viscous changes in the rubber, both its molecular weight and molecular weight distribution being altered as a function of the ongoing temperature rise, the strain, and the strain rate, imposed within the mixing cavity. Molecules of higher chain length are statistically more likely to rupture first. This sensitivity of chains to shear is very noticeable in natural rubber, but is observed in other polymers, such as SBR, as well.
This mechano-chemical breakdown makes the polymer more easily deformable and less elastic. Practical men concerned with mixing recognise the attainment of this stage, by listening to the sound generated by the rubber in the mixer. (Scientifically, it is possible to identify this point in the mixing cycle by noting batch temperature or from a consideration of the energy consumed by the mixer thus far.

The next stage is the addition of powders into the now receptive bulk of the polymer, and predominantly the introduction of black will be considered here. Cure activators, antioxidants, and sometimes curing additives and accelerators, are added as well but the progress of these in mixing is similar to that of carbon black. If certain ingredients are soluble in rubber, laminar/simple mixing completes the cycle, as happens in the case of oils, waxes and polymer blends.

When the black is first added, it is in the form of large agglomerates (pellets) which are first subdivided into smaller ones purely by the physical forces generated within the mixer. The now easily deformable rubber is folded over clumps of filler agglomerates completely enclosing the material. This folding is encouraged by the action of the mixer rotors, according to the flow visualisation studies of Freakley and Wan Idris \(^{17}\); one rotor wing moves material placed under the ram into the path of the wing of the other which then causes material (by now comparatively fluid) to engulf the particulate additive. This progressively leads to a wetting out of the filler by the rubber, and the gradual elimination of voids, the mix becoming more and more incompressible with time, and the whole stock forming a continuum. Power requirements rise to a peak since the stock viscosity is at the highest level just after the wetting stage (see Chapter 3) and this and subsequent stages are shown as power traces for the mixing operation derived from four sources of reference \(^{18-20,23}\).
FIGURE 2.10
Expanded trace of power consumption during internal mixing

- Time
- Power
- First phase of filler dispersion
- Incorporation/wetting
- Rubber breakdown
- Addition of filler
- Continued homogenisation and dominant rubber degradation.
- Inflection
- Scorch
- Further degradation

FIGURE 2.9
Generalised trace of power consumption during internal mixing

- Time
- Power
- Dispersion
- Incorporation and wetting
- Rubber breakdown
- Ram down
The incorporated black is now broken down by dispersive mixing in the elongational and shear fields of the mixer. Figures 2.9 and 2.10 show the increase of power requirements to accomplish this breakdown of filler agglomerates. At this time dispersed filler is subjected to distribution by simple (or extensive) mixing with the rubber facilitated by the flow mechanisms described by Freakley and reference 21. Nominally, these distributive actions are longitudinal cut back, (or axial flow), lateral overlap, and kneading, coupled with voiding behind the rotor tip leading to a disordering of flow.

FIGURE 2.11 Specific Actions in an Internal Mixer
Dolezal and Johnson 20 observe a second dispersion phase (Figure 2.10) where evidently loose materials from dead spots (for instance under the ram) now enter the wetting stage and are dispersed. Homogenisation then proceeds, and the power demand is seen to decrease as the viscosity of the mix decreases with increasing temperature. Filler deagglomeration and dispersion are now largely complete, and the mix homogenises by simple and laminar mixing, to a point of uniform compound viscosity. Any further mixing action either causes a continued drop in energy requirements, caused by a degradation of the polymer at the (now) high levels of cumulative shear, or registers an increase caused by scorch. The inflexion is a sign that mixing has reached an excellent state.

Figure 2.12 shows these different mixing stages.

2.4 Estimating the Adequacy of Mixing

It has been stated that even though mixing is a process that is common, and vital to a wide variety of industries, no one universal measure of the goodness of mixing has been developed, to date 22. The rubber industry is no exception, and several methods have been employed to characterise the goodness of mixing, and adequacy of dispersion prevalent in rubber compositions. The next chapter deals with these methods, their application, theoretical bases and the practical facets of their use.
FIGURE 2.12  The stages of mixing
Literature cited


In this chapter, industrial and research oriented methods for assessing the 'goodness' of carbon black/rubber stocks are discussed. The diversity of methods, and their sheer number indicates the overriding importance attached to the monitoring of the state of the mixed material. In industry, the level of mixing specified is a compromise between energy consumption combined with labour utilisation, and the standards of quality imposed by the end users of the ultimate product.

The justification of a review as extensive as this, is that several of the tests described are central to the arguments and discussions presented in the remainder of this dissertation. These tests (and their theoretical bases) will be dealt with in fair detail here, while others (not used in this research) will be subjected to the usual review scrutiny, accompanied by references.

3.1 Test Groupings

For convenience, the wide range of tests used to assess dispersion and mixing is divided into broad groupings.

**Processing properties** - these tests are those which indicate how a rubber stock will behave in subsequent operations such as extruding, calendering, vulcanising and so on and applies therefore to unvulcanised compounds.

**Vulcanisate properties** - this group is further subdividable into static, dynamic, and wear tests. In static tests the applied deformation is comparatively slow, and also importantly, one cycle in nature. Strength tests (where the ultimate aim is fracture/rupture of the specimen) and stiffness tests (where the consistency of a specimen
is evaluated) make up the major part of this subsection. The dynamic tests are those in which samples are subjected to repeated straining (multicyclic) at various frequencies of imposition. These may be either destructive or non-destructive. The wear tests are multicyclic, but result in removal of material from the bulk of the sample. Tests applied to vulcanised rubbers which do not conveniently fit this or any proceeding categories are called 'other' tests.

**Polymer modifications** — considered here are those tests which do not consider black dispersion as the indicator of mixing, but instead monitor the changes the rubber itself undergoes during the intensive mixing operation.

**Black-rubber interaction** — during mixing, chemical/physico-chemical attachments form between rubber and filler. These tests attempt to quantify mixing by measuring the magnitude of the phenomenon.

**Electrical/or energy based tests** — this segment concentrates firstly on electrical testing done either in the AC or DC mode. The energy based tests consider those using other radiation to monitor a characteristic of mixing.

**Viscoelastic properties** — here are described either stress relaxation or creep tests used to evaluate dispersion.

**Surface characterisation** — it is known that different dispersions yield surfaces of varying roughness. The mechanical methods of surface characterisation discussed attempt to correlate topography with degree of mixing.

**Miscellaneous methods** — under this category is included the methods that do not fall into any of the headings above.

**Optical/microscopical methods** — this class includes visual tests without magnifying aids, optical methods, electron microscopy and microradiography techniques used to explore black dispersion in rubbers.
3.2 Processing Properties

Several important processing properties have been assessed and related to the state of black dispersion in rubber. Certainly, the most widely used measure has been Mooney viscosity\(^1\), first used by Dannenberg\(^2\) and Drogin\(^3\). The former reported a negative response for Mooney (MV) with increasing time of mixing for cold SBR and butyl stocks containing HAF and EPC type blacks. High frictional resistance of contacting carbon black aggregates, within the matrix was advanced as the explanation for high viscosity at low mixing times, the effect being progressively eliminated with mixing. Dannenberg noted a contrary trend in polychloroprene ('G' type) which he ascribed to the marked tendency for this type to 'set up' or crosslink during mixing, to the elevated temperatures generated during the operation. Drogin found that cold SBR (CSBR), oil extended SBR (OESBR), CSBR/OESBR blends, natural (NR) and butyl (IIR) rubbers mixed with ISAF, HAF, FEF, EPC, and MPC blacks all showed decreasing MV with increasing mixing, the extent of the effect being dependent on the rubber and black under consideration.

A great many other workers have confirmed the relationship between Mooney and level of mixing (whether described by energy, time or temperature). Railsback et al\(^4\) worked with polybutadiene (BR)/Hot SBR (HSBR), BR/NR with ISAF (N220). Woods and Krosky\(^5\) found a drop in the property with progressing extruder mixing of a powdered nitrile (NBR) rubber with FEF (N550) as did Boonstra and Medalia\(^6\) with SBR 1712 and ISAF black during internal mixing. References 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21 and 22 along with many others have used this relationship either as a primary argument to show increasing efficiency of mixing, or as a secondary observation during mixing, to reinforce conclusions arrived at by other tests. Tokita and Pliskin\(^23\) in a generalisation for all polymers, state that MV decreases monotonically until the second power peak during mixing (see 2.3) is reached, after which it levels off.

Many papers have been published to explain the Mooney variation with mixing more quantitatively than the original frictional argument
of Dannenberg, Kraus and Medalia proposed the concept of rubber, occluded by the filler. A simple spherical model of filler is assumed as is a filler loading in the rubber of $\phi$. This is defined as the volume fraction of filler when its individual particles are separated by the matrix.

In the early stages of mixing, the particles are ill dispersed and are agglomerated with one another. Each agglomerate contains not only filler, but also rubber occluded between the particles during the wetting process referred to in 2.3. In this situation, the entity (filler + occluded rubber) behaves as a single filler particle. Thus, the effective volume fraction of filler ($\phi_e$) in the early stages of mixing is always larger than that of the filler in the well mixed compound.

Thus:

$$\phi_e(t) = \phi + \phi_{or}(t)$$  \hspace{1cm} 3.1

where $\phi_e(t)$ is the effective volume fraction of filler at time $t$, and $\phi_{or}(t)$ the occluded rubber volume fraction at that time. At early mixing times, the effect is that of a higher concentration of filler, and lower concentration of rubber than is to be found at longer mixing times. As a consequence, the viscosity is lower after extended mixing. Figure 3.1 schematically shows the comparative situations.

Real carbon black particles are not spheres, but instead more complex, geometrically. Each aggregate can occlude some rubber, even in a highly dispersed stock the fraction of which will be higher for a high structure than a low structure black, since the void volume in the former is larger than the latter.
\[ \phi_c(t) = \phi + \phi_{or}(t) \]

**FIGURE 3.1** Schematic diagram of composite morphology

Other methods of viscosity measurement too have been used for characterising the state of a rubber mix. The Monsanto curemeter (ODR) has been employed, the minimum torque on the cure curve being considered analogous to Mooney. (Despite the small angle oscillating mode, different from the rotation in the older instrument). Butyl, SBR and NR stocks have been tested for dispersion by the means 19, 20, 27 where, as previously noted, viscosity falls in response to increased mixing. In Ref. 27, the range of minimum ODR torque, measured from successive samples within a batch is also used as an indicator of mixing; curves resulting from different samples taken from the same mix are widely separated if from a poorly mixed stock, and are superimposed if from a well dispersed one.

Wan Idris 20 used Wallace rapid plasticity 28 (WRP) as a measure of viscosity and found the plots of log WRP versus log unit work of mixing to be linear with a negative slope. Buskirk et al 16 had noted this relationship previously for Mooney viscosity.
It has been apparent for some time now that single point viscosity measurements are insufficient to predict elastomer processability, since in practice, a stock passes through multishear rate processes from which the low shear strain rate Mooney (and other) measurements are far divorced. Capillary rheometers are able to provide a range of practical shear rates at which polymers could be characterised. By computation of the shear stress ($\tau$) at various shear strain rates, ($\dot{\gamma}$), the apparent viscosity ($\eta_a$) which equals $\tau/\dot{\gamma}$ might be calculated at the several $\dot{\gamma}$ points. Since polymers approximately follow a power law

$$\tau = K \dot{\gamma}^n$$

where $K = \text{shear stress at values of log } \dot{\gamma} = 0$ and $n = \text{flow index}$

A plot of log$\tau$ versus log$\dot{\gamma}$ will yield a straight line from which the slope ($n$) and the intercept (log $K$) can be extracted.

For plots of $\eta_a$ vs $\dot{\gamma}$ for stocks differing in mixing history, a generalised family of curves\textsuperscript{20} is obtainable, which takes the form shown in Figure 3.2.
If iso shear rate curves are considered \(^{13}\) (for example at \(\gamma_c\)) viscosity is seen to decrease with increasing severity of mixing in accordance with the occluded rubber theory\(^ {24,25}\).

Cogswell\(^ {29}\) pointed out that elongational or tensile flow occurs in any case of converging flow such as which occurs through a capillary rheometer die. Converging flows may be analysed in terms of their extensional and simple shear components and Cogswell derived equations from which the viscosities and modulii under these two modes of deformation could be calculated. Using these equations, Wan Idris\(^ {20}\) calculated these quantities in both simple shear and tension, for a series of SBR and NR mixes produced by systematic mixing changes. As with both one point and capillary shear derived viscosities, the corresponding quantity in both modes decreased with increasing mixing energy. The modulii determined for both components also decreased, and the importance of this observation will be appreciated in the section on stiffness properties, and the effects of mixing on these.

Two widely used tests for evaluating the mixedness of elastomeric compositions have been the closely related ones of post extrusion, shrinkage and die swell. These properties (only separated by simple geometrical considerations) are associated with the viscoelasticity of a rubber mix. After extrusion there is a retraction of the extrudate on cooling, and a corresponding increase in diameter, by the constant volume assumption. Dizon\(^ 8\), Boonstra\(^ 6\), and Vegvari\(^ 17\) all report increasing extrusion shrinkage with mixing time for SBR, SBR/BR mixes filled with N220 and N330 blacks, the former two references noting a maximum being reached.

Drogin\(^ 3\) calculated extrusion shrinkage by\(^ {30}\)

\[
S\% = \frac{D^2 - d^2}{D^2} \times 100
\]

3.(3)
which, more accurately, refers to swell, and it is evident, that with increasing die swell, $S^\%$ will increase (note - $D$ is extrudate diameter, and $d$ die diameter). Drogin\textsuperscript{3} found for SBR, OESBR, OESBR/SBR, NR and IIR mixed with N220, N550, S300 (EPC), S301 (MPC) shrinkage decreased with increasing time of mixing, without exception. This is contradictory to previous findings and he states that the nerve inherent in rubbers reduced by longer mixing is responsible for the fall. The elastic effects resulting from carbon black/rubber interaction are not considered.

Moving on to die swell, references 9, 12, 13, 15, 16, 20, 21, 23, 31, and 32 report increases in this quantity with increasing time or energy input of mixing. Most also document a maximum and a subsequent fall in the property, in line with the majority observations on extrusion shrinkage. The maximum appears to correspond to the second power peak\textsuperscript{23} referred to in 2.3 which in turn is caused by progressively improving filler dispersion. The decrease in the swell after long mixing can be attributed to the shear breakdown of polymer chains and an elasticity reduction, the actual location of the maximum die swell being a function of the shear sensitivity of the polymer. Wan Idris\textsuperscript{20}, found after comparatively short mixing energies (ca 600 MJ/m$^3$) NR stocks decreased in die swell while SBR stocks reached their maxima at 2000 MJ/m$^3$ and thereafter remained constant in value.

(NB: most previous workers use relaxed die swell measurements. Running die swell measurements are possible using modern instruments\textsuperscript{33}).

In the above context, Pliskin\textsuperscript{34} refers to a compound's rheological behaviour as being either 'dispersion controlled' (up to the die swell peak) or 'mastication controlled' (when die swell is decreasing). It would seem that this is perfectly true in NR, but in less shear sensitive polymers the distinguishing line becomes more obscure.

Drogin's\textsuperscript{3} die swell observations with mixing must now be viewed more closely with the weight of opinion being firmly against him.
On scrutiny of his paper, it is noted that his least mixed stocks were subjected to a Banbury mixing time of 3.5 mins and his best stocks to a period of 14 mins of mixing at the following conditions.

**TABLE 3.1**

<table>
<thead>
<tr>
<th>Process Variable</th>
<th>First Stage</th>
<th>Second Stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fill factor</td>
<td>0.72</td>
<td>0.72</td>
</tr>
<tr>
<td>Rotor speed</td>
<td>116</td>
<td>60</td>
</tr>
<tr>
<td>Ram air pressure (psi)</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Starting temperature (°F)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Circulating water temperature (°F)</td>
<td>85</td>
<td>85</td>
</tr>
</tbody>
</table>

It is evident that all Drogin's\(^3\) experimentation was carried out in the 'mastication controlled' area of mixing, since we deduce from the present state of knowledge, that the dispersion of carbon blacks in rubbers by Banbury mixing is complete shortly before 3.5 minutes under the above conditions. Thus, the apparent anomalies with regard to extrusion die shell, in fact confirm the findings of other workers in that a decrease is observed after long mixing times. Drogin's Mooney viscosity findings were in line with popular opinion since the property shows a decrease whether in dispersion or in the mastication controlled area of mixing, the only perceptible differences, being the rate of drop. (MV falls faster at earlier mixing times, than at the later mastication controlled stage, due to dominant filler deaggregation during the early stages).

To generalise, with mixing, the decrease in effective filler volume fraction results in increasing die swell and shrinkage. From previous discussions it is evident that the viscosity of the composite increases with increasing volume fraction of filler due to
the excess energy dissipation caused by the presence of this material. Though expressions have been propounded which quantify this aspect\textsuperscript{37}, no completely successful equations have been introduced to explain the changes in the elastic memory of a composite system. The last attempts have been less than satisfactory\textsuperscript{35,36}. Even though quantification of this elasticity phenomenon has not thus far been possible, by observation it is indeed clear - the elastic memory of a composite increases with decreasing effective volume fraction of filler\textsuperscript{23}.

Scorch time has been also correlated with mixing. This is defined as the time taken at a particular temperature, for the viscosity of a rubber (as measured by the Mooney viscometer, Monsanto ODR or like instrument) to increase by a given value. This signifies the onset of crosslinking in rubbers. Drogin monitored this property\textsuperscript{3,22} and found that its response to increased mixing depended on the particular rubber/black combination used. SBR/EPC, NR/HAF, SBR/HAF, NR/EPC, and SBR/SAF showed increases while in NR/SAF scorch time decreased. This property must be viewed with doubt as a reliable measure of mixing.

Finally, time to 95% cure as calculated from ODR data was noted by Railsback\textsuperscript{4} to increase with increasing mixing severity, for a BR/NR/N220 stock. This has been ascribed to being caused by a heat history effect, but the present author suggests that this increase in cure time is caused by an adsorption of curative onto the progressively higher surface area of filler, presented with mixing. It is further possible that in bad dispersions, since so much rubber is immobilised by occlusion, the effective curative:polymer ratio increases causing quicker curing.

3.3 Vulcanisate Properties

3.3.1 Static tests

3.3.1.1 Strength properties - Tensile strength, as measured by procedures similar or identical to the British Standard\textsuperscript{38} have been
long used for identifying the state of mixedness of a carbon black filled matrix. The great majority of researchers have found the property to increase with increasing mixing. (Refs. 39, 9, 20, 8, 5, 19, 2, 17, 31, 18, 40, 6, 10, 41, 4). Many of these workers found tensile strength to pass through a maximum, at a critical level of mixing. Drogin\textsuperscript{3,22} using the extraordinary long mixing times, found with his compounds that tensile strengths either fell with increasing mixing or remained constant. Again, it is evident that the length of the mixing cycles used, were too protracted for the observation of any tensile peak. Drogin found NR compounds at these lengthy times to increase in tensile strength, perhaps rather surprisingly, given the shear sensitivity of the base elastomer.

It could be generalised however that for practical mixing times (where energy inputs are realistically from 0-2100 MJ/m\textsuperscript{3}), tensile strength increases rapidly to a maximum, after which it either remains, or, conversely falls.

Another property measured concurrently with tensile strength is elongation at break\textsuperscript{38} (EB), calculated as the extension of a specified length of sample at rupture, divided by the original length of this sampling distance, expressed as a percentage. Workers have found this property to follow similar trends as tensile strength with mixing time, increasing quickly to a maximum value, subsequent to which a slow fall in the parameter value is observed (Refs 5, 6, 8, 9, 19, 20, 40, 2, 13, 17, 31, 18 and 39). Drogin\textsuperscript{3,22} finds EB to fall with his long times of mixing, as explained for tensile strength, above.

The unanimity of the findings regarding the responses of the above properties to mixing cannot be denied. Boonstra and Medalia\textsuperscript{6} in their extensive study noted that there were possibly two factors that caused these observations. Increasing mixing time eliminates large agglomerates, as well as improving the fine dispersion of black
These authors suggest that poor tensile properties (the term embraces EB as well) associated with inadequate mixing are more due to the former than the latter. This was demonstrated (but not proven unequivocally) by mixing about 40 phr, black into a rubber until well dispersed, and then, in the very last seconds of the mixing cycle, adding 10 pph more of black, and then offloading the stock. By comparing the stock with another of identical recipe, but in which the total 50 pph black had been added at once and only mixed for a short time, the properties were found to be almost the same. This was despite the better colloidal dispersion in the two-stage mixed stock, which led to their conclusion that the dominant feature affecting the tensile properties was the presence of the large agglomerates, unbroken due to insufficient mixing.

The present author believes that the second stage addition (of the balance 10 pphr black) comprises an unrealistically large concentration of agglomerates. This works out to 20% of total black, and in a practical system, one will not find 80% black in a colloidalp dispersed form and the rest as extremely large agglomerates. Thus, the experimental design itself encourages a domination of the large aggregates. If this aggregate percentage were reduced to a more realistic concentration (possibly 5-10% of total black) then, it is speculated one would find the two stage mix to have higher tensile properties than the bad one stage preparation. By the same token, a 100% colloidalp dispersed black stock would have the best properties of all. It is the present author's belief (based on past experimental work\textsuperscript{19}) that both the aggregate and the colloidal states affect property responses.

With mixing, the increasing fineness of the colloidal dispersion (by virtue of increasing the surface area in contact with the matrix) causes an increasing reinforcement effect. If large aggregates are present then these must act as stress concentrators, initiating cracks and magnifying true stresses that manifest themselves within the matrix, when the bulk is deformed. Complex internal localised stress fields occur, which result in premature rupture
in these areas. For complete rupture through a specimen, in realistic bad dispersions, the crack must propagate through areas of colloidal black, and despite Boonstra's agglomerate rupture theory the state of the fine dispersion too, must be important. In the model compounds (loaded with a high percentage of agglomerates as they were) crack propagation from large particle to large particle must have been the dominant phenomenon, thus explaining the conclusions these researchers arrived at.

Tear strength, as measured by the standardised load to rupture of a nicked sample, has been used to measure the adequacy of mixing. Boonstra and Medalia noted no changes in tear strength with mixing, even when 10% of microspheres 16 μm and 67 μm in diameter were deliberately introduced into otherwise well dispersed black compounds. Dannenberg claimed trends towards increasing tear strength with mixing, though on close scrutiny his results are somewhat doubtful. Railsback shows a maximum to be attained for BR/SBR blends, and despite increasing dispersion (as assessed microscopically), a subsequent fall. Both Drogin and Martin document decreases in tear strength with mixing time, but the assertion that the former results apply only to very long mixing times has already been made. On balance, tear strength must be viewed as a doubtful candidate for discriminating mixing levels of carbon black in rubbers.

Intuitively though, this conclusion is somewhat surprising. Andrews and Walsh indicate that tearing is not a simple plane surface propagation through the material in filled rubbers, but that the rupture will travel from one filler unit to an adjacent one. Since the path taken will be that requiring the least energy, it must follow that the weakest filler particles in a matrix will be isolated in this manner. Since these would be the largest (i.e. non dispersed) aggregates which at the same time have minimum void penetration by rubber, tearing behaviour should theoretically indicate dispersion admirably. It is however probable that the tear behaviour criterion (simple tear strength) used by researchers thus far has been lacking in discrimination rather than the property
itself. It is surprising to note that, despite tear energy being
the fundamental tear criterion it has not been used in an attempt
to distinguish different dispersions.

Why then does tensile behaviour reflect dispersion and not

tear strength? Obviously tensile strength can justifiably be
called a special case of tearing, even though the stress gradients
encountered are vastly different, the underlying mechanisms are
largely the same. Tensile strength corresponds to tear strength
with a minimum size for inadvertent failure - initiating stress
concentrations (under the normal circumstances of acceptable dis-
persion and so on). This might lead to the speculation that the
stress gradients introduced during nick cutting for tear testing
are so unrealistically large that they swamp out the effects of
any but the most dreadful of dispersions.

A final word now about tensile properties as a measure of
dispersion. In addition to considering mean values, yielded by
a test sampling as being indicative of the tensile strength of
the population of that batch, certain researchers have also corre-
lated the variation in tensile strength (and other properties)
within a batch as an indicator of mixing. The rationale behind this
philosophy must be the same as discussed in 2.1, in simple mixing.
The better the mixing, the more random the mixture, and thus the
less variation between individual observations taken from the same
batch. Extending the argument to the laminar/dispersive modes
dominant in rubber/black mixing, the more efficient the process,
the lower the probability of gross inhomogeneities affecting rup-
ture properties. One treatment possible is that utilised by Wan
Idris, who calculated the standard deviation of a series of indi-
vidual observations from the mean value, and combined these two
quantities, in terms of a ratio, expressed as a percentage, styled
the coefficient of variation. This quantity was noted to have a
low value (signifying low in-batch variability) in adequate mixes,
while the opposite was noted in poorly dispersed stocks. May noted
that tensile strength values follow a Doubly Exponential distribution
function (DEF), as do EB observations as well (Figure 3.3).
By plotting the data on probability paper valid for the DEF all the typical points fall on a single straight line. The ordinate of the point, where this line intersects the zero line of the abscissa corresponds with the mode, the slope of the line representing the standard deviation of the distribution. May showed two carbon black dispersions differing in intercept, the better having a higher modal value than the other. The slopes however were substantially parallel indicating similar in batch variability. It is suggested that the large agglomerates in the batch of bad dispersion were scattered evenly within the matrix, and thus there were no areas of high concentration of black which would have led to large variations in individual observations and thence to a higher probability slope.
3.3.1.2 Stiffness Properties

As with EB, modulus (stress at a specified extension) is commonly measured during tensile testing. Specific extensions at which the property is measured are 100, 200 and 300%, and the accruing quantity is really a measure of the stiffness of the polymer, in the tensile mode, at these deformations. Evidence as to the response of the property to mixing has been divided, certain workers showing the modulus to decrease with increasing mixing in specific systems (SBR, SBR/BR and IIR). Hess observed no change in the parameter in other systems, (Epichlorohydrin(ECO) and EDPM), and in yet others, workers have shown modulus to increase with mixing documents an initial increase, followed by a subsequent fall, with mixing.

Within the above references contradictory trends have been documented, even when the same base polymer type has been studied. A consideration of the theoretical aspects returns one to occluded rubber and the principles of rheology of suspensions. The former has been dealt with already (3.2) and some of the hydrodynamic aspects of filled rubbers will be detailed next. This area originated with Einstein's well known treatment of the viscosity of a liquid with suspended spheres at infinite dilution. This first order treatment has been modified by many authors to take into account the mutual disturbance caused by spheres at higher concentrations, leading to various equations of which that of Guth and Gold is perhaps the most familiar. (n is the viscosity of the composite, \(n_0\) that of the continuous phase, and \(\phi\) is the volume of fraction of the filler). More modern equations have been propounded but these, for our purposes, say no more than the Guth-Gold equation.

\[
n = n_0 \left(1 + 2.5 \phi + 14.1 \phi^2 \ldots\right) \quad 3.(3)
\]
That is, the viscosity of a composite material increases to $\eta$ from $\eta_0$ by a function related to volume fraction of the filler. Given that the effective volume fraction of the filler decreases during rubber mixing, this must mean that by equation 3.1, $\eta$ decreases as well. Viscosity in its simplest form is defined as shear stress ($\tau$)/shear strain rate ($\gamma$). If for a solid the term $\gamma$ (the shear strain), replaces $\dot{\gamma}$ (the shear strain rate) in the fluid equation above, then the term $\eta$ is supplanted by modulus $^{51,52}$. On the basis of the filler phase in a polymer is rigid and the elastomer has a Poisson's ratio of $^{190}$0.5, theoretically, modulus should (like viscosity) fall with increasing mixing time, even though this response has been practically found to be debatable. Since hardness as measured by an indentation instrument $^{53}$ is interpreted as an indicator of the rubber modulus at low deformations, the same argument could be applied to this property as was with modulus. Indeed, references 19, 2, 40, 13, 17, 31, 8, 43, 22 and 4 all agree that hardness falls with increasing mixing. It is surprising that some of these researchers have found in the same series of stocks that modulus increased. The fact that the "modulus" as measured by the stress at a given elongation is not a truly fundamental quantity, as are shear or extensional modulii, probably has something to do with this discrepancy. It is to be noted that Drogin $^3$ states that hardness at long mixing times is unaffected by mixing and Bittel $^{13}$ shows an increase contrary to most evidence.

Static compression as measured by a Goodrich flexometer is an indicator of compression modulus and hardness and Boonstra $^6$ found the compression to increase, with severity of mixing indicating stocks with successively softening consistency.

Another measure of modulus more akin to a true modulus is that obtained by observing the maximum torque after a curemeter test. Both Ebell $^{19}$ and Wan Idris $^{20}$ used this method for distinguishing the state of mixing and found the quantity to follow theoretical predictions of decrease with increasing mixing time. Farrel BV $^{27}$ use the maximum torque information on several runs from a batch to
calculate torque variability and found better mixed stocks to be less variable, as noted here before for other properties.

### 3.3.2 Wear properties

No property of rubber presents more difficulty in its evaluation than wear, more specifically abrasion. Both in laboratory instruments in which the sample is worn away against an abrasive surface\textsuperscript{55,56} and in actual product testing, the conditions of shear, rate of removal of rubber, temperature and so on affect both the result and the validity of comparisons between one material and another.

No less simple are the properties of a rubber which affect its abrasion resistance. Schallamach\textsuperscript{57,58} indicated that tensile strength plays a part in regulating the abrasion loss from a surface subjected to sharp abrasives.

Buist and Davies\textsuperscript{59} found statistical correlations between abrasion and hardness, and tensile strength, while Thornley\textsuperscript{60} was able to demonstrate similar findings with abrasion and tensile product. Champ\textsuperscript{61} et al proposed a simple theory relating abrasion to the fundamental strength property of crack growth of the rubber. Southern and Thomas\textsuperscript{62} extended this theory, to include the angle at which the cracks grow into rubber and the tearing energy of the rubber (in turn related to crack growth). Without delving into fine theoretical detail, we realise that abrasion is not a fundamental property in itself, but is possibly related to several of these. Knowing as we do at present (as discussed previously) that these abrasion related properties are a function of filler dispersion within the matrix, it is possible to infer that the composite property abrasion too should relate to dispersion.

Indeed, consideration of one of the models of failure in mechanical abrasion\textsuperscript{90}, shows that all these properties interact during the process.
FIGURE 3.4  An Abrasion Model

Other workers have shown the rate of abrasion loss to depend on the rubber surface - the rougher the surface for an equivalent compound, the quicker the abrasion from it. Since it is known that a bad carbon black dispersion in rubber manifests itself at surfaces by roughness (and visual dullness), whereas a well mixed stock surface is smooth (and glossy), this is possibly another factor attributable to the correlation between black dispersion and abrasion.
Dannenberg\(^2\) in his study, found a dramatic increase in the abrasion resistance of SBR stocks reinforced with HAF and EPC blacks, with increasing mixing time. In the former case, after a dramatic fall in abrasion loss from 0.5 to 1.25 minutes of internal mixing, any further lengthening of mixing time improved abrasion loss only minutely. With the latter, despite a similar large rise in abrasion resistance from 0.33 to 1.25 minutes of mixing, continuous improvement was noted up to 8 minutes. The general trends for NR, NBR and CR stocks was as above.

Boonstra and Medalia\(^6\) showed abrasion resistance to increase up to 3 minutes in a BR Banbury for SBR 1712. Also in their experiments it was found that for deliberate inclusion of large hard particles greater than 1 \textmu m in diameter abrasion resistance was radically decreased as were the related properties of tensile and tear strength. Drogin\(^3\) reported appreciable decreases in abrasion loss in SBR and NR compounds reinforced with ISAF, HAF, FEF and EPC when mixing times increased from 3.5 mins to 14 mins. For oil extended SBR however, no improvement in the abrasion property is recorded, this being ascribed to slippage. Presumably, this refers to the clogging up of pores of the abradant by the soft oil extended stock, and also possibly to a lubricant effect the high concentration of oil present might be responsible for. For butyl no trends were noted. In a subsequent experiment, Drogin et al\(^22\) noted negligible effects on abrasion in SBR and NR when mixed for times ranging from 5 to 20 mins in a Banbury mixer with possibly the exception of NR filled with EPC black, which showed a slight increase in resistance to abrasion.

It is probably from bearing in mind the suspect nature of a laboratory abrasion test that certain other authors attempted to relate dispersion to treadwear in a real tyre situation. Dizon and Papazian\(^8\), Hess et al\(^31\) report increased tread wear with a better dispersion level.

Railsback\(^4\) showed treadwear loss to decrease with improving dispersion for SBR/BR, NR/BR, and solution SBR/BR blends. For the first
series, improvements in the property were shown up to 8 minutes mixing in a BR Banbury.

Davies and Domingo\textsuperscript{10} quote Wood\textsuperscript{64} as stating that no correlation exists between average treadwear rating and optical dispersion rating. The reason advanced for this conclusion was that abrasion was a function of microdispersion (rather than the presence of large aggregates). Microdispersion (as will be discussed subsequently) is not measured by standard optical transmission microscopy. In view of what was said in 3.3.1.1 regarding the roles the dual facets of colloidal black and aggregated black play in the strength properties of rubber, this assertion would seem to reinforce and bear out the arguments advanced in that previous section.

3.3.3 Non-destructive dynamic properties

The application of a low amplitude sinusoidal oscillation to a rubber results in the ensuing strain lagging behind the stress by a phase angle $\delta$. This is because of the viscoelastic nature of rubber.

The total stress is the vectorial sum of two stresses, the elastic stress (in phase with strain) and the viscous stress (in phase with the strain rate). The position is depicted phasorially below (Figure 3.5).

![Stresses generated in an oscillated rubber](image)

**FIGURE 3.5** Stresses generated in an oscillated rubber
where \( AE = \) strain amplitude
\( AB = \) elastic stress
\( AD = \) viscous stress
\( AC = \) total stress
\( \delta = \) phase angle

so that

\[ AC = AB + j AD \quad 3.(4) \]

and

\[ \frac{AC}{AE} = \frac{AB}{AE} + j \frac{AD}{AE} \quad 3.(5) \]

or

\[ G^* = G' + j G'' \quad 3.(6) \]

where \( G^* = \) the complex modulus
\( G' = \) the in-phase (elastic) modulus
\( G'' = \) the out-of-phase (viscous) modulus

and

\( j \) is the complex number operator.

\[ \tan\delta = \frac{G''}{G'} \quad 3.(7) \]

\( \tan\delta \) is a measure of the hysteresis (energy loss) exhibited by the rubber at low strains.

In 1942 Stambaugh\(^67\) reported that the dynamic modulus of NR gum stock rubbers was almost independent of vibrational amplitude, but found that a large change in the modulus with amplitude occurred with black filled rubber stocks. The shape of the curve of in-phase modulus vs log amplitude was as shown in Figure 3.6.
Many workers, notably Payne\textsuperscript{68,69,70}, attempted to explain this phenomenon, the so-called amplitude effect. In the commonly accepted terminology, $G'_0$ is the limiting value of shear modulus at low strains, and $G'_\infty$ the value at very high strains. Payne also noted that for normal black loadings ($\approx 50$ pphr) in general purpose rubbers, $G'_0$ showed values of up to some two orders of magnitude greater than that for a gum rubber, while $G'_\infty$ in black loaded stock was less than one order of magnitude greater than that of the gum vulcanisate. Payne ascribed the difference between the two limits ($G'_0 - G'_\infty$) which represented the change of dynamic modulus with strain to a structure breakdown of carbon black aggregates.

Carbon black does not exist as single spherical particles but forms itself into a rodlike primary structure during manufacture. These rodlike structures form into an aggregated network, probably held together by Van der Waals-London attraction forces. It is the breakdown of these links during vibration that causes the amplitude dependence of dynamic modulus.

Payne\textsuperscript{71} verified that the modulus decrease with strain amplitude was indeed due to aggregate breakup by experimentally showing the same effect with carbon black mixed in paraffin. This showed
it was a filler (rather than a matrix) regulated property. On the other hand, Smit\textsuperscript{79} explained the dependence of dynamic modulus on amplitude as originating from the desorption of bound rubber from the aggregates, rather than their breakdown.

Medalia\textsuperscript{72}, in the following diagram (3.7) showed that there were additional effects contributing to the increase of dynamic modulus from gum to filled stocks, apart from that caused by interaggregate interaction.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{diagram3.7.png}
\caption{From Ref. 72}
\end{figure}

In addition, the parameters $G''$ and $\delta$ (expressed commonly as tan$\delta$) are also sensitive to amplitude effects in filled rubbers (Figures 3.8 and 3.9).
G'' and tanδ in gum rubbers are largely independent of amplitude of oscillation.

The phase angle effect (Figure 3.9) above has been qualitatively interpreted, on the assumption that hysteresis results from breakdown and reformation of filler-filler (interaggregate) linkages. At low amplitudes (A) there is little breakdown of interaggregate linkages, therefore little hysteresis. At intermediate amplitudes (B) considerable reformation and breakdown takes place giving high hysteresis. At very high amplitudes (C) network structure is broken down so extensively that the rate of reformation of structure is very much lower than cycle time, and hysteresis (or tanδ) falls again. Since G'' is a hysteretic parameter too, the same theory could be advanced to explain the shape of its curve.

Payne next demonstrated that rubber/black mixes with poor dispersions lead to large amplitude effects (large \( G'_0 - G'_\infty \)) whilst in good dispersions they were reduced. He also showed similar decreases in out-of-phase modulus and phase angle with increasing time of mixing at a given strain.
FIGURE 3.10 Dispersion/amplitude dependance of $G'$

FIGURE 3.11 Dispersion/amplitude dependance of $G''$

FIGURE 3.12 Dispersion/amplitude dependance of $\delta$
These dispersion controlled effects have been explained as follows.

The reduction in $(G'_o - G''_o)$ with mixing is attributable to reduction in the extent of interaggregate interaction as the agglomerates are broken down during mixing. The decrease in viscous modulus is to be expected from the theoretical predictions of occluded rubber$^{24,25}$ and the rheology of suspensions$^{48}$; the volume fraction of filler decreases with mixing, causing modulus to drop$^{74}$.

![Figure 3.13](From Ref 74)

The overall reduction in the magnitude of the hysteretic parameter tan$\delta$ is explained by the observation that (as in $G'$) less structure is present in a good dispersion than in an equivalent poor one. On the assumption that the size of the parameter is governed by the extent of network break-up and reformation, it is not surprising that tan$\delta$ at a given strain (especially at large strains), is much lower in well mixed stocks than in those of unacceptable quality.
Many researchers have then attempted to use these dynamic parameters to practically assess filler (black) dispersion in rubber.

Studebaker, Davies, Payne, Medalia, and Ebell used the elastic modulus (either in compression or shear) at small strains to correlate with dispersion, and noted the previously mentioned decrease in $(G'_0 - G'_\omega)$ or $(E'_0 - E'_\omega)$. Additionally, the same workers and also Wan Idris and Barker used $\tan \delta$ (or $\delta$) the phase angle as a dispersion discriminator and found without exception at equivalent strains this quantity to decrease with progressive mixing, again for the reasons given previously. Studebaker documents $\tan \delta$ as rising up to very short mixing times, then falling slightly and remaining constant after. Payne found the out-of-phase modulus to decrease practically at constant strain with improved dispersion.

One notable exception to the unanimity of the above findings has been noted in literature. Hess, Ulmer and Chirico while working with a stock base of NR mixed with N327 black found that both the elastic and the viscous modulii increased with increasing dispersion as shown by light microscope measurements. They went on to suggest that more than one mechanism is responsible for changes in dynamic properties with processing, i.e. a combination of state of dispersion, carbon black network and bound rubber development, to explain this disparity with the majority of findings.

Hysteresis, (the dissipation of mechanical energy in the form of heat) and the magnitude of the dynamic viscous modulus are directly related by

$$H = \pi \varepsilon^2 E''$$

where $H$ is the hysteresis (energy lost per unit volume per cycle) $\varepsilon = $ one half the peak to peak dynamic strain and $E'' = $ viscous modulus
E' is thus a direct measure of hysteresis under dynamic conditions at any given strain amplitude; Drogin,3 Boonstra6, Dannenberg2 and Davies10 have, not surprisingly, found hysteresis to decrease with increasing mixing time and have attributed their findings to the reduction in carbon black frictional losses as dispersion is improved10,6,2. This widely used term is an alternative for network breakup/reformation and relates to the same concept.

Rather than directly measuring input and output energies to calculate hysteretic losses, as is done in the Pirelli Hystereometer29 or in torsional hysteresis equipment6, a rather more simple principle is used in machines such as the Goodrich, Firestone and St Joe flexometers81. Here, cylindrical samples of rubber are compressed and cyclically deformed; the difference between input and output mechanical energy due to hysteretic dissipation is liberated as heat, and this is reported as ΔT, the heat rise for a set cycle of test. Boonstra6, Davies10, Vegvari17, Hess31 and Railsback4 all noted a decrease in heat build up (allied to a reduction in hysteresis) with progressive mixing. Drogin3 showed that heat build up increased with varying degrees of long mixing when the Goodrich Flexometer was used, but when the identical stocks were tested in the Firestone machine the trend was reversed. He ascribed the apparent paradox to machine factors. In a subsequent study Drogin22 indicated that using the Goodrich Flexometer SBR stocks decreased in heat build up with mixing time, while the effect in NR stocks seemed dependent on the type of black filler utilised (with SAF, heat build up increased while with HAF and EPC it decreased slightly with increasing mixing).

Also closely related to those dynamic properties is the resilience of a rubber composition. A highly elastic material will show high resilience, while a 'lossy' material (one with a large viscous component) will exhibit low rebound resilience. Indeed, Marvin82 derived an expression relating resilience (R) expressed as a fraction (not as a percentage as is customary) to tanδ,
\[ R = e^{(-\pi \tan \delta)} \] 3. (9)

The higher the \( \delta \), the lower is resilience.

Resilience can be measured in a great many ways, for instance, by using the Lupke pendulum \(^{83}\), the Goodyear-Healey \(^{84}\) or Dunlop \(^{83}\) tripsometers. Dannenberg \(^{2}\), Vegvari \(^{17}\), Raitsback \(^{4}\) and Hess \(^{31}\) found the quantity to show a positive response to mixing in keeping with the theoretical predictions, for a great majority of their stocks evaluated. The exceptions were compounds filled with low structure blacks, whose initial low hysteresis probably was responsible for masking changes during mixing, for, after all, resilience as measured by pendulum methods is not too sensitive a test.

3.3.4 Other physical properties

One property that does not conveniently fall into any of the foregoing, is that of permanent set. This is usually measured by deforming (usually compressing) a sample (either to a constant strain or by a constant stress) and after a period of time under load and another period of recovery, its height is measured \(^{65}\). This is expressed in terms of a reference height, and quoted as a % referred to as permanent set. Basically it is a measure of the recovery of the sample.

Boonstra \(^{6}\) reported permanent set measured on the Goodrich Flexometer as decreasing with increasing mixing time. Drogin \(^{3}\) found his experimental data to indicate that mixing had a varied effect on compression set depending on the rubber and the carbon black therein. Here too, the occluded rubber theory could be introduced to explain these experimental observations. As with unvulcanised rubbers, as effective filler volume fraction falls during mixing, elasticity increases. This has been evidenced before by die swell. With a vulcanised compound, even though an overall rise in elasticity will be noted by virtue of crosslinking, the filler effect too must be super-
imposed. It is to be inferred therefore, that vulcanised, well mixed stocks are more elastic than their poorly dispersed counterparts. Permanent set, being a viscoelastic phenomenon, is therefore affected by mixing efficiency.

3.3.5 Destructive dynamic tests - cut growth and flex fatigue

These properties are practically important in rubbers since most products are subjected to some form of fatigue loading. Failure may be caused by flaws induced in service or more important in this instance, by adventitious flaws, such as carbon black agglomerates\textsuperscript{85}. Topci\textsuperscript{86} showed this to be the case and emphasised the need for good dispersion to ensure acceptable fatigue life in tread compounds.

As with tear and tensile strength, failures in flexure are initiated by flaws which act as stress concentrators. The initiated crack, produced by these inhomogenieties then undergo as an irreversible kinetic process of growth, which, in the extreme case, causes rupture\textsuperscript{87}.

The difference between fatigue and tensile or tearing failure is that fatigue failure, being a slower process than the former two, is affected by environmental factors such as temperature, which then influences the patterns of propagation. But, after this induction period of slow growth, fatigue failure often culminates in a characteristic rapid spontaneous tear. There is a thread of continuity between the mechanisms for all three types of failure. All involve nucleation of failure at microstress concentrations, concurrently at many points. The propagation of failure is by transfer of some of the relieved stress to similarly highly stressed elements, so that the main failure advances as the localised stresses coalesce.

Lake and Lindley\textsuperscript{88} developed an empirical equation that predicted the fatigue life of gum SBR vulcanisates, to be inversely proportional to the third power of cut size, using deliberately introduced
cuts. Dizon et al.\(^{85}\) extended this treatment to black loaded stocks. They postulated that:

\[
N = \frac{G}{3 (2kW)^4 C_0}
\]  \hspace{1cm} \text{(10)}

where \(N\) = cycles to failure
\(G\) = a material constant (dependent mainly on black structure)
\(k\) = a function of the extension ratio \(\lambda\) reached during deformation
\(W\) = strain energy per unit volume

and 
\(C_0\) = the size of flaws (black agglomerates) expressed in equivalent cut length calculated by

\[
C_0 = \frac{\pi D^2}{2t}
\]  \hspace{1cm} \text{(11)}

where \(t\) = specimen thickness
\(D\) = diameter of (assumedly spherical) flaws

Thus, as the diameter of the flaw increased, so did \(C_0\), and under constant conditions of \(G\), \(k\) and \(W\), \(N\) decreased. This equation was used by Dizon et al.\(^{85}\) to predict \(N\) for stocks containing different particle sizes of black, when it was noted that fine particle sized fillers (e.g., HAF (L/S)-N327) gave inferior fatigue properties to coarser blacks (such as SRF (H/S)-N765). This is due to the inherent tendency of the former class of filler to form a small percentage of large agglomerates in rubber (shown microscopically\(^{85}\)). This analysis showed that the agglomerated carbon black in an 85% dispersion (one in which 85% of the total black is present in aggregates of smaller than 9 \(\mu m\) in linear dimension), exists in a size distribution ranging from 20 \(\rightarrow\) 200 \(\mu m\), and mainly in the 20 \(\rightarrow\) 100 \(\mu m\) class.
Using Dizon's equation to relate to the problem of dispersion assuming constant black type (and thus G), k, and W, it is evident that as aggregate size D increases, N progressively falls. In addition to flex fatigue cycles to failure being low for a badly dispersed compound, crack propagation under flexing will be faster since the stress concentrations will be physically closer together, offering a preferential low energy path of rupture through the bulk.

In the light of this discussion it is not surprising that a very high dispersion level is required for a maximum flex fatigue resistance level to be achieved, since elimination of the small percentage of large agglomerates is crucial to the property. It is also true to say that cut growth slows down long before this maximum flex resistance is achieved with mixing time. Even though the large agglomerates still exist (as shown by low cycles to failure) these will be increasingly far apart and agglomerate to agglomerate failure paths will become less probable as mixing proceeds. Indeed this is clearly borne out by the results from Davies, which show that to reach a maximum flex fatigue resistance a dispersion rating of greater than 96% is required. By contrast, to attain an optimum cut growth level, a dispersion of only about 85% is shown to be necessary.

Boons showed cut growth to slow down as mixing improved, and Wood noted rapid treadgroove cracking in poorly dispersed tyre stocks. Wood, Hess and Vegvar noted that mixes with very poor dispersion had low measured fatigue lives, which increased about 10 to 15 fold when dispersion was classified as excellent. Drogin found that mixing time affected flex resistance variably, depending on rubber and type of black utilised.

Dizon employed a statistical treatment of successive fatigue to failure observations and found that the Weibull distribution function adequately described most data involving single polymer systems and the use of at least twelve specimens. By using this function, it is possible to estimate for a given sample population,
the characteristic life (the mode), the 'Wiebull slope' - or the shape factor (- a constant that will produce a function that will fit the distribution being studied), and an estimate of the fatigue life of the lowest 10% of test pieces in the distribution. Dizon found that with increasing energy input of mixing the characteristic life rose markedly, but the 10% life only fell very slowly with increasing mixing; he suggested that this was due to the persistence of a small number of large agglomerates even at high mixing times (or mixing energies).

3.4 Measurement of Polymer Modifications

In 2.3 it was noted that the effects of the cumulative deformation of rubber during mixing changed its elasticity and viscosity, by a reduction in average molecular weight. Polymers contain very long chain molecules in their composition, and these longer molecules are much more statistically probable to rupture first, thus causing considerable molecular weight distribution change during mixing. It is possible to measure molecular weight (either number, weight, or Z average) by osmometry or light scattering and practically note the decrease that signifies more intensive mixing, of the rubber quotient only.

The rupturing of long molecules affect computed $M_w$ (weight average molecular weight) more than $M_n$ (number average molecular weight) since $M_w$ is more biased towards longer chains. The ratio $M_w/M_n$ (heterogeneity index) decreases as mixing proceeds. This ratio is obtainable either by separate $M_w$ (by light scattering) and $M_n$ (by osmometry) measurements or directly by Gel Permeation Chromatography as performed on the polymer solution extracted from a mixed stock. However, as noted earlier neither of these methods yields any information on the state of carbon black dispersion in the matrix.
3.5 Measurement of Black-Rubber Interaction

It is now widely recognised, that during the mixing of a carbon black with rubber, the polymer molecules are ruptured by the shearing action and the free radicals generated at the ends react with active sites on black particles forming more or less permanent attachments\textsuperscript{94,95,96}. It is evident that the more intensive the mixing, the larger the number of reactive polymer ends in the system, and also the greater the area of active sites of carbon black produced, by virtue of the increasing filler surface presented to the polymer with continuing dispersive mixing. There is also the possibility of physical attachments being formed such as through Van der Waals absorptive forces\textsuperscript{97} on highly active sites on the black surface.

A model for the system has been developed by McBrierty et al\textsuperscript{98} embodying the following features:

i) polymer-polymer crosslinking (caused by two active polymer ends reacting

ii) polymer-black interaction (by an active end chemically reacting with a filler surface site)

iii) physical interactions caused by penetration of rubber molecules into the porous surface of the black particle

iv) linkages between black particles by a tie molecule of rubber

v) multiple absorptive attachments of polymer molecules onto the black surface

vi) the presence of unterminated chains and folds in molecules.

In this light, the bonding between the rubber and filler is seen to exist as loosely bound and a tightly bound component. (Figure 3.14).

Due to this physico/chemical effect in the unvulcanised form, the rubber molecules anchored to the reinforcing filler are no longer soluble in the usual rubber solvents. The percentage of rubber that is so affected is called "bound rubber" and is left as a gel (with the carbon black) after the solubilised (non-bound) portion is decanted
A. PHYSICAL ATTACHMENT
B. CHEMICAL ATTACHMENT
C. CROSS LINKED RUBBER MOLECULE
D. LOOSE FOLD
E. TIGHT FOLD
F. MULTIPLE ADSORPTIVE ATTACHMENTS
G. INTER-PARTICLE LINKAGE MOLECULES
H. CILIA MOLECULES.

FIGURE 3.14 Molecular model of the carbon black filled composite
off after a period of immersion in solvent. Evacuation of residual solvent and weighing of the dry residue (when expressed variously as a percentage of the original stock weight used as a sample) gives an estimate of bound rubber.

This quantity has been widely used as a measure of dispersion. Studebaker and Beatty, Berry and Cayre, Bittel, Turetzky et al, Van Buskirk and co-workers and Sweitzer et al found that the quantity increased to a plateau with increasing mixing time. Ulmer, Watson and Ebell have found it to attain a maximum and then drop off slightly with increasing mixing for NR and IIR systems. Wan Idris found SBR systems to reach a steady value while his NR mixes dropped off in bound rubber very rapidly after mixing energies of about 1000 MJ/m³. This effect is ascribed to polymer breakdown, yet if this is the case, more active ends will be generated for bonding with black surfaces, resulting in an increase in bound rubber, not the observed decrease.

Recently McBrierty proposed a technique for measuring the bonded rubber (the tightly bound segment, but not the bound rubber) of his postulated model. He used low resolution Nuclear Magnetic Resonance (NMR) Spectroscopy. He noted that for black filled rubbers, at fixed temperatures well above glass transition, the spin-spin relaxation time (T2) was very short compared to unfilled materials. A short T2 characterises fairly rigid material while larger T2's indicate molecular motions possessed by unhindered materials. This in turn meant that for filled systems rubber molecules are severely motionally hindered. By identifying the intensity of the T2 due to the bonded rubber component it was found that for a large amount of bonded rubber (good dispersion) it was large while for a poor dispersion containing little bonded rubber it was smaller. McBrierty claimed correlation between microscopical assessments, both in reflected and transmitted light, and also in a factory situation isolated compounds that subsequently processed less than satisfactorily, due to dispersion problems.
When unvulcanised filled stocks are immersed in solvent, as in a bound rubber determination, the insolubilised gel absorbs a certain weight of solvent. When this weight is expressed as a ratio of the total weight of insoluble rubber in the jelly, a parameter known as swelling index is obtained. On the supposition that a variety of 'crosslinking' occurs between the rubber and the black, the higher the bound rubber, the lower the swelling index, because of a tighter 'network' formation. This is borne out by Southwart who found a linear dependence of swelling index on bound rubber for a range of immersion times, storage times, and filler contents. Studebaker calculated a quantity $V_r$ (presumably the reciprocal of swelling index) which increased with mixing time.

3.6 Electrical Properties and Other Energy Based Tests

Morrel, in a review of electrical methods used to characterise dispersion has noted that d.c. resistivity passes through a minimum as dispersion is improved. The reasons ascribed to this increased conductivity at low dispersions have been that the large aggregates present at this stage are in close proximity to each other and conductive paths are formed. Void penetration by rubber also evidently increases conductivity, but as mixing progresses since the aggregates are broken up and separated from each other, resistivity begins to rise.

Several workers have noted this phenomenon while yet others, without noting the minimum, have noted an increase with dispersion. While the majority of these tests have been carried out in the cured state, Boonstra, Ford and Wan Idris tested uncured samples with the same general findings except that no exponential increase was noted by the last worker for SBR (linear instead). Boonstra, in addition applied the statistics of variation to his resistivity observations and found (as with physical properties discussed before) the variation to fall with progressive mixing. Usachev et al measured resistivity
continuously by inserting two needle probes (the contacts) into
the chamber of an internal mixer and found the differences in
resistance between the two selected microareas fell to a low
constant value as mixing approached completion.

A.C. resistivity was measured on a series of mixes having
different dispersions by Woods and Krosky\(^5\). They found good corre-
lation between their a.c. parameter and processing as well as vulcanisate
properties of the stocks.

Other miscellaneous electrical (or radiation) based methods
for assessing mix uniformity have been as follows: Zaitseva et
al\(^{118}\) and Fedyukin et al\(^{120}\) used the variability of attenuation
of microwaves and ultra high frequency radio signals respectively,
while Havenhill et al\(^{119}\) measured the electrostatic contact poten-
tial developed in an internal mixer. The last work related to
incorporation, since it indicated when there were no more loose
powders left on the elastomer surface.

3.7 Measurement of Viscoelastic Properties

3.7.1 Stress Relaxation

As mentioned before, rubbers are complex materials, neither
purely elastic nor completely viscous; they are made up of a combination
of these two components, thus belonging to a class of materials
known as viscoelastics. Although the presence of such reinforcing
fillers as carbon black enhances the desirable properties in a
rubber composition, inevitably, the inclusion of such rigid mate-
rials leads to the reduction of rubber elasticity properties.

Thus, in the filled material certain properties such as creep
and stress relaxation rates are noted to be much faster than for
gum stocks of otherwise identical composition. Creep is the increa-
sing deformation noted with time when a rubber sample is held under
constant stress. Stress relaxation is the decay in stress noted when
a rubber is held at a constant deformation over a period of time.
The main factors affecting the viscoelasticity of filled stocks are postulated as being the following: changes in configuration of molecular chains, manifested as resistance to relative movement; chain length, and the number of possible points of attachment governed by this factor; and importantly, the interaction between polymer and filler. Several powerful arguments have been put forward claiming the invalidity of processability tests that consider either elasticity or viscosity of rubber as separate entities. After all, if a polymer is a viscoelastic material, is the balance between the relative magnitudes of the viscous and the elastic elements not more important than their individual contributions? It is mainly to answer such questions that tests for measuring the stress relaxation and creep properties of unvulcanised rubber have come into being.

Stress relaxation tests can be done following three fundamentally different approaches; in tension, bulk compression, or shear.

Several instruments have been developed solely to measure stress relaxation. The Monsanto Processability Tester (MPT), which is basically a sophisticated capillary rheometer, also has a secondary function of measuring SR. At the end of a fixed shear rate extrusion, the piston can be held steady, the electronics of the machine noting an initial stress on the bulk of the rubber in the extrusion chamber and a stress relaxation constant (the time taken for the initial stress to drop to a predetermined value). Another machine which accomplishes stress relaxation testing as a secondary function is the Rotary Rheometer developed by Avon Co. and by Sondes Place Research Institute. Moghe's machine and this last one bear certain similarities in that they both act in shear, the shearing member being a rotor which moves in a cavity of a set geometry. Again, the rotor is turned against the rubber in the cavity to a given deflection; the peak stress is noted as is the time to reach a given fraction of this. Additionally in the DSR (Dynamic Stress Relaxometer) of Moghe, it has the additional
capability of integrating the area under the stress relaxation curve to any time \( t \). The machine described by Berry and Sambrook (SRPT - Stress Relaxation Processability Tester) works in bulk compression, and depends on the deformation of a given volume of rubber of set dimensions by two parallel platens. Again peak stress is observed, as is the reference stress after a pre-set period of relaxation. The terminology of bulk compression must be queried here since no constancy of volume is encouraged.

Using the DSR, Myers and Newell noted a decrease in the integrated area of the SR curve to a given time with increasing unit work of mixing, indicating as expected the faster relaxation. More filler/polymer interactions form with longer dispersive mixing times, and slippage occurs from these links when an uncured polymer is deformed.

Using the SRPT, Leblanc and Price approximated the stress relaxation curves to a power law form

\[ P = K t^{-a} \]  \hspace{1cm} 3.12

where \( P \) is the decaying pressure, \( t \) the time, \( K \) and \( a \) the characteristic parameters of the relaxation curve, the former giving a measure of stiffness and the latter giving a relaxation rate.

Leblanc and Price found that \( K \) correlated with Mooney viscosity and decreased monotonically with mixing energy input, for both SBR/HAF and SMR (NR)/HAF stocks, \( a \) was found to increase and then plateau with mixing time, signifying an increasing relaxation rate. The above workers also noted that the deviation from linearity in their log \( P \) vs Log \( t \) plots was related to lack of homogeneity in the stock, and correlated this feature with the correlation coeffi-
cient \((r^2)\) from linear regression on the experimental \(P\) and \(t\) datum.

Freakley\(^{191,192}\) and Basir\(^{126}\), using the SPRI/Avon rotary rheometer utilised two different stress relaxation parameters. The former describes the use of a relaxation constant which is analogous to the quantity \(K\) in equation 3.12, derived similarly, from a stress relaxation curve. The quantity is shown to increase with intensiveness of mixing, which is contrary to Leblanc's and Price's\(^{121}\) findings in respect of their constant. Freakley's\(^{191,192}\) results are for a PVC-nitrile blend, which due to the non-elastomeric component, could give rise to values not totally predictable by previous findings with all-rubber stocks. The second treatment used by these workers\(^{126}\) uses the \(\log t\) versus \(\log G\) stress relaxation plot from which the intercept was equated to a function of shear modulus \(G\). The quantity was found to decrease with increasing energy input of mixing in the majority of instances; the exceptions to this were noted for other settings of the mixer variables (such as rotor speed and cooling water temperature).

Again, the influence of the non elastomeric component (the PVC) is significant, its presence sometimes causing the expected established responses to pure rubber/filler mixing to be reversed or changed somewhat.

3.7.2 Creep

Several models have been put forward to explain the viscoelastic behaviour of rubber. These are based mainly on perfectly elastic (Hookean) springs and Newtonian dashpots. The simplest models which deal only with one of each component are the Maxwell and the Voigt (or Kelvin)\(^{127}\) models which consider the spring and dashpot in series, or in parallel, respectively. However real polymers do not behave as single Maxwell or Voigt models and thus a profusion of more complex models have sprung up where a plurality (or an indefinite number) of Maxwell and Voigt models are combined in a variety of ways. Obviously the greater the number of elements
the closer the viscoelastic behaviour of polymers will be modelled by such "generalised" or "composite" models, since in the extreme, a continuous distribution of relaxation mechanisms will exist, closely duplicating individual molecular viscous and elastic behaviour. The determination of a distribution function combining and accounting for the differences between the various model components (the relaxation spectrum for stress relaxation or the retardation spectrum for creep) will totally describe the viscoelastic response of a polymeric material. This requires however accurate and long experimentation, which cannot be considered for a rapid estimate of rubber processability. Even more complicated models having non-Newtonian dashpots and non-linear elastic springs have been postulated, but these will be relegated to the background due to their extreme complexity. An example of practical creep testing only will be considered here.

Using a basic creep test, at constant loading with unvulcanised cord type samples, Wan Idris obtained a family of curves from his mixes of differing energy inputs.

\[ \text{FIGURE 3.15 The dependence of creep behaviour on mixing energy} \]
The creep rate was found to increase (Figure 3.15) with increasing mixing. Approximating (as Leblanc\textsuperscript{121} did for stress relaxation) the creep curve to a power law

\[ \gamma = K t^n \]  

where \( \gamma \) = strain  
\( t \) = time  
\( K \) = constant  
and \( n \) = power law index,

Wan Idris found that \( n \) showed a tendency to decrease with mixing while \( K \) (the creep rate) increased.

The same researcher obtained plots of true stress versus elongation rate for his unvulcanised cord type samples, using an elongational testing machine. He obtained a family of curves as follows (Figure 3.16), where it was observed, elongational modulus and surprisingly, breaking stress and strain were all noted to decrease with increasing energy inputs of mixing.
In addition Wan Idris\textsuperscript{20} used the T.M.S. model\textsuperscript{128,129} postulated by Turner and co-workers in an attempt to find a theoretical base for his observations in elongational testing and creep. This model is another of the profusion of spring/dashpot models noted earlier, but since these results do not have any practical significance, they shall not be reviewed here.

3.8 Surface Testing

The fact that a carbon black/rubber composite (whether vulcanised or unvulcanised) when cut with a sharp razor blade leaves a surface indicative of the nature of the dispersion of filler in the polymer has been known for some time\textsuperscript{130}. This is due to the fact that the carbon black agglomerates deflect the cut path, because of their higher hardness relative to the surrounding matrix. Thus, the worse the dispersion, the larger the aggregates, and thus the rougher the surface generated.

Mechanically based roughness testers have been used before and a stylus type device was used as early as 1941\textsuperscript{131} for measuring the surface roughness of panels of synthetic resins, paints and so on. In 1945 Mooney\textsuperscript{60} described a Rugosimeter for measuring the roughness of calendered rubber sheets but surface testing came into its own in the metal engineering sector of industry, where stylus techniques were developed mainly to meet the need for quantitative assessment of the surfaces of manufactured components\textsuperscript{133,134}.

The basic instrument comprises a pick-up, mechanical system, electronic unit and a metering and/or recording device. When being used, a sharply pointed stylus is rested lightly on the test surface and carefully traversed across it. The up and down movements of the stylus relative to a suitable datum are magnified and a profile graph recorded and/or some meter value noted.

The texture of a surface may be defined by a number of parameters\textsuperscript{135,136} (Figure 3.17).
ROUGHNESS

PROFILE

CENTER LINE

Figure 3.17
Profile - the contour of a section perpendicular to a surface unless some other angle is specified.

Roughness - the finer irregularities in surface texture, the height, width and direction of which establish the predominant surface pattern.

Waviness - the irregularities of the surface texture which are of greater spacing than roughness (roughness is superimposed on waviness).

Roughness height is the arithmetic average deviation measured normal to the centre line which passes midway between the peaks and valleys. Roughness width pertains to the spacing between repetitive units of the surface pattern and is measured parallel to the surface. Many other parameters may be obtained from the profile graph such as the ISO 10 point height parameter ($R_z$), average wavelength-average ($\lambda_a$), or r.m.s. ($\lambda_q$), average slope of profile ($\Delta a$ or $\Delta q$), maximum or average peak to valley height within assessment length ($R_{max}$ or $R_t$), skewness (the shape factor for the amplitude distribution curve $R_{sk}$), high spot count from a given datum (HSC), mean spacing between high spots ($S_m$), bearing ratio ($t_p$) or ratio curves (showing how bearing ratio varies with level) and maximum profile height or average profile height ($R_p$ or $R_{pm}$) and so on.

Hess and Vegvari used a stylus type machine to investigate the profiles obtained from cut surfaces (both vulcanised and unvulcanised) of a variety of rubbers (SBR/BR, SBR, IIR, NR/BR, CSM, ECO, CR, EPDM, and NBR) reinforced with a profusion of fillers (black and white, reinforcing and nonreinforcing) mixed under different input energy conditions.

From their profile graphs, they obtained estimates of parameters $f$ and $T$, the roughness peak frequency per centimetre and the average peak height in $\mu m$ respectively. They found both $f$ and $T$ decreased, suggesting a smoother surface with progressive mixing.
For this is not a surprising finding, but in actuality, should increase as agglomerates that are broken down to a smaller size, thus also increase in number. This is possibly due to the resolution problem presented with an instrument of finite stylus size (5 μm diameter) and obviously signifies the decreasing frequency of comparatively large agglomerates with mixing. Peak frequency (f) however was noted as the single most important factor by Hess and Vegvari relating to changes in black dispersion. Using microscopical estimates of percentage carbon black dispersed, the above authors correlated it with their parameters as follows:

\[
D.I. = 100 - 10 \exp [A \log (f^2 N) + B]
\]

3. (14)

thus using a combined measure of \(f^2 N\) for surface roughness (\(f^2 N\) will decrease with increasing dispersion).

The dispersion indices calculated by the authors correlated with a whole range of rubber properties indicative of dispersion. These were Mooney viscosity, stress strain properties, flex fatigue, electrical resistivity, compression set, hardness, abrasion (treadwear) resistance, heat build-up, extrusion swell and rebound resilience.

These workers document unvulcanised compounds to have rougher surfaces than equivalent vulcanised surfaces, but also emphasise the problems associated with porosity in the former class. No damage is seen to result from up to 15 successive tracks down the same line in vulcanised samples, but some breakdown by the repetitive action of the stylus was noted in uncured samples.
3.9 Miscellaneous Other Methods

Boonstra and Medalia\textsuperscript{6} measured the specific gravity of black stocks subjected to different mixing times and noted that at the very early stages of mixing (<1.5 minutes) low values were noted. This was probably due to the inclusion of air within the black agglomerates in the early stages of mixing before complete void penetration by the rubber had taken place. After 1.5 minutes of mixing in a BR Banbury there was no change noted in S.G. even though other measured properties were changing very quickly indeed soon after this period of time.

Gerke\textsuperscript{139} et al patented a method for judging the dispersion of a black in rubber by dissolving the unvulcanised rubber in a solvent and measuring the amount of light transmitted. The higher the percentage light transmitted through the solution, the worse the dispersion. A fine dispersion would form a very dense suspension and thus transmittance would be low.

Dannenberg\textsuperscript{2}, had criticisms of the above for several reasons. It was (he said) extremely difficult to dissolve a rubber stock containing normal loadings of black, without utilising high temperatures or agitation to promote the process (these would destroy the features needing preservation). He also said that even if extreme care was taken, the swelling of the rubber prior to dissolution might itself contribute to aggregate breakdown. Dannenberg found that no heating or agitation was necessary if a 0.05\% solution of benzoyl peroxide in benzene was used as solvent. The peroxide peroxidised the gel, and a stable and well dispersed system was produced. By diluting to 0.001\% solutions (calculated on black) he found a negative effect on transmittance when dispersion improved.

Tokita and Pliskin\textsuperscript{140} note a related property to specific gravity; specific volume of material in the mixer decreases with increasing mixing time abruptly in the early stages and then reaches a constant value. The attainment of this constant value coincides with the end of the wetting stage (shown by the torque curve for the...
mixer), a maximum Mooney being reached and the lowest extrusion die swell level. The writers have ascribed the attainment of this minimum to the formation of a single mass of filler and rubber in which penetration of the filler voids, by the elastomer, has occurred.

3.10 Microscopy

3.10.1 Light microscopy

Dispersion is a visually discernible phenomenon. Indeed, effects caused by dispersion and observable by eye have been documented. Thus a good dispersion is noted to have a shiny finish, while a bad one is dull and rough. In really bad cases, pieces of black can be seen with the naked eye. As early as the 1920's however microscopical methods were being used by early workers in the field of carbon black dispersion. In the last few decades considerable improvements in techniques have given new impetus to the use of microscopy that stemmed from these early precursors.

The first part of this section considers light microscopy while electron microscopical and microradiographical techniques will be dealt with in the second.

The earliest "microscopical" method probably used was by a supervisor or mixing shop manager using a hand lens to inspect the surface of the rubber. Reflected light techniques have become very popular chiefly because of the simplicity of sample preparation which entailed either looking at the surface of a stock produced, or tearing or cutting a piece of the material and looking at the exposed face. Stumpe and Railsback viewed cut specimens in a bright field under reflected light at about x60 magnification and evolved ten photographic comparators consisting of a range of dispersions from poor to excellent. As noted earlier surface topography is affected by dispersion and thus variously sized bumps and depressions
will be produced by the cut on the surface. Bussemaker\textsuperscript{148} noted that the method would not be applicable to stocks containing reclaim and allied materials, since these would contribute to roughness irrespective of dispersion. (It could be suggested that the superimposed roughness due to reclaim would be of a different nature to that produced by the carbon black aggregates, and could be compensated for by means of a series of controls). Sample preparation in the above case was simple and entailed cutting through the sample with a vertical stroke of a mounted razor blade.

Torn surfaces may be prepared by making a vulcanised sheet sample, nicking it and then pulling (manually or by machine) steadily, whence the tear propagates. The problem with this method, lies in the difficulty of obtaining planar surfaced samples that present a uniformly focussed field down the microscope, especially when comparatively large areas are viewed, as during low power observation. Medalia and Walker\textsuperscript{149}, Sweitzer and co-workers\textsuperscript{150,151,152}, Grenquist\textsuperscript{156}, Stumpe and Railsback\textsuperscript{130} all used this technique coupled with the use of photographic comparators which has now been embodied in an American standard\textsuperscript{153}. In an attempt to adapt this method (highly subjective by virtue of the required visual comparisons) to process control, Persson\textsuperscript{154} used split field microscopy in reflected light, whereby half the microscopical field was occupied by the sample, and the other half by the comparator. As with the previous work, (Refs. 150,151,152,130), ten comparators were used, but here, in the form of transparencies, each of which could be moved easily into the relevant half field for comparison with the sample. Persson\textsuperscript{154} also suggested the cutting or tearing of the sample from a Monsanto oscillating disc curemeter microdie moulding produced routinely in process control.

Fletcher\textsuperscript{158}, while examining a swollen vulcanisate sample by reflected light in another context, felt that this technique might be used to indicate uneven dispersion of compounding ingredients. The MRPRA\textsuperscript{159} have described the stretching of a de Mattia flex
fatigue test piece and found visual examination of this to correlate with dispersion.

Coming now to transmitted light microscopy, where a beam of light passing through the sample is the source, several methods of sample preparation have been used. "Squeeze-out" methods are described by Pavlova et al.\textsuperscript{161}, Allen\textsuperscript{160}, Loewen\textsuperscript{162}, Danneberg\textsuperscript{163} and Pohle\textsuperscript{164}. In principle, this consists of pressing a small sample of unvulcanised rubber between flat surfaces, the rubber having been presofterned either by heating or the action of a swelling solvent. There seems little doubt that this treatment will alter the dispersion/distribution patterns present in the original. A variant of this method (again with the same limitations) was used by Drogin\textsuperscript{155} who pressed unvulcanised samples initially between ferrotype plates, and then further reduced the thickness to about 0.1 mm by stretching the sheet over the top of a beaker. Hills\textsuperscript{165} described a rather unusual method for transmitted microscopical examination, when he recovered the used test piece from a Wallace Rapid Plastimeter. The top paper was pulled away, and the film of rubber adhering to it was examined. Ladd\textsuperscript{91} described a rub-out method based on smearing.

All these methods described up to now have gone to great trouble to reduce the thickness of the specimen such that trans-illumination is possible. The widest used method for doing this has been by using microtomy of frozen rubber samples. Hess\textsuperscript{166}, described methods of sectioning using either base sledge or rotary microtomes while Pavlova et al.\textsuperscript{161} have used an ultramicrotome, using dry ice and nitrogen respectively; these agents restrict the flexibility of the sample by chilling the polymer to approximately its glass transition point. Glass and metal knives of differing configurations have been used, (dry or wetted with solvent) with the aims of obtaining section thicknesses of about 2 \( \mu \text{m} \), ideal for the light microscopy of black filled rubbers.
Several workers have used this basic method both qualitatively for visual assessment of dispersion, and also with the quantitative formula and methods proposed by Leigh-Dugmore and Medalia. Both methods use a common starting point. The sections obtained are viewed in low power (ca x77) transmitted light, after they have been swollen in a suitable solvent (e.g. xylene) which makes the task of spreading the specimens out on a slide much easier. A graticule is contained in the eyepiece of the microscope. Black aggregates in the field occupying more than half a graticule square are counted. Since a graticule square is 13 μm in dimension, this ensures that only aggregates of greater than 84 μm² are included in the total.

According to stereological theory, this technique (called areal analysis) is recognised as being one of the methods for estimating the volume fraction of a disperse phase in a matrix, assuming that the thickness of the section is much smaller than the size of the agglomerates. It is immediately apparent that this counting procedure could be tedious, especially if particularly bad dispersions are being studied. In such cases, the count is usually estimated by inspection.

Having obtained the number of squares counted on each field (U) and averaging five of these for a given sample (Ū) one of two widely used calculations are employed.

Leigh-Dugmore's formula was as follows:

\[ D = 100 - \frac{S U}{L} \]

where

- \( D \) = amount of carbon black dispersed (%)
- \( S \) = area of swollen section
- \( L \) = area of unswollen section
- \( L \) = carbon black (volume percent loading) in the compound

\[ 3.15 \]
(1.86 is the specific gravity of carbon black, originally determined by helium displacement).

Several puzzling features have been observed when using this calculation, in particular that dispersion values of \( D \) less than zero are obtainable in bad dispersions.

Equation 3.15 tacitly assumes\(^{169} \) that the agglomerates as well as the individual particles of carbon black have an S.G. of 1.86, since it is only on this assumption that the volume ratio of agglomerates to total carbon black can be set equal to the fraction of undispersed black. This assumption is non-tenable, and one must arrive at the total volume of carbon black present in the agglomerates, rather than just the total volume of the agglomerates to arrive at the fraction of undispersed black when division by \( L \) is effected.

Meldal\(^{169} \) assumed a value of carbon black in agglomerates of 0.4 of the value of the agglomerates, but added the proviso that this is not known with any accuracy and may be different in different stocks. He proposed the following formula which took into account both this above problem and the possibility that the agglomerates themselves might swell, due to occluded rubber.

\[
D = 100 - \frac{\nu \cdot S}{A \cdot L} \tag{3.17}
\]

where the new terms \( \nu = \) volume fraction of carbon in the agglomerates and \( A = \) areal swelling factor of agglomerates.

Thus if \( A = S \), the equation simplifies still further. This equation still yields negative values from extremely badly dispersed stocks, but the improvement is considerable (e.g. \( D \) by Leigh-Dugmore is -364%, by Meldal = -21% as compared to a 'true' estimated rating of 10-20%).
In sum, even though these methods yield quantitative data, the sectioning and counting techniques at best are difficult and time consuming and require a fair degree of operator skill. Since the established methods specify glass knives for sectioning, this adds to the time spent in sample preparation, as glass knives cannot be stored even for relatively short periods due to glass flow. Further, the counting procedure does not appear to be sensitive enough to discriminate between slightly differing levels of good dispersions. While it cannot be denied that properties are adversely affected by agglomerates of greater than 9 μm in linear dimension, an additional factor appears to be of importance, that is the microdispersion in the matrix or the state of the carbon black features of less than 9 μm. Wood showed this to be so for abrasion resistance, which showed no correlation to optical dispersion rating.

As an alternative to the counting method Medalia suggested the use of a classification chart to estimate dispersion ratings in transmitted light. Forty two comparators are illustrated, each of which bear a letter and number rating. The number ratings refer to agglomerate sizes (1-6) while the letter rating refers to the state of the dispersed black (A-H). Thus A1 would be an excellent dispersion while H6 would be very poor. Again, subjectivity enters the assessment, especially when the sample being viewed consists of a different volume loading of black to that used in the standard.

Pavlova et al used higher power magnification (x350) in transmitted light and by a highly tedious manual procedure counted aggregate areas and diameters, the number of discrete sized aggregates, the total area examined, and the proportion of the total area of the sections examined occupied by aggregates of a given size. No results are given or correlations made with other established methods.

As will be noted, bright field methods have been used exclusively by workers studying carbon black/rubber dispersions. No other higher contrast methods are documented, perhaps because the black/rubber
mixture already represents a fairly high contrast system. Morrel\textsuperscript{105} however suggests that infra-red microscopy might be advantageous due to the different IR absorptions of carbon black and rubber.

One automated technique has been described by Kadunce\textsuperscript{172}. He prepared samples for reflected light observation by using metallographic techniques employed previously for rubbers\textsuperscript{174,173}. Long preparation times are quoted (about 20 hours) and polished mirror like specimens are obtained ready for analysis. Kadunce\textsuperscript{172} also states that thin sections could also be used for the automated image analysis. The AMEDA system used, point counts individual constituents, discriminated by light intensity (optical density) either reflected or transmitted. The sample used (whatever its form) traverses the microscope at a fixed rate and the signals received are analysed and categorised for intercept length. Distributions of particle sizes are thus obtained, as well as total count ($P$), counts on undispersed phase ($P_B$), and total intercepts ($N_x$). Kadunce gives a formula for a dispersion rating

$$D_{\text{AMEDA}}(\%) = (1 - \frac{V}{L}) \times 100$$ \hspace{1cm} (3.18)\\

where $V = \text{volume fraction of C/B in agglomerates} = 0.40$ $V = \text{volume percentage of undispersed (size nominated)}$ \hspace{1cm} particles from $L = \text{volume loading of black in compound as in the L-D\textsuperscript{168}}$ or \textit{Medalia}\textsuperscript{169} formulae.

From his data, Kadunce was also able to characterise the sample stereologically by calculating the volume $\%$ of undispersed agglomerates, mean free path in the matrix ($\bar{x}_X$), mean intercept length of particles ($\bar{x}_B$), variability index (V.I.) general anisotropy, degree of patternness and the mean spatial neighbour distance ($\bar{x}_Y$)\textsuperscript{175,176,177}. 
Spatial relation of stereological parameters in volume element; volume % agglomerates, ($\bar{z}_a$) mean free path length, ($\bar{z}_y$) mean special nearest neighbour distance, ($\bar{z}_l$) mean intercept length, (VI) variability index, (AR) anisotropy ratio

**FIGURE 3.18**

Twelve minutes total scanning time is required to view a sample. No estimate is given of the time taken for analysis and presentation of data. The reference gives no correlation with practical physical properties. There is no doubt though, that this method is by far the most complete analysis for carbon black dispersion in operation to date.

3.10.2 Microangiography

Microangiography, using very soft X-rays in the 1-5 kV range ($\lambda = 3-12$ A) has been used for studying the dispersion of inorganic
fillers and compounding ingredients in rubber. Early studies were carried out by Brock, Ladd and Ladd, and later on by Sweitzer et al., Hess and Hess and Ford. Advantages over light microscopy include the fact that thicker microtomed sections can be examined (20-40 μm). Wan Idris used a squeeze out method, but appeared to lose contrast as a result of his thickness (300 μm).

The method relies on the absorption differential of X-rays in the specified range between carbon black (or other material considered) and rubber. When the sample is backed by the recording film and exposure is made, the contact negative will bear areas of varying optical density, as a result of the differences in absorption. It is noted, however, that the resolution yielded by this method is not as good as light microscopy in resolving small carbon agglomerates.

3.10.3 Electron microscopy

The transmission electron microscope (TEM) whilst giving higher resolving power than the optical microscope, examines such a small field of vision that statistically misleading results might be obtained. The agglomerates seen in many electron microscopes are much smaller than those observed under the optical microscope and are often primary structures of fused carbon particles. In addition there is the problem of obtaining the extremely thin (100 nm) sections required for TEM. Thus apart from the attempts at thin sectioning with ultramicrotomes, replication, cast films and squeeze moulding techniques have been used to prepare specimens suitable for TEM examination. In addition pyrolysis of the rubber to recover the carbon black, supposedly in situ, has been used by Hess et al., but Heckman and Medalia infer that such a process will not preserve the agglomerate state.
3.11 Discussion

From the preceding extensive review, it is obvious that a myriad of methods are used for assessing the goodness of mixing between rubber and carbon black. Though most have scientific validity, various infringing factors make many of them unsuitable for process control assessment of dispersion. The factors that should be inherent in such a test are simplicity, non-subjectivity, cheapness, economy of effort, quickness of sample preparation, reproducibility, repeatability and discrimination over a wide range of possible mixes. It should also be effective for assessing unvulcanised rubbers and should correlate well with service properties related to dispersion. By examining the tests described, one is able to eliminate most of these as possible candidates for process control, while others in satisfying the majority of the above nominated criteria, fall short with regard to the remainder.

Of all the processing properties discussed, Mooney viscosity remains the outstanding choice in terms of the requirements for a process control test. ODR minimum torque tests are rather non-discriminating, while capillary viscometry remains an expensive and time consuming task, even with the advent of automatic testers such as the HPT. Wallace rapid measurements are a likely candidate, but the smallness of the sample requires many replications. Also, the test has not been widely used to assess mixing efficiency. Die swell is a realistic starter, especially if a small extruder is used exclusively for this purpose, rather than the current practice of combining the test with capillary rheometry. The use of laser dimensioning techniques if applied to a laboratory extruder would provide an immediate measure of die swell. On the basis of our preference for unvulcanised compound testing, all the vulcanisate properties would appear to be eliminated as likely candidates as process control tests, especially since there is the invariable need for repetitive testing in the light of statistical variance of test results commonly obtained. Dynamic properties are very discriminating
of dispersions, but again often there is the need to bond and cure samples for vibration. Also the best machines are very high capital investments. There is however the possibility that if unvulcanised dynamic samples may be quickly prepared, a simple dynamic tester (possibly working at only one frequency and small amplitude) would be a satisfactory tool in a mill room. The tests which measure rubber molecular weight or molecular weight distribution only consider the "mastication controlled" region of mixing and are therefore not adequate for characterising factory mixes. The NMR technique appears especially attractive, since a robust low resolution NMR spectrometer is available relatively cheaply, but again it has not been adequately proved with real compounds in practical situations. Ordinary bound rubber tests take far too long to be effective, and also need heavy replication for statistical accuracy. Electrical properties on unvulcanised compounds appear an attractive proposition, but the results obtained appear to be extremely dependent on test method.

Some viscoelastic properties (such as the basic creep test) are too long term in their response, and will serve as research/development tools. Others though (predominantly the DSR and the SRPT) are very fast in operation, and yield much useful information relevant to process control. These certainly do show possibilities for use in an on-line production situation as monitors of mixed material. Surface testing of rubbers has made significant advances in the recent past, and would seem an ideal method, especially since it (as the most recent paper states) is now fully automated. Again expense may be the limiting factor, in the form of the equipment, which at present has a dedicated Minc (DEC) PDP 11 computer interfaced to the stylus apparatus. There is no reason why a cheaper and smaller non-dedicated computer cannot be used to develop this technique even further. The results have been extensively tested, and this is the most favourable of all methods assessed to date. Light transmission on colloidal suspensions is also apparently very simple to operate, but one wonders why it has not received more extensive publicity. This probably is due to the inherent risk of agglomerate break-up.
Microscopy of sections appears to be too time consuming for process control work, while the microscopy of surfaces suffers from its subjectivity and operator dependence. Electron microscopy is without doubt too sophisticated, delicate and expensive for process control, whereas the image analysis methods are much too reliant on long preparation times.

3.12 The Definition of a Further General Objective

In addition to the broad objective demarkations, set out in Chapter 1, an additional general experimental aim will now be specified.

In the light of the foregoing it is evident that there is a strong need for a rapid and accurate method for determining dispersion in a practical environment. Such a technique should then be able to specify whether a mixed compound is suitable for further downstream processing or not.

It is hoped that just such a method can be developed which would satisfy the criteria specified earlier on in this section.
Literature cited

1. ASTM D-1646.


33. J L LeBlanc, presented at the 8th International Congress on Rheology, Naples, Italy (1980).


38. BS. 903: Part A2; 1971.
42. BS 903: Part A3; 1956.
44. W May, read at a meeting of the Midlands Section of the IRI, Birmingham (December 1963).
53. BS 903: Part A26; 1969.
55. BS 903: Part A9; 1957.
56. DIN 53516.
64. E C F Wood, IRC, Brighton (1972).
69. Exploration et chiffage des economies possibles sur l'énergie absorbée pendant les operations de mise en œuvre dans l'industrie due caoutchouc (Premiere partie) Rapport Technique No 102 (Mai 1976).
83. BS 903: Part 22; 1950.
84. ASTM D1054 (1955).
102. V J McBrierty, Communication to the PED, SERC (then SRC).


138. 'Surface Measurement in Depth', Technical Publn., Rank Taylor Hobson Ltd.


153. ASTM D-2663.


156. E A Grenquist, ibid, 4, 29 (1931).


159. NRPRA (now MRPRA), Tech. Inf. Sheet, 63 (1964).


162. H Loewen, Gummi-Ztg, 27, 1301 (1913).

163. H Dannenberg, Kautschuk, 2, 276 (1926).


174. P Brueil, Caoutchouc and Gutta-Percha, 2, 82 (1905).


177. S Chandrasekhar, Rev. Mod. Physics, 15, 86 (1943).


CHAPTER 4

THE DEVELOPMENT AND PROVING OF A NEW MICROSCOPICAL TECHNIQUE FOR ASSESSING DISPERSION OF CARBON BLACK IN RUBBERS

It is perhaps pertinent at the beginning of this experimental chapter to restate the features that should be built into any new dispersion measurement technique; just another addition to the already numerous methods available is undesirable and must be avoided at all costs.

The method must incorporate:

a) Quick, simple and cheap sample preparation,
b) Non-subjectivity and a minimum dependence on operator skill,
c) Discriminatory ability between various levels of good dispersion as well as the ability to distinguish easily between good and bad dispersions; that is, effectiveness through the whole range of dispersion levels obtainable in practice.

and

d) Flexibility in sample preparation and analysis, by designing in the possibility of using both vulcanised and unvulcanised samples.

For the simple reason that dispersion is a visually observable phenomenon, microscopy was selected as being the most obvious general base from which a prospective method could be constructed. In addition (and quite providentially) an excellent polymer light microscopical set-up was in existence at the Institute of Polymer Technology in Loughborough, staffed by experts. Thus it was felt that a lead was developed straight away, in that a valuable back-up (so necessary in a project such as this) was readily available. Also since service requirements and standard specifications are of high priority to both consumers and suppliers of rubber products, there was another criterion that the developed microscopical test should satisfy; that it correlates with physical and processing properties
as measured by the variety of methods described in the last chapter.

The main problems of the hitherto used microscopical methods have been in sum, economics, sample preparation difficulties, the alteration of dispersion during sample preparation, subjectivity of methods and non-discrimination at high dispersion levels; time consuming counting procedures and ignoring the 'microdispersion' state as being contributory to reinforcement, leading to an exclusive preoccupation with the 'macrodispersion' state.

It must be emphasised that the method that is described in the bulk of this chapter evolved through unsuccessful methods investigated by the writer which were extremely valuable in illuminating and tracing a logical path to the one to be proposed. It is strongly felt by the author that a brief discussion of these first forays into polymer microscopy will not be out of place here. Indeed, they will serve to focus the mind on the central problem.

4.1 Research Leading up to the Main Method

The first method explored was based on observation of diffraction patterns produced by coherent light (a laser source) passing through a thin section of the mix cut using a base sledge microtome and a chisel edged steel knife.

The principle of this method was as follows. In a transmission microscope an object is magnified by the objective lens to give an image. The object itself acts as a diffraction grating. This object plane information gives rise to a diffraction pattern of the 'grating' in the back focal plane (bfp), by a Fourier transform of the spatial information in the object. The light waves that proceed from these 'diffraction spots' interfere with one another to different extents, resulting in the formation of an image in the image plane.
Thus, if one inspects the back focal plane (or diffraction plane) instead of the image plane, the diffraction pattern from the object is perceived. In practice this is done by substituting the eyepiece of the microscope with a field telescope focused on the bfp.

All light beams, leaving the specimen at a given angle, pass through a single point in the diffraction plane, the light being diffracted at the largest angles lying furthest from the axis of the microscope. Since the angle of diffraction will be a function of feature size, the observation of a particulate type object in which the particles are randomly oriented (e.g., a black/rubber dispersion) should give rise to rings in the bfp, the diameter of the rings being inversely proportional to the size of the feature (or particles) causing it.

Thus, a diffraction pattern presents an integrated view of the structure sizes present in the object.

This experiment employed certain model samples to begin with. Two types of sample were prepared. Firstly, several types of carbon black of different particle sizes were taken and suspensions of equivalent concentration of these were made up in immersion oil of 1.513 refractive index (approximately equal to the r.i. of rubber). These suspensions were agitated similarly and drops of each placed between a slide and cover slip.

The second set of samples was made by taking just one black type and making up a suspension in oil in the same manner as above. The suspension was divided into three samples and two of these were subjected to differing severities of agitation so as to break down the aggregates of black in suspension. Thus, the non-agitated sample would contain the coarsest particles, with the second having finer and the third sample finest particles of the three. These samples too, were placed between slide and cover slip.
Diffraction trials on these samples were done using a Zeiss microscope and an objective of high numerical aperture, so as to capture as much of the diffracted light from the sample as possible. Illumination was achieved by using a mercury lamp of high power and the beam was narrowed down by inserting a stop of 100 \textmu m diameter in the condenser iris and centering it carefully. A camera was mounted on the monocular which bore the field telescope.

Fairly long exposure times were employed (about 8 seconds) and while the film was being exposed, the stage bearing the sample was rotated about its axis, so that the 'noise' in the diffraction pattern might be averaged out and any maxima present would be manifested as circles in the diffractogram. The basic technique of optical diffractometry has been described by Agar and Keown\textsuperscript{2}.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{strip_diffractograms.png}
\caption{Strip diffractograms}
\end{figure}

Figure 4.1 labelled A-I shows radial strips cut from the diffractograms obtained as described above. The table below identifies black types used in A-F, while G-I represent diffractograms of the black with increasing degrees of agitation.
TABLE 4.1 Black types used for model studies

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>Average Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Medium thermal - MT (N990)</td>
<td>470</td>
</tr>
<tr>
<td>B</td>
<td>New Technology black - NTB (N375)</td>
<td>24</td>
</tr>
<tr>
<td>C</td>
<td>General purpose Furnace - GPF (N660)</td>
<td>53</td>
</tr>
<tr>
<td>D</td>
<td>Super Abrasion Furnace - SAF (N110)</td>
<td>20</td>
</tr>
<tr>
<td>E</td>
<td>High Abrasion Furnace - HAF (N330)</td>
<td>27</td>
</tr>
<tr>
<td>F</td>
<td>No sample</td>
<td>-</td>
</tr>
</tbody>
</table>

F was a control to judge the diffraction common to all the patterns due to optical defects in the microscope components.

The diffractograms themselves showed very little systematic changes. This was disappointing but could have been due to the fact that even though the samples of blacks had different ultimate particle sizes, the aggregates which consisted of these particles and which were produced by light agitation in all these cases were approximately of the same size. Any differences in diffractograms would signify differences in aggregate strength (resistance to agitation) and no more.

The samples G, H and I might shed some light on the above if the diffractograms show substantial differences, because aggregate breakdown was guaranteed by the treatment of agitation imposed on them. However these diffractograms too seem inconclusive, as there are no dominant maxima, and it would seem therefore that two factors contribute to the failure of this technique.

1. The diffraction caused by optical defects in the system (F) appears to dominate all the samples, and
2. Smaller particles which would diffract at high angles would appear not to enter the objective and thus are non-contributory to the diffraction pattern.
Thus, any diffraction observed additional to that caused by the optical defects would be due to the larger agglomerates which would not be characteristic of the black type.

For the sake of completeness, sections of two black containing rubber compounds of different dispersion levels were tested as above. A laser source was used to obtain the high intensity through the section, but the diffractograms showed no appreciable differences. The next method attempted was the examination of samples by dark field light microscopy.

Briefly, dark field microscopy uses a hollow cone of light rather than the usual solid cone to illuminate the sample. The angle of the cone is such that with no specimen in place, or with a completely homogeneous specimen, the light rays converge in the specimen plane, but then pass on to fall outside the aperture of the objective (Figure 4.2a).

When a heterogeneous specimen is used, scattering and diffraction effects change the distribution of the light so that it now falls within the objective aperture. The boundary lines in the specimen appear in the microscope as bright lines, contrasting with the dark background.

Since carbon black scatters light strongly, this method was thought to be ideal. The principle behind the reasoning for using this technique will now be briefly explained. The smaller the particle size of black the more surface area per given volume it exposes to the elastomer. Stereologically, the perimeter length per given area of field may be related to surface area exposed per given volume. Thus, in dark field, the smaller the particle size the greater the collective boundary length per given field, and the higher the intensities of all the boundaries are, when integrated.

In bad dispersions low surface areas of filler are exposed to polymer and thus large particles are present. The larger the particles, the less the collective intensity of the boundaries in a given field.
(a) No specimen

(b) Heterogeneous specimen

FIGURE 4.2  The Principle of Dark Field Microscopy
These were the predictions of the behaviour of such a system, based on theory. Thus, intensities could be used (it was thought) to grade dispersion. Integrated intensities are obtainable as explained earlier by observation of the back focal plane. Thus, if a television camera observed the bfp, this plane then being displayed on a television monitor, the whole image on the monitor being scanned for intensity by feeding the signal into an oscilloscope, the overall height (in volts) of the trace shown thereby would be proportional to the integrated intensities in the back focal plane of the microscope.

Thus, in sum,

Oscilloscope peak height \( \alpha \) Integrated intensity in bfp
\[ \alpha(\text{average aggregate size in field})^{-1} \]

To verify this hypothesis, model compounds consisting of a suspension of HAF carbon black in cedarwood oil were used (concentration of suspension was 100:2::oil:black). Figures 4.3 - 4.6 show the appearance of these models in transmitted dark field compared with their bright field (trans-illuminated) views. It is possible to see the contrasting bright boundaries (or pin points for the fine specimens) as described earlier.

**TABLE 4.2 Model compounds and agitation times**

<table>
<thead>
<tr>
<th>Coding</th>
<th>Sample</th>
<th>Agitation time (seconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>Figure 4.3</td>
<td>0</td>
</tr>
<tr>
<td>M</td>
<td>Figure 4.4</td>
<td>15</td>
</tr>
<tr>
<td>N</td>
<td>Figure 4.5</td>
<td>30</td>
</tr>
<tr>
<td>O</td>
<td>Figure 4.6</td>
<td>120</td>
</tr>
</tbody>
</table>
FIGURE 4.3 Suspensions of HAF/cedarwood Oil (no agitation)

(a) Bright field  (b) Dark field

100 µm
FIGURE 4.4 Suspensions of HAF/Cedarwood Oil (15 secs agitation)

(a) Bright field  (b) Dark field

100μm
FIGURE 4.5 Suspensions of HAF/Cedarwood Oil (30 secs. agitation)

(a) Bright field

(b) Dark field

100μm
FIGURE 4.6  Suspensions of HAF/Cedarwood Oil (120 secs. agitation)

(a) Bright field  (b) Dark field

100 μm
Another sample which consisted of a medium thermal type (N990) black was also made up and agitated for the same time as sample 0.

Voltage peaks from the oscilloscope representing intensity in the bfp were as follows (averaged over 5 fields of view each).

TABLE 4.3 Model compounds and corresponding intensities

<table>
<thead>
<tr>
<th>Sample</th>
<th>Voltage (V x 100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>17</td>
</tr>
<tr>
<td>M</td>
<td>29</td>
</tr>
<tr>
<td>N</td>
<td>35</td>
</tr>
<tr>
<td>O</td>
<td>36</td>
</tr>
<tr>
<td>Medium Thermal Sample</td>
<td>96</td>
</tr>
</tbody>
</table>

Thus there appears to be from this preliminary experiment a relationship between time of agitation and voltage output. The medium thermal sample had the highest intensity, but has the largest ultimate particle size. It can be confidently said that the blacks are not therefore breaking down into their ultimate particle sizes by this agitation, only into progressively smaller aggregates. The aggregates produced by agitating the suspension of medium thermal black are smaller than the corresponding HAF sample since the former is a softer black, consisting of easy to destroy aggregations.

Since the oscilloscope signal was a summing of the intensity distribution of each scan line of the television monitor, the trace did not consist of a single line, but a combination. The trace appeared as in Figure 4.7, and by widening it electronically, it was possible to isolate the intensity line due to the diametral bfp scan.
FIGURE 4.7 Schematic oscilloscope trace through diameter of bfp

This figure indicates that there is a relatively dark area at the centre of the bfp surrounded by a bright annulus. To obtain the maximum amount of information, the height of the trough (T) was measured as well as the peak height (P).

In addition, during successive operation, the aperture iris of the objective lens was closed down to minimum and opened up to maximum to decrease or increase respectively the numerical aperture of the lens and to regulate the amount of scattered/diffracted light collected by the optical system.

To summarise, shoulder and trough heights were observed in volts from the oscilloscope trace, for each of the model samples, first with the objective iris closed and secondly with it open. Results were averaged over five fields of view and are shown in Table 4.4.

The following general comments may be made on these results:
1. Intensities, as shown by shoulder and trough heights increase with increasing agitation for both aperture settings.
TABLE 4.4

Model compounds and their bfp intensities (in volts), trough and shoulder, aperture open and closed

<table>
<thead>
<tr>
<th>Aperture/Sample</th>
<th>SAMPLE L</th>
<th>SAMPLE M</th>
<th>SAMPLE N</th>
<th>SAMPLE O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Shoulder Height</td>
<td>Trough Height</td>
<td>Shoulder Height</td>
<td>Trough Height</td>
</tr>
<tr>
<td>Aperture closed</td>
<td>0.18</td>
<td>0.08</td>
<td>0.27</td>
<td>0.14</td>
</tr>
<tr>
<td>Aperture open</td>
<td>0.25</td>
<td>0.08</td>
<td>0.33</td>
<td>0.14</td>
</tr>
</tbody>
</table>
2. Trough height remains the same for any one reading when the aperture is either open or closed.

3. Aperture opening increases shoulder intensity in all samples examined.

4. Shoulder:Trough height ratio decreases with increasing severity of agitation.

5. Coefficient of variation $\left[ \frac{\text{standard deviation}}{\text{mean}} \times 100 \right]$ of intensities for each of the five fields observed per listed sample decreases with increasing agitation, whether aperture is open or closed (Table 4.5).

**TABLE 4.5**
Coefficients of variation (CV) % of model compound intensities

<table>
<thead>
<tr>
<th>Aperture position</th>
<th>L</th>
<th>M</th>
<th>N</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aperture open</td>
<td>22.5</td>
<td>18.0</td>
<td>11.0</td>
<td>4.8</td>
</tr>
<tr>
<td>Aperture closed</td>
<td>24.5</td>
<td>18.2</td>
<td>10.9</td>
<td>4.7</td>
</tr>
</tbody>
</table>

It is suggested that the above observations are caused by the following.

Consider the interaction of a ray and a particle of greater dimension than $\lambda$ (the wavelength of the incident radiation). Substantially all the incident radiation is diffracted in this situation and a schematic diagram follows (Figure 4.8).
FIGURE 4.8 Diffraction from a feature

In the example above, the bfp will collect the first, second and third order diffractions, and in two dimensions, beam B will also produce the same pattern in the bfp. The combination of these produces the following

FIGURE 4.9 Back focal plane caused by diffraction in Figure 4.8
Thus, the shape of the trace from the oscilloscope with its two shoulders and trough. When the iris of the objective is closed, some of the stronger diffraction is cut out, resulting in lower shoulder trace height overall noted in Table 4.4. Also, the trough height remains unchanged from iris open to iris closed positions as that order of diffraction making up the less intense middle area of the bfp is unaffected by the iris opening.

Also, from Table 4.4, an increase in trough height is noted with increasing agitation times (progressively smaller agglomerate sizes). This cannot be due to diffraction, since distance of diffraction maxima from the zero order spot increases with decreasing size. It is not improbable then that scattering is beginning to occur as certain particles are attrited to below λ (= 600 nm in dimension). This mainly results in high angle scatter (Figure 4.10).

![Diagram](image)

**FIGURE 4.10** High angle scatter
Low angle scatter would either fall outside the optical system, or contribute to the 'bright ring' in the back focal plane which is increasing anyway. As the attrition increases it seems that more particles become responsible for high angle scattering, since the central spot intensity increases with increasing mixing time.

The increase of shoulder height with time is due to more particles falling within the size range for diffraction at that angle as mixing severity increases. Thus, in the back focal plane the cumulative effects of both scattering and diffraction phenomena are seen. Decreasing size of large (> λ) particles up to linear dimension λ result in increasing outer ring intensity in the bgp. Decreasing size of small (< λ) particles result in a bright central area of bgp. Thus it appears that in dark field viewing, the effect of many small particle boundaries in a given volume is to produce a higher total intensity than that produced by fewer large particle boundaries in the same field.

The observation noting systematic changes in CV would be in keeping with the well known principles of the kinetics and statistics of simple mixing. It is stated that "as mixing increases, so in-batch variance of some parameter related to mixing efficiency (the tendency toward randomness) falls".

Having had encouraging results from the model experiments, it was decided to attempt similar work with sections of known good and bad dispersions of a carbon black in butyl (isoprene-isobutyl) rubber. The sections were cut from vulcanised sheet. An ultramicrotome was used with the wet glass knife technique; temperature of cutting was established as being optimum at -60°C (Cryokit attached, with liquid nitrogen). The trimming of the specimen prior to cutting was also carried out under these preceding conditions.

Sections had to be of identical thickness since intensities were being monitored and transmission through the specimen would be a function of sample thickness. Section thickness was measured by
interferometry, using the Jamin-Lebedeff system. Thicknesses were established as being 1.5 μm as signified by an interference colour of second order yellow. (Figures calculated from optical path differences estimated from Michel-Levy chart).

Intensities were measured as described earlier on fifteen samples of each of the dispersions. The mean intensities, their standard deviations and the corresponding coefficients of variation were calculated (Table 4.6) in arbitrary units.

<table>
<thead>
<tr>
<th>Calculated parameter</th>
<th>Acceptable dispersion</th>
<th>Poor dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean Intensity</td>
<td>1.06</td>
<td>1.05</td>
</tr>
<tr>
<td>Standard deviation (SD)</td>
<td>0.18</td>
<td>0.46</td>
</tr>
<tr>
<td>Coefficient of variation (%)</td>
<td>17.3</td>
<td>43.58</td>
</tr>
</tbody>
</table>

Again, disappointingly, the mean values of intensity were almost identical. The SD and CV values indicative of the spread of results, yielded the expected relationship: that the worse the dispersion the more variable the mix.

The reasons to be advanced for the failure of the intensity parameter to show up differences in mixing are based on the feature sizes present in the rubber samples. In the model compounds, (see Figures 4.3-4.6) the biggest agglomerates were measured at 200 μm across progressing down to about a tenth of that value as mixing progressed. In rubbers the largest particles (even in a poor dispersion) are only about (at worst) 50 μm across, and these are superimposed on a field of sub-micron particles of black in the rubber matrix. In the model compounds the background is less dominant than in an actual rubber compound, and the big particles are more obvious as these sizes are much larger than in rubber mixes. Thus the effect of intensity differences due to dispersions varying in degree was masked by these two above factors. This leads to the conclusion that measurement of intensities in the bfp is insufficient.
to characterise dispersion. If enough samples were examined the statistical measures (SD & CV) would point to dispersion differences. The problem here is the cutting of similarly thick specimens, by the relatively long process of frozen ultramicrotomy.

It was obvious that there had been a departure from the original objective i.e the setting up of a simple, quick and effective method for microscopical determination of dispersions, and it was resolved then to consider the problem afresh.

4.2 Proposed New Method

Any microscopical work consists of the following basic steps:

1. Specimen preparation
2. Image formation
3. Analysis of image
4. Processing the data.

One of the easiest methods of specimen preparation for rubbers is that of making a cut surface. This is viewed in reflected light. If this image could be analysed by a method which perceives and recognises different dispersions of black within the rubber matrix, an excellent starting point for the development of a new method would have been reached. This analysis in the first stage of the research could be manual, with the proviso that if it worked, it could be automated later.

In the previous chapter, the surface testing method used to assess dispersion was considered. It had the basis that carbon black dispersion samples, when cut for surface examination, vary in topology. In a badly dispersed sample, a cut pulls out from, or leaves large agglomerates on the surface, leaving a very rough, irregular topography. In a good sample, since dispersive mixing has taken
place, the aggregates are much smaller and in more intimate contact with the rubber. A cut through such a sample leaves a smooth, uniform surface. It was thought that this visual aspect could be exploited in the high contrast dark field reflected light microscopy, since on initial exploration, these varying dispersion levels, showed up as totally different image types.

Given the aforementioned four areas for consideration in microscopical examination, the method selected was to use dark field light microscopy, employing low-medium magnifications, in reflected light. The image from the microscope would be exhibited using a conventional television system, whose signal was analysed by an oscilloscope. The advantages that were thought should accrue from this system are tabulated below.

TABLE 4.7 Innovations and advantages of the proposed system

<table>
<thead>
<tr>
<th>Light microscopy</th>
<th>Economical (standard equipment)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dark field mode</td>
<td>Increased contrast</td>
</tr>
<tr>
<td>Use low-medium magnification</td>
<td>To take into account macro and micro dispersion states</td>
</tr>
<tr>
<td>High Numerical Aperture (NA) lens</td>
<td>To increase resolution</td>
</tr>
<tr>
<td>Television system</td>
<td>For signal input</td>
</tr>
<tr>
<td>Oscilloscope (running at television line frequency)</td>
<td>For signal analysis</td>
</tr>
</tbody>
</table>
4.3 Description of the System Equipment

The heart of the equipment was a Reichert microscope with trinocular head set up for reflected light work in the dark field mode, and using white light. (Magnifications of x350 derived from a x10 eyepiece, x28 Epi objective of $NA = 0.55$ and x 1.25 tube factor). A Philips television system received the image signal and this segment consisted of a television camera looking down the eyepiece, linked to a control unit which in turn fed into a black and white monitor. The analogue signal from the television was fed into an oscilloscope (Tektronix, type 529 waveform monitor) with a single line strobing facility. That is, the instrument has the capability of scanning any one line of a multiline television signal and of displaying a trace of the intensity distribution across that image line on its screen. The television signal line manually selected for scan analysis by the oscilloscope appears as a bright up pulse on the monitor, showing the area of the image being analysed. Thus, as many lines as required may be analysed separately from a given field of view, by the expedient of altering the location of the bright up pulse, and thus altering the scan region of the oscilloscope. Figure 4.11 shows the system in operation.

FIGURE 4.11 The dark field reflected light dispersion analysis system
An Olympus OM1 camera was positioned on a tripod a constant distance away to photograph the trace on the oscilloscope screen for recording purposes.

4.4 Specimen Preparation

The aim was to produce a sample for reflected light examination, free of knife marks and other artefacts. For this purpose a new, single edged razor blade was used (Polaron) and this was affixed to a holder which in turn was accommodated in the rubber sample cutting equipment which moved the blade in a vertical plane (Figure 4.12). This is roughly the same manner in which previous
workers concerned with rubber surfaces obtained their samples. The nature of the surface is found to be dependent on the state of black dispersion within the matrix.

When the blade (washed in trichloroethylene to remove traces of wax used in manufacture) was 'in situ', a small strip from a vulcanised rubber sheet about 10 mm x 20 mm x 3 mm was placed under the blade, and with a quick downward motion a clean cut surface in the plane parallel to the height dimension was produced. The sample strip was then moved along without any lateral motion, and a second cut made parallel to and about 4 mm from the first cut surface. The same operation could be adopted with unvulcanised rubbers, except that these required a pressing prior to cutting to rid the bulk of porosity that exists when stock is offloaded from a batch-off mill. This could be conveniently done by sandwiching between "Melinex" sheet and pressing between the platens of a Mooney viscometer at about 100°C for 3 or 4 minutes, or (as was done here) a special multicavity plate mould was machined so that more than one sample at a time could be so pretreated. In this case, pressing was done in an hydraulic rubber moulding press under the same temperature conditions as in the Mooney instrument.

Whatever the rubber type, the cutting operation produced a level block which was knife mark and dust free; and the technique needed very little practice to perfect. The specimen was then picked up with tweezers with the first cut surface upwards and placed on a glass slide ready for microscopical examination.

4.5 Experimental Procedure

The microscope was set-up paying particular attention to the centering of the lamp to obtain an evenly intense field. This was easily done by referring to the oscilloscope screen, which showed a horizontal line when the light was evenly distributed. The lamp was set to a constant intensity, and the microscope switched to dark field operation.
The slide bearing the sample was focused on using the free ocular of the microscope. Specimens bearing knife marks, or dust contamination were rejected immediately. Specimens where faces were not parallel, could produce focusing problems due to depth of field and their wedge shape, and in these instances, the sample block was mounted on plasticine on the glass slide. By pressing lightly with a grease free glass slide, the top face of the sample could be made parallel with the objective plane, and thus rendered in focus at all points of a given field.

The image was then transferred to the television screen through the camera and a line on the screen selected by means of a rotary control on the oscilloscope. As mentioned earlier a bright up pulse signifies the portion being analysed in the field. Several options are available for actual positioning of the pulse. The scan position could be fixed, from sample to sample, or several set or random positions of the pulse could be selected for each field of view. Thus the effects of changing field while still observing one fixed line, and also the effects of shifting the observed line to various points of a given field could be studied.

4.6 Analysis of Results

When a rubber sample cut surface has been subjected to dark field reflected light (DFRL) microscopy and the image converted into a television signal, the television monitor bears a picture as in Figure 4.13. (Note the bright up pulse across the screen, signifying the area of scan). The oscilloscope registers the intensities across this line, and a trace of intensities (as voltages) will be presented on the oscilloscope screen (Figures 4.14 and 4.15).
Again it must be noted that previous workers\textsuperscript{4-7} have shown that different dispersions yield cut surfaces that differ in topography, the poor dispersions showing rougher and more variable surfaces than the good. Indeed by another inspection of Figures 4.14 and 4.15, it will be seen that the oscilloscope traces arising from diffractions from surface features are quite different too. Figure 4.14 is the trace of a cut surface from a good dispersion, while Figure 4.15 is that from a poor one. In the bad dispersion the trace is uneven and peaky, showing the high diffraction that has occurred in this case. In the good one, the trace is much more even, and the peak heights are less than in the previous instance.

Having noted clear differences between the traces resulting from viewing different dispersions by dark field reflected light (DFRL) microscopy, a choice of trace characterising parameters must be made. Very complex analytical methods such as fast Fourier analysis and frequency octave analysis were rejected as being unnecessary at this early stage. The simplest viable choices were the statistical parameters, calculated from the individual peak heights comprising each
FIGURE 4.14 Oscilloscope trace from a good dispersion

FIGURE 4.15 Oscilloscope trace from a bad dispersion
photographed trace.

Thus, a base line was ruled in joining the lowest troughs of each trace, and manual measurements were made on the peak heights. These were then combined to give standard deviations from mean and mean height by

\[
\text{mean } (\bar{x}) = \frac{\sum_{i}^{n} x_i}{n} \quad 4.1
\]

\[
\text{standard deviation } (S) = \sqrt{\frac{\sum (x_i - \bar{x})^2}{(n-1)}} \quad 4.2
\]

\(x\) being the individual peak heights for a series of \(n\) peaks/trace.

Additionally \(n\) (the number of peaks in each trace) was noted since intuitively, in a bad dispersion the number of diffracting centres per field length would be larger and consequently less in number. Conversely, in a good dispersion \(n\) will be large.

By applying the calculations noted above, the bad dispersion (which would produce a peaky and irregular oscilloscope trace) would yield large \(\bar{x}\) and \(S\) values, while for the trace observed for the good dispersion, these values should be numerically lower.

To verify these initial experimental observations a full scale experiment design was drawn up, where a number of compounds, differing only in dispersion levels, were produced and analysed.

4.7 Mixing the Experimental Proving Compounds

Five curative masterbatches of the following recipe were made up by mill mixing (approximately 2.3 kg batch weight each) designed for safety from scorch in view of the long mixing times later used.
Styrene Butadiene Rubber SBR 1502 100.00 2000.0
(ML 1 + 4 @ 100°C = 55)
(Cold emulsion polymerised)
Zinc Oxide 6.00 120.0
Stearic Acid 4.00 80.0
N,N-Dicyclohexyl-2-benzothiazyl sulphenamide 0.60 12.0
2,2'-Methylene bis (4-ethyl-6-tert. butylphenol) 1.00 20.0
Sulphur 4.00 80.0

These were then mill crossblended with each other several times such that the resultant batches were of closely matching Mooney viscosity (28.5 ± 0.5 MU) and curing characteristics as measured by the Monsanto OOR (minimum torque 6 lb-in, maximum torque 62 ± 1 lb-in, cure time 16:75 ± 0.5 mins all at 180°C). Mooney scorch at 120°C was > 16 mins. The reason for this rather tedious process was unavailability of a production sized mill to mix the required 12 kg master batch in one operation. In any case, superior homogeneity is obtained by the method used here.

Several identical weights of the masterbatch were next taken and each mixed with 40 pphr N375 carbon black in a Farrel Bridge BR Banbury of 1500 ml cubic capacity. The black chosen was a particularly difficult one to disperse (since it had been wet pelleted) supplied by Cabot Carbon, and made in Ravenna, Italy. This filler had pellets of high cohesive strength which would resist dispersion. The Banbury was operated at the following conditions:

Starting machine temperature 16°C
Specific ram pressure 0.56 MPa
Rotor speed 77 rpm
Fill factor (based on the chamber capacity) 0.65
Several batches were thus mixed, (809 gm M/B: 280 gm filler) each varying only in the degree of mixing received, ranging from 15 seconds to 10 minutes. The author is aware that energy input would have been a more modern dump criterion to use, but the technique used still serves the purpose. In the event, dump temperatures of each batch were monitored, and Figure 4.16 shows the relationship between time and temperature, for the reader more at ease with dump temperature as the drop criterion.

The initial process of producing a curative masterbatch will now be appreciated, the prime reason being to produce batches with initially identical curing characteristics. Any difference in properties observed subsequently could be ascribed to the different states of carbon black dispersion within the rubbers. If a one stage mixing was carried out, at the very short times of mixing very uneven curative distribution would have been present. In this eventuality, it would have been impossible to divorce the effects of varying curative dispersion thus resulting, from the main effect of systematic changes in filler aggregation within the matrix.

The dumped batches were passed through a mill running at even speed, at a nip opening of 8 mm, such that the dispersion obtained in the internal mixer would only be affected minimally (and hopefully by a constant factor).

After 76 hours storage, each of the batches thus produced was tested by a wide variety of means, both processing and vulcanisate tests. In addition, cured and uncured samples were prepared by the previously described methods for DFRL analysis. Further surface exploration was carried out by scanning electron microscopy, and mechanical stylus measurements. The details of the tests now follow.
FIGURE 4.16  Mixing Time vs Dump Temperature
4.8 Compound Testing/Microscopy

**Cure Properties** – all batches were curemetered on the Monsanto ODR with microdie at 170°C, 100 cpm and ±3° arc with no preheat time. Minimum and maximum torque was noted, and time to 95% of maximum crosslinking calculated. All vulcanisate property tests carried out subsequently used samples cured for this period of time at the above temperature in a Bradley and Turton hydraulic press at 17 tons on an 8" ram.

**Mooney Viscosity**$^8$ – this was carried out at 100°C with a large rotor with 1 minute preheating time (ML 1 + 4 - 100°C).

**Capillary Rheometry and Die Swell Measurements** – These tests were carried out using the Monsanto Processability Tester (MPT)$^9$ sited in the Monsanto Technical Centre, Louvain La Neuve, Belgium. The instrument is an automated, programmable, constant rate extrusion rheometer, equipped with a laser beam detector for the measurement of running and relaxed die swell$^{10}$. Eight shear strain rates ($\dot{\gamma}$) were employed, ranging from 10 - 180 s$^{-1}$. A die of 1.5 mm diameter (L/D = 20), and a chamber temperature of 100°C was used. At the end of each imposed shear rate stage, a 120 second swell pause was introduced, such that laser beam dimensioning and calculation of the swell was made possible.

Assuming the power law to hold, log shear stress ($\tau$) was plotted against log shear strain rate ($\dot{\gamma}$) and the slope ($n$) and the intercept ($k$) were calculated by linear regression. $k$ and $n$ were plotted versus mixing time. (These two constants are the flow and consistency indices respectively). Correlation coefficients of the regression all very closely approached unity signifying with 99.9% confidence that a linear relationship existed between $\log \tau$ and $\log \dot{\gamma}$. A family of curves for all the compounds with different mixing histories resulted.
Knowing \( n \) and \( k \) for each compound, it is now possible to apply:

\[
\eta_a = k \cdot \gamma^{n-1}
\]  

(4.3)

(where \( \eta_a \) is the apparent viscosity) and calculate \( \eta_a \) at each shear rate for each compound. Another family of curves results when \( \eta_a \) vs \( \gamma \) is plotted for each of the compounds, and incorporated in a composite graph.

By deriving iso-shear rate curves from the graph, it is possible to plot \( \eta_a \) vs mixing time, at a constant selected \( \gamma \).

Die swell is measured by the laser beams during a 120 second pause between shear rate changes, while the extrudate is maintained in a constant temperature chamber.

Similarly, die swell values are calculable at each shear rate for each compound. A fourth family of curves was thus drawn, of swell% vs shear rate, and as above iso-shear rate curves were derived once again for each compound. Swell % vs mixing time curves were then constructed at constant \( \gamma \).

**Stress Relaxation** - In the MPT, at the end of the 100 s\(^{-1}\) shear rate extrusion stage, the ram is held stationary and the time taken for the barrel pressure to decay to 80% of the original pressure needed to maintain 100 s\(^{-1}\) at the die wall is noted. This is a measure of stress relaxation, and was monitored for each compound.

**Bound Rubber** - About 0.3 gm from each test compound in the form of an approximately cubical test piece was weighed accurately. Each sample was then immersed in 10 ml of toluene SLR, and contained in a tared boiling tube in a water bath at 20\(^0\)C. The tube was corked to prevent evaporation of the solvent. After 72 hours, the sol fraction was decanted off. There appeared now to be a sol
fraction so viscous that it did not pour out, and therefore a second addition of solvent was made to dilute this portion. This would not affect the swollen gel, since equilibrium would have been attained. After a further four hours the second sol fraction too was decanted off and the swollen gel vacuum dried at 50°C at 760 mm of mercury for 12 hours. % BR was calculated from

$$\frac{W_D - W_I}{W_R} \times 100$$

where  
- $W_D = \text{weight of dried residue}$
- $W_I = \text{weight of insolubles in original weight of specimen}$
- $W_R = \text{weight of rubber in original weight of specimen}$

**Hardness** - After the moulding of three test sheets of approximately 2.5mm thickness from each of the compounds using ODR calculated cure times, a microhardness test was carried out on each sheet; from a sum of twenty four observations, based on eight observations per sheet for three sheets, mean ($\bar{X}$) and standard deviation ($S$) were calculated, on the normal distribution assumption. In addition, coefficient of variation ($100 \frac{S}{\bar{X}}$) was calculated, in an attempt to measure in batch variability with mixing time.

**Tensile Properties** - From the sheets referred to above, type dumbell tensile test pieces were cut, and values of ultimate tensile strength (UTS), elongation at break (EB), stress at 100, 200 and 300% extensions calculated, where possible. (if breakage did not occur prior to a specified strain being reached). Force and extension information were recorded, originating from a load cell and optical extensometer respectively.

In the case of the "modulus" at set extensions, the distribution is known to be normal, and mean, standard deviation and coefficient of variation were calculated under this assumption.
In the case of the other two parameters, UTS and EB which follow a double exponential distribution, the modal value, standard deviation and coefficient of variation were computed according to the recommended BS procedure\textsuperscript{14}.

In all the above cases, replication level was 3 x 8 as for hardness.

*Dynamic Properties* - Samples for dynamic testing in the shear mode (Figure 4.17) were moulded in a two cavity, three piece transfer mould from a 10 gm blank. End piece metals were roughed up and treated with Chemlok 205/220 before moulding.

![Dynamic Test Piece for shear testing](image)

**FIGURE 4.17** Dynamic Test Piece for shear testing

The author was fortunate to have access to the "Automatic dynamic response apparatus" (DRA)\textsuperscript{15} sited at Dunlop Technology Division, Birmingham. A block diagram of the machine is repro-
The following summarises the salient points of operation:

a) A moving coil vibrator (peak force 90N) drives a cylindrical test piece (12.5 mm long and 9 mm diameter) in sinusoidal extension/compression. The shear mode was used here rather than the compression and this is dictated by the geometry of the test piece.

b) Three oscillating frequencies are possible 1.5, 15 and 150 Hz.

c) Force is measured by using a quartz load cell.

d) Displacement is measured by a similar cell, calibrated by a steel spring of known characteristics.

e) The test was carried out at room temperature.

f) The machine is programmed to perform tests at six different single strain amplitudes ranging from ±20% to ±0.005%, the exact displacement depending on test piece hardness.
g) After 16 successive cycles of displacement (which keeps hysteretical temperature rise to an acceptably low level) at each amplitude, and at the three frequencies, the displacement, amplitude, force and phase information is input into a data logger.

h) Paper tape from the logger is computer processed (ICL 4120 computer, program written in Fortran).

i) After programme analysis the results are processed in tabular form.

Disturbing frequency was 1.5, 15 and 150 Hz. Tans, G' and G'' were noted at small strain amplitudes.

One modification to the existing Dunlop programme was requested by the author. This was that of beginning the displacement programme for each frequency at the smallest strain and working up to the larger ones. This was essential since structure breakdown was one of the properties requiring measurement. The existing Dunlop programme operated directly opposite to that above. The change was implemented by D.T.D., where it has been found extremely useful in certain areas of their work.

*Fatigue Tests* - The Wallace-MRPRA fatigue tester[^16][^17] was kindly made available for use by the MRPRA, Tun Abdul Razak Labs., Hertfordshire. The test pieces in the form of a standard Schopper ring (52.6 mm OD, 44.6 mm ID, 1.5 mm thick) were cut from moulded sheets of stock nominally 1.5 mm thick. Six rings per sheet were tested, at a frequency of 300 cpm, and at 23°C, at 0-75% preset tensile strain. The rings were deformed cyclically in tension and the number of cycles to failure was recorded for each sample as a measure of the fatigue resistance of the material. Again, distribution of results is known to follow a double exponential type function, and median, mode, high/low ratio, and standard deviation were calculable.
Test testing - Tear testing was carried out on standard crescent test pieces, cut from moulded sheets and as described in BS\textsuperscript{18}. In addition, tear energy determinations were made for each test piece, by calculating the area under each of the force/deformation curves as obtained from the JJ Tester chart recorder. Replication was 3 x 8 for each compound under examination.

Microscopical Testing - "Percent carbon black" dispersed in the stocks to be evaluated was calculated by the procedure and counting methods of Leigh-Dugmore\textsuperscript{19} and Medalia\textsuperscript{20} discussed in Chapter 3. Thin (1 \micro meter) sections were obtained by freezing and base sledge microtomy, using a 45° facet angle (D-profile) chisel edged steel knife.

Scanning electron microscope examination - Vulcanised sheets of the test compounds were used to cut test pieces for SEM examination, in exactly the same manner as samples were prepared for DFRL examination (by verticut with a new, single edged razor blade).

These samples were sputter coated with gold to prevent electron charge build-up during electron microscopy and consequent loss of contrast. The gold coating also improves the secondary electron emission from the sample surface. Sputter coater settings were as follows:

\begin{tabular}{|l|l|}
\hline
Coating time & 2 x 1 minute \\
Argon gas & to maintain vacuum of 2 x 10^{-2} torr \\
Current & 25 amps \\
Voltage & 6 volts \\
\hline
\end{tabular}

The SEM viewing was accomplished under a nominal magnification of x700, using a 10 kV accelerating voltage. Photographs of each test compound surface were taken during scanning.
4.9 Mechanical Surface Roughness Measurements

Since the most recent technique of carbon black measurement is that of testing the surface roughness of cut samples, it was resolved to attempt this novel test, even though the exact equipment used by the workers who developed the technique was not available to hand. The most modern version of this equipment used by Vegvari, Hess, Chirico and Wiedenhaefer is documented, as being a stylus type roughness tester of the Federal Products (formerly Gould) Model 2000 Surfanalyser type, linked to a dedicated DEC Minc PDP 11 computer. The principle of such a test has been detailed in the previous chapter, and very simply consists of a fine stylus being passed over a rubber surface; the electronics and recording equipment of the system amplifies the original signal, and traces a magnified profile graph of the surface, and calculates several stated parameters which relate to the topography.

It was possible to arrange for the use of an alternative British make of stylus tester, the Talysurf model with the kind cooperation of the manufacturers, Rank Taylor Hobson of Leicester. Obviously the American workers had modified the system as originally used in surface metrology for use in rubbers. Since no such machine was directly available here, the settings on the Talysurf had to be changed to match as closely as possible the conditions used by the previous workers. These were as follows:

- **Operation** - Skidless in roughness mode so that gross profile differences inherent in the cutting of a soft material could be filtered out.
- **Tracking force** - 100 mgf (1.00 mN)
- **Stylus** - diamond, $90^\circ$ four-sided pyramid
- **Tip radius** - 2.5 $\mu$m
- **Width cut off** - 0.8 mm
- **Probe tracking speed** - 30 mm/minute
- **Tracking length** - 2 cm
- **Vertical magnification** - between x1000 and x10,000 as dictated by the surface roughness of each sample
Horizontal magnification - 50 μm per scale division.
Sample size - 2.5 cm x 1.5 cm x 0.3 cm prepared by razor cutting

As described in Chapter 3, Vegvari and co-workers\textsuperscript{5-7} used two parameters of surface roughness, \( f \) the number of peaks per unit length, and \( \bar{H} \), the mean peak height. These were combined as \( f^2 \bar{H} \) to give an index of dispersion or surface roughness.

In equipment used here mean height was not a standard metrological parameter, and therefore was not calculated automatically. However, the computation was simply done by using the profile trace yielded by the pen recorder. At known vertical magnification factors, it is possible to ascribe a real value for each chart division. For example, in the trial part trace shown (Figure 4.19), the vertical magnification was set at x5000. That is, 10 mm on the chart would equal 2 μm in actual stylus deflection. Horizontal scale was set constant at x20 where 10 mm on the chart would equal 0.5 mm in reality. At the beginning of the trace (see Figure 4.19) upward pointing and downward pointing "blips" indicate the magnifications selected, and then follows a straight line at the mean peak height. This is quite simply obtained in microns by drawing two horizontal lines (A and B in Figure 4.19) to signify the highest and lowest points on the trace (marked * and + respectively on Figure 4.19). A third horizontal line can now be drawn in by extending the mean trace line (C). One is now able to specify maximum peak to valley height of the trace BA and the mean peak height BC, in this case 25 mm and 11 mm, or in real terms, 5 μm and 2.2 μm. The latter quantity is used as \( \bar{H} \), in this research.

The term \( f \) presented more of a problem, since again this was not a standard metrological parameter, and also, it was impossible to count the peaks manually from the chart paper, in view of some minute ones present as well as the dominant promonitories. However, peak count \( (P_c) \) is a standard in metal surface testing and is defined
FIGURE 4.19  Part of a profile trace obtained from surface tester
as the number of peak/valley pairs per unit length projecting through a band of width $b$ centred about the mean line (Figure 4.20).

$\text{FIGURE 4.20} \quad \text{The parameter } P_c$

$P_c$ was obtained for $b = 0.1 \ \mu\text{m}$ and $0.0 \ \mu\text{m}$. In the latter case, $P_c$ is the peak/valley pair intersection with the mean line.

In addition to these stated parameters that paralleled those of Vegvari and co-workers, certain other metrological measures were taken. These were:

- $R_{\text{max}}$ - is the maximum peak-to-valley height within a sample length $L$,
- $R_{\text{tm}}$ - is the average $R_{\text{max}}$ calculated from five sampling lengths within the assessment length $A$
- $R_a$ - the universally recognised parameter of roughness, and is the arithmetic mean of the departures $y$ of the profile from the mean line. Normally determined as the mean results of several consecutive sampling lengths $L$. 

Assessment Length

\[ R_{tm} = \frac{R_{max_1} + R_{max_2} + R_{max_3} + R_{max_4} + R_{max_5}}{5} \]

\[ = \frac{1}{5} \sum_{i=1}^{5} R_{max_i} \]

**FIGURE 4.21** The parameter \( R_{tm} \)

**FIGURE 4.22** The parameter \( R_a \)

HSC - the high spot count is the number of profile peaks projecting above the mean line or a line parallel to the mean line at a peak distance \( p \) from it. \( p \) was nominated as 0.1 \( \mu m \) above the mean line.
4.9.1 Operating Procedure

The machine used was a Talysurf 10 operated with settings as stated previously. Chart recorder for profile traces, an integral microprocessor, VDU and hand held keyboard for interactive operation were the peripherals. The interactive operation option enabled one to select parameters required for measurement, and also to manipulate the VDU graphs. A video printer gave hard copy of the VDU display if required at any time.

Rubber samples used for surface analysis were prepared exactly as for DFRL microscopical examination. All the stocks prepared by mixing carbon black/curative masterbatch were then analysed in the vulcanised form only.

The sample was clamped in the equipment vice, levelled manually with a gauge block, and the probe was then manually run over the surface to be profiled. The pen recorder would indicate an out of level surface, in which case the arm of the instrument could be moved with respect to the rubber surface until the pen indicator showed no gross out of level.
The parameters required for display were selected by means of the keyboard (the programme asked prompt questions, in the form of a 'menu' on the VDU).

The stylus traverse was started, and at the end of the run, the VDU displayed values of measured parameters. A record of this could be obtained via the printer (see Figure 4.25). As can be seen it consists of graphics and text. The graphics side consists of two curves, the amplitude distribution of the surface analysed, and the Abbot Firestone (A-F) bearing curve.

$R_{sk}$ or skewness is a measure of the shape of the amplitude distribution curve.

The A-F is a curve of high spot count (HSC) vs bearing ratio ($t_p$). The bearing ratio is the length of bearing surface (expressed as a percentage of $L$) at a depth $p$ below the highest peak. Thus, for the construction of the Abbot-Firestone curve, $p$ is varied from $0 \mu m$ (when HSC = 0) to $p$ = maximum peak-to-valley height (when $t_p$ = 100%). In sum, the bearing ratio curve shows how $t_p$ varies with the level.

The text side of the video printout gives the values ascribed to the roughness parameters discussed. The profile graph shown previously (Figure 4.19), is output from the pen recorder.
### Roughness Assessment

**Filter Cut-Off 0.8 mm**

5 Cut-Offs Assessed

<table>
<thead>
<tr>
<th>Slice Level</th>
<th>Height</th>
<th>Depth</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.0 μm</td>
<td>0.0 μm</td>
</tr>
</tbody>
</table>

**Amplitude Distribution**

<table>
<thead>
<tr>
<th>Zone Width</th>
<th>0.0 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pc</td>
<td>88 cm²</td>
</tr>
</tbody>
</table>

**Roughness Parameters**

- Ra: 0.4 μm
- Rq: 0.5 μm
- Rmax: 4.4 μm
- Rtm: 3.1 μm

**HSC @ 0.10 μm Height**: 34

**Tp @ 0.10 μm Height**: 43.7 %

**Pc @ 0.10 μm Zone Width**: 350 cm²

**Figure 4.25**: Hard copy of the VDU obtained during surface testing
A word on the selection of magnifications; these are selected by operating the hand held keyboard, directly after the instrument measures the surface, but prior to results being shown on the VDU. The VDU displays a selection of possible magnifications, the largest magnification, giving a pen trace as close to out of scale as possible, without actually overshooting the vertical scale. Obviously, this depends on the roughness of the sample analysed, and ranged from x1000 (for very rough rubbers) to x10,000 for the smoothest samples. x5000 was a commonly opted for magnification.

Replication levels were 3 profile runs from each of three sample blocks for each compound (3 x 3).

Microscopical examination (both by scanning electron microscopy and differential interferometry) was carried out on the surfaces analysed by Talysurf, after coating, and under the conditions described previously to assess any damage caused by the stylus.

4.10 Results and Discussion

Since the DFRL microscopical technique is the main subject of this section it will be a convenient starting point to discuss the DFRL results first.

Figures 4.26 and 4.27 show the visual differences when surfaces from two differently dispersed stocks are viewed by the present method. The poor dispersion (Figure 4.26 - 30 sec mixing) shows up as diffuse areas of light intensity on a dark background, while the better dispersion (Figure 4.27 - 5 mins mixing) produces a finer, more granular texture.

The following figures (4.28 - 4.38) show the television images as photographed directly from the VDU. Thus, these figures are of much lower resolution than of those taken looking directly
FIGURE 4.26  Surface of a poor dispersion viewed by dark field reflected light microscopy (vulcanised sample)

FIGURE 4.27  Surface of a good dispersion viewed by dark field reflected light microscopy (vulcanised sample)
down the eyepiece of the microscope. Again, the bright up pulse is seen, signifying the area being scanned. It is quite evident from the VDU that a progressive change is taking place in the texture of the image. In the worst dispersion (15 secs mixing) broad diffuse bands are seen, superimposed on an undulating background of black or grey. As we go through the dispersion spectrum, it is noted that the broad banded image quickly disappears to be replaced by one which again has large diffuse areas but not of banded appearance. These areas become smaller with time of mixing, a background consisting of points of light gradually becoming dominant. After about 2.5 mins of mixing, the granular and fine texture dominates the image, which changes not at all from this time to the maximum experimental time of mixing, ten minutes.

So far, vulcanised stocks only have been considered. The next series of pictures show the television images of unvulcanised surfaces with progressively better dispersion. Only three of these are shown for space saving reasons, a bad dispersion (Figure 4.39i - 15 secs mixing), an intermediate one (Figure 4.40 - 1 min mixing) and an excellent dispersion (Figure 4.41 - 10 mins mixing). Again the poor dispersion, as in the similarly mixed vulcanised sample, broad intensity bands on a background are noted. In fact the images vulcanised/unvulcanised are very similar. The intermediate dispersion shows a considerable reduction in the banded structures, a tendency to form large near circular bright areas being seen. A little development of the fine texture is also appearing at this stage. A comparison of the unvulcanised/vulcanised images for this mixing time (1 min) shows considerable differences. The unvulcanised have many more large structures than the cured. The image of the unvulcanised excellent dispersion shows an almost total disappearance of the large features seen previously, to be replaced by a granular texture; but are quite different in scale from the vulcanised image. To summarise, one sees similarities between vulcanised/unvulcanised images at very early stages of dispersion, the vulcanised samples however consisting of finer structure than
FIGURE 4.28
Television image, DFRL - 15 seconds mixing (Vulcanised sample)

FIGURE 4.29
Television image, DFRL - 30 seconds mixing (Vulcanised sample)

FIGURE 4.30
Television image, DFRL - 45 seconds mixing (Vulcanised sample)
FIGURE 4.31
Television image,
DFRL - 60 seconds mixing
(Vulcanised sample)

FIGURE 4.32
Television image,
DFRL - 90 seconds mixing
(Vulcanised sample)

FIGURE 4.33
Television image,
DFRL - 120 seconds mixing
(Vulcanised sample)
FIGURE 4.34
Television image, DFRL - 150 seconds mixing (Vulcanised sample)

FIGURE 4.35
Television image, DFRL - 180 seconds mixing (Vulcanised sample)

FIGURE 4.36
Television image, DFRL - 300 seconds mixing (Vulcanised sample)
FIGURE 4.37
Television image, DFRL - 420 seconds mixing (Vulcanised sample)

FIGURE 4.38
Television image, DFRL - 600 seconds mixing (Vulcanised sample)
FIGURE 4.39
Television image,
DFRL - 15 seconds mixing
(Unvulcanised sample)

FIGURE 4.40
Television image,
DFRL - 60 seconds mixing
(Unvulcanised sample)

FIGURE 4.41
Television image,
DFRL - 600 seconds mixing
(Unvulcanised sample)
corresponding unvulcanised specimens, at the longer mixing times. Estimating roughly, an unvulcanised sample from a 10 minute mix has a similar image to a vulcanised 45 secs sample.

We next inspect the oscilloscope traces arising from both the vulcanised and unvulcanised samples just studied, remembering that the oscilloscope trace will be a record of intensity on one selected line of the television signal, versus distance scanned along that line. Figures 4.42 - 4.52 show the oscilloscope traces resulting from the vulcanised surface microscopy in dark field, and Figures 4.53 - 4.55 show the traces for the previously discussed unvulcanised stocks.

It is evident that the progressively differing images produce progressively changing traces. In the vulcanised series for bad dispersions, one notes a variable, generally highly peaky uneven trace, made up of relatively few peaks, when compared to that from a very good dispersion (2.5 minutes mixing time onwards). In addition note the height of an imagined base line joining the lowest troughs in each trace. A gradual increase is seen in its height from the bottom of the screen. This is a measure of the increasing reflectivity of the sample surface, as better and better dispersions are realised. A bad dispersion has a matt black surface, while a good one is very shiny.

When the unvulcanised traces are inspected, it is immediately evident that the first trace (from a badly dispersed sample of 15 secs of mixing) is almost identical to its vulcanised companion. This perhaps is not a surprise in the light of the previous observations on image similarity. The other two unvulcanised traces, however, are markedly dissimilar to their corresponding vulcanised stocks, the unvulcanised ones being much more peaky, and rough. The remarks made about reflectivity of the samples in the vulcanised state would appear to also hold for the current samples, the effect however being less marked. Again, because a good unvulcanised sample surface is less reflective that its vulcanised twin,
FIGURE 4.42
Oscilloscope trace,
15 seconds mixing
(Vulcanised sample)

FIGURE 4.43
Oscilloscope trace,
30 seconds mixing
(Vulcanised sample)

FIGURE 4.44
Oscilloscope trace,
45 seconds mixing,
(Vulcanised sample)
FIGURE 4.45
Oscilloscope trace,
60 seconds mixing
(Vulcanised sample)

FIGURE 4.46
Oscilloscope trace,
90 seconds mixing
(Vulcanised sample)

FIGURE 4.47
Oscilloscope trace,
120 seconds mixing
(Vulcanised sample)
FIGURE 4.48
Oscilloscope trace,
150 seconds mixing
(Vulcanised sample)

FIGURE 4.49
Oscilloscope trace,
180 seconds mixing
(Vulcanised sample)

FIGURE 4.50
Oscilloscope trace,
300 seconds mixing
(Vulcanised sample)
FIGURE 4.51
Oscilloscope trace, 420 seconds mixing (Vulcanised sample)

FIGURE 4.52
Oscilloscope trace, 600 seconds mixing (Vulcanised sample)

FIGURE 4.53
Oscilloscope trace, 15 seconds mixing (Unvulcanised sample)
FIGURE 4.54
Oscilloscope trace, 60 seconds mixing
(Unvulcanised sample)

FIGURE 4.55
Oscilloscope trace, 600 seconds mixing
(Unvulcanised sample)
but more so than a worse dispersed unvulcanised sample, this observation would be intuitively correct.

At this point it is judicious to stop, and ask why differently dispersed compound surfaces yield different dark field images and lineal intensity traces. To do this, the SEM photographs of the surfaces must be included in the argument. Figures 4.56 - 4.66 display these and in a strikingly visual manner it is possible to demonstrate that the theories of previous researchers regarding variably dispersed surfaces were correct. The worst dispersed surface shows oriented features, indicating an isotropic structure, which would explain the bands of light in its DFRL image. Progression through the range of dispersions show rough, cratered surfaces to begin with, improving till featureless expanses are seen in the better dispersed compounds.

The above mentioned previous workers investigating surface changes with dispersion (both the bright field reflected light microscopy and the mechanical surface testing approaches) noted the reasons for this progressive change. When a filled compound is cut with a sharp razor blade, the filler agglomerates deflect the cut path, because of their higher hardness relative to the surrounding matrix. It is the authors' considered opinion that the blade could cut through loose agglomerates leaving a basically plane surface, or pull out particles from the matrix (leaving a hollow) or deflect an agglomerate pushing it down into the matrix, and leaving it to recover and form a bump, when the deforming influence (the blade) is removed. Indeed, consideration of the Figure 4.57 (30 seconds mixing) shows pictorial evidence for these three phenomena taking place synchronously. As far as visual assessment of roughness goes, this one appears the roughest, the least mixed stock image (15 seconds) consisting of a relatively smooth area of gum rubber. The isotropy of the image would probably be due to compacted (incorporated) streaks of carbon black running in the direction of sheeting off on the mill. In the 30 sec surface, the features appear to be about 15-25 \( \mu \text{m} \) across at an average height of about
FIGURE 4.56
SEM micrograph,
15 seconds mixing
(Vulcanised sample)

FIGURE 4.57
SEM micrograph,
30 seconds mixing
(Vulcanised sample)

FIGURE 4.58
SEM micrograph,
45 seconds mixing
(Vulcanised sample)
FIGURE 4.59
SEM micrograph, 60 seconds mixing (Vulcanised sample)

FIGURE 4.60
SEM micrograph, 90 seconds mixing (Vulcanised sample)

FIGURE 4.61
SEM micrograph, 120 seconds mixing, (Vulcanised sample)
FIGURE 4.62
SEM micrograph
150 seconds mixing
(Vulcanised sample)

FIGURE 4.63
SEM micrograph,
180 seconds mixing
(Vulcanised sample)

FIGURE 4.64
SEM micrograph,
300 seconds mixing
(Vulcanised sample)
FIGURE 4.65
SEM micrograph
420 seconds mixing
(Vulcanised sample)

FIGURE 4.66
SEM micrograph,
600 seconds mixing
(Vulcanised sample)
10-15 μm. As the dispersion gets better, so the SEM surfaces tend to increasing smoothness. Indeed in the 45 sec surface, a considerable smooth area is seen. This could either be gum rubber into which no carbon has trespassed, or it could be a well dispersed area amidst a dominant bad dispersion. At 1 min. the feature size has reduced to a uniform 10 μm or less and after 1.5 mins very little progressive change in surface is noted. One important point of note in these photographs is the virtual absence of blade marking, very strongly stating the effectiveness of the specimen preparation system used here. (Note the SEM, the DFRL and the stylus testing samples were prepared in exactly the same manner). This would add credibility to both previous and future observations, in that no artefacts are evident to divert arguments away from the main theme.

Thus, from the foregoing it is evident that the varying DFRL images (and the resultant oscilloscope traces) are produced by the generation of a source of contrast, that systematically differs with progressive mixing. The SEM photographs very clearly point to the origin of this contrast, and it would appear that the DFRL system distinguishes between surfaces of different topography.

A diversion into how this is so follows.

The principle of the transmitted dark field microscope has already been examined (Figure 4.2). In reflected light, the instrument functions as shown schematically in Figure 4.67.

Again a 'hollow beam' of light is produced, this time by a stop, situated in front on the illuminating source. This beam is diverted onto the sample by a system of reflective mirrors, such that it does not pass through the objective lens. On reflection from the sample, the non-diffracted light is returned, outside the objective lens. The diffracted fraction passes through the objective and is admitted into the optical system, where an image is perceived at the eyepiece. Thus, as in transmitted dark field microscopy, diffracting centres
OBJECTIVE
LENS

FIGURE 4.67  Dark Field Reflected Light Microscopy

FIGURE 4.68  Diffraction at a Step
show up as light boundaries on a dark background. The situation is effectively summarised in Figure 4.68, which shows reflection from a smooth, homogeneous sample (A) and diffraction from a step, which will show up in DFRL as a bright boundary against a dark background. In the real case of filled rubber surfaces, the situation may be compared to a reflected light echelon grating, consisting of a variable number of steps and in addition these steps being irregularly ranged in relation to one another.

It appears that the deeper the step, as in the case of the badly dispersed sample, the higher the peaks, and also the more variable the peak heights; since the carbon black agglomerates causing these depressions and elevations would not be evenly dispersed, and will give rise to alternate very rough and then smooth regions on the cut surface, due to the wide range of particle sizes and also due to other areas free of filler.
In the well dispersed black/rubber surface, the black aggregates would have reached a regular small size, and these would be evenly distributed about the matrix. Thus this case could approach that of a perfect diffraction grating, and give rise to evenly spaced peaks of equal height.

![Oscilloscope Peaks](image1)

![Diffraction surface](image2)

FIGURE 4.70 Oscilloscope peaks from a diffraction grating

Another factor to be considered is the total number of peaks per scan. Intuitively this would seem the best measure of particle size and dispersion in a lineal scan; this possibly could be another parameter by which the efficiency of mixing could be adjudged.

To verify the preceding hypothesis, that the presence of a step causes diffraction, and also, the deeper the step the greater the amount of light diffracted, a simple experiment was conducted.

A crude reflection echelon grating was made up by first layering together (minimising air traps) ten strips of Sellotape. A sharp razor blade was then used to slice through the layers at an angle of about 70° from horizontal.

Three clean glass slides were taken and a single strip of one layer of Sellotape was applied to each. This served as a uniform base
for the gratings. The gratings themselves were made by removing one, then three, thus leaving six of the layers in the originally made composite. These three strips consisting of one, three and six layers of Sellotape were now applied to the slides giving three different steps at the identical angle to the horizontal. These three wedges were viewed in reflected light dark field. Firstly, the step formed a bright line on an otherwise dark field, indicating a step that would indeed diffract light.

Intensities were measured for each grating, and as expected the longer the step, the higher was the field intensity. In the case of the longer step length an intensity scan across it would show as a higher and broader peak than for a short step length.

A parallel between this simple experiment and the real case of the elastomer surfaces could be drawn. The larger the aggregates, the deeper/longer would be the 'step lengths' produced, thus the higher, and broader (and fewer per a given field) the peaks in an intensity trace. The smaller the aggregates, the shorter the step lengths; thus, the narrower the peak width, the more numerous the peaks per given field and the smaller the peaks.

Thus from the simple model trial, the height, width and number of peaks have been established as being realistic characterising parameters for a diffraction trace.

Based on the foregoing then, the analysis of the dark field reflected light oscilloscope traces is done on the following specified lines.

Mean peak height from a defined baseline (h) - This would be a measure of the mean height of the real analysed surface. The badly dispersed samples, having larger peaky surfaces should have high mean height overall.
Standard deviation of peaks from the mean (S) - this would be a measure of unevenness or roughness. The badly dispersed surfaces, being more variable, should have a higher SD value than their better dispersed counterparts.

Number of peaks (n) - as dispersion proceeds aggregate sizes fall, and thus there will be more diffracting centres, and consequently more peaks. This increase will presumably cease at the resolution limits of the system.

The parameter linked to reflectivity (baseline height) was not measured in this series of trials.

Figures 4.71 - 4.76 depict the variations in these nominated parameters, with mixing time, for both vulcanised and unvulcanised stocks. Considering $\bar{H}$, the tendency in both types of stock is for the quantity to decrease with time, which is in line with the predictions based on the research of other workers concerned with surface roughness. In the vulcanised stocks, a rapid decrease with mixing time is noted, until at about 2.5 mins $\bar{H}$ levels out and remains constant. In the unvulcanised stocks, $\bar{H}$ starts off at approximately the same level as in the corresponding vulcanised stock, but the initial decrease is much slower, with a constantly increasing rate of change as mixing time increases. This suggests that even though the nett effect is the same for cured/uncured stocks (a decrease in $\bar{H}$), the mechanics of the decrease are somewhat different. Apart from the visual surface roughness differences between cured and uncured stocks of identical mixing histories (the uncured is rougher due to slight smearing during cutting) there is also the probability of the persistence of microporosity in the uncured stocks: these joint contributions would result in an overall higher surface mean level in the uncured stock. Thus, in the early stages of mixing, surfaces of uncured stocks would slowly be developing overall smoother surfaces, the retardation effect being contributed by smearing and microporosity the effects of which mask surface texture contributed to by filler. In vulcanised stocks, both smearing and porosity are eliminated by the
FIGURE 4.71 $\bar{n}$ vs mixing time (vulcanised stocks)
FIGURE 4.72 $\bar{H}$ vs mixing time (unvulcanised stocks)
Figure 4.73: $S$ vs mixing time (vulcanised stocks)
FIGURE 4.74  S vs mixing time (unvulcanised stock)
No. of peaks per trace (n)

Log mixing time (sec)

FIGURE 4.75 \( n \) vs mixing time (vulcanised stocks)
FIGURE 4.76  $n$ vs mixing time (unvulcanised stocks)
curing process, and thus the surface changes due to filler de-aggregation are dominant, resulting in the noted sharp decrease of $\bar{\eta}$. The continuing decrease in $\bar{\eta}$ in the unvulcanised stocks as opposed to its levelling off in the cured stocks, is ascribed to the molecular weight reduction causing smearing to be reduced (which should become evident from other tests carried out), and also the expulsion of air during mixing resulting in the reduction of microporosity. The effect is not noted in vulcanised stocks as they are of networked composition and thus molecular weight of the chains is of secondary importance.

The second parameter standard deviation ($S$) which is a measure of unevenness of surface, also shows a drop with mixing time (as predicted) for both types of stock. Again $S$ in vulcanised stocks follows very closely the trends of $\bar{\eta}$, showing a rapid exponential drop and levelling off. In the unvulcanised stocks $S$ starts off at 15 secs at again approximately the same level as in the cured compounds, but the fall in $S$ is slow, following a linear relationship. The remarks in the previous paragraphs explain this effect too, that of uncured stock surfaces being appreciably rougher than those of corresponding vulcanisates.

Figures 4.75 and 4.76 show the changes in peak frequency with mixing and increases are noted in both instances, the vulcanised peak count increasing considerably faster than the unvulcanised. The initial thoughts on this aspect have been confirmed; these stated that due to increasing numbers of decreasingly small aggregates per unit length peak frequency should rise, levelling off at the limits of resolution. Again, the number of peaks in an unvulcanised stock overall are less than for vulcanised, even though the starting counts (at 15 secs mixing) are roughly the same. Microporosity and smearing are counted as large agglomerates in this instance, reducing the sensitivity of the parameter for uncured stocks.

It must be concluded on the basis of the above that $S$, $\bar{\eta}$ and $n$ reach their maxima/minima at approximately 2.5 mins of mixing in
vulcanised stocks.

In addition to the stated surmises of the causes of the differences in unvulcanised/vulcanised compounds, it must also be added that differences in cutting behaviour and reflectivity contribute to the different extents of the parameter changes.

A word now on test precision. The values in the graphs are the mean values of seven observations per sample. As an additional test for reproducibility three samples representative of bad, fairly poor and commercial quality dispersions were assessed by the DFRL method. These corresponded to dispersion (mixing) times of 15 secs, 1 and 2 minutes. Twenty trace analyses on each sample were carried out, and composite graphs (4.77 - 4.79) show the observed scatter of the three parameters $n$, $S$ and $\bar{n}$.

Peak frequency ($n$) appears to be the parameter which exhibits the least discrimination between the three dispersion levels selected, since some infringement of the scattergrams of the 1 and 2 minute mixing times is noted. When the means yielded by the twenty traces are considered, they show the same trends as in the main graph of peak frequency versus mixing time: that is, peak frequency increases with increasing mixing (40.8, 55.1 and 60.1 respectively).

The other two parameters ($S$ and $\bar{n}$) show very good discrimination, no infringement being noted in the scattergrams at all. The average of the means of peak height from the traces as noted previously falls with increasing mixing (52.8, 27.5, 12.0) as does the standard deviations of the traces when averaged up (32.3, 14.7, 6.2). No quantification was made for parameter variation associated with dispersion level, since twenty observations was reckoned to be insufficient for statistical analysis.

These results are encouraging because, in sum, they indicate that the current method, with considerably less than 20 scans per sample, (in the case of $\bar{n}$ and $S$) can identify differently mixed stocks with ease.
FIGURE 4.77 Reproducibility tests on $S$
Mean peak height ($\bar{h}$)

15 seconds mixing

60 seconds mixing

120 seconds mixing

Observation number

FIGURE 4.78 Reproducibility Tests on $\bar{h}$
FIGURE 4.79 Reproducibility tests on $n$
Figures 4.80 - 4.90 show conventional transmitted light micrographs of the experimental compounds showing the state of dispersion causing the changes in surface noted by dark field reflected light, the oscilloscope traces, and the scanning electron micrographs. It is obvious that the dispersion changes from large immeasurable 'clumps' of carbon black (15 secs) to large sized agglomerates of about 100 µm in size, reducing progressively to 50 µm, 20 µm and 10 µm or less. Note also the increasing microdispersion, shown by the darker background as mixing progresses. This is colloidal dispersed black, which is the primary component of a good dispersion (the other is the macrodispersion or aggregate state). After 2-2.5 minutes, the transmitted light sections remain roughly the same. Graphs 4.91 and 4.92 show how the Leigh-Dugmore\textsuperscript{19} and Cabot (Medalia\textsuperscript{20}) dispersed fraction changes with mixing time. Table 4.8 summarises these results.

### TABLE 4.8 Quantitative microscopy on the test compounds

<table>
<thead>
<tr>
<th>Compound mixing time (secs)</th>
<th>Cabot dispersion (%)</th>
<th>Leigh-Dugmore dispersion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>75.5</td>
<td>-373.8</td>
</tr>
<tr>
<td>30</td>
<td>62.5</td>
<td>-87.58</td>
</tr>
<tr>
<td>45</td>
<td>98.4</td>
<td>92.1</td>
</tr>
<tr>
<td>60</td>
<td>99.2</td>
<td>96.2</td>
</tr>
<tr>
<td>90</td>
<td>99.86</td>
<td>99.3</td>
</tr>
<tr>
<td>120</td>
<td>99.91</td>
<td>99.53</td>
</tr>
<tr>
<td>150</td>
<td>99.99</td>
<td>99.94</td>
</tr>
<tr>
<td>180</td>
<td>99.95</td>
<td>99.74</td>
</tr>
<tr>
<td>300</td>
<td>99.95</td>
<td>99.74</td>
</tr>
<tr>
<td>420</td>
<td>99.95</td>
<td>99.74</td>
</tr>
<tr>
<td>600</td>
<td>99.99</td>
<td>99.94</td>
</tr>
</tbody>
</table>

Firstly in the Cabot dispersion ratings, after one minute of mixing, the rating was calculated at greater than 99%. It is commonly held that any dispersion rating of greater than 98% is
FIGURE 4.80
Thin section,
15 seconds mixing

FIGURE 4.81
Thin section,
30 seconds mixing

FIGURE 4.82
Thin section,
45 seconds mixing

100 \mu m
FIGURE 4.83
Thin section, 60 seconds mixing

FIGURE 4.84
Thin section, 90 seconds mixing

FIGURE 4.85
Thin section, 120 seconds mixing

100 μm
FIGURE 4.86
Thin section, 150 seconds mixing

FIGURE 4.87
Thin section, 180 seconds mixing

FIGURE 4.88
Thin section, 300 seconds mixing

$100 \mu m$
FIGURE 4.89
Thin section
420 seconds mixing

FIGURE 4.90
Thin section
600 seconds mixing
FIGURE 4.91 Leigh-Dugmore Dispersion vs mixing time
FIGURE 4.92 Cabot dispersion vs mixing time
exhibited by a compound whose physical properties (processing, and vulcanisate) cannot be further improved by further prolonging or intensifying the mixing cycle. Thus, it must be concluded, by this hypothesis that the optimum mixing time for the compounds mixed here must range from 45 secs to 1.5 mins.

True, there is an increase from 99.86 to 99.99 giving a difference of 0.13% dispersion rating from 1.5 min to 2 min after which variations in ratings are possibly masked by counting errors. The point is, that to give a difference of 0.13% dispersion by Cabot (or a 0.64% difference by Leigh-Dugmore), a difference in field counts (\(\bar{U}\)) of only just less than two aggregates (greater than 85 \(\mu m^2\) in area) is necessary. This difference may be seen as the variation from field to field within the same sample, and could be statistically unreliable. Definite changes as shown by the counting procedure, occur up to 1.5 minutes; after this, the count variation between different fields of the same sample, and between different samples, are noted to be the same.

Additionally, the Leigh-Dugmore method yielded negative values at short dispersion times. The reason for this has already been discussed in Chapter 3, and shall not be dealt with further.

The graphs show that an optimum dispersion in terms of these Leigh-Dugmore and Medalia parameters is reached after about 1.5 minutes of mixing. This is at variance with the findings of the DFRL method, which predict an optimum mixing time of about 2.5 mins. On this preliminary evidence then it could be stated that the established transmitted light microscopical methods are non-discriminatory of good dispersions. Indeed this question has been raised before by other workers involved in mixing studies\(^{21,22,23,24}\). The fact remains, as verified by the accompanying light micrographs that after 1.5 mins of mixing, the large (> 85 \(\mu m^2\)) aggregates of black stay approximately the same in number, the small aggregates (< 85 \(\mu m^2\) and not counted by either technique) fall in number, and the background becomes less grainy, signifying a progressively finer microdispersion state being achieved. The counting procedure by light
microscopy concentrates only on the former, and chooses to ignore the latter two factors, which also (especially the third one) contribute significantly to dispersion and properties accruing\textsuperscript{22,23}.

It has already been proven that surface roughness varies with dispersion. Indeed, in the following figures (4.94 - 4.103) confirmation of this is obtained in the shape of the mechanical surface testing results. Each figure consists of a portion of the profile trace (about a third of the total trace, meaning that about 7 mm of the sample surface is represented), and also a section of the VDU printout, showing amplitude dispersion and the Abbot Firestone curve. In each profile trace, the lowest trough and the highest peak has been marked off and the distance between these recorded. It is to be pointed out that in addition to the extra length of profile chart not presented here, each sample was replicated (3 x 3) times to obtain sufficient reliable information.

The first point to note about these measurements is that the roughest sample surface (derived from the 15 second mix) was not amenable to this form of testing. Even at the lowest magnification (x 1000) a consistently out of range profile was obtained, and thus, this compound was left out of this part of the experimental work. To consider the remaining compounds, it is noted as expected that the overall profile is smoother as dispersion proceeds. Except for the thirty second mix, all the other compounds were analysed using a vertical magnification factor ($V_v$) of 5000 so that direct comparison can be made. The 30 second mix proved too rough for this magnification and $V_v$ of x2000 was employed in this instance. Note the progressive decrease in the range value too, decreasing from 24.5 \(\mu\)m in the 30 second sample to approximately 2 \(\mu\)m in the better dispersed ones. Note also, the tendency to decreasing width of the amplitude curve as dispersion proceeds, signifying the narrowing of the agglomerate size distribution curve with mixing time.
1 - DECREASE DEPTH
0 - INCREASE DEPTH

AMPLITUDE DISTRIBUTION

ROUGHNESS ASSESSMENT
FILTER CUT-OFF 0.8 mm
5 CUT-OFFS ASSESSED

<table>
<thead>
<tr>
<th>SLICE LEVEL</th>
<th>HEIGHT</th>
<th>DEPTH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7.3 μm</td>
<td>0.0 μm</td>
</tr>
</tbody>
</table>

HSC
0

BEARING RATIO

ZONEWIDTH
0.0 μm
Pc
75 cm²

R²H

FIGURE 4.94 30 seconds mixing
1. DECREASE DEPTH
O-INCREASE DEPTH
AMPLITUDE DISTRIBUTION
ROUGHNESS ASSESSMENT
FILTER CUT-OFF 0.8 mm
5 CUT-OFFS ASSESSED

FIGURE 4.95
45 seconds mixing

ZONE WIDTH
Hz 0.0 µm
120 cm4

AMPLITUDE DISTRIBUTION

HEIGHT DEPTH
0.1 µm
3.2 µm

SLICE LEVEL BEARING RATIO

HSC 0
TP 0.1 µ
ROUGHNESS ASSESSMENT
FILTER CUT-OFF 0.8 mm
5 CUT-OFFS ASSESSED

SLICE LEVEL
HEIGHT
4.3 \( \mu m \)
DEPTH
0.0 \( \mu m \)

BEARING RATIO
HSC
0

ZONEWIDTH
0.0 \( \mu m \)
Pc
100 cm

FIGURE 4.96
60 seconds mixing
FIGURE 4.97  90 seconds mixing
ROUGHNESS ASSESSMENT
FILTER CUT-OFF 0.8 mm
5 CUT-OFFS ASSESSED

SLICE LEVEL
HEIGHT 4.7 μm
DEPTH 0.0 μm

BEARING RATIO
HSC 0

ZONEWIDTH
0.0 μm
Pc 83 cm²

1-DECREASE DEPTH
0-INCREASE DEPTH

AMPLITUDE DISTRIBUTION

8TH

FIGURE 4.98 120 seconds mixing
ROUGHNESS ASSESSMENT
FILTER CUT-OFF 0.8 mm
5 CUT-OFFS ASSESSED

SLICE LEVEL
HEIGHT 5.2 μm
DEPTH 0.0 μm

BEARING RATIO
HSC 0

ZONEWIDTH
0.0 μm
Pc 45 cm

150 seconds mixing

FIGURE 4.99
1. DECREASE DEPTH
0. INCREASE DEPTH

AMPLITUDE DISTRIBUTION

ROUGHNESS ASSESSMENT
FILTER CUT-OFF 0.8 mm
5 CUT-OFFS ASSESSED

SLICE LEVEL
HEIGHT 2.2 μm  DEPTH 0.0 μm

BEARING RATIO

ZONE WIDTH 0.0 μm
Pc 73 cm²

Tp 0.0 %

NTH

FIGURE 4.100  180 seconds mixing
1 - DECREASE DEPTH
0 - INCREASE DEPTH

ROUGHNESS ASSESSMENT
FILTER CUT-OFF 0.8 mm
5 CUT-OFFS ASSESSED

SLICE LEVEL
<table>
<thead>
<tr>
<th>HEIGHT</th>
<th>DEPTH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7 µm</td>
<td>0.0 µm</td>
</tr>
</tbody>
</table>

BEARING RATIO
HSC 0

ZONEWIDTH
0.0 µm
Pc 63 c.m²

Tp 0.0 %

FIGURE 4.101
300 seconds mixing
ROUGHNESS ASSESSMENT
FILTER CUT-OFF 0.8 mm
5 CUT-OFFS ASSESSED

1-DECREASE
DEPTH
0-INCREASE
DEPTH

AMPLITUDE
DISTRIBUTION

SLICE LEVEL
HEIGHT
1.9 µm
DEPTH
0.0 µm

BEARING RATIO

HSC
0

Tp
0.0 %

ZONE WIDTH
0.0 µm
Pc
70 cm²

FIGURE 4.102 420 seconds mixing
FIGURE 4.103

ROUGHNESS ASSESSMENT
FILTER CUTOFF 0.8 mm
5 CUTOFFS ASSESSED

1 - DECREASE DEPTH
0 - INCREASE DEPTH

AMPLITUDE DISTRIBUTION

SLICE LEVEL
HEIGHT
4.0 μm
DEPTH
0.0 μm

BEARING RATIO
HSC
0

ZONE WIDTH
0.0 μm
Pc
78 cm²

Tp
0.0 %

R²TH

600 seconds mixing
The peak heights as deduced from the profile graphs, very closely match the observations on size made on the basis of the SEM images, features of about 15 μm in height in the worst sample being seen, and then decreasing through 10 μm to less than 5 μm. In the better samples, occasional features of about 3 μm in size are noted; these would correspond to the bright areas on the corresponding DFRL micrographs or the slight perturbations on the SEM micrographs, or the residual aggregates in the transmission light micrographs.

Table 4.9 summarises the calculated parameters of roughness for our experimental compounds.

$R_{\text{max}}$ shows a decreasing tendency with time, though the results show a fair band of scatter. Also if $R_{\text{max}}$ at 600 secs is noted, the danger in taking what amounts to one point readings is made evident. In this instance, $R_{\text{max}}$ (7.57 μm) was obviously caused by a cutting artefact.

$R_{\text{rms}}$ values, being averaged $R_{\text{max}}$ values over a range of assessment lengths, again show a strong decreasing tendency (see Graph 4.104) showing decreasing peak-to-valley heights of agglomerates with increasing mixing.

HSC values too show a decreasing tendency with mixing time. Simply, this signifies the presence of a greater number of high peaks in the surface of badly mixed compounds. However this parameter does not take into account at all where the average level lies, and is measured at a decreasing level as mixing time proceeds and agglomerate sizes fall. To generalise, HSC (in our case at 0.1 μm below maximum peak height), will indicate the decreasing tendency for the higher peaks to be present with mixing. It must be noted that the HSC reference measuring line lowers itself with respect to a given baseline as mixing proceeds and agglomerates become smaller.

$P_c$ at 0.1μm zone width either side of the mean shows no trends at all, considerable scatter being noted. However, $P_c$ at the mean line shows a decreasing tendency with increasing mixing, signifying
<table>
<thead>
<tr>
<th>Mean Compounds</th>
<th>$R_{\text{max}}$ $\mu$m</th>
<th>$R_{\text{tm}}$ $\mu$m</th>
<th>Mean $\mu$m</th>
<th>$R_a$ $\mu$m</th>
<th>HSC (cm$^{-1}$) @ 0.1 $\mu$m</th>
<th>$P_c$ (cm$^{-1}$) at 0.1 $\mu$m zone width</th>
<th>$P_c$ (cm$^{-1}$) at 0 $\mu$m z/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 secs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30 &quot;</td>
<td>15.97</td>
<td>11.6</td>
<td>8.8</td>
<td>2.13</td>
<td>26</td>
<td>68</td>
<td>68</td>
</tr>
<tr>
<td>45 &quot;</td>
<td>5.9</td>
<td>4.67</td>
<td>2.5</td>
<td>0.73</td>
<td>40</td>
<td>53</td>
<td>108</td>
</tr>
<tr>
<td>60 &quot;</td>
<td>7.83</td>
<td>5.2</td>
<td>3.0</td>
<td>0.83</td>
<td>42</td>
<td>37</td>
<td>109</td>
</tr>
<tr>
<td>90 &quot;</td>
<td>6.08</td>
<td>3.4</td>
<td>1.87</td>
<td>0.40</td>
<td>32</td>
<td>106</td>
<td>110</td>
</tr>
<tr>
<td>120 &quot;</td>
<td>5.1</td>
<td>3.7</td>
<td>2.4</td>
<td>0.47</td>
<td>32</td>
<td>217</td>
<td>85</td>
</tr>
<tr>
<td>150 &quot;</td>
<td>5.23</td>
<td>3.17</td>
<td>2.17</td>
<td>0.37</td>
<td>21</td>
<td>92</td>
<td>58</td>
</tr>
<tr>
<td>180 &quot;</td>
<td>3.5</td>
<td>2.1</td>
<td>1.43</td>
<td>0.23</td>
<td>24</td>
<td>79</td>
<td>63</td>
</tr>
<tr>
<td>300 &quot;</td>
<td>2.9</td>
<td>1.8</td>
<td>1.7</td>
<td>0.27</td>
<td>17</td>
<td>213</td>
<td>58</td>
</tr>
<tr>
<td>420 &quot;</td>
<td>2.8</td>
<td>1.4</td>
<td>0.93</td>
<td>0.27</td>
<td>13</td>
<td>48</td>
<td>54</td>
</tr>
<tr>
<td>600 &quot;</td>
<td>7.57</td>
<td>2.57</td>
<td>1.6</td>
<td>0.27</td>
<td>12</td>
<td>50</td>
<td>53</td>
</tr>
</tbody>
</table>
FIGURE 4.104  $R_{tm}$ vs mixing time
FIGURE 4.105  Mean height of profile (μm) vs mixing time
FIGURE 4.106 $R_a$ vs mixing time.
the resolution by the stylus of fewer and fewer peaks as mixing proceeds. It is noted that this parallels the finding of Vegvari and co-workers $^5-^7$, with regard to their parameter $f$ (peak frequency).

Graph 4.105 indicates the trends observed in the mean peak height (corresponding to $H$ of Vegvari et al $^5-^7$). Indeed, as noted by these workers mean peak height decreases with mixing. Further, the range figures for mean from good to bad dispersions are approximately 1.5 $\mu$m - 9 $\mu$m, which match the findings of the American workers. It is also interesting to note that the shape of the curve of mean versus mixing time closely matches that of the DFRL trace, mean plotted against mixing time. A levelling out at about 3 minutes is noted.

The same comments could be addressed to the next graph of $R_a$ vs mixing time. Though Vegvari $^5-^7$ has not used this parameter, it is seen that it offers a very definite relationship with time of mixing.

This parameter (being a measure of roughness) is directly comparable to the DFRL parameter of standard deviation ($S$). The shape of the curve is identical, showing a minimum roughness to be reached at about 3 mins.

Combining the mean heights as obtained here, with $P_c$ at 0 $\mu$m, Vegvari's parameter $f^2H$ is approximately duplicated. It is re-emphasised that this is the product these workers found to be indicative of dispersion. Graph 4.107 shows how his composite parameter was found to vary with mixing time in this series of experiments. Again a strong tendency to exponential decrease is noted, a levelling off taking place at around 3 mins.

It is thus evident that the Talysurf measurements carried out bear out the arguments put forward during the SEM and DFRL analysis regarding improving surfaces formed with mixing efficiency.
Figure 4.107: "Talysurf composite index vs mixing time"
It is also pertinent to note a few points regarding the operation of the Talyurf system, since in effect, it is another method of dispersion measurement.

It was found that the mechanical surface testing method was not economical from the point of view of time. Thirty three samples took approximately 5 hours to analyse. This was mainly taken up by levelling and setting up time.

An important factor was that the worst dispersed compound could not be tested on the apparatus, since it was out of range even at the lowest magnification. Given an extra low magnification pick-up (12.5 μm radius) could have been used here, but further time would be spent in the change, and fine resolution would have suffered due to the tip size.

There was noted a tendency to move away from promonitory features when the instrument indicated profile out of range even in the better dispersions. The tendency is therefore to choose a profile that underestimates the roughness in poor to medium dispersed samples.

Obvious imperfections such as blade marks, air bubbles in the bulk, and so on cannot be seen by this technique since it does not involve visual examination at all. Thus, such artefacts will be erroneously included in the analysis, in this case overestimating the roughness in fine dispersions.

In defence of the system, it must be stated that all samples were examined after traversing, by stereo microscopy, SE microscopy, and differential interference contrast microscopy, to check for stylus damage. There was no destruction of structures noted at all; of course, this examination would not eliminate the possibility of stylus deformation at the time of testing, and recovery after.

We now examine the variation in physical and processing properties caused by varying mixing histories. Graphs 4.108 - 4.138 show these changes.
First, minimum torque by Monsanto ODR. The graph shows a trend to falling minimum torque with increasing mixing and this is in keeping with the findings of previous workers who used this as a measure of mixing\textsuperscript{25-27}. A minimum is reached at about three minutes of mixing for the experimental compounds.

Maximum rheometer torque shows a considerable scatter, with a less evident tendency for decrease with mixing, than the previous property. No optima can be derived for this property. Cure times calculated as time to 95\% crosslinking, show high scatter at the early stages of mixing, but reach cure times of consistently between 18 and 19 minutes, after 1.5 minutes of mixing.

Scorch time calculated as time to reach 2 torque points above minimum was the same for all compounds irrespective of mixing history (about 2.5 mins @ 170\textdegree C).

The next graph considers Mooney viscosity. It is clear that this measure increases to a peak at times around 60 seconds of mixing and then monotonically decreases to reach a steady value at around 3 mins of mixing. The decrease is not surprising, if other workers results are considered, (numerous references in Chapter 3) unanimity is evident. What has not been noted before is the initially rapid rise to a peak at low mixing times. This rise is very similar to that observed in the power/time curve during mixing, soon after addition of filler. It is believed that this initial increase in Mooney viscosity observed at the short times of mixing is due to the same phenomenon that causes the rise in the mixing power curve; that is, it signifies the gradual increase of wetting out of the filler by the rubber, which when complete, causes the property (and the instantaneous power) to reach its highest level. After this, dominant filler deaggregation effects cause the drop in Mooney, explainable by the previously alluded to theories of occlusion, and the rheology of suspensions.
Minimum rheometer torque (in lbs)

Log mixing time (secs)

FIGURE 4.108  Minimum torque vs mixing time
**FIGURE 4.109** Maximum torque vs mixing time
FIGURE 4.110  Cure time vs mixing time
FIGURE 4.111  Mooney viscosity vs mixing time
Moving on now to capillary rheometry, Graph 4.112, shows selected curves obtained (assuming the power law to hold) when logT vs Log\(\dot{\gamma}\) is plotted. (Note that no changes were made to the calculated shear stresses and shear strain rates by applying the Bagley end correction or Rabinowitsch correction for obtaining true T and \(\dot{\gamma}\) values). Given that very high correlation coefficients were yielded by linear regression (> 99.9% significance) linearity can be safely assumed. The next graph 4.113 shows the values obtained for k and n, the constants of the power law equation for each of the mixed compounds. Generalisations that n decreases monotonically and k increases with mixing can be made by inspection of these graphs. Further, what is also notable is that a peak (in the case of the n graph) and a trough (in the k graph) is a precursor to the dominant trend. It is interesting to note that this peak/trough arises at the identical time as the peak in the Mooney graph, and is therefore probably caused by the filler wetting effect. The generalised major effects noted would mean that, practically, a better dispersed stock would process less energetically at given shear rates in subsequent processing, as a direct result of the low values of n associated with such stocks. Well dispersed stocks (by virtue of a high k value), would be more stable than poorly dispersed ones, showing little low shear flow under storage conditions.

The next graph, again derived from the capillary viscometry shows the partial family of curves obtained when calculated \(n_a\) is plotted against shear strain rate for each stock.

Iso-shear rate curves are derived from this graph to yield \(n_a\) vs mixing time, and the next graph shows the relationship between these at selected shear rates. Low shear rates result in more viscous stocks overall, the general effect though being the same as that obtained with the Mooney viscometer, that is a rapid rise to a wetting peak and then an exponential drop due to deaggregation. It is surprising to note that the much maligned low shear rotational Mooney viscometer is as sensitive as a modern variable shear programmable capillary
FIGURE 4.112  Representative flow curves for experimental stocks
FIGURE 4.113  Flow and consistency indices vs mixing time
FIGURE 4.114  Apparent viscosity vs shear strain rate for selected stocks
FIGURE 4.115 Apparent viscosity vs mixing time for selected shear rates
instrument (the MPT).

It will be observed that $\eta_a$ as determined by capillary viscometry ceases to change appreciably after about 3 minutes of mixing (the rate of change $\delta \eta_a/\delta t_m$ prior to this is very high) but continues to drop slowly. This continued drop picked up by this sensitive instrument is ascribed to the "mastication controlled" stage of mixing since the "dispersion controlled" stage of mixing would be complete by this time. A molecular weight drop due to cumulative shear in the rubber, is the direct cause of the observed slow viscosity change at long mixing times.

Next, the die swell figures calculated at different shear strain rates during capillary viscometry. Graph 4.116, shows certain curves of calculated extrudate swell% vs Log\(\gamma\). Derived from this family of curves, are (as for $\eta_a$) isoshear rate curves, of die swell vs mixing time. An increase in the quantity is noted with mixing time, irrespective of shear rate. As known previously, an increase in shear rate leads to increase in die swell, up to a critical rate, after which melt instabilities occur. This is noted for certain stocks in Graph 4.116 (the ones with mixing times 30 and 60 seconds), while in the better mixed stocks (for example the 180 second material) the maximum is approached but not actually reached. It is noteworthy that the attainment of a peak die swell followed by a decrease, with mixing time noted by other workers, was not seen here. This (despite the suggestions made by the $\eta_a$ observations, pointing to some polymer breakdown) is possible in this instance, since SBR (the base used here) is not excessively shear sensitive. Thus, despite some breakdown, the increasing contribution to the elastic component by filler disaggregation would seem to balance out these viscous component losses. Again, large changes in die swell occur up to about 3 minutes of mixing, after which further changes are very slow.

The stress relaxation results obtained from the capillary rheometer as previously described, are depicted in the Graph 4.118. The time taken for decay of a given stress was monitored for each compound, the smaller the time, the higher being the stress relaxation rate.
Figure 4.116  Die swell vs shear rate for selected mixing times
FIGURE 4.117 Die swell vs mixing time at selected shear rates
FIGURE 4.118  Relaxation time vs mixing time
The results are scattered, but the general trend of slower relaxation in the better mixed compounds is evident. It is thought that the swift relaxation time noted at low mixing times is caused by a "strain amplification" effect. That is, since the black and rubber exist in the bulk in basically separate phases, at these times a strain imposed on the bulk would result in a larger strain operating on the rubber phase due to the presence of rigid inelastic filler clumps. A larger strain would result in a quick relaxation time, this slowing down with mixing due to progressively decreasing strain amplification. The approximate plateau in relaxation times is reached at about 2 minutes of mixing. Previous workers Myers and Newell\textsuperscript{29} have noted faster relaxation in better mixed compounds. No literature has been seen that documents stress relaxation behaviour at low mixing times.

The next property measured was bound rubber and Graph 4.119 shows a continuously increasing trend with time of mixing. Considerable scatter is observed at low mixing times and that section of the curve is necessarily an approximation. Though some agreement with previous workers is noted here, in that the quantity quite definitely increases during mixing, neither the plateau nor the peak and subsequent decrease was noted in this instance. From the evidence presented here, possibly the approach of a peak would occur after 10 minutes of mixing, but it does seem an inordinately long time to mix for development of maximum bound rubber.

In the case of hardness, in keeping with previous findings, the expected drop is seen with mixing time, due to the modulus effect explained in Chapter 3. Again, scatter is present, but the bulk of the changes in hardness seem to have occurred before 3 minutes of mixing. The low initial hardness would be due to high concentration of rubber, gradually increasing to a peak (at 45 secs) due to the high apparent volume fraction of filler in the rubber. Deaggregation and a consequent modulus drop explains the main decrease in hardness, small decreases at high mixing levels being ascribable to minor polymer chain shear degradation.
FIGURE 4.119  Bound rubber vs mixing time
FIGURE 4.120  Hardness vs mixing time
The next graph shows in batch variation as measured by using several observations of hardness and then deriving a coefficient of variation, based on a standard deviation estimate and mean value. As noted by previous workers for other properties (see Chapter 3) in batch variation falls appreciably up to about 2 minutes of mixing.

When tensile properties are considered, ultimate tensile strength (Graph 4.122) shows the expected increase with mixing time to a peak, and then a slight fall at longer mixing times. An optimum mixing time for tensile strength would appear to be about 2.5 minutes, while the same conclusion could be reached for the other measured property, elongation at break. Again, this shows an identical trace to that of tensile strength vs mixing time. No trends in coefficient of variation were noted, Table 4.10 summarises the findings for these two parameters, as well as for CV for stress at 100 and 200% extensions, carried out concurrently.

<table>
<thead>
<tr>
<th>Compound (mixing time)</th>
<th>CV % (ts)</th>
<th>CV % (eb)</th>
<th>CV % (M \textsubscript{100})</th>
<th>CV % (M \textsubscript{200})</th>
<th>Mod 200 (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 secs</td>
<td>16.7</td>
<td>19.6</td>
<td>11.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>8.2</td>
<td>11.0</td>
<td>5.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>45</td>
<td>10.4</td>
<td>8.8</td>
<td>10.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>60</td>
<td>8.6</td>
<td>8.8</td>
<td>9.7</td>
<td>-</td>
<td>10.9</td>
</tr>
<tr>
<td>90</td>
<td>13.0</td>
<td>9.6</td>
<td>5.9</td>
<td>1.5</td>
<td>15.4</td>
</tr>
<tr>
<td>120</td>
<td>12.5</td>
<td>9.7</td>
<td>4.3</td>
<td>4.2</td>
<td>9.1</td>
</tr>
<tr>
<td>150</td>
<td>18.3</td>
<td>13.2</td>
<td>10.6</td>
<td>3.7</td>
<td>12.5</td>
</tr>
<tr>
<td>180</td>
<td>13.5</td>
<td>9.2</td>
<td>6.2</td>
<td>6.3</td>
<td>12.5</td>
</tr>
<tr>
<td>300</td>
<td>10.6</td>
<td>7.8</td>
<td>3.5</td>
<td>6.2</td>
<td>12.6</td>
</tr>
<tr>
<td>420</td>
<td>7.5</td>
<td>6.1</td>
<td>7.2</td>
<td>5.0</td>
<td>12.5</td>
</tr>
<tr>
<td>600</td>
<td>19.0</td>
<td>13.8</td>
<td>6.5</td>
<td>3.8</td>
<td>12.9</td>
</tr>
</tbody>
</table>
FIGURE 4.121  Coefficients of variation (CV) vs mixing time
(Hardness as parameter)
FIGURE 4.122  Tensile strength vs mixing time
FIGURE 4.123  EB vs mixing time
In the case of mean modulus values the Mod\textsubscript{200} results are shown in the table above. Except to say that after 2.5 minutes of mixing the value remains constant, generalisations are not possible. The M\textsubscript{100} values are shown on Graph 4.124, which very closely duplicates the curve obtained for hardness vs mixing time. Since hardness is a measure of modulus at small deformations, according to the theoretical stance adopted in the previous chapter, it would be realistic to expect this superimposition of the two related graphs. Like the hardness curve, this modulus graph predicts an optimum mixing time to be reached around 2.5 minutes.

Next the dynamic property results. Plots of elastic stress modulus G' vs single strain amplitude (SSA) yield the family of curves of characteristic shape as discussed in Chapter 3. By fixing SSA at 1%, it is possible to draw curves of G' at this strain versus mixing time. This is analogous to the (G_0 - G_\infty) of Payne\textsuperscript{30}. (NB: Only G_0 and not the difference between G_0 and G_\infty is taken as the measure here, since in our case G_\infty for all stocks studied will be independent of the state of black dispersion and therefore constant). As predicted by Payne and other workers (see Chapter 3) G' shows a decrease with mixing time whatever the frequency. Also note that the overall levels of G'_0 increase with increasing frequency. Some scatter is noted in the 15 Hz and 150 Hz graphs, but to generalise, the bulk of the changes in G'_0 seem to have disappeared after approximately 3 minutes of mixing.

The next three graphs deal with the changes in G'' (the loss modulus) with mixing time at 1% SSA derived exactly as above. As previous workers have noted, G'' at given strain falls with decreasing volume fraction of filler (increasing mixing time). No plateau or slowing down of the effect is noted however, and it must be assumed that G'' continues to fall with progressive mixing.

Similarly values of Tan\h at 1% SSA and at the three frequencies used in this study were isolated. No trends were noted in the results, these being summarised in Table 4.11.
$M_{100}$ vs mixing time

**Figure 4.124** $M_{100}$ vs mixing time
FIGURE 4.125  $G'$ @ 1.5 Hz and 1% SSA vs mixing time
FIGURE 4.126  $G'$ at 15 Hz and 1% SSA vs mixing time
FIGURE 4.127  \( G' \) at 150 Hz and 1% SSA vs mixing time
FIGURE 4.128  G'' at 1.5 Hz and 1% SSA vs mixing time
FIGURE 4.129  $G''$ at 15 Hz and 1% SSA vs mixing time
FIGURE 4.130  $G''$ at 150 Hz and 1% SSA vs mixing time
TABLE 4.11 Changes in loss angle with mixing time and frequency

<table>
<thead>
<tr>
<th>Compound (mixing time in secs)</th>
<th>Tanδ @ 1% SSA 1.5 Hz</th>
<th>Tanδ @ 1% SSA 15 Hz</th>
<th>Tanδ @ 1% SSA 150 Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.22</td>
<td>0.22</td>
<td>0.36</td>
</tr>
<tr>
<td>30</td>
<td>0.19</td>
<td>0.20</td>
<td>0.36</td>
</tr>
<tr>
<td>45</td>
<td>0.19</td>
<td>0.21</td>
<td>0.34</td>
</tr>
<tr>
<td>60</td>
<td>0.19</td>
<td>0.19</td>
<td>0.30</td>
</tr>
<tr>
<td>90</td>
<td>0.17</td>
<td>0.18</td>
<td>0.30</td>
</tr>
<tr>
<td>120</td>
<td>0.17</td>
<td>0.18</td>
<td>0.31</td>
</tr>
<tr>
<td>150</td>
<td>0.18</td>
<td>0.18</td>
<td>0.29</td>
</tr>
<tr>
<td>180</td>
<td>0.20</td>
<td>0.20</td>
<td>0.32</td>
</tr>
<tr>
<td>300</td>
<td>0.19</td>
<td>0.19</td>
<td>0.31</td>
</tr>
<tr>
<td>420</td>
<td>0.19</td>
<td>0.22</td>
<td>0.34</td>
</tr>
<tr>
<td>600</td>
<td>0.15</td>
<td>0.17</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Except that there appears in all three series of results to be an initial reduction in Tanδ at very early mixing times, the rest of the values are spotty and inconclusive. Tanδ values at 1.5 and 15 Hz are very similar, but an overall increase (almost a doubling) is seen at the highest frequency (150 Hz).

The results of the fatigue tests are found in the next graph, which indicates a rise of flex resistance with mixing time up to about 2.5 minutes and then a very rapid degeneration of the property. This increase is ascribable to a progressive reduction in the size and population of filler aggregates (which act as stress initiating centres). The fall again, as noted for tensile properties, and viscosity, might well be due to the effects of cumulative shear imposed at long mixing times on the base polymer, resulting in a reduction of average molecular weight.

Finally, the tear results bear examination. Normal tear strength measurements yielded values that were inconclusive, except
Figure 4.131  Fatigue life vs mixing time
FIGURE 4.132  Tear strength vs mixing time
to emphasise that at very low mixing times tear strength was low, which then increased rapidly to a plateau with mixing, and then decreased once again. The best level of tear strength was achieved at surprisingly low levels of mixing (60 secs).

Indeed these results would seem to contradict those of Boonstra and Medalia\textsuperscript{31} who report no changes in tear strength with dispersion. Railsback\textsuperscript{32}, however notes a rise and a subsequent fall in his experiments, corresponding to the observations here.

The tear energy vs mixing time results show similar trends to the flex fatigue series, almost duplicating the curve shape. Why tear energy is sensitive to mixing and tear strength is not, is an imponderable, but what could make the difference is the fact that in the former case strain is taken into account, while in the latter this deformation is ignored. Thus though peak stress levels would be approximately the same through the series, the time taken for the cut to propagate would be dependent on the state of the disperse phase. Tear energy, like fatigue, peaks at around 2.5 minutes of mixing. The dependence of tear energy on strain is further reinforced by an inspection of the graph 4.123 for elongation at break versus mixing time, which shows a pattern very similar to the property under discussion.

4.11 Conclusions

It is evident from an inspection of the DFRL surface photomicrographs, that systematic differences arise from changes in dispersion within the sample. It is also concluded that these image differences noted arise from topographical variations from sample to sample: as deduced by two methods, the scanning electron microscope and the stylus surface measuring device. It is thus not surprising that even by visual analysis, both the SEM and DFRL micrographs show a considerable and systematic image change up to approximately 2.5 minutes of mixing of the compound used in this part of the work, after which the image remains the same even at extended mixing times.
FIGURE 4.13.3  Tear energy vs mixing time
Mechanical measurements of roughness as indicated by the parameters $R_{tm}$, mean peak height, $R_a$, and Vegvari's composite parameter (adapted here) $f^2/N$, all show very rapidly changing surface characteristics up to the same time pinpointed by the SEM and the DFRL photographs i.e. 2.5 minutes.

Thus, it is established that the present method is sensitive to changes in surface roughness (as shown also by the Sellotape models) these differences arising from the change of the state of the disperse phase in the elastomeric matrix. This last assertion is backed up by 'a priori' knowledge that time of mixing affects filler dispersion, and also by reference to the transmitted light micrographs of the stocks dealt with later.

The systematic variation in the DFRL information with surface roughness (and thus dispersion) has been established. The statistical parameters of the trace thus obtained, $h$, $S$, and $n$ correlate with the light microscopical, SEM and Talysurf results. This indicates that these calculated quantities adequately characterise the intensity vs distance DFRL trace, such that they may be used as indicators of dispersion.

It is thought that the parameter $h$ is proportional to the mean peak height of the surface examined, while $S$ is related to the roughness or unevenness of that surface. $n$ will be a measure of the number of diffracting features on the scan line. In graphs 4.134 - 4.136 these parameters are plotted against the corresponding mechanical stylus roughness related quantities. The first graph, $h$ vs mean peak height (Talysurf), shows strong grouping at the lower left indicating mean peak height by Talysurf is not very sensitive to mixing after 60 seconds. An elbow is noted in the graph which corresponds to 45-60 secs of mixing, and shows the extreme sensitivity of the DFRL method in that region. Note that the Talysurf mean height is between 2.5 and 3.0 μm in this area, which is not very different from the group values in the left lower corner of the graph. The elbow is caused by the point at 30 seconds of mixing, in which
FIGURE 4.134  Mean peak heights: Talysurf vs DFRL method
FIGURE 4.135 $R_a$ vs DFRL S
FIGURE 4.136 $P_c @ 0 \mu m zw$ vs DFRL n
region the mechanical stylus method seems very sensitive, much more so than the DFRL system. Similar observations are made for the next graph, of $S$ vs $R_a$. Overall, $R_a$ appears to be a more sensitive measure of surface than Talysurf mean peak height (in view of the spread of points in the $R_a$ vs $S$ graph, over a wide range). The next graph of $n$ vs $P_c$ at 0.0 $\mu$m zone width, even though highly scattered, shows a decrease in the stylus derived quantity with mixing, as did Vegvari for a corresponding parameter $f$. Note that optical peak frequency increases with mixing time.

It is accepted that at best a single figure is a compromise for characterising dispersion, which is in reality a distribution of sizes of the particulate component. In the discussions with industrialists following the development of this method, opinions remain divided as to whether these selected parameters $h$, $n$ and $S$ are adequate for characterising a dispersion. More elaborate methods of signal analysis have been suggested, such that frequency/amplitude distribution spectra might be obtained. The author is firmly of the belief that for process control purposes (for which this equipment is ideally suited) a single number which indicates either a satisfactory or bad stock to the operative is more than sufficient. What other simple means of specifying a distribution than a standard deviation and mean? It is accepted that for research purposes, a further refinement of data may be possible using roughness width, peak to peak distances, and other distributional aspects of the amplitude and frequency information held in the signal trace. As will be seen in the next chapter, such analysis is well within the capabilities of an automated device.

The transmitted light micrographs also show evidence of continuously changing dispersion up to about 2.5 minutes of mixing, after which time both numbers of aggregates per field and texture of background remain the same. Due to the procedure used in the Cabot and Leigh-Dugmore counting methods however, the majority of change is estimated to have taken place at between 60 and 90 seconds of mixing, after which dispersion ratings are calculated as being greater than 99%.
True, very small changes in the % dispersed are noted after this, but as explained, these are within error bands; the counting methods are found to be non-discriminating of high levels of dispersion. In addition they do not take into account background texture signifying colloidally dispersed black.

Vulcanisate and processing tests on the differently mixed stocks reinforce the findings of previous workers and in some cases supplement them. Viscosity as measured by minimum Monsanto ODR rheometer torque, Mooney and capillary rheometry show overall trends to decrease with mixing time. The latter two measures of viscosity show a rise to a peak at short mixing times, attributed to completion of incorporation, which has not been documented before. This peak at short mixing times (between 45-90 seconds) is noted graphically for several other properties; n (flow index), hardness and modulus at 100% extension vs mixing time. The reasons for the individual responses have been detailed, and it is concluded that in the compound, incorporation is complete at an approximate 60 seconds of mixing time. It is also relevant to note that all the properties that show this effect are dependent on occluded rubber which relate to the effective volume fraction of the filler developed at any point in the mixing cycle.

Decreases with mixing are noted for in batch variation, elastic and loss dynamic modulii at different frequencies with mixing. Positive dependences on mixing times are seen for consistency index (k), die swell and bound rubber, a levelling off being noted in the former two instances.

Critical mixing times are evident for the properties of elongation at break, tensile strength, tear energy, and fatigue life, these properties increasingly rapidly and then decreasing equally so after the attainment of a maximum. Tear strength shows trends to a maximum at about 90 seconds after which a decrease could be deduced with further mixing.
The times taken to reach a reasonable level of mixing (as predicted by each measured response) are tabulated next (Table 4.12).

**TABLE 4.12** Optimum mixing times predicted by properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Derived optimum time of mixing (mins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum torque (ODR)</td>
<td>3</td>
</tr>
<tr>
<td>DFRL trace analysis (vulcanised stock)</td>
<td></td>
</tr>
<tr>
<td>h</td>
<td>2.5</td>
</tr>
<tr>
<td>s</td>
<td>2.5</td>
</tr>
<tr>
<td>n</td>
<td>2.5</td>
</tr>
<tr>
<td>SEM</td>
<td>2.5</td>
</tr>
<tr>
<td>Mooney viscosity</td>
<td>3</td>
</tr>
<tr>
<td>Capillary viscometry ($n_a$)</td>
<td>3</td>
</tr>
<tr>
<td>Die swell</td>
<td>3</td>
</tr>
<tr>
<td>k</td>
<td>4</td>
</tr>
<tr>
<td>n</td>
<td>4</td>
</tr>
<tr>
<td>Leigh-Dugmore microscopy</td>
<td>1</td>
</tr>
<tr>
<td>Cabot microscopy</td>
<td>1.5</td>
</tr>
<tr>
<td>Stress relaxation</td>
<td>2 - 2.5</td>
</tr>
<tr>
<td>Bound rubber</td>
<td>&gt;10</td>
</tr>
<tr>
<td>Hardness</td>
<td>3</td>
</tr>
<tr>
<td>CV (based on hardness)</td>
<td>2</td>
</tr>
<tr>
<td>Modulus (100%)</td>
<td>2.5</td>
</tr>
<tr>
<td>$G'$ (1.5, 15 and 150 Hz)</td>
<td>3</td>
</tr>
<tr>
<td>$G''$ (1.5, 15 and 150 Hz)</td>
<td>&gt;10</td>
</tr>
<tr>
<td>Fatigue resistance</td>
<td>2.5</td>
</tr>
<tr>
<td>Tear energy</td>
<td>2.5</td>
</tr>
<tr>
<td>Tear strength</td>
<td>1</td>
</tr>
</tbody>
</table>

Note that cure time, maximum ODR torque, scorch time and tanδ were found not to vary significantly with time of mixing.
With reference to the table above, it will be seen that the weight of overwhelming evidence states that to obtain satisfactory processing and physical properties, a mixing time of 2.5 to 3 minutes is essential.

The present method is seen to correlate achievably with the property findings as regards a 'best' mixing time. Since processors and manufacturers of rubber goods are more interested in properties attained than just dispersion values the method is envisaged to be of extreme interest to the rubber industry.

The method itself has inbuilt a quick, simple and cheap method of sample preparation. No further refinements are required for vulcanised stocks, though unvulcanised materials do present their own special problems. As stated in the objectives, the method developed does satisfy the set criteria of non-subjectivity and independence of operator standards and skill. The method is reproducible and precise, with distinct values of \( h \), \( n \) and \( S \) being obtained for different levels of dispersions. It is discriminating and can identify differences in dispersion at the low, medium and high ends of the scale of practical mixes.

The problem with the method at present is the need to photograph the oscilloscope trace and manually analyse the signal. This is the current bottleneck in an otherwise swift and effective characterising test. In these days of advanced electronics however, it is surmised that equipment which will digitise analog information, store and manipulate it arithmetically as required and then output the selected roughness characterising parameters will not be inordinately difficult to manufacture. This reasonable amount of sophistication (and thus expense) appears to be tolerable, especially since the results shown, justify and validate the basic method.

The main disadvantages of the method are as follows:

1. It does not yield a true measure of carbon black dispersed, as do the Cabot, Leigh-Dugmore and AMEDA methods. Since the latter method has been acknowledged as being the most complete
dispersion analysis technique to date, it may be possible in future work, to relate the trace characterising parameters (at standard settings) to the AMEDA information. By use of mathematical techniques it may be possible to derive values of constants for groups of rubber compounds; by which, in conjunction with the observed h, S and n values, it may be possible to arrive at fairly complete dispersion information.

2. Extreme surface cleanliness of the sample is required, for otherwise, diffraction may occur from dust, fingerprints and so on. Experience has shown that it is not difficult to obtain and maintain surfaces in pristine condition, once the technique of sample preparation has been mastered.

3. The method might present a problem if the stock being examined contains such ingredients as reclaim, crumb rubber and unfluxed plastic resin. These materials will produce undulations during the cutting process, which may then be confused for dispersion features.

4.12 A Case Study

To evaluate the existing technique further, it was resolved to examine two dispersions of unknown physical/processing properties produced by different mixing methods.

The compound used was of the following recipe:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysar Butyl 301</td>
<td>100.0</td>
</tr>
<tr>
<td>Carbon black (N660)</td>
<td>44.0</td>
</tr>
<tr>
<td>Magnesium carbonate sulphur</td>
<td>1.5</td>
</tr>
<tr>
<td>Tetramethyl thiuram disulphide</td>
<td>1.5</td>
</tr>
<tr>
<td>Mercaptobenzthiazole</td>
<td>1.0</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5.9</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>153.0</strong></td>
</tr>
</tbody>
</table>
The compound was mixed, (one-stage) by Banbury mixing at the following conditions:

- Mixing time: 2.25 minutes
- Ram pressure: 0.414 MPa
- Starting temperature: 37.5 °C

Two batches were mixed, one at a fill factor of 0.4 and the other at 0.6.

<table>
<thead>
<tr>
<th>Material</th>
<th>0.4</th>
<th>0.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubber</td>
<td>459.6</td>
<td>689.5</td>
</tr>
<tr>
<td>Black</td>
<td>202.2</td>
<td>303.4</td>
</tr>
<tr>
<td>MC Sulphur</td>
<td>6.9</td>
<td>10.3</td>
</tr>
<tr>
<td>TMTD</td>
<td>6.9</td>
<td>10.3</td>
</tr>
<tr>
<td>MBT</td>
<td>4.6</td>
<td>6.9</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>23.0</td>
<td>34.5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>703.2</td>
<td>1054.9</td>
</tr>
</tbody>
</table>

Vulcanised sheets were prepared and samples for DFRL analysis made up as described previously. Three scans for each sample were made, and the parameters below are the average of these three scans.

**TABLE 4.13 Trace parameters for the two stocks**

<table>
<thead>
<tr>
<th>Trace characterising parameter</th>
<th>0.4 fill factor</th>
<th>0.6 fill factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>h (mean peak height)</td>
<td>13.6</td>
<td>8.6</td>
</tr>
<tr>
<td>S (SD from mean)</td>
<td>11.1</td>
<td>3.4</td>
</tr>
<tr>
<td>n (peak frequency)</td>
<td>37</td>
<td>55</td>
</tr>
<tr>
<td>Area under trace (arbitrary units)</td>
<td>1.76</td>
<td>1.0</td>
</tr>
</tbody>
</table>
By the previous reasoning it is established by the DFRL technique that the 0.4 fill factor batch has the inferior dispersion (large mean peak height, standard deviation and low peak frequency) consisting of a rougher surface and less (larger) diffracting centres compared to the stock mixed at the fill factor of 0.6. In addition, perhaps not surprisingly, the area of the traces (space enclosed by the baseline and peaks) is different, the rough sample showing a higher figure than the smoother.

Figure 4.137 shows a distribution histogram of amplitudes, comprising the traces; the better dispersion has a sharper distribution peak shifted to the right side, signifying an overall smaller trace amplitude. The badly dispersed distribution is broader and skewed towards the higher amplitude peaks.

The question is again, do the physical and other properties bear out the prediction that the 0.4 fill factor stock is inferior to the other? Table 4.14 shows the summarised results.

TABLE 4.14 Comparative properties of case study compounds

<table>
<thead>
<tr>
<th>Properties</th>
<th>Fill factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.6</td>
</tr>
<tr>
<td>Unit work of mixing MJ/m²</td>
<td>658</td>
</tr>
<tr>
<td>Dump temperature (°C)</td>
<td>83</td>
</tr>
<tr>
<td>Bound rubber (%)</td>
<td>66</td>
</tr>
<tr>
<td>Cabot dispersion (%)</td>
<td>99.91</td>
</tr>
<tr>
<td>Hardness (IRHD)</td>
<td>58</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>12.3</td>
</tr>
<tr>
<td>Modulus at 100% extension (MPa)</td>
<td>2.3</td>
</tr>
<tr>
<td>Modulus at 300% extension (MPa)</td>
<td>7.2</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>490</td>
</tr>
<tr>
<td>E' at 1% SSA and 1.5 Hz (MPa)</td>
<td>8.7</td>
</tr>
</tbody>
</table>
POOR DISPERSION
(0.4 fill factor)

GOOD DISPERSION
(0.6 fill factor)

FIGURE 4.137 Trace parameter histograms
Unequivocally, the 0.6 fill factor is found to give the better dispersion since it has a higher unit work input, dump temperature, bound rubber percentage, Cabot dispersion, tensile strength and elongation at break than its competitor. Its hardness, modulus (at 100 and 200% extensions) and dynamic in phase modulus is lower than the 0.4 fill factor stock; this combined evidence leaves us in no doubt at all, that the assertions of the microscopical method are correct.

It is thus seen that the method so successful for SBR, can be extended to butyl rubber stocks as well. The applicability of the method to process control is reinforced even further, by this brief verificatory segment of work.
Literature cited


14. BS 5324: 1976, 'Guide to application of statistics to rubber testing',


34. D A Hemsley, Private communication.

35. Carl Zeiss (Jena), Promotional publication.
CHAPTER 5
THE EVALUATION OF A PROTOTYPE AUTOMATIC DISPERSION TESTER

5.1 Description of the New Equipment

Due to the close collaboration encouraged between academy and the polymer industry by the Science and Engineering Research Council (SERC), the general principles of the dispersion tester described in the last chapter were made known to a cross-section of rubber companies. Dunlop Ltd Technology Division (DTD) (formerly Research Centre), declared a great deal of interest in the technique as a potential process control tool, and offered their electronics expertise to contribute to the development of the signal analysis segment of the equipment. It will be remembered that, in the existing method, this particular aspect required obvious improvement, if the method was to be practically viable.

Thus, DTD and the IPT cooperated on this phase of the research, the basic optical set up as described in the last chapter being retained, as was the television equipment for obtaining a signal of the microscope image. The Dunlop Design and Performance Engineering team set out to automate the hitherto manual process of photographing the trace, measuring peak heights and arithmetically manipulating these quantities to give the characterising parameters.

Appendix 1 describes this section of the system in great detail and is extracted from an internal DTD report by Burdock, Smith and Keyte.

To summarise, the image signals from the television system monitor (instead of being input into an oscilloscope) are accepted by a microcomputer, via an interfacing board. The signal is digitised and stored in the memory of the computer. At the line of sampling a bar is superimposed on the television image. (A vertical and not a horizontal line as used in the original method is utilised here,
due to the type of analogue to digital converter (ADC) contained in the video interface board. Several microseconds are required to digitize the analogue signal, thus horizontal scanning is impractical). Effective magnification was found to be x1000 on the VDU, equivalent to scanning a lineal dimension of 300 μm of sample.

The software (held presently on diskette) manipulates these digitized signals and gives a choice of several user selected processing functions for interactive operation which result ultimately in the computation of the dispersion related parameters.

The output is via a second video display unit (VDU) and is in the form of graphics/text. Hard copy is obtained by activating a thermal printer. A photograph of the system is appended, as well as a block diagram. (Figures 5.1 and 5.2).

FIGURE 5.1 The automatic dispersion tester
FIGURE 5.2 Block diagram of ADT
FIGURE 5.3 Trace from a poor dispersion
FIGURE 5.4 Trace from a good dispersion
In the automatic mode, the computer will take a number of sampling lines at regular intervals across the television image of the microscopical view, and calculate the output parameters for each scan. A record of the traces may be obtained from the printer and the hard copy resulting from the analysis of a poor and a good dispersion is shown in Figures 5.3 and 5.4. The flags over the trace signify the peak counts and the mean values shown in the text are averages of multiple line scans.

The reader will note that in addition to the original trace characterising parameters ($n$, $\bar{n}$ and $s$), two other quantities are calculated. These are threshold and variance. The latter is the square of standard deviation $S$, and yields no additional information. The former relates to the intensity of the lowest trough in the trace of any given scan (see Figure 5.5).

![Threshold level](image)

**FIGURE 5.5**

The parameter threshold

A glossy surfaced sample was noted to have a higher threshold than a matt sample; the value is believed to indicate the reflectivity of the sample being examined.
Note also the generalisations possible from these traces as with the original oscilloscope traces: the good dispersion yields a non-variable flattish trace, while the poor dispersion produces a peaky, uneven one.

To prove the new system, the following plan was devised. Firstly, the SBR compounds evaluated in the previous chapter provided a convenient and readily available set of variable dispersions for primary testing of the automatic dispersion tester (ADT). Next, it was intended to broaden the applicability of the technique by using a hitherto unutilised polymer in which again, varying dispersions of carbon black were prepared. In addition, various levels of black were used, as well as different black types, to examine the effects of these variables on the now established test.

5.2 Experimental

Vulcanised samples of the SBR compounds used in the previous chapter were cut as described and subjected to dark field microscopical analysis using the new system. Three samples were examined from each stock, five fields being used per sample, and five scans per field being analysed. Thus, each stock had a (3 x 5 x 5) trace replication level.

In addition, the importance of adequately focussing the microscope was explored, since this was one variable that could arise in a process control situation. A poor and a good dispersion were compared at different levels of focussing.

Also, two manufactured step heights were evaluated with this system. The step heights were produced by depositing aluminium on a glass slide by means of a metal shadowing apparatus; after the initial deposition, a square cover slip was placed on the first metal layer covering one section and leaving the rest bare. A further
shadowing operation was carried out, the time being varied for two such deposit slides. The result was a metal deposit with a step (where the cover slip lay) one step being higher than the second, due to the larger depositing time in the former instance.

This operation produced step thicknesses closer to the region of interest than in the first 'Sellotape step' samples used to explain diffraction observed in the last chapter. Step heights in the micron range were obtainable by using longish coating times (= 30 mins).

The new compound used for further testing was based on natural rubber and, as before, a curative master batch of the following recipe was prepared in a Banbury BR model mixer at 80 rpm, 50°C starting temperature, 0.4 MPa ram pressure, and at 0.8 fill factor (rate of flow of cooling water was 15.77 litres per minute).

<table>
<thead>
<tr>
<th>Actual Weights</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMR 5</td>
<td>988.0</td>
</tr>
<tr>
<td>Dutrex R</td>
<td>99.0</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>49.4</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>29.6</td>
</tr>
<tr>
<td>Isopropyl paraphenylenediamine (IPPD)</td>
<td>17.3</td>
</tr>
<tr>
<td>Cyclohexyl benzothiazyl sulphonamide (CBS)</td>
<td>7.9</td>
</tr>
<tr>
<td>Sulphur</td>
<td>17.8</td>
</tr>
<tr>
<td></td>
<td>1209.0</td>
</tr>
</tbody>
</table>

Dump temperature was 90°C after 6 minutes of mixing.

Several batches of this recipe were Banbury mixed, and cross-blended on a large (60") mill at MRPRA, Tun Abdul Razak Laboratory, Hertfordshire. This was, as before to ensure homogeneity, which was
checked by the usual Q.C. tests of Mooney viscosity and Monsanto ODR curemetry.

To prepare various levels of carbon black dispersion in this NR curative master batch, a Brabender Plastograph of 80 ml volume with mixing head was used. The rotor speed was set at 60 rpm, starting temperature to 55°C by means of a thermostatically controlled water bath regulating the inlet water temperature. Ram pressure was held at a constant but indeterminate value (the ram was one specially designed by MRPRA for their Brabender, which was often used as a small experimental internal mixer).

A chart recorder linked to the instrument recorded both batch temperature (by means of a thermocouple within the chamber walls) and also torque generated during the mixing operation in kg.m. with respect to time.

Four series of test stocks were produced from the basic NR master batch, containing 20, 50 and 80 pphr HAF (N330) black and 50 pphr GPF (N660) black. The specific gravity of the masterbatch was 0.96, and for ease of computation, equivalent volume loadings (55 ml of the total mixer capacity of 80 ml) were decided on for the Brabender mixing of the filled stocks: thus, the four compound series were mixed at 0.69 fill factor. To obtain equivalent volume loadings, the following mass loadings were required, given that the compound series had varying specific gravities (Table 5.1).

<table>
<thead>
<tr>
<th>Mix</th>
<th>Compound</th>
<th>SG</th>
<th>Wt of total (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>NR + 20 pphr HAF</td>
<td>1.03</td>
<td>57</td>
</tr>
<tr>
<td>B</td>
<td>NR + 50 pphr HAF</td>
<td>1.11</td>
<td>61</td>
</tr>
<tr>
<td>C</td>
<td>NR + 80 pphr HAF</td>
<td>1.18</td>
<td>65</td>
</tr>
<tr>
<td>D</td>
<td>NR + 50 pphr GPF</td>
<td>1.11</td>
<td>61</td>
</tr>
</tbody>
</table>
Table 5.2 shows the actual filler/masterbatch weights used for the four mixes (all weights in gm).

**TABLE 5.2**

<table>
<thead>
<tr>
<th>Components/Mix</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Masterbatch</td>
<td>49.0</td>
<td>43.3</td>
<td>39.0</td>
<td>43.3</td>
</tr>
<tr>
<td>Filler</td>
<td>8.0</td>
<td>17.7</td>
<td>26.0</td>
<td>17.7</td>
</tr>
</tbody>
</table>

'So, for each series, the relevant weight of rubber was made up from thinly sheeted masterbatch, and cut into small strips for inserting into the stationary Brabender. The ram was brought down and the rubber was allowed to warm up at 55°C for 3 minutes. The rotors were switched on, and mastication allowed to proceed for 30 secs. The required weight of filler was then added into the machine by raising the ram at this point. The filler addition took approximately 15 seconds to accomplish. The ram was brought down, and several stocks from each series were prepared varying only in dispersion by ranging the time of mixing from 0.25, through 0.5, 0.75, 1, 1.25, 1.5, 1.75, 2, 3, 5 to 7 minutes.

The stocks were removed from the Brabender by detaching its side and revolving the rotors at exceedingly slow speed. The stocks were sheeted out by one pass on a 6" x 3" mill at 4 mm nip setting at 20 rpm and even speed.

After cleaning the Brabender chamber and hopper, subsequent batches were mixed in the same manner as above. Thus, several different dispersion levels were obtained for the four classes of stock (three concentrations of HAF black, and one concentration of GPF).

Check weights were noted after each mixing, and dump temperatures were read off the chart recorder. Unit work of mixing was calculated according to the formula of Buskirk et al.
Unit work = $2\pi \times \text{Rotor speed} \times 9.8 \times 10^{-6} \int_{t_0}^{t_{\text{max}}} T(t) \, dt/V_b$ (MJ/m$^3$) 5.1

where rotor speed = 60 rpm in this case,

$$\int_{t_0}^{t_{\text{max}}} T(t) \, dt = \text{integrated torque time curve from time } 0 \text{ to end of mix (} t_{\text{max}} \text{) in Kg.m.min}$$

$V_b = \text{volume of mix in m}^3 = 5.5 \times 10^{-5} \text{m}^3 \text{ for all four series of mixes}$

Thus the above formula reduces to

$$K \int_{t_0}^{t_{\text{max}}} T(t) \, dt$$ 5.2

where $K = \left( \frac{2\pi \times \text{Rotor speed} \times 9.8 \times 10^{-6}}{5.5 \times 10^{-5}} \right) = 67.17$

The area under the torque/time curve was measured with a planimeter in cm$^2$ and converted to kg.m.min. by multiplying by a calculated scaling factor of 6.67 x $10^{-2}$.

Cure times for all stocks were evaluated using an ODR, and cured sheets were prepared by moulding for the cure time calculated to 95% crosslinking. Samples for analysis in the ADT were cut exactly as described before from these sheets.

5.3 Results and Discussion

First, a discussion of the model step findings. A diagram of the ADT traces obtained from each step (high and low) is found
below. (Note: no actual step measurements were carried out, and the steps will be referred to as high and low).

**Low step**

![Low step diagram]

**High step**

![High step diagram]

FIGURE 5.6

**Intensity peaks from steps**

The steps were positioned such that they were horizontal on the VDU screen, and any selected vertical scan line then would encounter the step.

The first point of note was that the diffracted light in the image at the steps caused a noticeable intensity peak in each case along the vertical line of scan which was certainly distinguishable from noise. Secondly, this peak was higher for the step of greater depth than for the shallower one. Next, to consider the trace characterising parameters relating to these traces. To be sure, this is an idealisation of the real case of a surface, since in these models, only one step is taken into account. In a real surface several of these steps, each possibly at different angles to the horizontal must exist.
The averaged trace parameters for several scans of the steps are shown in Table 5.3.

TABLE 5.3
Model step findings

<table>
<thead>
<tr>
<th>Step type</th>
<th>Threshold</th>
<th>Peak Frequency</th>
<th>Mean Height</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>High</td>
<td>58</td>
<td>18</td>
<td>68</td>
<td>26</td>
</tr>
<tr>
<td>Low</td>
<td>60</td>
<td>19</td>
<td>61</td>
<td>21</td>
</tr>
</tbody>
</table>

The values of threshold and peak frequency are not significantly different in the two cases. Thus, not surprisingly, the reflectivity of the two surfaces was deduced to be the same since they both comprise of aluminium. Since only one step is under examination in both cases, the number of peaks remain approximately the same. (Noise counts are inevitable in an electronic device such as this, and the noise tended to vary slightly even when successive scans were made over the identical lines).

The mean peak height ($\bar{n}$) and standard deviation ($S$) figures however are significantly different even allowing for noise interference. The high peak caused by the deep step pushes the values of both these parameters up. The mean level of the surface (as measured by $\bar{n}$) from the baseline is higher in the case of the high step, according to the assertion here. This reflects an obvious geometrical conclusion. The variability of the surface is more in the case of the deep step (by virtue of a greater $S$) and this reflects a statistically foregone conclusion once the step heights are known to be different.

Thus, as with the crude Sellotape models of the previous chapter, again it is seen that the DFRL system perceives step heights by virtue of the different extent of diffraction that occur from such surfaces.
Next, the exploration of the effects of looking at real rubber surfaces, but varying focussing. Two types of surface were examined, from good and poor dispersions. Focussing was varied in each case from sharp focussing, through slight and lastly gross defocussing. Tables 5.4, 5.5 and 5.6 summarise the findings, the figures quoted being averages of several scans from a plurality of fields. The good dispersion chosen was of commercially acceptable standards, while the bad one was only slightly outside a high specification (Cabot ratings shown in brackets).

### TABLE 5.4
Sharply focussed samples

<table>
<thead>
<tr>
<th>Dispersion Level</th>
<th>Threshold</th>
<th>Peak Frequency</th>
<th>Mean peak Height</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Good (99.9%)</td>
<td>81</td>
<td>21</td>
<td>46</td>
<td>13</td>
</tr>
<tr>
<td>Poor (99.2%)</td>
<td>69</td>
<td>28</td>
<td>76</td>
<td>33</td>
</tr>
</tbody>
</table>

### TABLE 5.5
Slightly defocussed samples

<table>
<thead>
<tr>
<th>Dispersion Level</th>
<th>Threshold</th>
<th>Peak Frequency</th>
<th>Mean peak Height</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Good (99.9%)</td>
<td>84</td>
<td>15</td>
<td>37</td>
<td>7</td>
</tr>
<tr>
<td>Poor (99.2%)</td>
<td>78</td>
<td>20</td>
<td>64</td>
<td>29</td>
</tr>
</tbody>
</table>

### TABLE 5.6
Highly defocussed samples

<table>
<thead>
<tr>
<th>Dispersion Level</th>
<th>Threshold</th>
<th>n</th>
<th>H</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Good (99.9%)</td>
<td>85</td>
<td>16</td>
<td>35</td>
<td>8</td>
</tr>
<tr>
<td>Poor (99.2%)</td>
<td>77</td>
<td>17</td>
<td>64</td>
<td>22</td>
</tr>
</tbody>
</table>
The first table indicates that the better sample is more reflective (higher threshold), has a lower overall peak height (lower $\bar{h}$) and is a less variable surface (lower $S$) than the bad sample.

What is different from the previous findings using the manual equipment, is that peak frequency falls as a dispersion improves. This is as a direct consequence of the software governing the extraction of trace data. As used, it specifies that only peaks above a given level are to be counted for inclusion in the parametric computation. This, as mentioned earlier, is to avoid counting small noise peaks which are present in abundance, in all the traces irrespective of the state of dispersion studied. As a consequence, some of the smallest non-artefactual peaks which would be produced by a good dispersion are ignored and not counted, whereas, in a poor dispersion which does not itself produce small peaks, all its constituents are taken into account. Thus, this system will be seen to produce a directly opposite effect to that noted in the original system. Because of the cut-off introduced, peak counts are noted to decrease with improving dispersion, rather than reflecting the increase in filler aggregate numbers per given line dimension taking place in reality with proceeding mixing.

In the slightly defocussed samples, the relationships stay constant, the better sample showing higher threshold, and lower $n$, $\bar{h}$ and $S$. The differences are still appreciable, and one is able to pick-out the better dispersion with no trouble. In the worst case of defocussing, the parameters $\bar{h}$ and $S$ are still amazingly discriminatory of dispersion, but the differences in $n$ and threshold value (even though still in the right order for picking out dispersion differences) appear to have lost some significance.

Considering all the tables together, threshold tends to rise with defocussing, since sharp points of light become more diffuse contributing to greater fraction of the image as focussing is made worse. Peak frequency falls with defocussing for very much the same reason as peaks become lower and lower in height and fusion of pre-
viously discrete peaks occur. A combination of the rising baseline (threshold) and the falling peak height renders the parameter \( h \) a decreasing value with progressive defocussing, and the general flattening out effect makes the \( S \) parameter fall as well. It is notable however, that despite the closeness of the dispersion characteristics of the two compounds, even under viciously defocussed conditions, it is possible to differentiate between the two.

Proceeding to the real rubber compounds, firstly the SBR stocks used in the previous segment of the work (the 'proving' compounds).

Graphs 5.7 - 5.10 show the changes in the trace parameters as yielded by the ADT on vulcanised stocks. All datum points are means of the \( 3 \times 5 \times 5 \) repeats on each stock. In the first two graphs, the trends in \( S \) and \( h \) are similar to those perceived before with the original equipment, a monotonic fall being noted. One point of dissimilarity from the original tests was noted to be the values of \( S \) and \( h \) ascribed to the worst mixed stock, that is the one offloaded at 15 secs of mixing. Mean values of \( S = 33.6 \) and \( h = 89 \) were lower than expected. The author would accept these values of being more representative of the sample in view of the high levels of replication used in this experimental sector. In the previous work, due to the time constraints on the manual process, it was not possible to obtain such high replication factors (the equivalent would have meant 75 photographs per analysed stock). The reason for this overestimation in the original case is plain - the highly non-distributed character of the stock in question would result in several categories of area being scanned. Some would have high concentrations of black agglomerates, others none at all, while in a smaller percentage, black dispersion would be in its initial stages. It is pertinent to note here that gum rubbers when cut exhibit smooth, reflective surfaces, and thus would yield regular intensity vs distance traces. Obviously, the concentration of such areas considerably affects the values which are then significantly decreased compared to a bad dispersion which is evenly distributed, such as the second point on the graphs corresponding to a 30 second mix.
FIGURE 5.7  Peak height S.D. vs mixing time
FIGURE 5.8  Mean height vs mixing time
FIGURE 5.9  Number of peaks vs mixing time
Threshold vs mixing time

FIGURE 5.10  Threshold vs mixing time
Thus, in the original equipment, only a bad area of dispersion would have been scanned, due to the low replication. With the high number of trace runs used with this method though, all areas have evidently contributed to the parametric values assigned to the 15 sec. mix, i.e. areas of pure rubber, distributed filler and agglomerated filler.

The next plot of peak frequency vs mixing time, falls as explained earlier, due to the noise cut-off level incorporated in the software of the equipment. The reversal of trend it is to be noted, but does not make this parameter any less effective for discriminating between good and poor dispersion. Again is noted the underestimations of the 15 sec mix for the reasons put forward earlier.

Graph 5.10 shows the trends in the new ADT parameter, threshold level. It is an obvious visual conclusion that reflectivity of sample surfaces increases with dispersion. Indeed, the shiny appearance on cutting has long been a reliable shop-floor indication of an acceptable dispersion level. That the lowest trough in a sample trace will indicate the 'mattest' point on a lineal scan is not in doubt either. The trend of this graph confirms this line of thought and again (given that the quantity is yielded by only one point per trace) it is surprisingly sensitive to dispersion changes, indicating a maximum level to be reached after 2.5 minutes of mixing. Note the enhanced reflectivity of the worst dispersion due to contributions from gum stock.

The ADT in sum yielded four parameters, three of which decrease with improving dispersion of carbon black (n, n and S) and the other, Threshold (T) which increases. An empirical composite parameter (C) was derived by

\[
C = \frac{n \times \bar{n} \times S}{T \times 100}
\]

5.3
FIGURE 5.11 Composite parameter vs mixing time
and the results of plotting C versus mixing time is shown in Figure 5.11. A curve with high discrimination at low-medium levels of dispersion is obtained, a slow decrease in C being noted even after 2.5 mins of mixing. It is seen however that the curve predicts the main changes (the deaggregation effects) in mixing to have ceased at around the critical 2.5 minutes, which again is in excellent agreement with the conclusions of the vulcanisate/processing characterisations of the previous chapter.

Next, consider the deeper exploration of the technique via the NR masterbatch, into which varying concentrations of HAF (N330) black and GPF (N660) were mixed.

Graphs 5.12 and 5.13 show the relationships between measured unit work of mixing (mixing energy per unit volume) and the concommitant measurements, dump temperature and mixing time respectively.

At equivalent unit work levels, batch temperatures are seen to vary systematically as a concentration effect, in the graphs relating to the 20, 50 and 80 pph HAF loadings. This is due to the more intense shear stresses developed, as a consequence of the increasing viscosity of the mixes with black concentration. At equivalent loadings of the different blacks (50 pph HAF and GPF) the former exhibits a higher dump temperature at equivalent energies, again due to the viscosity effect, this time introduced by the particle size differences between the two blacks (32 nm for the HAF and 60 nm diameter for the GPF).

These same effects are seen clearly in the unit work vs mixing time graph, where at a constant work input level, mixing time to that level increases with decreasing black concentration/increasing particle size. In an isochronous situation, less work is seen to be done at low concentration/low particle sizes than at high ones.

Apart from actually confirming known relationships between black concentrations and mixing time, energy and dump temperatures,
FIGURE 5.12 Mixing energy vs dump temperature (Brabender)
FIGURE 5.13  Mixing time vs mixing energy (Brabender)

80 pph HAF
50 pph HAF
20 pph HAF
50 pph GPF
these preceding graphs show the reader more accustomed to dump temperature and time their interaction with unit energy, which is used exclusively in the subsequent work.

(It is to be noted that these energy input levels consider only the mixing of black. The energy consumed during the manufacture of the masterbatch, as well as during mastication prior to addition of fillers has not been added on. This value was a carefully regulated constant equating to about 600 MJ/m$^3$. Thus to deduce the total amount of energy input into the rubber, this must be added on to the values of unit work on the following graph axes).

Having now clarified notation, it is possible to move on to considering how the established parameters of the ADT change with level of dispersion; also the effect particle size and concentration have on them. In the following graphs, dispersion parameter vs log unit work is plotted, in view of the broad span of energy inputs.

Graph 5.14 considers the changes in threshold (equated to reflectivity of surface) with progressive mixing for the compounds of varying HAF concentration. Note that the SBR proving compounds as analysed on the ADT would serve as an indicator and a baseline for proceeding discussion, and will be brought into the arguments frequently. However direct comparisons cannot be made since the SBR was filled with 40 pph N375 (a new technology type black) and thus several imponderables are introduced. The above graph matches the trends shown in the SBR compound analysis, in that first a decrease, following by an exponential increase and levelling out of threshold is noted with improving dispersion. The reasons for the initial comparatively high threshold value have been discussed before and are due to contributions to reflectivity by the gum still prevalent in stocks of low energy of mixing. As will be noted from the graph 5.14, at low energy inputs threshold is seemingly independent of black concentration, as is the initial rapid rise,
FIGURE 5.14  Concentration effects: threshold vs mixing energy
at medium/low dispersion levels. At high levels of dispersion however, the maximum threshold reached is significantly dependent on the level of the N330 black in the matrix. As is seen from practical experience, the highest concentration (80 pph) is confirmed by the ADT to be the glossiest, followed by the intermediate concentration (50 pph) and shows the surface of the stock containing only 20 pph black to be the mattest in character.

The next graph (5.15) shows the effects of particle size of black on threshold, and again it seems that at low levels of dispersion, this parameter is independent of black type. This observation continues up to fairly high/medium dispersions after which the more reinforcing the black, the higher the stock surface reflectivity. Indeed the gross effect observed between stocks containing different black types has been documented before, as being smoothness, decreasing with increasing particle size.

Next, the effect of concentration and particle size on the peak frequency as shown in Graphs 5.16 and 5.17, respectively. Again, as noted: for the SBR mixes, the effect of increasing dispersion on NR/HAF stocks is the same. (A decrease in the peak counts by the ADT with increasing dispersion). It must be remarked once again, that the apparent contradiction (peak frequency decreasing as dispersion increases) is an instrumental artefact, and relates only to a decrease in the comparatively large peaks (caused by large agglomerates) with mixing. The increasing small trace peaks (caused by the small aggregates) are masked, due to the noise cut-off and are not counted.

The effects of concentration on the counted parameter are not marked, all datum points (after an initial oscillation) falling on the same line. This even though contrary to intuition and logic, is explainable in terms of the noise cut-off level. Intuitively, the higher concentration should have the highest number of peaks at good dispersions, followed by the medium and low black concentration surfaces. In practice however the dominant very small particle size
FIGURE 5.15  Particle size effects: threshold vs mixing energy
FIGURE 5.16 Concentration effects: peak frequency vs mixing energy
FIGURE 5.17 Particle size effects: peak frequency vs mixing energy

Peak frequency vs mixing energy graph.
diffraction is not counted, due to the precaution of noise cut-out. The much less dominant large particle diffraction only is considered and this seems to vary little with concentration. Perhaps an improvement in the system could be made by eliminating the refinement of a cut-off (assuming noise to be constant) and thus making the ADT more sensitive to microdispersion, which is after all, as proved in the original DFRL technique, critical to the development of optimum properties.

Indeed this speculative thinking is borne out by the next graph 5.17, which shows the effect of particle size on peak frequency. As remarked before, the 50 pph HAF stock shows decreasing peak frequency with mixing. The GPF stock however exhibits an opposite trend, interestingly rising in peak frequency with dispersion. SEM photographs shown in another Dunlop Technology division confidential report by Walters and Keyte of stock surfaces containing small and large particle sized blacks, show that considerable roughness differences exist. Armed with this information it is possible to surmise with authority that the GPF stock yields a trace which is dominantly large peaked. Thus, the noise cut-off does not affect it significantly, as it does in small particle sized HAF stocks. It is possible to put figures to the GPF or HAF surface 'bumps' using the findings of Walters and Keyte, who generalise and indicate that aggregates of about 10 ultimate particle diameters exist in the best dispersed stocks.

Thus in HAF (32 nm particle size) and GPF (60 nm particle size) aggregates in average diameter of 320 nm and 600 nm exists in well dispersed stocks; somewhere between these two figures will lie a black type which, when mixed in natural rubber at different dispersions, will not show any change in ADT peak frequency with dispersion, since a balance between small/large aggregates will be reached.

(This somewhat chicken and egg situation of the present author quoting Dunlop reports which are based on the writer's original
work is another shining example of the interactive benefits that accrue when industrial and academic cooperation occurs in a properly regulated fashion).

On next to a consideration of how the third ADT parameter (mean peak height) reflects changes in concentration and black type. The graph 5.18 shows in general similar trends as observed before for changes in $\overline{n}$ with dispersion. There is without doubt a strong decreasing tendency. Note also the response of $\overline{n}$ vs energy input at low energies as observed previously - that is, the increase to a peak from initial moderate levels of the parameter, for all three N330 concentrations. The maximum value of $\overline{n}$ reached appears to be dependent on concentration, as does the initial $\overline{n}$ value. If, as supposed, this peak correlates with the end of the incorporation stage in mixing, then it is noted that incorporation involves high energies at high concentration and vice-versa at low. After the differing peak locations, the 20 and 50 pph concentration curves merge very early during the mixing and both sets of datum points are inseparable. The 80 pphr concentration though, is offset slightly signifying a markedly increased energy input to reach equivalent dispersions to those achieved by the lower concentrations. At high energy input (and high dispersion levels) this curve merges with the others (already united).

Mean surface height (as deduced by $\overline{n}$) thus is seen to remain the same for differing concentrations of a similar particle size, at high dispersions. The inequalities at the lower end of the dispersion scale would be due to a greater tendency for agglomeration at higher concentrations - this tendency being eliminated at high energy levels of mixing.

In graph 5.19 where the effect of black type on $\overline{n}$ is explored, after the now familiar equivalent initialisation, the curves are superimposed for a period of time. At high dispersion levels however, diversion takes place, the largest particle sized GPF showing a much higher minimum $\overline{n}$ (approximately 62 units) than the smaller particled black ($\overline{n} = 43$ units). It is very tempting to relate these quantities to the average 'bump height' ratios (1.88:1) calculable from the data
FIGURE 5.18 Concentration effects: mean peak height vs mixing
FIGURE 5.19  Particle size effects: mean peak height vs mixing energy
of Walters and Keyte\textsuperscript{4}, namely 600 and 320 nm respectively. In the light of this data, and the previous correlations with the Sellotape and shadowed metal models, evidence for a relationship between intensity of light diffracted in a reflection dark field system and step heights are very strong indeed.

Graph 5.20 shows changes in standard deviation (S) as measured by the ADT, and after identifiably different starts, all three curves merge into one, signifying that the average roughness of the surface at medium and high dispersions is independent of concentration.

The effects of black type on S (shown on Graph 5.21) show the GPF loaded stock to have a maximum value of S after which no initial increase (as noted for the HAF based compounds) is perceived. This would indicate that the GPF stock has reached the end of the incorporation stage during mixing faster than the finer particle sized black, and thus a uniform (though badly dispersed) stock is the result. This matches prior knowledge on the subject\textsuperscript{3}, which states that incorporation time increases with decreasing particle size. Returning to the graph under consideration, the rate of particle dispersion once the initial incorporation stage has reached its end, is much higher in the case of the finer particled black, probably in view of the higher shear stresses generated by the viscosity effect. At high dispersions, the parameter S not surprisingly, indicates that stocks containing GPF black are rougher in texture than those containing the finer HAF blacks. Reference is again made to the SEM photographs of Walters and Keyte\textsuperscript{4}, which visually prove this very observation extremely effectively. The general trends of the curves are as noted before in the SBR stocks.

The final graphs of this series indicate the changes taking place in the empirically derived composite parameter C. Again the general effect has been observed before with the original SBR compounds. Distinct starts are noted, and basically parallel curves are generated until very high dispersions are achieved when merging takes place. Iso-unit work observation indicates progressive tendency to good
FIGURE 5.20  Concentration effects: standard deviation vs mixing energy
FIGURE 5.21  Particle size effects: standard deviation vs mixing energy
dispersion from high to low black concentrations; emphasising in terms of energy the relative consumptions involved in mixing low, medium or highly loaded stocks to equivalent dispersions.

With regard to black type (Graph 5.23), C is seen to drop irrespective of particle size, the rate of drop being more favourable for the finer sized HAF. Maximum dispersion however is achieved at lower energy inputs (ca. 1200 MJ/m$^3$), in the GPF based stock, than the other (1350 MJ/m$^3$). The minimum value of C in the GPF stocks is higher than in the HAF compounds, due to the interdependence of C on $\overline{H}$, S, n and threshold (T).

5.4 Conclusions

This chapter has proved conclusively that a systematic relationship exists between dispersion (as varied by mixing time or energy input) and the selected ADT parameters $\overline{H}$, S, n and T. Also, $\overline{H}$, S and n undergo (in the case of the SBR mix containing 40 pph N375 black and the NR series of 20, 50 and 80 pphr N330), monotonic reduction to a steady level. In all cases considered T shows a positive trend with dispersion.

The combined empirical parameter C exhibits a negative response with increasing dump criteria severity, again showing a steady level to be reached at a critical level of mixing energy (or mixing time). This optimum level of mixing has been demonstrated for the SBR/N375 stocks to occur around 2.5 minutes of mixing. A glance at the ten foregoing graphs reveals that it is possible for the NR/N330 stocks (whatever concentration) to reach optimum mixing in terms of all the ADT parameters at 500 MJ/m$^3$, while for the NR/N660 an optimum energy input around 300 MJ/m$^3$ is required. It must again be stated that these figures relate to only the black mixing stage, and if the entire rubber mixing operation is considered (masterbatch mixing, mastication of masterbatch and filler dispersion) the above values become 1100 MJ/m$^3$ and 900 MJ/m$^3$ respectively. These, by 'a priori' knowledge and the work of other researchers$^5$ are reckoned to be in
FIGURE 5.22  Concentration effects: composite parameter vs mixing energy
FIGURE 5.23 Particle size effects: composite parameter vs mixing energy
the correct region for adequate mixing.

If these optimum energies are transcribed into optimum mixing times via the unit work/mixing time family of curves then the following table summarises the observations.

TABLE 5.7 Optimum mixing times for NR stock

<table>
<thead>
<tr>
<th>Compound</th>
<th>Optimum Mixing Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR/20 pph N330</td>
<td>4.5 (mins)</td>
</tr>
<tr>
<td>NR/50 pph N330</td>
<td>3.0 (mins)</td>
</tr>
<tr>
<td>NR/80 pph N330</td>
<td>2.0 (mins)</td>
</tr>
<tr>
<td>NR/50 pph N660</td>
<td>1.75 (mins)</td>
</tr>
</tbody>
</table>

The apparent anomaly of a lower concentration of black requiring a higher mixing time for efficient dispersion is observed. This is because input of energy is more rapid in the higher loaded stocks (because of the higher power peak) and viscosity increases (leading to shear stress magnification) make particle breakdown more efficient. The finding that coarser particles are quicker to mix than finer ones (N660 and N330, each at 50 pphr loading) is not at all novel, and is in agreement with the known facts of black mixing.

With regard to the effects both of concentration and black type on the ADT parameters, threshold effectively differentiates between varying concentrations, and particle sizes of black. As concentration increases, glossier stocks are produced, and the converse is seen with increasing particle size.

No evident effect of concentration on peak frequency is noted, for the reasons stated in the discussion. For the same reasons, the parameter n (which decreased in all other stocks) increased with mixing energy for the NR/N660 series of stocks.

The mean peak height (\(\bar{H}\)), was noted to be systematically different for varying concentrations of N330 black at low levels of mixing.
These differences rapidly vanished at good dispersions, with no variation in this parameter being noted with concentration. Due to inherent aggregate size differences, $n$ for the N660 stocks significantly differed from that corresponding to the N330 rubbers. The ratios of the values of $n$ obtained from these two different compound series match very closely the computed actual surface height ratios of 1.8:1.

The ADT parameter, $S$, shows no change with concentration; however, $S$ does vary with particle size at similar levels, of good dispersion. Again, from a consideration of aggregate or 'bump' sizes in the final mix, this is not a surprising observation, since one sample consists of uniformly dispersed largish aggregates while the other is made of similarly disposed smaller fragments.

The composite parameter $C$ indicates concentration differences at low and medium levels of mixing, which vanish at high energies of mixing. $C$ at any point in the mixing cycle is able to differentiate a small particle sized black (N330) from a large one (N660).

It is evident from the foregoing evidence, that considerably more than an embryonic method for assessing the dispersion of carbon black in rubber now exists. It is felt that here is the basis for a sophisticated though robust system which by its very nature, is ideally suited to a production environment, and matches the criteria set forth earlier in this dissertation.

Expansion of the technique is required, and it is now right that a prototype be used under production conditions, with scientific monitoring of the findings.

Further 'in situ' development work must follow on the lines suggested below.
5.5 Further Work

A priority for this area must be the institution of a setting up procedure by which the starting from a standard point is assured time after time. Reflection (step) gratings may be used profitably as an aid, to setting the electronic television system controls.

On the topic of the television system, it is possible to further compact the equipment by using a cheaper television camera and a less highly specified control system. One VDU may be eliminated from the system, the software providing an alternation between text, graphics, and image. In the same vein a less sophisticated microscope (possibly a basic metallurgical body, set up for dark field, with one objective) may be used, thus even further paring down costs, which one suspects will be critical for ensuring commercial acceptance of the system.

A concentrated attack must be made on the problems of preparing unvulcanised samples. It is thought that a suitable method already exists, for Vegvari, Hess and Chirico have already carried out extensive testing of unvulcanised stocks using their stylus system successfully. Unfortunately most of the work referred to in this thesis concentrated on the cured variety, since the priority was setting up and explaining a system that worked, within the obvious constraints of time. This necessitated the use of samples that were easily prepared.

Improvements have since been made to the software, and these include increasing the number of scans per field from five to twenty. This increases the time for analysis from four to ten minutes, but this is still better than the time requirements of the more commonly used methods for assessing dispersion.

Some work must also be carried out on alternative methods of analysing the trace. This necessarily involves aspects of communication theory, and signal analysis, but with the availability of computer subroutines which accomplish fast Fourier transforms and the like in microseconds, this alternative becomes increasingly attractive for planned research use of the instrument. The author however remains firmly convinced that the parameters specified here are more than
sufficient for routine process control.

The findings that threshold levels are related to reflectivity may be put on a sounder footing by a more complete measurement of trough levels. It is envisaged that an average threshold level calculated as the arithmetic mean of the trough levels making up a trace could be profitably added to the parametric selection in the software. This will make more complete the information extracted from the trace.

The method as it stands has been proved for SBR, NR, and IIR stocks, containing N330, N375, and N660, in varying proportions. There is no reason why the technique should not be able to handle other rubbers too, and blends one in another. Vegvari⁶ has shown his stylus technique to work on all types of commercial compounds and there is no reason why (once the basic premise that the ADT characterises surface is accepted) this should not hold for the present optical technique. Roughness differences similarly arise irrespective of black type (whether reinforcing, semi-reinforcing, or non-reinforcing) and again it could be safely assumed that the method will discriminate between dispersions of any black in any elastomer.

A limitation to the technique might be that large particle sized additives, or additives that form discrete lumps within the rubber will also be sensed (erroneously) as a contributor to dispersion. In the case of curatives for instance, this would presumably be desirable, since then a dispersion level which included contributions by the minor (in volume) components would indicate the overall state of the discrete multi-phase. With ingredients such as reclaim, non-fluxed high styrene resins and so on the limitations might become more serious, because such materials being present in relatively high proportions might mask the main black dispersion effects.

A further problem may arise with the use of the technique to investigate the dispersion of non black fillers in rubbers. Such light compounds, when viewed under dark field, may give rise to flare. This
is caused by a high ratio of background scatter to main scatter from the sample surface. Methods of reducing flare, such as metallising the surfaces before observation will work, but it is not thought that this technique will appeal to production controllers. This, and the other aspects discussed in the last three paragraphs are deserving of a systematic study if this technique pioneered here, is to be understood more fully. If, combined with these suggestions, wholesale visual surface characterisation by SEM was to be carried out, further extremely pertinent data regarding cut surfaces will be accumulated.

Finally, one aspect implied in the previous chapter bears repetition. Because of the varying parameter values yielded by different stocks, the method as it stands at present, cannot specify a dispersion level given one unknown sample. Given two unknown samples, from the same mother stock, it can analyse and grade the pair for comparative dispersion. It is emphasised therefore, that a high priority must be given to relating the parameters of this study to stereological information with the aim of obtaining relationships by which the true dispersion values pertaining to a sample might be derived. From the work done here, with varying fillers and filler contents, these relationships appear imminently possible to obtain.
Literature cited

1. W Burdock, J E Smith and D N Keyte - Dunlop Technology Division, restricted report TR81-44 "Methods of assessing the dispersion of fillers in rubber - I", (19.6.81).


4. M H Walters and D N Keyte, Dunlop Technology Division, Restricted report TR81-60, "Methods of assessing the dispersion of fillers in rubber - II", (10.8.81).


CHAPTER 6
THE EMPIRICAL MODELLING AND OPTIMISATION
OF THE INTERNAL MIXING PROCESS

6.1 Introduction

It was stated in Section 1.4 that there was a broad based need for a more complete understanding of the internal mixing process as applied to rubbers. Specifically, it was felt that the full potential of the internal mixing operation was yet to be achieved; what is known of how the main process variables affect the mixing operation, and more important perhaps, the interdependences between these, is superficial. However, it is important at this stage to collate the known facts regarding the influence the established variables have during this operation.

The variables considered here, are the five most used, to regulate the mixing process. They are:

- Ram pressure
- Starting temperature of the mixer
- Fill factor
- Rotor speed
- and the selected dump criterion for termination of mixing.

These variables have already been introduced in Section 1.1, and the reader will be familiar with their meaning. The next section will explore the established thoughts on the effects of their variation during the mixing process. It will be noted that there are other variables (both continuous and discontinuous) used in the field of internal mixing. For example, mixing techniques\textsuperscript{1,15} might be changed depending on the type of stock being mixed. Commonly, batches containing only a low percentage of rubber and large volumes of filler, are loaded 'upside down' or 'side by side', such that an effective volume for mixing is introduced into the mixer. In this section, only 'upside down' mixing is utilised, it being felt that the first priority was to obtain an understanding of the process.
variables.

Mixing also may be accomplished in discrete stages. Thus a separate mastication step might be introduced, when using natural rubber, or a masterbatch stage if using large quantities of filler. Similarly, two stage mixing is common if thermally sensitive curatives are used to prevent premature vulcanisation (scorch). Again, due to the priority needs of this study, in this section single stage mixing is used throughout, where all ingredients, rubber, fillers and curatives are added in the same mix cycle.

Recently, there has been interest in 'variable control' mixing. Here, ram pressure may be varied at different stages in a mix cycle\(^7\), as may temperature of coolant\(^1^1\) or rotor speed\(^7,2^4\). This method takes into account the different needs of the process at various stages in the mixing cycle, such as incorporation, dispersion, homogenisation and so on. This study ignores these advances, and concentrates on the more widely used technique of mixing where the mixing variables are held constant during a cycle.

6.2 The Variables of Internal Mixing and Their Effects on the Process

6.2.1 Ram pressure

Originally introduced as a variable during the reclaiming of rubber\(^2\), high pressure mixing of normal rubber stocks is now widespread in industry.

The need to shred and masticate the rubber sufficiently for the matrix to fill the flow channels in an internal mixer has already been emphasised. At low ram pressures, the rotors tend to slip past the rubber since the ram oscillates up and down in the throat of the mixer, and thus shredding cannot take place. It is only when the temperature builds up and the stock viscosity falls that flow in gaps can begin and efficient mixing commence. Increasing ram pressure increases the contact force between the rubber and
rotor surface, reducing slippage and increasing the critical stress for flow which then begins at a lower temperature. Also a decrease in the voids within the mixture and more intimate contact between ingredients is encouraged. The net effect of this is that more effective mixing is now possible as the stock temperature is lower (and thus its viscosity higher), and so peak power generated is also higher. It is because of this higher power peak generated that high ram pressure mixing is also known as 'High horsepower mixing'. Figure 6.1 from Bebris et al shows the effect of ram pressure on power consumption.

![Figure 6.1: Power consumed at different ram pressures](image-url)

**Figure 6.1** Power consumed at different ram pressures
Several workers have experimentally explored the effect of changing this mixing variable on the process. Most document a decrease in cycle time and/or improvement in dispersion with increasing pressure (Refs 1, 3, 4, 6, 7, 8, 9, 11 and 27), while yet others state that very high pressures lead to poor mixing. Certain researchers indicate that increasing ram pressure has an adverse effect on mixing/dispersion, when working at the dump criterion of batch temperature.

6.2.2 Temperature of mixer components

From a survey of literature, it is evident that the temperature selection for an efficient rubber mixer is dictated by opposing considerations. On one hand too low a temperature is deleterious, while on the other, high temperatures are exceedingly undesirable.

Rubbers are insulators, and thus to be cooled during mixing, fresh material must be continually exposed to the metal surfaces of the mixer. Cooling then takes place by conduction of heat away from the rubber to the metal surfaces in contact with the cooling medium. This exposure is achieved by a turbulent motion of the rubber in the chamber, and to promote this, it is essential that shearing between the metal components and the rubber takes place. This, in turn necessitates a gripping of the rubber by the mixing chamber wall and rotor surface.

This gripping is a function of temperature, which affects the coefficient of friction (μ) between the metal and rubber. The best temperature is the lowest possible which will give a sufficiently high value of μ for grip, which will depend on the polymer being mixed.

Too low a mixer temperature will cause μ to be low, and thus, instead of gripping, sliding of the rubber over the metal surface is the result. This sliding results in the generation of frictional heat, not contributory to mixing.
If now on the other hand temperature within the mixer is too high, several contributing effects can combine to retard mixing.

Firstly, consider the relationship between viscosity ($\eta$) and temperature in liquids:

$$\eta = A e^{(E/RT)}$$

where $A$ is a constant
$E$ is the activation energy
$R$ is the gas constant
and $T$ is the absolute temperature

Due to the Arrhenius type relationship, as temperature increases, fluid viscosity falls exponentially. The lower the viscosity, the lower the shear stress generated within the matrix at a constant shear rate. Thus, in rubber mixing, the effect of too high a temperature will be to reduce the dispersive mixing because of the degeneration of shear stress levels within the bulk of the stock.

Next, the materials used in the rubber industry are known to be temperature sensitive. Too high a temperature may cause polymer degradation during mixing, or, if curatives are present, premature vulcanisation may take place, rendering the batch useless for further processing.

Excessive temperatures could also cause the rubber to stick to the chamber wall or rotor surface; this causes a further runaway temperature rise within the bulk of the rubber, due to its insulation from the cool metal members by the offending adherent layer.

In the light of what has been said, a medium must be struck to prevent the disasters of either temperature extreme taking place. The temperature below which slipping occurs is about $12^\circ$C, and it
is generally recognised that mixer temperatures of greater than 80°C will cause the problems associated with extreme temperatures discussed above.

The practical findings relating to the effects of starting temperature variation on mixing are far from unanimous. References 17, 16 observe that high temperatures are beneficial, while others 6, 15, 10 document negative effects on mixing efficiency as a consequence. The indications from other sources 18 are that mixer temperature does not affect either stock properties or power demands.

6.2.3 Fill factor

As defined in Section 1.1, fill factor is the fraction of free mixer volume occupied by a batch of rubber stock. Due to the fluffy nature and low bulk density of the powdered ingredients to be mixed into the rubber, the total volume of ingredients in a batch is usually larger at the beginning of the mix cycle 10; subsequently, due to incorporation into the rubber this volume decreases, the degree of fill at this stage being quoted as the fill factor of the batch being mixed.

The optimum degree of filling depends on several factors. Mix viscosity, rotor and mixer geometry, filler type contained in the mix, nature and form of other compounding ingredients/base stock and quality of stock required, all affect the correct selection of batch size. Consensus of opinion points to a wide range of possible economical fill factors: 0.6 - 0.8 5,10,24,25,28 is a common choice opted for, others specifying even higher top levels, (e.g. 0.914). Most stocks are said to mix well at a fill factor of 0.719,22,23.

The reason for most researchers agreeing that fill factors of less than unity are conducive to efficient mixing is this; simply 10, the 'empty space' provides room for the rubber to be turned round in the chamber and this is essential for simple (or distributive) mixing.
This idea was expanded by Freakley and Wan Idris\textsuperscript{22}, and by means of colour photographs of rubber undergoing the rotor action in a transparent chamber, they explained qualitatively the dynamics of using different fill factors. At low volumes, the region between the rotor and chamber wall had large voids, with little flow of material past the tip. Flow was analogous to milling, material passing between the rotors, and not the high shear areas. At loadings of about 0.7, high shear and extensional flow occurred at the rotor tip, with accompanying flow instabilities. The material in the other regions of the mixer at this time were also undergoing shear flow of lesser magnitude. Void formation behind the rotor tips, essential for the disordered of streamline flow patterns, and the promotion of axial transfer of material (for distributive mixing action) is also encouraged at this level of fill factor. In addition\textsuperscript{11}, these combined actions result in the continuous presentation of new rubber surfaces to cooled metal components, thus achieving effective heat transfer from the bulk, enabling high viscosity levels to be maintained for efficient dispersive mixing. For very high volume loadings it was found that the general flow regimes remained unchanged, but distributive mixing (that is the material passing from one side of the chamber to the other, as well as one chamber half to the other chamber half) was greatly reduced.

Practically, oversized batches result in reduced uniformity\textsuperscript{26,28,10}, and long mixing times are required. Bad dispersions, high energy utilisation, dump temperatures and power consumption are noted. Under-sized batches are not subject to ram pressure, thus shear stresses generated are very low and slippage occurs\textsuperscript{10}. Long mixing times are therefore again needed\textsuperscript{28,14}, crumbing occurring in very low batch sizes on dumping. Ideally sized batches give the shortest mixing cycle\textsuperscript{24}, with small in batch variation\textsuperscript{10,7} and do not give rise to unacceptable amounts of loose black on discharge\textsuperscript{23}. A practical sign of the correct batch size is the ram, which in these cases, exhibits only small oscillations about its equilibrium position\textsuperscript{14}.

In view of the agreement of the majority of the findings that fill factor is indeed an important mixing variable\textsuperscript{22}, which has to be
set at considerably less than unity for efficient mixing to occur\textsuperscript{11,23,22,19}, it is interesting to note a totally opposed view taken by certain French workers in the field\textsuperscript{27}. They conclude that a fill factor of 1.1 yields the best mixed stock, with no adverse effects on in batch variability.

6.2.4 Rotor speed

The necessity for shear deformation during mixing has been pointed out by Irving and Saxton\textsuperscript{29}. Controversially, they state that this deformation alone determines the quality of mixer, and relegate shear stress and strain rate to the background. In reality, for materials such as rubbers it cannot be denied that shear stress is important for promoting intimate contact of ingredients, wetting and dispersive mixing. Similarly the rate at which the deformation is applied must affect the process: if too low, mixing times required will be unrealistic, while, if the shear strain rate is too high, power consumption and heat generation will be impracticably large.

Rotor revolution in internal mixing provides the necessary shear deformation, while the speed dictates the actual shear strain rates achieved during mixing\textsuperscript{36}.

\[ \gamma_a = \frac{V}{h} \]

where \( V \) is the velocity of an area \( a \) on a rotor
\( h \) is the clearance between \( a \) and the chamber wall
and \( \gamma_a \) is the shear rate at \( a \).

These shear rates approach 500 s\(^{-1}\) in many mixers\textsuperscript{10} at high speeds and those operating at low rotor speeds generate rates of about 100 - 250 s\(^{-1}\)\textsuperscript{31}. 
Given that high shear stress is a necessary condition for dispersive mixing (see Section 2.2) a high shear strain rate is necessary for the required levels of stress generation. For rubbers, the following approximation is acceptable:

\[ \tau = k \gamma^n \] \hspace{1cm} 6.(3)

This realisation pushed internal mixer rotor speeds up from the original 20 rpm in the first size Banbury to levels of greater than 100 rpm.

Of course, it has been pointed out that because of the power law type relationship in 6.(3) between \( \tau \) and \( \gamma \), a doubling of shear rate only increases shear stress by about 20%. (For 'average' rubber stocks at 100°C). 

This disproportionate increase in the shear stress generated is further affected adversely by the increasing heat generation caused by high rates of deformation. The Arrhenius relationship of 6.(1) causes apparent viscosity of the rubber stock to fall exponentially with temperature, thereby reducing shear stress and thus the intensity of dispersive mixing.

These then are some of the problems experienced by increasing rotor speeds to levels greater than optimum. If caution is exercised however and rotor speeds are set too low, then again by equations 6.(2) and 6.(3), shear stress levels reached will be inadequate for efficient mixing, as they may not exceed the cohesive strength of the filler aggregates waiting to be dispersed.

Again practical experimentation on mixing using different rotor speeds produces conflicting findings. Certain workers say that rotor speed has no effect on dispersion\(^6,33\), while others indicate\(^9,8,4,35\) a positive relationship between the two, especially with soft stocks.
Rotor speed is said to be inversely proportional to cycle time by some, while others oppose this view, due to complicating temperature effects. Whitaker agrees with the reduction in mixing time stemming from increases in rotor speed, but states that the effect on dispersion is indeterminate.

Rotor speed increases also mean linear increases in power requirements and, as ever, this must be weighed against any other benefits that accrue as a consequence.

6.2.5 Dump criteria

Mentioned briefly in Section 1.1, were several methods used to specify the termination of a mixing process. They were time, stock temperature, integrated power (or work done) per unit volume/weight of batch, and heat history.

All these are aimed at guaranteeing the quality of the end product, avoiding overmixing and reducing variation between batches. The object of the batch mixing step is to produce a material that has the ingredients sufficiently incorporated and dispersed so that it will process easily in the shaping step, cure efficiently and give the required end use properties. Any extension of the mixing process beyond these objectives is uneconomical.

Control of the mixer by elapsed time alone, however, does not adequately safeguard against the effects of changes in mixer temperature that take place particularly on short run production, or differences in individual mixer performance; nor does it provide indication of the mixer response to the various process functions that are performed. Also, it does not allow for time of addition of compounding ingredients, and batch to batch variation is common.

Any monitored criterion employing product temperature (dump temperature) as the basis for mix termination must be affected by the temperature of the metal mass surrounding the measuring element; also, note that the intimacy of contact between the element and the
mix might vary, causing further imponderables. The accuracy with which overall batch temperature can be measured is also in doubt.

It is to attempt to solve the individual problems of the above two criteria that, in effect, they were combined to give a measure of heat history (integrated temperature/time) experienced by the batch during mixing. This measure has not attracted many devotees, predominantly one supposes, since it still does not solve the problems highlighted with the individual time/temperature criteria.

The concept of unit work introduced by Van Buskirk et al as a dump criterion, directly related to mixing behaviour in an internal mixer. They showed that the power used at various stages of the mixing cycle was a function of the degree of mixing that had taken place, evolved the concept of power profiles and showed work per unit volume of compound to be a critical parameter. It related to the mixing processes (simple, dispersive and laminar - Section 2.1) and the physical changes taking place in the rubber mixing cycle (incorporation, dispersion, homogenisation and plastification - see Section 2.3) as well as the developed physical properties of mixes used to characterise 'mixedness' (see Chapter 3). It allows for the settings and levels of the other process variables, and because of all these factors, unit work has become the main method used to control mixing in the modern rubber industry.

Other means of control have been suggested, and will be documented for sake of completeness.

a) Combined reference to a power integrator and an instantaneous power recorder, in addition to a consideration of time and stock temperature.

b) Subjective measures used to identify the progress of internal mixing are listening to the noise of the mixer, and observing the movements of the ram.
Following up on the comments of Irving and Saxton, referred to in 6.2.4, Shikhirev et al.\textsuperscript{30} have shown experimental evidence to signify the exclusive dependence of mixing efficiency on shear deformation. As a consequence, this has been promoted as a controller of mixing\textsuperscript{3}, the total number of rotor revolutions being used in some instances as a measure of total shear strain\textsuperscript{7}; in other cases, it has been calculated as the product of the average shear rate and time of deformation\textsuperscript{30}.

In the following experimental work, unit work of mixing is used as the sole dump criterion.

6.2.6 General comment

From the foregoing, it is evident that contrary views regarding the influence of the mixer variables on the process exist. What is also clear is that several variable interdependences have been implied, though not investigated in detail. The reason for this neglect, has been that the experimenters in mixing studies have used the so-called variable screening (or Edisonian\textsuperscript{47}) approach to experimentation. That is, they observe the effect of changing one variable on a measured property while holding the levels of all the other variables constant. In a process as complicated as the internal mixing operation, there are complex interactions between variables, the effects of which cannot be recognised using the Edisonian method.

In addition to this neglect, there has evolved no universal measure of mixedness by which the process and the effects of the variables on it could be judged. Many indicators of mixing are known (as noted in Chapter 3) but each of these is found to yield a differing estimate of the extent of mixing that has taken place within a rubber stock. Thus, Mooney viscosity for instance, identifies only the changes of one component in the elastomer, while quantitative microscopy traces another. Bearing in mind these shortcomings of experimental procedure used hitherto, it is possible to frame a detailed set of aims for this section of the work.
6.3 The Objectives For this Area of Research

a) Firstly, there is the need for an experimental method that will clarify not only the effects of changing the individual variables of the mixing process, but also one that will identify the important interdependences between these.

b) The method will embody a means by which certain of the current dump criteria might be concommittantly observed, while one will be systematically varied; thus the influence of one on the other might be forthcoming.

c) Next, it is thought that to explain the mixing process in terms of the variables, the derivation of an unified function, relating to the 'goodness of mixing', within a rubber stock is highly desirable.

d) The relationships between the variables and the mixing function will be represented by a mathematical expression. However, since a technological subject is being dealt with here, some method by which any mathematical relationships postulated in the course of this section might be represented graphically, will increase its practical value. By using a graphical method one may more readily understand the workings of the mixing process, and grasp the importance of variable changes on the mixing function.

e) In addition, it should be possible to specify levels at which the variables must be set to obtain a certain degree of mixing. Also, the method must be able to isolate the best possible mix, and the conditions that produce it. It will also be useful if the method isolates the regions at which mixing is unsatisfactory. In this manner it will be able to identify a processing window within which the process may be operated successfully.
6.4 Some Background on Modelling

The rubber mixing process, already acknowledged, is a complex one to analyse. Mixing machinery comprises complicated geometries; the lines of flow within are also extremely intricate and these factors, together, give rise to non-uniform deformation rates, and non-steady state thermal conditions. The polymer undergoes complex mechano-chemical structural conversions, the compounding ingredients being subjected to various mixing mechanisms during the process.

Despite these almost insurmountable difficulties, many workers have attempted to mathematically model internal mixing, paying particular attention to detailed areas such as flow within mixers,(Refs. 42,43,45,46), temperature and pressure trends of mixing. As more details are incorporated into these models, their mathematical complexity and computational difficulties increase rapidly.

The above are known as 'mechanistic models', since their form attempts to reflect the structure of the supposed mechanism. These fundamental models, if representative of a process, are of considerable interest and utility to the machine designer and can provide the user with scale-up rules. However their accuracy within the wide range of an industrial process is poor and they are of little use for optimisation. Practical men require to know what factors may be controlled in the process of interest, the extent of their influence on the ultimate mixture, and how they quickly restore a process that has gone wrong back to normality. The usefulness of complex mechanistic models for these purposes is very limited indeed.

Other models (which do not take into account the mechanics of the process under consideration) have been used, to explain processes that are too complicated to be analysed mechanistically. The 'empirical models' as they are called specify generalised mathematical relationships between the variables of a process by which it is controlled (the independent variables) and measured properties of the product of such a process (the dependent variables or the responses).
In such models, a flexible graduating function $g$ (for example a polynomial) will often be satisfactory to express the relationship between the response $R$ and the $k$ important variables $X_1 - X_k$. In other words $g$ is an adequate approximation of the true relationship over the region of experimentation. The two most common forms of $g$ are the first order polynomials:

$$R = \beta_0 + \beta_1 X_1 + \beta_2 X_2 \ldots \ldots + \beta_k X_k$$  \hspace{1cm} (4)

and the second order polynomial

$$R = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \ldots + \beta_k X_k + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \ldots + \beta_{k-1,k} X_{k-1} X_k + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \ldots + \beta_{kk} X_k^2$$  \hspace{1cm} (5)

The quantity $\beta_0$ is the zero order constant term, while $\beta_1 - \beta_k$ are the linear coefficients, $\beta_{12} - \beta_{k-1,k}$ are the interaction coefficients and $\beta_{11} - \beta_{kk}$ are the quadratic coefficients to be estimated by experimentation.

In the internal mixing process as applied to rubbers, the independent variables or the controllers of the process are ram pressure, rotor speed, mixer temperature, fill factor and unit work of mixing. Thus, the properties of the material mixed under these conditions become the responses or dependent variables. So, Mooney viscosity is one possible response measured in a mix produced at a specific combination of the independent process variables, while bound rubber may be another. As stated earlier, the levels of these responses
or dependent variables are indicative of the mixed quality of the stock produced at the specific settings of the independent variables. The individual responses of course, will emphasise different aspects of the 'goodness' or 'badness' of a mix.

It was stated that the relationship between these responses and the mixer variables must be evaluated by experimentation to find the coefficients of the fitted model. This is then the next area to receive attention.

6.5 Selection of an Experimental Design for Estimating the Coefficients of a Polynomial Model

It has been observed that the Edisonian approach to experimentation is ineffective and misleading, especially if interaction between the variables of the study are expected, (where the effect of one variable depends on the level of another).

The most effective way to determine if a given variable has any significant effect, is to test it at two levels. This is the basis of factorial designs where if all combinations of variables, each at two levels, were run then a total of \(2^k\) test points or treatments result. If a full factorial design were used, the total test points for four and five variables will be 16 and 32 respectively. An example of such a two level factorial design in three variables is shown in Table 6.1.

**TABLE 6.1**
2 level full factorial design in 3 variables
Total test points = \(2^3 = 8\)

<table>
<thead>
<tr>
<th>Experiment No</th>
<th>Variable 1(V1)</th>
<th>Variable 2(V2)</th>
<th>Variable 3(V3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>2</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
</tr>
<tr>
<td>3</td>
<td>-1</td>
<td>+1</td>
<td>-1</td>
</tr>
<tr>
<td>4</td>
<td>-1</td>
<td>+1</td>
<td>+1</td>
</tr>
<tr>
<td>5</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>6</td>
<td>+1</td>
<td>-1</td>
<td>+1</td>
</tr>
<tr>
<td>7</td>
<td>+1</td>
<td>+1</td>
<td>-1</td>
</tr>
<tr>
<td>8</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
</tr>
</tbody>
</table>
(The levels of variables are coded: -1 is the low level, while +1 is the high).

Such designs are important for a number of reasons:

a) They require relatively few runs per factor studied; although they are unable to explore fully a wide region of factor space, they indicate major trends.

b) If more thorough exploration is required, they may be efficiently augmented to form composite designs.

c) The interpretation of the observations produced by the design can proceed largely by using common sense and elementary arithmetic.

Such designs enable one to estimate the main effects (the effect each individual variable has on the response) and the interactive effects (the dependence of the effect of one variable in the response, on the level of another). An excellent description of simple arithmetical analysis of factorial designs is given by Box, Hunter and Hunter 50.

Two level factorial designs however do not make possible the estimation of the quadratic effects of the variables. This effect (simply the response versus variable curvature) is generally important in complex systems. Thus, the analysis of the results of this research required to be more detailed than that allowed by the full two level factorial treatment alone. The factorial was augmented by a composite design. This design extended the experimental space by increasing and decreasing the highest and lowest variable levels respectively. Using the design with three variables, Table 6.2 shows the additional experimental design 51,52,53.

N.B. Coded values are used in these experimental designs for the following reasons; firstly, they give equal weighting to the independent variables, whose true levels differ widely in magnitude and units. Also, regression (especially if manual) and analysis of the yielded functions is made easier.
TABLE 6.2
Augmented 'star' design in 3 variables

<table>
<thead>
<tr>
<th>Experimental No</th>
<th>Variable 1(V1)</th>
<th>Variable 2(V2)</th>
<th>Variable 3(V3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>-1.68</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>+1.68</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
<td>-1.68</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>+1.68</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>0</td>
<td>0</td>
<td>-1.68</td>
</tr>
<tr>
<td>14</td>
<td>0</td>
<td>0</td>
<td>+1.68</td>
</tr>
</tbody>
</table>

This additional design uses the levels of variable set at ±1.68, calculated from:

\[ a = 2^{K/4} \]  \hspace{1cm} 6.(6)

where \( a = \) star point level, in this case = ±1.68
and \( K = \) number of experimental variables = 3 in the example.

The choice of the value of \( a \) from equation 6.(6) ensures rotatability; that is, the reliability of a predicted response will be constant at a constant distance from the centre of the design.

Note that the 'non-star' variables in each experimental run are set to 0, the centre of the factor space.

Finally, to augment the experimental area even further, all the variables are set at 0, the origin of the experimental space. By doing several replicate runs at levels of V1, V2 and V3 equal to 0, 0 and 0 it is possible from the \( n \) runs at these levels, to estimate experimental error, and thus how well the postulated model fits the data (see later).
6.6 Analysis of Data

The data accruing from an experimental design such as explained in the previous section, is analysed by multi-variate regression analysis (MVRA). The least squares method is described in Appendix 2, using the matrix approach. An exemplifying case study is also included.

Statistical computer programmes are available which take much of the tediousness out of the regression analysis calculations which become particularly formidable if multivariate regression analysis (MVRA) as required here, is used. The program used in this experimentation was GLIM (release 3), issued by the Royal Statistical Society, London and the Numerical Algorithms Group (NAG).

It is possibly pertinent at this point to note that thus far, an experimental design in several variables has been run, and for each combination of variable levels, responses (such as tensile strength etc. have been measured).
A THREE-FACTOR COMPOSITE DESIGN

FIGURE 6.2  Schematic representation of factor space
Appendix 3 describes the GLIM package, and its capabilities.

6.7 Judging the Adequacy of Estimation by an Approximating Response Function

Up to this stage, the experimental design has yielded observations of a response at certain levels of the process variables. This raw data has been analysed by MVRA to give estimates of the parameters of the postulated model. It is possible to obtain a model for any data subjected to MVRA, even 'nonsense' or random figures. It is important in our case to check on the adequacy of the fitted model, as follows.

The deviance referred to in Appendix 3 is the sum of squares of the residuals. This in turn is a measure of the departure of the model from a perfect fit. After all, if the model fitted each observation perfectly, then the deviance would be zero. However the total quantity known as deviance is made up of contributions from two sources. Firstly, pure error (a run to run variation) in the observations and secondly, lack of fit, caused by the nominated model.

This is where the replication at the centre points (Table 6.3) of the experimental design becomes so useful. Each of the response observations \(Y_n\) at the levels of variable 0,0, ... 0 is used in the following equation:

\[
V_c = \frac{\sum_{n=1}^{n-1} (Y_n - \bar{Y})^2}{SS_c} = \frac{SS_c}{d}
\]

where \(\bar{Y}\) is the mean value of the \(n\) observations at the centre point and \(n-1\) is the degrees of freedom. \(V_c\) is the variance due to pure error of the centre points. \(SS_c\) in equation 6.7 is an estimate of the sum of squares due to pure error of the centre points and by sub-
tracting $SS_c$ from the deviance of the model, the sum of squares of the residuals of the rest of the experimental points (the star and the factorial points) and the sum of squares due to lack of fit is obtained, $SS_r$. By dividing $SS_r$ by the balance of the degrees of freedom left in the model $m$, (original degrees of freedom $- d$) another estimate of variance is obtained ($V_r$).

If the model fits perfectly, $V_r/V_c$ will be close to unity, since all the residuals will be accounted for by run to run error. In fact, the ratio $F$ fluctuates around 1 due to random error. The larger the ratio, the more certain one can be that the model does not fit. An $F$ table entered at $m$ and $d$ degrees of freedom will tell how large the ratio has to be before it can be concluded that the model does not fit with any chosen degree of confidence. Thus, for example, for degrees of freedom 10 and 7 a ratio of 1.69 can be expected about 25% of the time, while a ratio of 6.62 can be expected only 1% of the time. If a ratio of 6.62 or greater was obtained, the chance of being correct, (when postulating that the model has inadequate fit) is 99%.

In such instances, other terms may have to be added to the model, or the data subjected to transformation or a different model tried to enable fit to be improved.

6.8 Presentation of Results (Experimental Section A)

Having obtained the polynomial equation and having established adequacy of fit, the next stage was to select a method of presentation, easily assimilable by the reader. There have been reviews of methods of presentation of multivariate data, but none of the methods seemed particularly suited to the present needs. Three possibilities were considered.

Firstly, the presentation of results in the form of simple two dimensional graphs of response versus one variable, holding the levels of the other independent variables constant. These 'held levels'
may be changed systematically to show the varying functional differences between the X and Y axis variables that accrue as a result. (See Figure 6.3). The method is however wasteful of time and space, if all the observed interactions between variables are to be noted.

For an exploration of the next two methods of presentation, the Butyl (IIR)/N660 black compounds used in a previous exercise by the present author will be considered. These arose from an experimental design of the type referred to before, a full factorial (16 runs), Star (8 runs) and centre point replicates (8 runs), using four variables of internal mixing as the independent variables. These were, mixing time, ram pressure, starting machine temperature and fill factor. At each of the total thirty two experimental runs, several responses were measured. They were unit work, dump temperature, Mooney viscosity, bound rubber, hardness, $M_{100}$ (stress at 100% strain) and in-phase compression dynamic modulus at a small fixed amplitude.

Table 6.4 gives the coded values of the independent variables of this study, and their equivalent real values.

**TABLE 6.4**

Relationship between the coded values and the real values of the independent variables

<table>
<thead>
<tr>
<th>Independent variable/Code level</th>
<th>-2</th>
<th>-1</th>
<th>0</th>
<th>+1</th>
<th>+2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing time (mins)</td>
<td>1.5</td>
<td>1.88</td>
<td>2.25</td>
<td>2.63</td>
<td>3.0</td>
</tr>
<tr>
<td>Starting temperature (°C)</td>
<td>25</td>
<td>31</td>
<td>37.5</td>
<td>44</td>
<td>50</td>
</tr>
<tr>
<td>Specific ram pressure (MPa)</td>
<td>0.28</td>
<td>0.42</td>
<td>0.57</td>
<td>0.71</td>
<td>0.85</td>
</tr>
<tr>
<td>Fill factor</td>
<td>0.4</td>
<td>0.5</td>
<td>0.6</td>
<td>0.7</td>
<td>0.8</td>
</tr>
</tbody>
</table>
FIGURE 6.3  *Simple two-dimensional representation*
Polynomial equations in terms of linear, quadratic and second order cross-product terms were derived from GLIM, and the adequacy of fit ratios calculated for each of the responses (10 and 7 degrees of freedom).

**TABLE 6.5**
F ratios (df 10, 7) for each response

<table>
<thead>
<tr>
<th>Dependent Variable</th>
<th>Variance Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit work</td>
<td>4.7x</td>
</tr>
<tr>
<td>Dump temperature</td>
<td>4.4x</td>
</tr>
<tr>
<td>Mooney viscosity</td>
<td>5.4+</td>
</tr>
<tr>
<td>Bound rubber</td>
<td>2.8*</td>
</tr>
<tr>
<td>Hardness</td>
<td>3.6*</td>
</tr>
<tr>
<td>Modulus at 100% extension</td>
<td>2.3*</td>
</tr>
<tr>
<td>In-phase dynamic modulus (peak at 15 Hz)</td>
<td>3.8x</td>
</tr>
</tbody>
</table>

* Significant at a level of > 5%
+ Significant at a level between 1 and 2.5%
* Significant at a level between 2.5 and 5%

Despite these values being not as close to unity as would be hoped, it was decided to use the resulting polynomials to show how mixing conditions affect individual responses.

Five variables in all are present, totalling the independent and the dependent variables. Computer programmes for the two methods of visual presentation explored were already available\(^59\). (Appendix 4, Appendix 5).
The first, made use of the method of computer graph plotting by contour diagrams. Such graphs depict lines of equal response versus two independent (the axial) variables. Thus for any contour plot the effects of two variables on response could be drawn. A matrix of nine of these graphs could be assembled on a single page, through which the other two (non-axial) independent variables could be changed at three levels of each. For example, if fill factor and starting temperature were the axial variables, the non-axial ones (specific ram pressure and mixing time) could be varied as in Table 6.7, each number representing a graph of the contours of response versus the axial variables, at various levels of the non-axial variables.

**TABLE 6.7**

The Visualisation matrix

<table>
<thead>
<tr>
<th>Specific ram pressure</th>
<th>LOW</th>
<th>MEDIUM</th>
<th>HIGH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Medium</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>High</td>
<td>7</td>
<td>8</td>
<td>9</td>
</tr>
</tbody>
</table>

Looking across the top row, one could note the effects of changing ram pressure at short mixing times, or medium or long mixing times for the middle and bottom row; similarly for mixing time at various constant ram pressures by looking down the columns of the matrix.

Isometric projections could be used in an identical manner to the above. (An isometric projection is an orthogonal projection of a surface in which the coordinate axes make equal angles of \( \tan^{-1}\sqrt{2} \) with the line of sight). In this case therefore the graph could have three axes, the z axis showing change in response with varying levels of independent variable (the x and y axes), where it is possible to fix one axial independent variable and observe the effect on the response of changing the other axial variable, and then examine the
interactions between them. As with the contour depiction, a 3 x 3 matrix of these graphs would show the effects of changing non-axial independent variables.

6.9 Results and Discussion of Experimental Section A

Figure 6.5 shows a series of isometric projections for the response unit work, while the contour graphs (Figures 6.4 and 6.6 - 6.11) for the seven responses measured are all included. The non-axial variables are specified in the nine partition box in the top left hand corner of each figure. The variables and the response studied are labelled at the bottom left hand corner.

(Axial variables are chosen by scrutiny of the MVRA coefficients. The largest interaction coefficient is caused by the two variables together having the greatest effect on the relevant response, and these two are chosen as the axial variables).

For ease of interpretation one may divide the measured responses into two categories, dump criteria (Figures 6.4 - 6.6) and process/vulcanisate tests (Figures 6.7 - 6.11).

6.9.1 Dump criteria

Figures 6.4 and 6.5 show the expected increase in unit work with increase in ram pressure, increase in fill factor at greater than 0 level of fill factor and ram pressure respectively, and also with lengthening of mixing time. Also clearly shown is the increase in unit work content with increasing starting temperatures. This may be due to the incorporation stage occurring quicker due to the reduced viscosity at higher temperatures, and consequently causing a longer period of dispersive mixing at constant mixing time.

A tendency for a fall in unit work with increasing fill factor, at low levels of ram pressure is noted. A partially 'stagnant' area is likely to occur in the mixer throat, by the pushing
FIGURE 6.4  Contour representation: unit work
FIGURE 6.5
Isometric projections - unit work

[Diagram showing isometric projections with unit work indicated.]
FIGURE 6.6 Contour representation - dump temperature
FIGURE 6.7 Contour representation - Mooney Viscosity
FIGURE 6.8  Contour representation - bound rubber
FIGURE 6.9  Contour representation - hardness
FIGURE 6.10 Contour representation - $M_{100}$
FIGURE 6.11 Contour representation - G' @ 15 Hz and 1% SSA
up of the ram by the batch; the proportion of material undergoing effective mixing progressively becoming smaller or even remaining the same with increasing degree of fill.

In Figure 6.6, increasing fill factor appears to be the main factor affecting dump temperature, which increases with increasing fill factor; the rate of change appearing to be largely independent of mixing time. At all but the very highest levels of fill factor, dump temperature increases with increasing mixing time between 1.5 and 3.0 mins. This agrees with work carried out elsewhere\(^{27}\). At these high levels of fill, increasing time of mixing appears to have very little or no effect on dump temperature. Graphs 3 and 7 of Figure 6.6 however, show contrary dump temperature trends with increase in mixing time. Graph 3 shows an increased dump temperature, probably caused by the high levels of power input at the particular combination of the nonaxial variables. In graph 7 there is a dump temperature increase with increasing mixing time. Overall temperature here is higher than in graph 3 (about \(110^\circ C\) as compared with \(95^0 C\)). This observation cannot be explained at present and perhaps, a detailed study of the dynamic energy balance during mixing is necessary to clarify this.

The expected relationship between starting temperature and dump temperature is also depicted in Figure 6.6, both increasing together, illustrating clearly the dependence of the temperature dump criterion on initial mixer temperatures.

6.9.2 Processing/vulcanisate properties

As mentioned before in Chapter 3, several of the above properties are used as measures of the efficiency of mixing. They do this indirectly and are therefore called 'proxy variables'. By equating their known responses to mixing (as discussed in Chapter 3) it will be possible to indicate whether the process variables at the various levels in the contour and isometric presentations affect mixing; for
the better, for the worse, or not at all.

Considering Figures 6.7 - 6.9 together we note the following features:

In all cases, increasing fill factor at low starting temperatures causes increased mixing efficiency, i.e. decreasing hardness and Mooney viscosity, and increasing percentage of bound rubber. Considering Figures 6.10 and 6.11 we note a drop in $E'$ and $M_{100}$ with increasing fill factor, signifying an improvement in dispersion, according to the references reviewed in Chapter 3.

At high starting temperatures, the result of increasing fill factor is not as consistent as the previous observation. Hardness increases (Figure 6.9), Mooney viscosity, $M_{100}$ and $E'_m$ either increase or stay constant (Figures 6.7, 6.10 and 6.11) and bound rubber falls (Figure 6.8). It would be reasonable though, by the established criteria, to conclude that high starting temperatures would be deleterious or at best non-conducive to improving mixing efficiency. This supposition is reinforced by observations at high (constant) fill factor levels and increasing starting temperature, where all the proxy variables point to decreasing mixing efficiency.

Next, considering the effect of increasing starting temperature at low (constant) fill factors, a surprising reversal is noted. In this instance all the proxy variables indicate increasing mixing efficiency with increasing starting temperature.

In the previous case of high fill factors and high starting temperatures, temperature rise is rapid, resulting in lowering of polymer viscosity and stresses within the mixing chamber. Mixing is therefore less intensive than at low starting temperatures. At low fill factor however, low shear stresses are present in the chamber. Incorporation (which is accompanied by folding over of the polymer on clumps of filler) is difficult under these circumstances. As temperature increases, incorporation takes place quicker, and then more time is available (under constant mix time regime) for dispersive mixing to take place, bearing in mind that less heat...
build up within the chamber will occur than in the high fill factor instance.

The effect of changing ram pressure is also very dependent on the levels of the other variables. At the most effective conditions of mixing (high fill factor, low starting temperature) increasing ram pressure appears to have little effect on Mooney viscosity and hardness. $E'_m$ increases slowly with increasing specific ram pressure. The analysis of the other two is more complex, bound rubber increasing as ram pressure is increased at the low and medium mixing times, but appears to drop with increasing pressure at high mixing times. M100 decreases with increasing ram pressure at the low and medium mixing times, but rises with increasing pressure at the high mix times. These findings may indicate that ram pressures greater than 0.57 MPa may well be unnecessary if other conditions are favourable. Indeed, very high ram pressures (0.85 MPa) may cause restrictions of flow in the mixing chamber, leading to insufficient randomisation and mixing.

The effects of combining high fill factors and high starting temperatures and then increasing ram pressures are almost identical to the foregoing, the only change being a consistent drop in bound rubber, whatever the mixing cycle length.

The effect of increasing mixing time in all cases is to increasing mixing efficiency, at high fill factor, low starting temperature and medium ram pressures. High ram pressures cause $E'_m$, bound rubber, hardness and M100 to change in directions contrary to mixing efficiency, but not Mooney viscosity, which continues to fall, with increasing ram pressure.

It must be pointed out that many of the graphs presented here are wholly outside the region of the data, which is specified by $\sqrt{4}$ in this design. (This will be explained more fully in 6.13.3). For instance the corner plots in Figures 6.4 - 6.11 are at levels at non-axial variable ±2, ±2. Even with the axial variables at 0, this gives rise to space far greater than $\sqrt{4}$ being explored.
These plots may be used as a guide to the trends of the process, but individual predictions from such plots outside experimental space must be tempered with caution.

6.10 Conclusions on Experimental Section A

Taking all the responses indicative of mixing efficiency, together, it is possible to delineate an operating window, for the compound and the mixing technique used here. The BR Banbury variable settings under which mixing appears to be most satisfactory, are as follows; the operating window will surround these unique values of variable.

- Medium high fill factor = 0.7
- Low starting temperature = 30°C
- Medium ram pressures (specific) = 0.5 MPa
- and mixing time = 2.5 mins

At these levels the properties used as mixing indicators appear to be at their best levels. Also, within the window changes in property level (if any) are taking place very slowly indeed; so that a small variation (either positive or negative) in the mixing variables by accident or design, will not affect the mixed material properties critically.

Moving away from quantitative conclusions, the foregoing has demonstrated the effective use of specialised graphing techniques to map a multivariable system. The main effects and the interactions between the variables of the experiment are made manifestly evident by use of such techniques; their utilisation allows the non-mathematician (as most technologists are) to appreciate the techniques used here, without recourse to the common interpretation methods of response surface methodology (RSM), such as canonical analysis\textsuperscript{50}. 
For further work here, a choice of the best visualisation method was made. It was decided to use the contour graphing techniques in preference to the isometric projections. This was done since the former are more conducive to inter-graph comparison. An unfortunate effect of the computer package used to draw the projection was that it scaled its Z axis to the maximum/minimum values of each individual graph, and not for the maximum/minimum values of the response as a whole. Consequently, the Z axis changes from graph to graph within any one response, making the assessment of the effects and interactions due to the non-axial variables very difficult indeed.

6.11 Experimental Section B

6.11.1 Introduction

Several valuable lessons had been learnt during the exploratory stages of the application of statistical experimental design to the mixing of rubbers. The present authors preliminary work\(^{11}\) represented the first analysis of the rubber mixing operation by this method. This technique has since been used by Williamson\(^{60}\), Basir and Freakley\(^{61,63}\) and Freakley\(^{62}\) to explain both the mixing process for selected polymer systems and also to trace rheological changes during mixing. The original use of RSM in the mixing of plastics is credited to Meyuhas\(^{65}\), and Meyuhas and Tadmor\(^{64}\), which was followed by the research by Fernando\(^{66}\) into mixing of polyethylene and carbon black systems.

It is notable that most of the documented work emphasises mixed stock properties resulting from variable settings on the Banbury mixer. No doubt this is important, but more vital is the exploration of the total mixing process in terms of its variables. Seldom are polymer processors interested in establishing what conditions are required to produce, say, a specific tensile strength, or viscosity level. Instead, their priority is that the overall conditions for good mixing are achieved. What is required is a function that relates
to the mixing process as a whole, taking into account all the properties of concern to the producer and user.

6.11.2 The Desirability Function

This function was developed to provide a mathematical solution for the following problem: to provide a means of combining several responses obtained from experimentation, into a single index. From this index, the efficacy of each experimental treatment could be simply judged, and the most suitable one identified.

In rubbers, the quality of a mix is seldom defined (as discussed above), by a single quantity. Rather, quality is a composite of a family of properties, which are often interrelated; each of varying importance, and measured in a variety of units. It has been shown by experience that there is no simple procedure for combining several properties into a single quantitative measure of overall quality. In the desirability function this combination is effected by the transformation of the measured properties to the desirability scale (d).
TABLE 6.6
The desirability scale

<table>
<thead>
<tr>
<th>Scale of $d$</th>
<th>Quality equivalents of the scale of $d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>Represents the ultimate in quality, the improvement beyond which would have no appreciable value</td>
</tr>
<tr>
<td>0.99 - 0.8</td>
<td>Acceptable and excellent. Represents unusual quality, well beyond anything commercially available</td>
</tr>
<tr>
<td>0.79 - 0.64</td>
<td>Acceptable and good. Represents an improvement over the best commercial quality</td>
</tr>
<tr>
<td>0.63</td>
<td>Best commercial quality</td>
</tr>
<tr>
<td>0.62 - 0.4</td>
<td>Acceptable but poor. Quality is acceptable to the commercial limits; improvement is desired</td>
</tr>
<tr>
<td>0.39 - 0.3</td>
<td>Borderline. Some of the products will be outside specifications</td>
</tr>
<tr>
<td>0.29 - 0.01</td>
<td>Unacceptable</td>
</tr>
<tr>
<td>0.00</td>
<td>Completely unacceptable</td>
</tr>
</tbody>
</table>

The scale of $d$, so developed, is a dimensionless scale to which any property may be transformed, such that it may be interpreted in terms of utility or desirability for any specific application.

For rubber properties allied to efficiency of mixing, a special form of the Gompertz growth curve is applicable. Figure 6.12 represents the curve of $d$ vs tensile strength.
Thus, if good tensile (all other factors being constant) is equated with good mixing the best mixing is at $d = 1.0$. The same scale holds for properties like Mooney viscosity, except that the $Y$ axis is reversed. That is, the highest Mooney represents the worst mix and vice versa. (Note these relationships have been established in Chapter 3).

The first step in the process is a judgement step, backed by experience. For any one response, values of $d$ are allocated to two values from the series: scaled values ($Y'$) of the actual response values ($Y$) are then obtained by transforming the $d$ values, using the following equation.

$$ Y' = -[\ln (-\ln d)] $$ 6.8

From these paired values of $Y$, and $Y'$, the constants of the linear transformation equation of the form

\begin{figure}
\centering
\includegraphics[width=\textwidth]{d_scale.png}
\caption{$d$ scale for one sided specification}
\end{figure}
is obtained, by solution of the simultaneous equations. This results in ascribing values to $b_0$ and $b_1$:

Using these values in 6.(9), each value of the specific response under consideration is transformable to its corresponding $Y'$. Figure 6.12 is a plot of $d$ vs $Y'$ which takes the form

$$d = e^{-e^{-Y'}}$$

Now using the calculated $Y'$ values for each experimental run, $d$ is calculated using 6.(10). If the process is repeated for each response measured a matrix of $d$'s will result, the columns being the $d$ values for each experimental run of the same response; the rows will be the $d$'s of differing responses for identical experimental treatment combinations.

The overall effect of each of the experimental variable combinations is obtained by multiplying the $d$ values of each row together, and then solving for their geometric mean:

$$D = \sqrt[n]{d_1 d_2 d_3 \ldots \ldots d_n}$$

The basic premise is this: if any one property is so poor that the product is not suitable to the application, the product will not be acceptable, regardless of the level of the other properties. A flow diagram for a computer programme that accomplishes these steps (specified later) is to be found in Appendix 9.

The $D$ in 6.(11) which is a measure of overall quality is completely analogous to any other measure of quality. Thus, it is ame-
nable to mathematical and statistical analysis, optimisation by response surface methods and so on, as if it were a measure of a single property.

6.11.3 The experimental strategy

Having explored a method for unifying the responses measured in an experiment, and also now having decided on the method for presentation of the forthcoming results, a full scale new experiment was initiated. This involved the following discrete stages.

1. The selection of a compound representative of the most common group of compounds mixed in the rubber industry.

2. The selection of a suitable experimental design, through which, the mixing variables could be altered systematically, and a batch of rubber compound mixed under each of these treatment combinations.

3. Several responses were to be measured on each batch thus produced.

4. These responses were to be combined into the overall desirability function, thus indicating the combination effects of each of the experimental treatment combinations.

5. The quantity D in the above, was then subjected to MVRA, and the coefficients of the proposed model thus evaluated.

6. The adequacy of fit of the regression equation was to be assessed by the technique referred to earlier.

7. In addition two responses noted for each batch during the experimental mixing, mixing time and dump temperature were to be modelled and assessed for fit as in (5) and (6) above. (Note the dump criterion used in this series of experiments was to be mixing energy).
8. The entire mixing process, in terms of the desirability function was to be depicted in the form of contour graphs; the individual responses mixing time and dump temperature were also to be depicted.

Details of the above experimental strategy now follow.

6.12 Experimental Work

The following compound was selected as being representative of a general purpose stock mixed commonly in the rubber industry.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>pphr</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR 1712</td>
<td>137.5</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>6.0</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>4.0</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>1.0</td>
</tr>
<tr>
<td>Di-cyclo benzthiazyl sulphenamide</td>
<td>0.6</td>
</tr>
<tr>
<td>Sulphur</td>
<td>4.0</td>
</tr>
<tr>
<td>Carbon black (N375)</td>
<td>40.0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>193.1</strong></td>
</tr>
</tbody>
</table>

The machine selected for mixing the rubber stocks was the OOC model Banbury sited at Farrel Bridge Ltd, Rochdale. The capacity of this machine was 2.85L, and it was equipped with integrating power meter, water tempering unit, and infinitely variable rotor speeds. Also, a stop clock for measuring cycle time; batch temperature, and water inlet and outlet temperature recorders. Coolant throughput was approximately 34 litres per minute.
6.12.1 The experimental design

In all, five machine variables were to be changed systematically. These were unit volume work of mixing (UW), starting temperature (ST) of machine, rotor speed (RS), ram pressure (RP) and fill factor (FF). These were combined into a full factorial experimental design at two levels (32 runs at $2^5$), and this was augmented with the star points and centre point replicates. In the previously referred to design it was found that the star points sometimes produced unreliable values, which tended to influence the regression curve very strongly. To make the observations more reliable at these points of experimental space, it was resolved to augment the star points, by duplication of each of the 'star runs'. Ten centre point replicates were used. An abbreviated experimental matrix is shown in Table 6.7.

Again, the coded extreme values of the variables work out to ±a = 2 since the value for a central composite design with full factorial, duplication at axial points and 10 replicates at the centre is given by

$$a = 2^{[(k-1)/4]}$$  \hspace{1cm} 6.12

and for number of variables = k = 5, a = 2.

Table 6.8 gives the relationships between the absolute and coded values of the variables of mixing.
### TABLE 6.7
Abbreviated experimental matrix

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>ST</th>
<th>RP</th>
<th>FF</th>
<th>RS</th>
<th>UW</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>2</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
</tr>
<tr>
<td>3</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
<td>-1</td>
</tr>
<tr>
<td>...</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
</tr>
<tr>
<td>33</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>34</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>...</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>+2</td>
</tr>
<tr>
<td>52</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>+2</td>
</tr>
<tr>
<td>...</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>...</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>62</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
TABLE 6.8
Coded and absolute values of variables

<table>
<thead>
<tr>
<th>Independent Variable</th>
<th>-2</th>
<th>-1</th>
<th>0</th>
<th>+1</th>
<th>+2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting temperature (°C)</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td>50</td>
<td>60</td>
</tr>
<tr>
<td>Specific ram pressure (MPa)</td>
<td>0.14</td>
<td>0.22</td>
<td>0.31</td>
<td>0.40</td>
<td>0.48</td>
</tr>
<tr>
<td>Fill factor</td>
<td>0.5</td>
<td>0.6</td>
<td>0.7</td>
<td>0.8</td>
<td>0.9</td>
</tr>
<tr>
<td>Rotor speed (rpm)</td>
<td>30</td>
<td>45</td>
<td>60</td>
<td>75</td>
<td>90</td>
</tr>
<tr>
<td>Unit work (MJ/m³)</td>
<td>300</td>
<td>600</td>
<td>900</td>
<td>1200</td>
<td>1500</td>
</tr>
</tbody>
</table>

The upper and lower levels of each variable were established such that the risk of crumbling at insufficient levels of mixing or scorch at severe levels of mixing was just averted.

The relation between specific ram pressure on the batch and line air pressure is shown in Appendix 6. Specific formulations of the rubber stock for fill factor level -2 to +2 are shown in Appendix 7.

The order of experimental runs was not done in the experimental order of Table 6.7. Instead, a random number generator was used to determine the order of experimentation. This precaution, eliminates unsuspected sources of disturbance affecting the comparisons in a systematic way and ensures that each run is effectively independent of the previous one.

6.12.2 Mixing procedure and testing of the compounds

a) Identify weighed up ingredients for each experimental run. The rubber was cut into standard sized pieces of about 7 cm in cubic dimensions.

b) Random checks of viscosity on various samples of the rubber were carried out to check in batch variability.
c) Select the run corresponding to random number 1 of the experimental sheet.

d) Set starting temperature, and switch coolant pump on. Allow an equilibration time of 15 minutes.

e) Bring ram down onto empty chamber and set the required air line pressure to generate the specific pressure wanted. Allow 2 minutes for equilibration and recheck gauge.

f) Raise ram.

g) Ensure machine is clean, and no tajlings prevent drop door from shutting flush.

h) Start machine.

i) Set rotor speed to about 20 rpm more than required.

j) Switch on recorders.

k) Check that timer and power integrator read zero.

l) Close door.

m) Final check on ram pressures, starting temperature and rotor speed.

n) Introduce powders and rubber (upside-down method).

o) Ram down.

p) Start timer; power integrator starts automatically.

q) Check rotor speed: on load, the speed falls, thus the speed excess of 20 rpm set with the machine running free must now approximately equal the desired level of speed. Make fine adjustments quickly.
r) At prescribed energy level (calculated from required unit work level and fill factor for the specific experimental run), dump batch.

s) Note time of mixing, dump temperature.

t) Check batch weight.

u) Clean Banbury with air line, ready for next batch.

v) Sheet batch by passing through sheeting mill at 3.5 rpm and 6 mm nip.

w) Identify mixed batch and store for two weeks.

x) Curemeter by Monsanto ODR at 170°C to obtain cure time (90%), maximum and minimum torque.

y) Measure Mooney viscosity for each batch.

z) Cure sheets/samples for time to 90% crosslinking in hydraulic press and quench samples on removal from moulds to prevent further vulcanisation taking place.

After a conditioning time of 72 hours, test samples were cut from the sheets and tensile strength, elongation at break, modulus at 100% strain, hardness, tear energy and tear strength tests were carried out as described in Chapter 4. In addition, abrasion testing on the DIN tester sited at Dunlop Ltd. Technology Division was accomplished.

This test uses standard preweighed test pieces rotated against an abrasive roller moving at a specified speed. The sample is held under a standard force. After a length of 40m has been traversed by the specimen on the abradant roller, it is removed and weighed. The weight loss was computed. (Note - the standard recommends volume loss as the parameter for determining abrasion resistance. This was not observed).
The results sheet, showing the measured property levels for each of the 62 experimental runs is tabulated in Appendix 8.

6.12.3 Assigning values of the Desirability Function to each of the experimental runs

This segment of the work was accomplished by using a computer programme written in Basic. The flow chart, and a printout of the programme is presented in Appendix 9 and 10. The programme was interactive, questions being asked constantly as well as checks being effected on the input data. An example of the printout for one response is shown in Appendix 11.

Two points are to be made here: first, that even though the option of weighting the d's calculated from the individual responses was included in the programme, it was not used here. Thus, each measured response was assumed to bear equal importance as an indicator of mixing efficiency. This assumption was made by reasoning that several response types has been used; processing, strength, stiffness and wear properties had been evaluated, in approximately equal numbers of tests per category. Secondly, since the values of D referred to previously were small (less than 1), the values were multiplied by 1000 to eliminate the decimal point. Thus, at a very high level of mixing D = 1000, while at predicted bad mixing conditions D = 0.

Values of the desirability function thus calculated, for each of the 62 experimental runs are presented in Appendix 12.

6.13 Results and Discussion

6.13.1 The regression of D, mixing time and dump temperature

Using GLIM as described before, MVRA was applied to the results thus far obtained. The model postulated in all three cases, was a general polynomial in the five variables of mixing, which included
five mean, five quadratic, ten second order and ten third order
terms. Assigning names to the five variables of mixing as follows:

Starting temperature = T
Ram pressure = P
Fill factor = F
Rotor speed = S
Unit work = U

Tables 6.9 - 6.11 gives the values of the coefficients of
the regression equation, in terms of the dependent variables D,
mixing time and dump temperature respectively. Also, tabulated
are the corresponding standard errors (Note TT, PP etc are the
quadratic terms of starting temperature and ram pressure respec-
tively. Similarly, TP, TF, TPF, etc. are the second order and third
order cross product terms of the main variables). Also the devia-
nces of each model, and the relevant degrees of freedom are given in
the tables. % GM is the grand mean, or zero order term.

6.13.2 Adequacy of fit of the three fitted models

Adequacy of fit was determined for all three models as descripted in 6.7, with one important modification.

An additional estimate of the sum of squares due to pure error

is available from the duplicated star points of the design used here. Thus, by adding the sum of squares calculated from the centre points and the above experimental points, a total sum of squares assigned to pure error variation is obtainable. This will have a total of 19 degrees of freedom (comprising 9 df from centre point values and 1 each df from each of the duplicated values at the star points of the design).

Subtraction of this combined error sum of squares from the
total model deviance leaves a sum of squares with (31-19 =)12 degrees
TABLE 6.9
Coefficients of fitted model and standard errors for response — desirability function

Deviance = 0.2530E 06 DF = 31

<table>
<thead>
<tr>
<th>Estimate</th>
<th>S.E.</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1  702.4</td>
<td>27.78</td>
<td>%GM</td>
</tr>
<tr>
<td>2  0.2104E-01</td>
<td>13.04</td>
<td>T</td>
</tr>
<tr>
<td>3  10.04</td>
<td>13.04</td>
<td>P</td>
</tr>
<tr>
<td>4 -17.46</td>
<td>13.04</td>
<td>F</td>
</tr>
<tr>
<td>5 -33.86</td>
<td>13.04</td>
<td>S</td>
</tr>
<tr>
<td>6  177.1</td>
<td>13.04</td>
<td>U</td>
</tr>
<tr>
<td>7  -6.003</td>
<td>12.03</td>
<td>TT</td>
</tr>
<tr>
<td>8  -38.26</td>
<td>12.03</td>
<td>PP</td>
</tr>
<tr>
<td>9  2.652</td>
<td>12.03</td>
<td>FF</td>
</tr>
<tr>
<td>10 -2.472</td>
<td>12.03</td>
<td>SS</td>
</tr>
<tr>
<td>11 -51.69</td>
<td>12.03</td>
<td>UU</td>
</tr>
<tr>
<td>12 -22.32</td>
<td>15.97</td>
<td>TP</td>
</tr>
<tr>
<td>13  31.89</td>
<td>15.97</td>
<td>TF</td>
</tr>
<tr>
<td>14  6.576</td>
<td>15.97</td>
<td>TS</td>
</tr>
<tr>
<td>15 -3.913</td>
<td>15.97</td>
<td>TU</td>
</tr>
<tr>
<td>16 -23.66</td>
<td>15.97</td>
<td>PF</td>
</tr>
<tr>
<td>17 -9.707</td>
<td>15.97</td>
<td>PS</td>
</tr>
<tr>
<td>18  5.188</td>
<td>15.97</td>
<td>PU</td>
</tr>
<tr>
<td>19 -24.42</td>
<td>15.97</td>
<td>FS</td>
</tr>
<tr>
<td>20  50.43</td>
<td>15.97</td>
<td>FU</td>
</tr>
<tr>
<td>21  2.738</td>
<td>15.97</td>
<td>SU</td>
</tr>
<tr>
<td>22  5.506</td>
<td>15.97</td>
<td>TPF</td>
</tr>
<tr>
<td>23 -13.90</td>
<td>15.97</td>
<td>TPS</td>
</tr>
<tr>
<td>24  8.776</td>
<td>15.97</td>
<td>TPU</td>
</tr>
<tr>
<td>25  0.2934</td>
<td>15.97</td>
<td>PFS</td>
</tr>
<tr>
<td>26  37.30</td>
<td>15.97</td>
<td>PFU</td>
</tr>
<tr>
<td>27  22.71</td>
<td>15.97</td>
<td>FSU</td>
</tr>
<tr>
<td>28 -33.06</td>
<td>15.97</td>
<td>TFS</td>
</tr>
<tr>
<td>29  8.338</td>
<td>15.97</td>
<td>TFU</td>
</tr>
<tr>
<td>30  9.717</td>
<td>15.97</td>
<td>TSU</td>
</tr>
<tr>
<td>31  47.57</td>
<td>15.97</td>
<td>PSU</td>
</tr>
<tr>
<td>Estimate</td>
<td>S.E.</td>
<td>Parameter</td>
</tr>
<tr>
<td>----------</td>
<td>------</td>
<td>-----------</td>
</tr>
<tr>
<td>1 218.4</td>
<td>3.761</td>
<td>%GM</td>
</tr>
<tr>
<td>2 4.564</td>
<td>1.765</td>
<td>T</td>
</tr>
<tr>
<td>3 -7.469</td>
<td>1.765</td>
<td>P</td>
</tr>
<tr>
<td>4 -9.678</td>
<td>1.765</td>
<td>F</td>
</tr>
<tr>
<td>5 -63.18</td>
<td>1.765</td>
<td>S</td>
</tr>
<tr>
<td>6 69.16</td>
<td>1.765</td>
<td>U</td>
</tr>
<tr>
<td>7 -0.2688</td>
<td>1.629</td>
<td>TT</td>
</tr>
<tr>
<td>8 1.874</td>
<td>1.629</td>
<td>PP</td>
</tr>
<tr>
<td>9 4.372</td>
<td>1.629</td>
<td>FF</td>
</tr>
<tr>
<td>10 18.17</td>
<td>1.629</td>
<td>SS</td>
</tr>
<tr>
<td>11 1.299</td>
<td>1.629</td>
<td>UU</td>
</tr>
<tr>
<td>12 -1.382</td>
<td>2.162</td>
<td>TP</td>
</tr>
<tr>
<td>13 -0.7375E-01</td>
<td>2.162</td>
<td>TF</td>
</tr>
<tr>
<td>14 -2.421</td>
<td>2.162</td>
<td>TS</td>
</tr>
<tr>
<td>15 -1.400</td>
<td>2.162</td>
<td>TU</td>
</tr>
<tr>
<td>16 -1.588</td>
<td>2.162</td>
<td>PF</td>
</tr>
<tr>
<td>17 2.309</td>
<td>2.162</td>
<td>PS</td>
</tr>
<tr>
<td>18 -3.874</td>
<td>2.162</td>
<td>PU</td>
</tr>
<tr>
<td>19 6.418</td>
<td>2.162</td>
<td>FS</td>
</tr>
<tr>
<td>20 1.293</td>
<td>2.162</td>
<td>FU</td>
</tr>
<tr>
<td>21 -22.48</td>
<td>2.162</td>
<td>SU</td>
</tr>
<tr>
<td>22 0.4625</td>
<td>2.162</td>
<td>TPF</td>
</tr>
<tr>
<td>23 0.3762</td>
<td>2.162</td>
<td>TPS</td>
</tr>
<tr>
<td>24 -2.014</td>
<td>2.162</td>
<td>TPU</td>
</tr>
<tr>
<td>25 -0.3831</td>
<td>2.162</td>
<td>PFS</td>
</tr>
<tr>
<td>26 2.038</td>
<td>2.162</td>
<td>PFU</td>
</tr>
<tr>
<td>27 -1.323</td>
<td>2.162</td>
<td>FSU</td>
</tr>
<tr>
<td>28 1.814</td>
<td>2.162</td>
<td>TFS</td>
</tr>
<tr>
<td>29 2.725</td>
<td>2.162</td>
<td>TFU</td>
</tr>
<tr>
<td>30 0.6500E-01</td>
<td>2.162</td>
<td>TSU</td>
</tr>
<tr>
<td>31 3.628</td>
<td>2.162</td>
<td>PSU</td>
</tr>
</tbody>
</table>
TABLE 6.11
Coefficients of filled model and standard errors for response -
dump temperatures
Deviance = 290.2     DF = 31

<table>
<thead>
<tr>
<th>Estimate</th>
<th>S.E.</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 120.6</td>
<td>0.9410</td>
<td>%GM</td>
</tr>
<tr>
<td>2 4.021</td>
<td>0.4416</td>
<td>T</td>
</tr>
<tr>
<td>3 1.021</td>
<td>0.4416</td>
<td>P</td>
</tr>
<tr>
<td>4 14.52</td>
<td>0.4416</td>
<td>F</td>
</tr>
<tr>
<td>5 9.104</td>
<td>0.4416</td>
<td>S</td>
</tr>
<tr>
<td>6 6.896</td>
<td>0.4416</td>
<td>U</td>
</tr>
<tr>
<td>7 0.5481</td>
<td>0.4075</td>
<td>TT</td>
</tr>
<tr>
<td>8 0.5481</td>
<td>0.4075</td>
<td>PP</td>
</tr>
<tr>
<td>9 3.798</td>
<td>0.4075</td>
<td>FF</td>
</tr>
<tr>
<td>10 -0.2019</td>
<td>0.4075</td>
<td>SS</td>
</tr>
<tr>
<td>11 -3.014</td>
<td>0.4075</td>
<td>UU</td>
</tr>
<tr>
<td>12 0.2812</td>
<td>0.5408</td>
<td>TP</td>
</tr>
<tr>
<td>13 -0.5938</td>
<td>0.5408</td>
<td>TF</td>
</tr>
<tr>
<td>14 -0.2188</td>
<td>0.5408</td>
<td>TS</td>
</tr>
<tr>
<td>15 0.2812</td>
<td>0.5408</td>
<td>TU</td>
</tr>
<tr>
<td>16 1.531</td>
<td>0.5408</td>
<td>PF</td>
</tr>
<tr>
<td>17 0.3125E-01</td>
<td>0.5408</td>
<td>PS</td>
</tr>
<tr>
<td>18 -1.219</td>
<td>0.5408</td>
<td>PU</td>
</tr>
<tr>
<td>19 1.281</td>
<td>0.5408</td>
<td>FS</td>
</tr>
<tr>
<td>20 2.406</td>
<td>0.5408</td>
<td>(FU</td>
</tr>
<tr>
<td>21 2.531</td>
<td>0.5408</td>
<td>SU</td>
</tr>
<tr>
<td>22 0.3437</td>
<td>0.5408</td>
<td>TPF</td>
</tr>
<tr>
<td>23 -0.3125E-01</td>
<td>0.5408</td>
<td>TPS</td>
</tr>
<tr>
<td>24 -0.3125E-01</td>
<td>0.5408</td>
<td>TPU</td>
</tr>
<tr>
<td>25 0.4687</td>
<td>0.5408</td>
<td>PFS</td>
</tr>
<tr>
<td>26 -0.6563</td>
<td>0.5408</td>
<td>PFU</td>
</tr>
<tr>
<td>27 1.219</td>
<td>0.5408</td>
<td>FSU</td>
</tr>
<tr>
<td>28 0.2187</td>
<td>0.5408</td>
<td>TFU</td>
</tr>
<tr>
<td>29 0.9375E-01</td>
<td>0.5408</td>
<td>TSU</td>
</tr>
<tr>
<td>30 0.3437</td>
<td>0.5408</td>
<td>PSU</td>
</tr>
</tbody>
</table>
of freedom; by obtaining two estimates of variance as described before, and calculating \( \frac{V_r}{V_{c+s}} \) a variance ratio results.

This is compared with the critical value in an F table, entering at 12 and 19 degrees of freedom.

Table 6.12 gives the values of F ratio obtained from the three postulated models.

**TABLE 6.12**

<table>
<thead>
<tr>
<th>Response</th>
<th>F Ratio</th>
<th>Degrees of Freedom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desirability function</td>
<td>0.95</td>
<td>12,19</td>
</tr>
<tr>
<td>Mixing time</td>
<td>2.51</td>
<td>12,19</td>
</tr>
<tr>
<td>Dump temperature</td>
<td>7.34</td>
<td>12,19</td>
</tr>
</tbody>
</table>

The ratio obtained for the desirability function is very close to unity and thus the sum of squares due to lack of fit is insignificant. In the case of the mixing time model, the F ratio is significant at a level between 2.5 and 5%, while the dump temperature model is somewhat less than satisfactory as shown by the high variance ratio.

6.13.3 The influence of the variables of mixing on the responses

The desirability function was derived from a host of properties on which mixing has established effects. Thus, the desirability function could be equated to a criterion of overall mixing efficiency. The model has been shown to fit adequately, and thus presentation of the results of the modelling (in the form of the contour graphs)
will indicate how the process variables influence mixing efficiency as a whole.

The following contour graphs (composite Figures 6.13 - 6.15) present the results as seen in the earlier section, using specified non-axial and axial variables in a 3 x 3 matrix. The effects of the fifth variable are studied by considering 3 such 3 x 3 matrices where the variable in question is changed three times; by looking 'through the pages' one is able to identify the effect of this extra non-axial variable.

To draw the above graphs, a colour graphics terminal was used, and its screen photographed. The programme for the mapping operation is due to Buxton\textsuperscript{59}, and is found in Appendix 13.

Two refinements of the previous graph plotting method will be observed. Firstly, the extreme values of all the independent variables of this study were limited to ±1. (±2 was used in the previous section). This was done so as to limit the area of inspection to the experimental region.

The experimental area is conservatively defined by:

\[
V_1^2 + V_2^2 + V_3^2 + V_4^2 + V_5^2 \leq 4
\]

since the data in the axial directions does not extend more than two units away from the centre of the experimental region ($V_n$ are the values of the independent variables).

The programme calculated the value of the axial variables that would be within the experimental area, for each plot, depending on the value of the non-axial variables. Thus, if the values of the three non-axial variables were 1, -1 and -1, the values of the two axial variables at the limit of experimental space would
Figure 6.13
<table>
<thead>
<tr>
<th>STARTING TEMPERATURE</th>
<th>RAM PRESSURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ROTOR SPEED</th>
<th>RESPONSE</th>
<th>DESIRABILITY FUNCTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>0</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>+1</td>
<td>7</td>
<td>8</td>
</tr>
</tbody>
</table>

FIGURE 6.14
STARTING TEMPERATURE +1  RAM PRESSURE

-1  0  +1

-1  1  2  3

0  4  5  6

+1  7  8  9

RESPONSE DESIRABILITY FUNCTION

FIGURE 6.15
be $\sqrt{T}$; at the 0, 0, 0 levels of non-axial variables, the axial values at the edge of the experimental region would be $\sqrt{T} = 2$.

As will be seen by inspection of composite Figures 6.13 - 6.15, this area is represented in each plot by a central dark circle. Extrapolation outside this area must be done with some caution, as the reliability of the information outside experimental space must be suspect.

The composite graphs show unit work (UW) and fill factor (FF) as the axial variables, with ram pressure (RP) and rotor speed (RS), as the non-axial variables. Starting temperature (ST) is varied through the thickness of the volume. (Note that a scaling factor of 10 is applied to some contour graphs, while no factor is applied in others).

The first of the composite graphs (Figure 6.13, ST = -1) shows the following: at the low temperatures used here, a very strong co-dependence of mixing efficiency on fill factor and unit work is noted.

In general at constant unit work, improving mixing is noted as fill factor progresses from 0.5 (-2) to 0.9 (+2). Under the conditions of this series of contour plots, no optimum fill factor is noted, as has been estimated by other workers at 0.7.

At constant fill factor, the expected effect of increasing unit work is seen; that is, an improvement in mixing. In this connection, a generalisation might be made, regarding the level of unit work beyond which only marginal improvements are observed. The critical level appears to be about 1000 MJ/m$^3$, (between 0 and +1 coded levels), where any further increase maintains contour heights at their particular level. The one exception to this rule is graph 1 of the composite figure 6.13, where increasing unit work causes continuous improvement in mixing. It is to be pointed out that the conditions of rotor speed and ram pressure of this graph
are at very low levels, and thus under these non-intensive conditions of mixing, the effect of increased unit work continue to be beneficial. The practical effects of low ram pressure and rotor speed will be, insufficient shear stress within the mixer, absence of a dominant power peak in the early stages of mixing and low shear strain rate.

Considering the non-axial variables of this series, increasing ram pressure from 0.22 (-1) to 0.4 MPa (+1) shows positive effects on mixing at constant unit work and fill factor, whether rotor speed is high, medium or low (75 - 45 rpm).

Increasing rotor speed from 45 to 75 rpm has an adverse effect on mixing, as seen by a vertical inspection of Figure 6.13. In all cases, at constant fill factor and unit work levels, irrespective of ram pressure, mixing efficiency falls. The fall is particularly serious at the high ram pressures (column 3).

By inspection, the four graphs (2, 3, 5, and 6) at the top right hand corner represent the best set of mixing conditions, based on the desirability function. Of these, graph 3 generates the maximum mix efficiency at constant levels of axial variable. Given a specific unit work and fill factor level (say 900 MJ/m³ and 0.7), a medium high ram pressure (0.4 MPa) and the lowest rotor speed permissible (45 rpm). This combination appears best for low starting temperature.

Diametrically opposite graph 3, graph 7 shows the worst conditions of mixing overall, the particular non-axial combination of high rotor speed (75 rpm) and low ram pressure (0.22 MPa) appearing to give particularly ineffective mixing.

Moving onto composite graph 6.14, one observes that a rotation of the contours has occurred here, compared to the previous series. That is, the dominant effect of fill factor has all but disappeared, leaving unit work as the strong axial variable. At constant unit work, increasing or decreasing fill factor hardly has any effect on mixing efficiency, indeed in graphs 8 and 9 increasing chamber loading, decreases the desirability function slightly.
The effect of increasing unit work is again, as expected, improving mixing, continuing up to 1200 MJ/m³. (Note that a plateau in mixing efficiency was observed at 1000 MJ/m³ in the last series of graphs).

The effect of ram pressure at constant unit work and fill factor regardless of rotor speed is increased mixing efficiency up to 0.31 MPa. Further increases are not beneficial, as the mixed material does not improve any further, constant mix quality having been reached before.

Again, as in the previous series of contours, the effect of increasing rotor speed is that it has a negative effect on mixing. This observation holds true whatever the ram pressure, unit work level or fill factor.

In this series of mixing contours too, the top right hand graphs (2, 3, 5 and 6) produce the conditions most conducive to effective mixing. Of this set, the first two present mixing as being the best attained in Figure 6.14. As before, this would indicate that even at a higher starting temperature, the combination of low rotor speed and medium-high ram pressure offers the best combination.

As before, graph 7 generates the worst mixing conditions, high rotor speed and low ram pressure being responsible.

The third composite graph Figure 6.15, completes the revolution of the contours of response, which are now noted to be at about 90° from their first position in Figure 6.13. The present series represents variation in the mixing variables at a high starting temperature (50°C). This appears to totally reverse the trend of the first graph (Figure 6.13), which suggested that increase of fill factor had a positive effect on mixing. This series shows at constant unit work, that increasing fill factor decreases mixing action.
Progressive positive changes in unit work increases mixing efficiency, this time up to 1350 MJ/m$^3$ after which very little change in the properties of the mixed material is noted.

Increases in ram pressure again, irrespective of unit work, fill factor or rotor speed levels, improves mixing up to intermediate levels (0.31 MPa). Definite deleterious effects are noted on the mixed material, if ram pressure is further increased. At these high starting temperature levels, heat generation within the mixer is rapid, and further ram pressure must only serve to exacerbate the situation, resulting in unfavourable temperature/viscosity balance. This effect is compounded at very high fill factor levels, where the mixed material has extremely low desirability function values (see graphs 3, 6 and 9).

Rotor speed again shows the now established effect of decreasing mixed material quality as it is increased.

The best conditions of this series are indicated by the graphs 2 and 5, with the former showing better contours of mixing overall. Again it would seem that medium high ram pressures in conjunction with as slow a rotor speed as practicable produces the best mixing conditions.

For the first time, the worst mixing location changes from graph 7 to graph 9, where the combined effects of high machine temperature, rotor speed and ram pressure make for inefficient conditions of internal mixing.

By a joint consideration of the three composite figures 6.13–6.15, the following might be said about the effects of starting temperature on mixing.

Increasing starting temperature causes a reversal of the effect of fill factor on mixing. At low temperatures (30°C) increasing fill factor has a positive effect on mix quality, while at 40°C, it does
not materially contribute as an effective mixing variable. At the high temperatures (50°C) high fill factors are an obstacle to mixing.

At higher temperatures the unit work of mixing required for generation of maximum material properties appears to be higher than at the lower temperatures. For example, at constant fill factor the general indications are for the critical mixing energy levels to increase from 1000 MJ/m³ to 1350 MJ/m³ with rising starting temperatures. This indicates that energy is being utilised more effectively at lower temperatures, possibly because of higher shear stresses being generated, at the higher viscosity of the rubber. Dispersive mixing must be accomplished more efficiently under these conditions.

Not surprisingly, in the light of the above speculative reasoning it is noted that high temperatures magnify the disastrous effects of increased rotor speed on mixing.

If high rotor speeds are to be used, it appears that the lower starting temperatures will minimise their negative effect on mixing.

High ram pressures are also particularly ineffective at high starting temperatures. The balance achieved with high pressures and low starting temperature of the mixer appears well struck if good mixing is desired.

Despite the unsatisfactory effects of high starting temperature when combined with extreme levels of ram pressure and rotor speed, at average levels of these (coded 0, 0) increasing temperature does appear to have a positive effect. Generalising across the whole range of variables, the starting temperature of 40°C (0) marginally appears to be most favourable for mixing.

Overall, across the entire range covered by the investigation, on the basis of the desirability function, the most favourable conditions of mixing were found to be:
and

Unit work  -  1500 MJ/m³
Fill factor  -  0.9
Starting temperature  -  30°C
Ram pressure  -  0.4 MPa
and
Rotor speed  -  45 rpm

The worst conditions were observed at:

Unit work  -  300 MJ/m³
Fill factor  -  0.9
Starting temperature  -  50°C
Ram pressure  -  0.4 MPa
and
Rotor speed  -  75 rpm

At a unit work level of 900 MJ/m³ and the rest of the mixing variables set at the same levels as above, the mixed material resulting is graded at only approximately one third as good as the best stock obtained. This conclusively indicates that at otherwise favourable mixing conditions, high rotor speed and starting temperature cause a direct reversal. In fact, a reduction in rotor speed at the higher temperatures (i.e. conditions of 900 MJ/m³ (UW), 0.9 (FF), 0.4 MPa (RP), 45 rpm (RS) and 50°C (ST) ) still does not make any improvement in mixed material properties, these remaining outstandingly less than the best mixed stock.

Despite the high F ratios of Table 6.12 for the mixing time and dump temperature models, a brief discussion on the main trends in these now follows.

Composite graph 6.16 represents contours of mixing time, at a constant unit energy of mixing (900 MJ/m³ - coded value, 0). Ram pressure and starting temperature are the axial variables while fill factor and rotor speed are the vertical and horizontal non-axial variables respectively. The findings are summarised below:
<table>
<thead>
<tr>
<th>FILL FACTOR</th>
<th>-1</th>
<th>0</th>
<th>+1</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>0</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>+1</td>
<td>7</td>
<td>8</td>
<td>9</td>
</tr>
</tbody>
</table>

**UNIT WORK**

**ROTOR SPEED**

**RESPONSE MIXING TIME**

**FIGURE 6.16**
1. At ram pressures below 0.35 MPa increasing starting temperature increases cycle time. This could conceivably be caused by a slippage of the rubber between the shearing surfaces of the mixer, at low ram pressures, aggravated by temperature. The higher ram pressure could force a gripping of the rubber, and consequently efficient shearing at the tips, the higher temperature causing a favourable coefficient of friction under these conditions.

2. It is observed at low and medium starting temperatures, increasing ram pressure has only small effects on cycle time due to slip taking place. Due to the factors stated above, at high starting temperatures, increasing ram pressure decreases cycle time.

3. The effect of increasing fill factor, at any rotor speed is to decrease cycle time. This is since higher shear stresses promoting dispersive mixing result from high chamber loadings. Also, higher power peaks are the consequence of high fill factors.

4. Increasing rotor speed in all cases decreases cycle time at constant unit work levels considerably, a 66% increase in speed resulting in a corresponding reduction in cycle time at high fill factors, and a 57% reduction at medium and low fill factors.

Figure 6.17 shows an incomplete composite for the contours of dump temperature at constant unit work, with again, fill factor and rotor speed as the non-axial variables.

1. Increasing ram pressure at low starting temperatures, decreases dump temperatures, probably due to less total shearing of the rubber, stemming from the slip phenomenon described earlier.
<table>
<thead>
<tr>
<th>UNIT WORK</th>
<th>ROTOR SPEED</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-1 0 1</td>
</tr>
<tr>
<td></td>
<td>-1 1 2 3</td>
</tr>
<tr>
<td>1</td>
<td>0 4 5 6</td>
</tr>
<tr>
<td>-1</td>
<td>-1 7 8 9</td>
</tr>
</tbody>
</table>

**Figure 6.17**

**Response Dump Temperature**
At high starting temperatures, where it was stated that gripping of the rubber between the shearing members would occur, increasing ram pressure increases dump temperature.

2. Not surprisingly, increasing starting temperature, has a positive effect on dump temperature.

3. Increasing rotor speed increases dump temperature, due to the increase in energy input rate. This increase is not balanced by a corresponding increase in heat output rate, and hence the internal energy of the system increases and temperature rises.

4. Increasing fill factor increases dump temperature, due to the higher stress levels within the mixer and primarily since there is a restriction on the presentation of new rubber surfaces to the cooled members of the mixer. There is thus less neat transfer away from the bulk of the rubber.

6.14 Conclusions

The methods of statistical experimental design, multivariate regression analysis and graphical presentation of results as applied here to rubber mixing is effective in showing the influence of the main processing variables on mixing. In addition it is seen that the mixing variables cannot be viewed in isolation, but must be thought of as part of an interactive operation, where the levels of all the mixing variables exert crucial influences on each other. Important interactions noted by graphics inspection have been starting temperature and rotor speed, starting temperature and ram pressure, fill factor and ram pressure, ram pressure and rotor speed.
The approach to deriving a unified mixing function in terms of material properties has proved credible, in that it has shown established responses to vary as predicted by previous work. With this reassurance, it is possible to use this function to explore territory yet unclear; to identify special areas of experimental space and specify their effects on material quality and also, to make observations of the effects of variables whose function in the mixing operation as a whole, are yet uncertain.

Indeed by use of this function, without any specialised graphical presentation, it is possible to select an area of desirable properties (see Appendix 12) and operate the process at those conditions producing it. No mathematical background or optimization knowledge is required to make such a specification.

For more research oriented workers, the specialised contour graphing techniques are extremely useful for examining in minute detail, the nature of a complicated, interactive process. The quality of presentation produced by the evolution from plotter graphics, to colour terminal graphics is evident from a scrutiny of the results, though necessarily both methods are expensive and are unsuited for industrial laboratory use, given the present 'state of the art' of computer graphics. The expense of plotting is likely to drop radically over the next few years, and thus it will be feasible to employ the method in industrial laboratories.

From the graphics it is possible to specify an operating window within which the process must be operated, for achievement of the desired stock quality. It is also possible to specify 'no-go' areas at which mixing will inevitably be disastrous.

By combining the contours of mixing efficiency and mixing time, one is able not only to specify the variables yielding best quality, but also, very importantly, to view the process in terms of productivity and economy. By combining the dump temperature contours with these, a mix schedule may be selected by which a good quality compound will be manufactured profitably, and also by which the heat history
developed will be at the correct level to ensure satisfactory processing further downstream.

It must not be forgotten that though digital computers are ever increasingly powerful and reliable, the technologist will only maintain contact with such data, and the reality of the problems by the commonsense use of 'pencil and paper' techniques in addition to the more powerful methods available. Failure to do this will result in the technologist being overwhelmed by computer print-out, and the elegance of the techniques utilised, and the abandonment of valuable human judgement. The graphical treatment employed here promotes the interaction between the experimenter and his data, in a manner which utilises his background knowledge, in a way which other techniques like mathematical optimisation do not.

To summarise, the technique used here is a powerful tool for examining the internal mixing process, and selecting desirable mixing conditions. It provides a viable method of avoiding the pitfalls and simplifications associated with fundamental models of mixing. The empirical nature of the model, unfortunately renders the results specific to the mixer size and geometry used and the compound employed in the experimentation. Extrapolation outside the experimental hyper-space must be made with extreme caution as random and uncontrolled fluctuations might result in an excursion over this boundary.

6.15 Recommendations for Further Work

A prime objective, if the technique is to be widely used, is that the experimental design be abbreviated. A design such as the one used here is rather extravagant of materials and time; however this was a sacrifice made to achieve reliability. In a pilot plant it is not thought that the deficiencies (or otherwise) of the model will be seriously felt, since trends would be of the essence; not detail. Thus, highly fractionated factorial designs could be used, as
might specialised screening designs, such as Plackett-Burman method. These would certainly indicate main effects, and if carefully selected, important interactions as well.

Finally, a further improvement in presentation (especially in a five independent variable case) could be made by 'three dimensional' contour representation, which if used here, would have reduced the number of graphs required for analysing the mixing process from twenty seven to just nine. Figure 6.18 indicates the potential use of such a graphics technique.

FIGURE 6.18 A three dimensional contour representation between four variables
Literature cited


27. Laboratoire de Recherches et de Controle du Caoutchouc, Rapport Technique No. 102, Mai (1976).


59. J R Buxton, Private communication, Dept of Eng-Maths, LUT.


68. DIN 53,516.

CHAPTER 7

THE INFLUENCE OF CERTAIN SECONDARY CARBON BLACK PROPERTIES
ON RUBBER STOCKS PRODUCED BY INTERNAL MIXING

7.1 Introduction

Early on in this dissertation, it was stated as an objective, that there was a need to explore the influences secondary carbon black properties exert on stocks produced by internal mixing.

The effects of the 'primary properties' of carbon black on mixing efficiency and stock properties have been rigorously investigated. Their influence on both these aspects is great, and their levels are crucial to final compound quality. These 'primary properties' are:

- Particle size and surface area
- Structure
- Amount of carbon per aggregate

In addition, other properties have been identified as being contributory to deficiencies (or otherwise) in practical rubber stocks. These are porosity, surface activity, surface chemistry and trace constituents.

Yet other attributes of the filler are called 'secondary' during this segment of the research. These are fines content of the black, mass pellet strength, bulk density, pellet size distribution, moisture content and individual pellet crush strength. They are thus named as they do not cause such evident effects as do the primary properties; however they are thought to be appreciable enough to merit consideration.

7.2 The Background of the Problem

Interest in the secondary properties of carbon black has been relatively recent. Two years ago, the present author found that
ostensibly similar carbon blacks manufactured by Cabot Carbon Ltd, by three manufacturing units were inherently different in dispersibility. Two black types were evaluated, N660 and N375, manufactured by plants in Stanlow in England, Ravenna in Italy and Hanau in Germany. These blacks were included in a Butyl (IIR) stock base, and mixed at identical conditions (derived from similar experimentation to that described in Chapter 6) designed to maximise shortcomings in dispersibility. That is, the mixing conditions selected, produced stocks whose dispersion allied properties were changing extremely rapidly, the conditions not being conducive to good mixing.

For both types of blacks, (N660 and N375) the physical tests showed a graded order of dispersibility. It was found that the blacks from Ravenna were the hardest to disperse, while the Hanau manufactured materials were graded next best. In both cases, the Stanlow black showed up as the easiest to disperse and mix.

Within each black type, the primary properties were similar, regardless of location of manufacture. Thus, iodine number (by which surface area, porosity and particle size are measured) within each black type was the same for all locations; as was tinting strength (estimates carbon content of aggregate), crushed DBP and DBP absorption (for estimating structure). These findings were not surprising, since the classification into black type is made on the basis of the above tests.

The differences observed in dispersibility were attributed to be possibly stemming from secondary properties, fines content, pellet size distribution and moisture levels within the blacks. These varied systematically, to match the observations on ease of dispersion.

The above properties are regulated and adjusted mainly in the pelletising process, carried out after the black has been formed from feedstock. The process of black manufacture (whether by the furnace or thermal methods mainly prevalent today, by the new tech-
ology process or the almost obsolete channel process) has been well documented\textsuperscript{28,10,11}. After carbon formation and quenching, the black aggregates are separated from the combustion gas stream by bag filters, for example.

The special needs of the rubber industry demand a densification of the black, which up to this stage is very fluffy (about 0.08 - 0.16 gm/cm\textsuperscript{3}). The industry requires bulk densities of between 0.32 - 0.48 gm/cm\textsuperscript{3} since:

a) Space required for packing, transportation and storage is thus minimised.

b) Such a pelletising treatment reduces dust hazards, which in turn, makes for a safer and more congenial working atmosphere.

c) It provides a free flowing material, and facilitates handling, particularly in the bulk, and

d) Within limits, pelletisation improves rubber compound processing: for instance, rate of incorporation.

As mentioned briefly in the first chapter, these needs of the rubber sector imposed pressures on the carbon black manufacturers to manufacture pellets where:

a) the purity of the black should not be affected by any additives added to promote pellet formation.

b) the treated black should disperse adequately in rubbers during mixing.

c) nevertheless, the modified black should survive handling and transport without reverting to dust, and

d) the process should be economical.
The pelletisation is carried out by several processes, and
patents relating to such processes and machines by which they are
accomplished are rife\textsuperscript{29-33}. Following the now obsolete mechanical
compression\textsuperscript{28} and two-liquid\textsuperscript{28} processes, the black industry is
dominated by two pelletising means. These are the pin-beading
process\textsuperscript{34} and the dry-beading process\textsuperscript{35}. The former uses wet
black as the base from which to obtain pellets, which are dried
afterwards, while the latter uses a 'seeding' technique, economi-
cal in fuel and plant costs.

Depending on the method used, the quality of the pellets
produced is found to depend on several features. The method of
addition of water, the speed of the pelletiser, the time of resi-
dence in the pelletiser, the degree of loading of the pelletiser,
the quantity of water added and the number of steps in which the
carbon was added are some of the variables by which the process may
be controlled\textsuperscript{36}.

Several of the secondary properties have been investigated,
in connection with the dispersibility of black. Some of these,
such as the mass pellet strength test\textsuperscript{20}, which was used widely till
about 1967 as being indicative of this property, has since lost
favour\textsuperscript{37} with manufacturers. It is still used to assess the bulk
packing tendency of black.

Eaton and Harris\textsuperscript{37,38} observe long incorporation times
for black pellets in rubber of either large (greater than 2.0 mm
diameter) or small (less than 0.25 mm in diameter) pellets. Pellet
sizes between this range are said to be desirable for incorporation.
Without any experimental evidence, the above authors specify an
'ideal' and a 'bad' size distribution of pellets, stating the cri-
teria of acceptability as being good bulk handling and disper-
sibility. These authors relate individual pellet strength\textsuperscript{26} to dis-
persibility, and give histograms of strength distributions of bad,
acceptable and best blacks.
Atkins and Boonstra\textsuperscript{39} state that the test relating to resistance of pellets of black to dust formation\textsuperscript{19} does not at all relate to the dispersibility of the material in rubber. Using the individual pellet strength test\textsuperscript{26} (IPS), they found a correlation between pellet strength (alternatively termed pellet hardness) and incorporation time for equivalently sized pellets. Incorporation time fell with increasing pellet strength. This effect was more marked the smaller the pellet. For large pellets incorporation time was longest. Dispersion was noted to increase, with reducing pellet strength.

Reynolds\textsuperscript{40} specifies a desirable hardness range for the 12/14 screen cut for dry pelleted blacks as being between 30 and 70 grammes and for the wet pelleted variety 70-120 grammes. Acceptable fines percentage is quoted as between 5 and 8\% (as shipped) for ‘flowability’ and processability. The above author states that pellet size distribution is unimportant, if pellet hardness is within the required range.

Daniell\textsuperscript{41} examined the effects of introducing various screen cuts (sieve fractions) of carbon blacks into rubber, and found no effects at all on dispersion, caused by the different pellet sizes added separately.

7.3 Objectives of this Segment of Research

The review revealed no information of any consequence which would lead to a solution of the original problem. That is, why do identical blacks from three manufacturing sources within the same company differ in inherent dispersibility? The following investigation was launched to attempt to clarify the observations.

a) It was stated that the three black types above differed in dispersibility when mixed under conditions not conducive to the process. The effects of mixing the identical blacks into
rubber at conditions of good mixing were to be investigated. After all, the first method indicates inherent dispersibility differences, but are these so severe that they still manifest themselves under conditions of intensive mixing? Since these conditions will be such as those used in industry, an indication of the seriousness of the observation would then be forthcoming.

b) A preliminary investigation into the possibility that significant trends in dispersibility accrue from systematic differences in fines content, pellet size distribution and moisture levels was instigated. One black type only (N375) was to be considered here.

Of necessity, these two areas had to be investigated fairly briefly, in view of the time constraints on the project. A third and deeper investigation into the following was also attempted.

c) Identical objectives as in (b), but using N660 as a base black, and applying a more probing approach to experimentation.

7.4 Experimental Methods Used

For the first part, batches of all three different source blacks of the two types were mixed into a Butyl (IIR) rubber base, of the following formulation:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysar Butyl 301</td>
<td>100.0</td>
</tr>
<tr>
<td>Carbon black</td>
<td>44.0</td>
</tr>
<tr>
<td>M.C. Sulphur</td>
<td>1.5</td>
</tr>
<tr>
<td>T.M.T.D.</td>
<td>1.5</td>
</tr>
<tr>
<td>(Tetramethyl Thiuram Disulphide)</td>
<td></td>
</tr>
<tr>
<td>M.B.T.S.</td>
<td>1.0</td>
</tr>
<tr>
<td>(Mercaptobenzo-thiazole)</td>
<td></td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5.0</td>
</tr>
</tbody>
</table>
As explained before, these stocks were mixed in a BR Banbury at good conditions for mixing.

These conditions were as shown in Table 7.1, the corresponding bad conditions used in the preliminary work also being shown, as a comparison.

TABLE 7.1
Mixing Conditions

<table>
<thead>
<tr>
<th>Mixing Variable Levels</th>
<th>Good mixing conditions</th>
<th>Bad mixing conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing time (minutes)</td>
<td>2.8</td>
<td>2.75</td>
</tr>
<tr>
<td>Starting temperature (°C)</td>
<td>32</td>
<td>25</td>
</tr>
<tr>
<td>Specific ram pressure (MPa)</td>
<td>0.4</td>
<td>0.27</td>
</tr>
<tr>
<td>Fill factor</td>
<td>0.7</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Rotors speed was set at 77.5 rpm.

The mixing technique too was as used before, an 'upside down' method being employed. Dump temperatures were monitored during mixing, and check weights observed after dump. Dumped batches were sheeted out on an even speed mill at an 8 mm nip. After curemetering, and vulcanisation to a 95% optimum crosslink level, in this first section, dynamic tension-compression test pieces were moulded, bonded to metal end pieces for testing in the DRA, as described in Chapter 4. In phase modulus at 1.5 Hz frequency and varying amplitude levels was measured on five test pieces from each of the six batches produced. As discussed at length in Chapter 3, in phase dynamic modulus is an extremely sensitive identifier of small dispersion differences with stocks. (Note that tension-compression testing replaces the usual shear dynamic testing in this instance).

In the experimental work, to swiftly achieve the second stated objective of this chapter, the following was done.
Firstly, a series of N375 blacks (obtained from the same production run from Cabot Carbon, Stanlow) differing only in fines content were made up. The term fines relates to that fraction of the black of less than 125 μm in size as measured by sieving\(^1\). This portion was extracted from a volume of black by the above means with a BS size 120 sieve. This ensured removal of fines, without materially affecting the size distributions of the other fractions within the black. To avoid any likelihood of separation of these fractions caused by sieving, the 'fines-less' black was re-randomised by gentle ball milling.

The extracted fines were reincorporated into the 'fines-less' samples, to make up the weights of carbon required for the mixing trials. One 'fines-less' complete sample too was made up. This entire process gave similar black weights, differing only in fines content (20%, 10%, 6.37%, 5% and 0%).

In the course of the above work, it was noted that the size distribution in the N375 corresponded not to the perfect pellet distribution of Eaton and Harris\(^3\),\(^4\) but approximated to the distribution said to be not ideal. Thus, sieve fractions were separated from the bulk of the carbon black\(^2\) and these differing sieve cuts reweighed to make up the perfect distribution of Eaton and Harris. This, it was thought, would serve as a comparator to give a baseline for acceptable dispersibility. Figure 7.1 shows these different distributions in the form of histograms.

The final black characteristic that was to be varied was moisture content. Moisture content in wet pelleted blacks is regulated in the drier stage after pelletisation. This would have been the easiest way of varying moisture levels, if access to the manufacturing plant was available. In dry pelleted blacks, moisture content is regulated elsewhere (at the quench stage), and thus for such blacks the regulation of moisture content was effectively out of the hands of the present author. Further, black wetness levels thus caused would change in the transport from manufacturing site to University laboratories.
FIGURE 7.1 Pellet size distributions - (Ideal, non-ideal and experimental N375 black)
Since swiftness was of the essence for this segment of experimentation, it was decided that a double pronged approach was called for to vary moisture, in the black. Firstly, the fact that the carbon black as stored had a certain level of moisture was made use of.

If varying percentages of this residual moisture could be extracted, then a series of test blacks of systematically varying percentage wetness could be achieved.

The extraction of these progressively increasing levels of moisture out of the black was effected by two means.

The first method was to heat weighed samples of black (of the order of batch weights required for the future mixing trials) and estimate rate of weight loss. An oven at 105°C was used, the temperature being low enough to prevent any surface modification of the black that would affect experimental observations taking place. Commencing at a starting moisture level of 1.8%, progressively longer heating times led to the production of batches of black of moisture contents 1.48%, 1.3%, 0.97% and 0%. A weight loss curve for the N375 black under the oven heating conditions, as described is shown in Figure 7.2. 5 hours heating was required to produce no further change in black weight.

In the event of the heat treatment of the black causing marked surface effects (or otherwise) in the material, an alternative method for extraction of moisture from the 1.8% base level was established. Here, vacuum dessication was applied to weighed black samples (at ambient temperature). The weight loss curve of this treatment is shown in Figure 7.3. Black samples of moisture contents of 1.8%, 1.48%, 1.3%, 0.97% and 0.65% were isolated by this means.

The blacks differing in fines content, the perfect pellet distribution sample, and the varying moisture level materials were mixed into the Butyl rubber stock as described before in a BR Banbury.
FIGURE 7.2  Weight loss curve - N375 (Oven at 105°C)
FIGURE 7.3  Weight loss curve - N375 (vacuum dessication)
Conditions of mixing selected were those not encouraging to an efficient process (Table 7.1, column 3).

In all cases, dump temperature and check weights were noted after mixing, and the following tests were carried out on the mixed batches. Mooney viscosity, Monsanto ODR curemetry, tensile strength, EB, modulus at 100% strain, microhardness, tear strength and tear energy. The techniques used for testing have already been described in Chapter 4.

The next series of experiments made use of the same principles described up to now, but a more detailed approach was adopted.

In this series, N660 carbon black from Cabot Carbon Ltd, was used exclusively. Again the influence of fines content on mixing and rubber properties was to be investigated.

The approach used here was to sieve out several size fractions from a standard production run of N660. The standard technique of fractionisation was used, sizes of pellets being obtained as follows; >1680, 1680-850, 850-450, 450-250, 250-125 and >125 μm. From these cuts several batches of black were made up, the non-fines distribution being kept constant, in all cases, while the fines % (pellets of less than 125 μm) was varied systematically. The range of fines contents used was from 0% through 2, 5, 7, 10, 12, 15, 20 and to 30%. Thus, while the fines level varied from batch to batch, so the non-fines concentration would also vary, but maintaining a standard distribution. Table 7.2 shows the distributions of the non-fine black fraction used throughout.

TABLE 7.2
Non-fines fraction

<table>
<thead>
<tr>
<th>Sieve cut</th>
<th>Percent weight of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;1680</td>
<td>0.22</td>
</tr>
<tr>
<td>1680-850</td>
<td>15.04</td>
</tr>
<tr>
<td>850-450</td>
<td>59.14</td>
</tr>
<tr>
<td>450-250</td>
<td>16.31</td>
</tr>
<tr>
<td>250-125</td>
<td>9.29</td>
</tr>
</tbody>
</table>
Each of the variable fines series was made up to two black weights, one to correspond to 0.4 and the other 0.7 fill factor. These artificially derived distributions were then rerandomised by ball milling (without pebbles) each batch for 5 minutes. Any suggestion of persisting separation of pellets would thus be eliminated. This method was also found to cause the desired randomisation without breakdown of pellets. It will be remembered that these two fill factors are quoted in Table 7.1 and would produce poor and excellent mixing conditions respectively. In total, 18 batches of black were made up, nine at each fill factor. Each of these batches was dried for 24 hours at 105°C in an oven before any mixing was done to keep moisture (or dryness) constant.

The next experimental series of blacks was to explore the effects of variable moisture on mixing and rubber properties. The approach to obtain the idealised pellet distribution has been described only here: fines formed a part of the constant total. Table 7.3 shows this, in terms of the weight fractions of each cut.

**TABLE 7.3**

Composite ideal distribution

<table>
<thead>
<tr>
<th>Sieve cut</th>
<th>Percent weight of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;1680</td>
<td>0.21</td>
</tr>
<tr>
<td>1680-850</td>
<td>14.31</td>
</tr>
<tr>
<td>850-450</td>
<td>56.29</td>
</tr>
<tr>
<td>450-250</td>
<td>15.52</td>
</tr>
<tr>
<td>250-125</td>
<td>8.85</td>
</tr>
<tr>
<td>&lt;125</td>
<td>1.63</td>
</tr>
</tbody>
</table>

Again, several of these fractions were combined by randomisation on a ball mill, to correspond both to 0.4 and 0.7 fill factors in a BR Banbury, based on the IIR compound specified earlier. Each of these batches was next dried at 105°C for 24 hours before the next step.
This next stage was to produce different levels of moisture within these batches. The original method used (vacuum dessication and/or oven heating progressively) was deemed satisfactory for a preliminary excursion, but not for an approach as detailed as this.

A technique which employed humidity fixed points of binary saturated aqueous solutions was used here, such that the dried carbon blacks could be stored for a period in fixed humidities, the total water absorbed by the black, depending on the specific humidity used.

The common methods of controlling humidity accurately use either a humidity generator\(^4\) or the equilibrium of a closed space with a chemical system\(^3\), which produces the desired equilibrium vapour pressure. The former method tends to be expensive, but the second system is much more economical. One method of preparing such a system is to dissolve a chemical in water at a particular concentration, whereby in a closed system it sets up an equilibrium vapour pressure. Special problems arise in this instance, because not only must the concentration be specified initially; but also since any humidity sources and sinks in the controlled space, and even the initial equilibration process can alter the solution concentration.

A specially useful variant of the chemical method is by the use of binary saturated aqueous solutions (primarily of single salts) in which the solute is highly non-volatile.

At specified temperature, the concentration of a saturated solution is fixed, and does not have to be determined. By providing excess solute, the solution will remain saturated, even in the presence of modest sources or sinks. Where a solute is a solid in pure phase, it is easy to determine that there is saturation, since precipitation is observed.
Table 7.4 shows the salts selected and the humidities they generate in closed spaces under equilibrium conditions.

**TABLE 7.4**
Salts for ensuring constant R.H[^44,45]

<table>
<thead>
<tr>
<th>Salt</th>
<th>Humidity (%)</th>
<th>Temperature °C</th>
<th>Solubility in gm/100 ml cold water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium sulphate ($K_2SO_4$)</td>
<td>97.59±0.53</td>
<td>20</td>
<td>12</td>
</tr>
<tr>
<td>Potassium chloride ($KCl$)</td>
<td>85.11±0.29</td>
<td>20</td>
<td>34.7</td>
</tr>
<tr>
<td>Sodium chloride ($NaCl$)</td>
<td>75.47±0.14</td>
<td>20</td>
<td>35.7</td>
</tr>
<tr>
<td>Sodium nitrite ($NaNO_2$)</td>
<td>66</td>
<td>20</td>
<td>81.5</td>
</tr>
<tr>
<td>Magnesium nitrate ($Mg(NO_3)_2·6H_2O$)</td>
<td>54.38±0.23</td>
<td>20</td>
<td>125</td>
</tr>
<tr>
<td>Potassium carbonate ($K_2CO_3·2H_2O$)</td>
<td>43.16±0.33</td>
<td>20</td>
<td>146.9</td>
</tr>
<tr>
<td>Calcium chloride ($CaCl_2·6H_2O$)</td>
<td>32.3</td>
<td>20</td>
<td>74.5</td>
</tr>
<tr>
<td>Potassium acetate ($KC_2H_3O_2$)</td>
<td>23.11±0.25</td>
<td>20</td>
<td>253</td>
</tr>
</tbody>
</table>

Saturated solutions (about 4 litres in volume, spread over a maximum surface area, by containing in a tray), were enclosed with the weighed, and dried black fractions. Also included in each chamber was a carefully weighed control of dried black (comprised of the same distribution) which would serve as a means by which the nett
quantity of moisture absorbed by each large sample of black could be gauged.

The chambers were 1m x 1m x 0.5m plastic bins, inverted over the black and the salt solutions placed on a table. The edges were sealed with masking tape, and a coat of rubber solution was painted over the whole. Equilibriation times allowed were 5 months, and each chamber was situated in a constant temperature room at a carefully regulated 20°C.

To ensure that the properties of the mixes produced by incorporation of the varying fines and moisture batches of black, would indicate only influences of these, a departure from the upside-down mixing procedure was warranted.

A curative masterbatch was mixed, of the Butyl (IIR) compound specified earlier. Table 7.5 shows the weights and ratios of this batch.

TABLE 7.5
Curative masterbatch

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts per hundred rubber</th>
<th>Weight (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysar Butyl 301</td>
<td>100</td>
<td>24.77</td>
</tr>
<tr>
<td>M.C. Sulphur</td>
<td>1.5</td>
<td>0.372</td>
</tr>
<tr>
<td>T.M.T.D.</td>
<td>1.5</td>
<td>0.372</td>
</tr>
<tr>
<td>M.B.T.S.</td>
<td>1.0</td>
<td>0.248</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5.0</td>
<td>1.239</td>
</tr>
</tbody>
</table>

The internal mixer used to mix this volume of the masterbatch was a Francis Shaw Intermix, K2A, sited at the Shaw Works at Manchester. The following mixing conditions were used. Starting temperature 38.6°C, time of mixing 3.0 minutes, coolant flow rate 293 litres/minute, ram ppressure 0.62 MPa, rotor speed 30 rpm. Dump temperature was 90°C, input energy used was 3.18 KJ/h. The dumped masterbatch was homogenised on an 80" mill at 10 mm nip setting.
The batch was checked for homogeneity by Monsanto ODR curemetry and Mooney viscosity.

After a storage period of about a week, the curative masterbatch was mixed with the variable fines, and variable moisture carbon blacks, under the two sets of mixing conditions in the BR Banbury. The two conditions in this case were not those specified in Table 7.1, as a curative masterbatch was used in this section and not a one stage mix. The conditions, except for mixing time, were maintained as in Table 7.1. The minimum mixing time to just avoid crumbing (in a normal batch) was found for the bad conditions of mixing to be 4.3 mins. Similarly for the good conditions of mixing the mixing time was reduced slightly from 2.8 to 2.5 mins.

Dump temperature and total energy consumed during mixing were observed as well as check weight after mixing.

The following tests were done on each batch thus produced. Mooney viscosity, ODR curemetry, and after vulcanisation to 95% optimum crosslinking, hardness, abrasion resistance, fatigue testing, dynamic properties, tear strength, tear energy, tensile strength, stress at 100% strain ($M_{100}$) and strain at rupture (EB), were measured. Test details were the same as those specified in Chapters 4 and 6.

7.5 Results and Discussion

First, an examination of the results obtained from the mixes containing the N375 and N660 blacks manufactured at the three different units. It will be remembered that these were mixed under conditions which would be used practically in industry. Table 7.6 summarises the findings regarding dump temperature of each batch mixed at identical conditions.
TABLE 7.6
Dump temperatures (°C)

<table>
<thead>
<tr>
<th>Manufacturing source</th>
<th>N660</th>
<th>N375</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ravenna</td>
<td>99</td>
<td>109</td>
</tr>
<tr>
<td>Hanau</td>
<td>106</td>
<td>109</td>
</tr>
<tr>
<td>Stanlow</td>
<td>105</td>
<td>106</td>
</tr>
</tbody>
</table>

Check weights were approximately the same in each case averaging about 97% of calculated batch weight. These weight results would indicate that the batches produced by the mixing would have in them the same quantity of carbon black and thus be comparable.

Figure 7.4 shows the results of the dynamic testing studies, where $E'$ (in phase compression dynamic modulus) was monitored against amplitude of deformation. Payne's work, which was described extensively in Chapter 3 and used in Chapter 5, indicates why the quantity is measured here. It is a very sensitive indicator of the dispersion of filler within the bulk of a rubber. Given identical mixing conditions, if the stocks exhibit different dispersions, black dispersabilities will be the direct cause.

The Figure 7.4 (in which the preliminary work on the blacks mixed at bad conditions of mixing is also included as a comparator) indicates the following.

Whereas definite dispersibility differences were manifested at bad conditions of mixing, Ravenna being the most difficult to disperse followed by the Hanau and the Stanlow N660's, the good conditions of mixing show that these differences are narrowed down greatly. Indeed within the bands of error, the three blacks appear to be indistinguishable in dispersion. The Ravenna black is still marginally higher in its modulus curve than the other two, but this is not thought to be very significant.
FIGURE 7.4 E' vs SSA for N660's Log amplitude
Also note that the general rationale behind two conditions of mixing being used, one conducive to, and the other minimising an efficient process, appears well founded. The overall dynamic modulii of the two sets of conditions are notably different, the bad conditions of mixing yielding higher modulii (and thus indicating worse dispersion). Note also that at high amplitudes, $E'$ is approaching similar values.

The results of Table 7.6 for the N660 blacks are particularly interesting, showing an order of gradation, under good conditions of mixing, indicating that the Hanau and the Stanlow blacks have been subjected to the highest intensities of mixing (dump temperatures of 106 and 105°C). The worst dispersed was the Ravenna black which only reached a dump temperature of 99°C.

From the foregoing it is to be appreciated the differences in inherent dispersibility that were found under the bad conditions of mixing, practically disappear under a favourable mixing regime.

Figure 7.5 shows the corresponding graph for the N375's. Again the preliminary results are included as a comparator. It must be emphasised at this point that the conditions for mixing of Table 7.1 were derived originally for the previous class of black. Thus, it is not expected, under the conditions optimised for a different black (N660), that the differences manifested due to pelletisation and other traits will be as clear cut as before.

Nevertheless, significant differences in $E'$ and thus dispersibility are seen, the Ravenna black being the most difficult to disperse, being followed by the Hanau and Stanlow varieties. This order prevails, whatever the conditions of mixing. In two cases (Ravenna and Stanlow), the noted reduction in modulii indicating better dispersion occurs when the mixing conditions are changed from bad to good; while in the Hanau material practically no change in peak modulus occurs with changes in conditions. Surprisingly, the badly mixed Stanlow black shows up as being better dispersed than the well mixed Ravenna and Hanau N375's by the measure of mixing used here.
FIGURE 7.5  $E'$ vs SSA for N375's
Comparing graphs 7.4 and 7.5, it is found that the corresponding N660's under any given set of conditions have lower modulii than their N375 counterparts. Only marginally lower differences are noted comparing the N660's to the N375's under the poor mixing conditions. Marked differences in modulus (stemming from the inherent primary properties) are observed at the severe conditions of mixing.

Next to be discussed will be the results from the N375 black mixes, varying in fines, pellet size distribution and moisture content. Check weights of the mixed batches, were approximately the same, through the series.

Table 7.7 summarises the results from the testing of the mixes containing variable fines. From a scrutiny of this table, it is evident that there is very little change in property levels in mixes manufactured from blacks containing the extreme ends of the fines spectrum. One fairly consistent feature however, as indicated by microhardness, Mooney viscosity, maximum Monsanto ODR torque, tear strength, Modulus$_{100}$ (stress at 100% strain), tear energy and in-phase dynamic modulus, is that at the medium level of fines, (5 and 6.4%) these properties indicate a mix somewhat inferior to the standards of those produced from other fines levels (less than 5% and greater than 6.4%). No concrete evidence can be shown to explain this observation, except to hazard a speculation that size distribution of filler might influence the ease of incorporation of black in a rubber during internal mixing. Packing efficiencies are known to vary with size distribution, and perhaps this critical fines level, makes for inefficient packing during incorporation. Obviously, from a handling point of view, the lower the fines content the better, and thus it may be stated that a fines content close to zero is the ideal. This finding is directly opposed to the views of Reynolds who specifies an ideal fines level (as shipped) of between 5 and 8%.

Table 7.8 summarises the property findings for mixes containing non-ideal and ideal pellet size distributions. Dump temperatures:
TABLE 7.7
Summary of results - varying fines content (N375 blacks)

<table>
<thead>
<tr>
<th>Fines Content (%)</th>
<th>Dump Temperature (°C)</th>
<th>Micro-hardness (°E)</th>
<th>Mooney Viscosity (M0)</th>
<th>Min. ODR torque (in lbs)</th>
<th>Max. ODR torque (in lbs)</th>
<th>Cure time for 95% cure (mins)</th>
<th>Tear Strength (N)</th>
<th>Tensile Strength (MPa)</th>
<th>E.B. (%)</th>
<th>Mod. 100 (MPa)</th>
<th>Tear Energy (kJ/mm)</th>
<th>E’ at peak 1.5 Hz (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>73.2</td>
<td>73.7</td>
<td>103.5</td>
<td>28</td>
<td>82.0</td>
<td>7.0</td>
<td>94.8</td>
<td>14.4</td>
<td>487</td>
<td>3.26</td>
<td>7.6</td>
<td>23.7</td>
</tr>
<tr>
<td>5</td>
<td>70.4</td>
<td>74.0</td>
<td>103</td>
<td>27</td>
<td>82.5</td>
<td>6.75</td>
<td>92.6</td>
<td>14.9</td>
<td>507</td>
<td>3.28</td>
<td>6.8</td>
<td>24.8</td>
</tr>
<tr>
<td>6.4</td>
<td>75.9</td>
<td>76.2</td>
<td>104</td>
<td>26.5</td>
<td>83.5</td>
<td>7.25</td>
<td>91.9</td>
<td>14.8</td>
<td>494</td>
<td>3.45</td>
<td>6.92</td>
<td>27.75</td>
</tr>
<tr>
<td>10</td>
<td>74.1</td>
<td>74.6</td>
<td>103.5</td>
<td>27</td>
<td>81</td>
<td>6.75</td>
<td>93.0</td>
<td>14.3</td>
<td>504</td>
<td>3.33</td>
<td>7.28</td>
<td>26.0</td>
</tr>
<tr>
<td>20</td>
<td>68.5</td>
<td>72.5</td>
<td>103.5</td>
<td>27</td>
<td>80.5</td>
<td>6.75</td>
<td>96.0</td>
<td>14.2</td>
<td>503</td>
<td>3.35</td>
<td>7.84</td>
<td>21.1</td>
</tr>
</tbody>
</table>
are identical, but on the basis of microhardness, Mooney viscosity, minimum and maximum Monsanto ODR torque, cure time, tear strength, Modulus$_{100}$, tear energy and elastic modulus, the ideal distribution yields the better mix. This would reinforce the assertion of Eaton and Harris$^{38,37}$ regarding the existence of an 'ideal' and 'non ideal' distribution of pellet sizes in carbon blacks. The tensile strength and strain at rupture (EB) results of Table 7.8 however, contradict this majority indication somewhat.

Next, we move onto the carbon black (N375) of varying moisture contents and examine the influence of this change on mixed material properties. Table 7.9 summarises these results for the oven dried series, while Table 7.10 presents those stemming from the vacuum dried sequence of blacks.

Note that in both these tables, the 1.8% moisture level black is the base, as it was from this level that the moisture content was reduced. First, a consideration of these tables individually. Table 7.9 indicates a considerable differing in dump temperatures, when the non-treated base black (1.8% moisture) and the oven heated blacks are compared (1.48 - 0% moisture). These evidently have undergone much more intensive mixing than the base black. Possibly the heat treatment (though only at 105°C) causes greater interparticulate interactions, leading to higher energy dissipation in the system, during dispersive mixing. There is also a considerable hardness drop, from non-heated to heated blacks. Mooney viscosity reflects a considerable decrease as drying increases, and tear strength, tensile strength, EB, tear energy and E' show general increases with decreasing moisture level. These indications would imply improved mixing with drier blacks, except for the increase in E' which by previous experience should decrease with better mixing. Modulus$_{100}$ shows a decrease, which would signify as do the majority of responses, an improved mixing as moisture levels in the black drop. If the speculation that increasing oven heating results in greater interparticle interactions in black is acceptable, this could explain the paradoxical E' results, in terms of the agglomerate breakdown
<table>
<thead>
<tr>
<th>Non-Ideal</th>
<th>Ideal</th>
<th>Distribution/Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>75.9</td>
<td>75.9</td>
<td>Dump temperature (°C)</td>
</tr>
<tr>
<td>76.2</td>
<td>74.7</td>
<td>Micro-hardness (°)</td>
</tr>
<tr>
<td>104</td>
<td>103</td>
<td>Mooney Viscosity (MU)</td>
</tr>
<tr>
<td>26.5</td>
<td>26</td>
<td>Minimum ODR torque (in. lbs)</td>
</tr>
<tr>
<td>83.5</td>
<td>81</td>
<td>Maximum ODR torque (in lbs)</td>
</tr>
<tr>
<td>7.25</td>
<td>6.75</td>
<td>Cure time to 95% cure (mins)</td>
</tr>
<tr>
<td>91.9</td>
<td>96.48</td>
<td>Tear Strength (N)</td>
</tr>
<tr>
<td>14.8</td>
<td>13.2</td>
<td>Tensile Strength (MPa)</td>
</tr>
<tr>
<td>494</td>
<td>457</td>
<td>E.B. (%)</td>
</tr>
<tr>
<td>3.45</td>
<td>3.21</td>
<td>Mod 100 (MPa)</td>
</tr>
<tr>
<td>6.92</td>
<td>7.6</td>
<td>Tear Energy (KN.mm)</td>
</tr>
<tr>
<td>27.75</td>
<td>25.0</td>
<td>E' at peak (1.5 Hz) (MPa)</td>
</tr>
</tbody>
</table>

**Summary of results - ideal and non-ideal pellet distributions**
### TABLE 7.9
Effect of moisture on mixed material properties - N375 black (oven dried)

<table>
<thead>
<tr>
<th>Moisture Level (%)</th>
<th>Dump Temperature (°C)</th>
<th>Micro-hardness (°)</th>
<th>Money Viscosity (mu)</th>
<th>Min. ODR Torque (in.1bs)</th>
<th>Max. ODR Torque (in.1bs)</th>
<th>Cure Time to 95% Cure (mins)</th>
<th>Tear Strength (N)</th>
<th>Tensile Strength (MPa)</th>
<th>E.B. (%)</th>
<th>Mod 100 (MPa)</th>
<th>Tear Energy (kJ/mm)</th>
<th>E' peak at 1.5 Hz (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8 (non-dried)</td>
<td>75.9</td>
<td>76.2</td>
<td>104</td>
<td>26.5</td>
<td>83.5</td>
<td>7.25</td>
<td>91.9</td>
<td>14.8</td>
<td>494</td>
<td>3.45</td>
<td>6.92</td>
<td>27.8</td>
</tr>
<tr>
<td>1.48</td>
<td>83.3</td>
<td>74.4</td>
<td>104</td>
<td>26</td>
<td>83.0</td>
<td>6.75</td>
<td>98.4</td>
<td>15.9</td>
<td>512</td>
<td>3.27</td>
<td>7.64</td>
<td>26.7</td>
</tr>
<tr>
<td>1.3</td>
<td>83.3</td>
<td>74.4</td>
<td>104</td>
<td>26</td>
<td>83.5</td>
<td>6.75</td>
<td>97.3</td>
<td>16.3</td>
<td>536</td>
<td>3.22</td>
<td>7.6</td>
<td>28.7</td>
</tr>
<tr>
<td>0.97</td>
<td>82.4</td>
<td>74.2</td>
<td>103</td>
<td>25.5</td>
<td>84.0</td>
<td>7.0</td>
<td>114.9</td>
<td>17.0</td>
<td>556</td>
<td>3.15</td>
<td>10.4</td>
<td>29.2</td>
</tr>
<tr>
<td>0</td>
<td>81.5</td>
<td>74.2</td>
<td>101</td>
<td>26</td>
<td>85.0</td>
<td>6.5</td>
<td>127.0</td>
<td>16.8</td>
<td>536</td>
<td>3.24</td>
<td>11.28</td>
<td>34.2</td>
</tr>
</tbody>
</table>
theory of Payne, discussed in Chapter 3. The progressively falling modulus $M_{100}$ is observed since, at these large deformations all evidence of agglomerate structure would be extinct, and the occluded rubber argument will prevail.

Moving onto Table 7.10 the dump temperature of the base black compound after mixing is this time higher than that produced by the vacuum dessicated blacks. Hardness shows a decrease, as do maximum ODR torque, and Modulus $M_{100}$ with lessening moisture levels. Increasing trends in tear strength, tensile strength, EB, and tear energy are noted. $E'$ shows no trends. Again, by consensus, mixing appears favoured by low levels of moisture, and the results suggest that the closer to a zero moisture level, the better.

Comparing the corresponding columns of Tables 7.9 and 7.10, the following generalisations may be made:

a) Dump temperatures are appreciably higher in the oven dried series.

b) Hardness levels follow the same pattern, oven dried blacks yielding higher hardness than the vacuum dessicated variety.

c) Maximum ODR torque values too are higher for oven dried blacks.

d) Mooney viscosity, cure time, tear strength, tensile strength, EB, modulus $M_{100}$, and tear energy levels do not appear to be affected by the method of moisture extraction.

e) $E'$ values in the oven dried sequences are comparatively higher than in the vacuum dried black mixes.

It appears from this preliminary examination that whatever the method of moisture extraction, mixing is favoured when drier blacks are used.

The results stemming from the final part of this investigation are now examined. It will be recalled that here N660 carbon black, with carefully regulated fines and moisture levels was internally mixed into a Butyl (IIR) rubber curative masterbatch.
TABLE 7.10
Effect of moisture on mixed material properties - N375 black (vacuum dried)

<table>
<thead>
<tr>
<th>Moisture Level (%)</th>
<th>Property</th>
<th>Drying Temperature (°C)</th>
<th>Micro-Vickers Hardness (°VH)</th>
<th>Mooney Viscosity (ML(1+4) 100s)</th>
<th>Min. ODR Torque (in. lbs)</th>
<th>Max. ODR Torque (in. lbs)</th>
<th>Cure time to 95% (mins)</th>
<th>Tensile Strength (MPa)</th>
<th>E.B. (%)</th>
<th>Mod 100 (MPa)</th>
<th>Tear Energy (KJ/m)</th>
<th>E' at peak at 1.5Hz (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8 (non-dried)</td>
<td></td>
<td>75.9</td>
<td>104</td>
<td>26.5</td>
<td>83.5</td>
<td>7.25</td>
<td>91.9</td>
<td>14.8</td>
<td>494</td>
<td>3.45</td>
<td>6.92</td>
<td>27.8</td>
</tr>
<tr>
<td>1.48</td>
<td></td>
<td>64.8</td>
<td>71.9</td>
<td>103.5</td>
<td>26</td>
<td>80</td>
<td>6.5</td>
<td>100.6</td>
<td>14.9</td>
<td>513</td>
<td>3.27</td>
<td>8.72</td>
</tr>
<tr>
<td>1.3</td>
<td></td>
<td>68.5</td>
<td>69.9</td>
<td>103.5</td>
<td>27</td>
<td>81</td>
<td>6.75</td>
<td>94.5</td>
<td>16.4</td>
<td>561</td>
<td>3.15</td>
<td>7.12</td>
</tr>
<tr>
<td>0.97</td>
<td></td>
<td>68.5</td>
<td>72.4</td>
<td>103.5</td>
<td>25</td>
<td>79.5</td>
<td>6.75</td>
<td>113.1</td>
<td>16.3</td>
<td>551</td>
<td>3.05</td>
<td>10.28</td>
</tr>
<tr>
<td>0.65</td>
<td></td>
<td>69.4</td>
<td>69.7</td>
<td>103.5</td>
<td>25</td>
<td>79.5</td>
<td>7.25</td>
<td>98.2</td>
<td>16.9</td>
<td>577</td>
<td>3.01</td>
<td>8.52</td>
</tr>
</tbody>
</table>
Figures 7.6 - 7.19 show the measured processing and property levels associated with mixing each of these test blacks. Each graph contains points both from the good and bad mixing conditions, for easy comparison. Maximum and minimum Monsanto ODR torque and cure times, even though measured, did not change, and are not presented here.

Figures 7.6 and 7.7 show the basic differences in mixing severity caused by the different mixing schedules. The batches mixed under conditions of mixing not conducive to the process have, not surprisingly, overall lower total energy consumption and dump temperatures. The total energy scattergram at bad conditions (Figure 7.6), shows low energies of mixing at constant time for those batches low in fines, and higher levels at higher fines contents. The dump temperature (Figure 7.7), almost totally reflects the mixing energy results, with the exception of the point at 2% fines for the same series. For the good conditions of mixing, both total work and dump temperatures are substantially the same over the entire fines range.

As for the Figures 7.8 - 7.19, the absence of any dominant effects on mixing, which could categorically be related back to fines levels is conspicuous. For the wide range of fines contents studied (0 - 30%, the latter figure being inordinately high), no effects are noted, certainly at the better mixing conditions. Fluctuations are random and are probably caused by experimental and testing error/material variation.

For the bad mixing conditions, one is tempted to generalise as above, but on close scrutiny, it is observed that the batch containing 15% of fines, in most of the graphs being considered, causes levels of properties associated with bad mixing. High values of Mooney viscosity, hardness, $G'$, $G''$, and modulus of 100% strain, combined with low values of fatigue cycles to failure, tensile strength, tear energy and EB lead to this observation. Despite this
FINES CONTENT% VS. PROPERTY [○-good mixing, □-bad mixing]
FINES CONTENT% VS. PROPERTY [ o - good mixing, □ - bad mixing ]

**FIGURE 7.18**

**FIGURE 7.19**
strong evidence of bad mixing, the batch has the highest observed abrasion resistance (Figure 7.9) of both series of compounds. Due to this paradox, the observation made earlier must be tempered with some uncertainty.

Right across the board, the proposed good conditions affect the indicators of mixing beneficially, exemplified by Mooney viscosity, hardness, ring fatigue, tear strength, tensile strength, modulus, tear energies and EB. Also noted is the less variable nature of the stocks mixed under good conditions. This is deduced by treating each of the batches mixed under any one of the conditions specified as being identical (not unreasonable in the light of the mostly negative findings regarding the effect of fines). The badly mixed batches are seen to fluctuate more around their mean, than the better mixed stocks.

Lastly, consider the blacks of varying moisture content, mixed at the two conditions of the process. Before moving on to the results, a word on how a moisture level was allocated to each black. It will be remembered that a small control sample of accurately weighed dry black was placed in each humidity chamber, along with the main black sample for humidifying. These were reweighed after the treatment and the calculated percentage moisture resulting for each humidity cabinet was plotted on a log-linear graph vs log quoted relative humidity at equilibrium in the cabinet. Linear regression by least squares was accomplished for these points to obtain the line of best fit.

A linear model with a logarithmic transform was used with reason, and that was because some data already existed on the moisture adsorption properties of the N660 carbon black in use here. This data, collected for three different humidities, 31, 55 and 79%, when plotted as above, yielded a straight line.

Figure 7.20 shows the results obtained in this research, and their regression line. Also is shown the datum line of Kirschbaum.
Weight % moisture in carbon black

- Kirschbaum
- Experimental/regression

Log equilibrium humidity in chamber (%)

FIGURE 7.20 Absorbed moisture vs humidity
for reference. Note that the regression line derived here is parallel to that of Kirschbaum but exhibits a different intercept. Perhaps this is a function of the varying chamber types used in the two series of humidifying experiments. Moisture levels assigned to the various blacks now to be discussed are derived from the coefficients of the regression equation:

\[ y = 2.78X - 3.77 \]  \hspace{1cm} 7.1

where \( Y \) = moisture estimated in carbon black, and \( X = \) log-equilibrium relative humidity in chamber

These calculated moisture levels were found to be 0.02, 0.41, 0.77, 1.05, 1.29, 1.46, 1.59 and 1.77% by weight of carbon black.

The fact that the effect of varying moisture was to be more critical than varying fines was realised during the mixing of these stocks. During the conditions of bad mixing, the four stocks containing the high moisture levels of black, emerged from the Banbury mixer in crumb form. On inspection, the batch containing 1.77% moisture had hardly incorporated its filler, and this situation became marginally better, through the series (1.59, 1.46%) up to the 1.29% moisture. Even though the batches were substantially crumbed, visual improvements were noted with increasing black dryness. In the same series, with moisture levels of less than 1.29% no further problems of mixing manifested themselves, the change in the dumped batch at 1.05% moisture (the next one down) when compared to that of the 1.29% moisture batch being remarkable, in the abruptness of its sudden tendency towards problem free mixing.

No such visual problems were noted when corresponding blacks were mixed at good conditions of mixing.

Going on now to the property relationships with moisture contents, Figures 7.21 - 7.36 summarise these. Cure times were all
MOISTURE LEVEL% VS. PROPERTY [○-good mixing, □-bad mixing]

**FIGURE 7.21**

Total energy consumed during mixing (MJ)

**FIGURE 7.22**

Minimum ODR torque (in lbs)

**FIGURE 7.23**

Maximum ODR torque (in lbs)

**FIGURE 7.24**

Dump temperature (°C)

**FIGURE 7.25**

Mooney Viscosity (HU)

**FIGURE 7.26**

Abrasion loss weight (%)
the same except for the two highest moisture containing stocks which took longer to cure. The total energy (Figure 7.21) and dump temperature graphs (Figure 7.24) only confirm the visual observations made earlier, for the bad conditions of mixing. For some reason, at high moisture levels, high shear mixing is discouraged. The stocks mixed at good conditions (even though they had showed no visual sign of this) also exhibit the same trends, the intensiveness of mixing decreasing markedly with high moisture levels in the carbon black.

Figures 7.22, 7.23 and 7.25 - 7.36 all amplify this main finding, that under adverse mixing conditions, highly moist blacks do not process at all well. All the properties depicted in these graphs show that at these unfavourable conditions moisture levels of greater than 1.05% without doubt cause inferior properties. Some of these properties were so bad that adequate measurement was not possible on the high moisture stocks. Abrasion loss and ring fatigue are examples of this inferiority. What is surprisingly evident from inspection of these scattergrams is that at moisture levels less than 1.05%, property levels abruptly improve, and are comparable to those levels exhibited by well mixed stocks. Incidentally, over the whole moisture range of the well mixed stocks, no trends are noted, property levels remaining similar, despite early indications to the contrary by the total work and dump temperature criteria. Practically, this indicates that those levels of moisture greater than 1% in N660 (even though critical at bad conditions of mixing), are tolerable in a production process.

7.6 Conclusions

This comprehensive study has considered two types of black (N375 and N660) in a butyl motherstock. The conclusions which follow apply only to the effects of the secondary properties studied on mixing efficiency. The important areas of their effects on handling
and storage of blacks were not considered during this research.

Firstly, it was observed that the novel technique used here for identifying good and bad mixing conditions has proved itself. The bad conditions highlight effects being studied, while the good effectively duplicates a production situation, and indicates the practical relevance of the findings. In all cases studied, certain differences are manifested under the adverse mixing conditions which disappear under the favourable ones. It is possible to form a general conclusion that under optimum conditions, the pellet properties and other secondary traits of blacks are non-critical.

In connection with the above argument it must be cautioned that by the very nature of a bad mixing schedule, wide variations in property will occur in-batch. This must be taken into account, and replication for statistical reliability must be high.

The following specific conclusions accrue from the different stages of experimentation presented here.

1. As shown by the dynamic testing of both the N375 and N660 black containing stocks, the fillers manufactured at Ravenna in Italy are the most difficult to disperse in the system used here. This is now thought to be due to the fact that pelletisation in this case is by the wet method. In the other blacks, the Hanau N375 and N660 was the next most difficult to disperse, and the Stanlow varieties proved to be the easiest. In all cases, these were the findings at the bad conditions of mixing. At good mixing conditions, these observed dispersibility differences all but vanished.

2. In the second series of experimentation, with the N375 blacks at only bad mixing conditions, it seemed that medium fines levels (= 6%) were not promotory of good mixing.
3. Previous ideas regarding ideal and non-ideal pellet size distributions were borne out by research on the same system used in 2. An ideal pellet distribution facilitated better mixing than a non-ideal one.

4. In the next segment of the work, moisture level was varied in N375 by two methods, vacuum dessication and oven drying. This series was mixed (only at bad conditions of mixing) into a butyl base. Apart from certain diversionary results arising on the relative effects of vacuum and oven drying on properties, it was indicated that whatever the method, mixing is better with drier blacks, 0 - 0.9% moisture being the recommended range.

5. The probing experimentation using N660 as the filler, varying fines and moisture, and mixing at both good and bad conditions was next considered. The thoughts on the effects of fines on mixing in 2 above, were not at all reinforced. No optimum level of fines was seen to exist at either set of mixing conditions. Over the wide fines range (0 - 30%) studied, no preferences were manifested in the testing. Appreciably worse dispersion linked properties were noted overall, at the bad conditions of mixing.

6. The next section on the blacks varying in moisture content and mixed under the two sets of mixing conditions yielded the most definitive results. At bad conditions of mixing, moisture levels of greater than 1.05% greatly affected mixing for the worse, as shown unanimously by the property levels. This finding is reinforced by 4 above, where N375 black showed the same trends. The importance of a critical level of moisture however is also conclusively seen to vanish at production type mixing conditions, where shear stresses/strain rates are stringent and conducive to an effective dispersive action.
7.7 Further Work

This segment of research concentrated on evaluating whether in fact, secondary properties of carbon blacks have any appreciable effect on mixing. Since the answer to that question is the affirmative (for moisture at least), it must next be asked why such an effect is noted. Is the answer a chemical one, in which bonds are formed between moisture monolayers and individual black particles, making them resist dispersive mixing? Alternatively, is the explanation a physical phenomenon simplified to a lubrication effect, preventing high shear?

The answers to these questions, even though not critical (since optimum mixing conditions disregard moisture in black in the range studied here as being important), could shed valuable light on the process of dispersive mixing as a whole, to the advantage of the rubber industry.
Literature cited


3. ASTM D3037-71T.


7. ASTM D1510-70.


9. ASTM D2414-65


15. ASTM D1618.
16. ASTM D1514.
17. ASTM D1506.
18. ASTM D1619.
19. ASTM D1508-60.
20. ASTM D1937-62T.
24. ASTM D1511-60.
25. ASTM D1509.
29. USP 3,927,988.
30. USP 3,931,377.
31. USP 3,969,457.
32. USP 4,005,170.
33. USP 3,993,739.
34. BP 754,124.
35. BP 638,863.


CHAPTER 8
SUMMARY AND CONCLUDING REMARKS

To facilitate analysis and discussion, the sections of this dissertation have been compartmentalised. Despite the discrete treatment, it must be emphasised that each segment is, in practice, inexorably linked with the others, and must be viewed as such.

The element of commonality in all four experimental chapters has been the internal mixing of black filled rubbers. This process (like any other) comprises input variables, which influence and regulate the quality of its output. The criterion of acceptability of a rubber stock is, in the final analysis, adequate performance in service. Prior monitoring of quality before service use, at the site of manufacture, is a vital need.

Chapters 4 and 5 describe the evolutionary development of a method for characterising mixed rubbers, suited to a process control environment in industry. Commercial acceptance and exploitation of the technique is probable.

Chapter 6 considered the input variables contributing to the process of rubber mixing and related these to a unique function; this was derived from numerous tests each relating to an aspect of mixing efficiency, in total contributing to an integrated view of product quality. Through the function, related to goodness of mixing, it was possible to explain and examine the process from several points of perspective; to enunciate the consequences of changing processing conditions not only on stock quality, but also on productivity and heat history as well.

Finally in Chapter 7, the effects of black properties on mixing efficiency and compound acceptability were studied. It is important
to remember that in addition to process control innovations, the success of an operation such as mixing depends critically on the quality and specifications of the raw material it utilises. Knowing exactly what range of property variation is tolerable is of utmost importance, if the frequent rejection of batches falling outside specification limits is to be avoided.

An efficient mixing department of the future will have to consider its main process anew. The aim of eliminating the production of unsatisfactory rubber stocks must be paramount; this consideration must be balanced by an awareness of the productivity demands of industry, in terms of labour effectiveness, and utilisation of raw material. Traditional rubber technology must move with the times and be augmented by the other sciences (both old and new) if it is to achieve these ends. It is fervently hoped that some indications of the path to this ideal have emerged from this work.
APPENDIX 1
APPENDIX I

AUTOMATIC ANALYSIS TECHNIQUE

1. Principles

Using the same basic principles as the Loughborough method, i.e. a microscope with a dark-field illumination and a television camera to monitor the image, DTD have developed an automatic analysis system based on a desk-top micro-computer. Fig 5.1 shows the general layout of the DTD system.

To interface the television camera to the computer it is necessary to convert the analogue video signal and sync signals produced by the camera into a suitable digital code that can be processed by the computer.

This conversion is carried out by the video interface board, which consists basically of analogue to digital converter (ADC) and a sample and hold circuit to produce a stable video signal for digitisation. The ADC used to digitize the video signal is of the successive approximation type; this type of device requires several computer clock cycles, i.e. several micro-seconds to digitize an analogue signal. Because of this it is not possible to digitize a line of the television signal, since only a few data points would be obtained per line. To overcome this problem the line and frame sync signals from the camera are interfaced to the computer, which enables the computer to synchronize to the camera so that the point at which the video is sampled is under computer control. By doing this the computer can take a sample at any point along each line of the television signal. Once the sampled video is stable the signal is digitized and stored in the memory of the computer. The point at which the sample is taken is displayed on a television monitor, along with the image of the test piece.

By programming the computer it is possible to take several samples automatically or manually across the surface of the test piece.
piece. Once the data is in the memory of the computer it can be processed to produce a graphical display of reflected light intensity from the sample and an analysis of the peak height and number of peaks above a threshold level. The results obtained from the analysis are analysed by the computer to produce figures relating to the level of carbon black dispersion in the sample, as in the Loughborough method.

A description of the video interface board and computer programs is given in Appendix A1 and A11 respectively.

ii) Mode of Operation

Figure 1 shows the basic sequence of operations required to produce a table of results relating to the level of carbon black dispersion in the test piece.

The first stage in the sequence is the preparation of the sample, details of which have already been given in Chapter 4. The microscope is then set up in accordance with the established technique for dark-field microscopy.

The following sequence of operations are carried out using the computer keyboard and the visual display units (VDU).

At each stage in the test sequence the computer displays on its VDU a prompt question and the form the answer must take. At the beginning of the sequence the computer requires the operator to enter test details; this can take the form of an alphanumeric string enabling the operator to enter special codes to identify the sample, this code is stored in the computer and printed out with the results.

The next prompt question requires the operator to select the mode of analysis, automatic or manual.

In manual mode the point at which the video signal is sampled is under the control of the operator. This enables the sampling bar to be positioned at any one of 170 points across the image dis-
played on the television monitor. Once the point has been selected
the computer is instructed to take a sample by pressing the 'RETURN-
key, the sampled video signal is displayed on the VDU as a trace of
light intensity versus line position down the screen. This dis-
play can be drawn out on the printer for a permanent record if
required. The sampled video signal is processed by the computer
and a table of results printed out at the end of the analysis.

In manual mode a single analysis can take less than two minutes,
if a hard copy of the intensity trace is not required.

If automatic mode is selected the computer will take twenty
samples at regular intervals across the image displayed on the tele-
vision monitor. At every sampling point the computer will display
the trace of reflected light intensity if the prompt question at
the beginning of the run is answered 'yes' (Y): this increases the
analysis time from about four minutes to ten minutes, depending upon
the sample being analysed. At the end of every sample the data is
analysed by the computer and stored in its memory: at the end of the
test the results from each sample are combined to produce an overall
figure relating to dispersion. These results are tabulated and
printed out on paper.

**PHOTOMETER METHODS**

As refinement of the Cabot reflected light method described
above, the subjective comparison of the 'reflectance' of cut or torn
surfaces with standard micrographs has been replaced by the measure-
ment of the intensity of light reflected from a cut surface, using
a photometer to monitor the intensity of a microscope image.

Two microscopes were used to evaluate the method. The M55,
which has a built-in photometer, and the M12 (ex Irish Research Cen-
tre) microscope, with a portable cadmium sulphide light-meter. Razor-
cut surfaces of cured and uncured rubber specimens were illuminated
obliquely (at about 45°) by the Xenon arc source of the M55, or by
twin fibre optic illuminators in the case of the M12 microscope.
A screen magnification of 175X was obtained on the M55, using a X10 objective, but a similar power objective on the M12 gave an inadequate light level for the cadmium sulphide photometer to respond to, and a X5 lens was used instead. The effect of knife-marks on the cut surfaces was minimised by arranging that the latter were illuminated along, rather than across, the direction of the razor-cut. However it was observed that some differences in light-intensity readings occurred between the 'with' and 'against' cutting directions, and the M55 readings were therefore made in each of these directions. (We presume this phenomenon to be due to the topography of the cut surface being slightly distorted in the direction of cutting).

FUTURE DEVELOPMENT

Micro-computer based system

The automatic analysis system developed by DTD is made up of several pieces of readily available commercial equipment with the exception of the video interface board and the computer program.

The system uses a readily available microscope with dark-field illumination and a separate television camera; this set-up presents slight problems in optical alignment. To overcome this problem the existing microscope and camera would have to be replaced by a microscope with a television camera attachment, the microscope having just the dark-field illumination system to keep the optics as cheap and as simple as possible. In the prototype a high quality television camera was used to monitor the image produced by the microscope; for future systems a lower quality camera could be used without loss of definition.

The computer used to process the signals from the video interface is an Apple II microcomputer with 5" floppy disc units for program storage, for future systems a basic Apple II could be used with a minimum store configuration and with a set of 'Read Only Memories' (ROM's) for program storage.
In the prototype, two VDU's were used, one to monitor the output of the television camera and one to display the output of the computer, it would be possible to replace the two units by one and use the computer to control which signal is viewed.

The basic future system could possibly consist of:

1. Microscope and camera.
2. Microcomputer, printer and VDU.
3. Video interface board.

**Photometer Method**

It is envisaged that for routine process-control assessment of filler dispersion, a relatively simple microscope fitted with a 10 x objective, 10 x eyepiece, and cadmium sulphide exposure meter should be adequate. Preferably the microscope should be of inverted design - that is, having its specimen stage above the objective - for ease of positioning the surface to be examined, and also to facilitate the attachment of a light source or sources is an integral part of the system. It has yet to be established whether illumination from a fibre-optic ring source (encircling the objective) is superior to twin illuminators on an axis parallel to any knife-marks in the specimen surface.

It is hoped to set up a suitable system to evaluate the method further, using a range of polymers, filler types (including non-black fillers), filler loadings, and mixing procedures. Further work on the production of representative surfaces, particularly with uncured compounds, is being undertaken, and already there is some indication that a 'razor-blade assisted tear' may avoid the 'smearing' effects described elsewhere.

In the ultimate, it might be possible to produce a more sophisticated form of analysis, wherein parameters related to the size of the reflecting features could be deduced by Fast Fourier analysis.
As further experience is gained, it may be possible with either method, to derive an algorithm involving the size and loading of the filler particles, which would permit the conversion of the arbitrary parameters produced by these techniques into 'absolute' dispersion values. This might be implemented by the equipment directly, or calculated externally.
APPENDIX AI

DESCRIPTION OF VIDEO INTERFACE BOARD

The operation of the video interface is best explained with reference to Figure 2.

The interface board consists of four basic units, these are:

1. Analogue to digital converter \( \text{ADC} \)
2. Digital to analogue converter \( \text{DAC} \)
3. Sample and hold \( \text{S & H} \)
4. Sync separator

The output signal from the television camera consists of three signals, an analogue video signal proportional to the light intensity and a mixed sync signal. The mixed sync signal consists of a series of line and frame sync pulses, the frame pulses occurring once every 20 milliseconds and the line pulses every 64.5 microseconds.

These pulses are separated from the video signal by the sync separator, both the line and frame pulses are interfaced to the data bus of the computers so as to provide timing signal for the computer. The line pulses are used to provide a ramp of length 64.5 microseconds, the ramp and an analogue signal from the DAC are then compared by the comparator; if the two signals are equal then a strobe pulse is produced which is used to enable the sample and hold. The output of the DAC is under the control of the computer program, therefore by increasing or decreasing the output voltage of the DAC it is possible to adjust the delay between the start of the line pulse and the strobe pulse.

When the strobe pulse occurs the sample hold is enabled, causing it to hold the value of the analogue video signal at its input, the sampled signal is now in a stable form for digitization by the ADC. Once the signal has been digitized the computer can
interrogate the ADC at any point in time before the next strobe pulse. The strobe pulse is recombined with the frame and line sync pulses to produce a visual indication on a television monitor of the sampling position.

The circuit diagrams of the analogue and digital sections of the interface cord are shown in Figures 3 and 4 respectively. Figure 5 gives a detailed layout and component list.
APPENDIX AII
COMPUTER PROGRAM

The Apple II microcomputer in its basic form can support two programming languages, BASIC a high level but relatively slow language, capable of performing floating point mathematics and an assembler language which enables high speed machine code routines to be written.

Both these languages are required in the dispersion analysis program, BASIC for the statistical analysis and graphics routines and the machine code for the control and data acquisition of the video signal.

The program can be split into two main sections, the data acquisition routine and the analysis routines. The operation of these routines is best explained with references to Figures 6 and 7.

Figure 7 shows the flow diagram of the machine code data acquisition routine; in this part of the program the signals from the video interface card are monitored by the computer. The frame and line sync signals are interfaced to the computer on bits 7 and 8 of address location C0C2. To sync the computer to the camera the program interrogates bit 8 until it locates a frame pulse. At this point the program branches into another loop where it interrogates the line sync pulse on bit 7; every time a pulse occurs the program logs the digitized video signal in memory location 4000,Y where Y is the line increment. A total of 255 lines are sampled and stored, each sample being greater than or equal to 0 or less than or equal to 255 depending upon the light intensity. When the Y increment reaches 255 the computer 'blesps' to indicate a complete frame sample and returns to the main BASIC program.

The main program has two modes of operation, manual and automatic as shown by the flow diagram in Figure 6, since both modes have a similar operating routine a general description is given.
With reference to Figure 6.

The first series of subroutines provide video interface initialization commands and a general set of operating instructions; at this point the operator can input to the computer test details and the mode of analysis. In each case the computer provides a prompt question and awaits a specific reply.

If manual mode is selected the computer displays the position of the sampling bar and its position relative to the surface of the sample on the television monitor. At this point the operator can position the sampling bar at any one of 170 positions across the screen. At the desired position the operator instructs the computer to sample the video signal, this is done by the machine code subroutine which stores the sampled data in successive memory locations starting at location 4000 Hex. The data is then displayed on the computer's VDU as a graph of reflected light intensity versus line position down the screen. Since the overall light intensity may vary from sample to sample the program reduces the data to a base level which is equivalent to the darkest point on the intensity trace. The program then sorts through the data looking for peaks above the base level and greater than a preset noise margin. The height of every peak located is stored in an array along with the number of peaks found on a particular scan. The positions of the peaks located are displayed on the VDU so that the progress of the program can be monitored.

Using the number of peaks found and the peak height the program calculates using standard statistical techniques, the mean peak height, variance and standard deviation for a particular scan. These results are tabulated and outputted on a small thermal printer. The program then returns to the beginning so that the process can be repeated.

In automatic mode the above sequence of operation is controlled completely by the computer program. Once test details and mode have been entered the computer increments the sampling bar a preset distance. At each increment the video is sampled and processed, the
results being stored in a set of arrays. A total of twenty samples are taken and at the end of the sampling period the individual results are combined together and statistically analysed to produce a mean peak height variance and standard deviation for the whole sample. These results are tabulated and printed out; when this has been completed the program returns to the introduction. In the automatic mode the operator can select to display the reflected light intensity as a graph or as a series of numbers relating to the peak height and number of peaks, the latter being approximately twice as fast.
1. Set up microscope & sample.

Input test details
(Test number, date etc)

Select mode?
A = Automatic
M = Manual

Display intensity trace?
[VDU] (Y/N)

Computer takes 20 samples automatically.

Plot waveforms?
(Hard copy) (Y/N)

Set sampling position.
(Left & right shift keys to move sampling bar, 0-170)

Press return to take sample & display intensity trace (VDU)

Print out of results.

Below this line all operations are computer controlled.
START
CLEAR AREAS, INTERROGATION, INITIATING VIDEO INTERFACE CARD.
INPUT TEST DETAILS
INPUT MODE A- AUTOMATIC M- MANUAL R- RE-START
SELECT MODE
A
M
R

Set Cursor Position - C -
CALL mic, LOG DATA
FIND Min BLACK LEVEL
FIND Peaks & Display
STATISTICAL ANALYSIS
STORE RESULTS
INC COUNTER C
TEST C = S
Y

DISPLAY INTENSITY OF SAMPLED VIDEO
CALL mic, LOG DATA
FIND Min BLACK LEVEL
FIND Peaks & Display
STATISTICAL ANALYSIS

OUTPUT RESULTS ON PAPER.
APPENDIX 2

ANALYSIS OF EXPERIMENTAL DATA -
MVRA BY LEAST SQUARES

Consider the model

\[ y = \beta_1 x_1 + \beta_2 x_2 + \epsilon \]  

(1)

in which we assume that the mean response \( y \) depends linearly on the two variables \( x_1 \) and \( x_2 \); the 'error' term, \( \epsilon \), is included to take account of the inevitable variations in response from run to run at fixed levels of \( x_1 \) and \( x_2 \). The estimates \( b_1 \) and \( b_2 \) of \( \beta_1 \) and \( \beta_2 \) are chosen so as to minimise the sum of squares of the deviations between the predicted and observed value (\( \hat{y} \) and \( y \) respectively) of the response.

\[ \hat{y} = b_1 x_1 + b_2 x_2 \]  

(2)

Using calculus, it can be shown that the least squares estimates of \( b_1 \) and \( b_2 \) may be obtained by solving the normal equations

\[ \Sigma (y - \hat{y}) x_1 = 0, \quad \Sigma (y - \hat{y}) x_2 = 0 \]  

(3)

(2) in (3)

\[ \Sigma (y - b_1 x_1 - b_2 x_2) x_1 = 0, \quad \Sigma (y - b_1 x_1 - b_2 x_2) x_2 = 0 \]  

(4)
Using the estimates of $b_1$ and $b_2$, as stated earlier, the sum of squares $S(b)$ is found to be uniquely minimised:

\[ S(b) = \Sigma (y - b_1 x_1 - b_2 x_2)^2 \]  

(5)

Matrices provide a convenient shorthand method for writing the important equations used in least squares calculations. If a graduating function linear in the parameters is used (where the levels of the variables are known for each experimental run and are not functions of the coefficients), then the mathematical models referred to in equations 6(4) and 6(5) may be written

\[ \gamma = X\beta + \epsilon \]

(6)

where $\gamma$ is the nx1 vector of the expected values of the response, $X$ is the npx matrix of independent variables and $\beta$ is the px1 vector of parameters.

Writing $X_1, X_2 \ldots X_p$ for the columns of $X$, the normal equations

\[ X_1' (y - \hat{y}) = 0, \quad X_2' (y - \hat{y}) = 0 \ldots X_p' (y - \hat{y}) = 0 \]

(7)

These can be combined to give

\[ X' (y - \hat{y}) = 0 \]

(8)

where the prime (') means transpose.
Equations (2) could be written in matrix form as

\[ \hat{y} = Xb \]  \hspace{1cm} (9)

and substitution of (9) into (8) gives

\[ X'(y - Xb) = 0 \]  \hspace{1cm} (10)

or

\[ X'Xb = X'y \]  \hspace{1cm} (11)

Since we suppose that the columns of \( X \) are linearly independent, \( X'X \) has an inverse and

\[ b = (X'X)^{-1}X'y \]  \hspace{1cm} (12)

To exemplify the above, the simple case of fitting a quadratic model

\[ y = \beta_0 + \beta_1 x + \beta_2 x^2 + \epsilon \]

to some 'real' data is used. This records the effect of rotor speed in internal mixing on tear strength of the rubber stock so produced. Table 1 summarises these results.
**TABLE 1**

Influence of rotor speed on tear strength in internal mixing

<table>
<thead>
<tr>
<th>Experiment No</th>
<th>Rotor speed (rpm)</th>
<th>Tear strength (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>73</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>90</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>91</td>
</tr>
<tr>
<td>6</td>
<td>25</td>
<td>87</td>
</tr>
<tr>
<td>7</td>
<td>25</td>
<td>86</td>
</tr>
<tr>
<td>8</td>
<td>25</td>
<td>91</td>
</tr>
<tr>
<td>9</td>
<td>30</td>
<td>75</td>
</tr>
<tr>
<td>10</td>
<td>35</td>
<td>65</td>
</tr>
</tbody>
</table>

The matrices required are:

\[
\begin{array}{ccc|c}
X_0 & X & X^2 & y \\
1 & 10 & 100 & 73 \\
1 & 10 & 100 & 78 \\
1 & 15 & 225 & 85 \\
1 & 20 & 400 & 90 \\
1 & 20 & 400 & 91 \\
1 & 25 & 625 & 87 \\
1 & 25 & 625 & 86 \\
1 & 30 & 900 & 75 \\
1 & 35 & 1225 & 65 \\
\end{array}
\]

\[
X = \begin{bmatrix} x_0 & x & x^2 \end{bmatrix}, \quad y = \begin{bmatrix} y_1 & y_2 & \cdots & y_n \end{bmatrix}, \quad b = \begin{bmatrix} b_0 \\ b_1 \\ b_2 \end{bmatrix}
\] (13)
\[
X'X = \begin{bmatrix}
\Sigma x & \Sigma x^2 & \Sigma x^3 \\
\Sigma x^2 & \Sigma x^3 & \Sigma x^4 \\
\Sigma x^3 & \Sigma x^4 & \Sigma x^5 \\
\end{bmatrix}
\begin{bmatrix}
10 \\
215 \\
5225 \\
\end{bmatrix} =
\begin{bmatrix}
10 \\
215 \\
5225 \\
\end{bmatrix}
\begin{bmatrix}
215 \\
5225 \\
138125 \\
\end{bmatrix}
\begin{bmatrix}
5225 \\
138125 \\
3873125 \\
\end{bmatrix}
\]

(14)

\[
X'y = \begin{bmatrix}
\Sigma y \\
\Sigma xy \\
\Sigma x^2y \\
\end{bmatrix}
\begin{bmatrix}
821 \\
17530 \\
418750 \\
\end{bmatrix}
\]

(15)

Substituting these into (11) we get the normal equations:

\[
\begin{bmatrix}
10 & 215 & 5225 \\
215 & 5225 & 138125 \\
5225 & 138125 & 3873125 \\
\end{bmatrix}
\begin{bmatrix}
b_0 \\
b_1 \\
b_2 \\
\end{bmatrix}
= \begin{bmatrix}
821 \\
17530 \\
418750 \\
\end{bmatrix}
\]

(16)

Specifically, the normal equations are:

\[
10b_0 + 215b_1 + 5225b_2 = 821 \\
215b_0 + 5225b_1 + 138125b_2 = 17530 \\
5225b_0 + 138125b_1 + 3873125b_2 = 418750
\]

The solution of (16) is

\[
\begin{bmatrix}
b_0 \\
b_1 \\
b_2 \\
\end{bmatrix}
= \begin{bmatrix}
10 & 215 & 5225 \\
215 & 5225 & 138125 \\
5225 & 138125 & 3873125 \\
\end{bmatrix}^{-1}
\begin{bmatrix}
821 \\
17530 \\
418750 \\
\end{bmatrix}
\]

(17)
That is $b_0 = 35.66$, $b_1 = 5.26$, $b_2 = -0.128$.

The same treatment is applicable to the polynomials 6(4) and 6(5) in Chapter 6, such that the coefficients of all the specified model terms are obtainable.

Note on estimation of standard errors

A measure of the precision of the estimates of the coefficients (say $b_1$ and $b_2$) of the regressors (say $X_1$ and $X_2$) is obtained as follows.

An estimate of the error variance $\sigma^2$ of the model is:

$$ S^2 = \frac{S_R}{n - p} \quad (1) $$

where $S_R$ is the deviance of the model and $(n-p)$ has been explained before as being the degrees of freedom of the model.

The formula (2) measures correlation between the two estimates $b_1$ and $b_2$

$$ \rho = \frac{-\sum X_1 X_2}{\sqrt{\sum X_1^2 \sum X_2^2}} \quad (2) $$
and using the calculated quantities $S^2$ and $\rho$ the variances of $b_1$ and $b_2$ may be written:

$$\hat{V}(b_1) = \frac{1}{(1 - \rho^2)} \frac{S^2}{\Sigma X_1^2} \quad (3)$$

and

$$\hat{V}(b_2) = \frac{1}{(1 - \rho^2)} \frac{S^2}{\Sigma X_2^2} \quad (4)$$

The standards errors of the estimates $b_1$ and $b_2$ are

$$\sqrt{\hat{V}(b_1)} \quad \text{and} \quad \sqrt{\hat{V}(b_2)}$$

respectively.
APPENDIX 3
THE GLIM PACKAGE

For each response the GLIM package accomplishes the following:

a) Performs a regression analysis and fits a curvilinear model relating the response to the nominated model terms (linear, quadratic and interaction).

b) It lists estimates of the coefficients of the model together with their standard errors. (See note at the end of Appendix 2). By comparing the terms and the standard errors, it is possible to determine whether the effect is statistically significant. A ratio of estimate/standard error is obtained, which is compared with the critical value of a Student's t table, entered at the degrees of freedom appertaining to the assigned model.

Table 1 (overleaf) considers an example where the polynomial is in five linear variables (T, P, S, F, U), five quadratic variables (TT, PP, SS, FF, UU), ten second order cross product terms (TP, TF, TS, TU, PF, PS, PU, FS, FU, SU) and six of the ten possible third order cross product terms (TPF, TPS, TPU, PFS, PFU, FSU) translated into the established notation, the model terms equate to:

\[
\begin{align*}
T &= X_1 \\
TT &= X_1^2 \\
TP &= X_1X_2 \\
TPF &= X_1X_2X_3 \\
P &= X_2 \\
PP &= X_2^2 \\
\vdots \\
etc &= etc \\
\end{align*}
\]

(1)
where \( y \) is the analysed response. In Table 1 of this appendix, 
\[
X_0 = 6.455, \quad b_1 = 0.9375 \times 10^{-1}, \quad b_{11} = 0.2410, \quad b_{12} = 0.1950, \quad \text{and} \quad b_{123} = 0.1269.
\]
The rest of the model coefficients may be extracted from the table.

The standard errors (SE) corresponding to each coefficient offers a measure of the significance of the coefficient. Thus, since the coefficient for the term \( F \) in Table 6 is \(-0.5667\) and its SE is \(0.1569\), a ratio of these two terms equals approximately \(3.6\): this indicates that the probability of the variable \( F \) having a real effect on the response is greater than \(98\%\) (by reference to Students \( t \) table - Ref 57 (in Chapter 6). By the same token, it is possible to state that the probability of \( T \) having a real effect on the response \( y \) is very low.

c) Glim also lists all the observed values (see Table 2) and the fitted values for response \( y \) predicted by the model. The residual is the difference between the fitted and the observed values of \( y \). These are of considerable interest, for example, to help locate points where the model fits badly.

In Table 2 a total of 62 experimental runs have been done. Thus, the 62nd run had an observed value of 6.77 units and a model fitted value of 6.455. Thus the residual equalled \((6.77 - 6.455) = 0.3147\).

d) The package (see Table 1) also calculates the deviance of the model (in this case \(= 41.37\)). The deviance is the sum of squares of the residuals, and as mentioned in Appendix 2, this quantity
### TABLE 1

Coefficients of model, with accompanying standard errors

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Deviance</th>
<th>DF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>41.37</td>
<td>35</td>
</tr>
</tbody>
</table>

Deviance = 41.37  DF = 35

<table>
<thead>
<tr>
<th>Estimate</th>
<th>S.E.</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.455</td>
<td>%GM</td>
</tr>
<tr>
<td>2</td>
<td>0.9375E-01</td>
<td>T</td>
</tr>
<tr>
<td>3</td>
<td>0.1492</td>
<td>P</td>
</tr>
<tr>
<td>4</td>
<td>-0.2887</td>
<td>S</td>
</tr>
<tr>
<td>5</td>
<td>-0.5667</td>
<td>F</td>
</tr>
<tr>
<td>6</td>
<td>0.3167</td>
<td>U</td>
</tr>
<tr>
<td>7</td>
<td>0.2410</td>
<td>TT</td>
</tr>
<tr>
<td>8</td>
<td>0.1210</td>
<td>PP</td>
</tr>
<tr>
<td>9</td>
<td>0.2873</td>
<td>FF</td>
</tr>
<tr>
<td>10</td>
<td>0.3466</td>
<td>SS</td>
</tr>
<tr>
<td>11</td>
<td>0.1173</td>
<td>UU</td>
</tr>
<tr>
<td>12</td>
<td>0.1950</td>
<td>TP</td>
</tr>
<tr>
<td>13</td>
<td>0.6562</td>
<td>TF</td>
</tr>
<tr>
<td>14</td>
<td>0.4700</td>
<td>TS</td>
</tr>
<tr>
<td>15</td>
<td>0.2487</td>
<td>TU</td>
</tr>
<tr>
<td>16</td>
<td>0.1688E-01</td>
<td>PF</td>
</tr>
<tr>
<td>17</td>
<td>0.2156</td>
<td>PS</td>
</tr>
<tr>
<td>18</td>
<td>0.3544</td>
<td>PU</td>
</tr>
<tr>
<td>19</td>
<td>0.4006</td>
<td>FS</td>
</tr>
<tr>
<td>20</td>
<td>0.8919</td>
<td>FU</td>
</tr>
<tr>
<td>21</td>
<td>0.3356</td>
<td>SU</td>
</tr>
<tr>
<td>22</td>
<td>0.1269</td>
<td>TPF</td>
</tr>
<tr>
<td>23</td>
<td>-0.1437E-01</td>
<td>TPS</td>
</tr>
<tr>
<td>24</td>
<td>-0.1644</td>
<td>TPU</td>
</tr>
<tr>
<td>25</td>
<td>0.3487</td>
<td>PFS</td>
</tr>
<tr>
<td>26</td>
<td>0.1587</td>
<td>PFU</td>
</tr>
<tr>
<td>27</td>
<td>-0.9625E-01</td>
<td>FSU</td>
</tr>
</tbody>
</table>
TABLE 2
Observed and fitted values for each experimental run

<table>
<thead>
<tr>
<th>Unit</th>
<th>Observed</th>
<th>Fitted</th>
<th>Residual</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.40</td>
<td>11.39</td>
<td>1.010</td>
</tr>
<tr>
<td>2</td>
<td>7.780</td>
<td>7.958</td>
<td>-0.1783</td>
</tr>
<tr>
<td>3</td>
<td>9.080</td>
<td>8.445</td>
<td>0.6351</td>
</tr>
<tr>
<td>4</td>
<td>7.780</td>
<td>6.741</td>
<td>1.039</td>
</tr>
<tr>
<td>5</td>
<td>7.550</td>
<td>7.402</td>
<td>0.1484</td>
</tr>
<tr>
<td>6</td>
<td>7.330</td>
<td>7.287</td>
<td>0.4258E-01</td>
</tr>
<tr>
<td>7</td>
<td>5.290</td>
<td>5.049</td>
<td>0.2409</td>
</tr>
<tr>
<td>8</td>
<td>5.980</td>
<td>5.892</td>
<td>0.8758E-01</td>
</tr>
<tr>
<td>9</td>
<td>10.81</td>
<td>11.04</td>
<td>-0.2258</td>
</tr>
<tr>
<td>10</td>
<td>10.71</td>
<td>9.044</td>
<td>1.666</td>
</tr>
<tr>
<td>11</td>
<td>9.350</td>
<td>7.616</td>
<td>1.734</td>
</tr>
<tr>
<td>12</td>
<td>6.560</td>
<td>7.352</td>
<td>-0.7916</td>
</tr>
<tr>
<td>13</td>
<td>4.570</td>
<td>4.577</td>
<td>-0.7421E-02</td>
</tr>
<tr>
<td>14</td>
<td>6.640</td>
<td>7.173</td>
<td>-0.5333</td>
</tr>
<tr>
<td>15</td>
<td>4.950</td>
<td>4.540</td>
<td>0.4101</td>
</tr>
<tr>
<td>16</td>
<td>8.620</td>
<td>8.092</td>
<td>0.5267</td>
</tr>
<tr>
<td>17</td>
<td>9.160</td>
<td>8.134</td>
<td>1.026</td>
</tr>
<tr>
<td>18</td>
<td>6.170</td>
<td>6.755</td>
<td>-0.5845</td>
</tr>
<tr>
<td>19</td>
<td>6.740</td>
<td>7.126</td>
<td>-0.3862</td>
</tr>
<tr>
<td>20</td>
<td>8.440</td>
<td>7.475</td>
<td>0.9655</td>
</tr>
<tr>
<td>21</td>
<td>5.670</td>
<td>6.263</td>
<td>-0.5928</td>
</tr>
<tr>
<td>22</td>
<td>7.890</td>
<td>8.201</td>
<td>-0.3112</td>
</tr>
<tr>
<td>23</td>
<td>6.350</td>
<td>5.848</td>
<td>0.5022</td>
</tr>
<tr>
<td>24</td>
<td>8.180</td>
<td>8.744</td>
<td>-0.5637</td>
</tr>
<tr>
<td>25</td>
<td>8.690</td>
<td>8.767</td>
<td>-0.7700E-01</td>
</tr>
<tr>
<td>26</td>
<td>7.300</td>
<td>7.513</td>
<td>-0.2128</td>
</tr>
<tr>
<td>27</td>
<td>7.900</td>
<td>7.710</td>
<td>0.7305</td>
</tr>
<tr>
<td>28</td>
<td>8.100</td>
<td>7.643</td>
<td>0.4572</td>
</tr>
<tr>
<td>29</td>
<td>5.640</td>
<td>5.441</td>
<td>0.1988</td>
</tr>
<tr>
<td>30</td>
<td>8.280</td>
<td>8.775</td>
<td>-0.4945</td>
</tr>
<tr>
<td>31</td>
<td>6.800</td>
<td>7.226</td>
<td>-0.4262</td>
</tr>
</tbody>
</table>

/Continued...
<table>
<thead>
<tr>
<th>Unit</th>
<th>Observed</th>
<th>Fitted</th>
<th>Residual</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>11.15</td>
<td>11.52</td>
<td>-0.3670</td>
</tr>
<tr>
<td>33</td>
<td>5.780</td>
<td>7.232</td>
<td>-1.452</td>
</tr>
<tr>
<td>34</td>
<td>6.490</td>
<td>7.232</td>
<td>-0.7418</td>
</tr>
<tr>
<td>35</td>
<td>7.480</td>
<td>7.607</td>
<td>-0.1268</td>
</tr>
<tr>
<td>36</td>
<td>8.510</td>
<td>7.687</td>
<td>0.9032</td>
</tr>
<tr>
<td>37</td>
<td>5.580</td>
<td>6.641</td>
<td>-1.061</td>
</tr>
<tr>
<td>38</td>
<td>6.870</td>
<td>6.641</td>
<td>0.2290</td>
</tr>
<tr>
<td>39</td>
<td>7.240</td>
<td>7.238</td>
<td>-0.2343E-02</td>
</tr>
<tr>
<td>40</td>
<td>6.650</td>
<td>7.238</td>
<td>-0.5877</td>
</tr>
<tr>
<td>41</td>
<td>7.620</td>
<td>8.738</td>
<td>-1.118</td>
</tr>
<tr>
<td>42</td>
<td>7.160</td>
<td>8.738</td>
<td>-1.578</td>
</tr>
<tr>
<td>43</td>
<td>5.280</td>
<td>6.471</td>
<td>-1.191</td>
</tr>
<tr>
<td>44</td>
<td>8.940</td>
<td>6.471</td>
<td>2.469</td>
</tr>
<tr>
<td>45</td>
<td>9.230</td>
<td>8.419</td>
<td>0.8107</td>
</tr>
<tr>
<td>46</td>
<td>7.880</td>
<td>8.419</td>
<td>-0.5393</td>
</tr>
<tr>
<td>47</td>
<td>6.240</td>
<td>7.264</td>
<td>-1.024</td>
</tr>
<tr>
<td>48</td>
<td>6.600</td>
<td>7.264</td>
<td>-0.6643</td>
</tr>
<tr>
<td>49</td>
<td>5.150</td>
<td>6.291</td>
<td>-1.141</td>
</tr>
<tr>
<td>50</td>
<td>5.680</td>
<td>6.291</td>
<td>-0.6110</td>
</tr>
<tr>
<td>51</td>
<td>6.420</td>
<td>7.558</td>
<td>-1.138</td>
</tr>
<tr>
<td>52</td>
<td>9.030</td>
<td>7.558</td>
<td>1.472</td>
</tr>
<tr>
<td>53</td>
<td>6.570</td>
<td>6.455</td>
<td>0.1147</td>
</tr>
<tr>
<td>54</td>
<td>6.270</td>
<td>6.455</td>
<td>-0.1853</td>
</tr>
<tr>
<td>55</td>
<td>6.200</td>
<td>6.455</td>
<td>-0.2553</td>
</tr>
<tr>
<td>56</td>
<td>6.150</td>
<td>6.455</td>
<td>-0.3053</td>
</tr>
<tr>
<td>57</td>
<td>6.970</td>
<td>6.455</td>
<td>0.5147</td>
</tr>
<tr>
<td>58</td>
<td>7.740</td>
<td>6.455</td>
<td>1.285</td>
</tr>
<tr>
<td>59</td>
<td>5.860</td>
<td>6.455</td>
<td>-0.5953</td>
</tr>
<tr>
<td>60</td>
<td>6.950</td>
<td>6.455</td>
<td>0.4947</td>
</tr>
<tr>
<td>61</td>
<td>6.490</td>
<td>6.455</td>
<td>0.3473E-01</td>
</tr>
<tr>
<td>62</td>
<td>6.770</td>
<td>6.455</td>
<td>0.3147</td>
</tr>
</tbody>
</table>
is minimised in least squares regression. Also the model is stated to have a specified degree of freedom (see Table 1) (DF), in the case above equalling 35. (For a total of \( n \) residuals, because of the need to calculate several sample quantities to replace unknown population parameters, several constraints, \( p \) in number, are induced on these residuals. Calculated sample quantities such as the deviance and the resulting sample variance will have \((n-p)\) degrees of freedom).

Since in this example \( n = 62 \), and \( p = 27 \) (the number of model coefficients estimated), \( DF = 35 \).

e) The programme has a facility by which the residuals may be plotted versus their corresponding fitted value (the linear predictor). Figure 1

FIGURE 1 Linear predictor vs residual scattergram

This gives a visual indication of validity of the assumption made that the variance of the model is roughly equal over the range studied.
END OF SEGMENT, LENGTH 538, NAME G-APMI

0090

FUNCTION QUAD(X,Y)

C) = 0.1, C1,X1,Y1,(Q,V)4,Y1

QUAD = (X*X)*(Y**2)*(Y0**2)**2*(Y0**2)**2*(X1*x)**2*(Y1*y)**2

END OF SEGMENT, LENGTH 40, NAME QUAD

0090

END
ISOMETRIC PROJECTION PROGRAM

0014 MASTER GRAPH
0015 C_ISOProj 2
0017 INTEGER V1,V2,V3,V4
0018 INTERNAL
0019 DIMENSION Z(640,4096),(10000),X4(4),Y4(4),VAR(4),E(2)
0020 COMMON C,XL,YL,X4,Y4,XY1
0021 EXTERNAL QUAD
0022 CALL C
0023 90 FORMAT (F0.0)
0024 91 FORMAT (F0.0)
0025 92 FORMAT (F0.0)
0026 93 FORMAT (F0.0)
0027 94 FORMAT (F0.0)
0028 95 FORMAT (F0.0)
0029 100 CONTINUE
0030 READ (4,30) VAR
0031 30 FORMAT (F0.0)
0032 31 FORMAT (F0.0)
0033 32 FORMAT (F0.0)
0034 33 FORMAT (F0.0)
0035 34 FORMAT (F0.0)
0036 35 FORMAT (F0.0)
0037 36 FORMAT (F0.0)
0038 37 FORMAT (F0.0)
0039 38 FORMAT (F0.0)
0040 39 FORMAT (F0.0)
0041 40 FORMAT (F0.0)
0042 41 FORMAT (F0.0)
0043 42 FORMAT (F0.0)
0044 43 FORMAT (F0.0)
0045 44 FORMAT (F0.0)
0046 45 FORMAT (F0.0)
0047 46 FORMAT (F0.0)
0048 47 FORMAT (F0.0)
0049 48 FORMAT (F0.0)
0050 49 FORMAT (F0.0)
0051 50 FORMAT (F0.0)
0052 51 FORMAT (F0.0)
0053 52 FORMAT (F0.0)
0054 53 FORMAT (F0.0)
0055 54 FORMAT (F0.0)
0056 55 FORMAT (F0.0)
0057 56 FORMAT (F0.0)
0058 57 FORMAT (F0.0)
0059 58 FORMAT (F0.0)
0060 59 FORMAT (F0.0)
0061 60 FORMAT (F0.0)
0062 61 FORMAT (F0.0)
0063 62 FORMAT (F0.0)
0064 63 FORMAT (F0.0)
0065 64 FORMAT (F0.0)
0066 65 FORMAT (F0.0)
0067 66 FORMAT (F0.0)
0068 67 FORMAT (F0.0)
0069 68 FORMAT (F0.0)
0070 69 FORMAT (F0.0)
0071 70 FORMAT (F0.0)
0072 71 FORMAT (F0.0)
0073 72 FORMAT (F0.0)
0074 73 FORMAT (F0.0)
0075 74 FORMAT (F0.0)
0076 75 FORMAT (F0.0)
0077 76 FORMAT (F0.0)
0078 77 FORMAT (F0.0)
0079 78 FORMAT (F0.0)
0080 79 FORMAT (F0.0)
0081 80 FORMAT (F0.0)
0082 81 FORMAT (F0.0)
0083 82 FORMAT (F0.0)
0084 83 FORMAT (F0.0)
0085 84 FORMAT (F0.0)
0086 85 FORMAT (F0.0)
0087 86 FORMAT (F0.0)
0088 87 FORMAT (F0.0)
0089 88 FORMAT (F0.0)
0090 89 FORMAT (F0.0)
0091 90 FORMAT (F0.0)
0092 91 FORMAT (F0.0)
0093 92 FORMAT (F0.0)
0094 93 FORMAT (F0.0)
0095 94 FORMAT (F0.0)
0096 95 FORMAT (F0.0)
0097 96 FORMAT (F0.0)
0098 97 FORMAT (F0.0)
0099 98 FORMAT (F0.0)
0100 99 FORMAT (F0.0)
0101 100 FORMAT (F0.0)
STOP
END

END OF SEGMENT LENGTH

FUNCTION QUAD(X,Y)
COMMON C, XL, YL, XQ, YQ, XQ, YQ
QUAD=(XL*XL)+(YL*YL)+(XQ*2)+(YQ*2)+(XQ*YQ)
RETURN
END

END OF SEGMENT LENGTH

FINISH
APPENDIX 6
CONVERSION OF AIR LINE PRESSURE TO SPECIFIC RAM PRESSURE
(BAMbury onC)

<table>
<thead>
<tr>
<th>Specific Ram Pressure (PSI)</th>
<th>Line pressure (PSI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.48 MPa</td>
<td>485</td>
</tr>
<tr>
<td>0.395 MPa</td>
<td>60</td>
</tr>
<tr>
<td>0.309 MPa</td>
<td>40</td>
</tr>
<tr>
<td>0.224 MPa</td>
<td>20</td>
</tr>
<tr>
<td>0.1379 MPa</td>
<td>25</td>
</tr>
</tbody>
</table>
APPENDIX 7

FORMULATIONS OF VARYING FILL FACTOR FOR
OOC BANBURY
(Weights in grammes)

<table>
<thead>
<tr>
<th></th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
<th>0.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR 1712</td>
<td>1100.0</td>
<td>1334.0</td>
<td>1554.0</td>
<td>1774.0</td>
<td>1994.0</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>48.0</td>
<td>58.2</td>
<td>67.8</td>
<td>77.4</td>
<td>87.0</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>32.0</td>
<td>38.8</td>
<td>45.2</td>
<td>51.6</td>
<td>58.0</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>8.0</td>
<td>9.7</td>
<td>11.3</td>
<td>12.9</td>
<td>14.5</td>
</tr>
<tr>
<td>Accelerator</td>
<td>4.8</td>
<td>5.8</td>
<td>6.8</td>
<td>7.7</td>
<td>8.7</td>
</tr>
<tr>
<td>Sulphur</td>
<td>32.0</td>
<td>38.8</td>
<td>45.2</td>
<td>51.6</td>
<td>58.0</td>
</tr>
<tr>
<td>Carbon black</td>
<td>320.0</td>
<td>388.8</td>
<td>452.0</td>
<td>516.0</td>
<td>580.0</td>
</tr>
<tr>
<td></td>
<td>1544.8</td>
<td>1874.1</td>
<td>2182.3</td>
<td>2491.2</td>
<td>2800.2</td>
</tr>
</tbody>
</table>
487

•,
•
5

•
•
•
,.
7

11
12

,."
"
"
z."
15
17

Z1

ZZ

",.
Z5
Z6

.
Z7
Z8

JO

",."

-\
-\
-1

-\
-\
-\
-\
-\
-\
-\

-\
-\
-\
-\

-1
-\

..

+\
+\
+1
+1
+\
+1
+\
+1
+1
+\

+1
+1

..
+\

+\

APPENDIX I:

fUlL EXPERINENTAl RESULTS

rs It

...1
-1
..1
-1

-1
+1
-1

17.5

sa

11.5

49

+.

-1
-1
+1
+1
-\

+1

-1

-1

.1

-1

+1

+\
+\

..1
-I.
-1
-1
..1
-1

.1

-1

• +1

-I

+1
+1

-1
-1
+1

.,+, _.,
+1

+1
+1
+\

+\
+\
+\

.
.."
..,
..
.\

'S

SO

"

52

"54

."
.."
..
.."
59

••

••

••
••
••
•o

o
o

•o•

54
48
58 5
53.5
51.5
56.5
49.5
52.5

132

.1
-1
.,

382 65
115.24
23i.05
21H.7
215.35
214.0
238 04
Z47.4
2" 89
218.38
210.90

135
Ha
167
11&
115
127
131
120
1Zt
125
123

+\

+\

o
o

-.

0

+Z

•

·· -.-.
o

16.5
12
18
13
13.5
1&
14.5
1] 5
1] 5
11.5
115.5
15
16

173.5

+1.

o

145
159
103
110
118
125
123
136

+,

.\

O.

n.5

109.61
22&.23
225.38
CS] 89
135 J]
25].74
189.36
421.27

..,

+\

+1
-\
-1

• -.
•
•• +.
••

12.5

156
102
109
114
120

+\
+\

o

135

133

-Z

+.

52.5

372.'

pS.2

o

••
•••
••
••

49

16

249.3
240.02
395,56
126.93
238.15

+1

".. -.-. •• • •o
,. +.+. •• •• oo
,. •• -. •• •o
. • +. • o
37

10.5

+1
..,
.1
-1

-\
-1
+\

+\
+\

247.94 113
168.8 127

-1

..1
-1
-1

-\

53.5
SI
49 5
54.75
50
48.5
55.75
515.5

+1
-\
-1

-1

-1
-1

+\
+1
+1
+1
-1
-1
-1
-\

156
97

ss

+\

-1

-\

245.,5
199.02

16
14
17.5
11
15.15
15.5
'4
IS.S
16 5

-\
-\

-\
-\
+1
+1
-\
-1
+\
+\

-1
-\
-1

97
103
110
11i
125
133
130

-1
+1
-1
+1
-\
+1
-1
+1
-1
+1
-\
+1
-1
+\
-1
+I
..I
+1

+1
+1

+.

+\

ZOS.S
430.33
127.72
250.9$
184.t8
396.18
122.05

0

+2

+.

o
o
o
o

o

o

o
o

o
o
o
o
o

407.04 100
123 34 113

258 16 108
248.44 104
217.46 169
222.48 169
417.95

"

o

448.37 102

o

151.16 140
149.76 136
80,49 .,
753
98

o

o

•

..2
-2

•

+2

361 88 126

o

0

+2

o

•

o
o
o
o

0
0
0
0

310
230
21]
218

o

0

•o ••
o
o

0
0

•

0

o
o
o

o
o

o
o
o

o
o

7 11'
48 123
42 119
1 121
224.70 122
21] 08 '22
201.74 127
220.46 124
215.4 122
220.15 123
223.92 12]

n.5
14
13.5
1&.5
16

"

'4.5
115.5

12
13.5

4'
46.5
57.25
55.5
55.5
54
54.5
51.5
56
49
50

54.5
55.5
51.5

48 5

16.25 55.5

15.5

56

11
12

55.5
50

14.5 54
12.75 48
'6
51.5
12
51
13.5 53

13.5
15

16
IS
1!.5
9.5

1]
1]

".5

54
51
51.5
49
54.5
44 5
50
49
53.25
51
54
52

12
15 5
12.5
12
so
14
55
14.75 52.5
15
54 S

POINT MIXING TRIAL

70.a
515 2

12.4
7.78

n.l

9.OB

615.0
74.S
62.3

7.78
7.55
7.33

340
277

311
282
266
282
n.] S.H 207
59.2
5.98 252
69.' 10.al 350
57.4 10.71 338
70 Z
9.35 288
SI.8
6.56 247
75.7
4.57 162
sa.I
6 64 ... 261
74.5
4 95~ 171
73.]
8 6Z 30]
74.5
9.16 295
56.!
6.17 242
70.2
6.74 226
59.8
a 44 262
225
7l.3 5.67
56.2 7.89
282
227
70.8 6.35
300
67.2 8.18
745 8.n
268
59.8 7.]
260
25]
73.9 7.9
58 15 8.1
243
73.] 5 64
20\1
322
151.1 828
715.] 6.8
187
70.8 11.15
281
240
67.2 5.78
66.6 6.49
251
68.4 7.4.
248
68.4 8.51
270
245
n.l 5.58
69.0 6.87
268
n.6 7.24
221
64.7 6 65
231
67.5 762
289
261
64 1 7.11
67. 5.28
203
294
78 t
8.94
67.2 9 2]
293
263
67.t 7.88
63.4
1511
873
76.3
68.0
51.3
67 8
64.7
67.2
68.4

6.!4
6.6
5.15
5.68
6.42
6.57
15.27
6.2
6.15

67.2

697

68.4

7.74

67.2

5 86

68.4
64.7
65.3

6.95
6.49

9.03

'.n

207
241
149
170
24]
337
245

3.17
2.35
2.59
2.13
2.49
Z 21
2.3]

58.!
54.]
515.7
57.8
5t.1

....

55.l
51 ••
57.7
54.8
57.3
5] 4
57.5
53.8
58.1

9 64
969
11.47
n.06
1098

t.S5
11..

4 05
7.72
3.65
5.04

104.7
1]3.9
91.5
10fi.]

4.39
5.sa

116.1

IOZ.'

4.1'
HI
5.2
101.,
4.69 105.1
!]
9.68
7.9! 132.0
2.64
t.57
4.34 103.9
2.09
10.14
5.72 108.
2'
1].",
5.32 lot.l
2.ll
9.88- 5.93 1150-- - - - - - 28
1201
3.42
91.9
2.5
54. 10.44
8.14 132.1
2.SZ
56.4
9 54
4.5a 113.3
227
55.9
t.94
I5.H 123.a
2.89. 55.] 10 •
4.38
99.7
2.B5
55.5
I.Bi
5.65 120.0
54 9
11.0
4.33 9fi 6
2.47
54.7
9.79 6.53 118.]
2.52
56.1
10.49 3.42 86 5
2 89
54.5
12 26 ti 62 133]
2.35
57 4
9 04 4.38 107.!
3 03
8.54 4.47 lOS.5
52.0
2.52
2.98
56.7
10.71 3.15 95.9
52
9.19 5.61 114.3
3.04
12.01 4.38 107.1
57.3
2.78
2.15
52.3
11.88 7.2 1329
60'0_ 11.78 3.14_91.4~ ______________
3.7
10.26 7.31 129.5
56.1
2.73
2.]3
46:6
9.73 4.96 101.1
56.8
2.4
9 68 6.11 119.1
2.14
4.5 105.5
57.1
9.45
2.86
857
8.71 148.1
57.0
2.22
51.8 15.61
7.7 122.'
2.44
55.9
8.1.
4.SS 104.5
8.46 • 5 29 11]••
54••
3.13
9.28
4 88 lee,
2.72
98
'.04 11&.9
2 44

1.95
! 53

1] 06
10.n

II

2 48

2.sa
2.51
2.n
2.157

2.1l

2.7
3.7
3.48
2.35
2.24
2••
243 2.51
260 2.59
212 2.71
2]7 2.n
250 2.715
211 2 54
227 2.91
2)1' t.64
247 %.57

........

I

1

10.~

57.7
54.6
50.9
56.1

10."
10.31

5.57 111.0
S.Ofi 109.5
7.32 136.5

10.43

& 43 122.1

57.4

8.79

59.5
54.2
62.1
54.'

'.54
12.62
12.77
13.22
8.63
10.79
10.71
10.66
9.05
13.00
10.13

55.6
53.5
55.1
51.0
63.5
57.0

57.3
58.1
56 5
58.0

ss.]
sa.6

8 at
9.42
t.74
t.lI
10.5t

5.25 115.7
5.67 112.&
4.76
97.5
3.74
4.19
5.85

663
$.70
0.58
5.94
6.38
6.24
4.1
6 ai
4.t3
5.66
5.15

91.2
95.4

111.1
115.1
113.4
115.4
114.'
122.7
121.4
104.5
11&.1
111.5
113.9
109.4


APPENDIX 9
FLOW CHART FOR PROGRAMME FOR CALCULATION
OF THE DESIRABILITY FUNCTION

START

INPUT: NUMBER OF DEPENDANT VARIABLES?
      : NUMBER OF EXPERIMENTAL RUNS?

ASSIGN DIMENSIONS

FOR EACH RESPONSE
INPUT: RESPONSE NAME
INPUT: INDIVIDUAL OBSERVATIONS AT EACH EXPERIMENTAL POINT
INPUT: WEIGHTING FACTOR FOR d
BUILD IN CHECKS
INPUT: WORST VALUE
INPUT: BEST VALUE

FOR EACH RESPONSE
CALCULATE: $b_1$, $b_0$
CALCULATE: $Y'$ FROM $Y$, $b_1$, $b_0$
CALCULATE: $d$ FROM $Y'$
CALCULATE: WEIGHTED $d$ FROM $d$ WEIGHTING FACTOR

FOR EACH RESPONSE
PRINT: RESPONSE NAME, BEST VALUE, WORST VALUE, $b_1$, $b_0$, BEST $d$, WORST $d$
PRINT: EXPERIMENT NO, $Y$, $Y'$, $d$, WEIGHTED $d$

WHEN THE ABOVE VALUES FOR ALL RESPONSES TO BE CONSIDERED ARE CALCULATED,
CALCULATE $D$ FOR EACH EXPERIMENTAL POINT. MULTIPLY $D$ BY 1000

PRINT EXPERIMENT NO; $D \times 1000$

END
<table>
<thead>
<tr>
<th>EXPERIMENT</th>
<th>RESPONSE VALUE</th>
<th>SCALED VALUE</th>
<th>LOW CASE D</th>
<th>WEIGHTED LCD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.65</td>
<td>-0.5</td>
<td>1.12</td>
<td>1.12</td>
</tr>
<tr>
<td>2</td>
<td>7.72</td>
<td>1.32</td>
<td>1.28</td>
<td>1.06</td>
</tr>
<tr>
<td>3</td>
<td>3.65</td>
<td>-0.94</td>
<td>0.86</td>
<td>0.86</td>
</tr>
<tr>
<td>4</td>
<td>5.34</td>
<td>0.53</td>
<td>0.57</td>
<td>0.57</td>
</tr>
<tr>
<td>5</td>
<td>4.33</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>6</td>
<td>5.98</td>
<td>-1.17</td>
<td>0.72</td>
<td>0.72</td>
</tr>
<tr>
<td>7</td>
<td>4.16</td>
<td>-0.78</td>
<td>0.57</td>
<td>0.57</td>
</tr>
<tr>
<td>8</td>
<td>5.69</td>
<td>2.38</td>
<td>3.13</td>
<td>3.13</td>
</tr>
<tr>
<td>9</td>
<td>3.29</td>
<td>0.23</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>10</td>
<td>7.32</td>
<td>2.31</td>
<td>3.13</td>
<td>3.13</td>
</tr>
<tr>
<td>11</td>
<td>5.24</td>
<td>1.33</td>
<td>0.72</td>
<td>0.72</td>
</tr>
<tr>
<td>12</td>
<td>5.33</td>
<td>2.33</td>
<td>3.13</td>
<td>3.13</td>
</tr>
<tr>
<td>13</td>
<td>5.99</td>
<td>3.14</td>
<td>0.57</td>
<td>0.57</td>
</tr>
<tr>
<td>14</td>
<td>4.33</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>15</td>
<td>3.14</td>
<td>3.14</td>
<td>0.57</td>
<td>0.57</td>
</tr>
<tr>
<td>16</td>
<td>4.33</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>17</td>
<td>4.33</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>18</td>
<td>3.14</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>19</td>
<td>4.33</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>20</td>
<td>2.02</td>
<td>0.57</td>
<td>1.32</td>
<td>1.32</td>
</tr>
<tr>
<td>21</td>
<td>3.42</td>
<td>1.64</td>
<td>0.94</td>
<td>0.94</td>
</tr>
<tr>
<td>22</td>
<td>2.31</td>
<td>0.57</td>
<td>1.32</td>
<td>1.32</td>
</tr>
<tr>
<td>23</td>
<td>2.31</td>
<td>0.57</td>
<td>1.32</td>
<td>1.32</td>
</tr>
<tr>
<td>24</td>
<td>2.31</td>
<td>0.57</td>
<td>1.32</td>
<td>1.32</td>
</tr>
<tr>
<td>25</td>
<td>2.31</td>
<td>0.57</td>
<td>1.32</td>
<td>1.32</td>
</tr>
<tr>
<td>26</td>
<td>2.31</td>
<td>0.57</td>
<td>1.32</td>
<td>1.32</td>
</tr>
<tr>
<td>27</td>
<td>2.31</td>
<td>0.57</td>
<td>1.32</td>
<td>1.32</td>
</tr>
<tr>
<td>28</td>
<td>2.31</td>
<td>0.57</td>
<td>1.32</td>
<td>1.32</td>
</tr>
<tr>
<td>29</td>
<td>2.31</td>
<td>0.57</td>
<td>1.32</td>
<td>1.32</td>
</tr>
<tr>
<td>30</td>
<td>2.31</td>
<td>0.57</td>
<td>1.32</td>
<td>1.32</td>
</tr>
<tr>
<td>31</td>
<td>1.32</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>32</td>
<td>1.32</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>33</td>
<td>1.32</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>34</td>
<td>1.32</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>35</td>
<td>1.32</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>36</td>
<td>1.32</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>37</td>
<td>1.32</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>38</td>
<td>1.32</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>39</td>
<td>1.32</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>40</td>
<td>1.32</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>41</td>
<td>2.14</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>42</td>
<td>2.14</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>43</td>
<td>2.14</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>44</td>
<td>2.14</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>45</td>
<td>2.14</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>46</td>
<td>2.14</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>47</td>
<td>2.14</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>48</td>
<td>2.14</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>49</td>
<td>2.14</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>50</td>
<td>2.14</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>51</td>
<td>2.14</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>52</td>
<td>2.14</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>53</td>
<td>2.14</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>54</td>
<td>2.14</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>55</td>
<td>2.14</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>56</td>
<td>2.14</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>57</td>
<td>2.14</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>58</td>
<td>2.14</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>59</td>
<td>2.14</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>60</td>
<td>2.14</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>61</td>
<td>2.14</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>62</td>
<td>2.14</td>
<td>-1.13</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>EXPERIMENT</td>
<td>DESIRABILITY FUNCTION</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>-----------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>422.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>377.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>324.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>460.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>222.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>742.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.5</td>
<td>514.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>152.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.5</td>
<td>562.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.0</td>
<td>221.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.5</td>
<td>553.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>311.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.5</td>
<td>133.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.0</td>
<td>134.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.5</td>
<td>587.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>645.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.5</td>
<td>455.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.0</td>
<td>535.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.5</td>
<td>499.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.0</td>
<td>533.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.5</td>
<td>136.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.0</td>
<td>37.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.5</td>
<td>695.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.0</td>
<td>544.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.5</td>
<td>347.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.0</td>
<td>491.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.5</td>
<td>456.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.0</td>
<td>559.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.5</td>
<td>559.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17.0</td>
<td>634.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17.5</td>
<td>705.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18.0</td>
<td>658.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18.5</td>
<td>751.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19.0</td>
<td>663.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19.5</td>
<td>719.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20.0</td>
<td>551.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20.5</td>
<td>611.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21.0</td>
<td>621.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21.5</td>
<td>368.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22.0</td>
<td>332.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22.5</td>
<td>771.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23.0</td>
<td>704.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23.5</td>
<td>721.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24.0</td>
<td>575.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24.5</td>
<td>688.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25.0</td>
<td>634.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25.5</td>
<td>716.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26.0</td>
<td>521.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26.5</td>
<td>721.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27.0</td>
<td>523.12</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**COMPUTER GRAPHICS COLOUR PROGRAM**

PR IIIE SYSB LINE 5
LOaIN PLERSE
LOaIN QWE,PTRS,PCE5
051
WORD?
E.~ION
LF/LUCC
COMPUTER
GRAPHICS
COLOUR
PROGRAM

LOGGED IN: RPT)IX
SLIST JR8CCC
INT:GER*2 N, NI:1, N!2, HR,

J!, J~,

C1., C;!,

C2.

CRESP,CON
INTEaER*4 NeREsp,VEND
INTEgE.

C.. XL .. VL, XQ, YQ, XR,.'I!Ul, HAXI, TE.''!P, RRNGE,

111NH,

!1A.<H", !NCR

REflL aIWD, Le6,

6), 0(0, 6),

Z(6,15), !Z(6,

2(1),

Z(18, '.9),

lW(lleoe.', VflL(6).I'EIaHTC6)

COI'!!10N /co/al1, L, Q, 12, IZ/QU/C, XL, YL, XQ,

XY!

IV/VflL/CONV.QR/C1,

C~/CONRES/C.~ESP/NOCO,'N,

fl!2,

NB

EXTERNlL CO£FF,QUflO

2COLOUR(!2)

COLOU!U!8~", COLOURC!l),

COLOUR(!~,,/

PEO

',

"GREEN", "PLUE",

"VTEL'

..,

'OU "fifPGE', 'NTA

'/

fD

IN NunS£R OF
'.~RIIlBLES
REIlD (5, *)

NI2=N*(N-l)/2

NI1=N.IN-l) OCN-2.'/6

liD

IN NllnES OF

1'I1.~

fRBLES
REIlD (5,28)

RVflR(I)

I

FORnIlT(f14)

DO 128 I=1,N

IF(VIlL(I)

LT

8

GOTO 128

IF(J I EO 8)GOTO 118

C2-1

GOTO 128

Cl-I

Jl=l

CONTINUE
WRITE(1, 110) YER(1)
FORMAT(1X, 'HORIZONTAL AXIS', 4X, A2)
WRITE(1, 120) YAR(A2)
FORMAT (1X, 'VERTICAL AXIS', 4X, A2)
LC AXIS OF EXP REGION ON PLOTS
SUM=0
DO 700 I=1,N
SUM=SUM+VAL(I)**2
CONRAD-SORT(N-SUM**2)
ITILISE COUNTER FOR NUMBER OF PLOTS
CON=1

EAR SCREEN AND REQUEST FRAME AND SCALE
CALL PICCEL(0)
CALL PICCEL(1)
CALL PICCEL(2)
CALL PICCEG(0)
CALL SETRAN(0)
WRITE (1, 150)
FORMAT ('TYPE NAME OF RESPONSE TO BE PLOTTED')
PEAD(1, 120) NCRESP
FORMAT( 14)
DO 160 I=1, NP
IF(SVAR(I) EQ NCRESP) NCRESP=1
CONTINUE

CALL SUBROUTINE TO CALG COEFFS OF QUAD
CALL COEFF
LOT CONTOURS
CALL FUNرد(QUAD, 40., -2 0.2 0.4 0., -2 0.2 0.2, 19000., N)
IF(CON NE 1) GOTO 720

RAW SCALE
CALL CHASIZ(3, 0 0)
CALL PENSEL(2, 0 0)
CALL DRACON(40., -2 0.2 0.4 0., -2 0.2 0.2, 19000., N)
CALL CHASIZ(6 0 0)
CALL CONSR(-2 0.0 0.0, XLL, YLL)
CALL CONSR(0 0.2 0.0, XBL, YBL)
XLL=XLL-21.0
YLL=YLL-5.0
XBL=XBL-18.0
YBL=YBL-22 0
CALL PENSEL(15 0 0)
CALL MOVTI(XBL, YBL)
CALL CHARR(VAR(2), 1, 2)
CALL MOVTI(XLL, YLL)
CALL CHARR(VAR(2), 1, 2)
HADE APER OUTSIDE EXPERIMENTAL REGION
CALL PENDEL(4 6560., 0)
CALL CONSR(0 0 0.0, XC, YC)
CALL CONSR(CONRAD 0 0, XSC, YSC)
CALL CONSR(0 0 0.0, XSR, YSR)
CALL CONSR(-2 0.0 0.0, XSR, YSR)
SLL=(XC-XSL)
SLL2=SLL**2
CALL PICCEG(1)
CALL PICCEG(1)
CALL MOVTI(YSC, YSC)
CALL ARCTO1(XC, YC, XSL, YSL, 1)
CALL LINTO2(XSL, YSL)
CALL LINEY2(0 0 0 1)
CALL LINEY2(SLL2 0 0)
CALL LINTO2(XSR, YSR)
CALL LINTO2(XSC, YSC)
CALL PICCEG(2)
CALL PICCEG(2)
CALL PICCEG(2)
CALL MOVTI(YSC, YSC)
CALL ARCTO1(XC, YC, XSL, YSL, 0)
CALL LINTO2(XSL, YSL)
CALL LINEY2(0 0 -SLL)
CALL LINTO2(XSR, YSR)
CALL LINTO2(XSC, YSC)
CALL PICCEG(2)
CALL PICCEG(2)
CALL PICCEG(2)
CALL MOVTI(YSC, YSC)
CALL ARCTO1(XC, YC, XSL, YSL, 0)
CALL LINTO2(XSL, YSL)
CALL LINEY2(0 0 -SLL)
CALL LINTO2(XSR, YSR)
CALL LINTO2(XSC, YSC)
CALL PICCEG(2)
CALL PICCEG(2)
CALL PICCEG(2)
CALL MOVTI(YSC, YSC)
CALL ARCTO1(XC, YC, XSL, YSL, 0)
CALL LINTO2(XSL, YSL)
CALL LINEY2(0 0 -SLL)
CALL LINTO2(XSR, YSR)
CALL LINTO2(XSC, YSC)
CALL PICCEG(2)
CALL PICCEG(2)
CALL PICCEG(2)
CALL MOVTI(YSC, YSC)
CALL ARCTO1(XC, YC, XSL, YSL, 0)
CALL LINTO2(XSL, YSL)
CALL LINEY2(0 0 -SLL)
CALL LINTO2(XSR, YSR)
CALL LINTO2(XSC, YSC)
CALL PICCEG(2)
CALL PICCEG(2)
CALL PICCEG(2)
CALL MOVTI(YSC, YSC)
CALL ARCTO1(XC, YC, XSL, YSL, 0)
CALL LINTO2(XSL, YSL)
CALL LINEY2(0 0 -SLL)
CALL LINTO2(XSR, YSR)
CALL LINTO2(XSC, YSC)
CALL PICCEG(2)
CALL PICCEG(2)
CALL PICCEG(2)
CALL MOVTI(YSC, YSC)
CALL ARCTO1(XC, YC, XSL, YSL, 0)
CALL LINTO2(XSL, YSL)
CALL LINEY2(0 0 -SLL)
CALL LINTO2(XSR, YSR)
CALL LINTO2(XSC, YSC)
CALL PICCEG(2)
CALL PICCEG(2)
CALL PICCEG(2)
CALL MOVTI(YSC, YSC)
CALL ARCTO1(XC, YC, XSL, YSL, 0)
CALL LINTO2(XSL, YSL)
CALL LINEY2(0 0 -SLL)
CALL LINTO2(XSR, YSR)
CALL LINTO2(XSC, YSC)
CALL PICCEG(2)
CALL PICCEG(2)
CALL PICCEG(2)
CALL MOVTI(YSC, YSC)
CALL ARCTO1(XC, YC, XSL, YSL, 0)
CALL LINTO2(XSL, YSL)
CALL LINEY2(0 0 -SLL)
CALL LINTO2(XSR, YSR)
CALL LINTO2(XSC, YSC)
CALL PICCEG(2)
CALL PICCEG(2)
CALL PICCEG(2)
CALL MOVTI(YSC, YSC)
CALL ARCTO1(XC, YC, XSL, YSL, 0)
CALL LINTO2(XSL, YSL)
CALL LINEY2(0 0 -SLL)
CALL LINTO2(XSR, YSR)
CALL LINTO2(XSC, YSC)
CALL PICCEG(2)
CALL PICCEG(2)
CALL PICCEG(2)
CALL MOVTI(YSC, YSC)
CALL ARCTO1(XC, YC, XSL, YSL, 0)
CALL LINTO2(XSL, YSL)
CALL LINEY2(0 0 -SLL)
CALL LINTO2(XSR, YSR)
CALL LINTO2(XSC, YSC)
CALL PICCEG(2)
CALL PICCEG(2)
CALL PICCEG(2)
CALL MOVTI(YSC, YSC)
CALL ARCTO1(XC, YC, XSL, YSL, 0)
CALL LINTO2(XSL, YSL)
CALL LINEY2(0 0 -SLL)
CALL LINTO2(XSR, YSR)
CALL LINTO2(XSC, YSC)
CALL PICCEG(2)
CALL PICCEG(2)
CALL PICCEG(2)
CALL MOVTI(YSC, YSC)
CALL ARCTO1(XC, YC, XSL, YSL, 0)
CALL LINTO2(XSL, YSL)
CALL LINEY2(0 0 -SLL)
CALL LINTO2(XSR, YSR)
CALL LINTO2(XSC, YSC)
CALL PICCEG(2)
CALL PICCEG(2)
CALL PICCEG(2)
CALL MOVTI(YSC, YSC)
CALL ARCTO1(XC, YC, XSL, YSL, 0)
CALL LINTO2(XSL, YSL)
CALL LINEY2(0 0 -SLL)
CALL LINTO2(XSR, YSR)
CALL LINTO2(XSC, YSC)
CALL PICCEG(2)
CALL PICCEG(2)
CALL PICCEG(2)
CALL MOVTI(YSC, YSC)
CALL ARCTO1(XC, YC, XSL, YSL, 0)
CALL LINTO2(XSL, YSL)
CALL LINEY2(0 0 -SLL)
CALL LINTO2(XSR, YSR)
CALL LINTO2(XSC, YSC)
CALL PICCEG(2)
CALL PICCEG(2)
CALL PICCEG(2)
CALL MOVTI(YSC, YSC)
CALL ARCTO1(XC, YC, XSL, YSL, 0)
CALL LINTO2(XSL, YSL)
CALL LINEY2(0 0 -SLL)
CALL LINTO2(XSR, YSR)
CALL LINTO2(XSC, YSC)
CALL PICCEG(2)
CALL PICEXIT(0)
CALL PENSEL(14,0,0)
CALL PIC0P(2,0)
CALL PENSEL(2,0,0)
CALL ADVY02(KSR,YSR)
CALL LINEV2(0,0,SL1)
CALL LINEV2(-SL2,0,0)
CALL LINEV2(0,0,-SL2)
CALL LINEV2(SL2,0,0)
CALL LINT02(KSR,YSR)
CALL CHAMOD
CALL SETFR(2)
CALL PENSEL(CRESP,0,0)

END

MIN AND MAX HEIGHTS

MIN=Z(1,1)

MAX=Z(1,1)

DO 800 J=1,40

TEMP=Z(J,J2)

IF (TEMP LT MIN) GOTO 830

IF (TEMP GT MAX) GOTO 830

GOTO 810

MIN=TEMP

GOTO 810

MAX=TEMP

CONTINUE

CONTINUE

CALC ARRAY OF HEIGHTS AT WHICH CONTOURS TO BE DRAWN

RANGE=MAX-MIN

MINH=MIN-(0.05*RANGE)

MAXH=MAX-(0.05*RANGE)

INCR=(MAXH-MINH)/6

DO 840 I=1,6

HEIGHT(I)=MINH+(I-1)*INCR

CONTINUE

LOT CONTOURS

DO 850 J=1,6

CALL ADDCON(HEIGHT(I),0.1000,W)

CALL CHAMOD

WRITE(1,170)

FORMAT(/'DO YOU WISH TO PLOT ANOTHER RESPONSE')

READ(1,180)YENO

FORMAT(A1)

IF(YENO.EQ.'NO')GOTO 190

CON=CON+1

GOTO 200

WRITE(1,210)

FORMAT(/'DO YOU WANT TO CHANGE VALUES OF INDEP VARS')

READ(1,220)YENO

IF(YENO.EQ.'YES')GOTO 220

CALL PICCLE

CALL DEVEND

CALL EXIT

END

SUBROUTINE COEFF

INTEGER*2 C1,C2,CRESP,IND

REAL XL,YL,QL,YO,XO,XQ,VAL,TERM

REAL GM(6),L(6,6),D(6,6),U(6,6),J(6,6),Z(6,6),VRH(6)

COMMON/CM/K,L,0,12,17/00/CXL,YL,YO,XO,XQ,

1/VRL/VPR/VR/VR/C1,C2/CONRES/CRESP/M/NC/M12,M13

C=GM(CRESP)

CALL LINEAR AND QUAD TERMS OF MODEL

DO 300 J=1,N

IF(J.EQ.C1)GOTO 210

IF(J.EQ.C2)GOTO 220

C=C+L(CRESP,J)*VAL(J)+O(CRESP,J)*(VAL(J)+2)

GOTO 200

VL=L(CRESP,J)

VO=0(CRESP,J)

GOTO 300

VL=L(CRESP,J)

VO=0(CRESP,J)

CONTINUE

CALL 2ND ORDER INT TERMS OF MODEL

J=0

N1=N+1

DO 330 J=1,N1

J1=J+1

DO 340 J2=J1,N

J2=J2+1

330 CONTINUE

340 CONTINUE
AN 3RD ORDER INT TERMS OF MODEL

J=0
NM=NM-2
DO 448 J1=J1+1
   J11=J11+1
   J2=J2+1
   J3=J3+1
   J=J+1
   IND=IND+1
   TERM *= TERM(J11)
   GOTO 488
   IF(J11 .GE. C1) GOTO 478
   IF(J11 .GE. C2) GOTO 488
   TERM *= TERM(J2)
   GOTO 488
   IF(J2 .GE. C1) GOTO 478
   IF(J2 .GE. C2) GOTO 488
   TERM *= TERM(J3)
   GOTO 488
   IF(J3 .GE. C1) GOTO 478
   IF(J3 .GE. C2) GOTO 488
   TERM *= TERM(J4)
   GOTO 488
   CONTINUE

RETURN
END

FUNCTION QUAD(X, Y)

REAL X, Y, XL, YL, XQ, YQ, XYI

COMMON /QUAD/C, XL, YL, XQ, YQ, XYI

QUAD=C+(XL*X)*(YL*Y)+(XQ*X**2)+(YQ*Y**2)+(XYI*X+Y)

RETURN
END