To my parents

AN INVESTIGATION INTO THE FATIGUE RESISTANCE OF NATURAL RUBBER VULCANISATES

by

VARAPORN KAJORNCHAIYAKUL

A Thesis submitted for the degree of
Master of Philosophy

of the

University of Aston in Birmingham

March 1986

DECLARATION

The work described in this thesis has been carried out between July 1984 and February 1986. It has been done independently and submitted for no other degree.

V. Kajornchaiyakul

V. Kajornchaiyakul

March 1986

AN INVESTIGATION INTO THE FATIGUE RESISTANCE
OF NATURAL RUBBER VULCANISATES

by

VARAPORN KAJORNCHAIYAKUL

Submitted for the Degree of M.Phil.

SUMMARY

The fatigue resistance of dicumyl peroxide (DCP) and conventional sulphur cured Natural Rubber (NR) vulcanisates have been investigated. The rubbers were examined both with and without hot acetone extraction under nitrogen, before and after vulcanisation. Extraction reduced the fatigue life of vulcanisates made by both procedures i.e., before and after vulcanisation. The non-rubber constituents of NR were shown to exhibit anti-fatigue activity in both vulcanisates, but the effect was more pronounced in DCP vulcanisates. Extra-network compounds produced by both vulcanising systems did not show any adverse effect on fatigue life.

The fatigue life of DCP vulcanisates was found to be very dependent on DCP loading. Below 2 parts per hundred of rubber, the fatigue life was found to be higher than a conventional sulphur vulcanisate cured to the same rheometer torque.

The structures resulting from DCP vulcanisation of NR have been studied by infra-red and it is shown that aromatic compounds, almost certainly derived from the cumyloxy radical, are attached to the crosslinked polymer.

In the presence of IPPD, the DCP cured rubbers have a lower modulus than the control, and attempts have been made to find coagents to compensate for this. Trimethylol propane trimethacrylate was shown to satisfy this requirement; however, it showed an adverse effect on fatigue life.

KEY WORDS

RUBBER
FATIGUE
VULCANISATION
PEROXIDE VULCANISATION

ACKNOWLEDGEMENTS

I would like to express my gratitude and appreciation to Professor G. Scott and Dr. M. Tavakoli for providing unfailing help, guidance and supervision throughout the course of this work.

I also wish to thank the technical staff of the Molecular Sciences (Chemistry) Department, especially to Mr. P. Hughes and Mr. S. Ludlow, for their assistance, and Mrs. L. Ludlow for typing the manuscript.

Appreciation is expressed to the Food and Agriculture Organisation of the United Nations and The Department of Agriculture in Thailand for the financial support, and to Dr. O. S. Peries and Mr. Lim Poh Loh for their support and encouragement.

Special thanks are due to my father, my sister - Chumnoon, my brother - Somkeit, my sister-in-law - Tasnee, my sons and my husband for their moral support and encouragement during my unexpectedly prolonged stay in England.

LIST OF CONTENTS

		Page
DEDICATION		1
TITLE PAGE		2
DECLARATION		3
SUMMARY		4
ACKNOWLEDGEMENTS		5
LIST OF CONTENTS		6
LIST OF TABLES		14
LIST OF FIGURES		15
CHAPTER ONE - LITERATURE SURVEY		16
1.1	Natural Rubber	17
1.2	Vulcanisation of Natural Rubber	18
1.2.1	Sulphur Vulcanisation	18
1.2.1.1	Introduction	18
1.2.1.2	Definition of Types of Sulphur Systems	20
1.2.1.3	General Course of Sulphur Vulcanisation	21
1.2.1.4	Properties of Sulphur Vulcanisates	23
1.2.2	Peroxide Vulcanisation	25
1.2.2.1	Introduction	25
1.2.2.2	Mechanism of Crosslinking of Rubber with Peroxides	26
1.2.2.3	Cure Behaviour	29
1.2.2.4	Effect of Additives	33
1.2.2.5	Properties of Dicumyl Peroxide - Cured Rubber	35
1.3	Crosslink Density	35

Page

1.3.1 Introduction 35

1.3.2 Determination of Crosslink Density 36

1.3.3 Relationship Between the Physical Properties of Vulcanisates and the Degree of Crosslinking 39

1.4 Oxidative Degradation 41

1.4.1 Oxidative Degradation of Unvulcanised Rubber 44

1.4.2 Oxidative Degradation of Vulcanised Rubber 45

1.5 Fatigue of Rubber 48

1.5.1 Mechanism of Fatigue 48

1.5.2 Factors Involved in Fatigue 49

1.5.3 Effects of Compounding 51

1.5.4 Effects of Vulcanising System and Crosslink Type 52

1.5.5 Effects of State of Cure and Curing Time 53

1.6 Protection of Rubber Against Fatigue Failure 54

1.6.1 Mechanisms of Antioxidant Action 54

1.6.2 Chain-breaking Antioxidants 56

1.6.2.1 Chain-breaking Acceptor (CB-A) Antioxidants 56

1.6.2.2 Chain-breaking Donor (CB-D) Antioxidants 57

1.6.2.3 Complementary Antioxidants Involving Both CB-A and CB-D 58

1.6.3 Preventive Antioxidants 59

1.6.4 Antifatigue Agent for Rubber 60

1.7 Scope and Object of the Present Project 61

Page

CHAPTER TWO - EXPERIMENTAL 65

2.1 Materials 66

2.1.1 Natural Rubber 66

2.1.2 Compounding Ingredients 66

2.2 Compounding 66

2.2.1 Base Formulations 66

2.2.2 Extraction of Raw Rubber 69

2.2.3 Preparation of Gum Compounds 69

2.2.3.1 CBS-Sulphur Gum Compounds 69

2.2.3.2 Peroxide Gum Compounds 70

2.2.4 Preparation of Black Compounds 71

2.3 Vulcanisation 73

2.3.1 Monsanto Oscillating Disc Rheometer 74

2.3.2 Press Curing 78

2.3.2.1 The Amount of Stock Used for Preparation of a Particular Test Specimen 79

2.3.2.2 Conditioning of the Test Sample 80

2.4 Physical Tests on Unvulcanised Rubber 80

2.4.1 Wallace Rapid Plastimeter 80

2.5 Physical Tests on Vulcanised Rubber 81

2.5.1 Fatigue Test 81

2.5.1.1 The Monsanto Fatigue to Failure Tester 82

2.5.1.2 Sample Preparation for the Monsanto Fatigue to Failure Tester 84

2.5.1.3 Operation of the Monsanto Fatigue to Failure Tester 85

2.5.1.4 Expression of Fatigue Results 85

2.5.2 Tensile Test 86
2.5.2.1 Sample Preparation for the E-Type Tensometer 87
2.5.2.2 Operation of the E-Type Tensometer 88
2.5.2.3 Expression of Ultimate Tensile Strength(UTS) 90
2.5.2.4 Expression of Elongation at Break (EB) 91
2.5.2.5 Expression of Modulus at 100% and at 300% Elongation 91
2.6 Extraction of Vulcansied Rubbers 92
2.7 Determination of Crosslink Density 94
2.7.1 Equilibrium Volume Swelling Measurements 94
2.7.2 Analysis of Data 95
2.8 Infra-red Spectroscopy 96
2.9 Ultraviolet Spectroscopy 97
2.10 Gas-Liquid Chromatography 97

CHAPTER THREE - ASSESSMENT OF VULCANISATION CHARACTERISTICS AND CROSSLINK DENSITY 99
3.1 Introduction 100
3.2 Wallace Plasticity Number 101
3.3 Assessment of Vulcansiation Characteristics 101
3.3.1 Conventional Accelerated Sulphur Vulcanisation 102
3.3.1.1 Results 102
3.3.2 Peroxide Vulcanisation 109
3.3.2.1 Results 109

Page

3.3.3 Discussion 111

3.3.4 Peroxide/Coagent Vulcanisation 122

3.3.4.1 Introduction 122

3.3.4.2 Experimental 123

3.3.4.3 Results and Discussion 124

3.4 Estimation of Crosslink Density 136

3.4.1 Time to Equilibrium Volume Swelling 136

3.4.2 Results 136

3.4.3 Discussion 143

CHAPTER FOUR - STUDY ON THE PEROXIDE VULCANISATION OF NATURAL RUBBER 145

4.1 Study of Structural Changes in Natural Rubber After Peroxide Vulcanisation by Infra-red (IR) Spectroscopy 146

4.1.1 Introduction 146

4.1.2 Preparation of Films for IR Measurements 146

4.1.2.1 Unvulcanised Natural Rubber Films 146

4.1.2.2 Vulcanised Natural Rubber Films 147

4.1.3 Estimation of Aromatic Ring Attached to Polymer Chain After DCP Vulcanisation 147

4.1.4 Results and Discussion 148

4.1.4.1 IR Spectra of Unvulcanised Natural Rubber 148

4.1.4.2 IR Spectra of DCP Vulcanised Films 151

4.1.4.3 Aromatic Ring Attached to Polymer Chain 154

4.1.4.4 IR Spectrum of DCP Vulcanised Film Containing IPPD 154

Page

4.2 Analysis of the Extra-Network Compounds (ENCS) of Peroxide Vulcanised Rubber 157
4.2.1 Ultraviolet Spectroscopy Analysis 157
4.2.2 Infra-red Spectroscopy Analysis 159
4.2.3 Gas-Liquid Chromatography(GLC) 164
4.2.4 Comment on the Analysis Results 164

CHAPTER FIVE - STUDY OF FATIGUE AND TENSILE PROPERTIES OF NATURAL RUBBER VULCANISATES 168
5.1 Introduction 169
5.2 Experimental 170
5.3 Effect of Extraction on Fatigue and Tensile Properties 170
5.3.1 Procedure 170
5.3.2 Results 172
5.3.3 Discussion 175
5.4 Effect of Vulcanisation Time on Fatigue and Tensile Properties 176
5.4.1 Procedure 176
5.4.2 Results and Discussion 176
5.4.2.1 Variation of M_{100} with Vulcanisation Time 176
5.4.2.2 Tensile Modulus (M_{100}) Against Rheometer Torque 178
5.4.2.3 Variation of Tensile Strength and Fatigue Life with Vulcanisation Time 179
5.4.2.4 Fatigue Life of DCP and Conventional Sulphur Vulcanisates Cured to the Same Rheometer Torque 181

Page

5.5 Dependence of Fatigue Life on M_{100} and Physical Crosslink Density 181
5.5.1 Procedure 181
5.5.2 Results and Discussion 183
5.5.2.1 Dependence of Fatigue Life on M_{100} 183
5.5.2.2 Dependence of Fatigue Life on Physical Crosslink Density 185
5.6 Effect of Non-Rubber Constituents (NRC), Extra-Network Compounds (ENCS) Formed During Vulcanisation and Olive Oil on Fatigue Life 187
5.6.1 Effect of NRC on Fatique Life 187
5.6.1.1 Procedure 187
5.6.1.2 Results 187
5.6.1.3 Discussion 189
5.6.2 Effect of ENCS Formed During Vulcanisation on Fatigue Life 190
5.6.2.1 Procedure 190
5.6.2.2 Results and Discussion 195
5.6.3 Effect of Olive Oil on Fatigue Life 195
5.6.3.1 Introduction 195
5.6.3.2 Procedure 196
5.6.3.3 Results and Discussion 197
5.6.4 Conclusions 198
5.7 Properties of Vulcanisates Containing IPPD and Coagents 199
5.7.1 Procedure 199

Page

5.7.2 Fatigue Life and Tensile Properties of DCP and Conventional Sulphur Vulcanisates Containing IPPD 200
5.7.2.1 Results 200
5.7.2.2 Discussion 200
5.7.3 Fatigue Life and Tensile Properties of DCP/IPPD/Coagents Vulcanisates 202
5.7.3.1 Results 202
5.7.3.2 Discussion 202
5.7.4 Fatigue Life of Black-filled Vulcanisates 204
5.7.4.1 Results and Discussion 204

CHAPTER SIX - CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK 206
6.1 Conclusions 207
6.2 Suggestions for Further Work 209

REFERENCES 210

LIST OF TABLES

Table	Page
1.1	21
2.1	67
2.2	68
2.3	68
3.1	107
3.2	108
3.3	110
3.4	117
3.5	118
3.6	127
3.7	127
3.8	128
3.9	129
3.10	135
3.11	137
3.12	139
3.13	140
3.14	141
4.1	156

Table	Page
5.1	171
5.2	173
5.3	182
5.4	188
5.5	193
5.6	194
5.7	197
5.8	201
5.9	203
5.10	205

LIST OF FIGURES

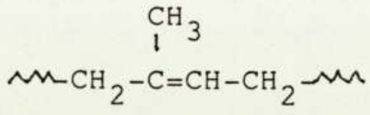
Figure	Page
1.1	19
1.2	22
1.3	24
1.4	29
1.5	37
1.6	38
1.7	39
2.1	73
2.2	75
2.3	76
2.4	76
2.5	83
2.6	89
2.7	90
2.8	93
3.1	104
3.2	105
3.3	106
3.4	112
3.5	113
3.6	114
3.7	115
3.8	116
3.9	130
3.10	131
3.11	132
3.12	133
3.13	134
3.14	138
3.15	142
3.16	142
4.1	149
4.2	152
4.3	155
4.4	158
4.5A, 4.5B	160
4.6A, 4.6B	161
4.7	162
4.8	163
4.9	167
5.1(a),5.1(a')	174
5.2	177
5.3	177
5.4	180
5.5	180
5.6	184
5.7	186

CHAPTER ONE

LITERATURE SURVEY

1.1 Natural Rubber

Cis-polyisoprene, the hydrocarbon component of natural rubber



$$\sim\sim\mathrm{CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2}\sim\sim$$

(NR) is fairly widespread in nature, having been identified in about 2000 plant species. Only Hevea Brasiliensis has become of major significance. Indigenous to the Amazon valley, it is the species on which all plantation rubber in Africa and the Far East is based. Recently efforts have been initiated to utilise the guyale shrub(1).

The coagulum obtained from Hevea Brasiliensis by treatment of the latex with acid, followed by washing and drying, contains a high proportion of a hydrocarbon, mixed with proteins, resins and other constituents. Commercial raw natural rubber has a small number of highly important non-rubber constituents. These may comprise as much as 5-8% of the total composition. Most important are the naturally-occurring antioxidants and activators of cure, represented by the proteins, sugars and fatty acids. A typical composition is: rubber 94.2%; ash 0.3%; protein 2.5%; acetone extract 2.5%; and moisture 0.5%(2).

1.2 Vulcanisation of Natural Rubber

Vulcanisation is the chemical reaction which brings about the formation of crosslinks between the long polymer chains, thus enabling useful products to be produced from the rubbery polymer.

NR and unsaturated synthetic rubbers e.g., styrene-butadiene rubber (SBR) and butadiene rubber (BR) can be vulcanised by sulphur and by a wide variety of non-sulphur crosslinking agents including organic peroxides, quinones and their oximes, and by means of high-energy radiation.

1.2.1 Sulphur Vulcanisation

1.2.1.1 Introduction

The most common system used for vulcanisation of NR employs sulphur which reacts with unsaturation in the polymer backbone(3). Vulcanisation is usually effected industrially by heating the mechanically plasticized rubber with sulphur and auxiliary vulcanising agents such as organic accelerators, zinc oxide, and long chain fatty acids (stearic acid or lauric acid) or the zinc soap of these acids as activators.

Heating is usually at 140°C for NR and somewhat higher for SBR and isobutene-isoprene rubber (IIR) (up to 150-160°C);

much lower temperatures are possible, however, if specially active accelerators such as the zinc dialkyldithiocarbamates are used(4).

In most cases the vulcanisation is achieved by a chemical reaction between the rubber and the vulcanising agent which produces covalent crosslinks between the rubber chains. For example, in the vulcanisation of NR with sulphur, mono- and polysulphide groups join the polyisoprene chains together.

According to Bateman(4), a typical structure of unaccelerated sulphur vulcanisation is shown in Figure 1.1.

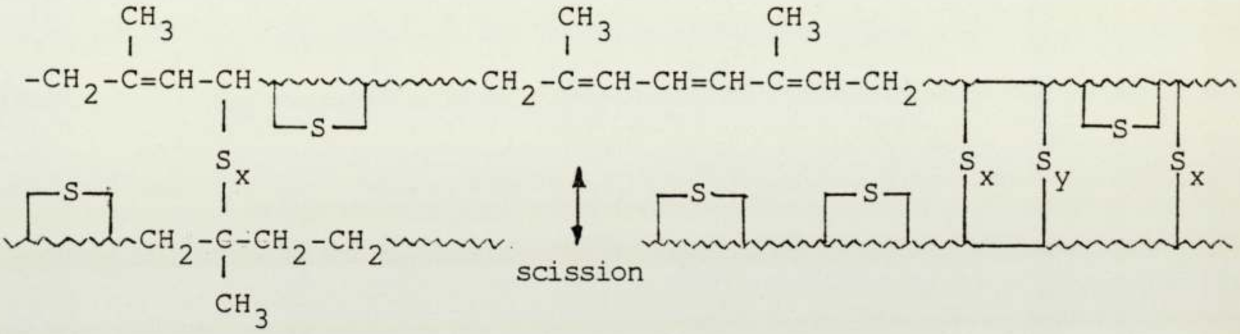


Figure 1.1 Main structural features of unaccelerated sulphur vulcanisate of natural rubber(4)

This illustrates the various transformations which natural rubber molecules undergo during unaccelerated sulphur vulcanisation, not only producing long polysulphidic crosslinks but also cyclic monosulphides which constitute important modifications of main chain.

Vicinal crosslinks are also formed,where they act physically as a single crosslink together with chain scission and dehydrogenation to form conjugated triene structures in the chain, where they constitute the main features of the rubber vulcanisate. The low crosslinking in unaccelerated NR systems is thus attributed to incorporation of the sulphur in the form of polysulphides and cyclic sulphides (see Figure 1.1).

The differences between accelerated and unaccelerated sulphur vulcanisation are that less cyclic sulphide structures are formed in the accelerated systems and the length of the polysulphidic crosslinks is much shorter and decreases rapidly with time.

The role of the accelerator in conjunction with auxiliary agents such as zinc oxide and fatty acids in the sulphur vulcanisation of natural rubber is to increase the reaction rate and prevent excessive side reactions of the sulphur with the rubber. The side reactions not only have an adverse effect on the physical properties of the vulcanisates but also accelerate the oxidative ageing, since the various sulphur structures on the chain act as loci for oxidative attack.

1.2.1.2 Definition of Types of Sulphur Systems

The amount of sulphur used in NR compounds (excluding ebonite) may vary from about 3.5 parts per hundred of rubber (phr) down to only 0.3 phr. As the amount of sulphur is reduced, an adequate degree of crosslinking is achieved by increasing the efficiency of the chemical reactions which provide the crosslinks. Thus the term "efficient vulcanising (EV)" is used to define these low sulphur systems(5-8). Since increased efficiency is obtained by an increase in the amount of accelerator, it is the relative concentration of sulphur and accelerator which determines the type of crosslink formed. A general division is made into conventional systems which contain a much higher concentration of sulphur than accelerator, and EV systems which contain a much lower concentration of sulphur than accelerator. Between these extremes are semi-EV systems. The approximate concentrations of sulphur and accelerator in the three systems when used in NR are as given in Table 1.1(9).

	Sulphur(phr)	Accelerator(phr)
Conventional	2.0 to 3.5	1.0 to 0.4
EV	0.3 to 0.8	6.0 to 2.5
Semi-EV	1.0 to 1.7	2.5 to 1.0

Table 1.1

1.2.1.3 General Course of Sulphur Vulcanisation

An outline reaction scheme for the course of sulphur vulcanisation, originally proposed for NR(4) is now generally accepted (Figure 1.2).

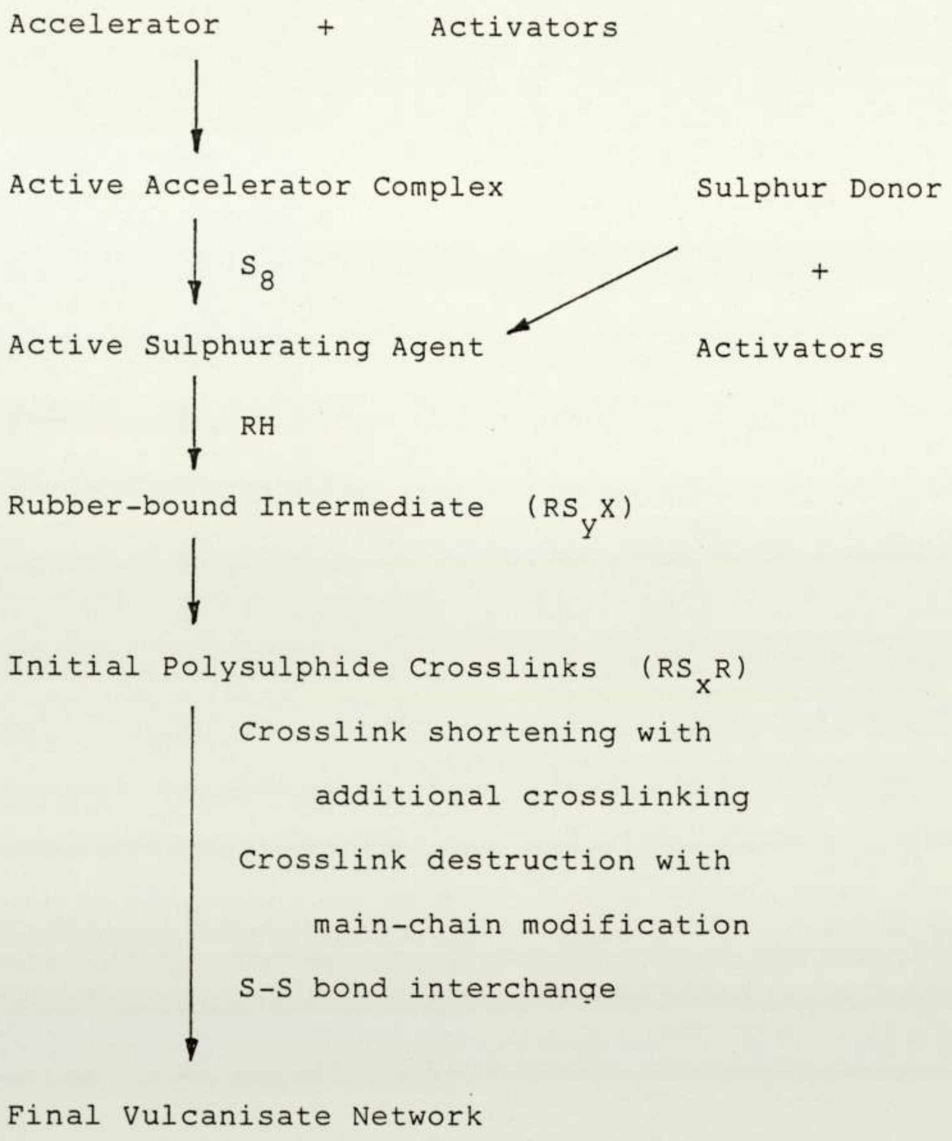


Figure 1.2 Outline reaction scheme for the sulphur vulcanisation of diene rubbers. R, represents the rubber chain and H is normally an allylic hydrogen atom; X = accelerator residue(10).

Since the scheme was proposed, further evidence for the existence and identity of the rubber-bound intermediate has been obtained(11-13); but there is as yet no general agreement on the chemical nature of the active sulphurating agent - in particular, as to whether it contains zinc or not(14-16).

1.2.1.4 Properties of Sulphur Vulcanisates

The properties of vulcanisates not only depend upon the degree of crosslinking, but they also depend to some extent upon the crosslink structure. In accelerated sulphur vulcanisation, diene rubbers form not only mono-, di- and polysulphidic crosslinks, but also pendent sulphidic groups terminated by an accelerator residue, cyclic sulphides, conjugated diene and triene units, cis-, trans- isomerised olefin units, and vicinal crosslinks (see Figure 1.3)(17,18). The networks formed with high proportions of polysulphide crosslinks display higher tensile strengths(19,20), tear strengths(21) and abrasion resistance(22) than networks prepared with monosulphide crosslinks. The main chain modifications formed by side reactions also appear to affect a variety of properties(17). The extent to which the type of crosslink and type and degree of main chain modification play a part in determining initial properties of vulcanisates varies considerably with the nature of the elastomer and other factors such as the presence of fillers and oils .

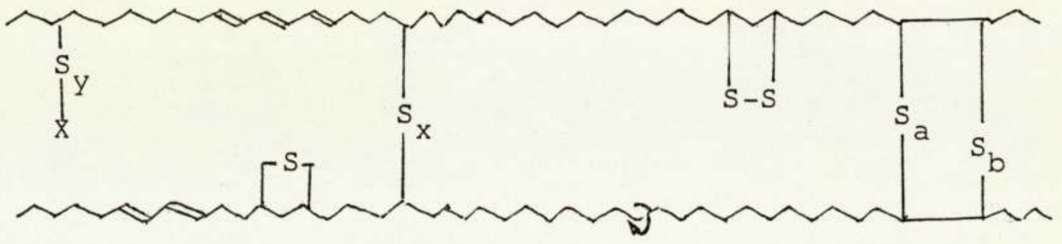


Figure 1.3 Generalised structure of an accelerated sulphur vulcanisate of a diene rubber. a, b, x, y =1-6; X=accelerator residue: 2-benzothiazolyl dialkylthiocarbamyl, etc.; curved arrow signifies cis, trans-isomerisation(17,18).

Di- and especially polysulphidic crosslinks not only display poor thermal ageing resistance but, as a consequence of the high chemical lability of the S-S linkage they also undergo thermal restructure. Thus conventional sulphur vulcanising systems are less satisfactory for applications which involve high vulcanising temperatures, or high service temperatures, or where resistance to creep or stress relaxation is important(7). This is because the high concentrations of sulphur and low accelerator concentrations used give vulcanisates containing mainly polysulphide crosslinks(4,9). There is however, some evidence that resistance to fatigue failure is enhanced in polysulphidic networks(21). The excellent ageing behaviour of the efficient vulcanising systems reflects not only the thermal stability of networks but the fact that monosulphidic crosslinks formed by EV systems are much less antagonistic than polysulphide crosslinks towards antioxidants(7). EV system gives vulcanisates with lower permanent set than rubbers cured with conventional system because monosulphidic crosslinks cannot exchange with one another under conditions of heat or stresses in the way that polysulphides do(7).

1.2.2 Peroxide Vulcanisation

1.2.2.1 Introduction

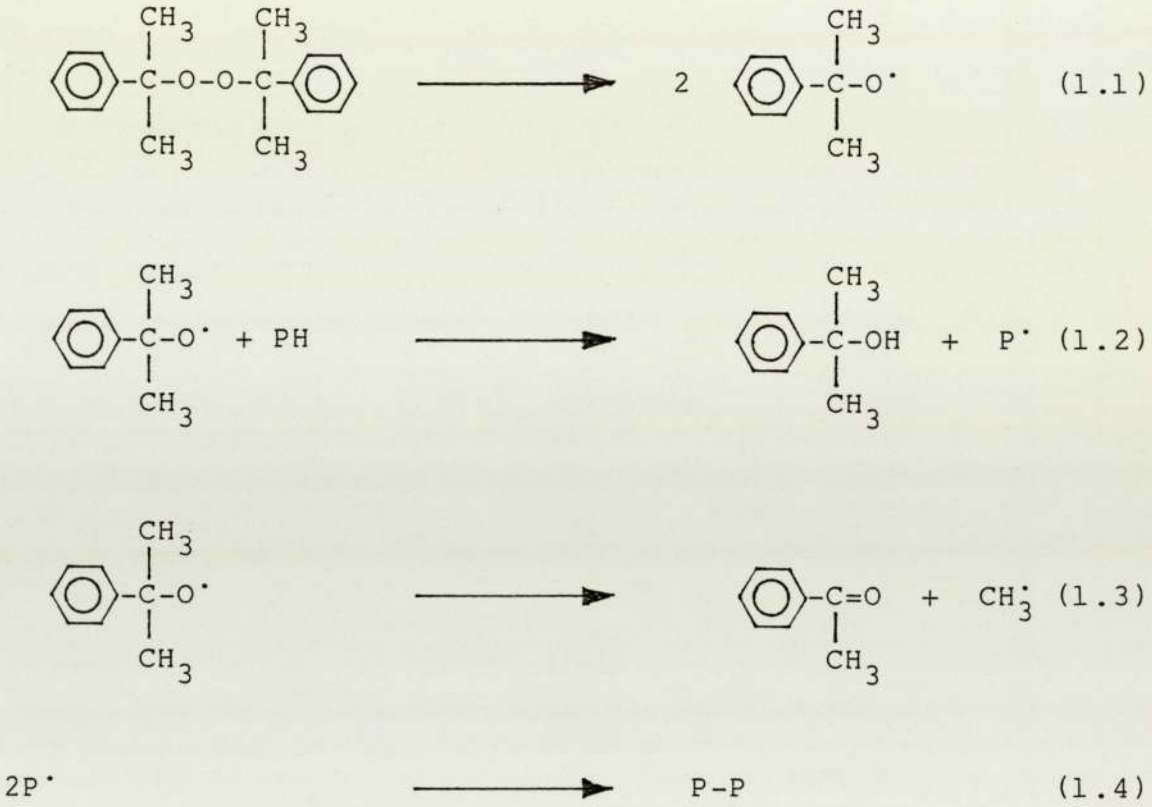
Elliott and Tidd(9) stated that "The formation of a network having solely carbon-carbon crosslinks has long been attractive to the research scientist. In principle, it enables physical and chemical changes in the network to be studied without the complication of crosslinks containing hetero atoms". Peroxides are capable of crosslinking rubbers by forming carbon-carbon crosslinks. Ostrominslensky(23) first proposed benzoyl peroxide as a crosslinking agent in natural rubber. The technological interest in the use of organic peroxides increased with the advent of fully saturated hydrocarbon polymers which cannot be cured by accelerated sulphur systems(9,24-27).

Peroxides may be used to crosslink either saturated or unsaturated elastomers, but, in practice, they are used primarily for the saturated elastomers, i.e., silicones, urethanes and highly filled polyethylene(27). This is because the unsaturated elastomers are more conveniently vulcanised with sulphur. However, butyl rubber cannot be crosslinked by peroxides since it undergoes serious degradation when it is treated(27).

Of several peroxides examined(28,29) as crosslinking agents for NR none was found to be as good as dicumyl peroxide [Bis(α,α-dimethylbenzyl)peroxide](28), because of its low volatility, high crosslinking efficiency especially in the presence of carbon black, and its reduced tendency to cause degradation of the unvulcanised rubber. This was recognised to be the most important peroxide crosslinking agent for NR and other diene rubbers as well as for saturated rubbers. The use of dicumyl peroxide (DCP) vulcanisation has been demonstrated practically in a wide variety of applications(30,31). DCP offers freedom from colour, opacity and resistance to ultraviolet light discolouration in white and transparent vulcanisates(32). In black stocks, DCP offers excellent low compression set, low temperature flexibility and ageing resistance, especially at high temperature(32).

1.2.2.2 Mechanism of Crosslinking of Rubber with Peroxides

The mechanism proposed for the crosslinking reaction of rubber with peroxides is, in principle, simple(28) and it has been reviewed by Loan(33). Unlike sulphur vulcanisation which is thought to proceed by a polar mechanism(4), peroxide-induced crosslinking is a free radical reaction. The initial step of dicumyl peroxide vulcanisation involves the thermal decomposition of the peroxide, thus yielding two cumyloxy radicals (reaction 1.1) which then react either by abstracting hydrogen atoms from the rubber to form α,α-dimethylbenzylalcohol (cumyl alcohol) and a polyisoprenyl radical (reaction 1.2) or by decomposing to acetophenone and a methyl radical (reaction 1.3). Intermolecular combination of pairs of the polyisoprenyl radicals gives rise to carbon-carbon crosslinks (reaction 1.4). They are represented by Scheme 1.1, reactions 1.1 to 1.4.



Scheme 1.1 Mechanism of dicumyl peroxide vulcanisation$^{(9)}$

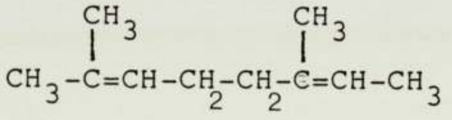
where PH, P$^{\cdot}$ and P-P denote a polymer molecule, polymer radical and crosslinked polymer respectively. The methyl radicals may also give rise to polymer radicals or may possibly dimerise to give ethane as shown in reactions 1.5-1.6.

$$CH_3^{\cdot} + PH \longrightarrow CH_4 + P^{\cdot} \qquad (1.5)$$

$$2CH_3^{\cdot} \longrightarrow CH_3-CH_3 \qquad (1.6)$$

Amberg and Willis(32) have shown that, easily cured elastomers such as NR and SBR are crosslinked mostly by reaction with cumyloxy radicals with the formation of cumyl alcohol, whereas saturated, very stable silicone rubber is crosslinked mostly by reaction with methyl radicals.

Although there is no unequivocal evidence that the exclusive fate of the polymer radicals is combination, experiments on the reaction of dicumyl peroxide with 2,6-dimethylocta-2,6-diene, I (a model for polyisoprene) suggest that it is the predominant reaction(34,35).



$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_3$$

(I)

The only complication that the above chemical equations do not take into account is the possibility of chain scission during the vulcanisation, and this, if it occurred, would vitiate any determination of crosslink density by physical measurements. However, sol-gel measurements on natural rubber vulcanisates crosslinked by dicumyl peroxide, by Bristow(36), showed that chain scission is a very minor reaction at the temperature normally used.

On the basis of experiments carried out by Moore et al (37) on the stoichiometry and mechanism of the reaction of di-t-butyl peroxide as the crosslinking agent for natural rubber and the reaction of dicumyl peroxide with 2,6-dimethylocta-2,6-diene by Park and Lorenz (35), it is possible to deduce the structure of peroxide crosslinked natural rubber vulcanisates. This is shown schematically in Figure 1.4 (4,27). Thus this network not only consists primarily of di-alkenyl carbon-carbon crosslinks, but may also contain some cyclic structures, presumably formed by intra-molecular addition of the alkenyl radicals to double bonds.

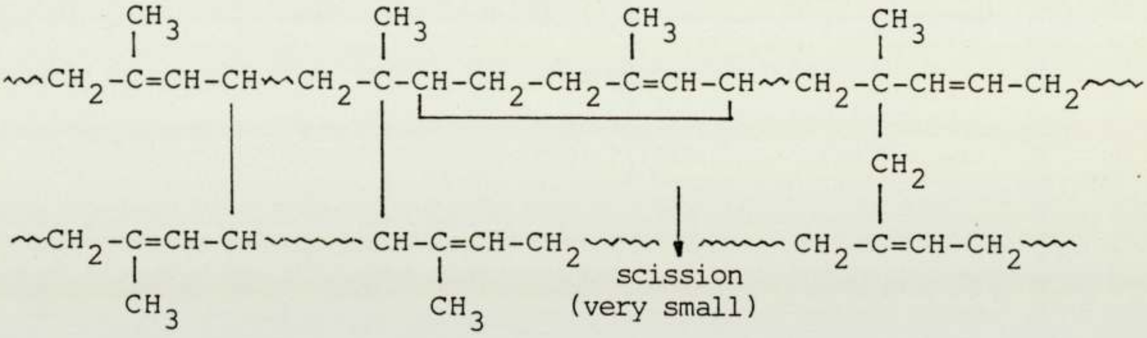


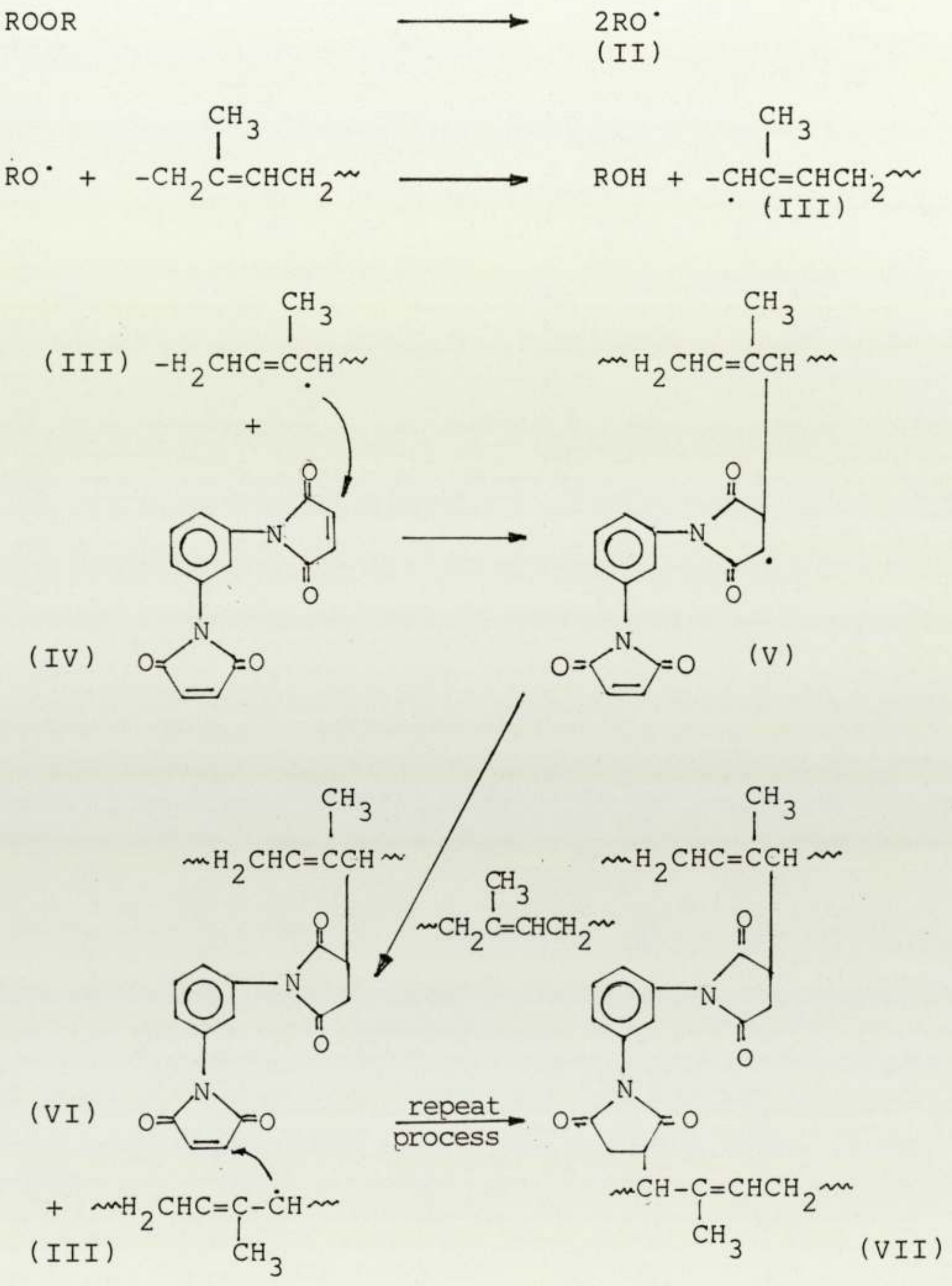
Figure 1.4 Structure of peroxide crosslinked natural rubber (4,27)

1.2.2.3 Cure Behaviour

The peroxide curing system is essentially non-reverting, i.e., modulus does not fall as cure time is increased, as attributed to the formation of very thermally stable carbon-carbon bonds. Thus vulcanisates which have equivalent states of cure can be prepared by varying the concentrations of peroxide and the time of vulcanisation. There are, however, disadvantages of such a procedure since any peroxide remaining undecomposed at the time of the vulcanisation period will act as a potent pro-oxidant during subsequent ageing. Continued vulcanisation by the undecomposed peroxide also produces inferior high temperature compression set behaviour(38). It is recommended that the rubber should always be vulcanised for at least five times the half life (97% decomposition) of the peroxide. Suggested minimum cure times for dicumyl peroxide crosslinked natural rubber are 1 h at 160°C, 3 h at 150°C or as long as 8 h at 140°C(39).

The main technical limitations of the dicumyl peroxide system are its low cure rate and the absence of an induction period to crosslinking i.e., it is scorchy. Other defects are sticky mould deposits caused by oxidised spew, unpleasant odour, and the production of a vulcanised rubber deficient in strength properties. Lewis(39) stated that "If scorch delay could be introduced without jeopardising the rate and efficiency of crosslinking, shorter and more economically attractive cure cycles should result because a higher moulding temperature could be tolerated".

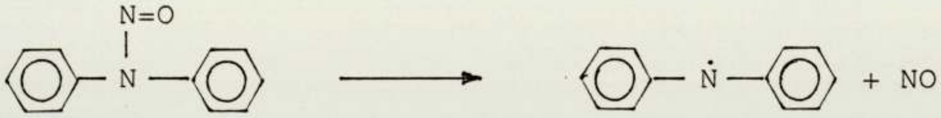
Some success in providing scorch delay has been achieved by the use of radical scavengers (N-nitroso diphenylamine) in peroxide-activated bismaleimide systems(40). In this system peroxide initiates the reaction by providing the free radicals. The bismaleimide takes part in the vulcanising reaction, by a mechanism proposed by Kovacic et al(41) which is given in Scheme 1.2.



Scheme 1.2 Mechanism of vulcanisation by peroxide-bismaleimide system(41)

The initiating free radical (II), formed by peroxide, abstracts an allylic α-hydrogen atom from the natural rubber, to give a rubber radical (III) on the rubber chain. Then (III) attacks a bismaleimide molecule (IV) to give the new free radical (V). After a chain-transfer reaction to give (VI), the other maleimide unit of (VI) proceeds through an analogous sequence, which results in a crosslink as shown in (VII).

At vulcanisation temperature, N-nitroso diphenylamine decomposes to give nitric oxide and diphenyl amine (see reaction 1.7) which react with peroxy radical (II) or rubber radical (III)(42). This results in some delay of the crosslinking reaction.



(1.7)

The crosslinks formed by bismaleimide compensate for the loss of crosslinks due to the radical scavenging of N-nitroso diphenylamine.

Other coagents designed to solve both the scorch and cure rate of peroxide system have been introduced(43), and the one adopted is the commercially available peroxide coagent and retarder, Saret 500®, which is based on trimethylol-propane-trimethacrylate and a nitroso radical-capture reagent, and has been evaluated in the NR/dicumyl peroxide system(44). In this system trimethylol-propane-trimeth-

---

® Saret is a registered trade name of Sartomers Resins Inc.,Essington Pa, USA.

acrylate is used to boost the modulus of the peroxide system which has been depleted by the inclusion of a nitroso radical capture reagent. It was found that Saret 500 increased both scorch safety and modulus, while reducing compound viscosity. When adjustments were made to the amounts of peroxide required to give a constant modulus with varying concentration of Saret 500, an almost linear relationship was observed between scorch time at $120^{\circ}C$ and concentration. The vulcanisates had good physical properties, including high rubber to metal bond strengths using proprietary bonding agents. Chow(40) showed that Saret 500 can improve fatigue life about 2 times and scorch time about 3 times, as compared with simple peroxide formulation. Wheelans(45) reported that Saret 500/DCP mix allowed satisfactory injection moulding at temperatures up to $200^{\circ}C$.

1.2.2.4 Effect of Additives

Amberg and Willis(32) have studied the reaction of dicumyl peroxide during vulcanisation in the presence of a variety of polymers, carbon black, fillers, plasticizers, accelerators, retarders and antioxidants, and have concluded that formation of free radical is a first-order, temperature dependent reaction alone, the time to decompose all the peroxide and therefore time to optimum cure, are not affected by compounding ingredients. However, the amount of dicumyl required is decidedly dependent on the kind and quality of components such as polymer, pigments, plasticizers and antioxidants.

Dicumyl peroxides are quite sensitive to acids. This sensitivity is less pronounced, however, in aliphatically substituted peroxides e.g., di-tert-butyl peroxide, than in aromatically substituted ones(46). If a rubber compound containing acidic ingredients is stored, the peroxides may be wholly or partly decomposed, which would greatly influence the vulcanisation. Most fillers reduce the efficiency of peroxides to some extent, this should be catered for by a corresponding increase in the proportion of peroxide.

Though dicumyl peroxide vulcanisation occurs predominantly through a radical mechanism, some ionic cleavage also occurs in the presence of acids (such as channel blacks and clays). Thus channel blacks increased the peroxide demand over a furnace black with the same surface area. Thermal and furnace blacks increase the amount of dicumyl peroxide for vulcanisation depending on the surface area of the filler.

Plasticizers should be selected such that they do not react with free radicals. This is particularly the case when the plasticizer is resinous, phenolic or acidic, or a naphthenic or aromatic mineral oil, some of which catalyse the heterolytic decomposition of peroxides more than the polymers do, or alternatively react with the peroxy radicals. Plasticizers for compounds vulcanised with peroxides should preferably be straight chain aliphatics. Nevertheless, the undesirable effects of plasticizers can also be counteracted in many cases by increased dosage of peroxide(46).

Antioxidants and antiozonants, being radical scavengers, increase the demand for dicumyl peroxide to compensate for their influence on the vulcanisation. These materials should therefore be used with great care(32).

1.2.2.5 Properties of Dicumyl Peroxide-Cured Rubber

The strength of peroxide-cured rubber is lower than that of most sulphur vulcanisates, particularly in gum and slightly filled compounds, and hot tear strength can be so poor that demoulding operations become difficult. The hot strength is also very critically dependent on crosslink density(47).

Crystallisation occurs fairly rapidly at temperatures around -25°C leading to considerable hardening in approximately 1 to 2 days. Not withstanding these deficiencies, peroxide curing is useful since it gives low compression set, low creep, low stress relaxation and outstanding resistance to ageing and reversion(48).

1.3 Crosslink Density

1.3.1 Introduction

The most important characteristic of an elastomeric network is unquestionably its degree of crosslinking, i.e., the number density of crosslinks joining the chains into a structure of sufficient permanence to give elastic recoverability rather than irreversible plastic flow(49). This aspect of network structure affects all of the elastomeric properties, including equilibrium properties such as the modulus, ultimate tensile strength, maximum extensibility, and the degree of swelling(49,50), and also dynamic mechanical properties such as viscoelastic losses(51,52). Its determination is thus of importance with regard to both the molecular interpretation of rubberlike elasticity and the rational design of materials having specified properties for a wide range of elastomeric applications.

1.3.2 Determination of Crosslink Density

Crosslink density is inversely related to M_c, as can be seen from Figure 1.5, which represents a portion of crosslinked rubber. It can be seen that each chain segment (of weight Mc) is terminated by two crosslinks, one at each end. Clearly, the central crosslink "possesses" completely one-half only of each of the four chain segments emanating from it (shaded area). Hence such a crosslink has associated with it 2Mc of polymer i.e., 2Mc of polymer contains one crosslink.

The crosslink density is determined as $\frac{1}{2}$Mc and it can be arrived at from stress-strain measurements in simple strain using the expression:

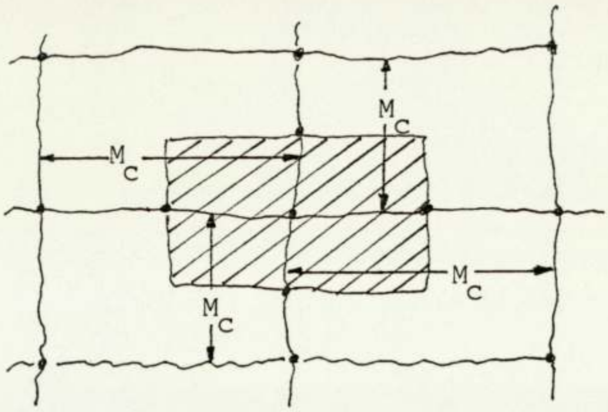


Figure 1.5 Portion of crosslinked rubber. M_c is the number average molecular weight of the rubber chains between crosslinks$^{(53)}$

$$f = \rho RTA_o^{-1}Mc^{-1}(\lambda-\lambda^{-2}) \qquad (1.8)$$

where f is the force to extend at a sample of cross-sectional area A_o to extension ratio λ, ρ is the density, R is the gas constant and T is the absolute temperature$^{(53-55)}$.

Alternatively, the Flory-Rehner equation$^{(56)}$ can be applied to the results of swelling the rubber in suitable solvents:

$$-[\ln(1-Vr) + Vr + \chi Vr^2] = \rho V_oMc^{-1}Vr^{\frac{1}{3}} \qquad (1.9a)$$

which simplifies to modified Flory-Rehner equation$^{(57)}$:

$$-[\ln(1-Vr) + Vr + \chi Vr^2] = \rho V_oMc^{-1}(Vr^{\frac{1}{3}} - Vr/2) \qquad (1.9b)$$

in order to obtain accuracy when the degree of crosslinking is large and therefore the equilibrium degree of swelling is small, where Vr is the equilibrium volume fraction of rubber in swollen gel, ρ the density of the rubber, χ an interaction constant characteristic of rubber and swelling liquid, and V_o the molecular volume of the swelling liquid.

The use of equation (1.9b) requires that the interaction constant, χ, be known. In practice this can only be obtained by assessing Mc by an independent method e.g., by stress-strain measurements, and measuring the corresponding Vr for this network. Mc determined from stress-strain measurement is Mc,phys, which may be changed to Mc,chem, by using the Moore-Watson-Mullins empirical calibration(55,58) (1.10) which is obtained from their results and illustrated graphically in Figure 1.6.

$$\tfrac{1}{2}\text{Mc,phys} \simeq (\tfrac{1}{2}\text{Mc,chem} + 0.35\text{x}10^{-4}) \qquad (1.10)$$

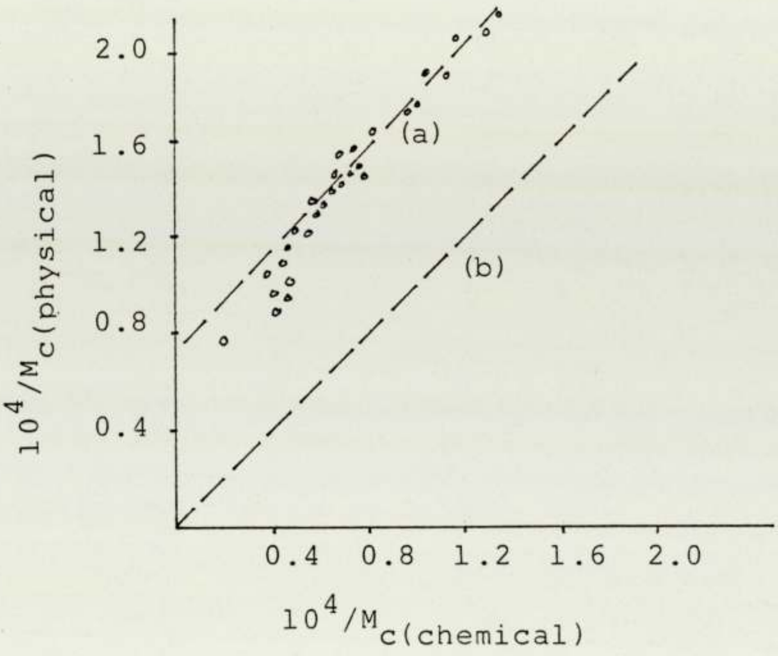


Figure 1.6 Comparison of estimates of crosslinking based on chemical and physical methods. The discrepancy between experimental results (a) and theory (b) is considered to be due to entanglements(58)

1.3.3 Relationship Between the Physical Properties of Vulcanisates and the Degree of Crosslinking

Several studies have been reported on the effect of the degree of crosslinking on the tensile strength of natural rubber gum vulcanisates(59-61). The tensile strength passes through a maximum as the degree of crosslinking is increased as is shown in Figure 1.7(62).

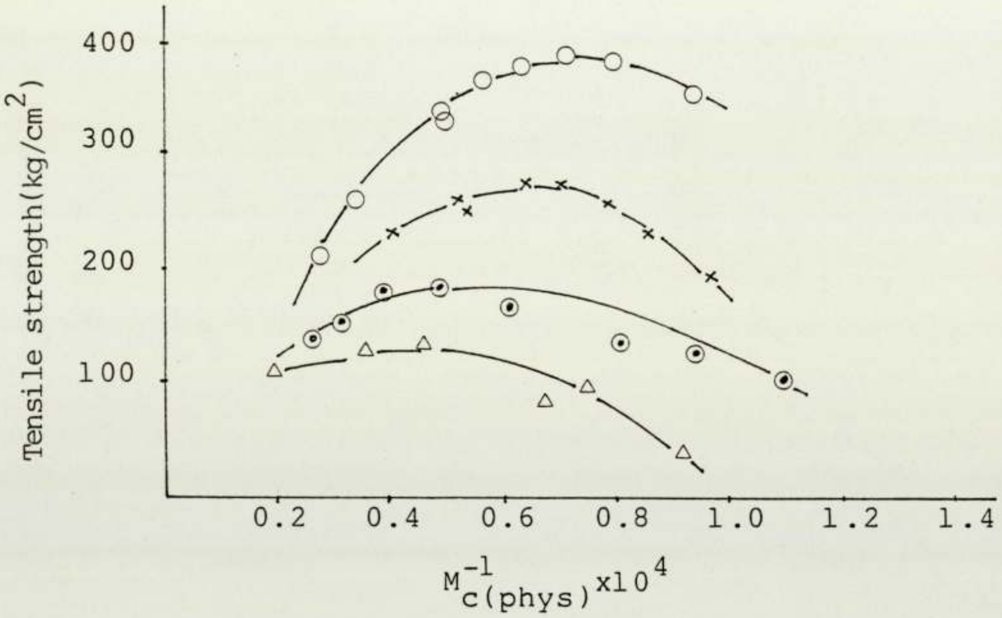


Figure 1.7 Tensile strength of pure gum natural rubber vulcanisates plotted against $M^{-1}_{c(phys)}$ for various vulcanising systems. (○) accelerated sulphur; (×) TMT sulphurless; (⊙) peroxide; (△) high energy radiation

It has been proposed that the tensile strength is low at high degrees of crosslinking because the breaking point is attained before the extension is sufficiently high for crystallisation to develop(59,60). In explanation of the low tensile strength at low degrees of crosslinking, Gee(59) suggested that, unless the degree of crosslinking is sufficiently high for a coherent network to be formed, plastic flow will occur and will prevent orientation of the chains to form crystallites.

The tensile stress of a vulcanisate at a given elongation (modulus) is substantially proportional to the number of crosslinks formed, and hence to the "degree of vulcanisation or crosslinking". The correlation between tensile stress at a given elongation and the degree of crosslinking is expressed in Equation 1.8.

As the degree of crosslinking increases, the hardness, which is related to the tensile stress at a given elongation, progressively increases until the steel-elastic state is reached i.e., until the material becomes ebonite(63).

The elongation at break and the permanent set (e.g., tensile set, compression set) become progressively smaller as the number of crosslinking increases(63). Therefore a high degree of crosslinking is always desirable in products which have to have a particularly low permanent set. Generally the degree of crosslinking is inversely proportional to the permanent set. Poor resistance to abrasion is found when the crosslinking is rather insufficient whereas the abrasion resistance deteriorates relatively little when it is excessive(63). The rebound resilience and consequently the dynamic damping and fatigue cracking, improve to some extent as the degree of crosslinking rises(63).

1.4 Oxidative Degradation

The rubber hydrocarbon containing double bonds and hence labile C-H bonds is highly susceptible to attack by molecular oxygen. This reaction is called "autoxidation", it proceeds autocatalytically since most oxidation products are, in general, more reactive towards heat, light and radicals than are parent polymers. The oxidation of polymers causes deterioration in physical properties, thus it is considered generally to be a deleterious process and therefore efforts have been devoted to its inhibition or suppression.

The formation of free radicals in uncured rubbers during mastication has been inferred by a number of workers from the rheological changes in the polymer(64) and from the chemical reactions which can be initiated in the rubber under conditions of shear(65-67). Direct evidence has been found for macro - radical formation by E.S.R. spectroscopy(68). Similar phenomena have been found during the milling of vulcanised rubbers(69) and in the presence of oxygen, the radicals were characterized as alkylperoxy radicals.

The oxidative degradation of polymers is a radical reaction and it proceeds by a free radical chain mechanism consisting of three important steps: initiation, propagation and termination$^{(70-72)}$ (scheme 1.3).

Initiation $\quad \mathrm{ROOH} \longrightarrow \mathrm{RO.} + \mathrm{HO.}$

$\mathrm{2ROOH} \longrightarrow \mathrm{RO.} + \mathrm{RO}_2^{\cdot} + \mathrm{H_2O}$

Propagation $\quad \mathrm{RO}_2^{\cdot} + \mathrm{RH} \longrightarrow \mathrm{ROOH} + \mathrm{R.}$

$\mathrm{R.} + \mathrm{O_2} \longrightarrow \mathrm{RO}_2^{\cdot}$

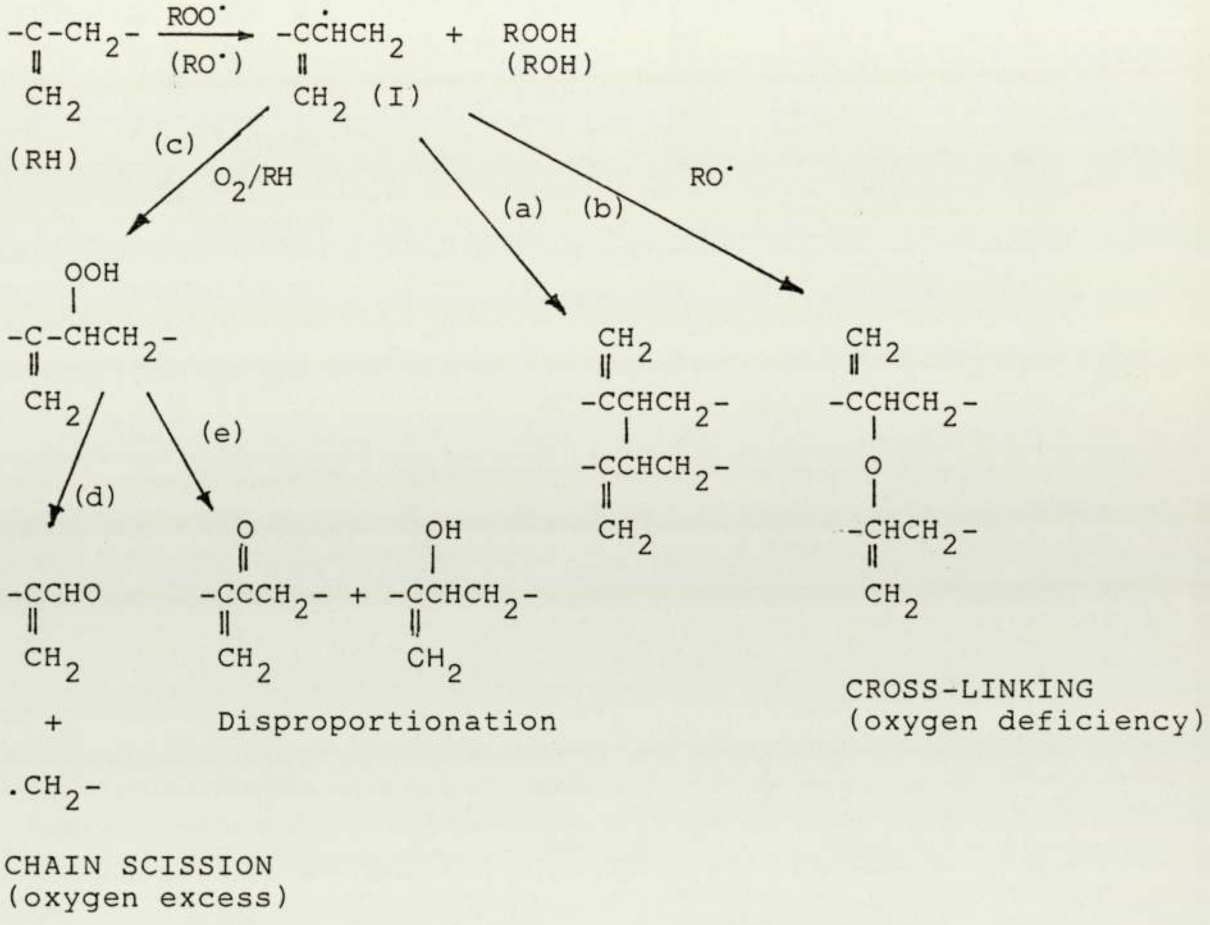
Termination $\quad \mathrm{2R.} \xrightarrow{(a)} \mathrm{R{-}R}$

$\mathrm{R.} + \mathrm{RO}_2^{\cdot} \xrightarrow{(b)} \mathrm{ROOR}$

$\mathrm{2RO}_2^{\cdot} \xrightarrow{(c)} \text{non-radical products} + \mathrm{O_2}$

Scheme 1.3 Oxidative degradation mechanism

In scheme 1.3, R. is the alkyl radical and $\mathrm{RO}_2^{\cdot}$ is the alkyl peroxyl radical derived from the organic substrate RH. The reaction is autocatalytic because hydroperoxide (ROOH) formed as the primary product of the reaction is also the source of free radical required to initiate the process. Termination of the oxidation chain normally occurs predominantly by reaction (a), (b) and (c). In the absence of antioxidant,reaction (c) in scheme 1.3 is responsible for termination at normal oxygen pressures. At low oxygen pressures, reactions 1.3(a) and (b) become much more important. For example, during the processing of polyethylene, where the rate of radical formation is high due to mechanical scission of the polymer chain and the only oxygen present is that initially trapped in the polymer, the predominant process occurring is molecular increasing through the allylic radicals (I) due to the crosslinking reactions (Scheme 1.4, reactions (a) and (b)). In the presence of excess oxygen, however, reaction 1.4(c) predominates and is followed by thermolysis of the hydroperoxide which can give rise to polymer chain scission by reaction 1.4(d).



Scheme 1.4 Alternative cross-linking and chain scission reactions in LDPE during processing(72)

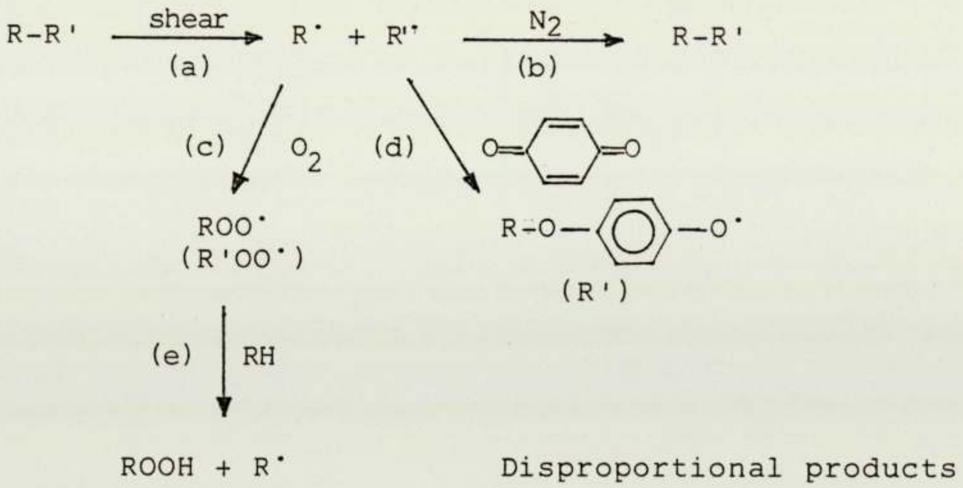
1.4.1 Oxidative Degradation of Unvulcanised Rubber

Unvulcanised rubber oxidises autocatalytically just as do simple hydrocarbons containing isolated double bonds and hydroperoxides as primary products are formed. The accepted mechanism is as shown in Scheme 1.3 and 1.4. The process of degradation of polymers can lead to a serious reduction in the useful life of the polymer.

Degradation of rubber is always undesirable in long term service of products, however, the process of mastication of rubber, subjecting rubber to high shearing forces in the presence of air, enables the incorporation of compounding ingredients into the partially degraded and less viscous rubber(73).

The mechanical scission of carbon-carbon bonds occurs in the polymer backbone when the polymer is subjected to high shearing forces(64). In the absence of oxygen the macroradicals produced by mechanical scission of the polymer molecule (Scheme 1.5, reaction (a)) are effective initiators for radical polymerisation(74). Oxygen behaves as an effective trap for macroalkyl radicals formed and this leads to the production of peroxy terminated molecular chains of similar molecular weight to the mechanically formed macro-radicals (Scheme 1.5, (a) and (c)). In the absence of oxygen, however (in nitrogen), other radical trapping agents (e.g., benzoquinone) behave in the same way as oxygen does (Scheme 1.5, (d)). In an inert atmosphere and in the absence of a radical trap, recombination occurs to give macro molecules of similar molecular weight to that of the original rubber (Scheme 1.5, (b)).

Oxygen clearly has an important influence on the mechanodegradation of rubber since not only does it prevent the recombination of macro-alkyl radicals but it also gives rise to macro-alkyl hydroperoxides which are initiators for oxidation (Scheme 1.5, (c), (e)).



Scheme 1.5 Reaction of mechano-radicals$^{(74)}$

1.4.2 Oxidative Degradation of Vulcanised Rubber

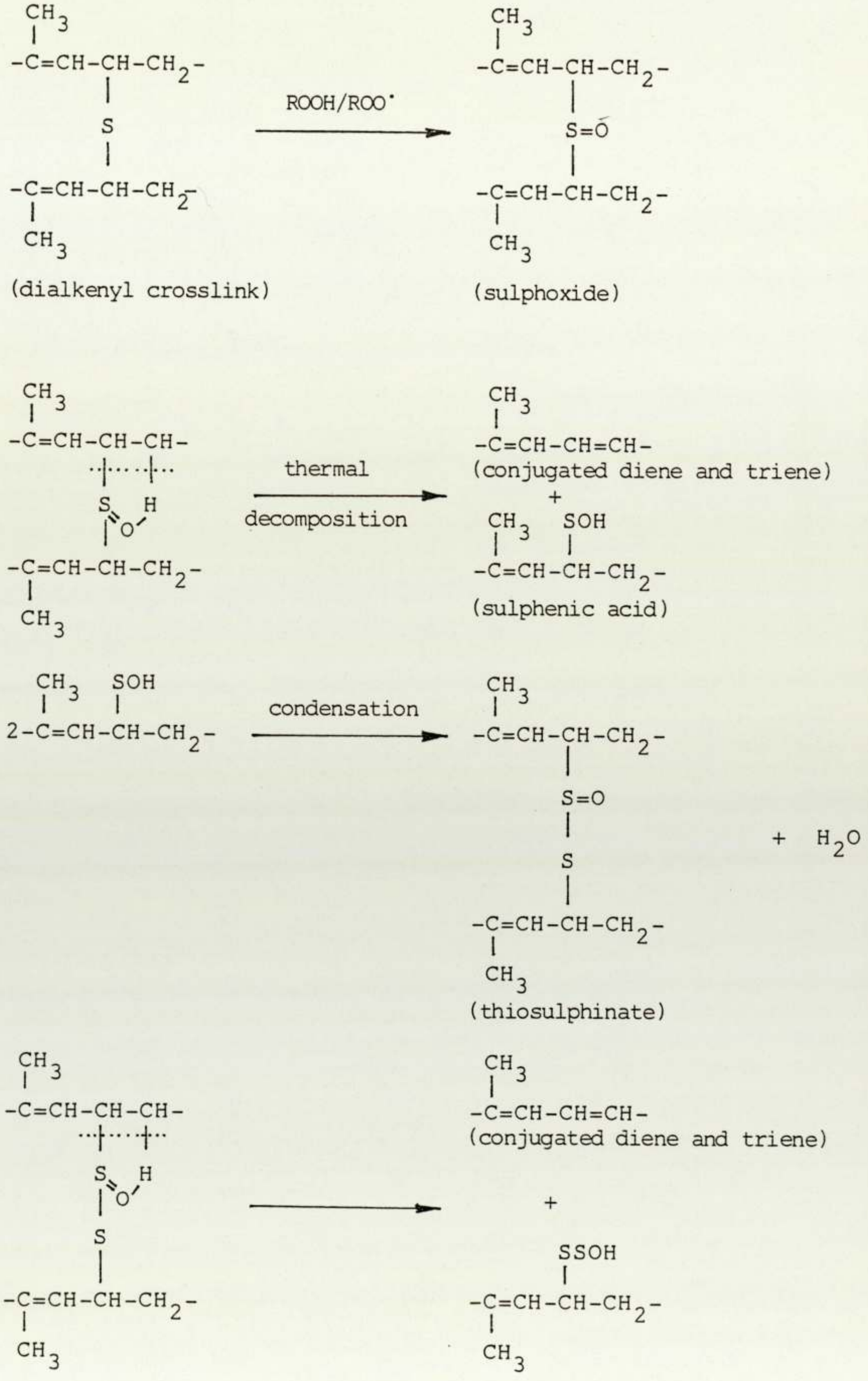
Oxidative degradation of sulphur vulcanised rubber differs considerably from that of raw rubber or peroxide vulcanised rubber. Peroxide vulcanisate oxidise in a similar way to unvulcanised rubbers, this is due to carbon-carbon links formed by peroxide and thus the oxidation process remains autocatalytic as in the case of raw rubber. The degradation of peroxide vulcanisate is therefore due to carbon-carbon bond scission(75,76). Oxidative degradation of sulphur vulcanisates are auto-retardation processes(77). Apart from main chain scission, C-S and S-S scission can also occur in degradation of sulphur vulcanisate.

Vulcanisate containing mainly monosulphidic crosslinks undergo oxidation by hydroperoxides or peroxy radicals to form sulphoxide which is thermally unstable leading to decomposition with scission at the C-S bonds to give sulphenic acid intermediates. The sulphenic acids undergo condensation giving a thiosulphinate crosslink which may also undergo scission by a similar mechanism(78,79). Conjugated dienes and triene groups are also formed along the main chain as a likely consequence of crosslink decomposition(78-80). The oxidation mechanisms are illustrated in Scheme 1.6.

In the case of disulphide crosslinks, oxidation by hydroperoxide occurs in a similar way to give thiosulphinate which undergoes a free radical disproportionation in the presence of peroxy compounds (reaction 1.11)(78,79).

$$\mathrm{RSSR} \xrightarrow{\mathrm{ROOH}} \mathrm{RSOSR} \longrightarrow \tfrac{1}{2}\mathrm{RSO_2SR} + \tfrac{1}{2}\mathrm{RSSR} \qquad (1.11)$$

This is ascribed to the more thermally labile $-\overset{\overset{\displaystyle O}{\|}}{S}-S-$



<u>Scheme 1.6</u> Oxidation of monosulphidic crosslink

linkage than the -S-S- linkage(72).

Little is known about oxidation of polysulphide crosslinks but it is believed that they may behave in a similar way(79).

1.5 Fatigue of Rubber

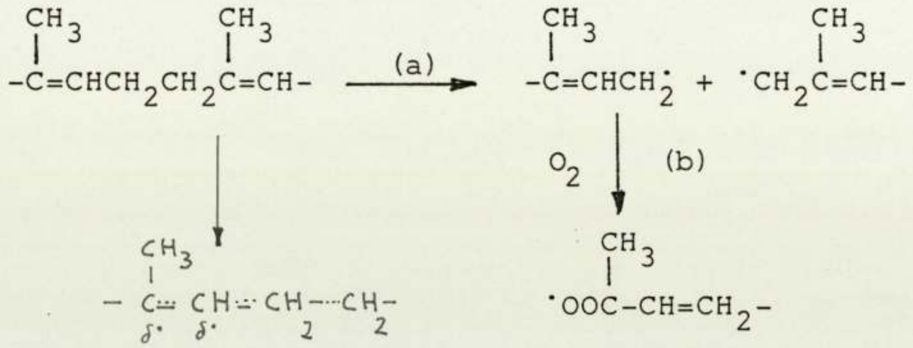
The term "fatigue" is frequently used to describe the mechano-degradation process which is a major cause of failure in rubber components subject to stress(74). Fatigue failure may occur under static loads, but is generally accelerated by cyclic stresses. Examples of fatigue failure are groove cracking in tyres tread and ply separation in tyres, etc.,(81).

1.5.1 Mechanism of Fatigue

Fatigue is a mechanochemical process causing gradual weakening of the rubber network and eventual fracture. Kuzminsky(82,83) showed that mechanically activated oxidative destruction take place during the fatigue rather than just mechanical destruction as suggested by others. Mechanical destruction is different from mechanically activated oxidation and these processes cannot be considered as identical. Potter and Scott(84) have observed an initial chain scission during mechanodegradation of peroxide cured rubber. Two processes have been proposed to account for the effect of fatigue in vulcanised rubber:

a) the homolysis of the weakest carbon-carbon bond in the polymer chain to give radicals(69,84,85)

b) the activation of the double bonds towards oxygen by distortion of the tetrahedral bond angle giving partial double bond character(84), as shown in Scheme 1.7.



Scheme 1.7

Both processes have the effect of increasing the rate of autoxidation by introducing mechanically formed macro radicals.

1.5.2 Factors Involved in Fatigue

There are many factors affecting the fatigue life of rubber such as inhomogeneities, strain cycles, atmosphere, accidental damage and composition(81). Various kinds of inhomogeneities, such as particulate material, areas of unequal cure, all have one thing in common, they serve as loci of fatigue failure by causing highly localised stress concentrations.

Busse(86) was the first to show the effect of strain cycle on fatigue life. The fatigue life increases as the cycle time of the same extension increases. Strain cycle effects on the fatigue life are noted in many products and contribute to their ultimate failure. The energy input in a deformation cycle is very important in its effect on fatigue life(87).

Beatty(81) stated that the atmosphere surrounding an elastomer specimen which is being subjected to repeated deformation can affect the time for complete failure in several different ways. The most important of these is an alteration of the physical properties of the specimen at or near its surface by chemical reaction of oxygen or ozone with the rubber, whether this surface be the original surface or the new surface being generated by growing flaws. If this reaction is such that it leads to a decrease in the ultimate elongation of the polymer at any given point, then the result will be to shorten fatigue life. This postulated effect of the atmosphere on fatigue life has been borne out by a number of experiments. The results of one of these showed that the number of cycles to failure of samples was greatly increased in very pure nitrogen and less in air (ozone-free) than in oxygen or ozone. Gent(88) reported that unprotected natural rubber vulcanisates showed an increase in fatigue life if the fatigue tests were carried out in the vacuo rather than air, and also stated that the effect of oxygen is more pronounced at low strain.

1.5.3 Effects of Compounding

Variations in compounding may affect the fatigue life of polymer in many different ways. However, it may be said on the basis of fatigue theory, that compounding variation affect fatigue life as a result of the effect of number and stability of crosslinks upon the physical properties at any given point in the rubber specimen.

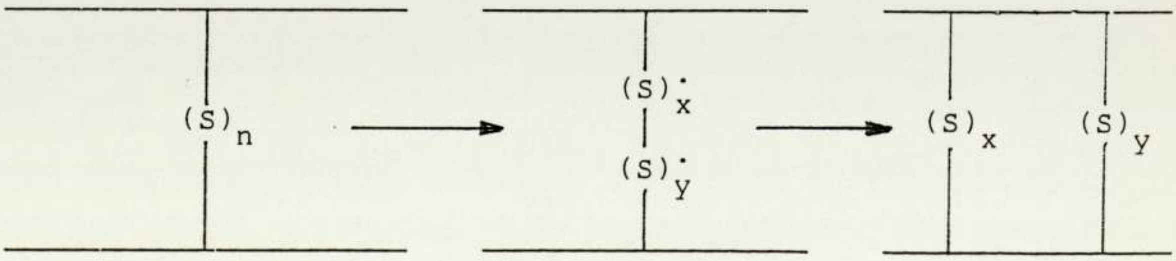
The most important variable affecting fatigue life is the nature of the rubber. The evidence showed that natural rubber and butyl rubber give the longest fatigue lives compared with SBR(hot polymerised rubber), Neoprene CN and NBR (Hycar 1001), when they were tested at 0 to 100% extension at ambient temperature and at 475 cycles per minute. The lower fatigue lives of these synthetic rubbers may be due to pendent vinyl groups arising from polymerisation process. These groups function as loci of crosslinking by interacting with peroxy and possibly other radicals(19). This resulting in a modulus increase so that the capacity of the molecule to re-orientate is reduced and the molecular stresses increase during fatiguing.

Small particle size fillers have been clearly shown to have little effect on fatigue life if comparisons with large particle fillers are made on equal energy input basis(87). However, the effect of fillers can be influenced not only by particle size but also be adhesion between the rubber and filler(89). Looser adhesion between the granules and the surrounding vulcanised rubber has been shown by Angioletti(89) to give greater stress concentrations and the possibility of local cracking is increased.

1.5.4 Effects of Vulcanising System and Crosslink Type

The fatigue strength of vulcanisates is markedly dependent on the nature of the network structure and hence the vulcanising systems. Baker(90) studied the characteristics imparted to natural rubber by a wide range of carbonblacks and reported that tension fatigue is controlled rather more by the vulcanising system than by the black type.

Rubber vulcanisates cured with conventional vulcanising systems (Table 1.1) are reported(19,91,92) to show superior properties to compounds obtained with nonelemental sulphur or peroxide curing systems. The superior fatigue resistance of the former is attributed to a relatively high proportion of polysulphidic crosslinks which impart a high degree of flexibility, able to break and reform during fatiguing(6,7,93,94).



where $n = x + y$

Efficiently vulcanised systems produce mainly monosulphide crosslinks which are thermally stable and unlike the polysulphidic type, cannot readily exchange or rearrange under high localised stresses, so that the fracture of the linkage results in a site which is a potential source of further crack growth(6,7).

Peroxide cures which promote the formation of carbon-carbon crosslinks(29,95) impart very good thermal stability, however, the fatigue life is known to be generally poor(96).

1.5.5 Effects of State of Cure and Curing Time

The fatigue characteristics of rubber vulcanisates depend not only on the type of crosslink but also on the state of cure and curing time(97). Increasing the degree of crosslinking decreases the fatigue resistance, presumably by reducing the capacity of the rubber molecule for re-orientation and hence increasing the molecular stresses(98). If the level of crosslink is too low, it may also lower resistance to crack growth(99).

Overcure in conventional vulcanisate leads to a significant decrease in polysulphidic crosslinks and generates more di- and mono- sulphidic crosslinks which causes a reduction in the fatigue resistance. Undercure produces a vulcanisate of low elasticity due to the insufficient formation of crosslinks, thus resulting in poor fatigue life.

1.6 Protection of Rubber Against Fatigue Failure

Various chemical and physical means of protection are used to stabilise vulcanised rubber for service under different loading conditions. Antioxidants are by definition agents which are added to inhibit oxidative deterioration either during processing or in service. Different technologies have their own terminology for the classification of antioxidants. Rubber technologists frequently use the term anti-degradant to encompass a range of protective functions (thermal antioxidants, anti-fatigue agents, anti-ozonants, etc)(74).

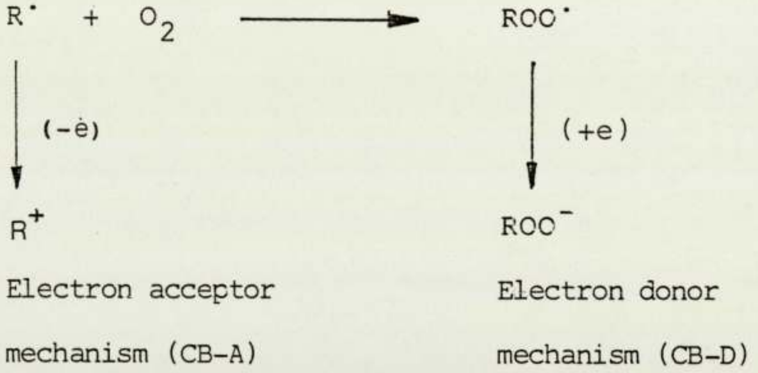
Only vulcanised rubber requires complex protection. Raw rubber, plastics and synthetic fibres do not need this variety of protective agents which may differ profoundly in their mechanism of action(100).

1.6.1 Mechanisms of Antioxidant Action(74,77)

Oxidation inhibition processes have been classified into two main types: (a) chain-breaking and (b) initiation prevention. The first type, by its reaction with alkyl and alkylperoxy radical break the propagation cycles and thus leads to new chain termination reaction. Examples of antioxidants functioning in this way are aromatic amines and phenols. The second type inhibits or retards the formation of free radicals in the initiation step, this includes hydroperoxide decomposers, the transition metal deactivators and U.V. stabilisers acting by the light absorption mechanism.

a) The chain-breaking (CB) mechanism

Consideration of the free radical oxidation chain reaction (Scheme 1.8) indicates two ways in which the chain might be interupted.



Scheme 1.8 Potential chain-breaking process during autoxidation

Alkyl radical deactivators are electron acceptors which oxidise the radical to a carbenium ion, which may subsequently give an olefin by loss of proton. Alkylperoxy radical deactivators are electron donors which reduce the oxygen radical to the corresponding anion (Scheme 1.8).

At ambient oxygen pressure alkylperoxy radicals are normally present in a large excess over alkyl radicals. Consequently termination occurs by reaction of alkylperoxy radicals with each other or with antioxidants. In this case the CB-D process is favoured over CB-A. The CB-A mechanism, on the other hand operates best in oxygen deficiency.

b) The preventive mechanism

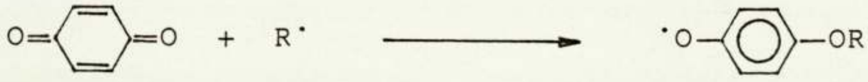
In the initiation step of the free radical chain mechanism of autoxidation, degradation of hydroperoxide to free radicals is accelerated by heat, light and metal ions(70,73,77,101) which can participate in electron transfer reactions. Preventive antioxidants stabilise the polymer by either removing hydroperoxide in a process which does not involve free radical formation, or protecting hydroperoxides from decomposition.

1.6.2 Chain-breaking Antioxidants(74,77)

1.6.2.1 Chain-breaking Acceptor (CB-A) Antioxidants

Macro-alkyl radicals are electron donors which are readily oxidised by electron acceptors. Those oxidising agents capable of removing alkyl radicals from an autoxidising system have antioxidant activities(77,102). Quinones, nitro compounds and "stable" free radicals of which nitroxyls and phenoxyls are the best known example of this class(77) (reaction 1.12-1.15). Quinones and nitro compounds have been shown to be effective alkyl traps for rubber during processing. However, they have little practical utility since they are not able to compete with oxygen in the presence of excess oxygen. Quinones have been shown to have some antifatigue activity, however(77).

$$RH + O_2 \longrightarrow R^{\cdot} + HOO^{\cdot} \qquad (1.12)$$



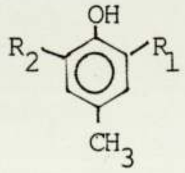
(1.13)

$$R'\text{-}N\text{=}O + R^{\cdot} \longrightarrow R'\text{-}\overset{R}{N}\text{-}O^{\cdot} \qquad (1.14)$$

$$R'_2\text{-}N\text{-}O^{\cdot} + R^{\cdot} \longrightarrow R'_2\text{-}N\text{-}OR \qquad (1.15)$$

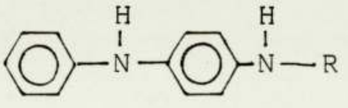
1.6.2.2 Chain-breaking Donor (CB-D) Antioxidants

The CB-D antioxidants function by electron or hydrogen atom donation to an alkylperoxy radical and thus terminate a kinetic chain. Hindered phenols (VIII) and aromatic amines (IX) are typical examples in this category. Both of them fit very well into the inhibitor model described in reaction 1.16 since they posses labile H atoms and the radical derived from the antioxidant (denoted here by $A^{\cdot}$) is sufficiently resonance stabilised not to cause abstraction of hydrogen from the substrate.



(VIII)

R_1=CH_3, t-Butyl, Phenyl
R_2=t-Butyl, CH_3, Phenyl



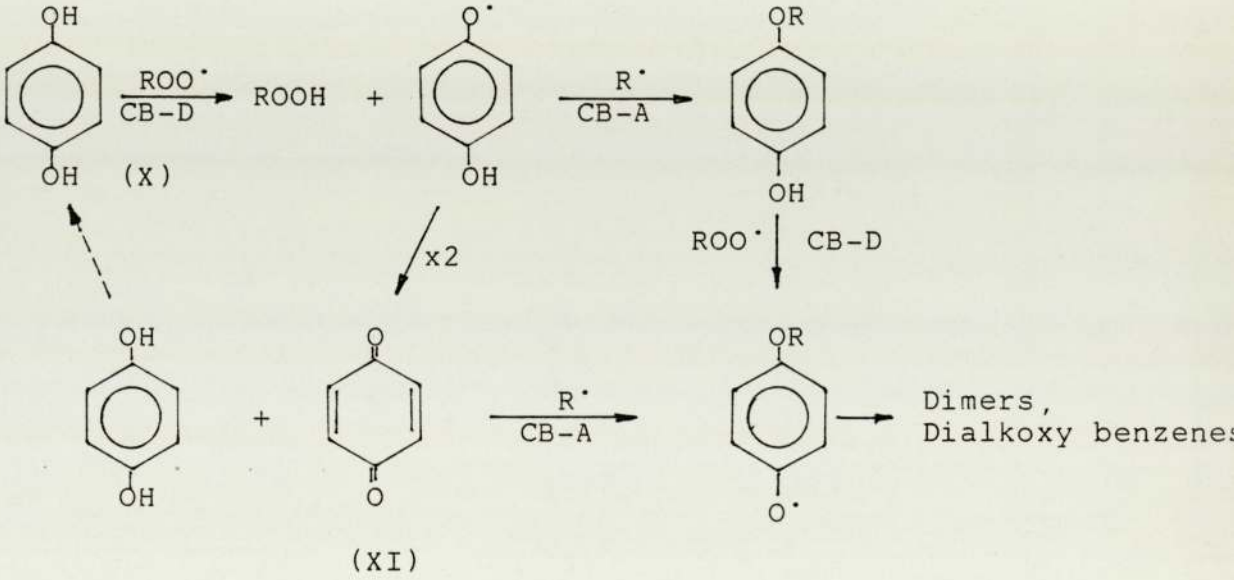
(IX)

R=Isopropyl, Di-octoyl

$$\begin{array}{ll} ROO^{\cdot} + AH \longrightarrow & ROO......H......A \\ & \quad\Big\downarrow \\ & ROOH + A^{\cdot} \qquad (1.16) \end{array}$$

1.6.2.3 Complementary Antioxidants Involving Both CB-A and CB-D

Antioxidants which exhibit both CB-A and CB-D mechanisms have an advantage over those operating by a single one since in most oxidation processes both alkyl and alkylperoxy radicals are present to some extent. A well known example which involves both mechanisms is hydroquinone(X). It is converted by the CB-D mechanism (Scheme 1.9) to benzoquinone (XI) which itself is a very effective alkyl radical trap and many radicals may be removed from the system before antioxidant inactive products are finally obtained.



Scheme 1.9 Complementary mechanisms involving CB-A and CB-D in antioxidant function of hydroquinone

1.6.3 Preventive Antioxidants(72,77)

This type of antioxidants can be divided into three groups: light absorbers, metal ion deactivators and peroxide decomposers(PD).

The function of the light absorbers as preventive antioxidants is to reduce the effect of light on the degradation of the peroxide and to reduce the photo-excitation effect on the oxidation of rubber by absorbing the ultraviolet light to a minimal electron excitation level and transmitting the absorbed energy in the form of harmless low light quanta and thermal energy(70,103,104). Ultraviolet stabilisation in rubber vulcanisates is not very important due to the presence of fillers, notably carbon black which is an effective light screen(70).

The role of metal ion deactivators is to deactivate the catalytic effect of metal ion upon hydroperoxide decomposition. Examples of transition metal ions that catalyse the decomposition of hydroperoxide are copper, manganese, nickel and iron. Inhibition of metal ion catalysis can be achieved by incorporating the metal ion in a complex using chelating agents.

Peroxide decomposers inhibit the chain initiation induced by the degradation of hydroperoxide by degrading the hydroperoxide to stable non-radical products, and they fall into two main classes: stoichiometric reducing agents (PD-S) and catalysts for peroxide decomposition (PD-C). The first one has the ability to reduce hydroperoxides to alcohols without the formation of free radicals. Phosphate esters such as trisnonylphenylphosphite (XII, Scheme 1.10), is an example of PD-S antioxidant. It is a commercial stabiliser for raw rubber.

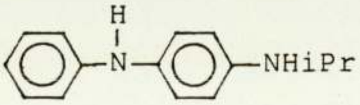
(XII)

Scheme 1.10

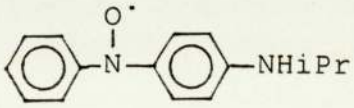
PD-C antioxidants have the ability to destroy hydroperoxide through the formation of an acidic product. A wide variety of sulphur compounds fall into this class. In all cases the antioxidant function is proceeded by a pro-oxidant stage and the importance of the pro-oxidant stage is a function of the structure of the sulphur compound.

1.6.4 Antifatigue Agent for Rubber(74)

Antifatigue agents are antioxidants but not all antioxidants are effective antifatigue agents. The most effective antifatigue agents so far identified are the diarylamine classes and the most widely used commercial agent is N-isopropyl-N'-phenyl-p-phenylene diamine (XIII, IPPD).



(XIII),IPPD



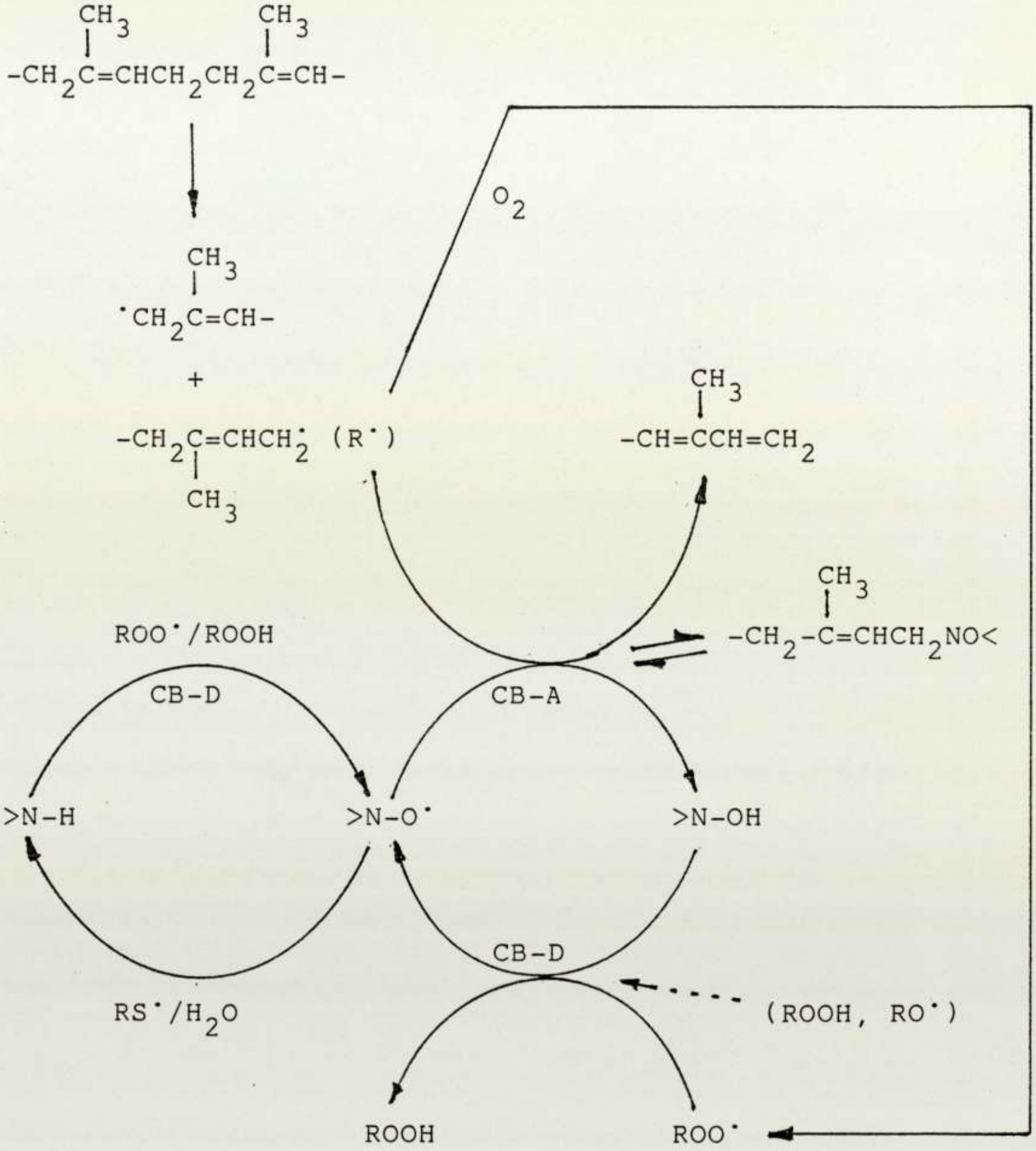
(XIV),nitroxyl radical

IPPD has been shown to be converted to the corresponding stable nitroxyl radical (XIV) in vulcanised rubber during fatiguing(85) and (XIV) then becomes involved in a cyclical catalytic mechanism in which both macro alkyl and macro alkylperoxy radicals are removed from the polymer.

The effectiveness of nitroxyl species as antifatigue agents for sulphur rubbers has been attributed to the fact that under reducing conditions found in sulphurated rubber networks, the nitroxyls are substantially reduced back to the parent amines which act as a reservoir for the formation of the nitroxyl/hydroxylamine couple which is involved in the removal of both alkyl and alkylperoxyl radicals in a catalytic antioxidant process (Scheme 1.11)(74,105).

1.7 Scope and Object of the Present Project

It has been generally accepted that polysulphidic networks can resist mechano-oxidation (fatigue) more than networks containing di- and monosulphides and even more than carbon-carbon crosslinks(19,91,92). This is attributed to the ability of more flexible polysulphide crosslinks to undergo interchain reactions to di- and monosulphide before failure occurs. Furthermore, polysulphide crosslinks are able to break and reform during the fatiguing operations, thus releasing local stresses and imparting a greater fatigue life to the vulcanisate.



Scheme 1.11 Catalytic activity of nitroxyl radicals during fatiguing of vulcanised rubber(74,105)

The rather attractive theory about the strength advantages of "labile" crosslinks has however, been largely disproven by the results of Lal(106), who prepared both sulphur and peroxide vulcanisates of natural rubber and noted the effect of the presence of either sulphur-sulphur bonds, carbon-carbon bonds, or a mixture of two. In the first place, it was noted that extraction of sulphur vulcanisates by triphenylphosphine, which is known to "strip" sulphur from polysulphides, did not reduce the tensile strength or flex life of the network. Furthermore, the introduction of sulphur-sulphur crosslinks into a peroxide vulcanisate, by means of "second stage" vulcanisation, did not enhance the strength as might have been expected.

In addition, there is evidence from recent work(107) which does not support the generally accepted conclusion mentioned above. This shows that peroxide vulcanisate of the same modulus to that of sulphur vulcanisate, both in the presence and absence of antioxidants, has superior fatigue resistance.

There is also evidence(108) that extra-network sulphur compounds act as antifatigue agents. Hence there does not appear to be any support for the theory that "weak" crosslinks actually lead to strong rubber networks, and the reasons for such differences in strength must lie elsewhere.

It is therefore of some interest to find out whether peroxide vulcanisates can give longer fatigue life than sulphur vulcanisate when they are cured to the same moduli. This is because this kind of comparison has normally been made in rubber vulcanisates whose moduli are different.

Another criticism that is sometimes made of peroxide vulcanisate is that it has never been considered to be practical for tyre formulations because of the absence of a significant induction period during vulcanisation. Some additives (coagents) have been examined (1.2.2.3) to increase the scorch time of NR/peroxide system and improve the fatigue life of the vulcanisate i.e., Saret 500 crosslinking agent, produced by Sartomers Resins Inc., Essington Pa, USA. It is thus of interest to look for chemicals as crosslinking coagents for this purpose.

The object of the present work is,therefore, concerned with the investigation of fatigue resistance of natural rubber, particularly in a peroxide system in comparison with conventional CBS-sulphur vulcanisate.

CHAPTER TWO

EXPERIMENTAL

2.1 Materials

2.1.1 Natural Rubber

Natural rubber used was SMR 10(Standard Malaysian Rubber, grade 10).

2.1.2 Compounding Ingredients

Compounding ingredients shown in Table 2.1 were used without further purification.

2.2 Compounding

The vulcanisation systems used in this work were conventional CBS-sulphur and peroxide. Gum vulcanisates prepared from unextracted and extracted SMR 10 were used throughout this work. The black filled vulcanisates were prepared only from unextracted SMR 10. Base formulations used are shown in Table 2.2 and 2.3.

2.2.1 Base Formulations

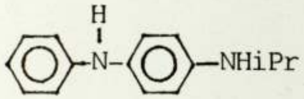
These are as shown in Table 2.2 and 2.3.

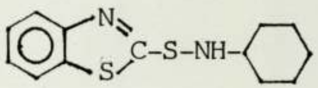
Table 2.1

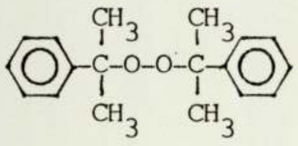
Compounding ingredients	Supplier
Zinc oxide (ZnO)	Amalgamated Zinc Ltd
Stearic acid	Anchor Chemicals Ltd
Sulphur (S)	Anchor Chemicals Ltd
N-cyclohexyl benzothiazyl sulphenamide (CBS), (XV)	Monsanto Chemicals Ltd
Dicumyl peroxide (DCP)-Dicup R, (XVI)	Hercules
N-isopropyl-N-phenyl-p-phenylene diamine (IPPD), (XIII)	Imperial Chemical Industries
High Abrasion Furnace Black (HAF)	Sevalco Ltd
Trimethylol propane trimethacrylate (TMPTMA), (XVII)	Aldrich Co
Triallyl cyanurate (TAC)*, (XVIII)	Degussa Ltd
Non-rubber constituents (NRC)**	-

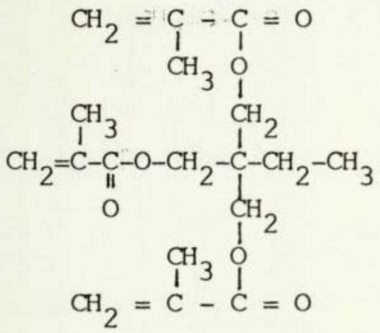
* Donated by Degussa, Teil unserer Welt, Metaff Chemie Pharma

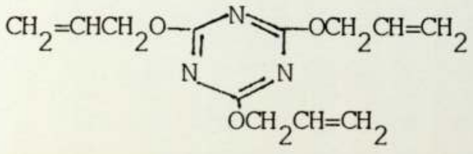
** Obtained by evaporation of acetone extract of SMR 10


IPPD (XIII)


CBS (XV)


DCP (XVI)


TMPTMA (XVII)


TAC (XVIII)

Compounding Ingredients(phr)	Gum Compound	Black Compound
SMR 10	100	100
HAF	-	40
Naphthenic Processing Oil	-	3.3
Zinc oxide	5	5
Stearic acid	3	3
CBS	0.6	0.6
Sulphur	2.5	2.5
Antioxidants:		
IPPD (variable)	0,0.5,1.0,1.5	0,0.5,1.0,1.5
Non Rubber Constituents(NRC)	0,1.0,1.5	-

Table 2.2 Conventional CBS - Sulphur formulation

Compounding Ingredients(phr)	Gum Compound	Black Compound
SMR 10	100	100
HAF	-	40
Naphthenic Processing Oil	-	3.3
DCP (variable)	1.5,2.0,2.5,3.0	3.0
Antioxidants:		
IPPD (variable)	0,0.5,1.0,1.5	0,0.5,1.0,1.5
Non Rubber Constituents(NRC)	0,1.0,1.5	-

Table 2.3 Peroxide formulation

2.2.2 Extraction of Raw Rubber

The raw rubber was sheeted out on a two-roll mill and extracted, when necessary, with hot acetone under nitrogen for 48 hours, using a Soxhlet apparatus. This was done to remove naturally occurring non-rubber constituents of the rubber. After extraction the rubber was dried in a vacuum oven at about 40°C and stored in a vacuum desiccator until requried.

2.2.3 Preparation of Gum Compounds

2.2.3.1 CBS-Sulphur Gum Compounds

All compounding ingredients except sulphur and IPPD were mixed in a laboratory size, type B Banbury mixer (Farrell-Bridge).

1,100 gm of unextracted or extracted NR was cut into small pieces and 55 gm of ZnO, 33 gm of stearic acid and 6.6 gm of CBS were mixed with the rubber according to the following mixing schedule:

Temperature of the chamber was maintained at 50°C.

Time (mins)	Mixing Steps
0	Add unmasticated rubber, 1100 gm
	Masticate for 2 mins.
2	Add chemicals, ZnO + stearic acid + CBS
	Mix for 3 mins.
5	Dump.

The total cycle time in Banbury mixer was 5 mins. By this stage the temperature of the chamber had risen to 90°C.

This masterbatch was then divided into six parts, each of them was mixed with sulphur and IPPD or NRC (when required) on a 12" two-roll mill to obtain six gum CBS-sulphur stocks with the same formulation as in Table 2.2. A 12" water-cooled laboratory two-roll mill with a friction ratio of 1:1 was employed. The total compounding time on the mill was 5±1 mins.

2.2.3.2 Peroxide Gum Compounds

Extracted or unextracted SMR 10 was masticated and mixed with compounding ingredients on a 12" water-cooled laboratory two-roll mill adjusted at 1:1 friction ratio. In a typical milling cycle, the raw rubber was first passed several times through a tight nip before being allowed to band on to the rolls. IPPD or NRC or TMPTMA or TAC, when required, was added after mastication of rubber for five minutes then followed by the addition of DCP. The total mixing time was 11±1 mins.

2.2.4 Preparation of Black Compounds

60 phr masterbatch of HAF with 5 phr Naphthenic oil (Sunpar 2280), MB-1, was mixed in Banbury mixer.

Time (mins)	Mixing Steps
0	Add all rubber, 700 gm Masticate for 1 min.
1	Add oil, 35 gm Mix for 2 mins.
3	Add one half of black, 210 gm Mix for 2 mins.
5	Add remainder of the black, 210 gm Mix for 2 mins, and then for a further ½ mins.
6½	Dump.

The total mixing time in Banbury mixer was 6½ mins. During the mixing cycle, the temperature inside the chamber rose to 120°C.

The formulation for masterbatch-1 (MB-1) was:

	(phr)
SMR 10	100
HAF	60
Oil	5

The MB-1 was then diluted to MB-2 on an open mill, heated at 60°C, with fresh rubber. To ensure thorough mixing of the fresh rubber into MB-1, the rubber was milled for 5 mins.

The formulation for MB-2 was:

	(phr)
SMR 10	100
HAF	40
Oil	3.3

The MB-2 was used to prepare black compounds of both vulcanisation systems on the open mill. For CBS-S formulation, all ingredients except sulphur were first mixed until good dispersion was obtained. Sulphur was added at the end of mixing step and mixed until good dispersion was achieved. In the case of peroxide formulation, IPPD was first mixed then peroxide was added and mixed until a uniform dispersion was obtained.

The consistency of the initial plasticity of each batch were checked by Wallace Rapid Plastimeter.

The cure characteristics of each batch were determined by the Monsanto Rheometer.

2.3 Vulcanisation

Vulcanisation occurs in three stages(109): (1) induction period; (2) curing or crosslinking stage; and (3) reversion or over-cure stage; as shown in Figure 2.1. The induction period represents the time at vulcanisation temperature during which no measurable crosslinking occurs. It is of practical importance since its duration determines the safety of the stock against "scorch" or onset of vulcanisation during the various processing steps which precede the final vulcanisation. Following the induction period, crosslinking proceeds at a rate which is dependent on the temperature and the composition of the compound. When crosslinking proceeds to full cure continued heating produces an overcure which may result either in a further stiffening or softening of the compound.

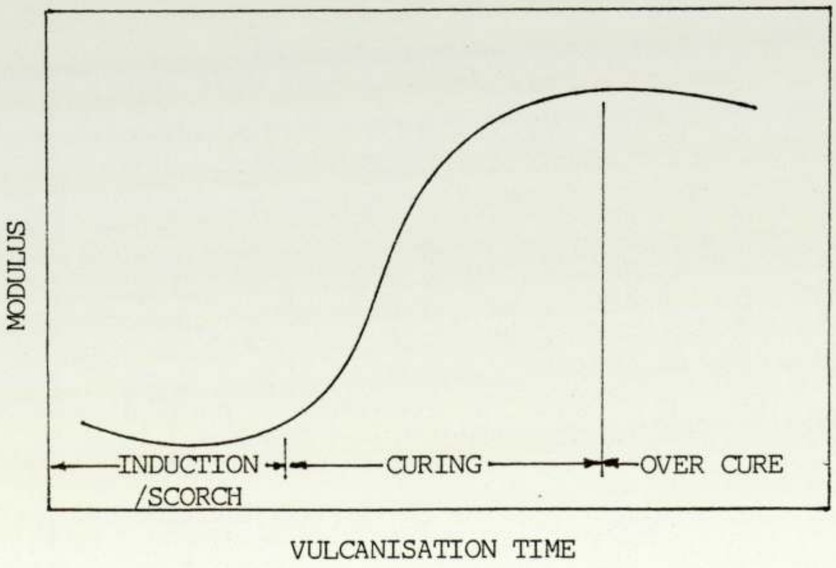


Figure 2.1 Steps in the vulcanisation process(109)

2.3.1 Monsanto Oscillating Disc Rheometer

The Monsanto Oscillating Disc Rheometer (Model 100)(110) was used to determine the cure characteristics of the compounded rubber before preparing vulcanised sheets for further testing. This instrument follows the resistance to motion of an oscillating rotor embedded on the rubber specimen held in a cavity at a chosen temperature (140°C for CBS-S stocks or 160°C for peroxide stocks). The cavity is formed by a fixed lower die and a movable upper die and is kept closed during test by a pneumatic ram (Figure 2.2). As the vulcanisation proceeds, the resistance of rotor oscillation through 3° arc is recorded in terms of torque against time to give a characteristic cure curve on a potentiometric flat-bed recorder.

A typical torque-time curve produced on the Monsanto Rheometer is shown in Figure 2.3. The scorch time may be obtained from this Rheograph by taking the time to an arbitrary rise in 5 units torque above the minimum. The rate of cure can be assessed from the slope of curve. However, more accurate results may be obtained for the scorch time and rate of cure by using the kinetic treatment of Coran(111,112), which assumes that the crosslinking formation is a first-order reaction after the end of the induction period, t_i; and that the rate of crosslink formation is inversely proportional to the crosslink

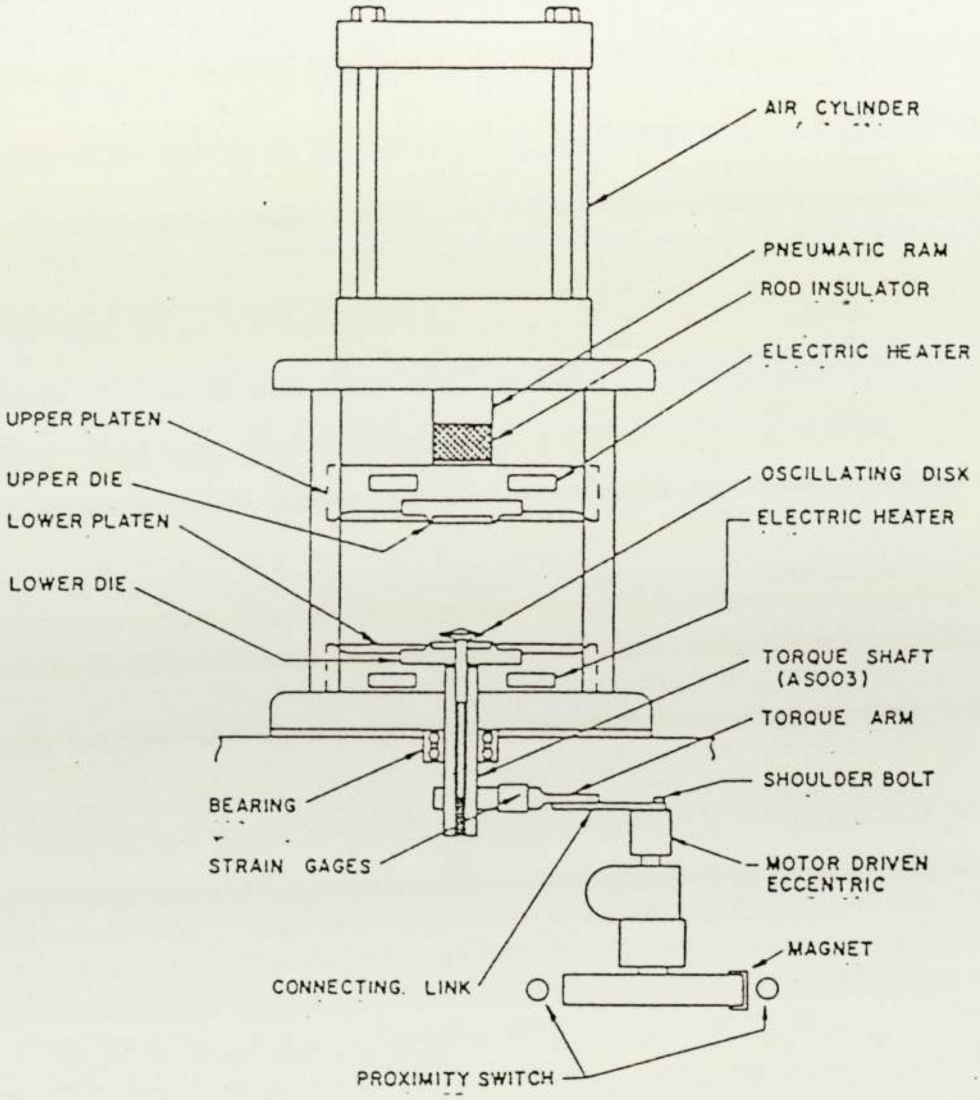


Figure 2.2 Oscillating disc system(110)

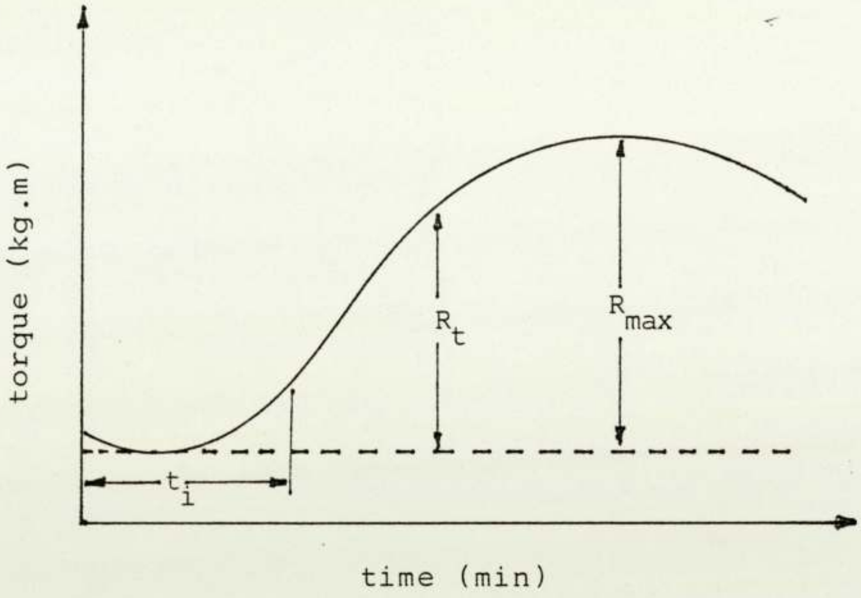


Figure 2.3 Typical Monsanto rheograph

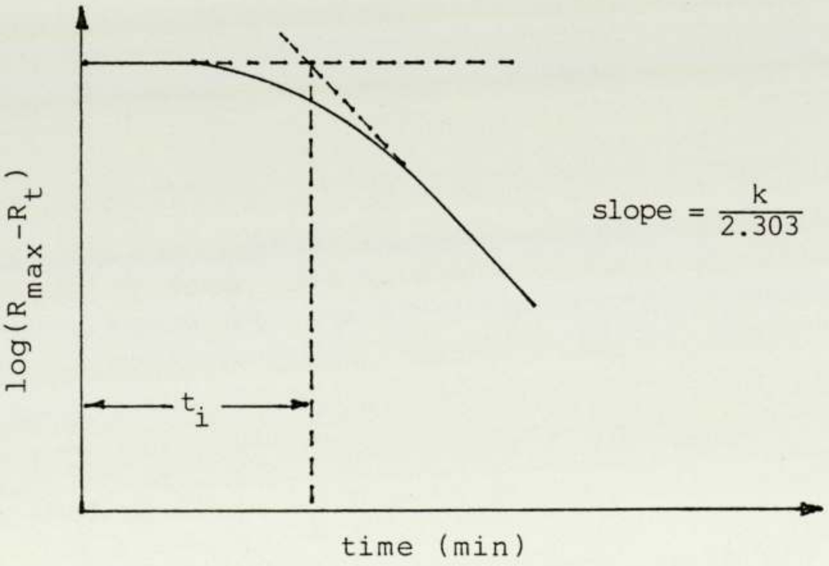


Figure 2.4 First order plot of $\log(R_{max}-R_t)$ against time according to the data obtained from the Monsanto rheograph

density. Since at maximum cure, the rate of formation of crosslinking is zero, then:

$$\frac{dV}{dt} = k(V_\alpha - V_t)$$

where k = the overall first order rate constant

V_α = the maximum crosslink density, and

V_t = crosslink density at time "t".

Thus on integration:

$$\int_{V_o}^{V_t} \frac{dV}{V_\alpha - V_t} = k\int_{t_i}^{t} dt$$

Hence,

$$\ln\frac{V_\alpha - V_t}{V_\alpha} = k(t - t_i) \tag{2.1}$$

Since the torque developed (R) is a measure of the crosslink density, therefore equation becomes:

$$\ln\frac{R_{max} - R_t}{R_{max}} = k(t - t_i)$$

or

$$\log(R_{max} - R_t) = \log R_{max} + \frac{k}{2.303}(t - t_i)$$

where R_{max} = the maximum torque attained

R_t = the torque at time "t"

t_i = the induction time

Then a plot of $\log(R_{max} - R_t)$ against time "t" gives a straight line with slope of $\frac{k}{2.303}$ and an induction period to t_i (Figure 2.4).

These parameters thus become characterised in a vulcanising system.

i) The induction time, t_i, which is, in the case of sulphur vulcanisation, a measure of the time for the formation of an active sulphurating agent, and the reaction of this with the hydrocarbon to form rubber-bound intermediate - a precursor to crosslink formation. For peroxide vulcanisation, t_i is a direct measure of the time for the peroxide to undergo homolysis and to abstract hydrogen atom from the rubber chain. This is due to the fact that peroxide vulcanisation is a free radical reaction.

ii) The overall first-order rate constant, k.

iii) The maximum torque developed, R_{max}, which is a measure of crosslink density.

2.3.2 Press Curing

Curing of all rubber stocks to give the required test samples were carried out in a mould placed between the heated platens of a press. A certain weight of the compound was placed in the appropriate mould and cured at a certain temperature. The mould was first sprayed with mould releasing agent before the curing process, in order to facilitate the removal of the vulcanised rubber, especially for peroxide stock, from the mould. The optimum cure time or any state of cure required were obtained from the Monsanto Rheograph. The vulcanisation temperature was varied according to the vulcanising system used, i.e., 140°C for CBS-sulphur system and 160°C for peroxide system. The time to vulcanise the compound was varied according to the state of cure required.

The vulcanisation was done in a steam heated single daylight press equipped with a thermocouple and maintaining a pressure at 55 tons on a twelve inch diameter ram.

2.3.2.1 The Amount of Stock Used for Preparation of a Particular Test Specimen

Test sample for	amount of stock (approx. in gm)	mould dimensions (cm x cm x cm)
Rheometer	9-10	-
Plasticity	5	-
Fatigue	45-55	22.9x7.6x0.16 with beaded edges
Tensile Properties	20-22	25.0x15.0x0.102
Infra-red	4.5-5.0	13.5x13.5x0.018

Samples were first sheeted out on a laboratory two-roll mill to about 3 mm thickness and then cured with the grain (pattern of lines formed during milling which are perpendicular to the direction of flow) direction along the length of the mould.

2.3.2.2 Conditioning of the Test Sample

As the properties of vulcanised rubber change continuously with time, and since these changes are particularly rapid during the first 16 hours after vulcanisation(113), thus no tests were carried out during this period. Samples were stored in a vacuum desiccator for 24 hours before testing.

2.4 Physical Tests on Unvulcanised Rubber

The plasticity number or viscosity of the rubber mixture is defined as its resistance to flow. Rubber, before vulcanisation, is in between the plastic and the elastic states; when warm it becomes more plastic and less elastic. Most rubbers are used in their elastic state, nevertheless, plasticity tests have been devised to measure the elastic as well as the plastic component of deformation, and are important because both determine the processibility of the material (see Section 3.2).

2.4.1 Wallace Rapid Plastimeter

The Wallace Rapid Plastimeter (the compression type) was used to measure the plasticity of rubber compound in the present investigations. Its principle is that the test piece is compressed between parallel plates under a constant force and the compressed thickness measured. To operate this plastimeter, the test piece is cut with a punch which will give a constant volume of $0.40 \pm 0.04 cm^3$, the thickness being approximately 3 mm and the diameter approximately 13 mm. The test piece is precompressed to a thickness of 1 ± 0.01 mm within 2 sec and heated for a further 15 sec. The test load of 10 kg is then applied for 15 sec further, then the test piece thickness is measured. The usual temperature of test is 100°C and the result is expressed as the thickness of the test piece at the end of the test in units of 0.01 mm and is called the "rapid plasticity number".

2.5 Physical Tests on Vulcanised Rubber

2.5.1 Fatigue Test

Fatigue cannot be defined as any change in the properties of a material caused by prolonged action of stress or strain, since this general definition would then include creep and stress relaxation. Fatigue is normally taken to cover only changes resulting from repeated cyclic deformation which means, in effect, long term dynamic irreversible changes in the rubber. In rubber testing it is normal to distinguish between two types of fatigue test; tests in which the aim is to induce and/or propagate cracks without subjecting the test piece to a large increase in temperature, and tests in which the prime aim is to cause heating of the specimen by the stressing process. The former type is generally referred to as flex-cracking or cut-growth tests and the latter as heat build-up. The "heat build-up" type of fatigue test is carried out on an apparatus generally called a "Flexometer". For flex-cracking tests, there are a variety of flex testers e.g., the De Mattia, the "flipper" or Torrens machine, Du Pont machine and the Ross machine. The essential feature of flexometer tests is that a cylindrical specimen is subjected to rapid alternating deformation in compression or shear or some combination of the two, the motion generally being superimposed on a fixed pre-stress or strain. The usual measurements are of temperature rise by using a thermocouple, permanent deformation and cycles to failure. The flex-cracking test differs from that of the flexometer test in that the strip test piece is subjected to mechanical action in the bending mode under circumstances where rise in temperature of the rubber is minimal and so investigates resistance to surface cracking.

2.5.1.1 The Monsanto Fatigue to Failure Tester(114)

In this investigation, the Monsanto Fatigue Tester (Figure 2.5) was used to determine the fatigue lives of

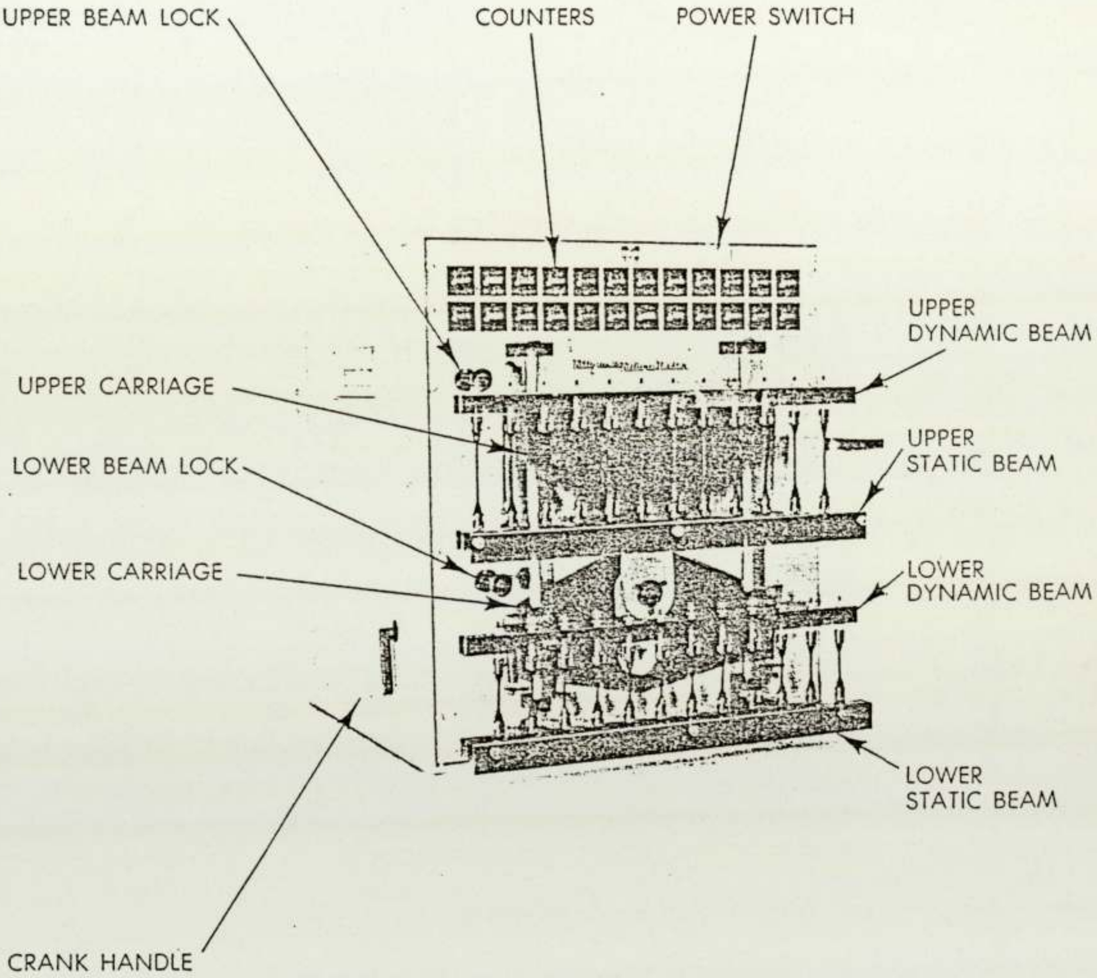


Figure 2.5 Fatigue to failure tester(114)

various vulcanisates. This machine was originally developed by the Natural Rubber Producers Research Association (NRPRA) to overcome the poor reproducibility associated with the De Mattia Flex Tester. In this test, dumb-bell shaped test specimens are subjected to a repeated strain cycle and the number of cycles to failure recorded automatically. During each extension, the test specimens are subjected to an increasing strain at uniform acceleration for a quarter of a cycle, then relax over the next and held at zero strain for the remaining half of the cycle. The maximum applied strain could be varied by changing the driving cams of the machine.

2.5.1.2 Sample Preparation for the Monsanto Fatigue to Failure Tester

Samples for fatigue tests were moulded and conditioned prior to testing (Sections 2.3.2.1 and 2.3.2.2). Dumb-bell shaped test pieces were cut from the vulcanised rubber sheet at right angles to the grain direction using a B.S. type "E" cutter. The die cutting edge was always kept evenly sharp and free from any grease or oil since any flaws at the sample edge, caused by faulty cutting, could cause premature failure. The fatigue mould used was designed to give marks at regular intervals along the beaded edge of the cured sheet so that the die can be correctly aligned before cutting each dumb-bell. All samples were examined for moulding or cutting imperfections before being tested.

2.5.1.3 Operation of the Monsanto Fatigue to Failure Tester

To ensure that fatigue samples were loaded in an unstrained state, the long axis of the chosen cams were aligned manually, using the crank handle to operate the main drive, with a horizontal line engraved on the equipment (both main beams are then resting on their stop and the distance between each set of top and bottom beams is identical) (Figure 2.5). Each sample holder was then adjusted by inserting a 6 cm long calibration metal rod between the upper and lower shackle and adjusting the thumb nut until a snug fit was attained. Eight test specimens from each stock were mounted in the sample holders. A cam No. 4 was used to obtain a single extension of 60% at a frequency of 100 cycles per minute. After the machine had been run for 1000 cycles, the power was turned off and the drive cams were set for zero extension by adjusting the thumb nut so that when the lower shackle was raised, a slight bow appeared in the sample. The machine was then run again and fatigue life was recorded as the number of cycles to failure.

2.5.1.4 Expression of Fatigue Results

Fatigue results are not very reproducible. This is due to the fact that fatigue failure is affected by a number of factors e.g., flaws which are caused by poor dispersion, inhomogeneous curing, the presence of foreign matter, physical defects in cutting the sample; and applied strain. The normal averageing methods are unsatisfactory because of the spread of results obtained. So a minimum of eight similar test pieces were fatigued and the fatigue life was quoted as the Japanese Industrial Standard (JIS) average(114) obtained from the four highest values using the formula:

$$\text{JIS average} = 0.5A + 0.3B + 0.1(C + D)$$

where A, B, C and D are the fatigue lives and where $A>B>C>D$. The sample with maximum fatigue resistance were selected because premature failure in the test piece may be due to flaws and surface imperfections caused by the moulding or cutting processes. The results would not reflect the true value of fatigue life if such imperfect samples were considered.

2.5.2 Tensile Test

Physical testing of rubber generally involves application of a force to a specimen and measurement of the resultant deformation or, conversely, application of a deformation and measurement of the required force. Two common modes of deformation are tensile and shear and test results are expressed in the form of stress-strain curves. Stress is the force per unit cross-sectional area i.e., F/A for either tensile or shear deformation, usually expressed in units of pounds per square inch (PSI) or in the SI system of International units the Newton per square meter (N/m^2) is used. Strain is the deformation per unit original length ($\Delta L/L_o$) in tensile tests or deformation per unit distance between the contacting surfaces in shear tests. This is usually expressed as per cent and is dimensionless since it is the ratio of two lengths. An elongation of 300%, for example, means that the specimen has been stretched to four times its original length. In the common practice of rubber technology, the stress required for a given elongation is used to represent the material stiffness. This quantity is called the modulus. A 300% modulus, for example, means the stress required to produce a 300% elongation. The machine used for tensile measurements was the E-Type Tensometer(115).

2.5.2.1 Sample Preparation for the E-Type Tensometer

Samples for tensile tests were moulded and conditioned prior to testing (Section 2.3.2.1 and 2.3.2.2). Dumb-bell shaped test pieces were cut from the vulcanised sheet using B.S. type "E" cutter.

Testpieces similar to those used in fatigue test as described in Section 2.5.1.2 were used for compounds which readily slip from the grip. These were particularly suited because the beaded edges ensured that the test pieces did not slip from the grips during stretching (see Figure 2.6).

All samples were examined for moulding or cutting imperfections before being tested. Cross-sectional areas were determined for each sample before testing.

2.5.2.2 Operation of the E-Type Tensometer

A dumb-bell shaped specimen is clamped between two jaws and the small clamps are placed along the middle section of the dumb-bell piece.

When the machine is switched on, the upper jaw automatically moves upwards, extending the sample using a certain predetermined load. The force and elongation required to break the sample is recorded on a chart paper.

The conditions for operating the machine used in this project are listed below.

Chart head drive control : Set on forward (F)
Cross head speed range : High
Attenuator : Medium
Motor Speed Range : Set to 10,000
Speed control : Set at 3525
Motor R.P.M. meter : 20"min^{-1}

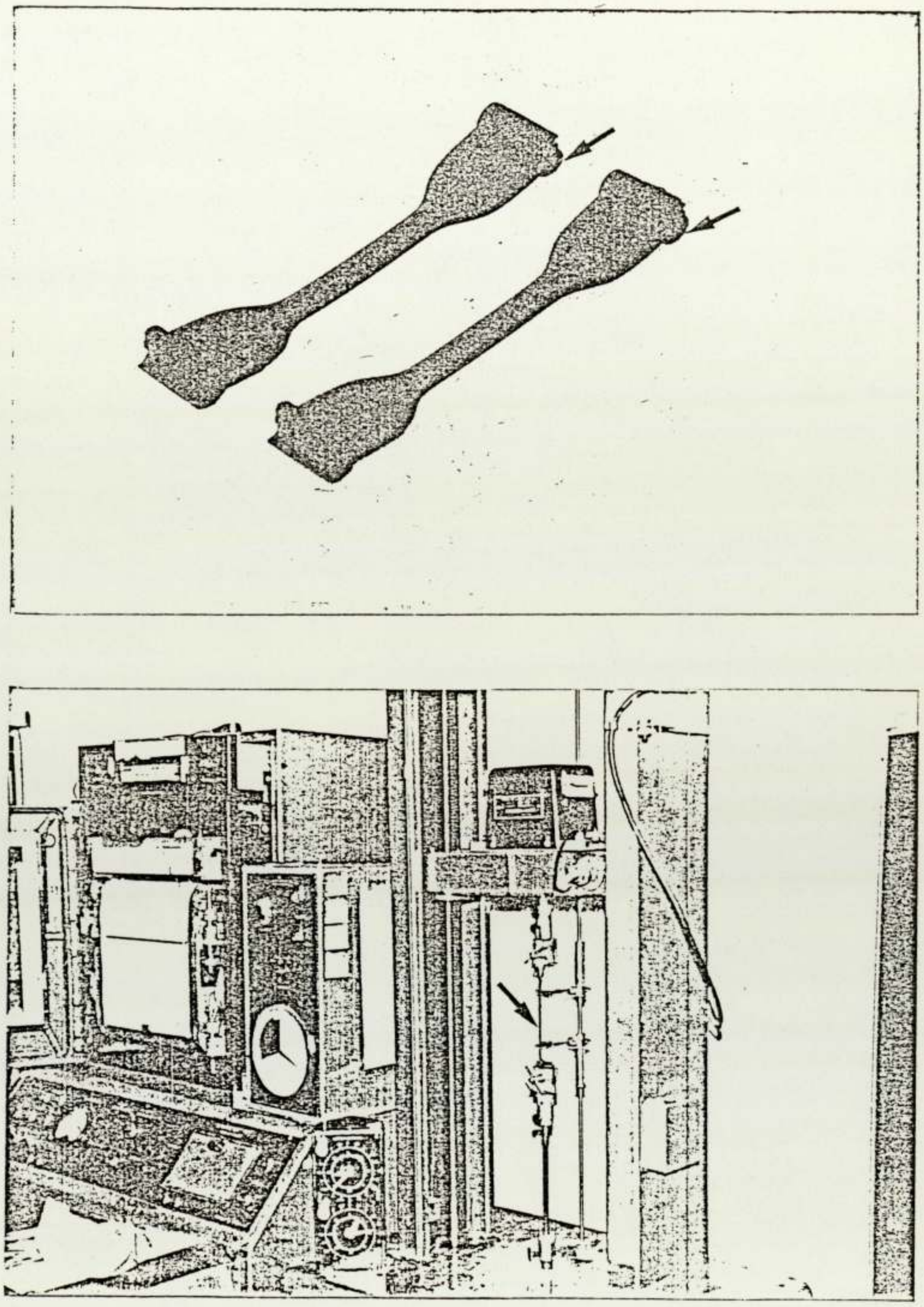


Figure 2.6 Fatigue test pieces having beaded edges (above, see arrow) and fatigue test piece being stretched on E-type Tensometer

Because of motor and chart speed range, 10" clamp separation is equivalent to 20" on the chart.

An average value for UTS, EB, M 100 and M 300 were obtained for six samples from each formulation.

2.5.2.3 Expression of Ultimate Tensile Strength (UTS)

A typical plot obtained from the E-Type Tensometer is shown in Figure 2.7.

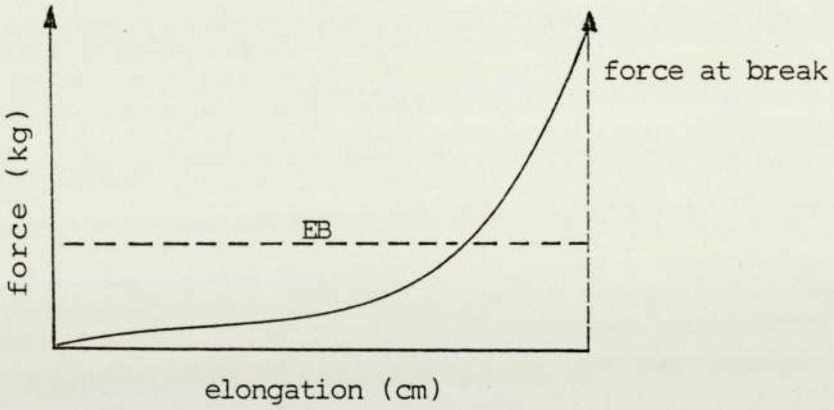


Figure 2.7 A typical Tensometer plot

Ultimate Tensile Strength is given by:

$$\text{UTS} = \frac{\text{Force}}{\text{Unstrained area (cross-sectional)}}$$

The force at break was measured directly from the chart paper and UTS evaluated in SI units.

2.5.2.4 Expression of Elongation at Break (EB)

Elongation at Break is given by:

$$\%EB = \frac{L - L_o}{L_o} \times 100$$

where L = extended length

L_o = original length

Since 20" on chart paper is equivalent to 10" extension of sample, and L_o = 1" (i.e., the initial separation of clamps) hence,

$$\%EB = \frac{(L/2 + 1) - 1}{1} \times 100$$

The extended length (L) is measured directly off the chart paper to evaluate %EB.

2.5.2.5 Expression of Modulus at 100% and at 300% Elongation

Modulus at 100% elongation (M_{100}) is given by stress at 100% elongation and Modulus at 300% elongation (M_{300}) is given by stress at 300% elongation.

$$\text{where stress} = \frac{\text{Force}}{\text{Cross-sectional area (unstrained)}}$$

2.6 Extraction of Vulcanised Rubbers

Vulcanised rubbers were extracted when there was the need to remove extra-network compounds (ENCS) which might otherwise interfere with network structure analysis. The extraction was carried out using a Soxhlet apparatus, with hot acetone under nitrogen. To ensure the ENCS were completely removed, the time to complete removal of ENCS was first estimated by monitoring acetone extraction over a range of times. Then the extracted rubbers were dried in a vacuum oven at temperatures below 40°C to a constant weight. Extracted rubbers were further extracted with iso-octane at room temperature for 48 hrs and the extracted solutions were analysed by U.V. absorbance. Figure 2.8 shows the U.V. spectra for extracted solutions derived from rubbers extracted with hot acetone for various times. The suitable time for hot acetone extraction was taken from the time that U.V. spectra show no absorptions due to aromatic $\pi\rightarrow\pi^*$ transitions of dicumyl peroxide at λ_{max} 258 nm and due to aromatic $\pi\rightarrow\pi^*$ transitions of acetophenone at λ_{max} 278.(see Figure 2.8 and Section 4.2.1). This was determined experimentally to be 24 hrs however, to ensure that complete removal of ENCS was achieved, a minimum of acetone extraction time of 48 hrs was subsequently used. The extracted vulcanised rubbers were dried in a vacuum oven at temperature below 40°C to a constant weight and stored in a vacuum desiccator until required.

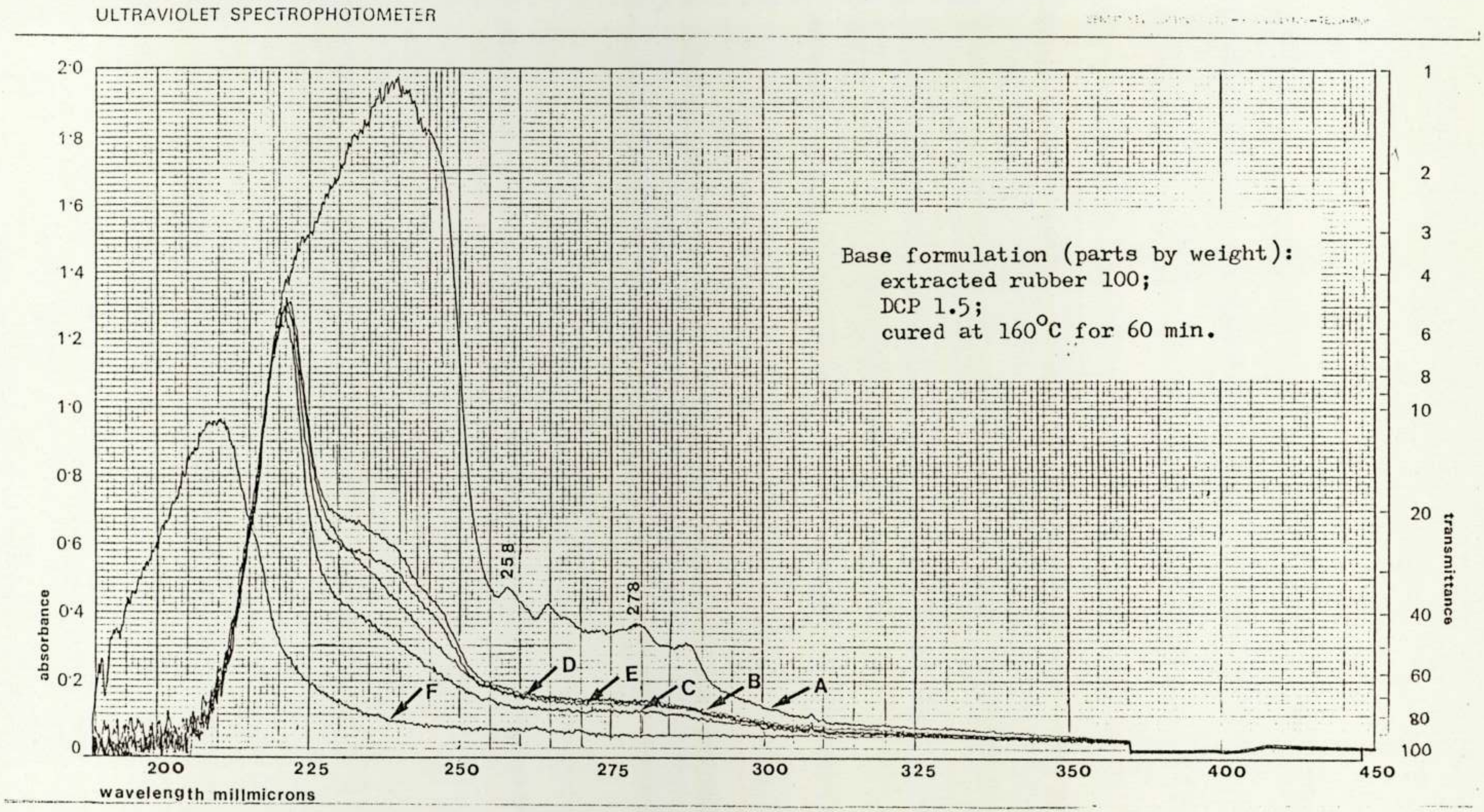


Figure 2.8 Spectra for cold iso-octane extract derived from 2gm of vulcanisates which first were hot acetone extracted for various times followed by cold iso-octane extracted for 48 hrs: acetone extracted for:- (A) None, (B) 24 hrs, (C) 48 hrs, (D) 72 hrs, and (E) 96 hrs; (F) pure iso-octane

2.7 Determination of Crosslink Density

The determination of crosslink density (M_c) by a chemical method is virtually impossible with an accelerated sulphur-cured diene rubber vulcanisate because of the complexity of the system and the formidable obstacles to analysis(116). Estimation of crosslink density in this project was determined by swelling measurements which give a related physical parameter $M_{c,phys}$ from which $M_{c,chem}$ may be estimated by the Moor-Watson-Mullins empirical calibration (see Equation 1.10).

2.7.1 Equilibrium Volume Swelling Measurements

The samples before testing were extracted in hot acetone under nitrogen for 48 hrs. The extracted samples were dried in a vacuum oven at a temperature of 25°C to a constant weight. The extraction was carried out in order to remove the non-rubber constituents which were known to effect the test results(117). The swelling agent used was n-decane, which swells rubber extensively without leading to detectable degradation of the network. This solvent has a sufficiently low vapour pressure to obviate the need for elaborate precautions to preclude loss of swelling liquid during the experiments(117).

Square specimens of approximately 3 mm side were cut from each of the fatigue test pieces, weighed accurately and placed in small weighing bottles. N-decane was added, the bottles covered with caps and placed in a thermostatically controlled water bath at 25°C. After the samples had been swollen to equilibrium, they were removed and the excess solvent on the surface was dried by pressing lightly between two filter papers. The samples were then weighed immediately in closed weighing bottles before they were deswollen under vacuum at 45°C to constant weight. The difference in weight between the swollen samples and the deswollen samples gave the weight of n-decane absorbed.

2.7.2 Analysis of Data

The volume fraction of rubber network (V_r) in the swollen vulcanisates, were calculated from the above measurements using the expression:

$$V_r = \frac{(W_2 - FW_1)\rho_r^{-1}}{(W_2 - FW_1)\rho_r^{-1} + W_3\rho_s^{-1}} \qquad (2.1)$$

where:

W_1 = unswollen weight

W_2 = deswollen weight

W_3 = weight of the absorbed solvent

F = weight fraction of insoluble components

ρ_r and ρ_s = densities of rubber and solvent respectively

The values of V_r were then used in the Flory-Rehner equation (equation 2.2), using the rubber n-decane interaction constant (χ) from the average of three results of Ihenyen$^{(118)}$ i.e., $\chi = 0.446$ for conventional CBS-S vulcanisate and $\chi = 0.441$ for peroxide vulcanisate.

The modified Flory-Rehner equation:

$$-[\ln(1-V_r) + V_r + \chi V_r^2] = \rho V_o M_c^{-1}(V_r^{\frac{1}{3}} - V_{r/2}) \qquad (2.2)$$

where:

V_r = equilibrium swelling ratio

χ = rubber solvent interaction constant

ρ = density of rubber (0.92 gm/cm^3 for natural rubber)

V_o = molar volume of solvent (194.918 cm^3/mol for n-decane at 25°C)

M_c = number average molecular weight of the rubber network chains between crosslinks

Then the physical crosslink density (CLD_{phys}) defined as:

$$CLD = \frac{1}{2M_{c(phys)}}$$

were calculated.

2.8 Infra-red Spectroscopy

A Perkin Elmer 599 B infra-red spectrophotometer was used to obtain the infra-red spectra of rubber film and of extract from dicumyl peroxide vulcanisate. This double-beam infra-red spectrophotometer provides the possibility of automatic elimination of the solvent absorption. In analysis for extra network compounds of peroxide vulcanisate, a demountable NaCl cell was filled with the extract derived from room temperature extraction of 5 gm of vulcanisate with 25 ml of CCl_4 for 48 hrs. Another NaCl cell was filled with CCl_4 in order to cancel out the absorption due to CCl_4 used for extraction, and this cell was placed on the reference beam. Thus the absorbance obtained was due to extra network compounds of vulcanisate. The absorbance of specific absorptions for rubber film and for extract are shown in Section 4.1.4 and 4.2.2 respectively.

2.9 Ultraviolet Spectroscopy

A Pye Unicam SP 800 B Ultraviolet spectrophotometer was used to analyse extra network compounds of dicumyl peroxide vulcanisate. The absorbance of specific absorptions used were discussed in Section 2.6 and are also discussed in Section 4.2.1.

2.10 Gas-Liquid Chromatography

The instrument used for GLC analysis was the Pye Unicam, Flame Ionisation which employed a high accuracy temperature programmer. The column used for the analysis of the

ENCS peroxide vulcanisate was a 6' glass column packed with 10% polyethylene glycol adipate on Celite 56. The temperature range was 60°C to 160°C. An initial temperature of 60°C was held for 2 minutes after which the temperature was programmed to rise at 8°C per minute until a temperature of 160°C was attained. The flame ionisation detector was used with nitrogen carrier gas at a flow rate of 30 mls/min.

CHAPTER THREE

ASSESSMENT OF VULCANISATION CHARACTERISTICS AND CROSSLINK DENSITY

3.1 Introduction

The purpose of vulcanisation is to convert the thermoplastic polymer to the elastic state with long term properties appropriate for adequate service life. This can be achieved by using an appropriate crosslinking system. Critical parameters related to the process of vulcanisation are the time elapsed before the onset of crosslinking (scorch time), the rate and extent of crosslinking. There must be sufficient scorch resistance to permit mixing, forming and moulding, followed by a rapid formation of crosslinks. These parameters: scorch time, cure rate and modulus level have in the past been measured by following the rheological changes in the rubber.

The initial technological properties of the vulcanisate are primarily a function of crosslink density and are affected by the type of crosslink, the nature of the polymer and the type and amount of compounding ingredients.

Long term properties are also affected by the vulcanisation process, for example, fatigue life increases at low crosslink densities but is reduced with increasing crosslink formation(119). Thus, the comparison between different vulcanisates must be made at approximately equal moduli.

3.2 Wallace Plasticity Number

The plasticity of the rubber mix i.e., its ability to flow, is the property used to assess the rheological properties for processing, and it is frequently used for process control purposes. Standardised plasticity tests use either the rotation (e.g., Mooney Viscometer) or the compression (e.g., Wallace Rapid Plastometer) principle. The latter was used in the present investigation and the test result obtained i.e., the thickness of compressed test piece in units of 0.01mm, is the plasticity number. The test procedure for plasticity measurement is described in Section 2.4.1.

The Wallace Plasticity Number were found to be 12 to 14 for gum stocks and 20 to 23 for black filled stocks. Therefore, the plasticity before vulcanisation did not vary significantly, and any difference in behaviour of the compound stock could be attributed to the nature and density of the crosslink and/or to the additive and not to the mastication time.

3.3 Assessment of Vulcanisation Characteristics

The vulcanisation characteristics of a vulcanising system may be described by the scorch time, the rate of cure and the optimum cure time. A study of these parameters was undertaken to compare the cure behaviour of the conventional accelerated sulphur and the peroxide vulcanising system with and without the additives. The vulcanisation characteristics were assessed using the Monsanto Oscillating Disc Rheometer as described in Section 2.3.1.

Unextracted and acetone extracted SMR 10 were used for the preparation of pure gum compounds and only unextracted SMR 10 was used for the preparation of black filled compounds. The extraction procedure and the compounding operation used were as described in Sections 2.2.2, 2.2.3 and 2.2.4.

3.3.1 Conventional Accelerated Sulphur Vulcanisation

The vulcanisation system was conventional accelerated sulphur (parts by weight: rubber 100, ZnO 5, Stearic acid 3, CBS 0.6, S 2.5), and the stocks were cured at 140°C for different times to give the same rheometer torque.

3.3.1.1 Results

The cure characteristics of unextracted and of extracted SMR 10 with and without antioxidant or non-rubber constituents are shown in Figures 3.1-3.3, and their corresponding cure parameters in Table 3.1. The variation in cure times to give a chosen rheometer torque are given in Table 3.2.

Results given in Table 3.1 show that the cure parameters of gum stocks prepared from extracted (a-e) and unextracted (f-h) rubber were slightly affected in the presence of IPPD. IPPD increased the scorch time but with further increase, the scorch time reduced, as did the rate of cure and the maximum torque, these are demonstrated in an extracted rubber. However, IPPD reduced the scorch time and rate of cure in an unextracted rubber. IPPD has more effect on the time to optimum cure of gum stocks made from extracted rubber than on that of unextracted rubber.

The incorporation of non-rubber constituents (NRC) which were added as compounding ingredient to extracted rubber (Table 3.1, d-e) slightly changed all the cure parameters as compared with the control (Table 3.1, a).

The results in Figures 3.1-3.3 and Table 3.1 show that at the level of IPPD or non-rubber constituents incorporation into the gum and IPPD into the black filled stocks, there was no significant change in cure characteristics from the control. Thus these results indicate that IPPD does not interfere with the CBS-S vulcanisation reaction. However, the effect of IPPD on the maximum torque of black filled stock is shown to be remarkedly increased as the concentration of IPPD is increased. This may be ascribed to the activity of the carbon black surface in accepting free radicals from rubber which then gives to additional cross-links.

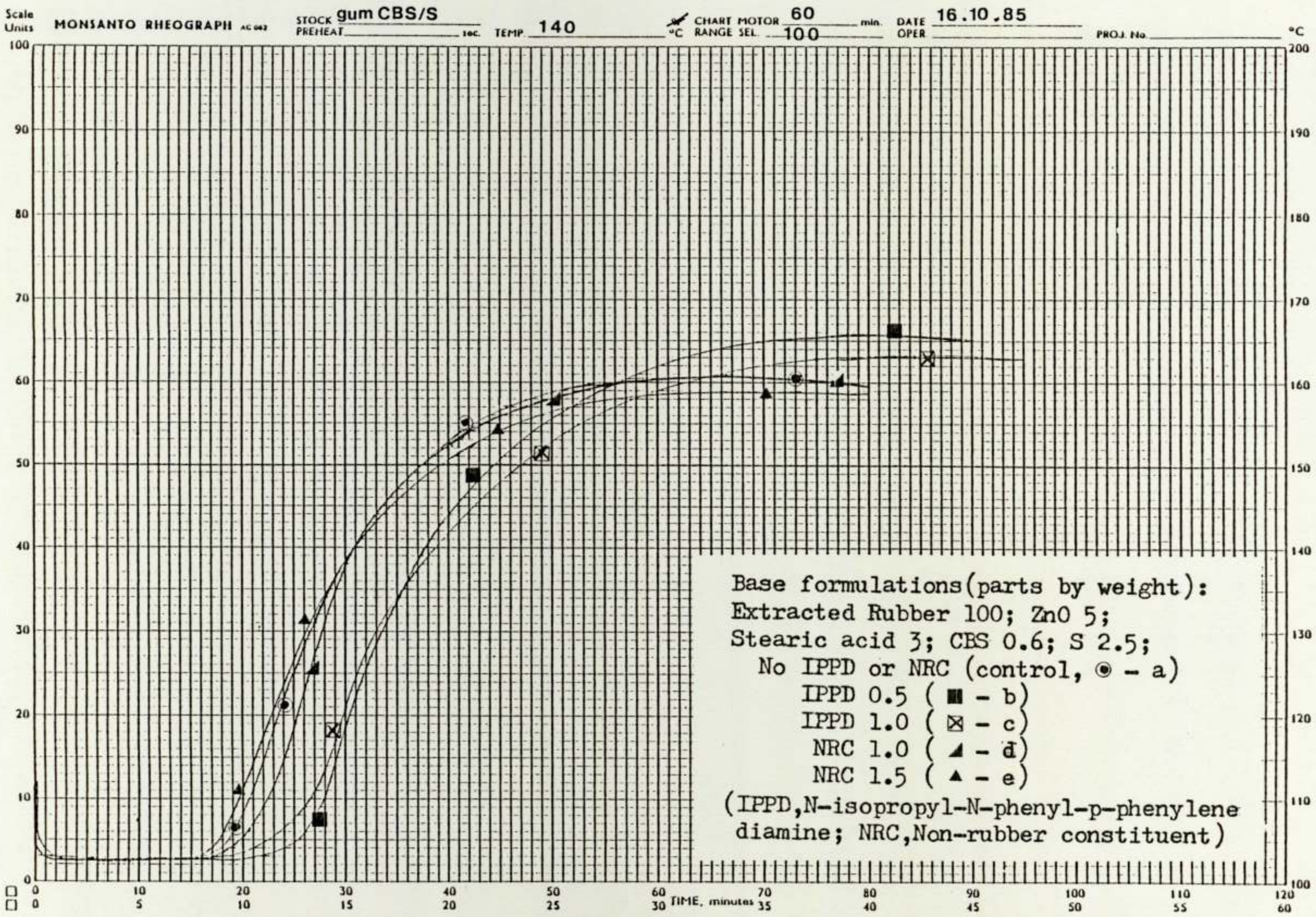


Figure 3.1 Monsanto Rheographs for extracted rubber vulcanised with CBS-S system (gum stocks)

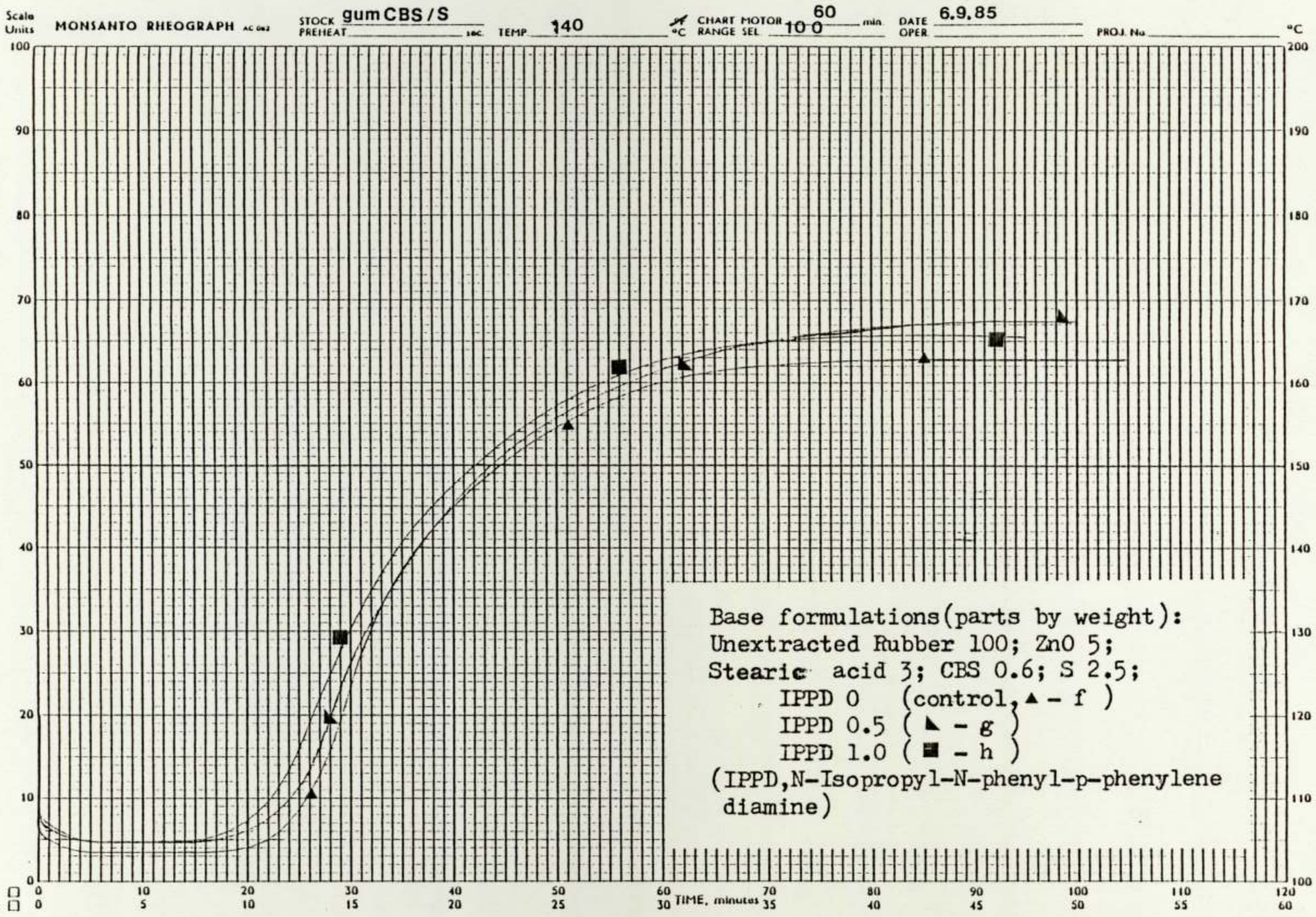
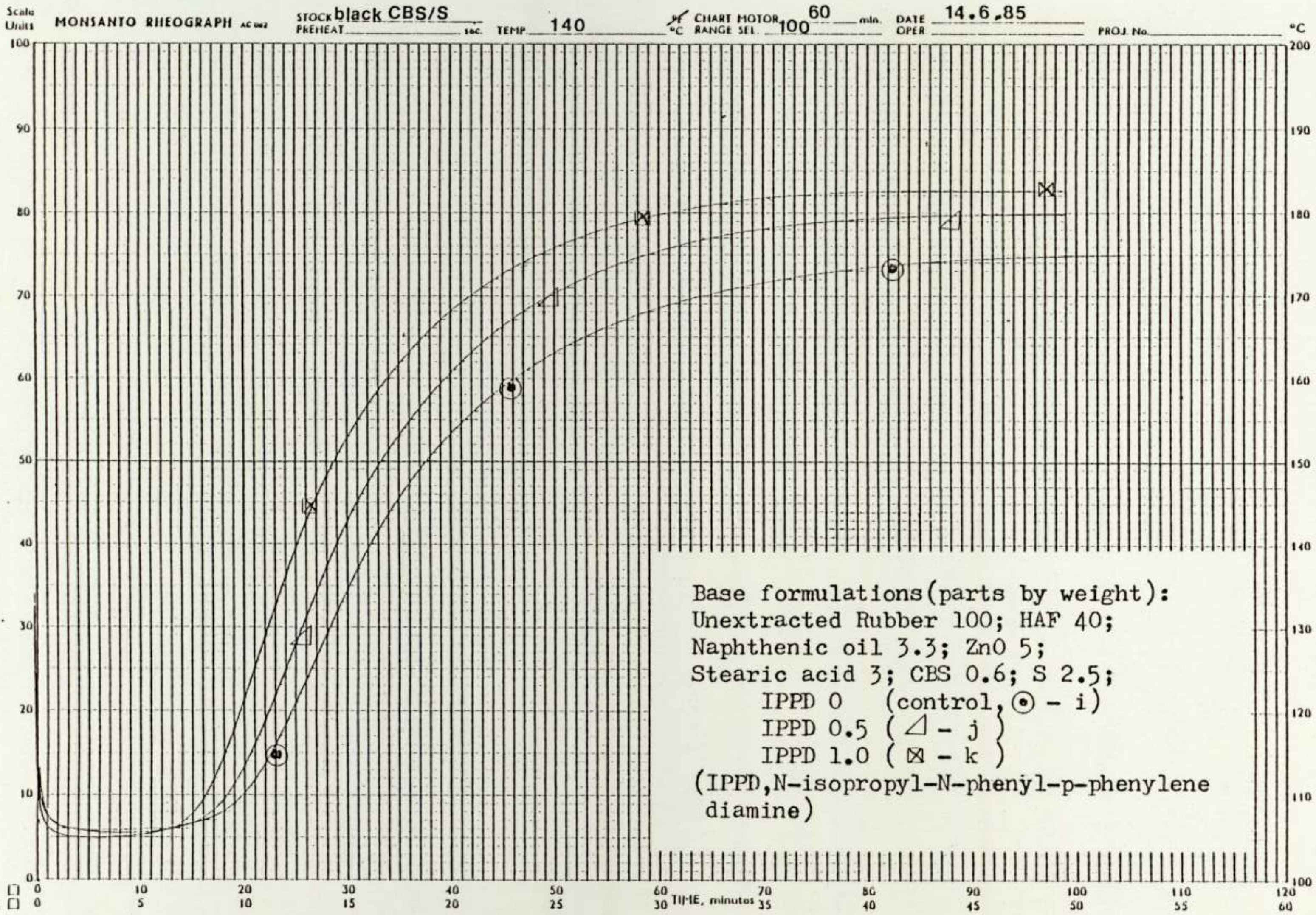


Figure 3.2 Monsanto Rheographs for unextracted rubber vulcanised with CBS-S system (gum stocks)



Base formulations(parts by weight):
Unextracted Rubber 100; HAF 40;
Naphthenic oil 3.3; ZnO 5;
Stearic acid 3; CBS 0.6; S 2.5;
IPPD 0 (control, ⊙ - i)
IPPD 0.5 (◁ - j)
IPPD 1.0 (⊠ - k)
(IPPD,N-isopropyl-N-phenyl-p-phenylene diamine)

Figure 3.3 Monsanto Rheographs for unextracted rubber vulcanised with CBS-S system (black filled stocks)

Stock(1)	Additive (phr)	R_{max} (kg.m)	Scorch time t_i (min)	Rate of cure k_i ($\times10^{-1}$ min^{-1})	Time to R_{max} - R_{min} (min)
a	No IPPD or NRC(2)	3.48	11	2.15	32
b	IPPD, 0.5	3.78	13.25	1.61	40
c	IPPD, 1.0	3.66	12.25	1.34	44
d	NRC, 1.0	3.48	10.5	2.14	33
e	NRC, 1.5	3.42	10.25	1.97	33
f	No IPPD	3.54	13	1.45	43
g	IPPD, 0.5	3.78	12	1.15	45
h	IPPD, 1.0	3.66	11	1.27	45
i	No IPPD	4.14	9	1.88	51
j	IPPD, 0.5	4.44	7.5	1.05	49
k	IPPD, 1.0	4.74	7	0.94	49

(1) Base formulations (parts by weight):
a-e, Extracted Rubber, 100; Zno, 5; Stearic acid, 3; CBS, 0.6; S, 2.5
f-h, Unextracted Rubber, 100; ZnO, 5; Stearic acid, 3; CBS, 0.6; S, 2.5
i-k, Unextracted Rubber, 100; HAF, 40; Naphthenic oil, 3.3; ZnO 5; Stearic acid, 3; CBS, 0.6; S, 2.5

(2) IPPD, N-isopropyl-N-phenyl-p-phenylenediamine
NRC, Non-rubber constituents

Table 3.1 Cure parameters of CBS-S vulcanising system (see Figure 3.1-3.3)

Rheometer torque (kg.m)	Cure time (min)										
	a	b	c	d	e	f	g	h	i	j	k$^{(1)}$
1.2	-	-	-	-	-	14	-	-	-	-	-
1.68	14	-	-	-	-	-	-	-	-	-	-
2.4	16	-	-	-	-	20	20	19	-	-	-
3.0	20	23	26	20	24	25	-	-	-	-	-
3.6	-	-	-	-	-	-	-	-	26	23	19

(1) Compound formulations are given under Table 3.1

Table 3.2 Variation in cure times to give the required rheometer torque of CBS-S vulcanising system

3.3.2 Peroxide Vulcanisation

Dicumyl peroxide was used for the peroxide vulcanisation system, and all stocks were cured at 160°C for different times to give the required rheometer torque.

3.3.2.1 Results

The cure characteristics of unextracted and extracted rubber with and without antioxidant or non-rubber constituents are shown in Figures 3.4-3.8 and their corresponding cure parameters in Tables 3.3-3.4. Variation in cure times to give the required rheometer torque are given in Table 3.5.

The data in Table 3.3 show that the higher the amounts of DCP, the higher the maximum torque, the shorter the scorch time and the higher the rate of cure attained for both the stocks from extracted (A-E) and from unextracted (A'-E') rubber. Figures 3.4 and 3.5 demonstrate the variation of rheometer torque with the level of DCP. The dotted lines in these Figures indicate vulcanisates with the same torque reading, showing how vulcanisates with equivalent cure states can be obtained by using different peroxide concentrations and by vulcanising for different times.

Table 3.4 shows the cure parameters of gum stocks prepared from unextracted and extracted rubber with and without

Stock(1)	DCP (phr)	R_{max} (kg.m)	Scorch time t_i (min)	Rate of cure k_i ($\times 10^{-1}$ min^{-1})	Time to $R_{max} - R_{min}$ (min)
A	1.0	2.16	1.75	1.15	60
B	1.5	2.76	1.5	1.15	60
C	2.0	3.6	1	1.26	60
D	2.5	4.2	1	1.26	60
E	3.0	4.8	0.75	1.05	60
A'	1.0	1.98	2.25	0.92	60
B'	1.5	2.7	2	0.99	60
C'	2.0	3.3	2	1.23	60
D'	2.5	3.84	1.75	1.30	60
E'	3.0	4.32	1.25	1.42	60

(1) A-E from extracted rubber; A'-E' from unextracted rubber

Table 3.3 Cure parameters of peroxide vulcanising system (gum stocks) containing variable amounts of DCP at 160°C (see Figures 3.4-3.5) additive and also of black filled stocks. Both gum stocks made from extracted (a'-c', g'-i') and unextracted (d'-f') rubber show a significant effect of IPPD on the cure parameters. The maximum torque is obviously decreased as the amount of IPPD is increased independently of DCP concentration. Results indicate some increase in scorch time and a tendency to slower rate of cure in the presence of IPPD in both kinds of gum stocks.

The incorporation of non-rubber constituents (NRC) (Table 3.4, j-k) into the DCP mixes by adding them as compounding ingredient shows some effect on the cure parameters i.e., it decreases maximum torque and rate of cure but increases scorch time when compared with control (g').

The effect of IPPD on the maximum torque of black filled stocks (Table 3.4, l'-n') is similar to that in gum stocks i.e., the higher the amount of IPPD, the lower the maximum torque attained. However, there is no significant change in the scorch time or rate of cure to be observed when IPPD is present in the black filled stocks.

3.3.3 Discussion

The chemical mechanism of sulphenamide accelerated sulphur vulcanisation is still not fully understood, particularly whether the predominant reactions are free radical or

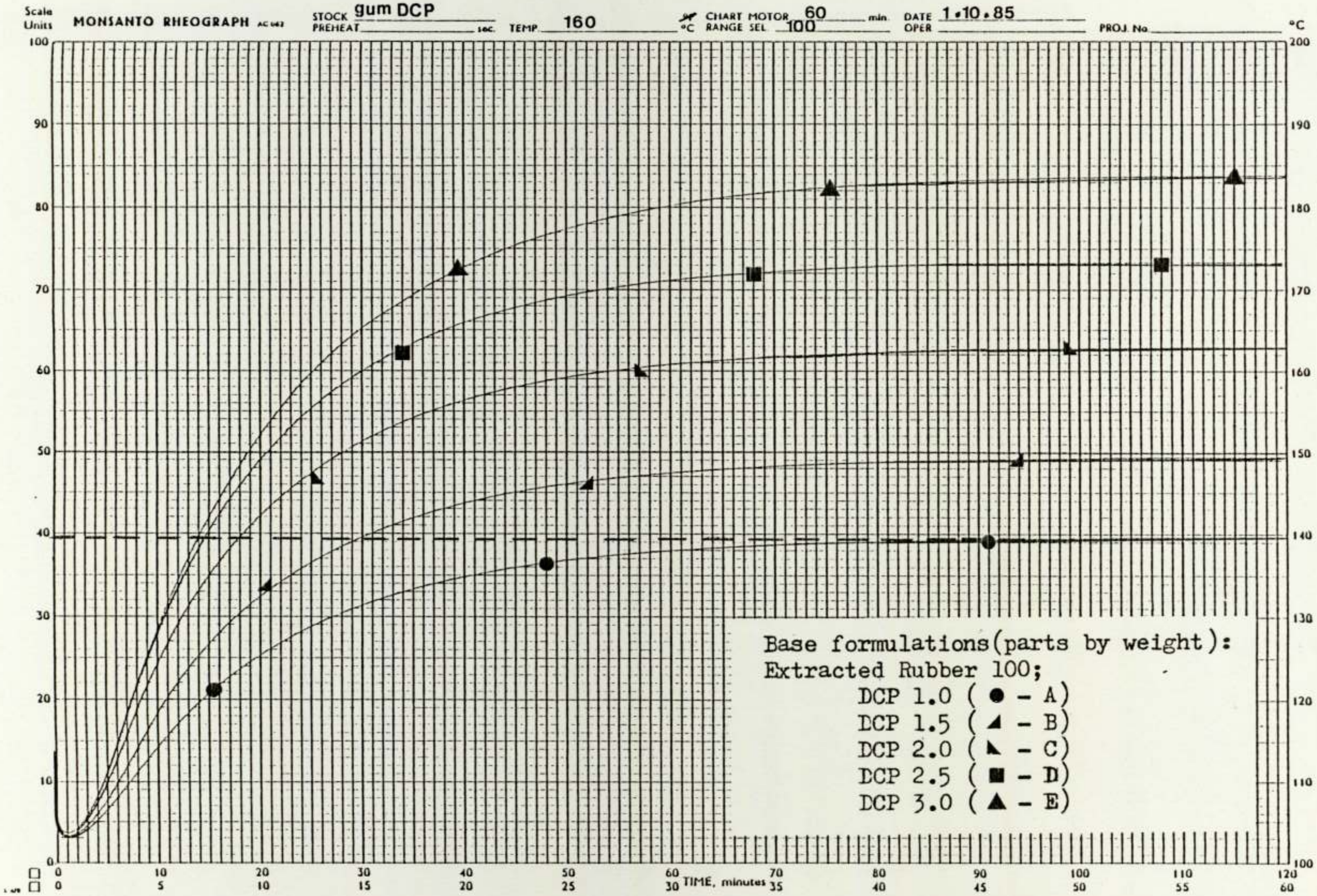


Figure 3.4 Monsanto Rheographs for extracted rubber vulcanised with variable amounts of DCP

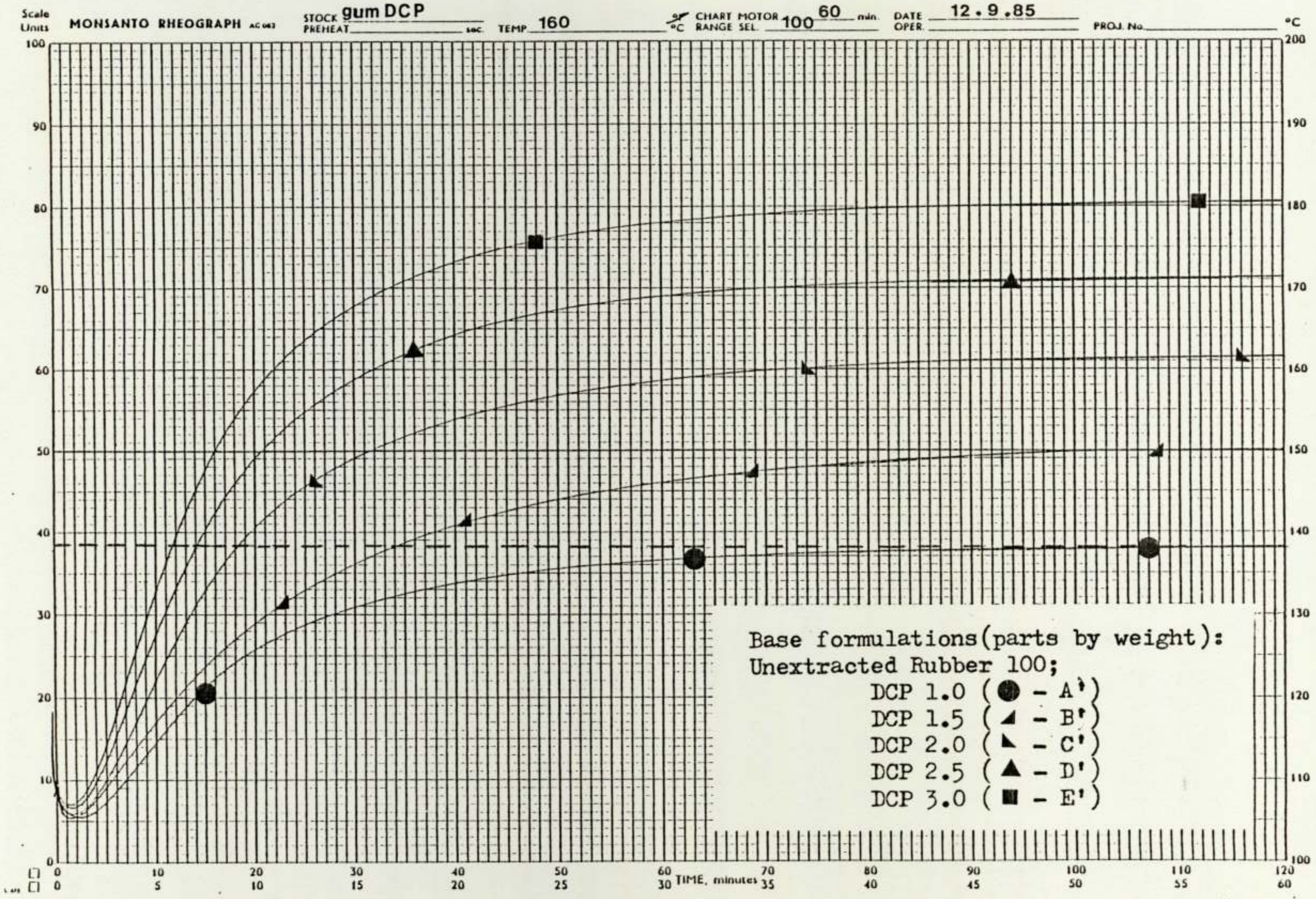


Figure 3.5 Monsanto Rheographs for unextracted rubber vulcanised with variable amounts of DCP

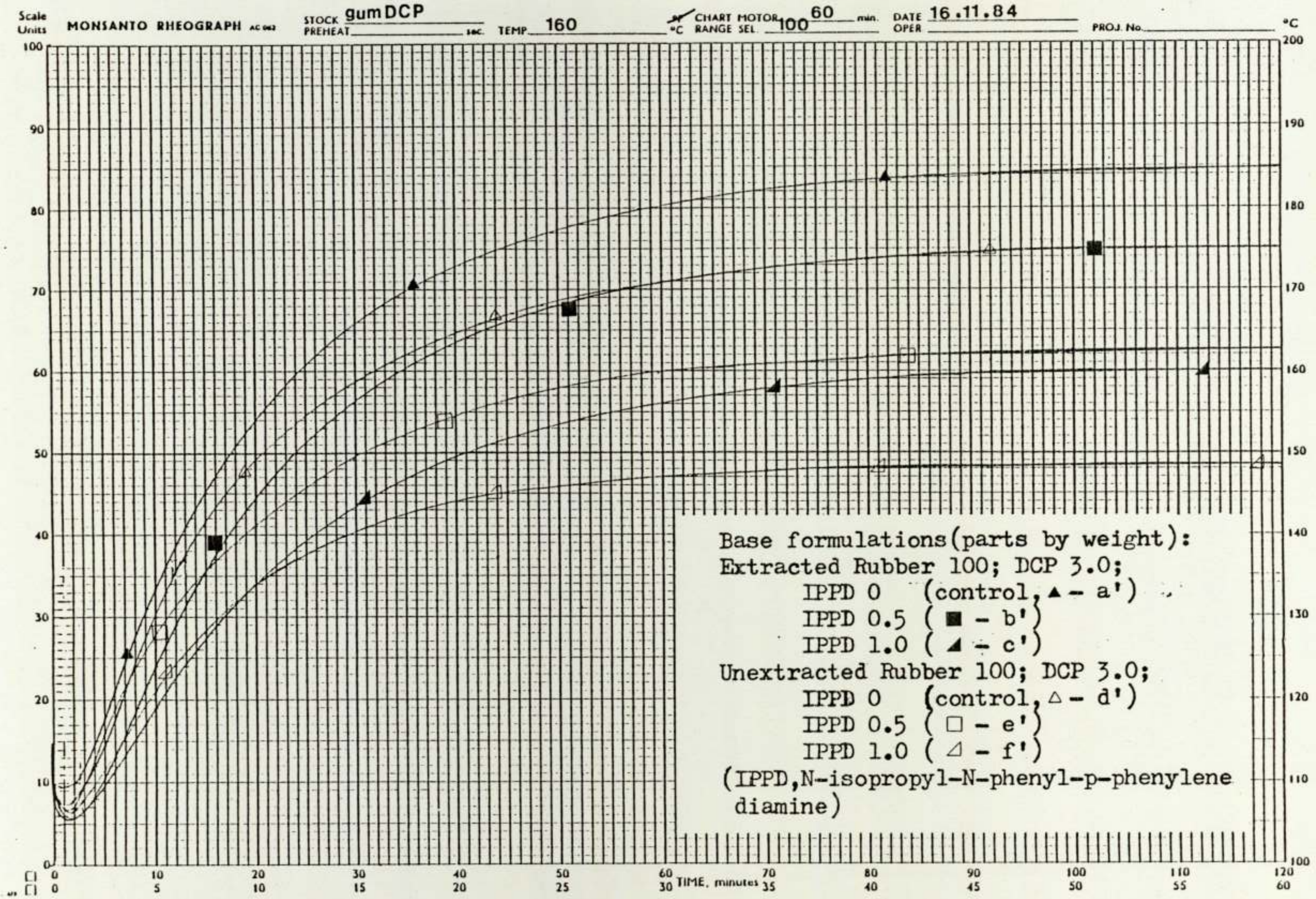


Figure 3.6 Monsanto Rheographs for extracted (a'-c') and unextracted (d'-f') rubber vulcanised with 3 phr of DCP

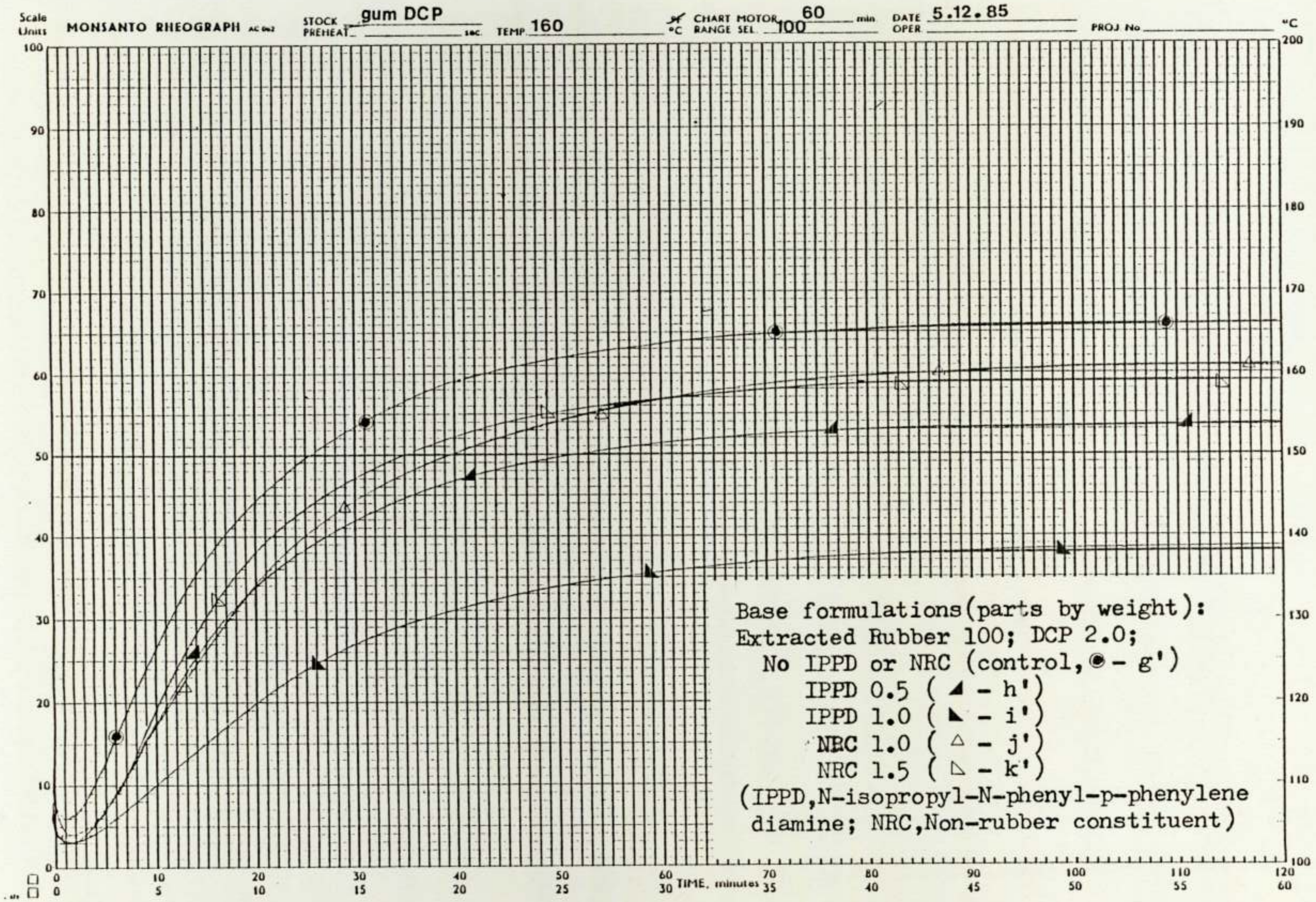


Figure 3.7 Monsanto Rheographs for extracted rubber vulcanised with 2 phr of DCP

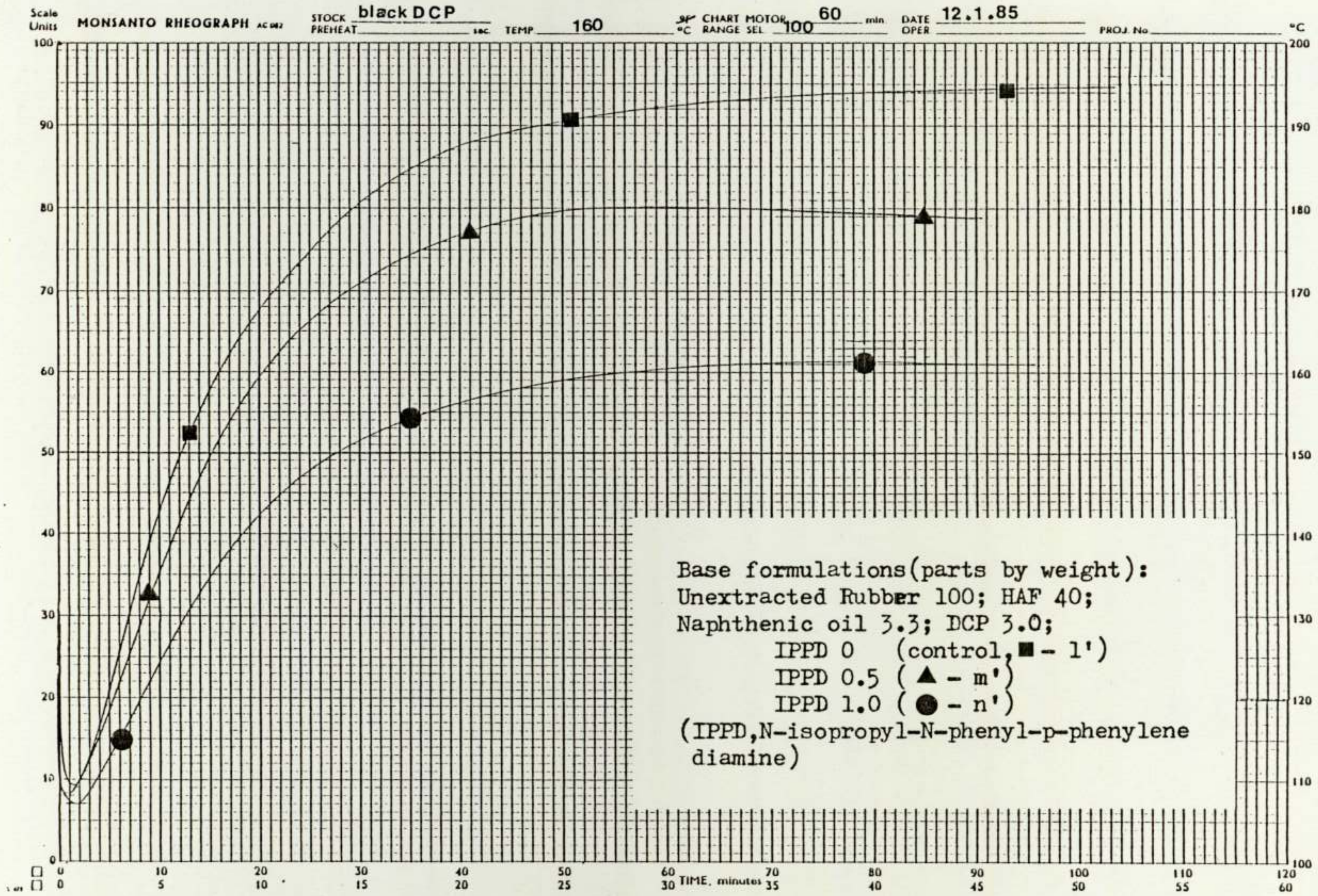


Figure 3.8 Monsanto Rheographs for unextracted rubber vulcanised with 3 phr of DCP (black filled stocks)

Stock(1)	Additive (phr)	R_{max} (kg.m)	Scorch time t_i (min)	Rate of cure k_i (x10^{-1} min^{-1})	Time to $R_{max}-R_{min}$ (min)
Gum:					
a'	IPPD 0	4.8	0.75	1.05	60
b'	IPPD 0.5	4.2	2	0.92	60
c'	IPPD 1.0	3.3	2	0.89	60
d'	IPPD 0	4.32	1.25	1.42	60
e'	IPPD 0.5	3.42	1.75	1.15	58
f'	IPPD 1.0	2.58	2	1.13	58
g'	IPPD,NRC 0	3.6	1	1.26	60
h'	IPPD 0.5	3.0	2.5	1.24	60
i'	IPPD 1.0	2.16	2.75	0.89	60
j'	NRC 1.0	3.42	2	1.01	60
k'	NRC 1.5	3.36	2	1.25	60
Black filled:					
l'	IPPD 0	5.28	1.25	1.36	49
m'	IPPD 0.5	4.32	1.25	1.47	31
n'	IPPD 1.0	3.24	1.25	1.47	36

(1) Base formulations (parts by weight) for gum stocks:
Extracted Rubber, 100; DCP, 3.0(a'-c'); 2.0(g'-k')
Unextracted Rubber, 100; DCP, 3.0(d'-f')
Base formulations (parts by weight) for black filled stocks:
Unextracted Rubber, 100; HAF, 40; Naphthenic oil, 3.3; DCP, 3.0(l'-n')

Table 3.4 Cure parameters of peroxide vulcanising system for gum and black filled stocks (see Figures 3.6-3.8)

Rheometer torque kg.m	Cure time (min)															
	A	B	C	D	E	a'	b'	c'	d'	e'	f'	j'	k'	l'	m'	n'(*)
2.16	35	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
2.28	60	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
2.4	–	16	11	8	8	–	–	–	10	14	45	–	–	–	–	–
3	–	–	16	12	11	12	16	50	–	–	–	24	24	8	10	23
3.6	–	–	35	19	15	–	–	–	–	–	–	–	–	–	–	–

(*) Base formulations (parts by weight):
A–E, Extracted Rubber,100;DCP,1.0(A),1.5(B),2.0(C),2.5(D),3.0(E)
a'–c', Extracted Rubber,100;DCP,3.0;IPPD,0(a'),0.5(b'),1.0(c')
d'–f', Unextracted Rubber,100;DCP,3.0;IPPD,0(d'),0.5(e'),1.0(f')
j'–k', Extracted Rubber,100;DCP,2.0;NRC,1.0(j'),1.5(k')
l'–n', Unextracted Rubber,100;HAF,40;Naphthenic oil,3.3;DCP,3.0;IPPD,0(l'), 0.5(m'), 1.0(n')

Table 3.5 Variation in cure times to give the required rheometer torque of peroxide vulcanising system polar in nature. There are extensive reviews(120-123) supporting a mixed radical and polar mechanism. The vulcanisation in the presence of CBS, S, ZnO and stearic acid is initiated by a radical mechanism but an ionic mechanism is operative in the major crosslinking period(121).

The chemical mechanism of peroxide vulcanisation, unlike the conventional CBS-S vulcanising system, is free radical in nature. In principle, the crosslinking process of natural rubber by dicumyl peroxide can be divided into three successive steps(124,125) as indicated in Scheme 1.1:

(I) The homolytic decomposition of the peroxide into cumyloxy radicals,
(II) hydrogen abstraction by the cumyloxy radicals from the polymer chain, resulting in stable peroxide decomposition products (cumyl alcohol and acetophenone),
(III) combination of two polymer radicals, whereby a crosslink is produced.

Peroxide mixes are scorchy and not very fast curing and even at 160°C, complete peroxide decomposition, and hence maximum rheometer torque, is only attained after some 60 minutes. Peroxide cured rubbers are essentially non-reverting and hence, vulcanisates which have equivalent states of cure can be prepared by the use of increased concentration of DCP and vulcanised for shorter periods.

Rheographs illustrating this approach are shown in Figures 3.4-3.5.

Data showing the effect of increasing amounts of peroxide on the cure parameters are given in Table 3.3. The maximum torque is noticably increased as the amount of peroxide is increased, this is essentially a reflection of the higher degree of crosslinking. Lower scorch time , becomes more pronounced as the peroxide concentration is increased. This is due to the fact that the rate determining step in the kinetics of peroxide vulcanisation is the decomposition of the peroxide (Scheme 3.1, reaction (i)). Reaction steps (ii) and (iii) are much faster than (i).

$$\mathrm{ROOR} \longrightarrow 2\mathrm{RO}^{\cdot} \qquad \text{(i)}$$

$$\mathrm{RO}^{\cdot} + \mathrm{PH} \longrightarrow \mathrm{ROH} + \mathrm{P}^{\cdot} \qquad \text{(ii)}$$

$$\mathrm{P}^{\cdot} + \mathrm{P}^{\cdot} \longrightarrow \mathrm{P{-}P} \qquad \text{(iii)}$$

where ROOR $\equiv$ an organic peroxide and PH $\equiv$ polyisoprene

Scheme 3.1 Mechanism of peroxide crosslinking

Insertion of crosslinks in a peroxide system is therefore first order with respect to the peroxide with no delay period. Addition of IPPD imparts some delay to the crosslink reaction and the rate of cure becomes slower than that of control (Table 3.4). This is attributed to the radical scavenger nature of IPPD which removes some of the $\mathrm{RO}^{\cdot}$ radicals as they are formed. The removal of radicals by IPPD lowers the crosslink yield and hence a reduction in maximum torque is observed. This is indicated by the rheometer traces shown in Figure 3.6-3.8.

The slight differences between the cure characteristics of the stocks made from extracted and those from unextracted rubber may be ascribed to the influence of the non-rubber constituents present in the unextracted rubber. These apparently compete with the polyisoprene chain for the peroxide-derived radicals, and so diminish the efficiency of the peroxide as a crosslinking agent. This is clearly indicated by the lower maximum torque i.e., 4.32 kg.m, of control d' than that, 4.8 kg.m, of control a' (Table 3.4). The evidence confirms the effect of the non-rubber constituents on maximum torque and is demonstrated in stocks j'-k' which contain non-rubber constituents as added ingredients (Table 3.4).

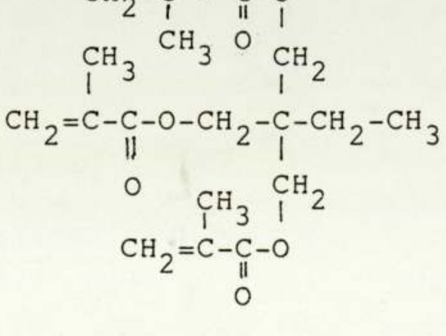
The effect of non-rubber constituents on tensile strength of natural rubber cured with di-tert-butyl peroxide was observed by Farmer and Moore(126). They performed the experiment by removal of non-rubber constituents from rubber in order to increase the maximum attainable tensile strength and also to reduce the peroxide concentration required to produce this maximum tensile strength.

Table 3.4 shows significant higher maximum torque for black filled stocks (l'-n') than for the gum stocks (d'-f'). This may be due to the additional crosslinks formed by carbon blacks and polymer radicals. However, carbon black does not influence the scorch time and the rate of cure of the vulcanisates.

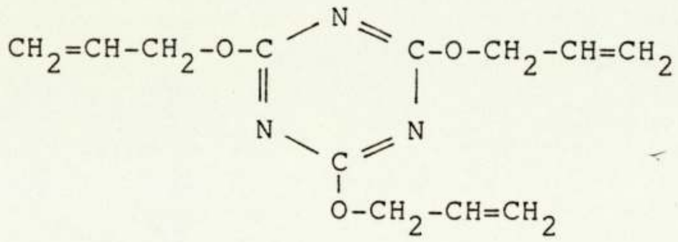
3.3.4 Peroxide/Coagent Vulcanisation

3.3.4.1 Introduction

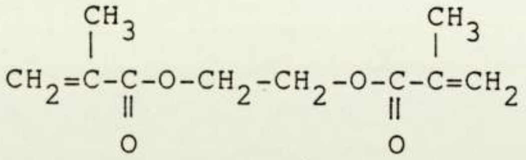
Co-curing agents are used with peroxide vulcanising agents in order to increase the efficiency of the crosslinking reaction i.e., to give more crosslinks, or tighter cure(127). Since peroxide crosslinking reactions occur by means of free radical reactions (see Scheme 3.1), it is to be expected that free radical scavengers, including all of the usual antioxidants, will interfere with those reactions to some extent. It was found that the coagent more than compensated for the loss of crosslinking efficiency due to the radical scavenger, so a decrease in the amount of peroxide could be made and consequently the scorch time was increased even more(127). Normally coagents are polyunsaturated compounds, such as:-



trimethylol propane trimethacrylate (TMPTMA, XVII)



triallyl cyanurate (TAC, XVIII)

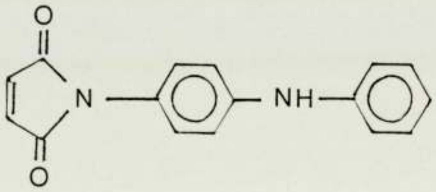


$$CH_2=C(CH_3)-C(=O)-O-CH_2-CH_2-O-C(=O)-C(CH_3)=CH_2$$

ethylene dimethacrylate (IXX)

3.3.4.2 Experimental

The coagents used in this project were:-



(APM, XX)

1) N-(4-Anilinophenyl)maleimide (APM, XX). This was given by N. C. Quinn, who prepared it according to the method described in his thesis$^{(128)}$. It was a red powder.

2) Triallyl cyanurate (TAC, XVIII). This was donated by Degussa Ltd. It was a white solid.

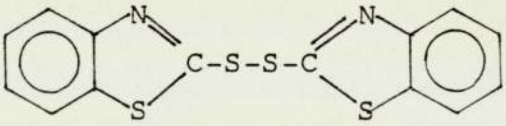
3) Trimethylol propane trimethacrylate (TMPTMA, XVII), from

Aldrich Chemical Co., was a viscous liquid and inhibited with 175 ppm hydroquinone monomethyl ether.

All these coagents were used without further purification, the amount of inhibitor presented in TMPTMA was very small since it was used only 3% (by weight) TMPTMA.

The radical scavengers used to improve the scorch time were:-

1) $[(CH_3)_3CNO]_2$, nitroso-tert-butane from Aldrich Chemicals Co.



(XXI)

2) Dibenzothiazyl disulphide (MBTS, XXI) from Monsanto Chemicals Ltd.

These were used as supplied.

The compounding operation was described in Section 2.2.3.2 and coagents or radical scavengers were added and thoroughly dispersed through the mix before addition of peroxide.

3.3.4.3 Results and Discussion

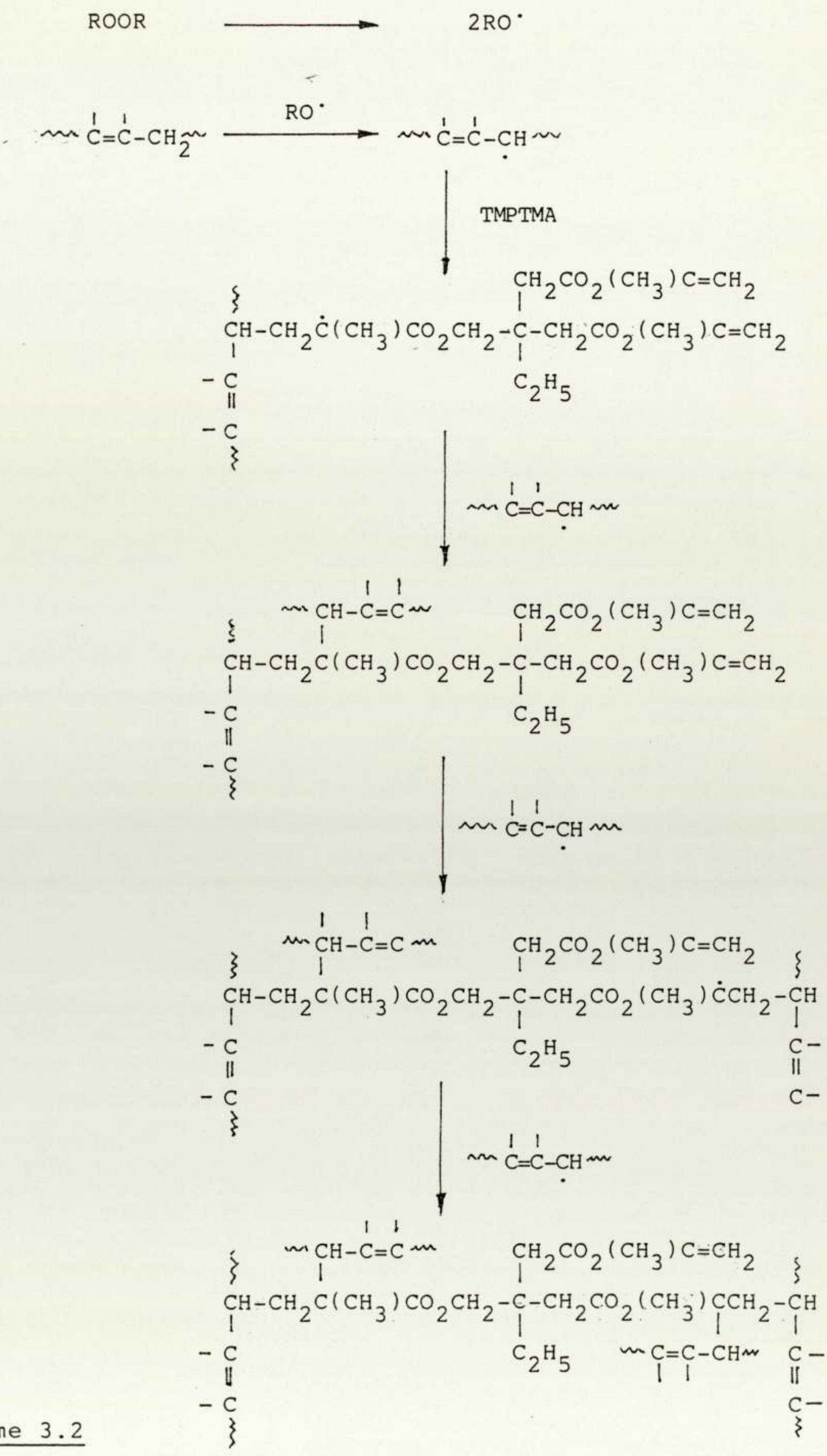
The variation in scorch time, cure rate and maximum torque with IPPD concentrations are shown in Table 3.6.

The cure parameters for simple peroxide and peroxide/APM coagent, peroxide/TAC coagent and peroxide/TMPTMA coagent are shown in Tables 3.7, 3.8 and 3.9 respectively.

The purpose of adding coagents was to boost the modulus of the peroxide system which has been depleted by the inclusion of IPPD radical capture reagent (see Table 3.6). N-(-4 Anilinophenyl) maleimide and triallyl cyanurate do not improve maximum torque as compared with control (see Tables 3.7 and 3.8). Table 3.9 shows that trimethylol propane trimethacrylate compensates the loss of cross-linking efficiency due to IPPD.

Increasing of crosslinking efficiency by peroxide/TMPTMA vulcanisation may be visualised as shown in Scheme 3.2. It shows that 4 polymer radicals gives 3 crosslinks, whereas normally 2 radicals gives 1 crosslink, thus statistically increasing the crosslinks for the same number of radicals.

Table 3.10 shows the cure parameters of peroxide/nitroso-tert-butane and peroxide/MBTS vulcanisations, their corresponding Rheographs are illustrated in Figure 3.13. Both nitroso-tert-butane and MBTS do not improve the scorch time but they increase cure rate. The reduction in maximum torque is attributed to the removal of peroxy radicals by nitroso-tert-butane and by MBTS.



Scheme 3.2

	parts by weight								
Formulation:									
Unextracted SMR 10	100	100	100	100	100	100	-	-	-
Extracted SMR 10	-	-	-	-	-	-	100	100	100
Dicumyl peroxide	3	3	3	3	3	3	2	2	2
IPPD	0	0.5	1.0	1.5	2.0	2.5	0	0.5	1.0
Rheometer, at 160°C/60 min:									
Scorch time, t_i (min)	1.25	1.75	2.0	2.25	2.25	2.75	1	2.5	2.75
Cure rate, k_i ($\times 10^{-1}$min)	1.05	1.15	1.23	1.15	1.15	1.25	1.26	1.24	0.89
Max. torque (kg.m)	4.08	3.42	2.58	1.98	1.56	1.32	3.6	3	2.16

Table 3.6 Variation in cure parameters with IPPD concentrations

	parts by weight a control	b	c	d
Formulation:				
Unextracted SMR 10	100	100	100	100
Dicumyl peroxide	1.5	1.5	1.5	1.5
APM	-	1	2	3
Rheometer, at 160°C/60 min:				
Scorch time, t_i (min)	1.5	1.25	1.5	1.5
Cure rate, k_i ($\times 10^{-1}$min)	1.06	1.47	1.32	1.26
Max. torque (kg.m)	2.7	2.16	2.34	2.46

Table 3.7 Cure parameters of simple peroxide and peroxide/APM coagent (see Figure 3.9)

	parts by weight							
	e control	f	g	h	i control	j	k	l
Formulation:								
Unextracted SMR 10	100	100	100	100	-	-	-	-
Extracted SMR 10	-	-	-	-	100	100	100	100
IPPD	-	-	-	-	1.0	0.5	1.0	1.5
Dicumyl peroxide	2	2	2	2	2	2	2	2
TAC	-	1	2	3	-	2	2	2
Rheometer, at 160^{o}C/60 min:								
Scorch time, t_i (min)	2	2.5	2.25	2	2.75	2.5	2.5	3.25
Cure rate, k_i (x10^{-1}min^{-1})	1.92	2.30	1.92	2.15	0.89	1.02	0.99	0.89
Max. torque, (kg.m)	3.18	3.18	3	3.12	2.16	2.55	2.06	1.46

Table 3.8 Cure parameters of simple peroxide and peroxide/TAC coagent (see Figures 3.10 and 3.11)

	parts by weight									
	m	n control	o	p	q	r	s control	t	u	v
Formulation:										
Unextracted SMR 10	100	100	100	100	100	-	-	-	-	-
Extracted SMR 10	-	-	-	-	-	100	100	100	100	100
IPPD	-	1.0	0.5	1.0	1.5	-	1.0	0.5	1.0	1.5
Dicumyl peroxide	2	2	2	2	2	2	2	2	2	2
TMPTMA	-	-	3	3	3	-	-	3	3	3
Rheometer, at 160^{o}C/60 min:										
Scorch time, t_i (min)	2	2.75	2.5	2.75	2.75	1	2.75	2.5	2.5	2.75
Cure rate, k_i (x10^{-1}min)	1.23	1.15	0.92	0.99	1.15	1.26	0.89	0.96	1.06	1.1
Max. torque (kg.m)	3.3	1.8	3.24	2.94	2.58	3.6	2.16	3.54	3.24	2.76

Table 3.9 Cure parameters of simple peroxide and peroxide/TMPTMA coagent (see Figure 3.12)

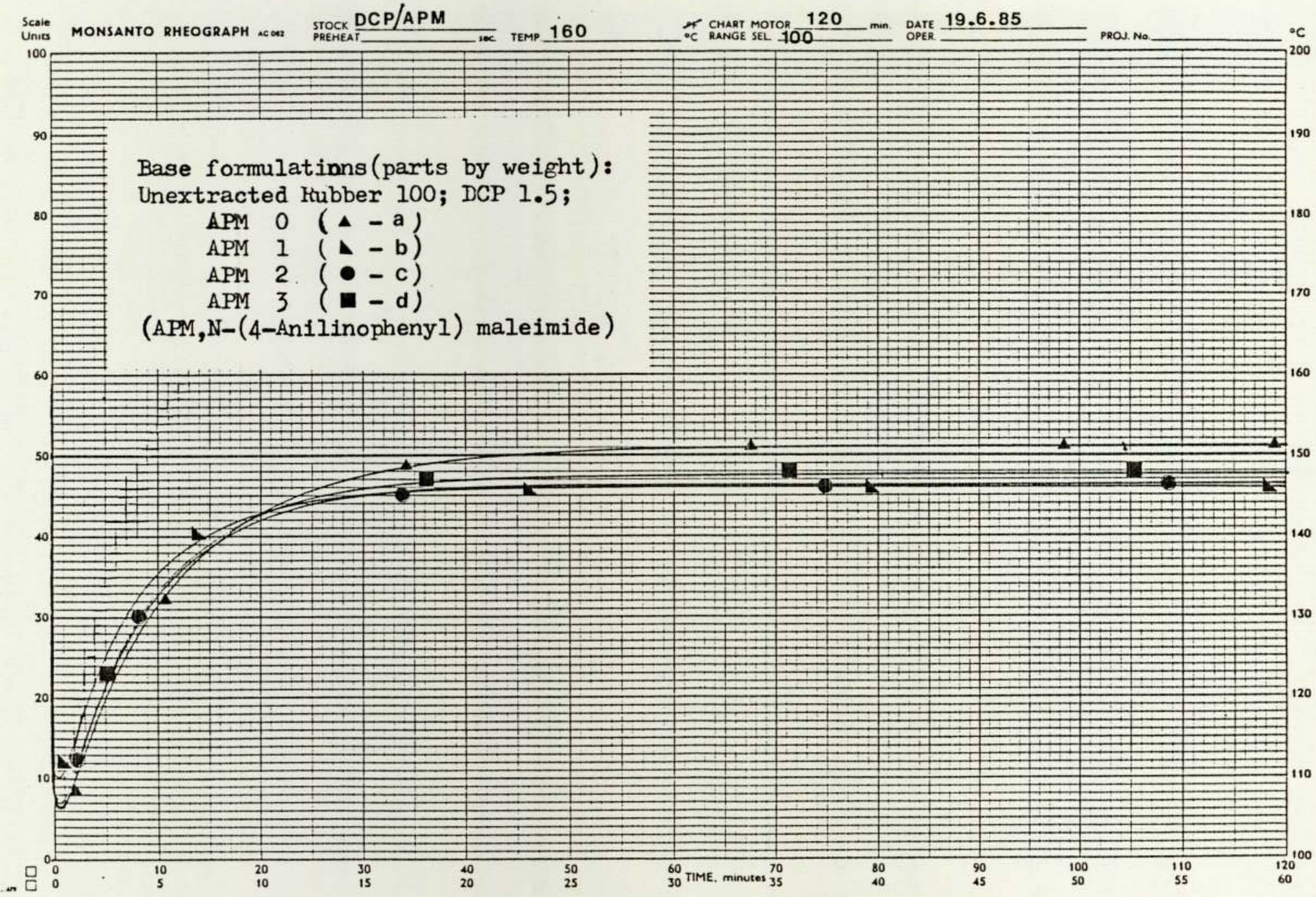


Figure 3.9 Monsanto Rheographs for DCP/APM vulcanisation

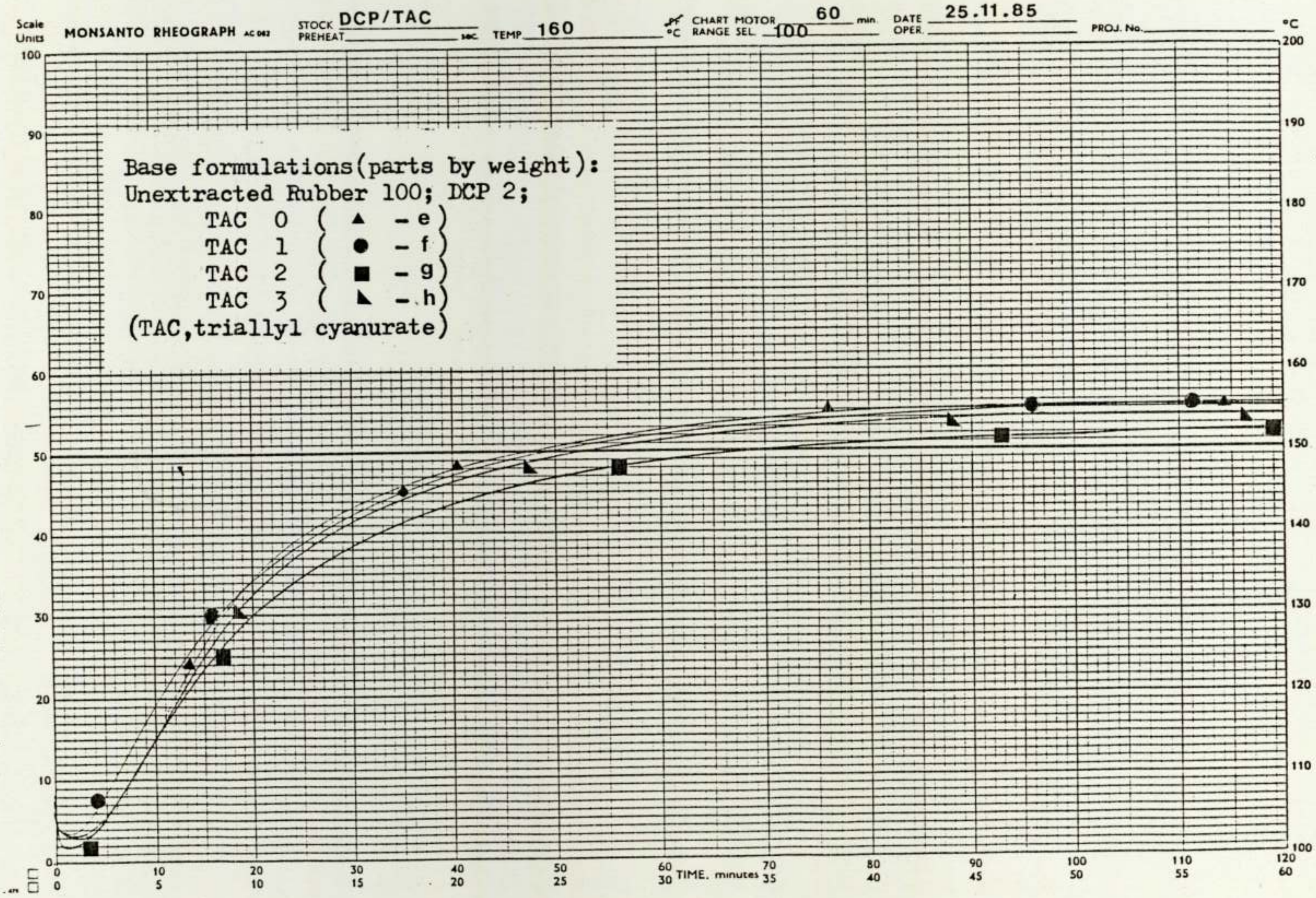


Figure 3.10 Monsanto Rheographs for DCP/TAC vulcanisation

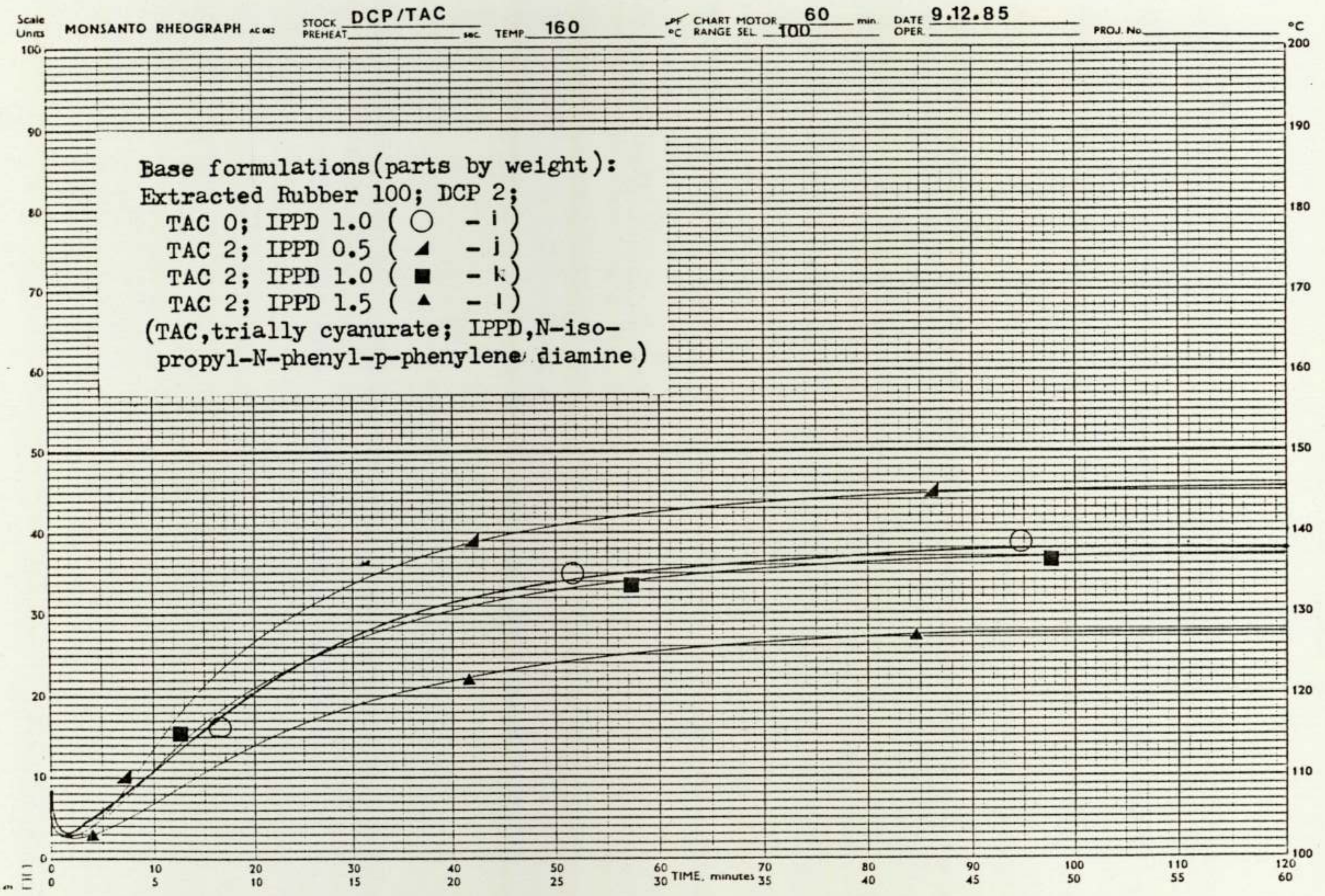


Figure 3.11 Monsanto Rheographs for DCP/TAC vulcanisation in the presence of IPPD

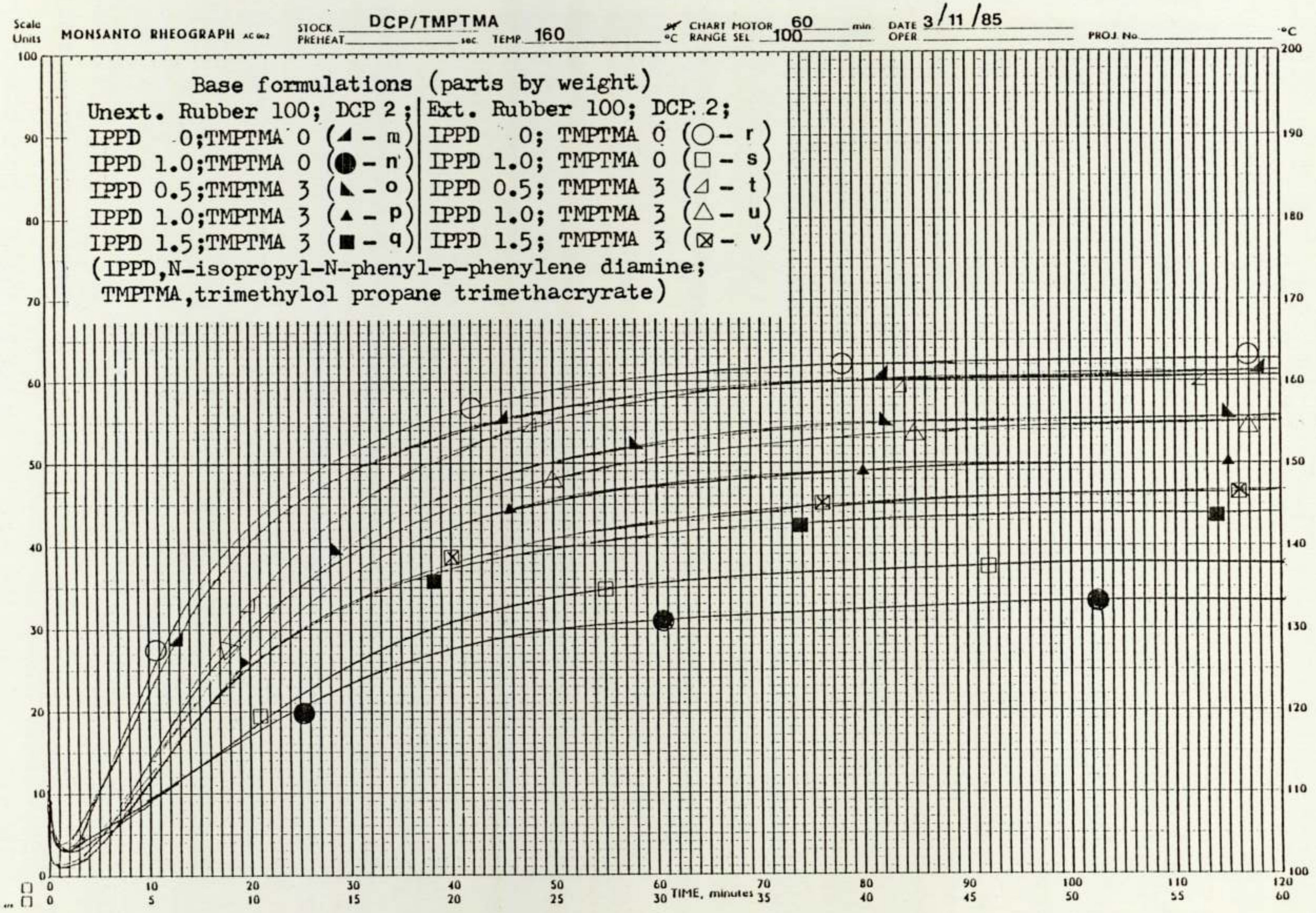


Figure 3.12 Monsanto Rheographs for DCP/TMPTMA vulcanisation in the presence of IPPD

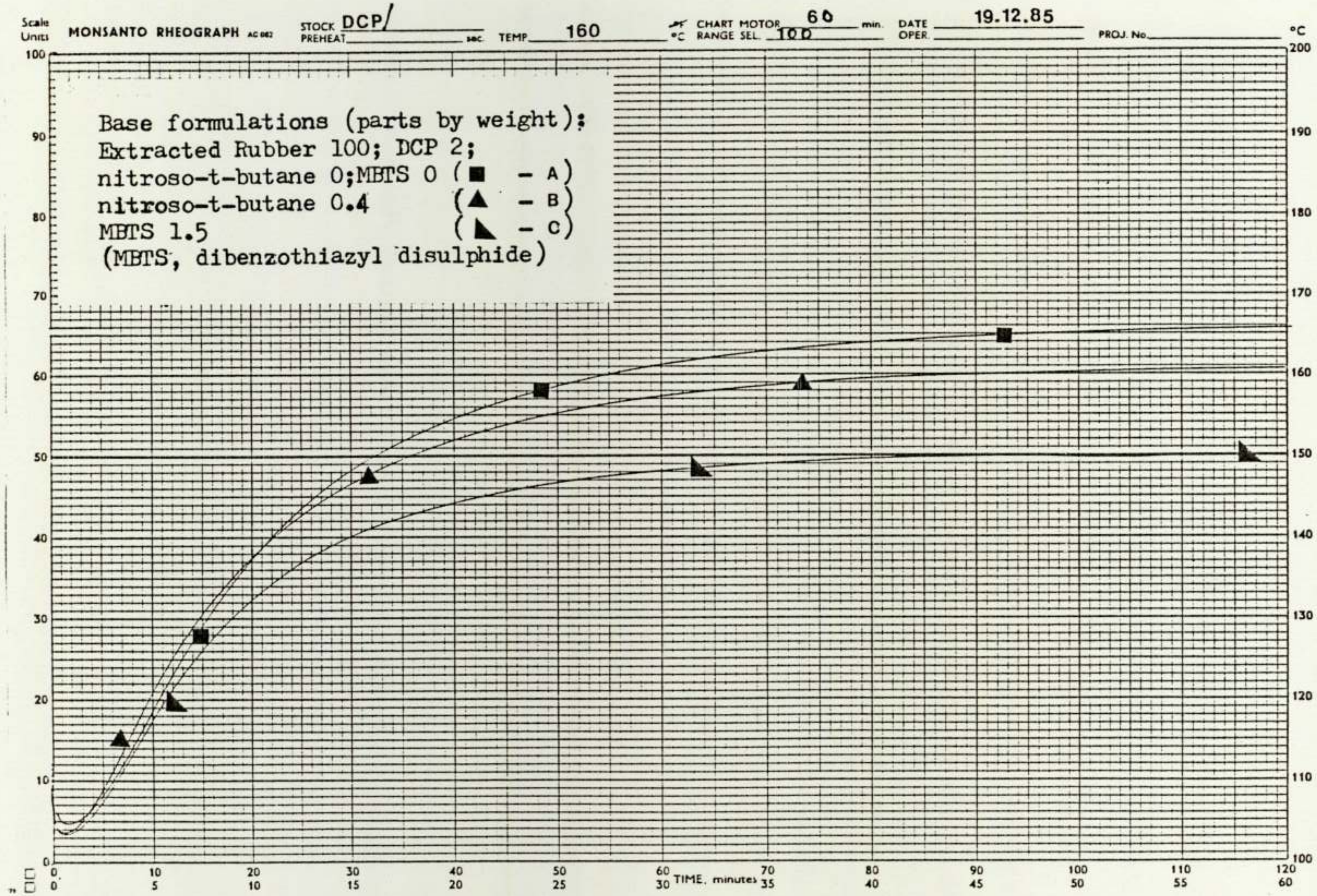


Figure 3.13 Monsanto Rheographs for DCP, DCP/nitroso-t-butane and DCP/MBTS vulcanisations

	part by weight		
	A (control)	B	C
Formulation:			
Extracted SMR 10	100	100	100
Dicumyl peroxide	2	2	2
Nitroso-tert-butane	-	0.4	-
MBTS	-	-	1.5
Rheometer, at 160°C/60 min:			
Scorch time, t_i (min)	2	2	2
Cure rate, k_i ($\times 10^{-1} min^{-1}$)	0.96	1.06	1.23
Max. torque, (kg.m)	3.6	3.42	2.82

Table 3.10 Cure parameters of peroxide/nitroso-tert-butane and peroxide/MBTS vulcanisations (see Figure 3.13)

3.4 Estimation of Crosslink Density

The estimation of crosslink density was performed according to the method described in Section 2.7. Tables 3.12-3.14 record the physical crosslink density of peroxide and of CBS-S vulcanisates and they are graphically illustrated in Figures 3.15 and 3.16.

3.4.1 Time to Equilibrium Volume Swelling

To ensure that samples were swollen to equilibrium during crosslink density determination, the time to equilibrium volume swelling in the solvent was first estimated by monitoring swollen weights over a range of times. Table 3.11 and Figure 3.14 show V_r as a function of time for NR vulcanisates in n-decane. The equilibrium swelling time was taken as the time to reach a constant value V_r. This was determined experimentally to be 20 hours. However, to ensure that equilibrium swelling was achieved, a minimum swelling time of 24 hours was subsequently used.

3.4.2 Results

Tables 3.12 and 3.13 show that the crosslink density of peroxide vulcanisates depends on: (1) whether the rubber is unextracted or acetone extracted before vulcanisation; (2) the concentration of peroxide. The data

Swelling	V_r					
Time	Sample number					
(hr)	1	2	3	4	5	6
5	0.235	0.234	0.231	0.210	0.210	0.211
10	0.228	0.225	0.225	0.200	0.200	0.201
15	0.223	0.223	0.223	0.198	0.197	0.199
20	0.221	0.223	0.233	0.197	0.197	0.199
25	0.221	0.223	0.222	0.197	0.198	0.199

Table 3.11 Equilibrium volume swelling time for NR vulcanisates in n-decane.

show that the removal of non-rubber constituents from the rubber by acetone extraction before vulcanisation leads to an increase in the crosslink density in both DCP and CBS-S vulcanisates.

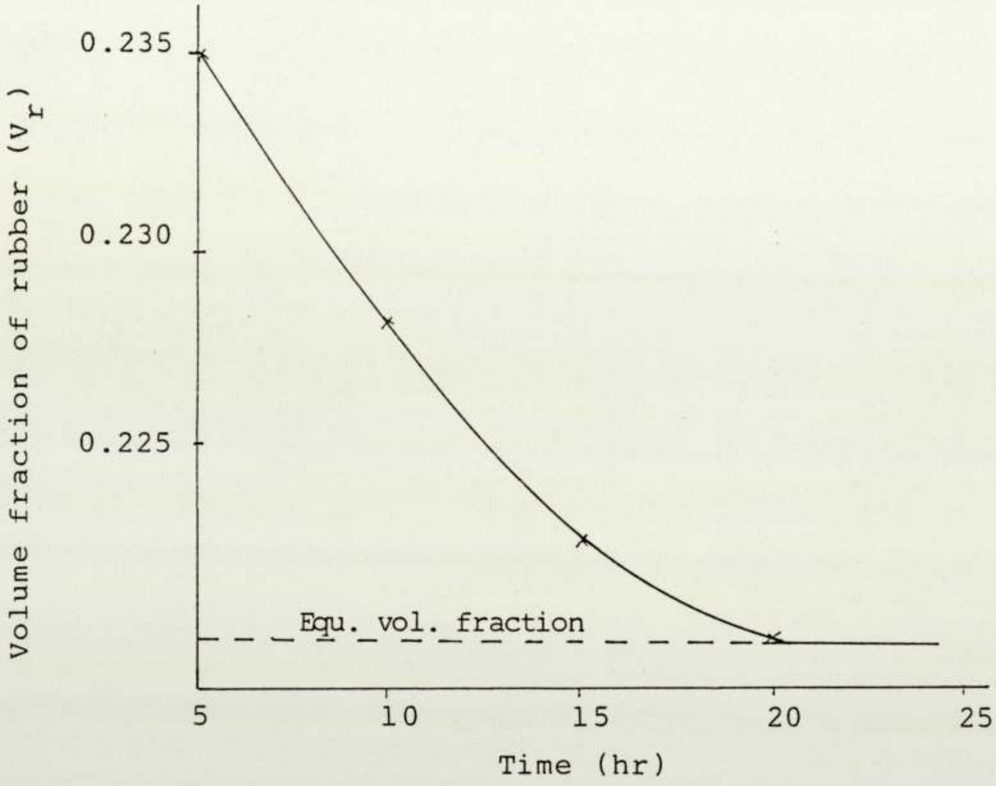


Figure 3.14 Dependence of volume fraction of rubber (V_r) on the swelling time

Increase in the peroxide concentrations increases the crosslink density (Table 3.12, Figure 3.15). These are in agreement with the experimental results of Bristow et al$^{(129)}$ for the crosslinking efficiency of peroxide vulcanisates.

Vulcanisation	Max.torque/Cure time (kg.m) (min)		$2M^{-1}_{c,phys}$ ($\times 10^{-5}$ mole/g.R)	
	Unext	Ext	Unext	Ext
DCP: 1.0 phr	1.98/60	2.16/60	2.15	2.63
1.5 phr	2.70/60	2.76/60	3.03	3.43
2.0 phr	3.30/60	3.60/60	3.46	4.11
2.5 phr	3.84/60	4.20/60	4.15	4.53
3.0 phr	4.32/60	4.80/60	4.51	5.23
CBS-S (conventional)	3.54/43	3.48/32	3.53	3.62

Table 3.12 Physical crosslink density of gum DCP and of CBS-S vulcanisates from unextracted and extracted rubber* cured to maximum rheometer torque.

* Base formulation (parts by weight) : Unext. or ext. rubber,100; DCP variable; Cured at 160°C. Unext. or ext.rubber,100; ZnO,5,Stearic acid,3; CBS,0.6; S,2.5; Cured at 140°C.

Rubber type	Cure time (min)	Rheometer Torque (kg.m)	$2M_{c,phys}^{-1}$ ($\times 10^5$ mole/g.R)
Ext.SMR10	14	1.74	3.84
(Mix D)	17	2.4	4.11
	19	3	3.79
	32	3.48(max)	3.62
Unext.SMR10	14	1.2	3.75
(Mix E)	21	2.64	3.79
	29	3.3	3.58
	43	3.54(max)	3.53

Table 3.13 Variation of physical crosslink density of gum CBS-S vulcanisates from unextracted and extracted rubber* with cure time

* Base formulations (parts by weight) : Unext. rubber,100; ZnO, 5; Stearic acid, 3; CBS,0.6; S,2.5; cured at 140°C.

	parts by weight			
	A	B	C	D
Formulations:				
Extracted SMR 10	100	100	100	100
Dicumyl peroxide	2.0	2.5	3.0	-
ZnO	-	-	-	5
Stearic acid	-	-	-	3
CBS	-	-	-	0.6
Sulphur	-	-	-	2.5
Rheometer:				
Temperature (^{o}C)	160	160	160	140
$R_{max}-R_{min}$ (kg.m)	3.6	4.2	4.8	3.48
Time to $R_{max}-R_{min}$(min)	60	60	60	32
Time to $R-R_{min}$ = 2.4 kg.m(min)	11	8	8	17
= 3 kg.m(min)	16	12	11	19
= 3.6 kg.m(min)	35	19	15	-
$2M^{-1}_{c,phys}$(x10^{5}mole/g) rubber:				
at Rheometer torque = 2.4 kg.m	4.04	4.76	5.24	4.11
= 3 kg.m	4.21	4.97	5.53	3.79
= 3.6 kg.m	4.11	4.60	5.59	-
= $R_{max}-R_{min}$	4.11	4.53	5.23	3.62

Table 3.14 Physical crosslink density of gum CBS-S and peroxide vulcanisates at variable

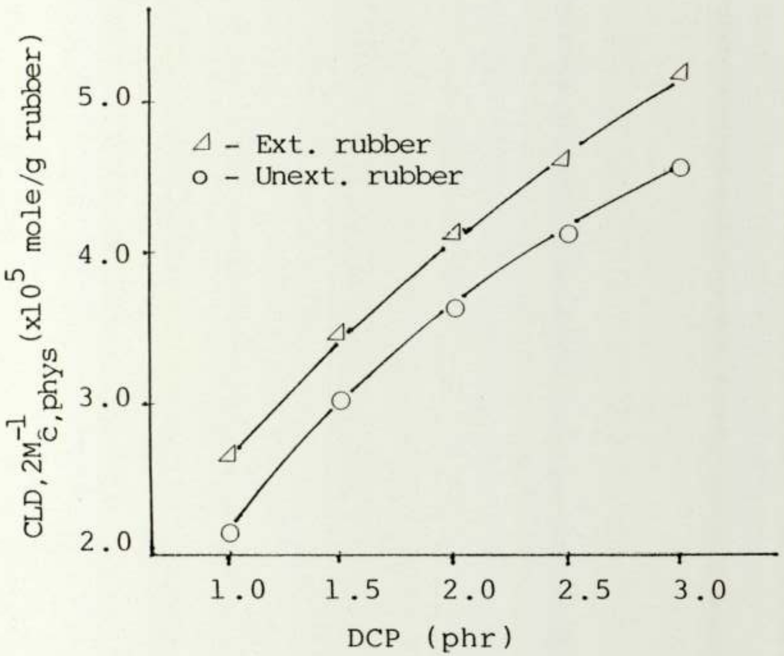


Figure 3.15 Variation of physical crosslink density, $2M^{-1}_{c,phys}$ with DCP concentration (see Table 3.12)

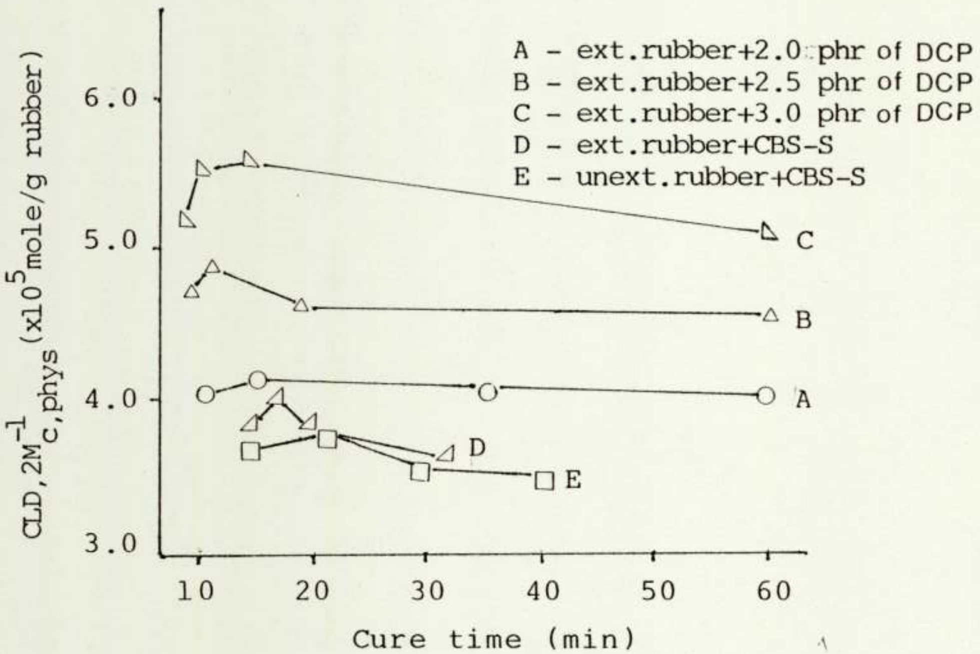


Figure 3.16 Variation of physical crosslink density, $2M^{-1}_{c,phys}$ with cure time (see Tables 3.13-3.14)

Tables 3.13-3.14 and Figure 3.16 show that the crosslink density of both CBS-S and peroxide system increases with increasing the cure time up to a certain time, beyond which they fall. The results are in agreement with the experimental results of Porter et al(130) for the high-sulphur CBS-accelerated vulcanisation system.

3.4.3 Discussion

The crosslink density of dicumyl peroxide is increased by acetone extraction of natural rubber before vulcanisation and by increasing the concentration of peroxide. This suggests that cumyloxy radicals react not only with hydrogen atoms of the rubber hydrocarbon but also with non-rubber constituents present in the rubber. The nature of the non-rubber constituents in natural rubber which scavenge some of the radicals and thus lower the crosslink density, is not known. However, the experimental results of Bristow et al(129) indicate that they cannot be solely nitrogeneous compounds, since there is no correlation between the cross-linking efficiencies of the peroxide and the nitrogen content of the rubber sample. The amount of reactive non-rubber constituents in a rubber sample must be very small (<<5%) relative to the rubber hydrocarbon present, and thus there will be only a limited amount of non-rubber constituents available, then the crosslink density should increase with increasing peroxide concentration as is observed experimentally. Similarly, the interference of non-rubber constituents to the CBS-S vulcanisation may be the reason for the low crosslink density of unextracted rubber. Since it is believed that CBS-S accelerated vulcanisation system is initiated by a radical mechanism(121), the interference by non-rubber constituents may occur at this stage.

The reversion in crosslink density of CBS-S vulcanisates on long cure is attributed to the low accelerator concentration(130). Polysulphide crosslinks are the primary products of the vulcanisation process, and these subsequently undergo thermal destruction.

Decrease in crosslink density as cure time is increased for dicumyl peroxide vulcanisation may be ascribed to chain scission.rather than crosslinking in the later stages.

The discussion on relation between physical crosslink density and physical properties of vulcanisates is given in Section 5.5.

CHAPTER FOUR

STUDY OF THE PEROXIDE VULCANISATION OF NATURAL RUBBER

4.1 Study of Structural Changes in Natural Rubber After Peroxide Vulcanisation by Infra-Red (IR) Spectroscopy

4.1.1 Introduction

IR spectroscopy has been widely applied in attempting to understand the reaction mechanism and the structure of vulcanised rubber. The investigations include natural rubber, raw and vulcanised under a variety of conditions(131-133). Linnig and Stewart(132) studied the spectra of vulcanised natural rubber made with a number of different curing systems, including di-tert-butyl peroxide. It was reported that there was no significant change of the spectrum of rubber vulcanised with di-tert-butyl peroxide(132).

In the present work, in order to elucidate structural changes occurring during dicumyl peroxide (DCP) vulcanisation, the infra-red spectra between 4000 and 200 cm^{-1} of raw natural rubber and of DCP vulcanised rubber were investigated using a Perkin Elmer 599 B infra-red spectrophotometer.

4.1.2 Preparation of Films for IR Measurement

4.1.2.1 Unvulcanised Natural Rubber Films

Unvulcanised natural rubber films were prepared from both unextracted and extracted SMR 10, the method for extraction of raw rubber was as described in Section 2.2.2 In both cases, the films were obtained by evaporating to dryness natural rubber solution which had been dissolved in benzene in the presence of air, sufficiently to give a film of satisfactory thickness, ca 0.1016 mm, on clean glass.

4.1.2.2 Vulcanised Natural Rubber Films

Specimens of vulcanised rubber were prepared by vulcanising the compounded rubber, made with extracted SMR 10 compounded with DCP in variable amounts and IPPD (when required) between sheets of cellophane on twelve inch diameter ram press at 160°C for 60 minutes. It was found that a pressure of 55 tons was sufficient to produce a specimen of suitable thickness i.e., somewhere between 0.1016 and 0.1524 mm.

4.1.3 Estimation of Aromatic Ring Attached to Polymer Chain After DCP Vulcanisation

It was found that after DCP vulcanisation, all the aromatic ring compounds derived from DCP were not extractable as evidenced by an absorbance at 700 cm^{-1}, using a Perkin Elmer 599 B infra-red spectrophotometer. This absorbance is the characteristic of mono-substituted aromatic ring.

The amount of aromatic ring present in vulcanised film after DCP vulcanisation was expressed as an index which is defined as the ratio of the absorbance of the aromatic peak to that of a reference peak. The characteristic absorption peak at 2700 cm^{-1} due to a C-H stretching, was used as reference since it was not considered that they would vary in concentrations during vulcanisation.

The baseline measurement technique(134) shown in Figure 4.1 was used to determine the absorbance.

The amount of aromatic ring attached to the polymer chain can be expressed by the following equation:

$$\%\text{Aromatic ring attached to polymer} = \frac{\text{Aromatic ring index after ext.}}{\text{Aromatic ring index before ext.}} \text{ x10}$$

4.1.4 Results and Discussion

4.1.4.1 IR Spectra of Unvulcanised Natural Rubber

Figure 4.2 shows the spectra of films of unextracted (A) and extracted (B) natural rubber. The films were obtained by the method described in Section 4.1.2.1. These spectra are essentially the same as those obtained by other investigators and some additional bands were also observed. Sheppard and Sutherland(131) suggest that the band at 3280 cm^{-1} may be due to the C-H stretching vibration of

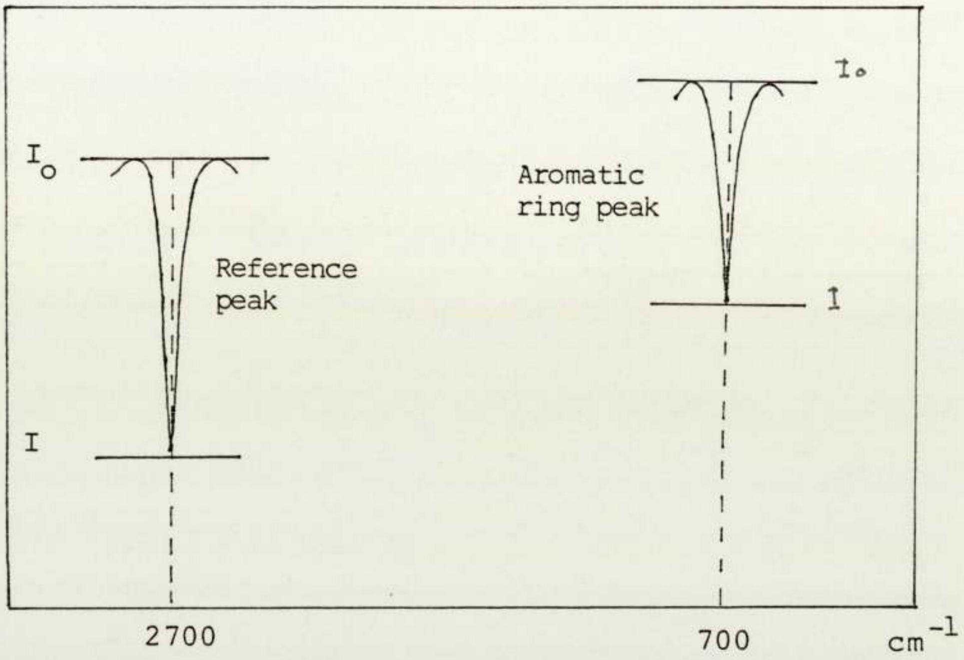


Figure 4.1 Aromatic ring index measurement by baseline technique

$$\text{Absorbance} = \log\frac{I_o}{I}$$

$$\text{Aromatic ring index} = \frac{\text{absorbance at 700 cm}^{-1}}{\text{absorbance at 2700 cm}^{-1}}$$

the ethylene bond in rubber. On the other hand, this band may be due to NH groups in proteins perhaps, or to OH groups, in which case its position indicates that these groups are strongly hydrogen bonded. However, this band is not markedly changed by extraction of rubber. This indicates that it is not related to resin or protein content of the rubber, which is greatly reduced on extraction, unless appreciable quantities of resin or proteinlike units are in some way part of the polymer chain. The spectrum of unextracted NR (Figure 4.2, spectrum A) shows two carbonyl absorptions near 1700 cm^{-1} and 1735 cm^{-1}; they may be due to carbonyls already present in the hydrocarbon chain, or formed by oxidation of the chain, or else to carbonyls in the resinous portion. The carbonyl absorption at 1700 cm^{-1} attributed to carboxylic acid was removed after extraction of the rubber, thus suggesting this band was caused by naturally occurring, low molecular weight carboxylic acids which were removed by extraction. The absorption at 1735cm^{-1} is the characteristic absorption frequency of an ester carbonyl which remains after extraction of the rubber. This evidence is consistent with the investigation made by Gregg et al(133), and they suggest that the band at 1735cm^{-1} may be due to part of the denatured protein which is attached to the rubber, probably at a lactone group.

The bands near 1030, 1080 and 1130 cm^{-1} which have not been reported by others, are the characteristic absorption frequencies of the C-O stretching of esters. These bands confirm the presence of carboxylic ester in the hydrocarbon chain which was suggested by Gregg et al(133).

The other assignments are:

Wave number (cm^{-1})	Assignment
2940, 2700	C-H stretching
1660	C=C stretching
1430, 1370, 1310, 1240	C-H bending
1000-750	$>C=C<^{H}$ bending

4.1.4.2 IR Spectra of DCP Vulcanised Films

Peroxide vulcanised films were prepared by the method described in Section 4.1.2.2. Figure 4.2 (C), represents the typical spectrum of vulcanised film derived from DCP (3 phr) mix. The spectrum C was obtained after removal of ENCS from the film by the method described in Section 2.6. Comparing the spectrum of vulcanised film (C) with that of unvulcanised film from extracted rubber (B), the carbonyl absorption at 1735 cm^{-1} of (C) was reduced. The overall absorptions are similar in both cases, except the appearance of a new band at 700 cm^{-1} after DCP vulcanisation. From literature evidence(135), this absorption is the characteristic absorption frequency of mono-substituted aromatic ring. The evidence to confirm the band at 700 cm^{-1} derived from DCP is shown in Figure 4.3(F), spectrum "u". The spectrum "u" in Figure 4.3(F) was

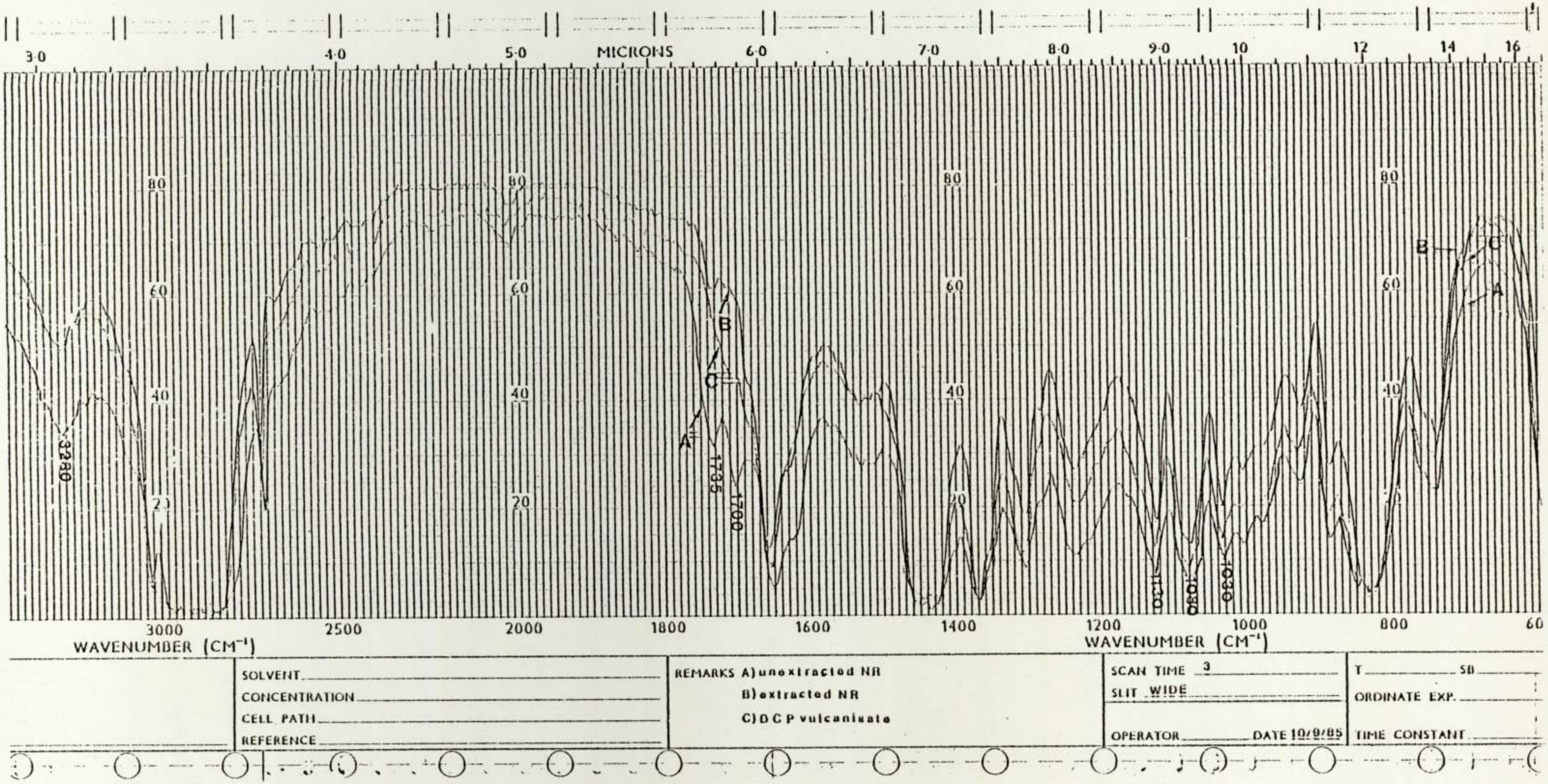


Figure 4.2 IR spectra of:- cast film of unextracted rubber (A), cast film of extracted rubber (B), and of DCP (3 phr) vulcanised film extracted after cure at 160°C for 60 mins (C).

obtained after swelling extracted film in DCP-benzene solution (1.5% w/v) for 24 hours and drying to constant weight in the vacuum oven. This suggests that during DCP vulcanisation, a side reaction involving polymer-peroxy radical combination occurs. The possible mechanisms are as follows:

$$\mathrm{ROOR} \longrightarrow 2\mathrm{RO}^{\cdot} \qquad (4.1)$$

$$\mathrm{RO}^{\cdot} + \mathrm{PH} \longrightarrow \mathrm{P}^{\cdot} + \mathrm{ROH} \qquad (4.2)$$

$$\mathrm{P}^{\cdot} + {}^{\cdot}\mathrm{OR} \longrightarrow \mathrm{POR} \qquad (4.3)$$

Reactions 4.1 and 4.2 are normal mechanisms for peroxide vulcanisation, reaction 4.3 is taken to account for side reaction i.e., the addition of peroxide radical ($\mathrm{RO}^{\cdot}$) to polymer radical ($\mathrm{P}^{\cdot}$) which is not a crosslinking process.

This evidence does not agree with the conclusion made by Thomas(136) that "none of the cumyloxy radicals become attached to the polymer during the crosslinking reaction". This conclusion was based on the quantitative estimation of acetophenone and cumyl alcohol together with that of the undecomposed peroxide which were then compared with the initial peroxide concentration. It should be pointed out that the reaction products of DCP vulcanisation used for this quantitative analysis were obtained from heating a Pyrex tube filled with solid rubber mix (DCP, 1.5 phr) in an oil bath and not by a normal vulcanisation procedure.

The spectrum did not show C-O stretching absorption of ether linkage when the cumyloxy radical is attached to the polymer chain. This is due to the fact that, as discussed in Section 4.1.4.1, the polymer chain itself has the absorptions due to C-O stretching of lactone group which mask the bands of interest.

4.1.4.3 Aromatic Ring Attached to Polymer Chain

The spectra given in Figure 4.3 (A-E) are typical of vulcanised films containing different DCP concentrations, and spectrum F is of DCP deswollen film which was prepared by the method described in Section 4.1.4.2. Films containing higher quantity of DCP show higher intensities of absorptions at 700 cm^{-1}. The amount of aromatic ring combined with polymer chain after DCP vulcanisation was estimated by the method described in Section 4.1.3, and is tabulated in Table 4.1 at different DCP concentrations. The variation of results is perhaps due to uncertainty of drawing the base line particularly at very low intensity of absorptions. However, the mean values for different compounds are similar, suggesting that the proportion of peroxide radicals bound to polymer is independent of DCP concentrations.

4.1.4.4 IR Spectrum of DCP Vulcanised Film Containing IPPD

The vulcanised films of DCP mixes containing various amounts of IPPD were prepared by the method described in

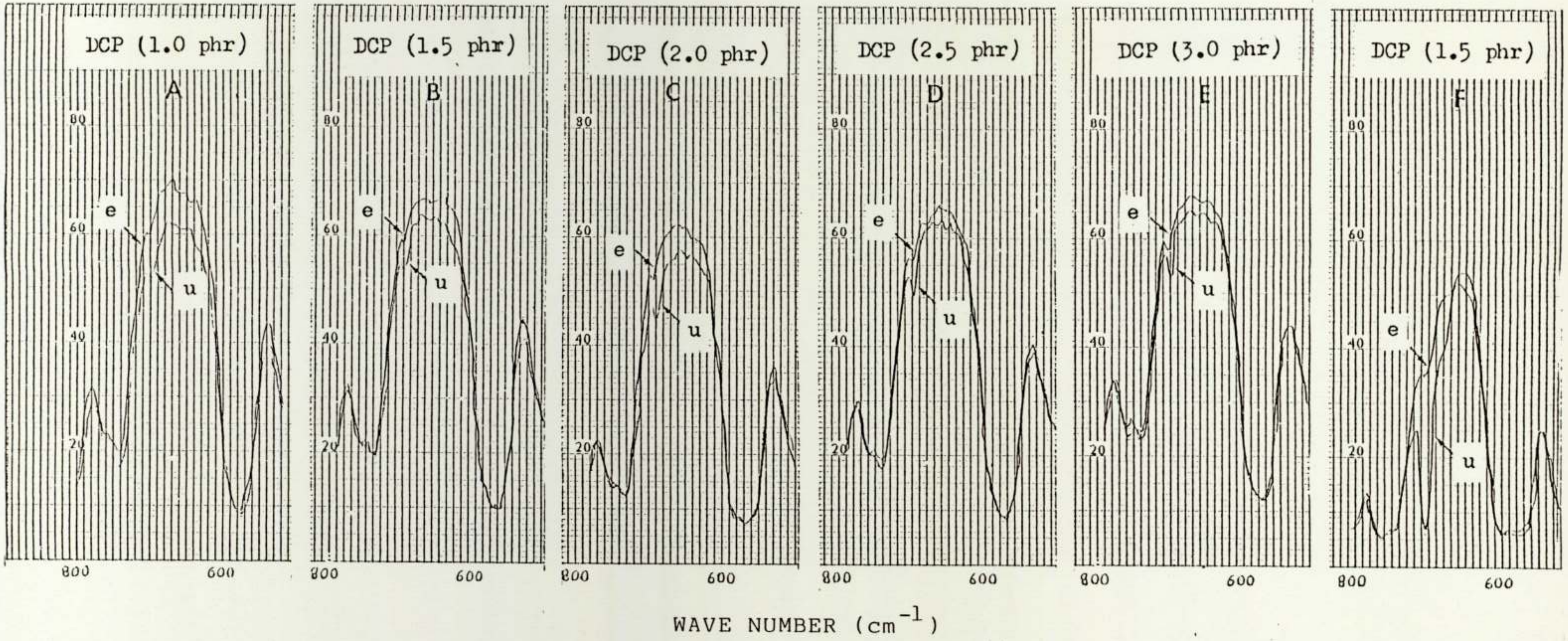


Figure 4.3 IR spectra of films derived from extracted rubber vulcanised with variable DCP concentrations at 160°C for 60 mins (A-E): (u) not extracted after cure, (e) extracted after cure; and from extracted rubber vulcansied with DCP (1.5 phr) at 160°C for 60 mins (F): (u) extracted film swollen with DCP-benzene solution (1.5% w/v), (e) extracted film not swollen

DCP (phr)	Aromatic ring attached to polymer (%)							
	Experiment 1			Experiment 2			arithmetic mean ($\bar{x}$)	standard deviation (SD)
	Sample			Sample				
	No. 1	No. 2	No. 3	No. 1	No. 2	No. 3		
1.0	42.55	34.47	31.10	36.28	32.29	41.40	36.18	4.74
1.5	37.35	32.21	47.39	33.69	42.39	35.95	38.16	5.73
2.0	32.20	47.52	45.73	42.13	35.58	31.25	39.07	7.09
2.5	39.19	41.80	47.52	35.63	37.02	40.23	40.23	4.20
3.0	40.74	37.31	30.01	35.64	33.93	38.96	36.09	3.83

Table 4.1 Estimation of aromatic ring attached to polymer chain after DCP vulcanisation

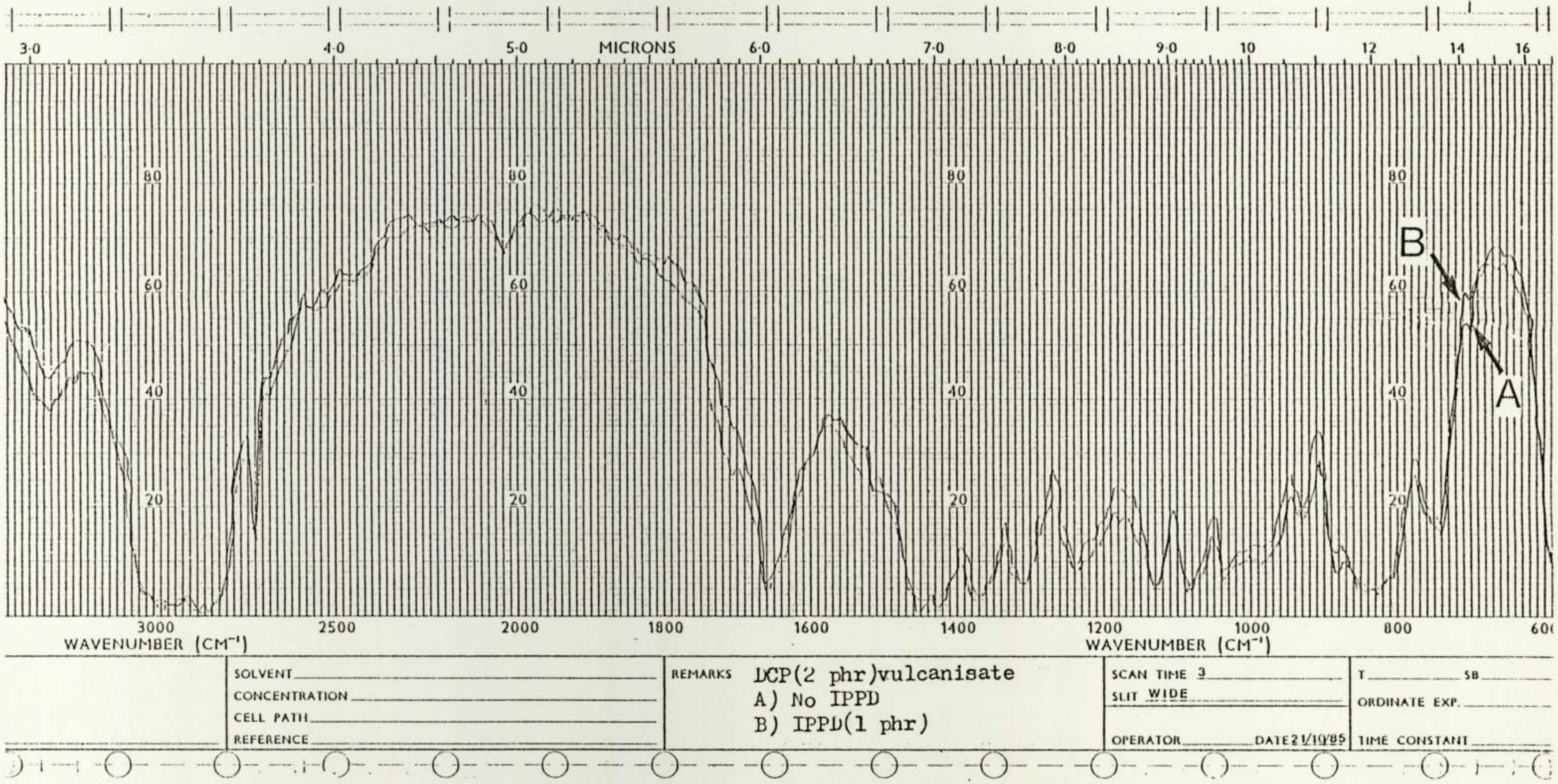
Section 4.1.2.2. Figure 4.4 represents the typical spectra of vulcanised films made with DCP (2 phr) stock without IPPD (A), and with 1 phr of IPPD (B), after hot acetone extraction. Both spectra are essentially similar demonstrating that no structural changes occur on addition of IPPD to DCP vulcanisation.

4.2 Analysis of the Extra-Network Compounds (ENCS) of Peroxide Vulcanised Rubber

During dicumyl peroxide vulcanisation most of the decomposed peroxide should be converted to cumyl alcohol and acetophenone (see Section 1.2.2.2). To determine the amount of these products, the vulcanised rubber was extracted at room temperature by swelling in a suitable solvent, which was carbon tetrachloride for infra-red analysis and iso-octane for ultraviolet analysis. In both cases, 0.2 gm of vulcanised rubber was immersed in 10 ml of solvent. The extraction time was 48 hours.

4.2.1 Ultraviolet Spectroscopy Analysis

Acetophenone and residual dicumyl peroxide were attempted to determine from the Pye Unicam SP 800 B Ultraviolet Spectrophotometer using the absorptions at λ_{max} 278 nm for aromatic $\pi \rightarrow \pi^*$ transitions of acetophenone and at λ258 nm for aromatic $\pi \rightarrow \pi^*$ transitions of dicumyl peroxide.



SOLVENT
CONCENTRATION
CELL PATH
REFERENCE

REMARKS DCP(2 phr)vulcanisate
A) No IPPD
B) IPPD(1 phr)

SCAN TIME 3
SLIT WIDE
OPERATOR
DATE 21/10/85

T
SB
ORDINATE EXP.
TIME CONSTANT

Figure 4.4 IR spectra of films derived from extracted rubber vulcanised with DCP (2 phr) at 160°C for 60 mins and extracted after cure: (A) No IPPD; (B) with IPPD (1 phr)

Typical absorptions attributed to electronic transitions for acetophenone and for dicumyl peroxide were obtained from a certain weight of reference compound in solvent which was used for sample extraction. Figure 4.5 shows UV spectra absorptions of acetophenone (A) and of dicumyl peroxide (B), and their corresponding calibration curves are shown in Figure 4.6 A and B respectively. Spectrum of mixture of acetophenone and dicumyl peroxide in iso-octane is shown in Figure 4.7, spectrum C. An attempt to analyse acetophenone and residual dicumyl peroxide of vulcanisates was performed by room temperature extraction of 2 gm of sample with 10 ml of iso-octane for 48 hours. From this extract the UV spectrum was then obtained.

4.2.2 Infra-red Spectroscopy Analysis

Cumyl alcohol was attempted to determine by infra-red analysis using the Perkin Elmer Infra-red Spectrophotometer as in the method described in Section 2.8. The characteristic bands attributed to O-H stretch: intermolecular hydrogen bonded, 3450-3200 cm^{-1}; C-H stretch: aromatic ring 3100-3000 cm^{-1}; C-H stretch: methyl, 2980-2840 cm^{-1}; were used to analyse the spectra of extract samples. Figure 4.8 shows IR spectra of cumyl alcohol and of extract derived from dicumyl peroxide vulcanisate.

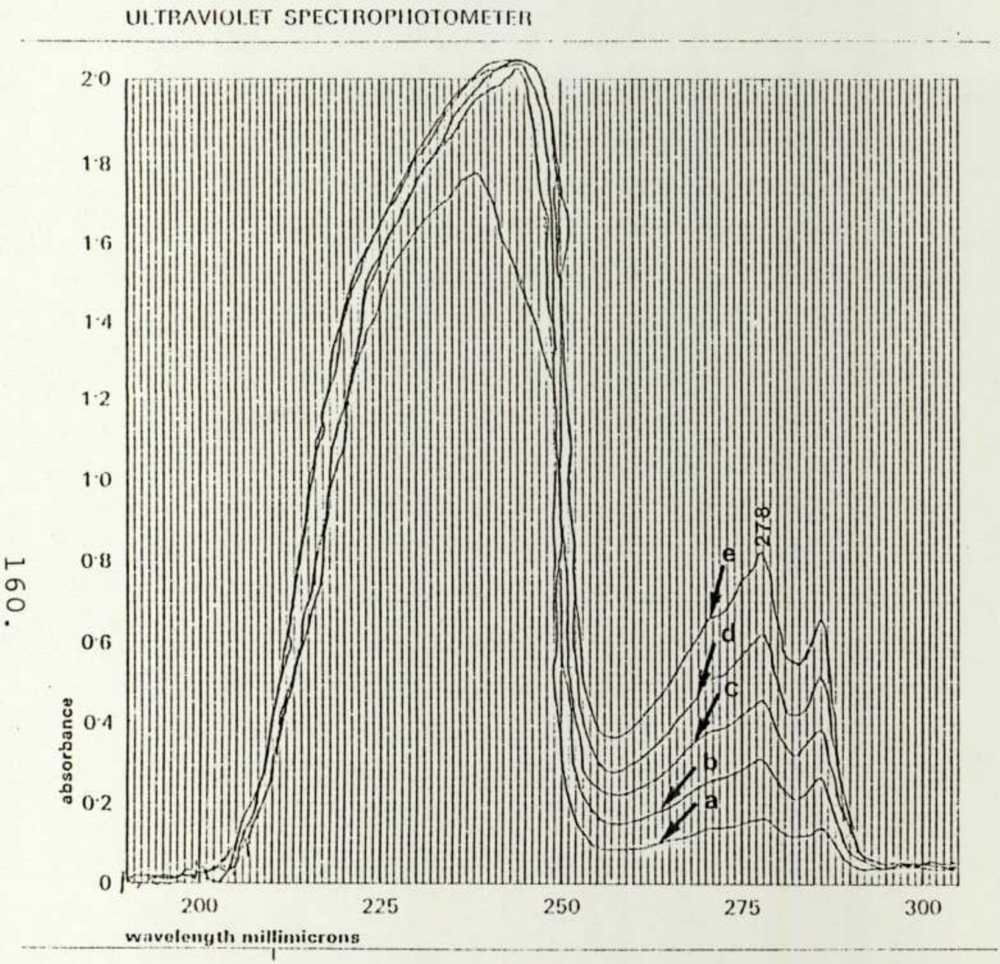


Figure 4.5A UV spectra of acetophenone in iso-octane, concentrations (x10^{-4}mole. litre^{-1}):1.6646(a), 3.3292(b), 4.9938(c), 6.6583(d), 8.3229(e)

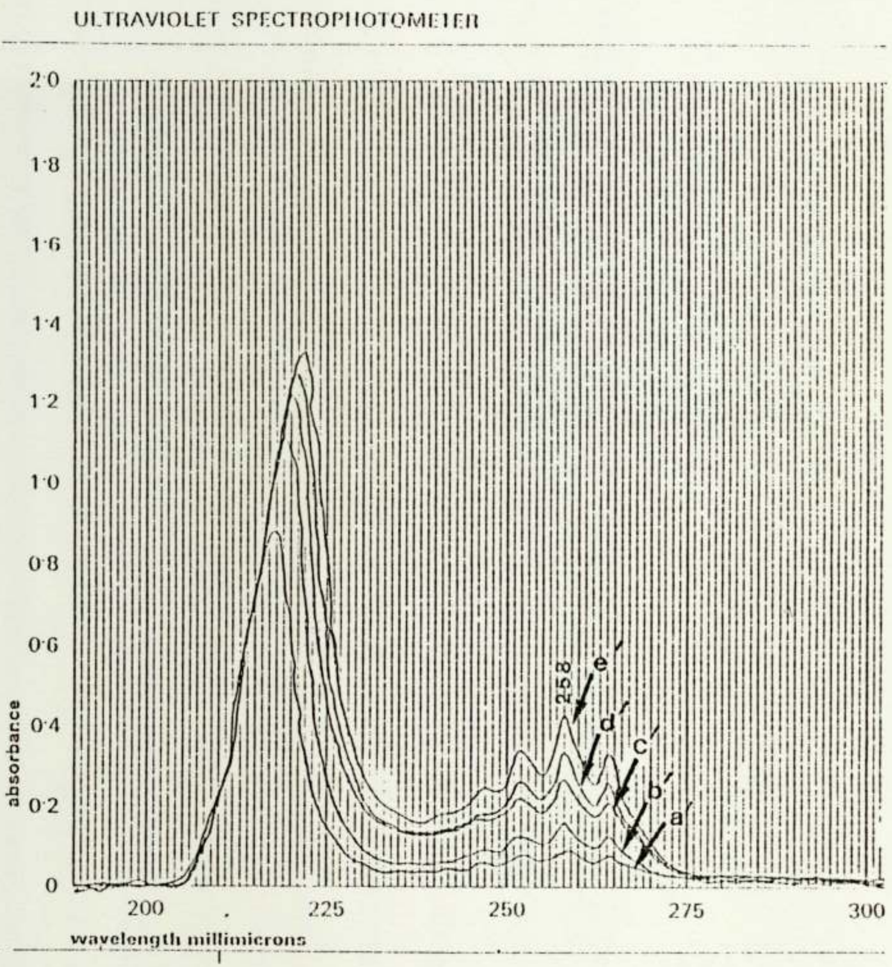


Figure 4.5B UV spectra of DCP in iso-octane, concentrations (x10^{-4}mole.litre^{-1}): 1.8519(a'), 3.7037(b'), 5.5555(c'), 7.4074(d'), 9.2593(e')

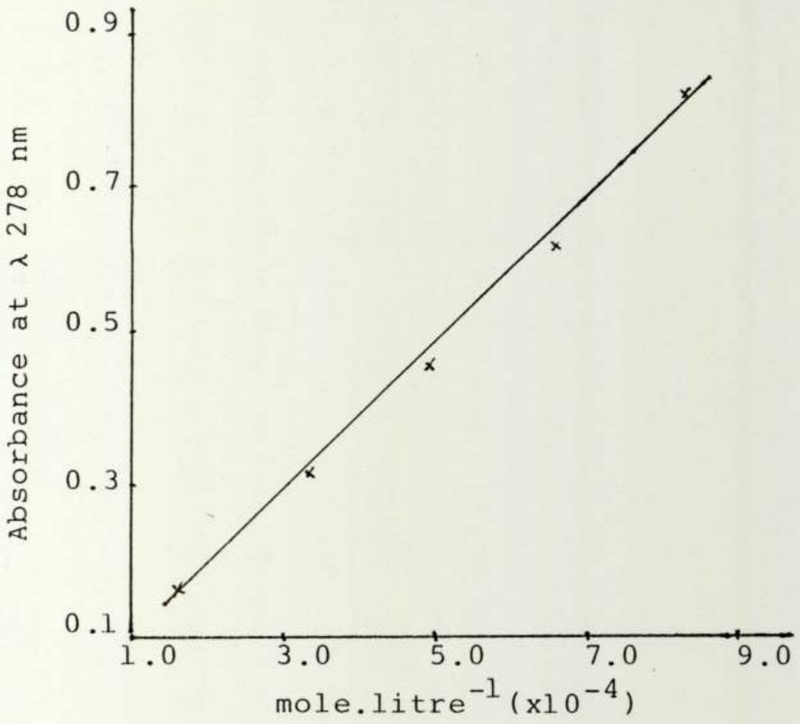


Figure 4.6A Calibration curve for acetophenone

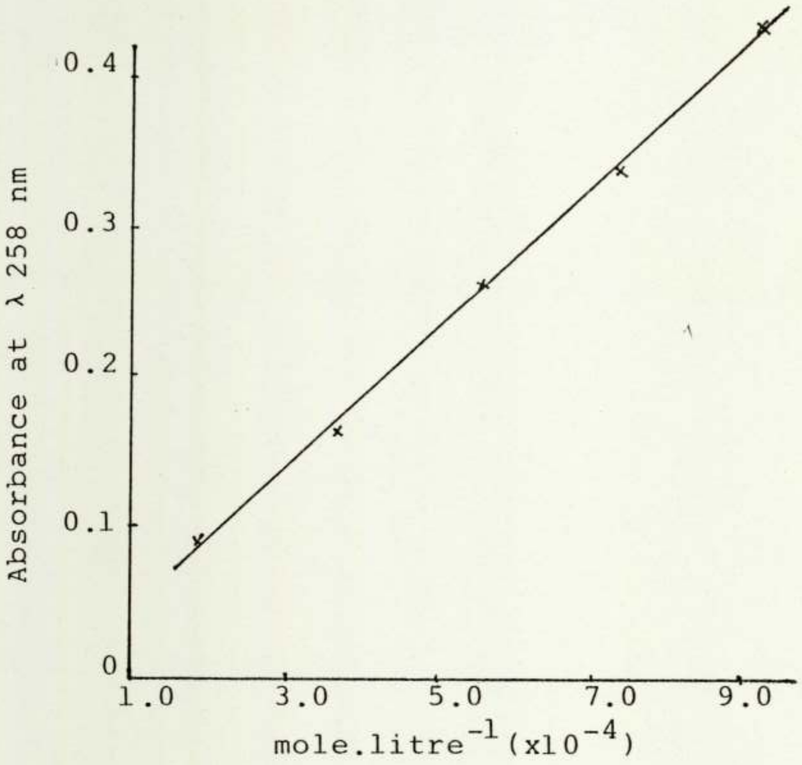
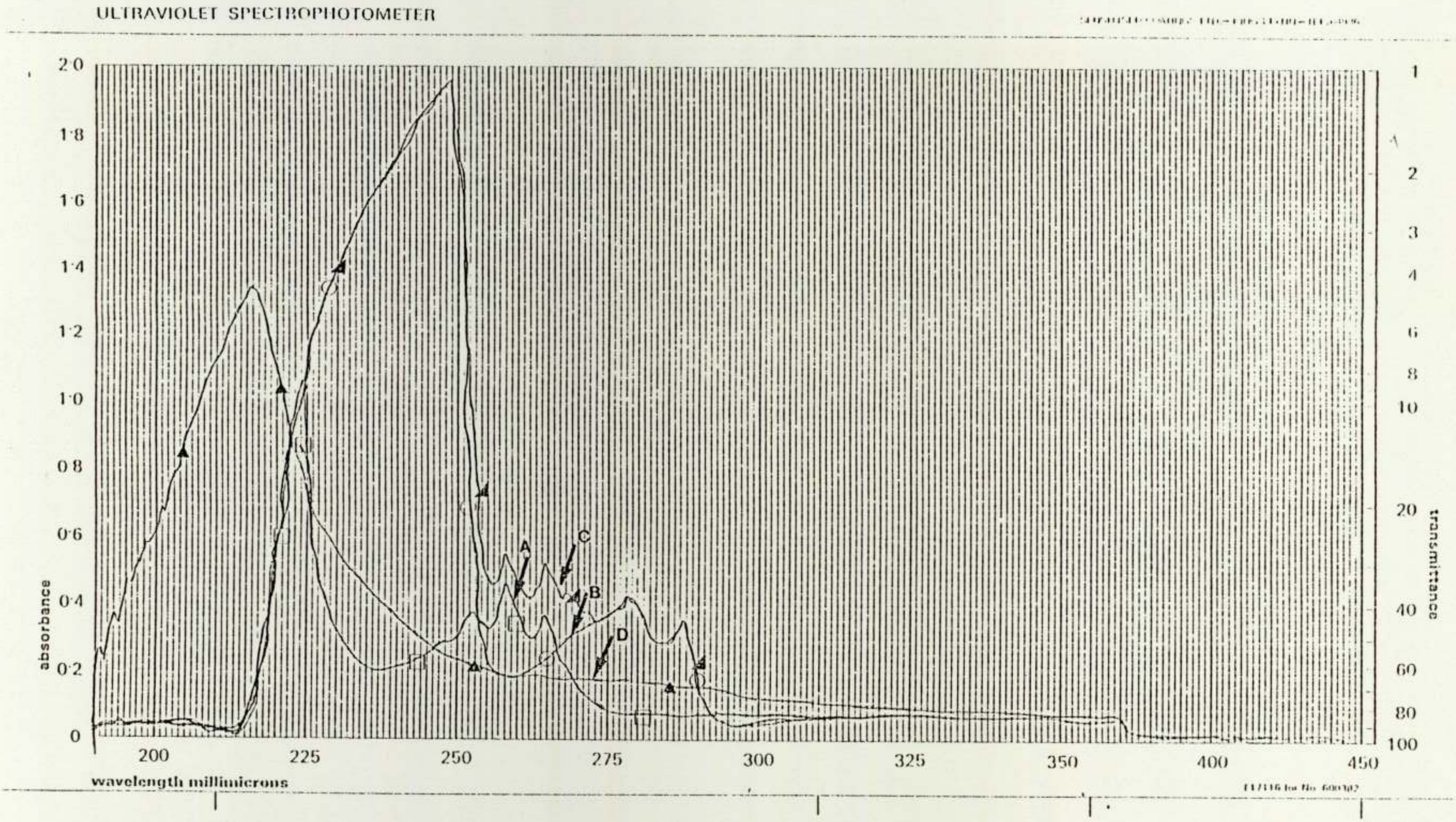


Figure 4.6B Calibration curve for DCP



<u>Figure 4.7</u> UV spectra of acetophenone/DCP in 10 ml iso-octane: 0.003 gm DCP (A,□), 0.0005 gm acetophenone (B,O), 0.003 gm DCP + 0.0005 gm acetophenone (C,◢), pure iso-octane (D,▲)

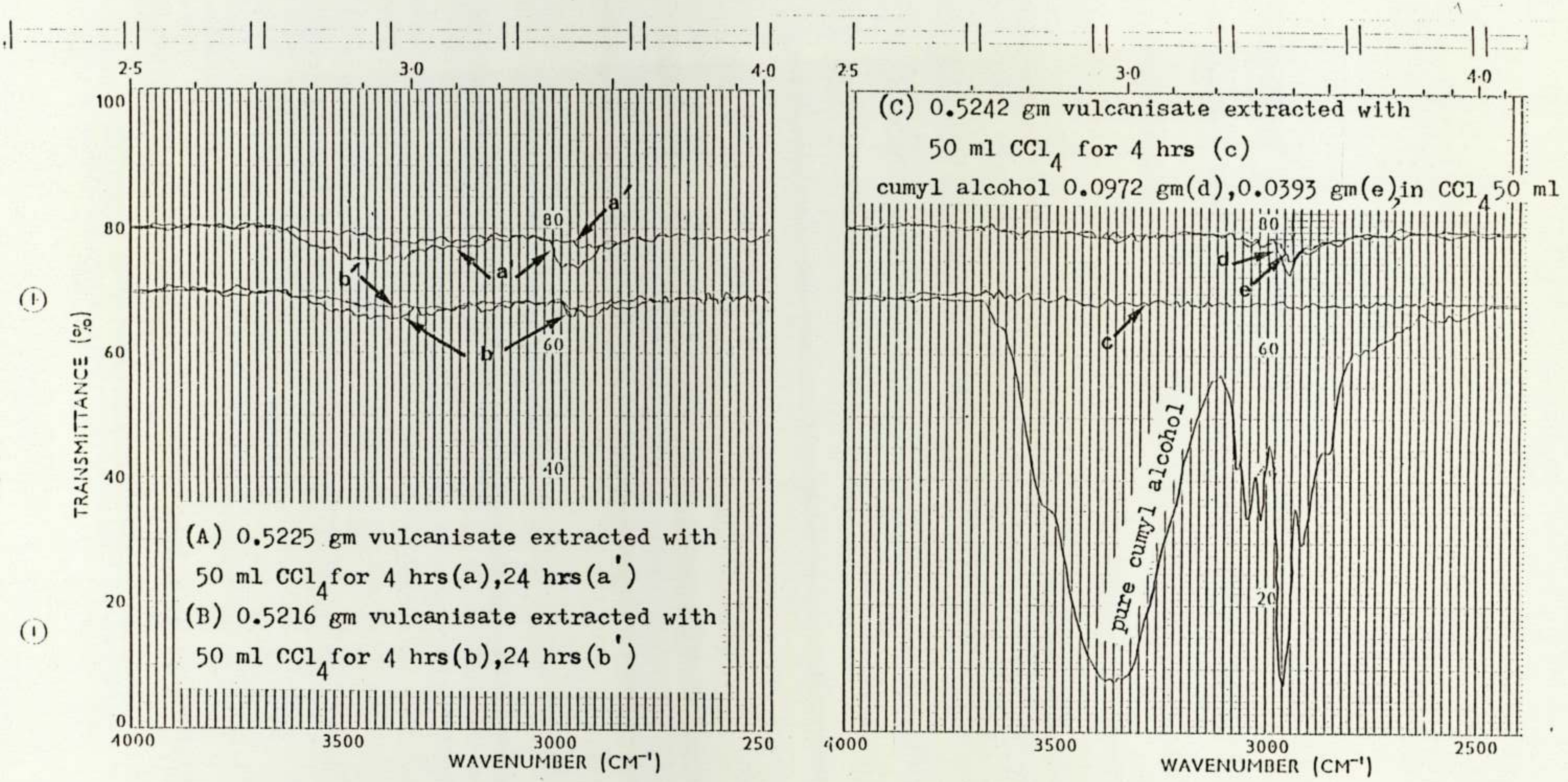


Figure 4.8 IR spectra of cumyl alcohol and of extract derived from DCP (3 phr) vulcanisates which were cured at 160°C for 14 mins and subsequently kept in bags with sealing (A,B), without sealing (C)

4.2.3 Gas Liquid Chromatography (GLC)

An attempt was made to determine the ENCS of dicumyl peroxide vulcanisate using GLC, the Pye Unicam GLC was used. The trial was carried out using the solution of recrystallised dicumyl peroxide in iso-octane as reference. Dicumyl peroxide used was recrystallised from ethanol.

4.2.4 Comments on the Analysis Results

The UV absorbance was shown to give incorrect results. The evidence (see Figure 4.7, spectrum C) is that absorptions due to dicumyl peroxide were interfered with by absorptions due to acetophenone when they were in admixture. This is due to the fact that the two compounds exhibit benzenoid bands (β-bands) which for acetophenone is at λ_{max} 278 nm and for dicumyl peroxide is at λ_{max} 258 nm. These were the selected wavelengths used for comparison with spectra of samples. Dicumyl peroxide has ethylenic bands (E-bands) at λ_{max} 223 nm. Acetophenone shows konjugierte (German) bands (K-bands) at λ_{max} 250 nm due to the carbonyl group being capable of conjugating with the aromatic ring. These $\pi \rightarrow \pi^*$ transitions (K-bands) are characterised by high molar absorpivity (see Figure 4.7, spectrum B). Figure 4.7 shows high intensity of absorption near λ_{max} 250 nm for acetophenone (spectrum B) thus interfering with the absorption at

λ_{max} 258 nm for dicumyl peroxide (spectrum A) resulting in increasing the intensity of the absorption at λ_{258} nm when acetophenone and dicumyl peroxide are in admixture (spectrum C).

Cumyl alcohol disappeared, perhaps by volatilisation before examination by the infra-red absorptions. There was evidence that vulcanised rubber kept in an unsealed bag gave the extract which showed no trace of absorbance due to O-H stretch at 3450-3200 cm^{-1} (see Figure 4.8, spectrum C). The vulcanised rubber for this analysis was subsequently kept in a sealed bag and the extraction was carried out as soon as possible. Figure 4.8, spectra a, b, for extract derived from 4 hrs extraction of rubber kept in a sealed bag, show some absorptions due to O-H stretch. However, on swelling the vulcanisate in CCl_4 for 4 hours, some of the ENCS were extracted by the solvent and were observed to contain OH groups on IR examination. After 20 hours, the extract was found to contain less OH groups by IR spectroscopy, probably due to volatilisation of cumyl alcohol. The amounts of cumyl alcohol present in dicumyl peroxide vulcanisates could not be measured reproducibly by IR spectroscopy.

In an attempt to analyse ENCS of a peroxide vulcanisate by GLC, a preliminary analysis was carried out with recrystallised dicumyl peroxide dissolved in iso-octane. On injecting into the column (see Section 2.10) two peaks of reference were observed (see Figure 4.9) perhaps because of on-column decomposition which gave rise to a mixture of products. This is possible because of the temperature range program which was set at 60° to 160°C, thus thermal decomposition of dicumyl peroxide occured on-column. Analysis of ENCS of a peroxide vulcanisate was not successful by GLC.

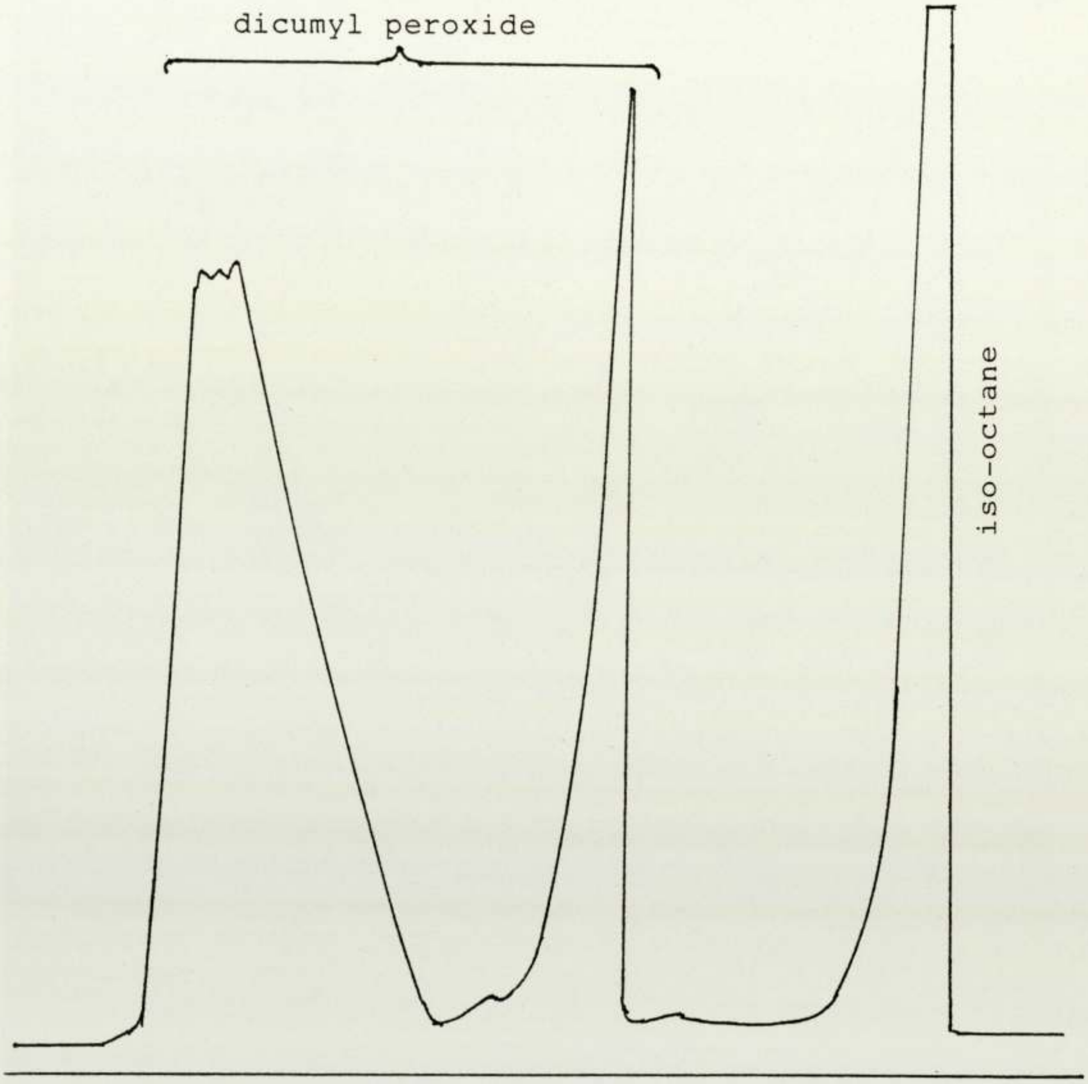


Figure 4.9 GLC chromatogram of dicumyl peroxide

CHAPTER FIVE

STUDY OF FATIGUE AND TENSILE PROPERTIES OF NATURAL RUBBER VULCANISATES

5.1 Introduction

Natural rubber vulcanised with a peroxide contains carbon-carbon crosslinks, while those prepared with a sulphur-accelerator system are likely to possess a variety of chemical crosslinks, namely, monosulphide, disulphide and polysulphide. The order of bond energies of these crosslinks is: carbon-carbon>monosulphide>disulphide>polysulphide(137). The hypothesis that weak crosslinks are essential for obtaining high tensile strength and fatigue life has been formally proposed(138). Several investigators(139-141) have compared the flex life of natural rubber vulcanisates prepared with a variety of curing systems and have concluded that vulcanisates containing polysulphidic crosslinks are superior to those containing carbon-carbon or monosulphidic crosslinks. However, recent studies(142,143) do not support this conclusion, and there is other evidence that a peroxide vulcanisate is more resistant to fatigue than a conventional sulphur vulcanisate when cured to the same rheometer torque. It has been shown that the initial modulus markedly affects fatigue resistance(144,145).

It was of interest to determine whether fatigue resistance really does depend only on the modulus of vulcanisate. The first approach was to cure the rubber with various concentrations of dicumyl peroxide to the same rheometer torque to those cured with a conventional sulphur system. The fatigue life and tensile properties of these vulcanisates were studied after acetone extraction before and after cure. The relation between fatigue resistance and crosslink density, and the effect of extra-network compounds (ENCS) of vulcanisates and of other additives on fatigue resistance were also investigated.

5.2 Experimental

Compounding operations were performed as described in Section 2.2 and the curing parameters were obtained from the Monsanto Oscillating Disc Rheometer as described in Section 2.3.1. The determinations of fatigue life by the Monsanto Fatigue to Failure Tester, tensile properties by the E-type Tensometer and crosslink density, were described in Sections 2.5.1, 2.5.2 and 2.7 respectively.

5.3 Effect of Extraction on Fatigue and Tensile Properties

5.3.1 Procedure

Rubber used was unextracted and extracted before mixing. The fatigue life and tensile properties of vulcanisates were investigated both with and without extraction after vulcanisation. Extraction procedures for raw rubber and vulcanisates were described in Section 2.2.2 and 2.6 respectively. The formulations and cure conditions used are shown in Table 5.1.

Compounding Ingredients	Parts by weight											
	A	B	C	D	E	F	A'	B'	C'	D'	E'	F'
Extracted SMR10	100	100	100	100	100	100	-	-	-	-	-	-
Unextracted SMR10	-	-	-	-	-	-	100	100	100	100	100	100
DCP	1.0	1.5	2.0	2.5	3.0	-	1.0	1.5	2.0	2.5	3.0	-
Zinc Oxide	-	-	-	-	-	5	-	-	-	-	-	5
Stearic Acid	-	-	-	-	-	3	-	-	-	-	-	3
CBS	-	-	-	-	-	0.6	-	-	-	-	-	0.6
Sulphur	-	-	-	-	-	2.5	-	-	-	-	-	2.5
Cure temp./time (^{o}C/min)	160 /60	160 /60	160 /60	160 /60	160 /60	140 /32	160 /60	160 /60	160 /60	160 /60	160 /60	140 /43
Rheometer torque (kg.m)	2.16	2.76	3.60	4.20	4.80	3.48	1.98	2.70	3.30	3.84	4.32	3.54

Table 5.1 Formulations and cure conditions.

5.3.2 Results

Figures 5.1 (a) and (a') show the effect of extraction after cure on fatigue life of the vulcanisates prepared from extracted rubber (a) and from unextracted rubber (a'). The results in Figures 5.1(a) and (a') were obtained from the mean data of three experiments and the variation was less than 10%. The results in Figure 5.1(a) and (a') show that (1) the lower the DCP concentrations, the better the fatigue resistance attained; (2) vulcanisates prepared from unextracted rubber are more resistant to fatigue than those from extracted rubber; (3) conventional sulphur vulcanisates (F, F') are more resistant to fatigue than peroxide vulcanisates containing DCP, 2.5 phr (D, D'); 3 phr (E, E') but lower than those containing DCP, 1 phr (A, A'); 1.5 phr (B, B'); and 2 phr (C, C'); (4) fatigue resistance of all kinds of vulcanisates are decreased on acetone-extraction after vulcanisation; (5) vulcanisates prepared from unextracted rubber show much more decrease in fatigue life when extracted after vulcanisation than those from extracted rubber do.

The data in Table 5.2 were obtained from the mean results of three experiments and the variation within three experiments was not greater than 10% for any sample. The results show that at optimum cure, extraction of the rubber before vulcanisation enhances M_{100} and M_{300} but lowers tensile strength and elongation at break for both

Vulcanising system*	M_{100} (MPa)		M_{300} (MPa)		TS (MPa)		EB (%)	
	Ext.	Unext.	Ext.	Unext.	Ext.	Unext.	Ext.	Unext.
1.0 phr of DCP (A,A')	1.48	1.43	2.97	2.69	8.58	13.71	510	625
1.5 phr of DCP (B,B')	1.86	1.75	4.24	3.91	7.83	9.22	420	470
2.0 phr of DCP (C,C')	2.42	2.26	6.18	4.92	7.44	9.01	350	350
2.5 phr of DCP (D,D')	2.60	2.51	-	-	6.62	7.11	270	280
3.0 phr of DCP (E,E')	3.13	2.94	-	-	3.42	4.26	140	180
Conventional sulphur (F,F')	1.05	1.01	2.69	2.37	26.19	29.21	700	980

* Formulations and conditions are shown in Table 5.1.

Key to abbreviations :

M_{100}	Stress (modulus) at 100% elongation
M_{300}	Stress (modulus) at 300% elongation
TS	Tensile strength
EB	Elongation at break
Ext	Rubber extracted before vulcanisation
Unext	Rubber unextracted before vulcanisation

Table 5.2 Tensile properties of unextracted and extracted rubber vulcanised with DCP and conventional sulphur systems to maximum rheometer torque.

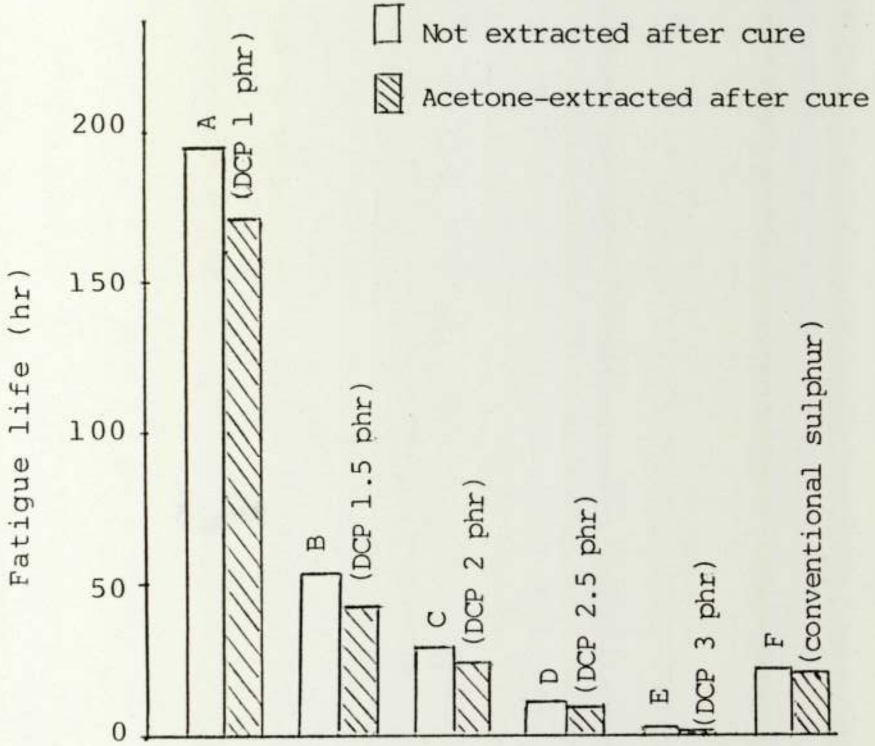


Figure 5.1(a) Effect of extraction after cure on the fatigue life of extracted rubber cured by DCP at 160°C, and by conventional sulphur system at 140°C, to maximum rheometer torque (see Table 5.1).

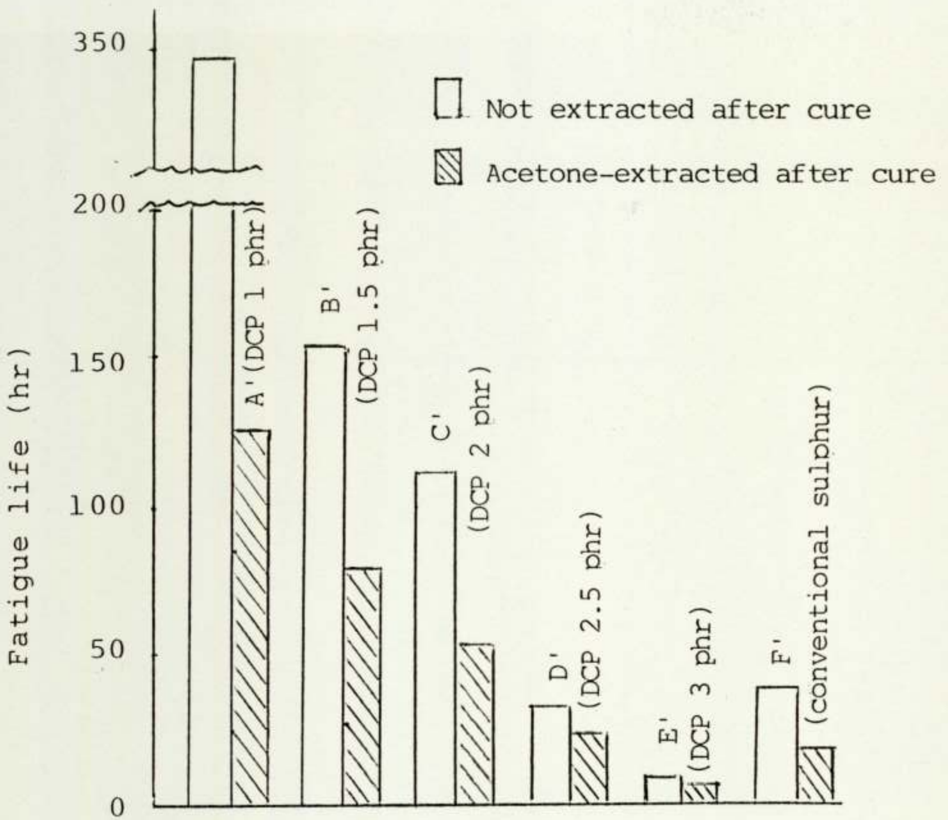


Figure 5.1(a') Effect of extraction after cure on the fatigue life of unextracted rubber cured by DCP at 160°C, and by conventional sulphur system at 140°C, to maximum rheometer torque (see Table 5.1)

peroxide and conventional sulphur vulcanisates. Vulcanisates prepared from both unextracted and extracted rubber show that the higher the DCP concentrations, the higher the M_{100} and M_{300}, but the lower the elongation at break and the tensile strength attained.

5.3.3 Discussion

The results presented in Table 5.2, Figures 5.1 (a) and (a'), indicate that extraction of the rubber before curing yields vulcanisates which have lower tensile strength and fatigue resistance than those derived from unextracted rubber. This suggests that non-rubber constituents are partly responsible for fatigue resistance and may play a part in improving tensile strength. Extraction after vulcanisation reduces fatigue resistance and the effect is more pronounced for vulcanisates derived from rubber unextracted before vulcanisation, presumably through the removal of both non-rubber constituents present in the original rubber and extra-network compounds formed during vulcanisation. This suggests that extra-network compounds of DCP and conventional sulphur vulcanisates account for part of antifatigue resistance. The evidence confirming this suggestion is given in Section 5.6.2.2. The low fatigue life of vulcanisates containing higher DCP concentrations may be attributed (1) to high degree of crosslinking (see Section 5.5.2.2); (2) to pendent groups formed by the addition of cumyloxy radical to the polymer chain (see Section 4.1.4.2). The effect of the modified structure on fatigue life may be explained in terms of greater impedance in the stressed structure than normal, thus leading to an increase in localised stresses in the network and hence to a reduction in fatigue life.

5.4 Effect of Vulcanisation Time on Fatigue and Tensile Properties

5.4.1 Procedure

Rubber was acetone extracted (see Section 2.2.2) before mixing. Vulcanisation times were varied in order to obtain the required rheometer torque.

5.4.2 Results and Discussion

5.4.2.1 Variation of M_{100} with Vulcanisation Time

Results for variation of M_{100} with cure time are shown graphically in Figure 5.2. The results demonstrate that M_{100} of conventional sulphur and DCP vulcanisates increased with increasing cure time up to a certain time, beyond which they fell. The change in M_{100} of DCP (2 phr) vulcanisate with cure time shows a similar trend at higher temperature to that of the conventional sulphur vulcanisate, except that the peak is later than it is for the conventional sulphur vulcanisate.

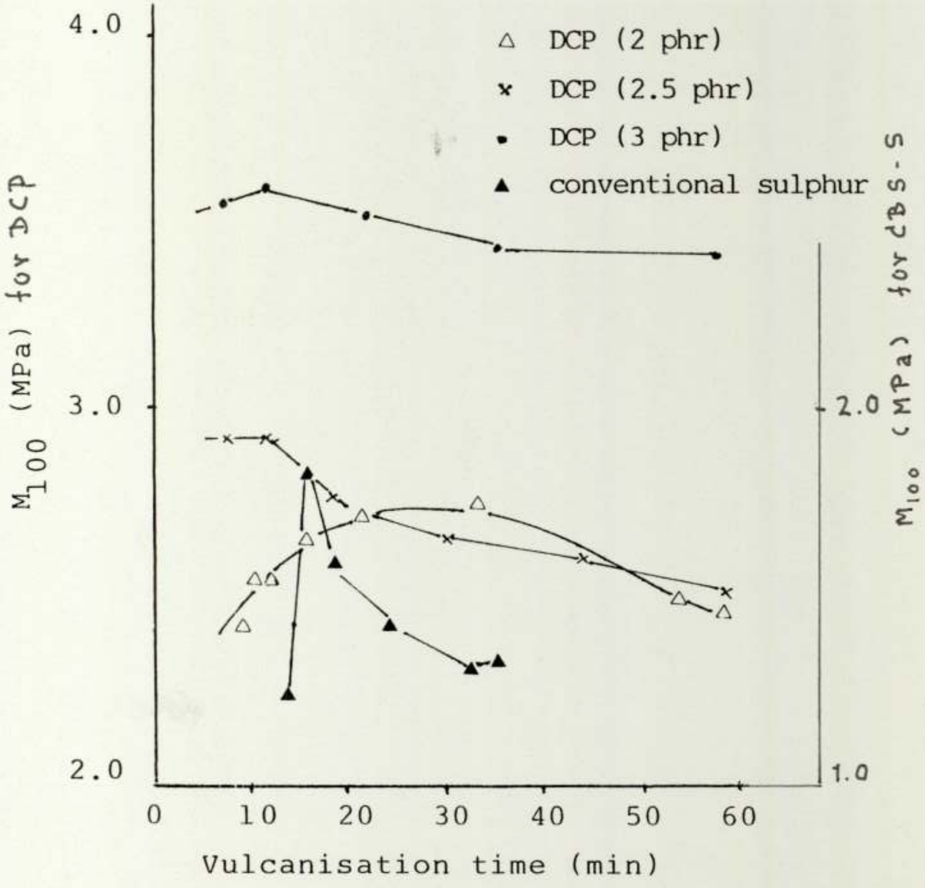


Figure 5.2 Variation of M_{100} with vulcanisation time for extracted rubber cured by DCP, 2; 2.5; 3 phr at 160°C; and by ZnO, 5; Stearic acid, 3; CBS, 0.6; S, 2.5 phr at 140°C

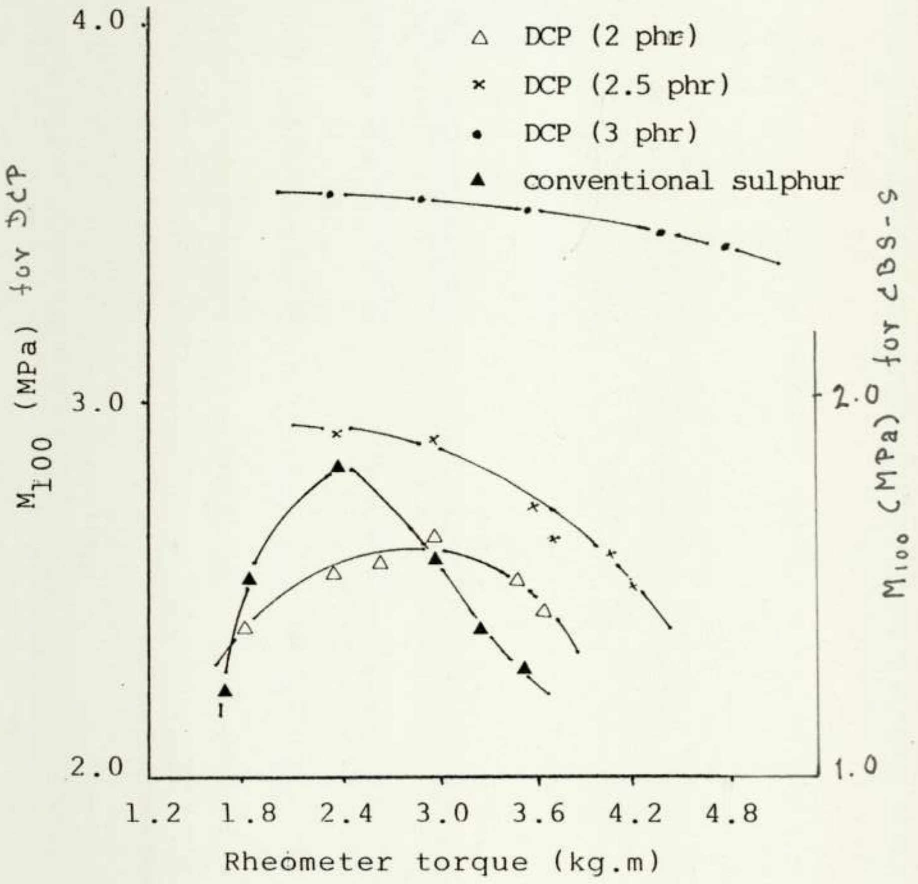


Figure 5.3 Plots of M_{100} against rheometer torque for extracted rubber cured by DCP, 2; 2.5; 3 phr at 160°C; and by ZnO, 5; Stearic acid, 3; CBS, 0.6; S, 2.5 phr at 140°C

M_{100} of DCP (2.5 phr) and DCP (3 phr) vulcanisates increase slightly at the early stage, thereafter they decrease gradually.

5.4.2.2 Tensile Modulus (M_{100}) Against Rheometer Torque

Figure 5.3 shows plots of M_{100} against rheometer torque. From Figure 5.3, it is evident that the curves for DCP (2.5 phr) and DCP (3 phr) are different from those for DCP (2.0 phr) and conventional sulphur vulcanisates. M_{100} of DCP (2.5 phr) and DCP (3 phr) decrease with increasing rheometer torque but M_{100} of DCP (2 phr) and conventional sulphur vulcanisates rise with increasing rheometer torque up to a certain point, thereafter they decline. The experimental results represented in Figure 5.3 demonstrate that beyond a rheometer torque of ca. 3 kg.m, M_{100} fell in all cases. This is presumably due to the fact that the strains in the measurement of these two parameters are different. The Oscillating Disc Rheometer measures the torque required to oscillate the rotor which is embedded in the rubber sample confined in a die cavity under pressure through 3^{o}. The sample is thus subjected to an oscillatory shearing action of small amplitude. As vulcanisation proceeds, the torque required to shear the rubber increases, since the rotor is straining the rubber, the torque value is directly related to the shear modulus of the rubber at small strains. The tensometer measures M_{100} by stretching the rubber continuously to 100% elongation. Thus at high degree of crosslinking, the strain produced by the tensometer is enough to break the rubber chain, therefore the stress is low. In contrast, at high degree of crosslinking, small strain produced by the rheometer is not enough to break the rubber chain, then the torque is high.

5.4.2.3 Variation of Tensile Strength and Fatigue Life with Vulcanisation Time

Plots of tensile strength and fatigue life against vulcanisation time are given in Figures 5.4 and 5.5 respectively. The results show that tensile strength and fatigue life of DCP (2 phr) and of conventional sulphur vulcanisates behave similarly i.e., they pass through a maximum as the vulcanisation time is increased. Tensile strength of DCP (2.5 phr), and DCP (3 phr) vulcanisates also reaches a peak and then declines, but their fatigue life decreases with vulcanisation time.

From the results of Section 5.4.2.1, 5.4.2.2 and 5.4.2.3, it is clearly shown that vulcanisates containing 2 phr of DCP and conventional sulphur system behave similarly in the effect of vulcanisation time on fatigue and tensile properties.

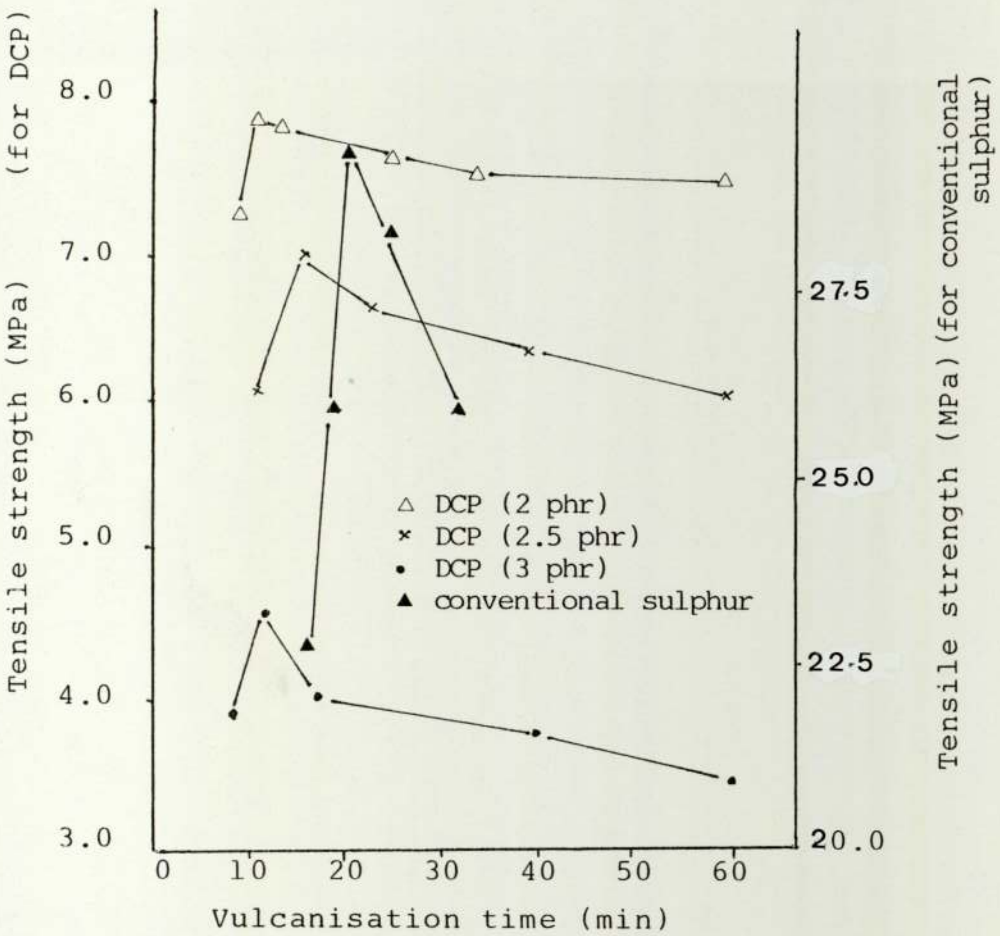


Figure 5.4 Variation of tensile strength with vulcanisation time for extracted rubber cured by DCP at 160^{o}C and by conventional sulphur system at 140^{o}C

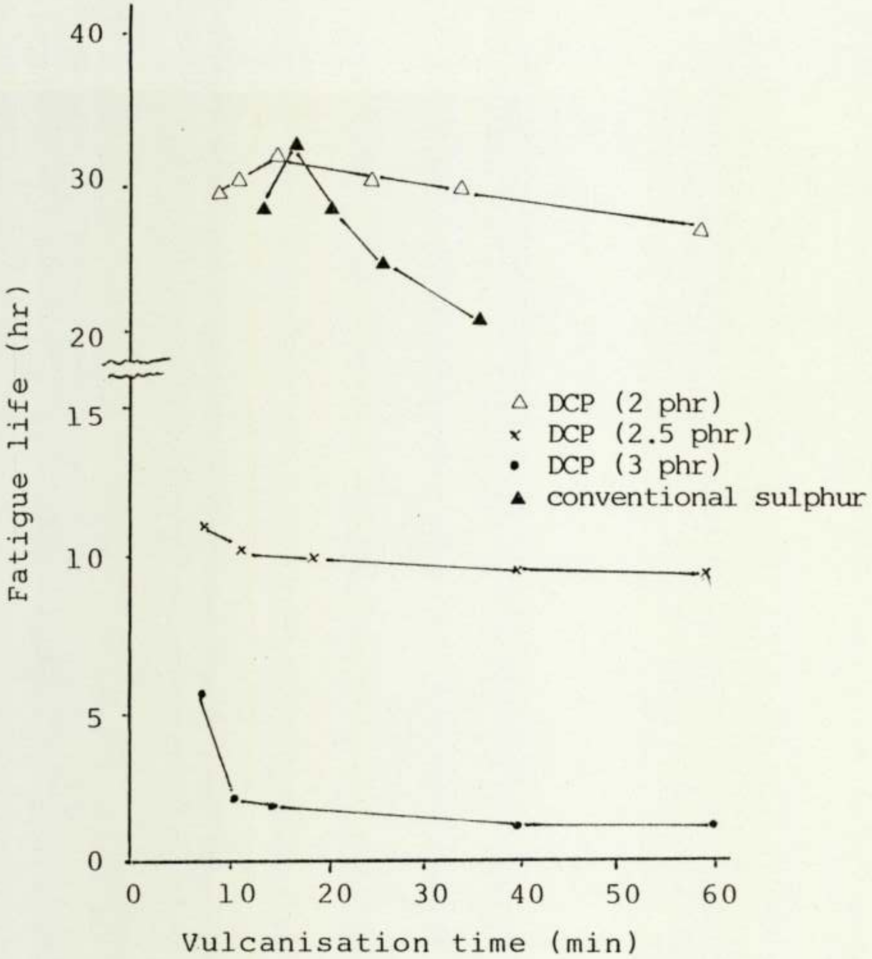


Figure 5.5 Variation of fatigue life with vulcanisation time for extracted rubber cured by DCP at 160^{o}C and by conventional sulphur system at 140^{o}C

5.4.2.4 Fatigue Life of DCP and Conventional Sulphur Vulcanisates Cured to the Same Rheometer Torques

Table 5.3 presents the modulus and fatigue life of DCP and conventional sulphur vulcanisates which were not extracted after cure. DCP and conventional sulphur vulcanisates were cured to various rheometer torques. At the same rheometer torque (not necessarily the same tensile modulus), vulcanisates containing higher DCP concentrations showed higher M_{100}. However, at equivalent rheometer torques, the fatigue life of vulcanisates decreases with increasing peroxide loading. A comparison of the fatigue lives of DCP vulcanisates with conventional sulphur vulcanisates at equivalent rheometer torques, DCP (2 phr) and conventional sulphur vulcanisates show similar results, but vulcanisates containing > 2 phr of DCP are less resistant to fatigue than are conventional sulphur vulcanisates.

5.5 Dependence of Fatigue Life on M_{100} and Physical Crosslink Density

5.5.1 Procedure

Rubbers used were unextracted and acetone extracted before mixing. Rubber mixes were cured to various times and M_{100} (see Section 2.5.2.2), fatigue life (see Section 2.5.1.3)

Vulcanising system*	Cure time (min)	Rheometer torque (kg.m)	M_{100} (MPa)	Fatigue life (hr)
DCP (1phr)	35	2.16	1.65	127.7
	40	2.23	1.46	146.3
DCP (1.5phr)	16	2.28	1.68	48.3
	60	2.88	1.69	47.8
DCP (2phr)	11	2.4	2.48	30.3
	16	3.0	2.65	31.8
	34	3.6	2.74	30.1
	60	3.66	2.42	28.5
DCP (2.5phr)	11	2.4	2.91	11.7
	16	3.0	2.87	10.6
	23	3.6	2.74	10.3
	60	4.2	2.68	9.1
DCP (3phr)	9	2.4	3.54	6.7
	12	3.0	3.53	3.5
	16	3.6	3.52	3.4
	60	4.8	3.42	2.7
Conventional sulphur	12	1.68	1.14	28.3
	16	1.8	1.24	32.5
	20	2.4	1.21	27.6
	25	3.0	1.21	25.2
	36	3.3	1.17	22.4

* Base formulations (parts by weight) : Extracted rubber, 100; DCP, 1.0; 1.5; 2.0; 2.5; 3.0; cured at 160°C. Extracted rubber, 100; ZnO, 5; Stearic acid, 3; S, 2.5; cured at 140°C.

Table 5.3 Modulus and fatigue life for DCP and conventional vulcanisates which were not not extracted after cure.

and crosslink density (see Section 2.7) were determined. In order to investigate the dependence of fatigue life on M_{100} and on crosslink density, the samples for these three tests were taken from the same vulcanisate sheet.

5.5.2 Results and Discussion

5.5.2.1 Dependence of Fatigue Life on M_{100}

Figure 5.6 shows plots of M_{100} against fatigue life for the above system. Results indicate a difference in behaviour between DCP vulcanisate made from unextracted and from extracted rubber i.e., the former shows an increase in fatigue resistance with increasing M_{100} while the latter shows some increase and then a slight decline. Conventional sulphur vulcanisates demonstrate similar trends for both unextracted and extracted rubber i.e., an increase in fatigue resistance with increasing M_{100} and then a slight fall. The traditional view is that fatigue resistance of vulcanisate at high modulus decreases because of high molecular stresses produced during fatiguing.

The M_{100} results obtained from DCP (2 phr) vulcanisate made with unextracted rubber may not be enough to show this effect. Non-rubber constituents are clearly very important in the case of DCP vulcanisate and this will be discussed further in Section 5.6.1.3.

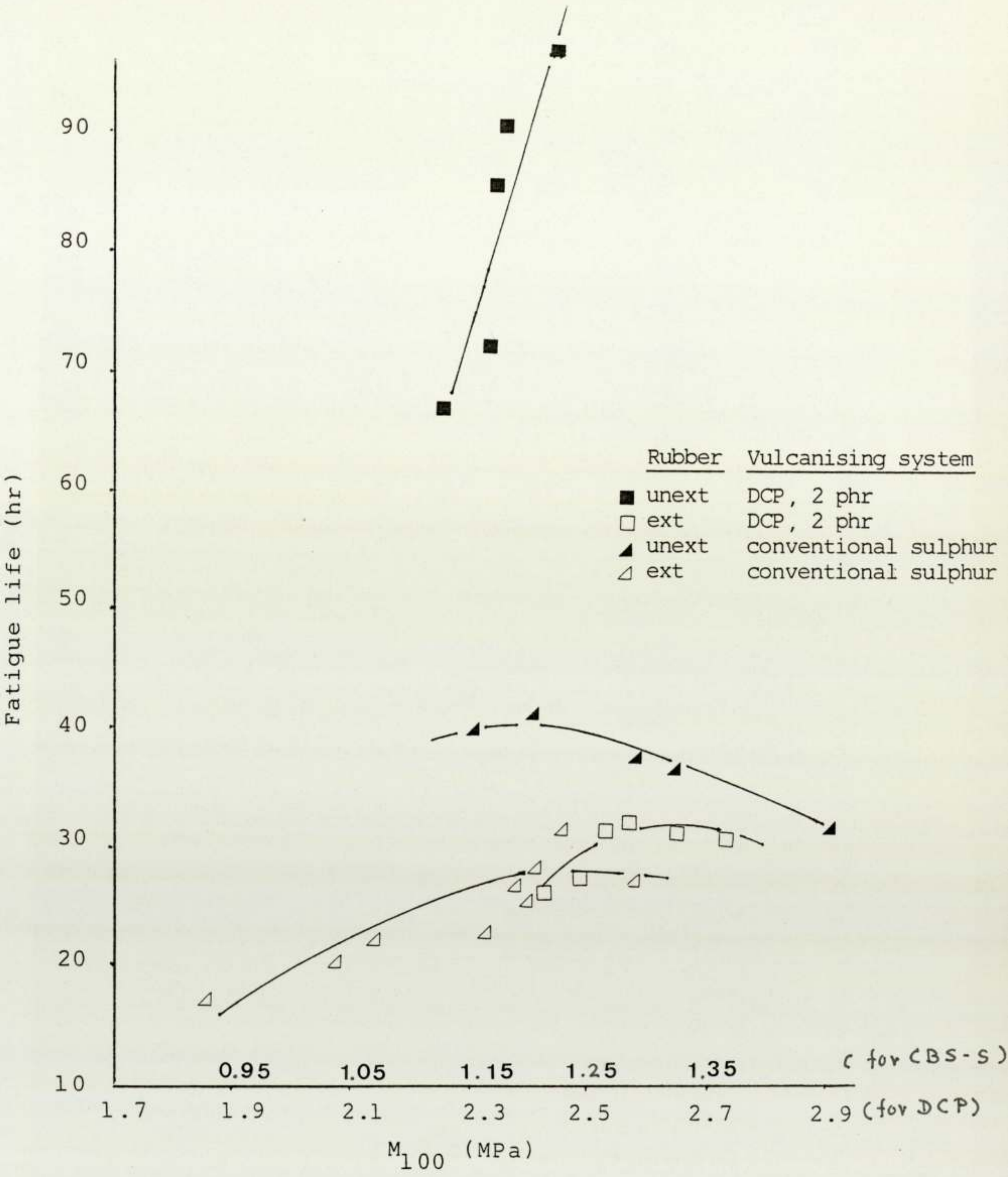


Figure 5.6 Plots of M_{100} against fatigue life for unextracted and extracted rubber with DCP, 2 phr; cured at 160°C; and with conventional sulphur system (ZnO, 5: Stearic acid, 3; CBS, 0.6; S, 2.5 phr); cured at 140°C (not extracted after cure).

5.5.2.2 Dependence of Fatigue Life on Physical Crosslink Density

Figure 5.7 shows plots of physical crosslink density against fatigue life for conventional sulphur and peroxide vulcanisates containing DCP, 2; 2.5; 3 phr. Conventional sulphur and DCP (2 phr) vulcanisates show that fatigue resistance increases as physical crosslink density is increased. Vulcanisates containing DCP, 2.5 and 3 phr demonstrate an increase in fatigue life with increasing physical crosslink density up to certain values, beyond which they fall.

The experimental results show that DCP (2 phr) vulcanisates having low physical crosslink density behave similarly in relation to the physical crosslink density and fatigue life, as do those for conventional sulphur vulcanisates i.e., fatigue life increases with increasing physical crosslink density. Good fatigue life at low physical crosslink density is attributed to the increased capacity of segments of rubber molecules to re-orientate. However, DCP (2.5 phr) and DCP (3 phr) vulcanisates possessing higher physical crosslink density show that increasing physical crosslink density decreases fatigue life and presumably, the capacity of segments of rubber molecules to re-orientate is reduced. Physical crosslink density of DCP (2 phr) and conventional sulphur vulcanisates may

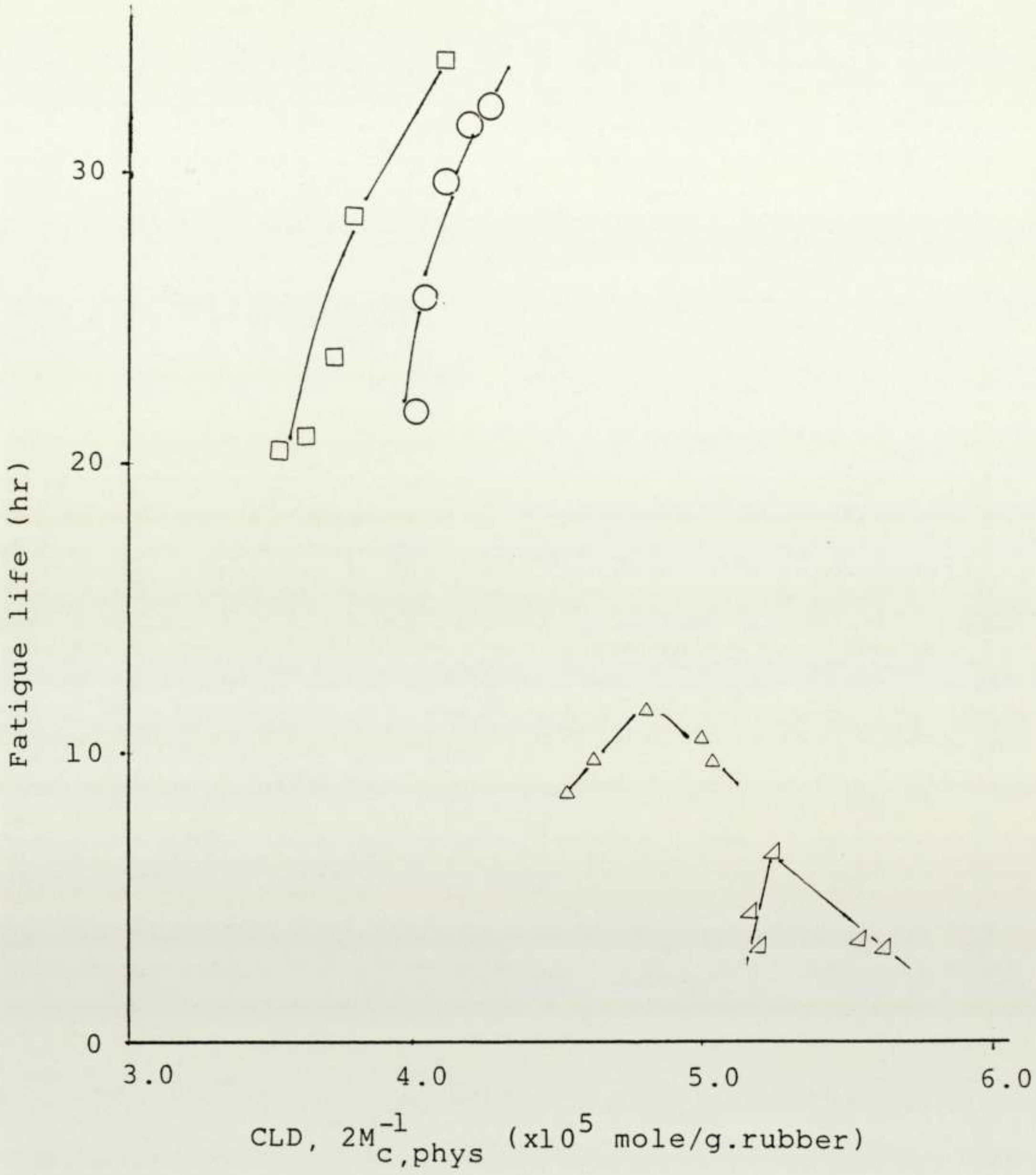


Figure 5.7 Plots of $2M_{c,phys}^{-1}$ against fatigue life for extracted rubber with DCP, 2 phr(○); 2.5 phr(△); 3 phr(◺); cured at 160°C and with ZnO, 5; Stearic acid, 3; CBS, 0.6; S, 2.5 phr(□); cured at 140°C

not be high enough to show the effect of reduction in capacity of segments of molecules to re-orientate during fatiguing, therefore reduction in fatigue resistance at high physical crosslink density was not observed.

5.6 Effect of Non-Rubber Constituents (NRC), Extra-Network Compounds (ENCS) Formed During Vulcanisation and Olive Oil on Fatigue Life

5.6.1 Effect of NRC on Fatigue Life

5.6.1.1 Procedure

To observe the effect of NRC on the fatigue life of vulcanisates, NRC used were obtained by evaporation of the extract derived from acetone extraction of SMR 10. NRC were mixed with rubber on a two-roll mill before adding DCP (for DCP vulcanisation system) and before adding sulphur (for conventional sulphur vulcanisation system). The fatigue lives of the vulcanisates were determined and the results are given in Table 5.4.

5.6.1.2 Results

The fatigue lives of vulcanisates containing NRC added as compounding ingredients are shown in Table 5.4. The results show that incorporation of NRC improves the fatigue lives of vulcanisates cured by DCP and conventional

Rubber used	Vulcanising system*	NRC (phr)	Cure time (min)	Rheometer torque (kg.m)	Fatigue life (hr)	
					Not ext. after cure	Ext. after cure
Unext.	2 phr DCP	0	60	3.36(max)	110	39
Ext.	2 phr DCP	0(control)	16	3.0	32	25
		0(control)	60	3.66(max)	26	23
		1.0	24	3.0	40.6	31.2
		1.0	60	3.66(max)	59.1	36.5
		1.5	21	3.0	78.1	56.9
		1.5	60	3.36(max)	105.4	37.5
Unext.	CBS-S	0	28	3.0(max)	37.1	20.5
Ext.	CBS-S	0(control)	20	3.0	24.8	24
		1.0	20	3.0(max)	25.2	20.5
		1.5	25	3.0(max)	39.6	28.1

* Base formulations (parts by weight) :Unext. or ext. rubber, 100; DCP, 2; cured at 160^{o}C. Unext. or ext. rubber, 100; ZnO, 5; Stearic acid, 3; CBS, 0.6; S, 2.5; cured at 140^{o}C.

Table 5.4 Fatigue life of DCP and conventional sulphur vulcanisates containing NRC sulphur systems, however, the effect is more pronounced for DCP than for conventional sulphur systems. The effect increases with NRC loading in both vulcanisates. It was noted that extracted rubber mixed with 1.5 phr of NRC produced vulcanisates with similar fatigue lives to those derived from unextracted rubber when they were cured to maximum rheometer torque. This effect was observed for both DCP and conventional sulphur vulcanisates. Extraction after cure lowered the fatigue life of vulcanisate, presumably through the removal of NRC.

5.6.1.3 Discussion

The experimental results indicate that NRC exhibit an anti-fatigue activity, although the reason or the detail of chemical species responsible for this effect is not yet known.

The composition of NRC present in dry rubber depends on the coagulation procedure used and in addition varies somewhat between clones, some high yielding types tending towards higher acetone extract and nitrogen (protein) content. Overall, typical analyses reveal acetone solubles 2.5-4.5%, nitrogen 0.3-0.5% and ash 0.2-0.6%(146). Fatty acids constitute the largest fraction of the acetone extract and it also contains esters of these acids(147). Ho et al(148) suggest that triglycerides are the principal constituents of the neutral lipids of the rubber phase;

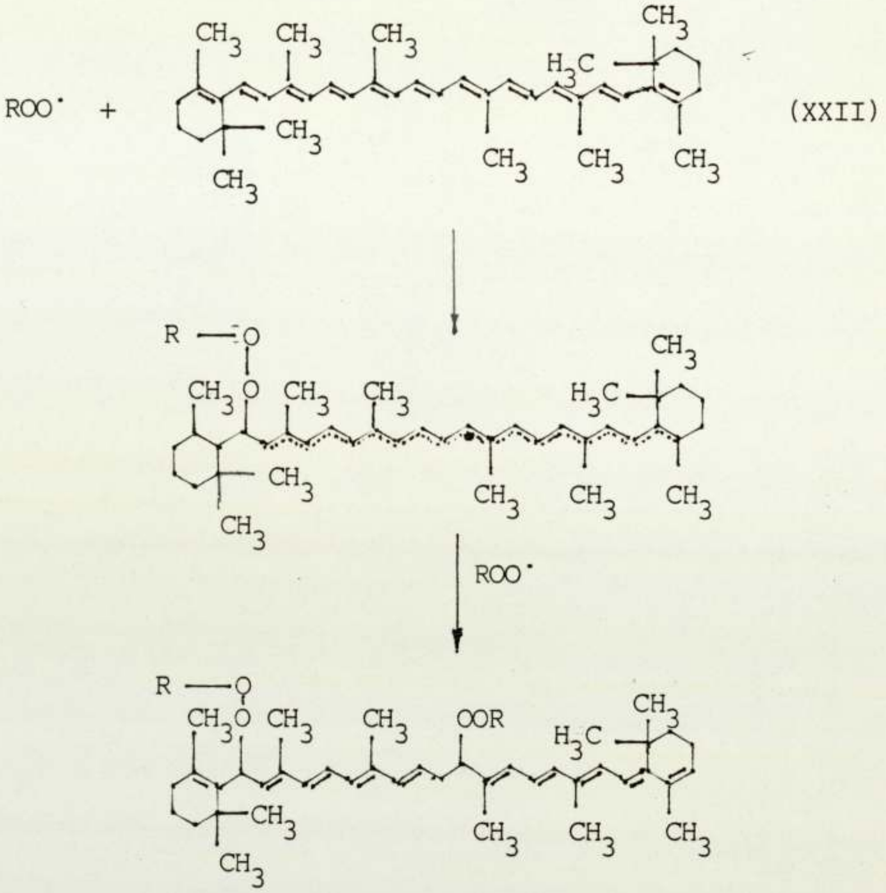
β-sitosterol and its isomers are also present in high concentration. The yellow colour of natural rubber is due to the presence of carotenoid pigments(149). Considering the composition of NRC present in natural rubber suggests that some of them may have an antifatigue activity by removing the alkyl radical or alkylperoxy radical formed during fatiguing.

According to Burton and Ingold(150), β-carotene (XXII) exhibits good radical-trapping antioxidant behaviour at the pressure of oxygen in air. They state that an inhibiting resonance-stabilised, carbon-centred radical is probably formed by the addition of $ROO^{\cdot}$ (and, perhaps also of an $R^{\cdot}$) radical to the conjugated system of β-carotene. Thus β-carotene present in natural rubber may act in this way during fatiguing and hence enhances fatigue resistance. The possible mechanism is shown in Scheme 5.1.

5.6.2 Effect of ENCS Formed During Vulcanisation on Fatigue Life

5.6.2.1 Procedure

The effect of ENCS formed during vulcanisation on fatigue lives of vulcanisates was investigated by two techniques. The first involved a DCP (1.5 phr) mix which was cured at



Scheme 5.1

160°C for 60 minutes. Fatigue test pieces cut from the vulcanisates were hot acetone extracted for 48 hours under continuous stream of nitrogen to remove ENCS of DCP vulcanisation and then dried under vacuum at 25°C. DCP and acetophenone were then swelled into the extracted samples. Various amounts of each compound in benzene (see Table 5.5) were prepared separately and extracted samples were placed each in different solutions under a continuous stream of nitrogen for 24 hours. The samples were then deswollen under vacuum at 25°C to constant weight and stored under vacuum before testing. The actual amounts of DCP and acetophenone present in the samples were determined by UV absorbance using the calibration curves (see Section 4.2.1).

The second involved DCP (2 phr) and conventional sulphur mixes which were cured at 160°C and 140°C respectively, for four different times in each case. Fatigue test pieces cut from each vulcanisate were cold extracted to remove ENCS. This was carried out by wrapping eight fatigue test pieces of each vulcanisate with aluminium foil and placing them in iso-octane. Samples cured by DCP and by conventional sulphur systems were immersed in iso-octane separately for 24 hours. The swollen samples were then dried under vacuum at 25°C to constant weight. The extracts containing ENCS were used for re-swelling the deswollen iso-octane extracted samples. This was carried out by re-swelling extracted samples (DCP) in the extract derived from conventional sulphur vulcanisates and vice versa, for 24 hours and drying under vacuum at 25°C to constant weight. The samples were then stored under vacuum before testing.

The fatigue lives of samples obtained by these two techniques were determined and compared to those of the controls, the results are given in Tables 5.5 and 5.6.

Compound	Concentration of solution (gm/100 ml benzene)	Compound present in sample (gm/100 gm rubber)	Fatigue life (hr)
Control*	-	-	58.8
DCP	0.0689	1.61	59.3
DCP	0.1795	4.53	63.9
DCP	0.2156	5.23	66.2
DCP	0.2300	5.85	63.5
Acetophenone	0.0950	0.45	75.2
Acetophenone	0.1985	0.84	74.9

* DCP (1.5 phr) vulcanisate acetone extracted after cure, fatigue life of vulcanisate unextracted after cure was 63.3 hours.

Table 5.5 Fatigue of DCP vulcanisates containing DCP and acetophenone by swelling technique.

Vulcanising system*	Cure time (min)	Fatigue life (hr)		
		Unext. after cure	Ext. after cure (control)	After swelling**
DCP (2 phr)	9	30.1	27.3	31.4
	14	31.5	28.2	32.5
	25	30.8	29.5	33.1
	60	29.3	27.2	29.8
Conventional sulphur	16	32.5	31.9	32.7
	20	27.6	23.1	23.5
	25	25.2	22.3	22.4
	36	22.4	20.7	21.8

* Base formulations (parts by weight): Ext.rubber,100;DCP,2;cured at 160°C. Ext.rubber,100;ZnO,5; CBS, 0.6; Stearic acid,3;S,2.5;cured at 140°C.

** DCP vulcanisates were swollen in extract derived from conventional sulphur vulcanisates and vice versa (see Section 5.6.2.1).

Table 5.6 Fatigue life of DCP and conventional sulphur vulcanisates containing ENCS by swelling technique

5.6.2.2 Results and Discussion

Table 5.5 shows the fatigue life of samples in which DCP and acetophenone were swelled by the first method described in Section 5.6.2.1. The results shown in Table 5.5 indicate that DCP or acetophenone present in a DCP vulcanisate enhances fatigue life. Although fatigue life decreases at the highest DCP or acetophenone concentration, it is still higher than the control. It thus appears that ENCS formed during DCP vulcanisation i.e., DCP and acetophenone do not have an adverse effect on fatigue life.

Table 5.6 shows the results obtained by the second method of incorporating ENCS into vulcanisates (see Section 5.6.2.1). The results show that, in almost every case, some increase in fatigue life occurs after the swelling technique as compared with the controls i.e., vulcanisates extracted after cure.

Both swelling techniques carried out in this experiment show that ENCS formed during DCP and conventional sulphur vulcanisations do not have an adverse effect on fatigue resistance as compared with the controls.

5.6.3 Effect of Olive Oil on Fatigue Life

5.6.3.1 Introduction

The results shown in Sections 5.6.1.2 and 5.6.2.2 indicate that NRC present in the original natural rubber and ENCS formed during DCP and conventional sulphur vulcanisation exhibit an antifatigue resistance of vulcanisates. It is therefore of interest to find out how these compounds behave during fatiguing of vulcanisates. NRC present in natural rubber are known to contain many chemical species including protein and lipids, this was discussed in Section 5.6.1.3. ENCS formed during vulcanisation of natural rubber by DCP contain α-cumyl alcohol, acetophenone and residual peroxide(32), and by conventional sulphur vulcanisation, residual vulcanising agents and their transformation products(5). It was decided therefore to incorporate some related compounds into the rubber by conventional compounding and observe the fatigue life of the vulcanisates so obtained. Olive oil was selected for this purpose as typical of the triglyceride lipid structure. The main components of olive oil are saturated (ca. 11.5%) and mono unsaturated e.g., XXIII (ca. 88.5%), fatty acids(151). Peroxide cured rubber was used to observe the effect of olive oil on fatigue resistance because of its simple crosslink structure.

$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ (XXIII)

Oleic acid

cis-9-octadecenoic acid

5.6.3.2 Procedure

Olive oil from Aldrich Co. was used as supplied. It was added gradually into rubber on a two-roll mill during compounding. Addition of a large quantity of oil at one time will cause difficulty in forming the band of rubber around the roll. DCP was added after the oil was mixed thoroughly into the rubber. The compounded rubber was then cured at 160°C for certain times to obtain the required torque. The fatigue lives of vulcanisates were determined and compared with the control, and the results are shown in Table 5.7.

	A (control)	B	C
Formulation:			
Extracted rubber	100	100	100
DCP	2	2	2
Olive Oil	-	2	4
Cure time at 160°C(min), (to obtain torque 3 kg.m)	35	27	32
Fatigue life (hr)	31.8	38.6	44.7

Table 5.7 Fatigue life of DCP vulcanisate containing olive oil

5.6.3.3 Results and Discussion

The results shown in Table 5.7 indicate that the incorporation of olive oil improves the fatigue life as compared with the control. The fatigue life of vulcanisates increases with increasing concentration of olive oil. This effect of olive oil on fatigue life is presumably due to its ability to act as a lubricant between the rubber chains. Such a process results in a decrease in stress concentration at individual sites in the vulcanisates and consequently an increased resistance to fatigue.

5.6.4 Conclusions

The experimental results reported in this work show that the NRC present in the original natural rubber, the ENCS formed during DCP and conventional sulphur vulcanisation and the olive oil, exhibit an anti-fatigue activity. Considering the effect of olive oil on fatigue lives of vulcanisates, this would suggest that some chemical species present in the non-rubber constituents and in the extra-network compounds may improve the fatigue resistance in the same way as olive oil does i.e., by lubricating between the rubber chains during fatiguing. A comparison between the effectiveness of olive oil (see Table 5.7) and NRC (see Table 5.4) on fatigue resistance indicates that NRC is more effective than olive oil. It thus leads to the conclusion that the lubrication ability of chemical species is only part of the reason for improving fatigue resistance. The major factor in improving fatigue resistance should be due to good radical-trap behaviour of β-carotene.

5.7 Properties of Vulcanisates Containing IPPD and Coagents

5.7.1 Procedure

The effect of IPPD on peroxide cure was discussed in Section 3.3.3 and the purpose of using coagents was given in Section 3.3.4.1.

An investigation into the fatigue life and tensile properties of DCP vulcanisate containing antifatigue agent, IPPD with and without coagent - trimethylol-propane-trimethacrylate (TMPTMA), triallyl cyanurate (TAC) was made with extracted rubber. IPPD or coagent was mixed before adding peroxide on two-roll mill (see Section 2.2.3.2). Mixing of IPPD in conventional sulphur system was described in Section 2.2.3.1. The fatigue life and tensile properties of gum stocks cured by DCP and conventional sulphur systems are shown in Tables 5.8 and 5.9. The black-filled stocks of DCP and conventional sulphur systems were made with unextracted rubber as the method described in Section 2.2.4 and the fatigue lives of black-filled vulcanisates are shown in Table 5.10.

5.7.2 Fatigue Life and Tensile Properties of DCP and Conventional Sulphur Vulcanisates Containing IPPD

5.7.2.1 Results

The fatigue life and tensile properties of DCP and conventional sulphur vulcanisates containing IPPD are shown in Table 5.8. Results demonstrate a similar effect of IPPD on the properties of DCP and conventional sulphur vulcanisates i.e., the higher the IPPD level, the lower is the M_{100} and tensile strength, but the higher is the elongation at break and fatigue life. However, the antioxidant improvement factor (I_F) relative to the control for the two vulcanisates is slightly different. At a low level of IPPD, I_F is similar for the two vulcanisates, but at a high level of IPPD, I_F for the DCP vulcanisate is higher than that for the conventional sulphur vulcanisate.

5.7.2.2 Discussion

The results shown in Table 5.8 indicate that the tensile properties and fatigue resistance of DCP vulcanisates are much more sensitive to the effect of IPPD than are the conventional sulphur vulcanisates. This is due to the fact that DCP vulcanisation results from free radical mechanism, thus IPPD, which is a radical scavenger in nature, inhibits the vulcanisation reaction and hence lowers the crosslink density. Both tensile properties

Vulcanising system*	IPPD (phr)	Cure time (min)	Rheometer torque (kg.m)	M_{100} (MPa)	T.S. (MPa)	E.B. (%)	Fatigue life	
							(hr)	I_F**
DCP	0(control)	16	3.0	2.42	8.61	380	32	-
	0.5	60	3.0	1.71	7.45	410	282	8.81
	1.0	60	2.13	1.09	6.75	450	589	18.41
CBS-S	0(control)	20	3.0	2.41	58.18	675	28	-
	0.5	23	3.0	2.18	57.98	680	242	8.64
	1.0	21	3.0	1.83	57.24	685	321	12.84

* Base formulations (parts by weight):extracted rubber,100:DCP,2;cured at 160°C;extracted rubber,100;ZnO,5; Stearic acid,3;CBS,0.6;S,2.5;cured at 140°C.

** Key to abbreviations: I_F antioxidant improvement factor - relative to the control. See also under Table 5.2.

Table 5.8 Fatigue life and tensile properties of DCP and conventional sulphur vulcanisates containing IPPD and fatigue resistance are dependent on crosslink density(81,152). The elongation at break decreases with increasing degree of crosslinking and the modulus is substantially proportional to the degree of crosslinking(22). The tensile strength and fatigue life pass through a maximum as the degree of crosslinking is increased(22).

5.7.3 Fatigue Life and Tensile Properties of DCP/IPPD/Coagent Vulcanisates

5.7.3.1 Results

The results obtained for the fatigue life and tensile properties of DCP/IPPD/coagent vulcanisates are given in Table 5.9. This indicates that in comparison with the control, TMPTMA increases M_{100} and tensile strength but decreases elongation at break and fatigue resistance. TAC improves elongation at break, however, it reduces M_{100}, tensile strength and fatigue resistance.

5.7.3.2 Discussion

The effects of coagents on tensile properties and fatigue resistance are probably through the effect on the degree

Coagent	IPPD	Rheometer torque (kg.m)	M_{100} (MPa)	T.S. (MPa)	E.B. (%)	Fatigue life (hr)
0(control)	0.5	3.0	1.71	7.45	410	282
0(control)	1.0	2.13	1.39	6.75	450	589
TMPTMA, 3.0	0.5	3.54	1.87	7.71	350	153
	1.0	3.24	1.57	6.78	360	162
	1.5	2.76	1.41	4.45	365	182
TAC, 2.0	0.5	2.55	1.59	4.74	500	280
	1.0	2.06	1.36	4.61	610	384
	1.5	1.46	0.98	4.59	800	-*

Key to abbreviations - see under Table 5.2 and Section 3.3.4.
* Too low modulus to get number flexing cycles when fatigued at 60% extension.

Table 5.9 Fatigue life and tensile properties of DCP (2 phr)/IPPD/coagent vulcanisates made with extracted rubber and cured at 160°C for 60 min of crosslinking. TMPTMA was found to compensate for the loss of crosslinking efficiency due to the radical scavenger but TAC was not, this was discussed in Section 3.3.4.3. The effects of degree of crosslinking on fatigue resistance and tensile properties were discussed in Sections 5.5.2.2 and 5.7.2.2.

5.7.4 Fatigue Life of Black-Filled Vulcanisates

5.7.4.1 Results and Discussion

Table 5.10 presents the fatigue resistance of black-filled vulcanisates for DCP and conventional sulphur systems cured to the same rheometer torque i.e., 3.24 kg.m. The results show that DCP vulcanisates containing 3 phr of DCP are less resistant to fatigue than are conventional sulphur vulcanisates. This characteristic is in agreement with both the controls and the vulcanisates containing IPPD. IPPD improves the fatigue resistance of both vulcanisates and the antioxidant improvement factor (I_F) for peroxide vulcanisates is higher than that for conventional sulphur vulcanisates. The low efficiency of IPPD on black-filled conventional sulphur vulcanisates is probably due to antagonistic effects of the polysulphides.

Vulcanising system*	IPPD (hr)	Fatigue life	
		(hr)	(I_F)**
DCP (3 phr)	0(control)	3	-
	0.5	32	10.67
	1.0	44	14.67
Conventional sulphur	0(control)	13	-
	0.5	80	6.15
	1.0	89	6.85

* Base formulations (parts by weight): Unextracted rubber,100;DCP,3; cured at 160°C. Unextracted rubber, 100;ZnO,5;Stearic acid,3; CBS,0.6;S,2.5;cured at 140°C.

** I_F antioxidant improvement factor relative to the control.

Table 5.10 Fatigue life of black-filled vulcanisates cured to the same rheometer torque (3.24 kg.m)

It may not involve any antagonistic effects in black-filled DCP vulcanisates and hence the efficiency of IPPD is high.

CHAPTER SIX

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

6.1 Conclusions

The investigations reported in this thesis focussed on the fatigue resistance of dicumyl peroxide (DCP) and conventional accelerated sulphur gum vulcanisates of natural rubber.

The cure characteristics and fatigue resistance of DCP vulcanisates were shown to depend very much on: (1) whether the rubber was acetone-extracted before vulcanisation and (2) on the concentration of peroxide. The results show that extraction of rubber before vulcanisation leads to an increase in maximum torque but to a reduction in scorch time and a marked reduction in fatigue resistance. An increase in the peroxide concentration caused an increase in maximum torque through the increase in physical crosslink density, but scorch time and fatigue resistance were reduced. A conventional accelerated sulphur vulcanisate was shown to be less sensitive to extraction so far as cure characteristics are concerned, but it did show a marked reduction in fatigue resistance. The effect of non-rubber constituents and extra-network compounds produced from these two vulcanising systems on fatigue life were investigated. The results lead to the conclusion that non-rubber constituents exhibit antifatigue activity. Extra-network compounds produced from DCP or conventional accelerated sulphur systems lead to improvement in fatigue resistance. Some of their effect may be by lubricating the rubber chains during fatiguing and hence reducing localised stresses. β-carotene present in natural rubber is likely the main chemical species responsible for improving fatigue resistance.

The present experimental results show that DCP vulcanisate containing DCP below 2 parts per hundred of rubber is more resistant to fatigue than is conventional accelerated sulphur vulcanisate when cured to the same rheometer torque. Surprisingly, conclusions from the present work are that vulcanisates of the same rheometer torque do not have the same tensile moduli.

An infra-red examination of a DCP vulcanisate showed that aromatic compounds, almost certainly derived from the cumyloxy radicals, are attached to the crosslinked polymer. The amount of aromatic compounds bound to the polymer is independent of DCP concentration, and amounts to $38\pm2\%$ of the DCP residues present in the unextracted vulcanisates.

Trimethylol propane trimethacrylate and triallyl cyanurate were used in order to compensate the lower modulus caused by the presence of IPPD in DCP vulcanisation. Only the first chemical was shown to satisfy this requirement, however, it showed an adverse effect on fatigue resistance.

6.2 Suggestions for Further Work

The fatigue resistance of DCP vulcanisate was improved by decreasing the peroxide loading and by using the natural rubber without extraction before and after vulcanisation. DCP vulcanisate showed better fatigue resistance than conventional accelerated sulphur vulcanisate did, this was observed only at the loading of DCP below 2 parts per hundred of rubber. Thus it would be of interest to study in more detail about the chemical species, which act as an anti-fatigue agent, of non-rubber constituents of the original natural rubber and extra-network compounds formed during DCP and conventional accelerated sulphur vulcanisation.

REFERENCES

<ins>REFERENCES</ins>

1. G.E.Broomfield,revised by G.M.Bristow,in "Rubber Technology and Manufacture,2nd Ed.,C.M.Blow,Ed.", Butterworth Scientific,London,1982,Ch.4.
2. S.T.Semegen,in "Rubber Technology,2nd Ed.,M.Morton, Ed.",Van Nostrand Reinhold Co.,1973,p.161.
3. H.L.Stephens,in Ibid.,p.28.
4. L.Bateman,et al,in "Chemistry and Physics of Rubber-like Substances,L.Bateman,Ed.",Maclaren and Sons Ltd., London,1963,Ch.15.
5. J.A.Brydson,Rubber Chemistry,Applied Science Publishers, London,1978,Ch.8.
6. T.D.Skinner,A.A.Watson,Rubber Age,<ins>99</ins>(11),76, and <ins>99</ins>(12),69,(1967).
7. M.Porter,NR Technol.,<ins>4</ins>,76,(1973).
8. E.J.Blackman,E.B.McCall,Rubber Chem.Tech.,<ins>43</ins>,651,(1970).
9. D.J.Elliott and B.K.Tidd,Annual Report of the Progress of Rubber Technology,<ins>36</ins>-<ins>37</ins>,83-107,(1973-1974).
10. N.J.Morrison and M.Porter,Rubber Chem.Tech.,<ins>57</ins>,63,(1984),
11. D.S.Campbell,J.Appl.Polym.Sci.,<ins>14</ins>,1409,(1970).
12. C.R.Parks,D.K.Parker,D.A.Chapman and W.L.Cox,Rubber Chem.Tech.,<ins>43</ins>,572,(1970).
13. C.R.Parks,D.K.Parker and D.A.Chapman,Ibid.,<ins>45</ins>,467,(1972).
14. A.Y.Coran,"Science and Technology of Rubber,F.R. Eirich,Ed.",Academic Press,New York,1978,Ch.7.
15. M.M.Coleman,J.R.Shelton and J.L.Koenig,Ind.Eng.Chem., Prod.Res.Develop.,<ins>13</ins>,154,(1974).

16. I.Field,"Organic Chemistry of Sulphur,S.Oae,Ed.", Plenum Press,New York,1977,Ch.3.

17. N.J.Morrison and M.Porter,Rubber Chem. Tech.,57,63, (1984).

18. Ref.4,

19. L.Bateman,J.I.Cunneen,C.G.Thomas,L.Mullins and A.G. Thomas,Ref.4,Ch.19.

20. F.P.Baldwin and G.Ver Strate,Rubber Chem.Tech.,45,709, (1972).

21. E.Southern,"Elastomers:Criteria for Engineering Design,C.Hepburn and R.J.W.Reynolds,Ed.",Applied Science Publishers,London,1979,Ch.16,p.287-294.

22. W.Hofmann,Vulcanisation and Vulcanising Agents, Maclaren and Sons Ltd.,London,1967,Ch.1.

23. S.H.Morrell,Ref.1,p.180-181.

24. L.P.Lenas,Ind.Eng.Chem.,Prod.Res.Develop.,2(3),202, (1963).

25. L.O.Amberg and A.E.Robinson,Rubber and Plastic Age, 42,875,(1961).

26. A.E.Robinson,J.V.Marra and L.O.Amberg,Ind.Eng.Chem., Prod.Res.Develop.,1(2),78,(1962).

27. M.Morton,"Developments in Polymerisation-3"R.N.Harward, Applied Science Publishers,London,and New Jersey,1982, p.207.

28. M.Braden,W.P.Fletcher,Trans.IRI.,31,No.6,1955,p.155-165.

29. M.Braden,W.P.Fletcher,G.P.McSweeney,Trans.,IRI.30, No.1,(1954),p.44-55.

30. L.M.Hobbs,R.G.Craig,C.M.Burkhart,Rubber World,136, 675,(1957).

31. C.H.Lufter,Rubber World,133,511,(1956).

32. L.M.Amberg,W.D.Willis,Proc.Int.Rubber Conf.,Washington, 1959,p.565.

33. L.D.Loan,Rubber Chem.Technol.,40,149,(1967).

34. C.G.Moore,W.F.Watson,J.Polym.Sci.,19,No.92,237,(1956).

35. C.R.Parks,O.Lorenz,Ibid.,50,287,(1961).

36. G.M.Bristow,J.Appl.Polym.Sci.,7,1023,(1963).

37. C.G.Moore,L.Mullins and P.McL.Swift,Ibid.,5,293,(1961).

38. G.M.Bristow,NR Technol.,7(3),61,(1976).

39. P.M.Lewis,"Developments in Polymer Stabilisation - 7,G.Scott,Ed.",Elsevier Applied Publishers,London and New York,1984,Ch.3.

40. Y.W.Chow,G.T.Knight,Proc.Int.Rubber Conf.,Brighton, IRI.,Vol.2,(1977),paper 24.

41. P.Kovacic and R.W.Hein,J.Am.Chem.Soc.,81,1187,(1959).

42. Ref.22,p.357.

43. J.E.Lohr,Rubber World,165,47,(Oct.1971).

44. D.Barnard,Proc.Rubber Res.Inst.Malaya,Planters Conf.,Kuala Lumpur,Malaysia,July 1973,p.483.

45. M.A.Wheelans,Proc.2nd.Annual Nat.Conf."Rubber Processing",1974,IRI.,London,p.37.

46. Ref.22,p.233.

47. A.G.Thomas,J.M.Wittle,Rubber Chem.Technol.,43,No.2, 222,(1970).

48. Ref.9,p.105.

49. P.J.Flory,"Principles of Polymer Chemistry",Cornell University Press,Ithaca,New York,1953.

50. A.N.Gent,"Science and Technology of Rubber,F.R. Eirich,Ed.",Academic Press,New York,1978,Ch.10.

51. J.D.Ferry,"Viscoelastic Properties of Polymers,2nd. Ed.",Wiley,New York,1970.

52. W.W.Graessley,Adv.Polymer Sci.,16,1,(1974).

53. J.Glazer and F.H.Cotton,"Applied Science of Rubber, W.J.S.Naunton Ed.",Edward Arnold(Publishers)Ltd., London,1961,Ch.12.

54. S.H.Morrell,Ref.1,Ch.5.

55. Ref.5,Ch.3 and 8.

56. P.J.Flory and J.Rehner,J.Chem.Phys.,11,512,(1943).

57. P.J.Flory,Ibid.,18,108,(1950).

58. L.Mullins,J.Appl.Polym.Sci.,2,1,(1959).

59. G.Gee,J.Polym.Sci.,2,451,(1947).

60. P.J.Flory,N.Rabjohn and M.C.Schaffer,Ibid.,4,435,(1949).

61. S.H.Morrell and J.Stern,Trans IRI,28,269,(1952).

62. Ref.4,Ch.10.

63. Ref.22,p.6.

64. W.Kauzman and H.Eyring,J.Am.Chem.Soc.,62,3113,(1940).

65. M.Pike and W.F.Watson,J.Polym.Sci.,9(3),229,(1952).

66. D.J.Angier and W.F.Watson,Trans,IRI.,33,(1),22,(1951).

67. D.J.Angier,E.D.Farlie and W.F.Watson,Ibid.,34(1),8, (1958).

68. Ye.V.Reztsova and G.V.Chubarova,Vysokomol Soyed 7, (8),(1965),1335,Translation,Polym.Sci.,USSR.,7,1481, (1965).

69. P.Yu.Butyagin,V.E.Drozdovskii,D.R.Razgon and I.V. Kolbanev,Fizika Tverd Tela 7,941(1965);Translation, Soviet Phys.-Solid State 7,(3),757,(1965).

70. J.R.Shelton,Rubber Chem.Tech.,45,359,(1972).

71. Y.Kamiya and E.Niki,"Aspect of Degradation and Stabilisation of Polymers,H.H.G.Jellinek,Ed.",Elsevier Scientific Publishers,Amsterdam,1978,Ch.3.

72. J.R.Shelton,"Developments in Polymer Stabilisation-4, G.Scott,Ed.",Applied Science Publishers,London and New York,1981,Ch.1 and Ch.2.

73. G.Scott,Atmospheric Oxidation and Antioxidant,Elsevier Scientific Publishers,London and New York,1965,p.466.

74. G.Scott,Brit.Polym.J.,15,208,(1983).

75. A.V.Tobolsky and A.Mercurio,J.Appl.Polym.Sci.,2,186, (1959).

76. A.V.Tobolsky,J.Appl.Phys.,27,(7),673,(1956).

77. G.Scott,Ref.72,Ch.1.

78. T.Colcough,J.I.Cunneen and G.M.C.Higgins,J.Appl.Polym. Sci.,12,295,(1968).

79. D.Barnard,M.E.Cain,J.I.Cunneen and T.H.Houseman,Rubber Chem.Tech.,45,381,(1972).

80. J.I.Cunneen,Rubber Chem.Tech.,41,182,(1968).

81. J.R.Beatty,Ibid.,37,1341,(1964).

82. A.S.Kuzminsky,Ref.72,p.73.

83. A.S.Kuzminsky,"The Ageing and Stabilisation of Polymers" Elsevier Scientific Publishers,Amsterdam,1971,p.48.

84. W.D.Potter and G.Scott,Europ.Polym.J.,7,489,(1971).

85. A.A.Katbab and G.Scott,Ibid,17,559,(1981).

86. W.F.Busse,Ind.Eng.Chem.,26,1194,(1934).

87. H.W.Greensmith,L.Mullins and A.G.Thomas,Ref.4,p.295.

88. A.N.Gent,J.Appl.Polym.Sci.,6,497,(1962).

89. A.Angioletti,Rubber Chem.Tech.,29,753,(1956).

90. C.S.L.Baker,NR Tech.,8(2),24,(1977).

91. J.C.Ambelang,"Vulcanisation of Elastomer,G.Alliger and I.J.Sjothun,Eds.",Reinhold Publishing Corp., 1964,p.126.

92. B.A.Dogadkin and Z.N.Tarasova,Rubber Chem.Tech.,27, 883,(1954).

93. G.J.Lake,Ibid,45,309,(1972).

94. W.L.Cox and C.R.Parks,Ibid.,39,785,(1966).

95. E.H.Farmer and C.G.Moore,J.Chem.Soc.,131,142,(1951).

96. Ref.22,p.17.

97. A.E.Juve and Jr.B.S.Gravey,Ind.Eng.Chem.,36,212,(1944).

98. Ref.73,p.473.

99. E.E.Auer,K.W.Doak and I.J.Schaffner,Rubber Chem.Tech., 31,185,(1958).

100. A.S.Kuzminsky,Ref.72,Ch.3,p.77.

101. J.R.Shelton,"Polymer Stabilisation,W.L.Hawkins,Ed.", Willy Interscience,New York,1972,Ch.2,p.31-42.

102. Ref.73,p.164-166.

103. D.M.Wiles and D.J.Carlsson,Polym.Deg.Stab.,3,61,(1981).

104. G.Scott,"Developments in Polymer Stabilisation-6, G.Scott,Ed.",Applied Science Publishers,London and New York,1983,Ch.2.

105. L.P.Nethsinghe and G.Scott,Rubber Chem.Tech.,57,918, (1984).

106. J.Lal,Ibid.,43,664,(1970).

107. A.Ogunbanjo and G.Scott,Europ.Polymer J.,21,No.6, 541,(1985).

108. M.S.S,Coker,G.Scott and H.A.A.Sweiss,Polym.Degrad. Stab.,4,33,(1982).

109. R.W.Wise,"Rubber Technology,2nd.Ed.,M.Morton,Ed.", Van Nostrand Reinhold Co.,1973,p.95.

110. Anon,Monsanto Rheometer 100 Operation and Service Manual.

111. A.Y.Coran,Rubber Chem.Tech.,37,689,(1964).

112. Ibid,38,1,(1965).

113. R.P.Brown,Physical Testing of Rubber,Applied Science Publishers,London,1979,p.59.

114. Anon,Monsanto Fatigue-to-Failure Tester Operation and Service Manual.

115. Anon,Tensometer Type E Instruction Manual.

116. J.R.Brydson,Rubber Chemistry,Applied Science Publishers,London,1978,p.199.

117. L.Mullins,J.Polym.Sci.,19,255,(1956).

118. G.A.Ihenyen,PhD Thesis,The University of Aston in Birmingham,1982.

119. A.Y.Coran,"Science and Technology of Rubber,F.R. Eirich,Ed.",Academic Press,New York,1978,Ch.7.

120. Ref.22,p.163,174.

121. S.P.Manix and S.Banerjee,Rubber Chem.Tech.,43,1311, (1970).

122. J.R.Wolfe,Ibid,41,1339,(1968).

123. J.R.Shelton and E.T.McDonel,Ibid,33,342,(1960).

124. Ref.1,p.325.

125. Ref.4,Ch.15.

126. E.H.Farmer and C.G.Moore,Rubber Chem.Tech.,24,777,(1951).

127. Ref.40.

128. N.C.Quinn,PhD Thesis,The University of Aston in Birmingham,1985.

129. G.M.Bristow,C.G.Moore and R.M.Russell,J.Polym.Sci., Part A,3,3893,(1965).

130. M.Porter,T.D.Skinner and M.A.Wheelans,J.Appl.Polym. Sci.,11,2271,(1967).

131. N.Sheppard and G.M.M.B.Sutherland,Rubber Chem.Tech., 9,67,(1946).

132. F.J.Linnig and J.E.Stewart,Ibid.,31,719,(1958).

133. E.C.Gregg,J.R. and J.H.Macey,Ibid.,46,47,(1973).

134. G.W.Ewing,Instrumental Methods of Chemical Analysis, 3rd.Ed.,McGraw-Hill Book Co.,(1969),p.137.

135. C.G.Creswell,Spectral Analysis of Organic Compounds, 2nd.Ed.,Longman,(1972),p.72.

136. D.K.Thomas,J.Appl.Polym.Sci.,6,No.24,613,(1962).

137. Ref.22,p.21.

138. Ref.4,Ch.19.

139. A.S.Kuzminsky and L.I.Lyubchanskaya,Rubber Chem.Tech., 29,770,(1956).

140. J.C.Ambelang,"Vulcanisation of Elastomers,G.Alliger and I.J.Sjiothun,Eds.",Reinhold Publishing Corp., (1964),p.126.

141. B.Dogadkin and Z.Tarasova,Rubber Chem.Tech.,26,759,(1953).

142. Ref.108.

143. Ref.107.

144. J.R.Beatty,Rubber Chem.Tech.,37,1341,(1964).

145. Ref.73,p.474.

146. Ref.1.

147. Le.Bras,Rubber:Fundamentals of Its Science and Technology,Chemical Publishing Co.,Inc.,New York,(1957),Ch.5.

148. C.C.Ho,A.Subramaniam and W.M.Yong,Proc.Int.Rubber Conf.,Kuala Lumpur,1975,p.441.

149. Ref.4,Ch.3.

150. G.W.Burton and K.U.Ingold,Science,224,569,(1984).

151. Kirt-Othmer,Encyclopedia of Chemical Technology,3rd. Ed.,John Wiley and Sons,New York,(1978).

152. Ref.4,Ch.10.