A STUDY OF THERMAL OXIDATIVE AGEING IN NATURAL RUBBER (NR)

VORAPONG PIMOLSIRIPHOL

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF SCIENCE
(POLYMER SCIENCE AND TECHNOLOGY)
FACULTY OF GRADUATE STUDIES
MAHIDOL UNIVERSITY
2005

ISBN 974-04-6273-1

COPYRIGHT OF MAHIDOL UNIVERSITY

Copyright by Mahidol University

Thesis
Entitled

A STUDY OF THERMAL OXIDATIVE AGEING IN NATURAL RUBBER (NR)

Vorapong Pimolsiriphol
Mr. Vorapong Pimolsiriphol
Candidate

.....
Assoc. Prof. Chakrit Sirisinha,
Ph.D. (Rubber Engineering)
Major-Advisor

.....
Assoc. Prof. Pranee Phinyocheep,
Doctorat de l' Universite' du Maine
Co-Advisor

.....
Mr. Pongdhorn Sae-Oui,
Ph.D. (Rubber Engineering)
Co-Advisor

.....
Assoc. Prof. Rassmidara Hoonsawat,
Ph.D.
Dean
Faculty of Graduate Studies

.....
Assoc. Prof. Taweechai Amornsakchai,
Ph.D. (Polymer Physics)
Chair
Master of Science Programme
in Polymer Science and Technology
Faculty of Science

Copyright by Mahidol University

Thesis
Entitled

A STUDY OF THERMAL OXIDATIVE AGEING IN NATURAL RUBBER (NR)

was submitted to the Faculty of Graduate Studies, Mahidol University
For the degree of Master of Science (Polymer Science and Technology)

On

3 June, 2005

Vorapong Pimolsiriphol
Mr. Vorapong Pimolsiriphol
Candidate

Assoc. Prof. Chakrit Sirisinha, Ph.D. (Rubber Engineering)
Chair

Pranee Phinyocheep
Assoc. Prof. Pranee Phinyocheep, Doctorat de l' Universite' du Maine
Member

Jatuphorn
Asst. Prof. Jatuphorn Wootthikanokkhan, Ph.D.
Member

Pongdhorn Saeoui
Mr. Pongdhorn Sae-Oui, Ph.D. (Rubber Engineering)
Member

Assoc. Prof. Rassmidara Hoonsawat, Ph.D.
Dean
Faculty of Graduate Studies
Mahidol University

Prof. Amaret Bhumiratana, Ph.D.
Dean
Faculty of Science
Mahidol University

Copyright by Mahidol University

ACKNOWLEDGEMENTS

This research project would not have been completed, succeeded without the extensive support and assistance from my major advisor, Assoc. Prof. Chakrit Sirisinha and my co-advisor, Assoc. Prof. Pranee Pinyocheep, Asst. Prof. Jatuphorn Wootthikanokkhan and Dr. Pongdhorn Sae-oui. I deeply thank them for their valuable advice and guidance throughout this research.

For the cooperation, I would like to thank Department of Chemistry, Faculty of Science, Mahidol University for the use of brabender rheomix, rubber process analyser, compression moulding machine, tensile tester, hot-air oven, dynamic mechanical thermal analyser, thermogravimetric analyser and fourier transform infrared spectroscope.

I wish to thank my friends, polymer graduate students and staffs of Polymer Science and Technology Program in Department of Chemistry, Faculty of Science, Mahidol University for their support and encouragement.

Finally, I would like to thank my lovely family and my parents, who always stand beside me during the difficult time and give me continuous support, for their love, inspiration, and endless encouragement throughout this entire study.

Vorapong Pimolsiriphol

Copyright by Mahidol University

A STUDY OF THERMAL OXIDATIVE AGEING IN NATURAL RUBBER (NR)

VORAPONG PIMOLSIRIPHOL 4536704 SCPO/M

M.Sc. (POLYMER SCIENCE AND TECHNOLOGY)

THESIS ADVISORS: CHAKRIT SIRISINHA, Ph.D. (RUBBER ENGINEERING), PRANEE PHINYOCHEEP, DOCTORAT DE L′ UNIVERSITE′ DU MAINE (POLYMER CHEMISTRY), PONGDHORN SAE-OUI, Ph.D. (RUBBER ENGINEERING)

ABSTRACT

Natural rubber (NR) has particularly been recognised in terms of its high green strength, low-temperature crystallisation and low hysteresis. However, NR has a main limitation in terms of poor thermal, oil and chemical resistances. A process known as vulcanisation, i.e., peroxide and sulphur, associated with the appropriate compounding ingredients can improve these negative properties of NR. Nevertheless, when sulphur-cured NR compounds are exposed to a thermal oxidative ageing environment, significant changes in physical and dynamic mechanical properties are observed. To overcome this problem, some compounding ingredients, e.g., antioxidants and reinforcing fillers are added to rubber mixes. Therefore, this study aims to investigate the influences of thermal oxidative ageing conditions and compounding ingredients on the ageing properties of sulphur-cured NR vulcanisates.

Results obtained from the part of the effect of ageing conditions show that types of curing systems (conventional vulcanisation, CV, and efficient vulcanisation, EV) and thermal oxidative ageing conditions (ageing temperature and time) affect the change of crosslink density, which strongly controls the ageing properties of NR vulcanisates. The thermal oxidative ageing dominantly causes the post-curing and chain-scission for CV and EV systems, respectively.

The second part focuses mainly on the antioxidant effect on ageing properties of NR vulcanisates. The results illustrate that the ageing properties of vulcanisates cured with a CV system depend strongly on types of antioxidants. By contrast, those cured with an EV system is independent of types of antioxidant.

Finally, the effect of reinforcing fillers (e.g., precipitated silica and carbon black) on ageing properties of NR vulcanisates was investigated. The results demonstrate that carbon black accelerates the curing process while precipitated silica retards cure. The ageing properties of carbon black filled-vulcanisates are independent of grade of carbon black.

KEY WORDS: NATURAL RUBBER / THERMAL OXIDATIVE AGEING / POST-CURING / CHAIN-SCISSION

108 P. ISBN 974-04-6273-1

Copyright by Mahidol University

การศึกษาการเสื่อมสภาพของยางธรรมชาติ(ที่เชื่อมโยงด้วยพันธะซัลเฟอร์)ภายใต้การบ่มเร่งด้วยความร้อน
(A STUDY OF THERMAL OXIDATIVE AGEING IN NATURAL RUBBER (NR))

วรพงษ์ พิมลศิริผล 4536704 SCPO/M

วท.ม. (วิทยาศาสตร์และเทคโนโลยีพอเมอร์)

คณะกรรมการควบคุมวิทยานิพนธ์ : ชาคริต สิริสิงห, Ph.D. (RUBBER ENGINEERING), ปราณี ภิญโญชีพ, DOCTORAT DE L′ UNIVERSITE′ DU MAINE (POLYMER CHEMISTRY), พงษ์ธร แซ่อุย Ph.D. (RUBBER ENGINEERING)

บทคัดย่อ

โดยปกติแล้วการนำยางธรรมชาติไปผ่านกระบวนการทำให้สุกด้วยซัลเฟอร์จะช่วยปรับปรุงสมบัติของยางธรรมชาติได้ อย่างไรก็ตามถึงแม้จะนำยางธรรมชาติไปผ่านกระบวนการทำให้สุกด้วยซัลเฟอร์แต่ยางผลิตภัณฑ์ที่ได้ยังไม่สามารถนำไปใช้งานภายใต้ความร้อนได้อย่างมีประสิทธิภาพ ดังนั้นงานวิจัยนี้จึงสนใจที่จะทำการศึกษาอิทธิพลของสารเคมีที่ใช้ในการผสมยางและสภาวะการใช้งานภายใต้การบ่มเร่งด้วยความร้อนต่อสมบัติของยางธรรมชาติที่ผ่านกระบวนการทำให้ยางสุกด้วยระบบซัลเฟอร์

ผลการทดลองในส่วนแรกพบว่า สมบัติของยางธรรมชาติที่ผ่านกระบวนการทำให้สุกด้วยระบบซัลเฟอร์จะขึ้นอยู่กับระบบที่ใช้ในการทำให้ยางสุกและสภาวะการบ่มเร่งด้วยความร้อน นอกจากนี้ยังพบว่าสมบัติของยางผลิตภัณฑ์ที่ได้จะขึ้นอยู่กับปริมาณการเชื่อมโยงของสายโซ่ของยางธรรมชาติที่เปลี่ยนแปลงขณะที่ยางธรรมชาติอยู่ภายใต้การบ่มเร่งดังกล่าว

ในการศึกษาส่วนที่สองเป็นการศึกษาอิทธิพลของสารยับยั้งการเสื่อมสภาพของพอลิเมอร์ต่อสมบัติของยางผลิตภัณฑ์ที่ผ่านการทำให้สุกด้วยระบบซัลเฟอร์ภายใต้การบ่มเร่งด้วยความร้อน ซึ่งจากผลการทดลองพบว่าสมบัติของยางธรรมชาติที่ผ่านกระบวนการทำให้ยางสุกด้วยระบบการคงรูปแบบดั้งเดิม (CV) ขึ้นอยู่กับชนิดของสารยับยั้งการเสื่อมสภาพของพอลิเมอร์ ขณะที่พบว่าสมบัติของยางธรรมชาติที่ผ่านกระบวนการทำให้ยางสุกด้วยระบบการ ไม่ขึ้นคงรูปแบบประสิทธิภาพ (EV) อยู่กับชนิดของสารยับยั้งการเสื่อมสภาพของพอลิเมอร์

ในส่วนสุดท้ายเป็นการศึกษาอิทธิพลของสารเสริมแรง (ซิลิกาและเขม่าดำ) ต่อสมบัติของของยางธรรมชาติที่ผ่านการทำให้สุกด้วยระบบซัลเฟอร์ภายใต้การบ่มเร่งด้วยความร้อน จากผลจากทดลองพบว่าเขม่าดำช่วยเร่งการเชื่อมโยงสายโซ่ยางธรรมชาติขณะที่ซิลิกาขัดขวางการเชื่อมโยงสายโซ่ยางธรรมชาติ นอกจากนี้ยังพบว่าสมบัติหลังผ่านการบ่มเร่งด้วยความร้อนดังกล่าวไม่ขึ้นกับชนิดของเขม่าดำ

108 หน้า ISBN 974-04-6273-1

Copyright by Mahidol University

CONTENTS

		Page
ACKNOWNLEDGEMENTS……		iii
ABSTRACT (in English)……....		iv
ABSTRACT (in Thai)……		v
LIST OF TABLES…….		ix
LIST OF FIGURES……...		xiv
LIST OF ABBREVIATIONS……...		xviii
CHAPTER		
1	**INTRODUCTION**……..	1
2	**OBJECTIVES**……..	3
3	**LITERATURE REVIEW**……..	5
	3.1 Natural rubber (NR)……	5
	3.1.1 Historical of NR……..	5
	3.1.2 Properties of NR……..	6
	3.1.3 Applications of NR……..	6
	3.2 Compounding of NR…….……..	6
	3.2.1 Activators…….	7
	3.2.2 Accelerators…….	7
	3.2.3 Antidegradants…….	8
	3.2.4 Reinforcing fillers…….…...	8
	3.2.5 Organic peroxides……	8
	3.2.6 Retarders and prevulcanisation inhibitors…...	9
	3.3 Vulcanisation……...	10
	3.3.1 Vulcanisation systems……..	11
	3.3.2 Peroxide vulcanisation…….	11
	3.3.3 Sulphur vulcanisation…….….	13

Copyright by Mahidol University

CONTENTS (Continued)

		Page
	3.2.4 Effect of crosslink density on properties of NR vulcanisates…… …….	16
	3.4 Rubber degradation……	17
	3.4.1 General approach for NR…….…….	17
	3.4.2 Oxidation of peroxide-cured vulcanisates by hydroperoxide……	18
	3.4.3 Oxidation of sulphur-cured vulcanisates by hydroperoxide……..…	20
	3.4.4 Oxidation of sulphides by oxygen…….	21
	3.4.5 Oxidative crosslinking in sulphur vulcanisates…….….....	22
	3.5 Protection against oxidative ageing……	24
4	**MATERIAL AND METHODS**…….	25
	4.1 Materials…….	25
	4.2 Apparatus……	26
	4.3 Mixing procedures and vulcanisation……	27
	4.4 Compound formulation……..	28
	4.5 Mechanical property measurement of vulcanisates…...	29
	4.5.1 Tensile properties……	29
	4.5.2 Dynamic mechanical properties…….	30
	4.5.3 Aging properties…….	30
	4.5.3.1 Aging temperature…….....	30
	4.5.3.2 Aging time……	30
	4.6 Determination of crosslink density…….	31
5	**RESULTS AND DISCUSSION**…….	33
	5.1 Effects of ageing temperature and time on properties of NR vulcanisates……..	33

Copyright by Mahidol University

CONTENTS (Continued)

	Page
5.1.1 Effect of ageing temperature on properties of NR vulcanisates……..	34
5.1.2 Effect of ageing time on properties of NR vulcanisates……	40
5.2 Effect of antioxidant on ageing properties of NR vulcanisates……	45
5.2.1 Effect of types of antioxidant…….	45
5.2.2 Effect of antioxidant concentration……	58
5.3 Effect of reinforcing fillers on ageing properties of NR vulcanisates…….	67
6 CONCLUSIONS…….	84
REFERENCES……	86
APPENDIX……..	91
BIOGRAPHY……..	108

Copyright by Mahidol University

LIST OF TABLES

Table		Page
3.1	Classification of accelerator groups and their relative curing speeds……....	7
3.2	Major commercial organic peroxides……	9
3.3	Advantages and disadvantages of the peroxide crosslinking……	11
3.4	Ratios of accelerator to sulphur for accelerated sulphur vulcanisation……....	14
4.1	Materials used in the present study……..	25
4.2	List of apparatus used in the present study……...	26
4.3	Mixing procedure used in the study……..	27
4.4	Compounding formulation used in the study of ageing condition effect…	28
4.5	Compounding formulation used in the study of antioxidant effect……....	28
4.6	Compounding formulation used in the study of reinforcing filler effect…	29
5.1	Sulphur versus peroxides bond strength……...	41
5.2	Sample codename of specimens used in the study of antioxidant effect..	46
5.3	Structure and reactivity of antioxidants used in the study…….	49
5.4	Effects of types and filler loading and ageing time on tensile strength of the vulcanisates cured with CV system……	68
5.5	Effects of types and filler loading and ageing time on M_c of the vulcanisates cured with CV system…….	70
5.6	Effects of types and filler loading and ageing time on M100 of the vulcanisates cured with CV system…….	72
5.7	Effects of types and filler loading and ageing time on E′ at 15^{o}C of the vulcanisates cured with CV system……	73
5.8	Effects of types and filler loading and ageing time on $\tan\delta_{max}$ of the vulcanisates cured with CV system……..	74

Copyright by Mahidol University

LIST OF TABLES (Continued)

Table		Page
5.9	Effects of types and filler loading and ageing time on tensile strength of the vulcanisates cured with EV system……..	76
5.10	Effects of types and loading and ageing time on M_c of the vulcanisates cured with EV system…….	78
5.10	Effects of types and loading and ageing time on M100 of the vulcanisates cured with EV system…….	80
5.12	Effects of types and filler loading and ageing time on E′ at 15^{o}C of the vulcanisates cured with CV system……	81
5.13	Effects of types and filler loading and ageing time on tanδ_{max} of the vulcanisates cured with EV system……	82
A1	Tensile strength of NR vulcanisates after thermal oxidative ageing at various temperatures……..	92
A2	%swelling of NR vulcanisates after thermal oxidative ageing at various temperatures……...	92
A3	M100 of NR vulcanisates after thermal oxidative ageing at various temperatures……	93
A4	E' at 15^{o}C of NR vulcanisates after thermal oxidative ageing at various temperatures……..	93
A5	tanδ_{max} of NR vulcanisates after thermal oxidative ageing at various temperatures…….	94
A6	Tensile strength of NR vulcanisates after thermal oxidative ageing at various times…….	94
A7	%swelling of NR vulcanisates after thermal oxidative ageing at various times…….	95
A8	M100 of NR vulcanisates after thermal oxidative ageing at various times……..	95

Copyright by Mahidol University

LIST OF TABLES (Continued)

Table		Page
A9	E' at 15^{o}C of NR vulcanisates after thermal oxidative ageing at various times…….	96
A10	tanδ_{max} of NR vulcanisates after thermal oxidative ageing at various times……..	96
B1	Sample codename of specimens used in the study of antioxidant effect……..	97
B2	Tensile strength of vulcanisates cured with CV system filled with various antioxidants after thermal oxidative ageing at various temperatures……..	98
B3	%swelling of NR vulcanisates cured with CV system filled with various antioxidants after thermal oxidative ageing at various temperatures……..	98
B4	M100 of vulcanisates cured with CV system filled with various antioxidants after thermal oxidative ageing at various temperatures	99
B5	E' at 15^{o}C of vulcanisates cured with CV system filled with various antioxidants after thermal oxidative ageing at various temperatures……..	99
B6	tanδ_{max} of vulcanisates cured with CV system filled with various antioxidants after thermal oxidative ageing at various temperatures……..	100
B7	Tensile strength of vulcanisates cured with EV system filled with various antioxidants after thermal oxidative ageing at various temperatures……..	100
B8	%swelling of vulcanisates cured with EV system filled with various antioxidants after thermal oxidative ageing at various temperatures……..	101

Copyright by Mahidol University

LIST OF TABLES (Continued)

Table		Page
B9	M100 of vulcanisates cured with EV system filled with various antioxidants after thermal oxidative ageing at various temperatures…….	101
B10	E' at 15^{o}C of vulcanisates cured with EV system filled with various antioxidants after thermal oxidative ageing at various temperatures……..	102
B11	tanδ_{max} of vulcanisates cured with EV system filled with various antioxidants after thermal oxidative ageing at various temperatures	102
B12	Tensile strength of aged NR vulcanisates cured with CV system at various 6-PPD concentration after thermal oxidative ageing at various temperatures……...	103
B13	%swelling of aged NR vulcanisates cured with CV system at various 6-PPD concentration after thermal oxidative ageing at various temperatures…….	103
B14	M100 of aged NR vulcanisates cured with CV system at various 6-PPD concentration after thermal oxidative ageing at various temperatures…….	104
B15	E' at 15^{o}C of aged NR vulcanisates cured with CV system at various 6-PPD concentration after thermal oxidative ageing at various temperatures…….	104
B16	tanδ_{max} of aged NR vulcanisates cured with CV system at various 6-PPD concentration after thermal oxidative ageing at various temperatures…….	105
B17	Tensile strength of aged NR vulcanisates cured with EV system at various 6-PPD concentration after thermal oxidative ageing at various temperatures…….	105

Copyright by Mahidol University

LIST OF TABLES (Continued)

Table		Page
B18	%swelling of aged NR vulcanisates cured with EV system at various 6-PPD concentration after thermal oxidative ageing at various temperatures…….	106
B19	M100 of aged NR vulcanisates cured with EV system at various 6-PPD concentration after thermal oxidative ageing at various temperatures…….	106
B20	E' at 15^{o}C of aged NR vulcanisates cured with EV system at various 6-PPD concentration after thermal oxidative ageing at various temperatures…….	107
B21	tanδ_{max} of aged NR vulcanisates cured with EV system at various 6-PPD concentration after thermal oxidative ageing at various temperatures…….	107

Copyright by Mahidol University

LIST OF FIGURES

Figure		Page
1.1	Chemical structure of NR……	1, 5
3.2	Effect of acid retarder and PVI on state-of-cure: curve A: without acid retarder and PVI; curve B: with PVI; curve C: with acid retarder…….	10
3.3	Polymer chains in unvulcanised and vulcanised rubber; the crosslinks are indicated by bullets…….	11
3.4	Peroxide crosslinking mechanism of elastomers (P-H)……...	12
3.5	Different types of sulphur crosslinks between elastomer chain; x = 2-30; Ac = accelerator fragment……	13
3.6	Mechanism of sulphur vulcanisation; R = rubber chain, H = allylic proton and X = accelerator residue……	15
3.7	Relationship between crosslink density and vulcanisate properties	16
3.8	Oxidation mechanism of NR……...	18
3.9	The oxidation of peroxide-cured vulcanisates by hydroperoxide…	19
3.10	Oxidation of monosulphides by hydroperoxide……	20
3.11	Crosslink scission of monosulphides by oxygen…….	22
4.1	Dimensions of the tensile specimen…….	29
5.1	Effect of ageing temperature on tensile strength of NR cured with CV and EV systems……..	34
5.2	Effect of ageing temperature on %swelling of NR cured with CV and EV systems…….	35
5.3	Sketch of relationship between crosslink density and tensile strength properties…….	36
5.4	Effect of ageing temperature on modulus at 100% elongation (M100) of NR cured with CV and EV systems…….	37

Copyright by Mahidol University

LIST OF FIGURES (Continued)

Figure		Page
5.5	Effect of ageing temperature on E' at 15^{o}C of NR cured with CV and EV systems…….	38
5.6	Effect of ageing temperature on tanδ_{max} of NR cured with CV and EV systems……	39
5.7	Effect of ageing time on tensile strength of NR cured with CV and EV systems……	41
5.8	Effect of ageing time on %swelling of NR cured with CV and EV systems……	41
5.9	Effect of ageing time on M100 of NR cured with CV and EV systems…….	42
5.10	Effect of ageing time on E' at 15^{o}C of NR cured with CV and EV systems……	43
5.11	Effect of ageing time on tanδ_{max} of NR cured with CV and EV systems…….	43
5.12	Effect of ageing temperature on tensile strength of NR vulcanisates cured with CV system filled with various antioxidants……	47
5.13	Effect of ageing temperature on %swelling of NR vulcanisates cured with CV system filled with various antioxidants……...	48
5.14	Effect of ageing temperature on M100 of NR vulcanisates cured with CV system filled with various antioxidants……	50
5.15	Effect of ageing temperature on E’ at 15^{o}C of NR vulcanisates cured with CV system filled with various antioxidants……	51
5.16	Effect of ageing temperature on tanδ_{max} of NR vulcanisates cured with CV system filled with various antioxidants……	52
5.17	Effect of ageing temperature on tensile properties of NR vulcanisates cured with EV system filled with various antioxidants……..	53

Copyright by Mahidol University

LIST OF FIGURES (Continued)

Figure **Page**

5.18 Effect of ageing temperature on %swelling of NR vulcanisates cured with EV system with various antioxidants……. 54

5.19 Effect of ageing temperature on M100 of NR vulcanisates cured with EV system filled with various antioxidants……. 55

5.20 Effect of ageing temperature on E' at 15^{o}C of NR vulcanisates cured with EV system filled with various antioxidants……. 55

5.21 Effect of ageing temperature on tanδ_{max} of NR vulcanisates cured with EV system filed with various antioxidants…….. 56

5.22 Effect of 6-PPD concentration on tensile strength of aged NR vulcanisates cured with CV system…… 58

5.23 Effect of 6-PPD concentration on %swelling of aged NR vulcanisates cured with CV system……. 59

5.24 Effect of 6-PPD concentration on M100 of aged NR vulcanisates cured with CV system…….. 60

5.25 Effect of 6-PPD concentration on E' at 15^{o}C of aged NR vulcanisates cured with CV system and antioxidants……... 61

5.26 Effect of 6-PPD concentration on tanδ_{max} of aged NR vulcanisates cured with CV system…….. 62

5.27 Effect of 6-PPD concentration on tensile strength of aged NR vulcanisates cured with EV system…….. 63

5.28 Effect of 6-PPD concentration on %swelling of aged NR vulcanisates cured with EV system…… 64

5.29 Effect of 6-PPD concentration on M100 of aged NR vulcanisates cured with EV system…… 64

5.30 Effect of 6-PPD concentration on E' at 15^{o}C of aged NR vulcanisates cured with EV system…… 65

Copyright by Mahidol University

LIST OF FIGURES (Continued)

Figure **Page**

5.31 Effect of 6-PPD concentration on $tan\delta_{max}$ of aged NR vulcanisates cured with EV system and antioxidants…… 66

5.32 Idealised form of a typical elastic modulus curve……. 69

Copyright by Mahidol University

LIST OF ABBREVIATIONS

NR	=	Natural rubber
IR	=	Isoprene rubber
SBR	=	Styrene butadiene rubber
BR	=	Butadiene rubber
IIR	=	Isobutylene isoprene rubber
NBR	=	Acrylonitrile butadiene rubber
EPDM	=	Ethylene propylene diene rubber
T_g	=	Glass transition temperature
G' or E'	=	Storage modulus
tanδ	=	Tangent of phase lag or hysteresis factor
δ	=	Phase lag
t_{c90}	=	cure time to achieve 90% complete cure
M_c	=	Molecular weight between crosslink
M100	=	Modulus at 100% elongation
CV	=	Conventional vulcanisation system
EV	=	Efficient vulcanisation system
Semi-EV	=	Semi-efficient vulcanisation system
DRC	=	Dry rubber content
ZnO	=	Zinc oxide
PVI	=	Prevulcanisation inhibitors
TBBS	=	N-tert-Butyl-2-Benzothiazole sulfenamide
TMQ	=	2, 2, 4-Trimethyl-1, 2-Hydroquinoline
6-PPD	=	N-(1, 3-Dimethylbutyl)-N'-Phenyl-P-Phenylenediamine
BHT	=	2, 6-di-tert-butyl-4-methylphenol
GPC	=	Gel permeable chromatography
RPA	=	Rubber process analyser

Copyright by Mahidol University

LIST OF ABBREVIATIONS (Continued)

DMTA	=	Dynamic mechanical thermal analysis
UV	=	Ultraviolet light

Copyright by Mahidol University

CHAPTER 1
INTRODUCTION

Natural rubber (NR) is produced from the milky secretion (latex) of various plants, but the only important commercial of the world natural source of rubber is the rubber from *Hevea brasiliensis*. The major component of NR is polyisoprene, consisting of isoprene units in a two trans-1,4 and a long sequence of *cis*-1,4 configurations [1], as shown in Figure 1.1.

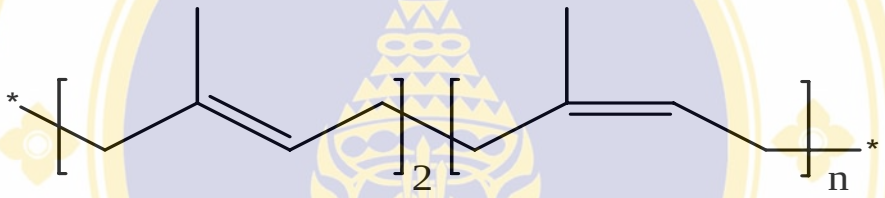


Figure 1.1 Chemical structure of NR [2]

Nowadays, NR has particularly been recognised in terms of its high green strength, low-temperature crystallisation and non-rubber components [3]. NR is still of great technical importance for the rubber industry, although there are many attempts to replace NR with some synthetic polymers. The main reason is, of course, the superior basic properties of NR, particularly the mechanical properties. However, NR has the main limitation in terms of its poor thermal, oil and chemical resistances. Oxidative thermal ageing of NR is a very serious problem in applications of NR since the oxidation of NR leads to chain scission, crosslinking, or formation of oxygen containing functional groups in polymer chains or their degradation products, resulting in severe changes of properties [4]. A process known as a vulcanisation associated with the appropriate compounding ingredients can remarkably improve these negative properties of NR.

Generally, elastomeric materials cannot be used without the chemical crosslinking. There are two main groups of chemical crosslinking, which are peroxide

Copyright by Mahidol University

and sulphur vulcanisation systems. However, sulphur vulcanisation is a regular system widely used in rubber industries due to the improvement in mechanical properties, chemical resistance as well as gas impermeability. Such properties mean that NR could be used in a wide variety of products. Nevertheless, when sulphur-cured NR products are exposed to a thermal oxidative ageing environment, severe changes in physical and dynamic mechanical properties are observed [5]. These changes are directly related to a modification of an original crosslink structure and/or a main-chain scission [5-9]. To overcome this problem, chemical substances, known as antioxidants, are added to rubber mixes for prolonging a service life of rubber vulcanisates. However, there are many kinds of antioxidants and each of antioxidant has different efficiency to protect vulcanisates from the thermal oxidative ageing. Thus, it is necessary to select the appropriate antioxidants for each application. In addition, reinforcing fillers, i.e., carbon black and silica, is generally used to improve physical and dynamic mechanical properties of rubber products. Nevertheless, the uses of reinforcing fillers may affect the thermal oxidative ageing of rubber products due to the difference in thermal conductivity between reinforcing fillers and NR [10]. Therefore, the correlations of amount and types of antioxidant as well as reinforcing filler with thermal oxidative ageing are necessary to be investigated.

Dynamic mechanical properties of rubber compounds are one of their important physical properties for tire applications as well as for other dynamic rubber products. Many studies on the dynamic mechanical properties of various rubber compounds have been reported, including the effects of the type and amount of rubbers [11–12] and fillers [13–16], the interaction between rubbers and fillers [17], the compounding ingredients and the state-of-cure [17-18]. It is found that changes in the crosslink structures (e.g., crosslink density and crosslink type) of NR vulcanisates cause variation in glass transition temperature (T_g), elastic modulus (G') and tanδ [5].

The major purpose of the present study is to investigate influences of thermal oxidative ageing conditions and compounding ingredients on ageing properties of sulphur-cured NR vulcanisates.

Copyright by Mahidol University

CHAPTER 2
OBJECTIVES

The principle objectives of this research are to study the effect of thermal oxidative ageing conditions and compounding ingredients on properties, including physical and dynamic properties as well as a crosslink density, of NR vulcanisates. The scope of this work consists of three main parts, as follows:

1. Effects of thermal oxidative ageing conditions on properties of NR vulcanisates

The objective of this section is to investigate the effects of thermal oxidative ageing conditions on properties of NR vulcanisates via crosslink density. Thereafter, the onset ageing temperature and ageing time (as determined from tensile strength) will be selected. Since types of curing systems (conventional vulcanisation, CV and efficient vulcanisation, EV) and thermal oxidative ageing conditions (temperature and time) are known to strongly affect the physical and dynamic properties, the relationship between curing system, thermal oxidative ageing conditions and mechanical properties will therefore be considered in the first part.

2. Influences of antioxidants on ageing properties of NR vulcanisates

There are many factors, which control the ageing properties of NR vulcanisates, such as nature of the elastomer and compounding ingredients, e.g., antioxidants and reinforcing fillers. Thus, it is necessary to investigate the effects of antioxidants and reinforcing fillers on ageing properties of NR vulcanisates.

The second part aims to investigate the effects of types and amount of antioxidant on ageing properties of NR vulcanisates. In this part, the NR vulcanisates with various antioxidants will be prepared for investigating their influences on ageing properties of NR vulcanisates. Then, the suitable antioxidant (based on tensile properties) will be

Copyright by Mahidol University

chosen for the subsequent study.

3. Effects of reinforcing fillers on ageing properties of NR vulcanisates

The final part will be focused on types and amount of reinforcing filler affecting the ageing properties, including tensile properties and dynamic mechanical properties, of NR vulcanisates. Various types and amount of carbon black and precipitated silica will be used as reinforcing filler and their influences on thermal ageing properties will be discussed.

Copyright by Mahidol University

CHAPTER 3
LITERATURE REVIEW

3.1 Natural rubber (NR)

3.1.1 Historical of NR

Natural rubber is obtained from the milky secretion (latex) of various plants, but the only important commercial source of natural rubber is the tree *Hevea brasiliensis.* Rubber from *Hevea brasiliensis* is therefore usually known as natural rubber (NR). NR latex, collected by tapping from *Hevea* rubber trees, is a colloidal suspension of rubber particles in an aqueous serum phase. The latex exuding from the tapping cut is called as fresh rubber latex or fresh field latex. Fresh field latex is composed of approximately 25-40% dry rubber content (DRC) and 5-10% non-rubber substances. These non-rubber components include proteins, carbohydrates, lipids and inorganic salts [19]. Proteins and lipids are major non-rubber substances in NR, which are believed to cover the surface of rubber particles and yield good green strength of NR [1]. In addition, other factors, such as long-chain branching and high molecular weight have been reported to play strong roles in the strength of NR [1, 20]. The major component of NR is polyisoprene, consisting of the isoprene units in a two trans-1, 4 and a long sequence of cis-1, 4 configurations, as shown in Figure 3.1.

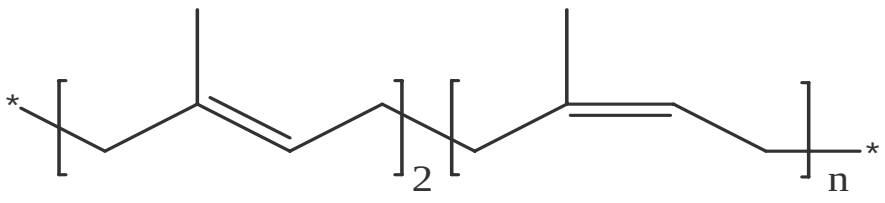


Figure 3.1 Chemical structure of NR [2]

Copyright by Mahidol University

3.1.2 Properties of NR

Nowadays, NR has particularly been recognised in terms of its high green strength, elasticity, low-temperature crystallisation and non-rubber components [3]. NR is thus of great technical importance for the rubber industries, although there are many trials to replace NR with some synthetic polymers. The main reason is, of course, the superior basic properties of NR, particularly the mechanical properties. However, due to the presence of unsaturation in NR main chains, poor resistance to ozone, wheather (heat and cold), oils and fuels is resulted.

3.1.3 Applications of NR

NR is still the best choice for many applications that require low heat buildup, such as large tyres, carcasses of passenger-car tyres, vibration mounts, springs and bearings. For special purposes, NR is used in hoses, seals, rolls, conveyor, belts, gaskets, elastic bands, rubberised fabrics and other products. Evidently, NR is chosen for various applications requiring high strength. In addition, NR can be blended with other diene rubbers such as isoprene rubber (IR), styrene butadiene rubber (SBR) and butadiene rubber (BR) to achieve desirable properties of the blends [2].

3.2 Compounding of NR

Regularly, compounding transforms NR into a range of materials suitable for applications. Such transformation is accomplished by an addition of a number of ingredients for instance, carbon black or non-black fillers or both, activators, accelerators, vulcanising agents, suitable antidegradants and sometimes retarders or prevulcanisation inhibitor. The objectives of compounding are; (a) to facilitate processing and fabrication; (b) to ensure a rapid throughput with minimal rejection rate; (c) to achieve the required balance in vulcanisate properties and (d) to provide durability, all at the lowest possible cost [21].

Copyright by Mahidol University

3.2.1 Activators

Activators are chemicals used to activate or extract the full potential from the organic accelerators. Useful activators include metal oxides (usually zinc oxide; ZnO), fatty acids and nitrogen containing bases. ZnO is the most widely used inorganic activator (lead and magnesium oxides are also used, but less often), while stearic acid is normally the organic activator of choice. For ZnO to be fully effective, ZnO must be present in a form that can react with the accelerator system. Stearic acid serves also as a plasticiser or lubricant to reduce the compound viscosity, and to solubilise the available zinc. Many rubber compounds nowadays incorporate a combination of ZnO and stearic acid in sulphur-cured compounds [22].

3.2.2 Accelerators

The vulcanisation process can generally be accelerated by adding small amounts of chemicals known as accelerators. The classification of these accelerators, in terms of their chemical composition and speed of vulcanisation, is shown in Table 3.1.

Table 3.1 Classification of accelerator groups and their relative curing speeds [23]

Type	Example	Relative curing speed
Guanidines	DPG	Slow
Dithiocarbamates	ZDBC	Very fast
Thiurams	TMTD, TMTM, DPTTS	Very fast
Thioureas	ETU	Fast
Thiophosphates	DIPDIS	Semi-fast
Thioazoles	MBT, MBTS, ZMBT	Moderate
Sulfenamides	CBS, MBS	Fast with delay-action

Functionally, accelerators are typically classified as primary or secondary accelerators. The former usually provides considerable medium to fast cure and good modulus development. The latter usually produces scorchy, very fast curing stocks. The secondary accelerators are seldom used alone, but generally are found in a

Copyright by Mahidol University

combination with primary accelerators to gain faster cures or greater product properties [22].

3.2.3 Antidegradants

Antidegradants are commonly used to protect rubber both in uncured and cured states. Normally, there are many kinds of antidegradants widely used in the rubber industries. The types of antidegradant can be classified by their duties, namely antiozonants and antioxidants, which are used to protect the rubber from ozone attack and oxidation of rubber, respectively. Types and applications of elastomer are the principle factor in considering the antidegradant used [23].

3.2.4 Reinforcing fillers

Reinforcing fillers are used to reinforce or enhance properties of elastomers while reduce cost of the compounds. In black-filled compounds, carbon blacks are used. For non-black compounds, silica, clay, calcium carbonate, etc. can be used depending on the properties required. The most commonly known reinforcing fillers are carbon blacks and silicas. Silicates, clays, whiting (calcium carbonate), and other mineral fillers are used extensively where a high degree of reinforcement is not essential [23].

3.2.5 Organic peroxides

Organic peroxides are curing agents that possess one or more oxygen-oxygen (R-OO-R) bonds. These chemicals are used commercially to produce free radicals, yielding the desired crosslinked networks in elastomer via hydrogen abstraction and/or addition at double bonds. The structure of the peroxides affects strongly their thermal and chemical stabilities, as well as the energy level of the free radicals generated [24]. There are generally seven major classes of organic peroxides as shown in Table 3.2.

Copyright by Mahidol University

Table 3.2 Major commercial organic peroxide classes [25]

Organic peroxide	10 h half life
Diacyl peroxides	21-75^{o}C
Peroxydicarbonates	49-51^{o}C
t-Alkyl peroxyesters	38-107^{o}C
Peroxyketals	92-112^{o}C
Dialkyl peroxides	115-131^{o}C
tert-Alkyl hydroperoxides	Not applicable
Ketone peroxides	Not applicable

Four classes of organic peroxides are used commercially for crosslinking and polymer modification of polyethylene and elastomers: diacyl, peroxyesters, peroxyketal, and the dialkyl type peroxides [26-28]. Each class of peroxide has a distinctive half-life (thermal stability). The most common peroxide used in the crosslink industry has traditionally been the dialkyl classes. However, there are several other peroxide types, which provide distinctive advantages, such as aromatic odorless, non-bloom, and liquid form, in many manufacturing operations.

3.2.6 Retarders and prevulcanisation inhibitors

Retarders and prevulcanisation inhibitors (PVI) are materials, which are used with sulphur vulcanised polymer, providing scorch safety with relatively little change in other properties. Acidic material such as salicylic acid, benzoic acid and phthalic anhydride are widely known as retarders, which are extremely efficient in some applications, but reduce the state-of-cure and rate of cure as negative results, as shown in Figure 3.3. The acid retarders are also not effective with sulfenamide accelerators and may function as activators instead [29]. In the case of PVI, it is found that PVI could increase scorch time with no influence on cure rate and state-of-cure.

Copyright by Mahidol University

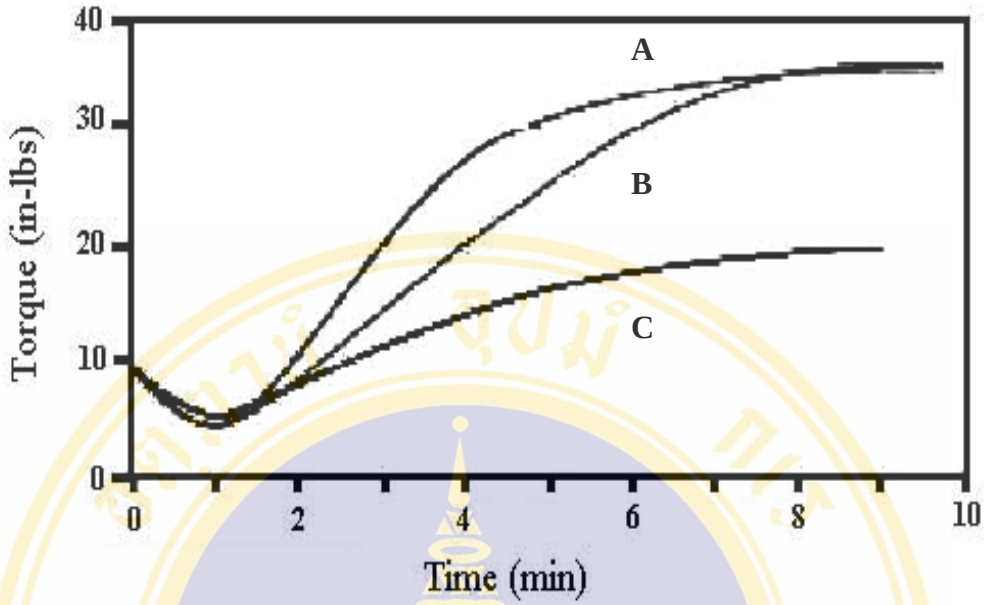


Figure 3.2 Effect of acid retarder and PVI on state-of-cure: curve A: without acid retarder and PVI; curve B: with PVI; curve C: with acid retarder [30]

3.3 Vulcanisation

Generally, rubber products, such as tyres and mechanical goods, cannot be used without vulcanisation due to their negative properties. Vulcanisation or chemical crosslink is a process by which rubber is changed from a plastic material to either elastic or a hard material depending on degree of crosslink. As a plastic material, the unvulcanised rubber readily undergoes permanent deformation whereas vulcanised rubber is highly elastic and has high resistance to plastic deformation. Vulcanisation involves the formation of chemical crosslink between long chains constituting the rubber molecules, as illustrated in Figure 3.2. Thus, the chains cannot move pass each other as readily as before vulcanisation, with elongation decreasing and resistance to deformation or modulus increasing. The three dimensional crosslinked structure renders vulcanised rubber more insoluble in solvents and more resistant to heat, light or chemicals [31-34].

Copyright by Mahidol University

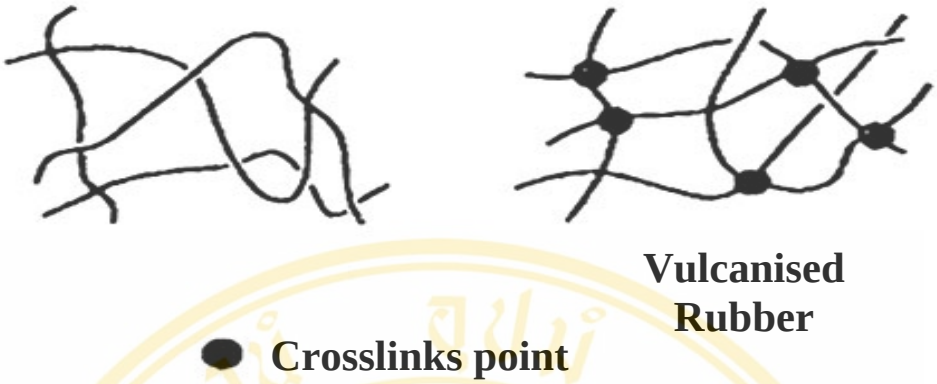


Figure 3.3 Polymer chains in unvulcanised and vulcanised rubber; the crosslinks are indicated by bullets [35].

3.3.1 Vulcanisation systems

3.3.1.1 Peroxide vulcanisation

A wide variety of peroxides can be used to crosslink most types of elastomer except butyl rubber (IIR) [36]. The importance of peroxides is the ability to crosslink not only unsaturated, but also saturated elastomers. Compared with sulphur vulcanisation, crosslinking by peroxides is a relatively simple process since there is no accelerator and activator required. Some advantages and disadvantages of peroxide crosslinking are summarised in Table 3.3.

Table 3.3 Advantages and disadvantages of the peroxide crosslinking [37]

Advantages	Disadvantages
Low tension set (i.e., high elasticity)	Possibility of thermal degradation in hot air curing
Simple compounding	Low mechanical strength
No mould contamination	Expensive crosslinking agent
Good heat ageing resistance	Possibility of cure inhibition by some antioxidants
Transparent rubber possible	Long cure time

Copyright by Mahidol University

The crosslinking reaction involves the homolytic decomposition of peroxides to produce alkoxy radicals (RO•) followed by a hydrogen-atom abstraction. The hydrocarbon radicals (P•) predominantly undergo coupling to form crosslinks between polymer chains. A peroxide crosslinking mechanism is shown in Figure 3.4.

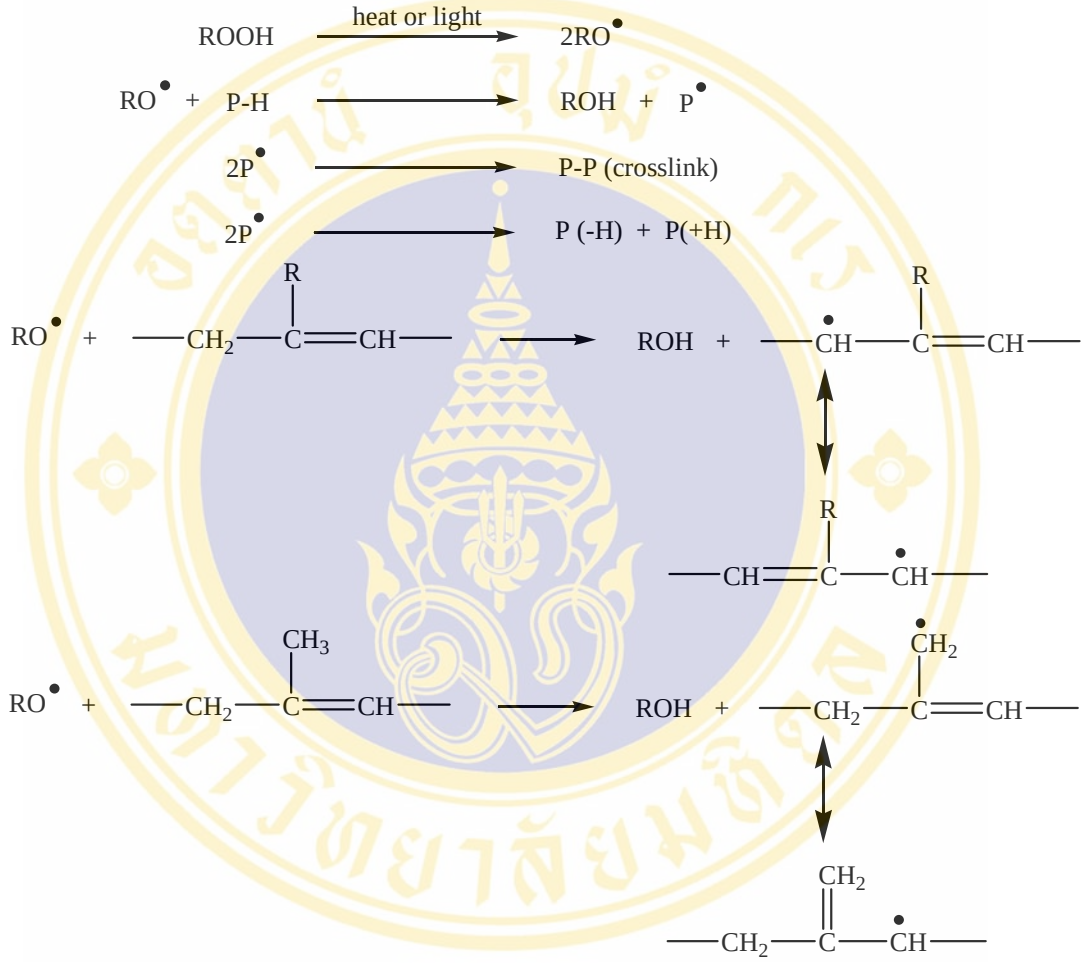


Figure 3.4 Peroxide crosslinking mechanism of elastomers (P-H).

Also, co-agent is often used to improve the rate and state of cure and to lower a peroxide dosage. As with peroxide cure, in general, the compounding ingredients should be selected with care since some acidic and unsaturated materials can seriously impair crosslink efficiency [2]. It can be seen that there are some major disadvantages of peroxide cure as illustrated in Table 3.3. As a result, the peroxide-free curing systems have been developed in order to overcome the limitation of peroxide vulcanisation [2, 38].

Copyright by Mahidol University

3.3.1.2 Sulphur vulcanisation

Generally, sulphur is the most widely used curing agent because it provides rubber vulcanisate with good mechanical properties. The main requirement for sulphur vulcanisation is the unsaturation in rubber molecules, i.e., the sulphur cure is not applicable to saturated rubber. By heating rubber with sulphur, long chains of the rubber molecules could simply be linked together by one or more sulphur atoms, as shown in Figure 3.5.

Figure 3.5 Different types of sulphur crosslinks between elastomer chain; x = 2-30; Ac = accelerator fragment

These sulphidic linkages radically modify the properties of rubber. As illustrated in Figure 3.5, some of the sulphur chains give intramolecular crosslinking and others yield intermolecular crosslinking. The change in properties resulting from vulcanisation is due to almost entirely to the intermolecular crosslinking compared to the intramolecular crosslinks [35].

Rubber vulcanisation by sulphur with no accelerators takes several hours and is therefore no longer of commercial importance. A vulcanisation process can be accelerated by adding small amounts of organic compounds known as accelerators. With the uses of accelerators, the optimum curing can be accomplished in periods as short as 2-5 min. Accelerated sulphur vulcanisation is suitable not only for NR and its synthetic counterpart (IR), but also for other synthetic rubbers such as polybutadiene

Copyright by Mahidol University

(BR), styrene butadiene rubber (SBR), nitrile rubber (NBR), butyl rubber (IIR) and ethylene-propylene-diene rubber (EPDM). An overall summary of the accelerated sulphur vulcanisation is illustrated in Figure 3.6. The accelerator complex initially forms, and then reacts with sulphur to yield the active sulphurating agent, which gives the rubber-bound intermediate (RS_yX). The rubber-bound intermediate form polysulfidic crosslinks, which are reduced the rank or destroyed upon network maturing. As the cure state continues, the accelerator residual can change polysulfidic linkages to mono- or disulfidic linkages [39-40]. In sulphur vulcanisation, quantity and types of crosslinks can be categorised into 3 main systems based on the ratios of accelerator to sulphur used in curing, namely, conventional vulcanisation (CV), efficient vulcanisation (EV), and semi-efficient vulcanisation (semi-EV) systems, as demonstrated in Table 3.4.

Table 3.4 Ratios of accelerator to sulphur for accelerated sulphur vulcanisation [41]

Curing systems	**Sulphur (phr)**	**Accelerator (phr)**	**Acc. / S_8**	**Crosslink (%)**		**Cyclic sulphide**
				S_2, S_x	S	
Conventional (CV)	2.0-3.5	0.4-1.2	0.1-0.6	95	5	High
Efficient (EV)	0.4-0.8	2.0-5.0	1.2-2.5	20	80	Low
Semi-efficient (semi-EV)	1.0-1.7	1.2-2.5	0.7-2.5	50	50	Medium

As for the CV system, the amount of accelerator is lower than sulphur, giving mainly the polysulfidic linkages (see Figure 3.5), and thus good mechanical properties, with the expense of thermal resistance. In EV system, the amount of accelerator is higher than sulphur, which yields mainly the monosulfidic linkages giving xxx to the rubber vulcanisates with main properties are good thermal resistance but low mechanical properties. The properties of the rubber vulcanisate cured with the semi-EV system are in between those of CV and EV systems.

Copyright by Mahidol University

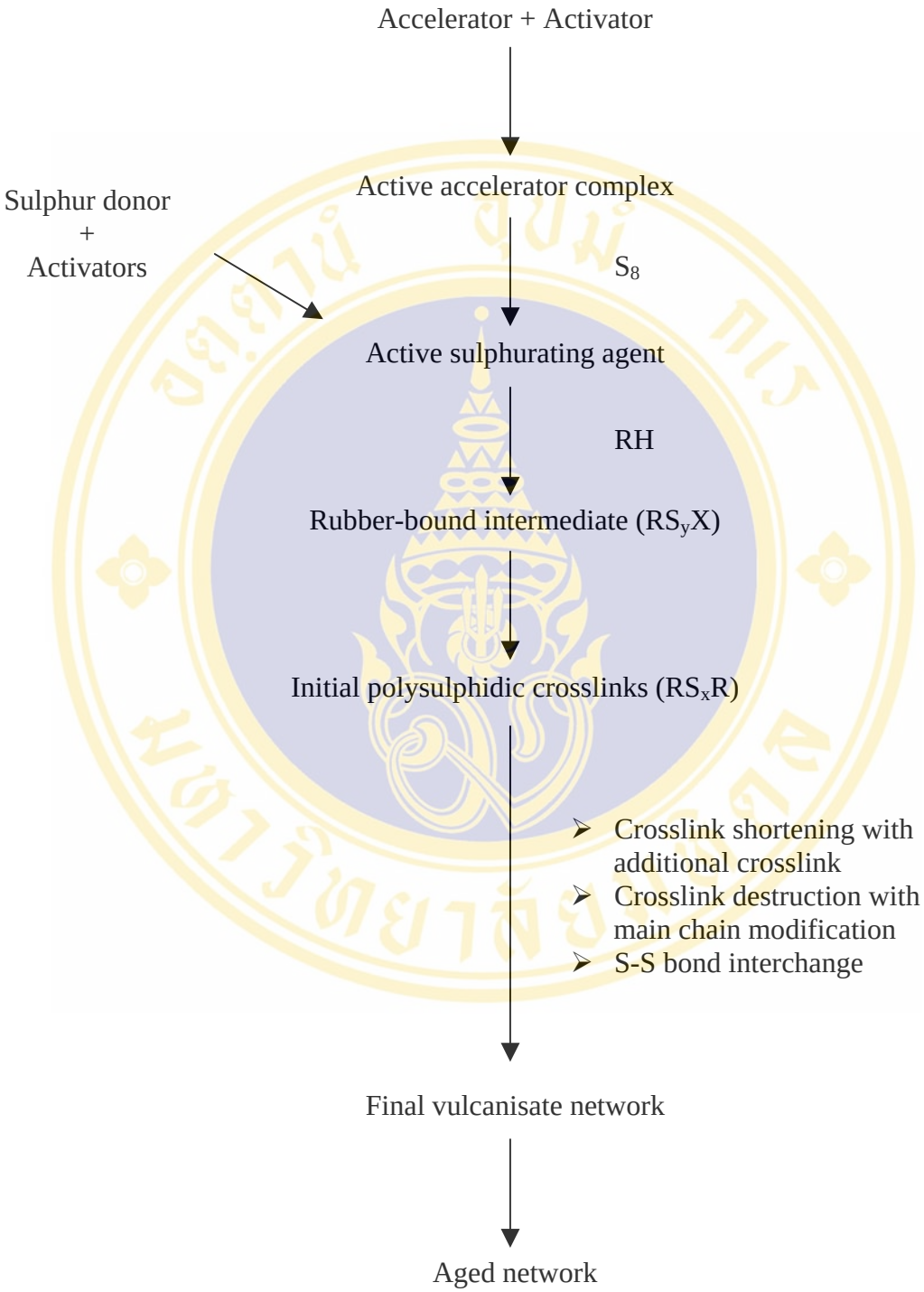


Figure 3.6 Mechanism of sulphur vulcanisation; R = rubber chain, H = allylic proton and X = accelerator residue [42-43].

Copyright by Mahidol University

3.3.2 Effect of crosslink density on NR vulcanisates

Vulcanisation of a rubber stock produces changes in properties [44]. Furthermore, NR vulcanisates with appropriate compounding formulation would provide excellent elasticity (i.e., the ability to snap back to their original shape after loading). NR has very good abrasion resistance, poor chemical resistance and good dynamic mechanical properties and is therefore used in tyres, rubber springs and vibration mounts [2]. The relationship between properties of vulcanisates and crosslink density is demonstrated in Figure 3.7.

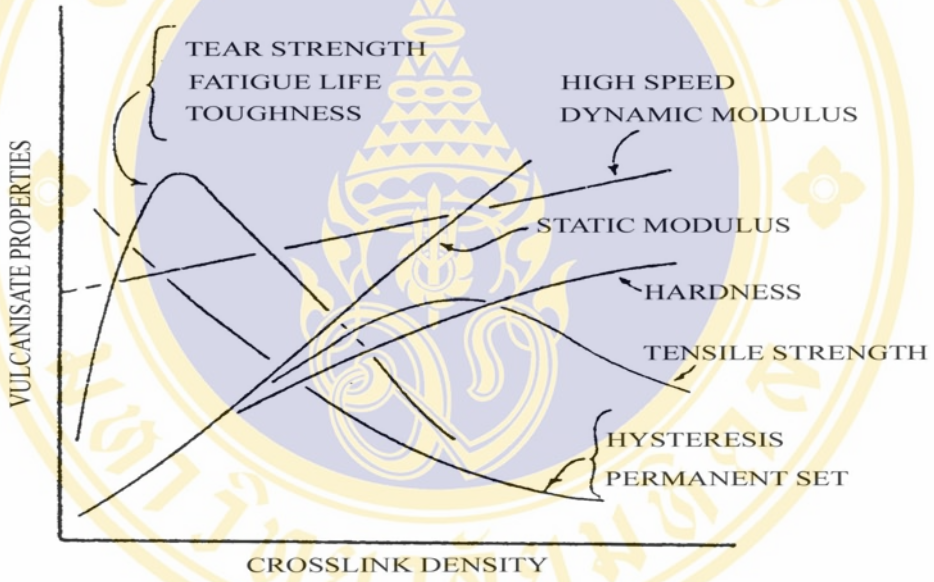


Figure 3.7 Relationship between crosslink density and vulcanisate properties

It has been shown, both theoretically and experimentally, that modulus and hardness of vulcanisates are proportional to crosslink density. Thus, as a number of crosslinks increases, the elastomer chains are more restricted in their motions and the force required to produce a given deformation (modulus) becomes greater. The increase in modulus with crosslinking is paralleled by a decrease in elongation at break. Nevertheless, the influence of crosslink density on physical properties depends on nature of the elastomers and, to a lesser extent, with other compounding ingredients (e.g., reinforcing fillers, cure system, plasticisers, etc.).

Copyright by Mahidol University

3.4 Rubber degradation

3.4.1 General approach for NR

Elastomers, like most organic materials, that contains high levels of unsaturation in the polymer backbone can be degraded by exposures to high temperature (thermal degredation), oxygen, ozone, ultraviolet light, moisture, radiation and chemical agents. Often multiple exposures, such as a combination of moisture and heat or oxygen and light, can result in accelerated deterioration [45]. The susceptibility to degradation depends strongly upon structure and environmental exposure. For example, saturated polymers are inherently more stable than unsaturated polymers due to the lack of double bonds in their backbones. The degradation is a complex process involving many reactions influenced by prevailing conditions such as singlet oxygen, ozone, mechanical force, heat, light, oil and heavy metal. Typically, polymer degradation occurs via free radical process, as shown in Figure 3.8. The main chain or side group of polymers can initially be dissociated by heating and/or mechanical shearing to generate polymeric free radicals (R•) known as the initiation step. Propagation, the second stage, occurs when atmospheric oxygen reacts with R• to form peroxy radicals (ROO•), and followed by the abstraction of hydrogen atoms from rubber chains (RH) by proton acceptor to generate hydroperoxide (ROOH) group and another macroradical site (R•). The unstable hydroperoxides will then decompose resulting in the formation of alkoxy (RO•) and hydroxyl (HO•) radicals. Therefore, if modified RO• could form t-alkoxy radical, chain scission at β position would take place, leading to a decrease in properties. For example, in the case of NR, the mechanism of thermal degradation is schematically in Figure 3.8.

Copyright by Mahidol University

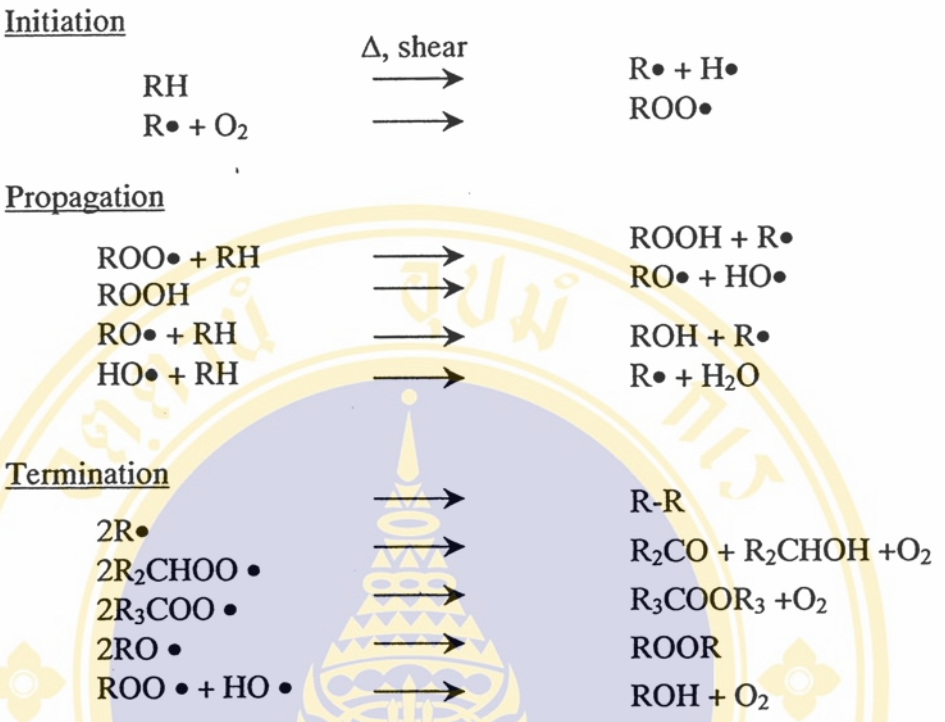


Figure 3.8 Oxidation mechanism of NR [46-48].

3.4.2 Oxidation of peroxide-cured vulcanisates by hydroperoxide

In the case of peroxide-cured vulcanisates, the crosslinks introduced are simply covalent bonds between the rubber chains. As the rubber is purified before vulcanisation and the residual peroxide is extracted after vulcanisation, the kinetics of oxidation of the thin samples of NR are very similar to those of simple polyisoprenes, such as squalene, except for short induction periods due to traces of natural antioxidants. The oxidation mechanism of peroxide-cured vulcanisates is demonstrated in Figure 3.9.

Copyright by Mahidol University

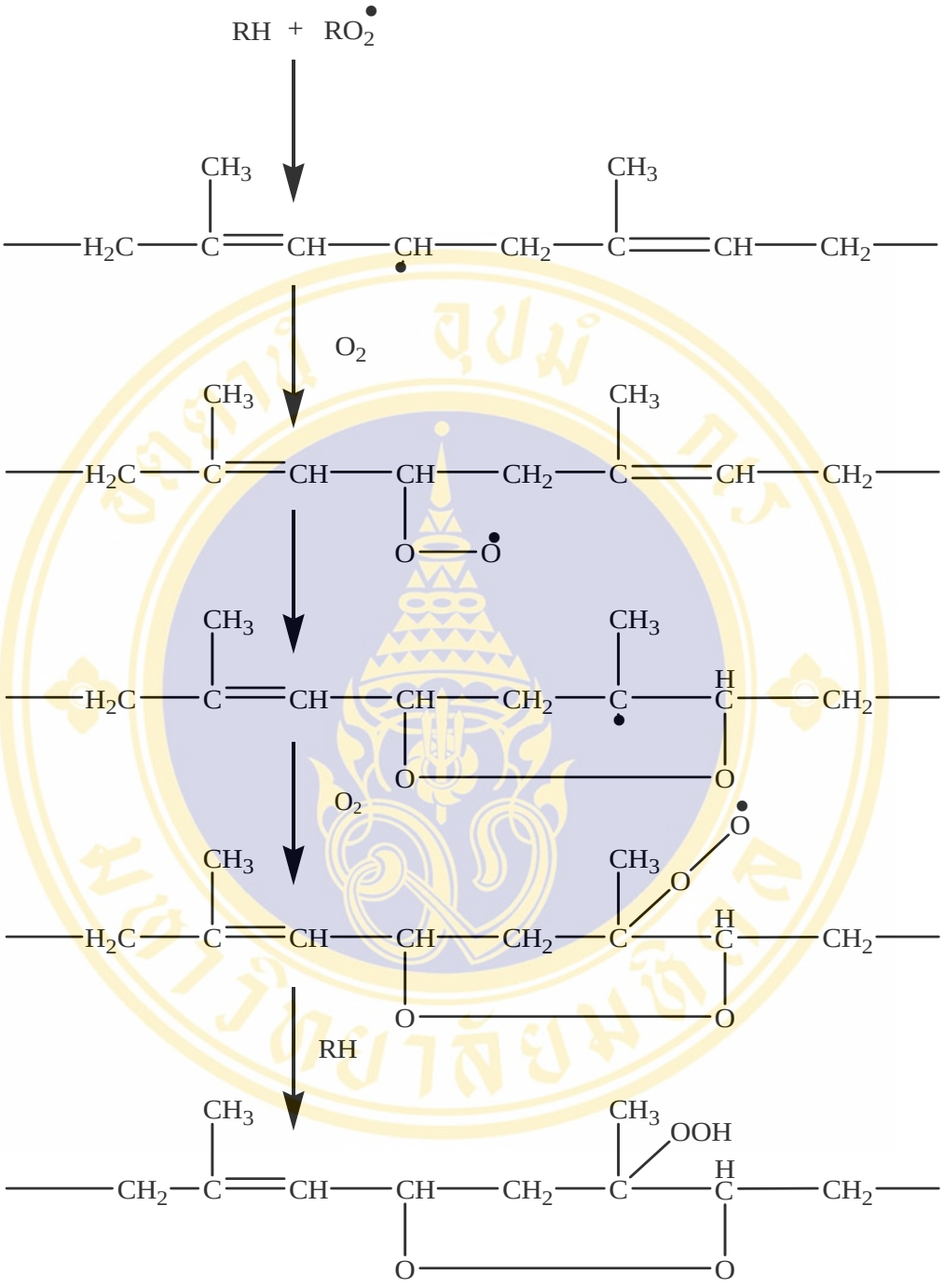


Figure 3.9 The oxidation of peroxide-cured NR vulcanisates by hydroperoxide [47]

The oxidation mechanism as illustrated in Figure 3.9 is not acceptable for vulcanisates cured with sulphur and accelerators with much more complex structure. Detail of oxidation in sulphur-cured vulcanisates will be discussed in the subsequent section.

Copyright by Mahidol University

3.4.3 Oxidation of sulphur-cured vulcanisates by hydroperoxide

When sulphur-cured NR compounds are exposed to a thermal ageing environment, significant changes in physical and dynamic mechanical properties are observed [5]. These changes are directly related to a modification of the original crosslink structure and molecular chain-scission. Dialkyl, alkyl-aryl and diaryl monosulphides (RSR) are oxidised to sulphoxides (RSOR) at rates decreasing in that order. The mechanism of the reaction has been elucidated by Bateman and Hagrave [49]. Alkyl alkenyl monosulphides are also oxidised to sulphoxides, but these are unstable, and its decomposition and side reactions become important [50]. Monosulphide crosslinks in an NR vulcanisate and the decomposition of the sulphoxides will result in crosslink scission, as shown in Figure 3.10, and also the sulphenic acids (RSOH), which are postulated as powerful antioxidants by Scott [51]. Thus, the presence of such monosulphides can initially increase oxidation rates via some redox type of radical initiation process with hydroperoxide (ROO•), but very quickly gives rise to a pronounced auto-inhibition.

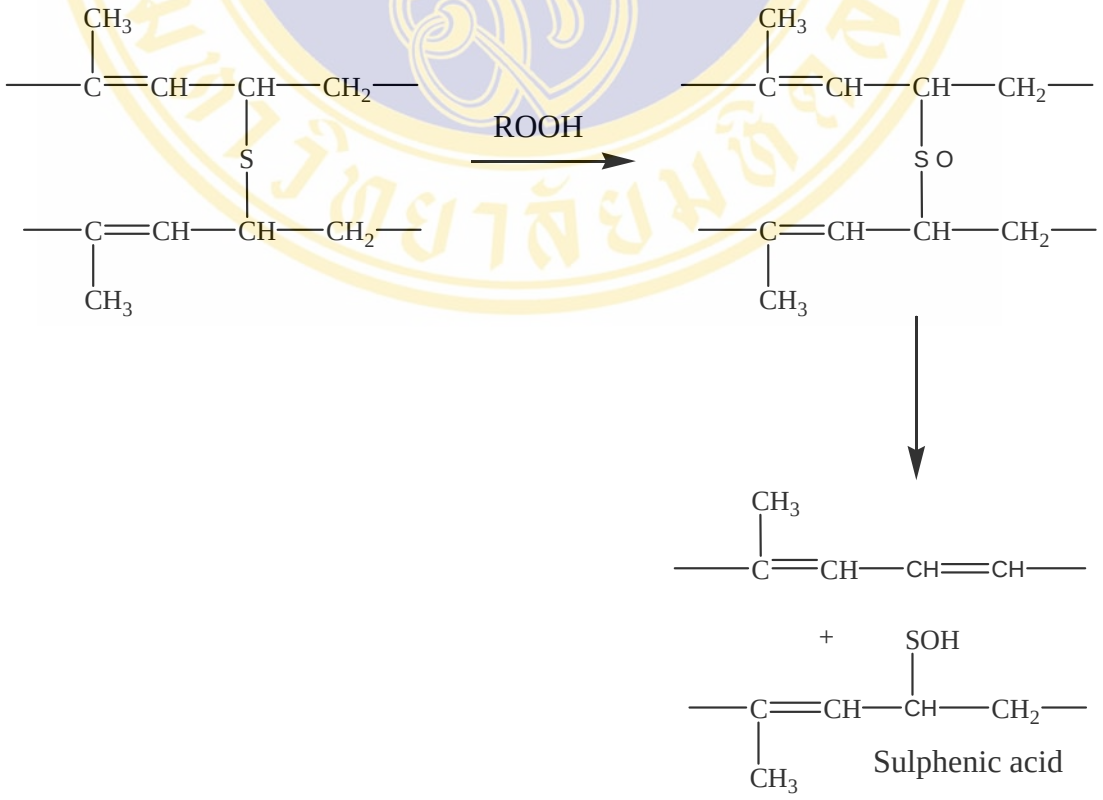


Figure 3.10 Oxidation of monosulphides by hydroperoxide

Copyright by Mahidol University

As can be seen in Figure 3.10, there is also the possibility of the introduction of conjugated unsaturation into the rubber chain, which will increase oxidisability. Disulphides (RSSR) react with hydroperoxides (ROO•) to give thiosulfinates (RSO•SR), which again are unstable and decompose into sulphenyl (RS•) and sulphinyl radicals (RSO•) [52].

The sulphenyl radicals (RSO•) can again give rise to sulphur acid (e.g., sulphenic acid) which function as a good antioxidant. Thus, disulphide crosslinks can be expected to give progressive inhibition of oxidation, and also to be susceptible to oxidation scission. The oxidative behaviour of polysulphides is little understood, but it is known that polysulphide possesses some antioxidant activity and at the same time is antagonistic to conventional antioxidants leading to poor resistance to oxidation [52].

3.4.4 Oxidation of sulphides by oxygen

Alkenyl alkyl or dialkenyl monosulphides are known to be oxidised directly by oxygen [53] but, this and the ensuring reactions leading to crosslink scission do not appear to be important. Disulphides and polysulphides are not appreciably oxidised by atmospheric oxygen. The crosslink scission of monosulphides by oxygen is shown in Figure 3.11.

Copyright by Mahidol University

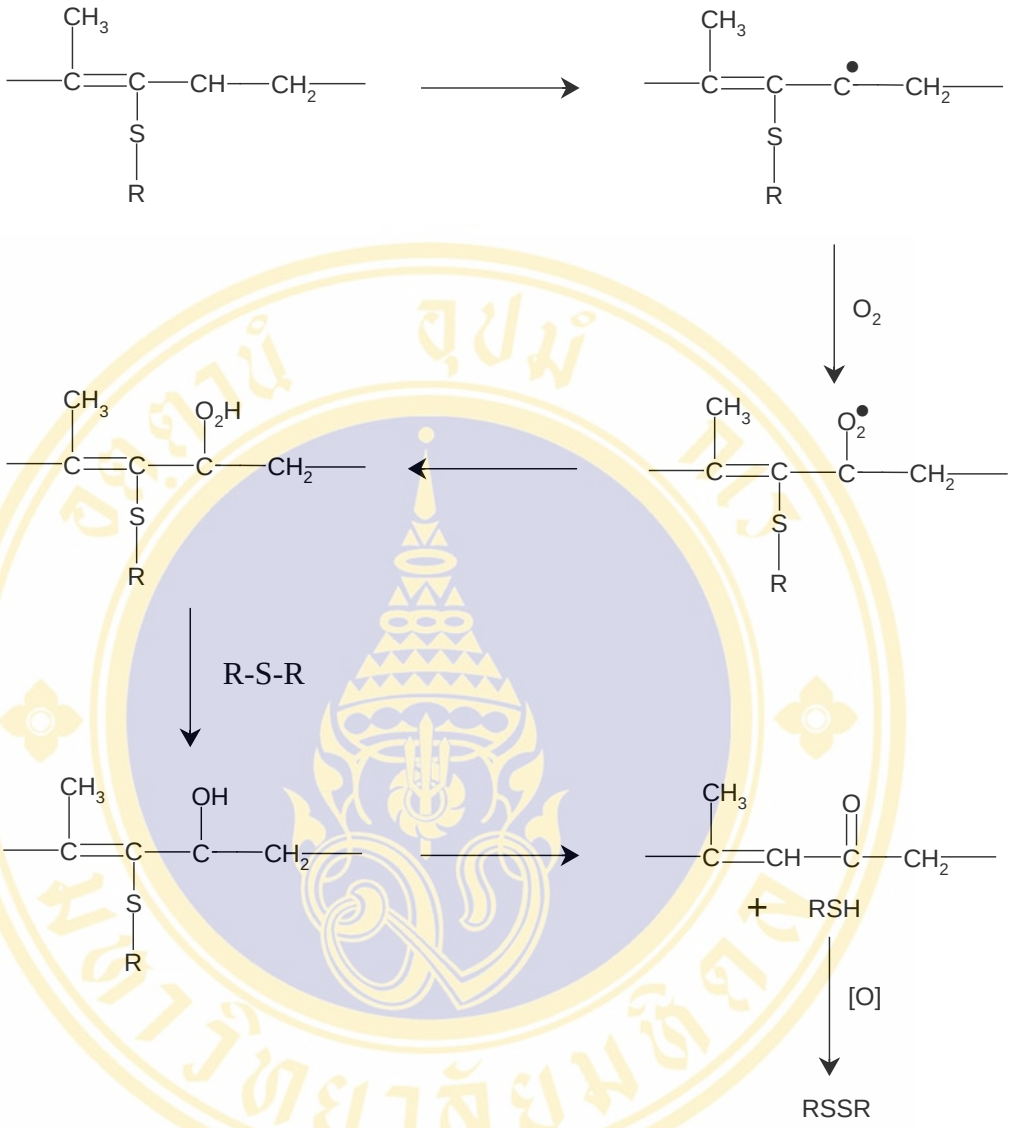


Figure 3.11 Crosslink scission of monosulphides by oxygen [54]

3.4.5 Oxidative crosslinking in sulphur vulcanisates

Normally, the oxidative ageing causes the degradation of polymer chains; nevertheless, the oxidative ageing can sometimes crosslink polymer chains leading to a tridimensional network structure. Practically, most types of sulphur-cured vulcanisates initially harden on ageing before degradation occurs. Also, a crosslinking accompanies the network scission in the oxidation of sulphur-cured vulcanisates, but not for peroxide-cured vulcanisates. The sulphur crosslinking is therefore connected with oxidative reactions of sulphur species in the network. Routes of the oxidative

Copyright by Mahidol University

scission of mono- and disulphides have been outlined previously and some of products could give rise to new crosslinks. Thus, sulphenic acids (RSOH) dimerise to give thiosulphinates (RSO_2 SR) [53].

$$2RSOH \longrightarrow RSO\bullet SR + H_2O$$

Sulphinyl radicals can also dimerise to give thiosulphonates,

$$2RSO\bullet \longrightarrow RSO_2\bullet SR$$

While thiols are oxidised readily to sulphides

$$2RSH \xrightarrow{[O]} RSSR + H_2O$$

However, the crosslink via such scission products can generate at best only fraction of the crosslinks originally broken, and another source of crosslink formation must exist. The most probable explanation is the oxidation of cyclic mono- or disulphides, and the further reaction of scission products give new crosslinks, although none has been lost.

A scission can quantitatively be detected by a number of techniques via either physical or chemical methods. The physical methods include gel permeable chromatography (GPC), osmometry, viscometry, sol-gel analysis, stress relaxation and stress-strain measurements. Physicals methods of estimating scission are extremely useful, but offer no insight to the mechanism of the scission reaction. For a chemical method to be successful, it is essential that:

(1) the scission reaction gives rise to well-defined chemical products;

(2) at least one of the products bears a consistent, although not necessarily stoichiometric relationship with scission is stable under the oxidations conditions, and can be analysed accurately at very low concentration.

The radiochemical labeling technique is one of the chemical methods, which is used for determining the chain scission. The use of radio-labelled reagents such as ^{14}C for very sensitive methods of analysis is well established [55].

Copyright by Mahidol University

3.5 Protection against oxidative ageing

Polymers usually degrade according to an oxidative-free radical reaction, which cannot be terminated. However, polymers can be stabilised from the oxidative-free radical reaction by the addition of antioxidants and/or other antidegradants. Antioxidants, which act as free-radical resistant agents, are effective stabilisers for oxidative degradation. The antioxidation action would ordinarily involve three functions. Firstly, the antioxidant will absorb the UV light, which catalyses the oxidation. Secondly, the antioxidant may be the decomposition of initiating peroxides, which are converted into non-radical products. Finally, the antioxidant will be the termination of the radical chain reactions. The phenol and amine antioxidants (HA), increase thermal stability of the rubber products by terminating the chain reaction as shown below:

The resultant free radical (A•) can link up with another radical to form a stable product or can react with peroxide radical:

Copyright by Mahidol University

CHAPTER 4
MATERIALS AND METHODS

4.1 Materials

The materials used in the present study are summarised in Table 4.1.

Table 4.1 Materials used in the present study

Chemical name	Grade/Supplier
Natural rubber (NR)	STR 5L, Thailand (ML1+4 @ 100^{o}C = 72)
Zinc Oxide (ZnO)	Commercial/ Chemmin Co., Ltd., Thailand
Stearic acid	Commercial grade/ Petch Thai Chemical Co., Ltd., Thailand
N-tert-Butyl-2-Benzothiazole sulfenamide (TBBS)	Santocure TBBS/ Flexsys Antwerp Belgium, Belgium
Sulphur	Commercial Grade/ Chemmin Co., Ltd., Thailand
2, 2, 4-Trimethyl-1, 2-Hydroquinoline (TMQ)	Vulkanox HS/ Bayer Co., Ltd., Germany
N-(1, 3-Dimethylbutyl)-N'-Phenyl-P-Phenylenediamine (6-PPD)	Santogard 6-PPD/ Flexsys Co., Ltd., Thailand
2, 6-di-tert-butyl-4-methylphenol (BHT)	Bayer Thai, Co., Ltd., Thailand
Carbon black	N330, N550 and N660/ Thai carbon product Co., Ltd., Thailand
Precipitated silica	Hisil 233/ PPG-Siam Silica Co., Ltd., Thailand

Copyright by Mahidol University

Table 4.1 Materials used in the present study (continued)

Chemical Name	Grade / Supplier
Toluene	AR grade/ Labscan Asia Co., Ltd., Thailand

4.2 Apparatus

The apparatus used in the present study is summarised in Table 4.2.

Table 4.2 List of apparatus used in the present study

Apparatus	Supplier/Trade mark
Brabender internal mixer	Brabender mix Germany R2000 with Banbury rotors
Two-roll mill	Labtech model LRM 150
Rubber process analyser (RPA 2000)	Alpha Technology model RPA 2000
Hydraulic hot press	Wabash Genesis Series model G30H
Dynamic mechanical thermal analyser (DMTA)	Gabo Qualimeter model Eplexor 25 N
Tensile tester	Instron universal tester model 4301
Ageing oven	Memmert Air Oven

Copyright by Mahidol University

4.3 Mixing procedures and vulcanisation

Apparatus: Brabender internal mixer

Chamber capacity: 410 cm^3 Temperature: 40^oC

Rotor speed: 40 rpm Fill factor: 0.65

Initially, NR was first charged into the mixing chamber and masticated for 2 mins, followed by the addition of ZnO and stearic acid, and mixed further for 7 mins. Then, all curatives were added and mixed for 3 mins. Finally, the compound was dumped, sheeted on the cold 2-roll mill and kept at room temperature for 24 hours before testing. Detail of mixing procedure is shown in Table 4.3.

Table 4.3 Mixing procedure used in the study

Action	Time (mins)
Add rubber	0.0
Add ZnO and stearic acid	2.0
Add reinforcing filler	4.0 [a]
TBBS, antioxidants and sulphur	9.0 [b], 12.0 [a]
Dump and sheet on the mill	12.0 [b], 15.0 [a]

a = Used in the study of reinforcing fillers effect

b = Used in the study of ageing condition and antioxidant effects

To prepare rubber vulcanisates for property measurement, uncured rubber sheets were compression moulded using a hydraulic hot press at 160^oC under pressure of 15 MPa. Cure time set for curing the sample agreed with the cure time to achieve 90% complete cure (t_{c90}) as determined from the Rubber Process Analyser or RPA 2000.

Copyright by Mahidol University

4.4 Compounding formulation

To determine the influence of thermal oxidative ageing conditions on properties of NR vulcanisates, the NR vulcanisates cured with conventional vulcanisation (CV) and efficient vulcanisation (EV) systems were prepared using the compounding formulation, as shown in Table 4.4. Ageing temperature and time were varied in the ranges of 60-120^{o}C and 1-10 days, respectively.

Table 4.4 Compounding formulation used in the study of ageing condition effect

Ingredients	CV (phr)	EV (phr)
NR	100.0	100.0
ZnO	5.0	5.0
Stearic acid	2.0	2.0
TBBS	1.0	4.0
TMQ	2.0	2.0
6-PPD	2.0	2.0
Sulphur	4.0	1.0

In order to investigate the effects of antioxidants on properties of NR vulcanisates, types of antioxidants were varied. The compounding formulation used in this part is shown in Table 4.5.

Table 4.5 Compounding formulation used in the study of antioxidant effect

Ingredients	CV (phr)	EV (phr)
NR	100.0	100.0
ZnO	5.0	5.0
Stearic acid	2.0	2.0
TBBS	1.0	4.0
TMQ or 6-PPD or BHT	2.0	2.0
Sulphur	4.0	1.0

Copyright by Mahidol University

To investigate the effect of reinforcing filler on properties of NR vulcanisates, types and loadings of reinforcing filler were varied. Detail of compound formulation used in this part is shown in Table 4.6.

Table 4.6 Compounding formulation used in the study of reinforcing filler effect

Ingredients	CV (phr)	EV (phr)
NR	100.0	100.0
ZnO	5.0	5.0
Stearic acid	2.0	2.0
TBBS	1.0	4.0
Antioxidant	2.0	2.0
Sulphur	4.0	1.0
Carbon Black or Silica	0.0, 10.0, 20.0, 30.0	0.0, 10.0, 20.0, 30.0

4.5 Mechanical property measurement of vulcanisates

4.5.1 Tensile properties

Tensile strength, modulus and elongation at break were measured per ASTM D 412-92 using the Instron universal tensile tester (model 4301) at a crosshead speed of 500 mm/min with the load cell of 1 kN. The NR vulcanisate sheets were cut into the dumbbell shape with the dimensions as shown in Figure 4.1 Thickness of the dumb-bell test pieces was measured. At least 5 pieces of test specimens were used for each measurement and the stress-strain curves were recorded.

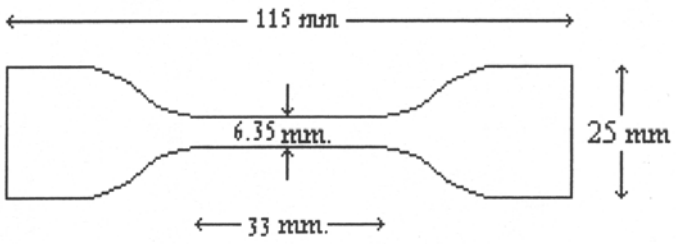


Figure 4.1 Dimensions of the tensile specimen

Copyright by Mahidol University

4.5.2 Dynamic mechanical properties

The Gabo Eplexor qualimeter was used for determining the dynamic mechanical properties of NR vulcanisate with tension mode of deformation. The set static and dynamic strains were of 1% and 0.1%, respectively, at the test frequency of 10 Hz. Temperature was swept from –90^{o}C to 20^{o}C at a heating rate of 2^{o}C/min. Storage modulus (E') and damping factor (tanδ) of NR vulcanisates as a function of temperature were recorded.

4.5.3 Ageing properties

Ageing test of NR vulcanisates was performed to determine the influences of elevated temperature and time on changes in physical and dynamic properties of vulcanised rubber, compared with unaged specimens, based on ASTM D 573-88.

4.5.3.1 Ageing temperature

The dumbbell specimens were placed in a hot-air oven at various temperatures of 60, 70, 80, 100 and 120^{o}C for 48 hours. At the end of the ageing period, the specimens were removed from oven, cooled to room temperature on a flat surface, and allowed to rest neither less than 16 hours nor longer than 96 hours before performing tests for tensile properties, %swelling and dynamic mechanical properties.

4.5.3.2 Ageing time

The dumbbell specimens were placed in a hot-air oven at a given temperature, for various ageing times of 1, 2, 4, 6 and 10 days. At the end of the ageing period, the specimens were removed from oven, cooled to room temperature on a flat surface, and allowed to rest neither less than 16 hours nor longer than 96 hours. Thereafter, the tensile strength, %swelling and dynamic mechanical properties were determined, and compared with those of the unaged specimens.

Copyright by Mahidol University

4.6 Determination of crosslink density

Small pieces of vulcanisates weighing approximately 0.3 g were immersed in 30-ml toluene for 7 days at room temperature. The swollen specimens were blotted with filter paper and transferred quickly to weighing bottles. Degree of crosslink density was presented in terms of a %swelling, which was determined from the quantity of solvent uptake of rubber vulcanisates, as shown in equation 1. In the case of filled vulcanisate, the swelling technique is not applicable due to the dilution effect provided by reinforcing filler. Therefore, the Florry - Rehner, as illustrated in equation 2, was used instead [56].

$$\%\text{swelling} = [(W_s - W) / W] \times 100 \quad (1)$$

where W = Weight of unswollen rubber (g)

Ws = Weight of swollen rubber (g)

$$\ln(1 - V_r) + V_r + \chi V_r^2 + 2\rho_r V_o V_r^{1/3}[X] = 0 \quad (2)$$

$$[X] = -[\ln(1-V_r) + V_r + \chi V_r^2] / (2\rho_r V_o V_r^{1/3})$$

$$M_c = 1 / 2[X]$$

$$V_r = [V_{rnet} / (V_{rnet} + V_{sol})]$$

$$V_{rnet} = (W / \rho_r) \times (\text{phr of NR / total phr})$$

$$V_{sol} = W_s / \rho_s$$

where [X] = Crosslink density

V_r = Volume fraction of rubber in swollen vulcanisates

V_{rnet} = Volume fraction of the rubber network

V_{sol} = Volume of solvent absorbed at equilibrium

V_o = Molar volume of toluene (106.3 cm3)

ρ_r = Density of natural rubber (0.92 g/cm^3)

Copyright by Mahidol University

ρ_s = Density of toluene (0.866 g/cm^3)

χ = Rubber-solvent interaction parameter (0.3795)

M_c = Molecular weight between crosslink

Copyright by Mahidol University

CHAPTER 5
RESULTS AND DISCUSSION

The discussion of this thesis consists of three main parts. In the first part, the effects of ageing temperature and time on properties, including tensile properties, crosslink density and dynamic mechanical properties, of NR cured with conventional vulcanisation (CV) and efficient vulcanisation (EV) systems will be presented. The second part deals with the influences of antioxidants on properties of NR vulcanisates after thermal oxidative ageing. In the final part, the filler reinforcing effect on properties will be discussed. The relationships between ageing temperature and time, types of antioxidant and reinforcing filler in NR cured with CV and EV systems will finally be drawn.

5.1 Effects of ageing temperature and time on properties of NR vulcanisates

Initially, the ageing temperature effect was investigated in order to gain a maximum service temperature of vulcanisates. Then, the optimum ageing temperature was drawn, and used for the study of ageing time effect. Properties to be discussed include tensile properties, crosslink density and dynamic mechanical properties.

Copyright by Mahidol University

5.1.1 Effect of ageing temperature on properties of NR vulcanisates

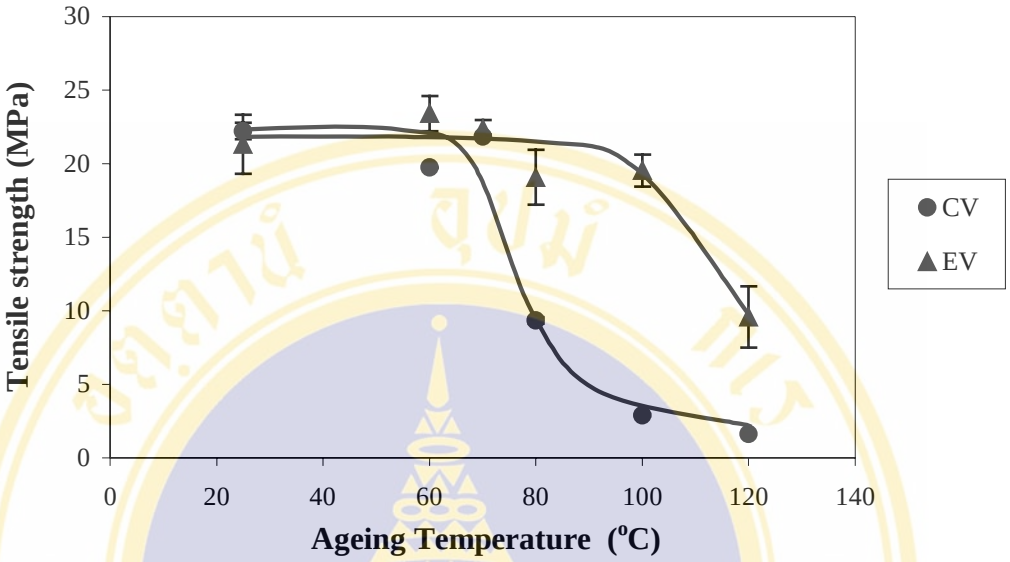


Figure 5.1 Effect of ageing temperature on tensile strength of NR cured with CV and EV systems.

Figure 5.1 represents the effect of ageing temperature on tensile strength of NR cured with CV and EV systems. It is observed that, at ageing temperature lower than 70°C, tensile strength of both NR vulcanisates is not dependent on vulcanisation system. This might be explained by an insufficient thermal history to break the polysulfidic linkages of the vulcanisates cured with CV system or mono- and disulfidic linkages of those with EV system. In addition, it is evident that tensile strength of NR vulcanisates shows sharp drops at ageing temperatures of approximately 70°C and 100°C for CV and EV systems, respectively. Theoretically, the decrease in tensile strength can occur from two main mechanisms that are chain-scission and too-high crosslink density of vulcanisates. The former gives a reduction in molecular weight and thus molecular entanglement while the latter results in the reduction in energy dissipation via the molecular mobility restriction. As for the chain-scission effect, it is known that polysulfidic linkages having relatively low bond strength is dominant in CV system while monosulfidic or di-sulfidic linkages having relatively strong bond strength is dominant in EV system. As a consequence, there are

Copyright by Mahidol University

relatively poor and relatively good thermal resistances in the vulcanisates cured with CV and EV system, respectively [57].

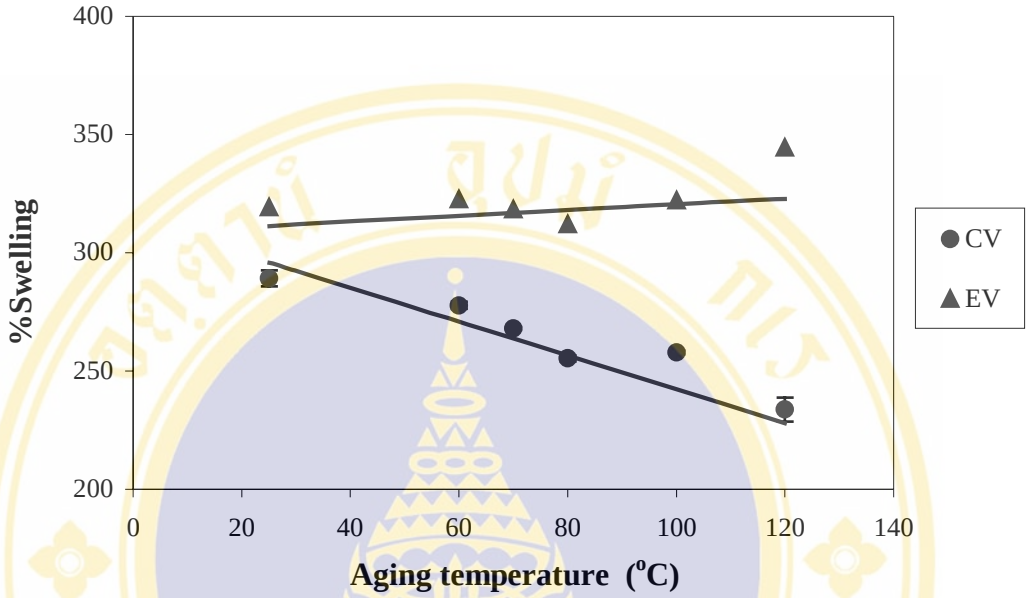


Figure 5.2 Effect of ageing temperature on %swelling of NR cured with CV and EV systems

Apart from the linkage type, the crosslink density could play strong role in tensile properties as illustrated in Figure 5.2. It is evident that the %swelling, as an indicator for crosslink density, of NR vulcanisates cured with EV system is higher than that of the vulcanisates cured with CV system, which means the vulcanisates cured with CV system has higher crosslink density than those cured with EV system at any given ageing temperature. This result can be explained by the amount of sulphur added to the vulcanisates, which is larger in case of the vulcanisates cured with CV system. Also, the %swelling of the specimens cured with CV system decreases as ageing temperature increases. This phenomenon might be explained by the post-curing effect, which tends to increase if ageing temperature increases [58]. The increase in crosslink density via the post-curing effect causes the sharp drop in tensile strength since the density of crosslink is too-high for energy dissipation via the molecular mobility (i.e. from zone 2 to zone 3 in Figure 5.3).

Copyright by Mahidol University

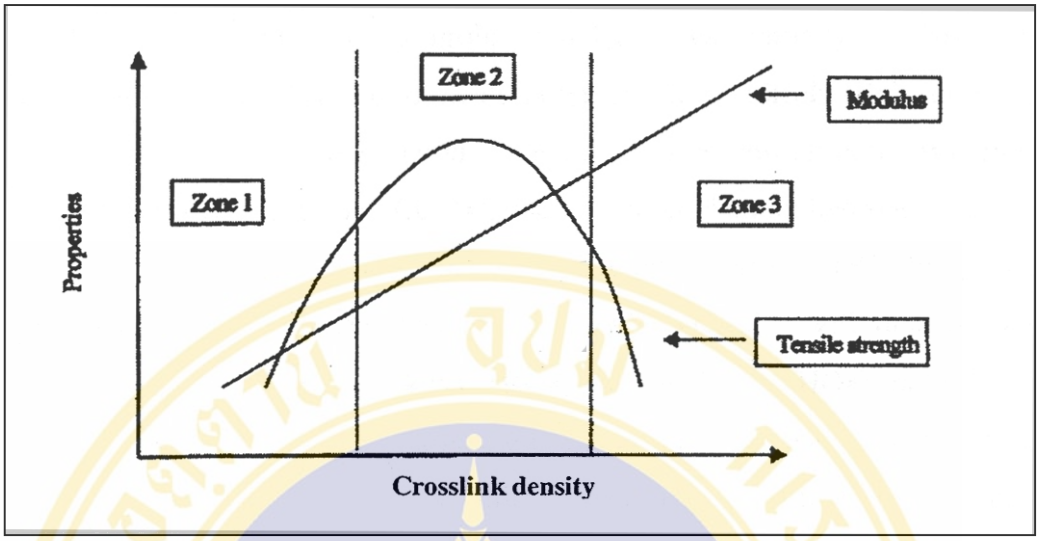


Figure 5.3 Sketch of relationship between crosslink density and tensile strength properties [59]

The influence of crosslink density on tensile strength of NR and SBR vulcanisates has been studied by Naris and Teh [60]. They found that the tensile properties increase with increasing amount of crosslink density until the critical crosslink density is reached. Beyond this crosslink density, the tensile properties decrease as a function of crosslink density as represented in Figure 5.3. Similarly, Bristow and Tiller found that properties such as resilience, tensile strength, and energy to break improve substantially in some sulphur-cured NR, as the crosslink density increases [61]. The tensile strength firstly increases and subsequently decreases with crosslink density.

By contrast, in NR cured with EV system, it is observed from Figure 5.2 that the %swelling marginally increases, as ageing temperature increases. At high ageing temperature, the chain-scission in the vulcanisates cured with EV system seems to override the post-curing effect. The result of swelling test agrees well with the tensile strength result shown earlier in Figure 5.1.

Copyright by Mahidol University

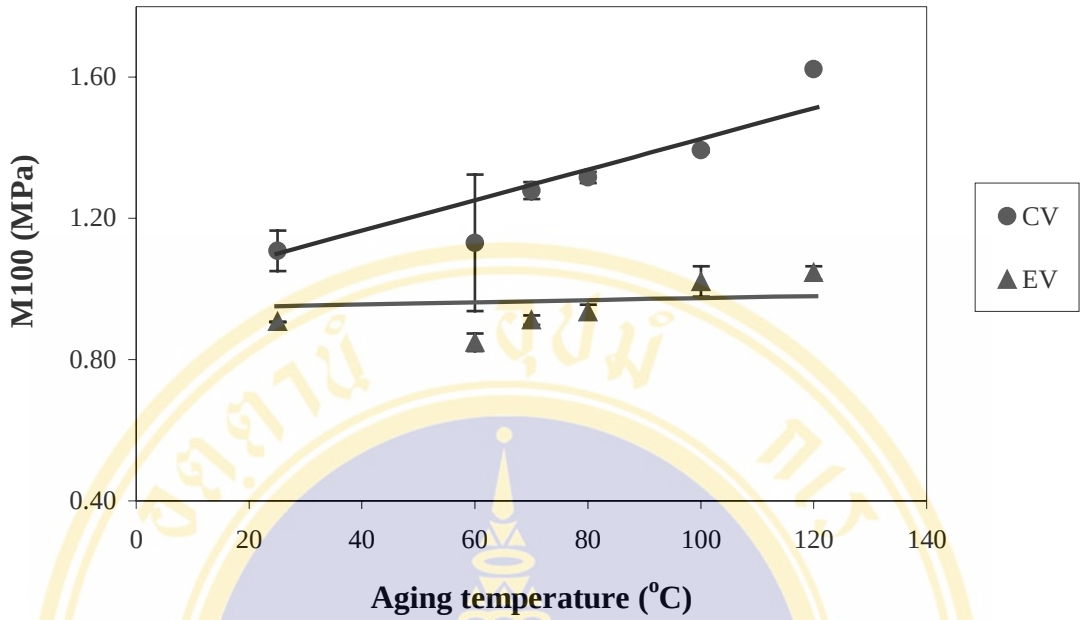


Figure 5.4 Effect of ageing temperature on modulus at 100% elongation (M100) of NR cured with CV and EV systems

Figure 5.4 illustrates the effect of ageing temperature on modulus at 100% elongation (M100) of NR cured with CV and EV systems. In theory, M100 is found to depend on crosslink density, as shown in Figure 5.3, so M100 could be another indicator for tracking the change in crosslink density after thermal oxidative ageing. It is evident that M100 of the specimens cured with CV system is higher than that of the specimens cured with EV system, which supports the proposed explanation that the NR vulcanisates cured with CV system has higher crosslink density than EV system at any given ageing temperature. Moreover, M100 of the vulcanisates cured with CV system increases as the ageing temperature increases. This can be explained by the post-curing effect as discussed previously. Unexpectedly, M100 of the specimens cured with EV system does not obviously change with increasing ageing temperature. The unexpected result is believed to be due to the insufficient sensitivity of M100 to a crosslink density.

In order to support the proposed explanation, the dynamic properties determined from a dynamic mechanical thermal analyser are used. In the rubbery region, rubber is neither purely elastic nor purely viscous in its dynamic behaviour, i.e., during the deformation, elastomeric materials store some portion of energy and dissipate the

Copyright by Mahidol University

other portion. Generally, the elastic component (E') represents the immediate response to the applied force while the viscous component (E″) represents energy dissipated as heat. The amount of offset between the measured stress and applied strain is a direct measure of a phase lag (δ). A tangent of phase lag (tanδ) or hysteresis factor is defined as the ratio of E″ to E', and therefore is a measure of the energy dissipated by various processes, such as molecular mobility [62-63], breakdown and reformation of the filler particles [63] or slippage of rubber molecules under high strain amplitudes [64]. In the present work, two main points of dynamic mechanical properties are of interest. The first point is a storage modulus (E') at 15°C, which is an elastic response corresponding directly to the crosslink density of rubber in the rubbery state. The other is a $\tan\delta_{max}$, which can be related to the crosslink density of rubber. In other words, the results of dynamic mechanical properties will be used to support the result of crosslink density determined from the swelling test.

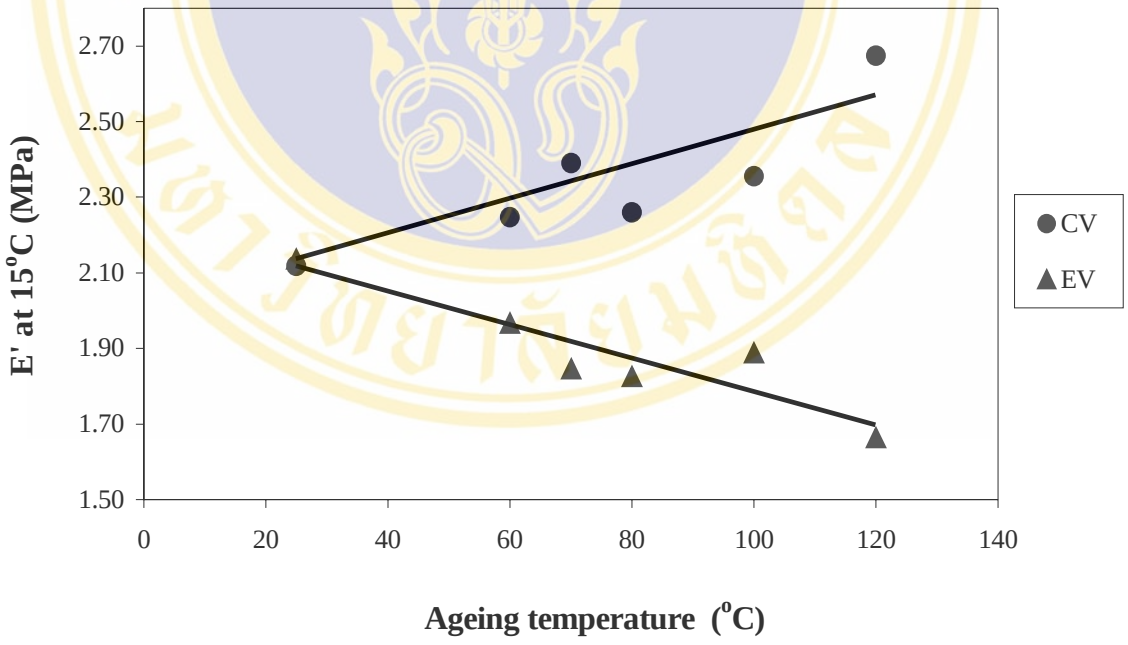


Figure 5.5 Effect of ageing temperature on E' at 15°C of NR cured with CV and EV systems

The E' and $\tan\delta_{max}$ of the NR vulcanisates, as a function of ageing temperature are illustrates in Figures 5.5 and 5.6, respectively. It is evident from Figure 5.5 that E' of the vulcanisates cured with CV system increases whereas that of the vulcanisates cured with EV system decreases with increasing ageing temperature. The increase of

Copyright by Mahidol University

E' can be explained by the post-curing effect, which takes place during thermal oxidative ageing, as discussed previously. By contrast, the decrease in E' of the vulcanisates cured with EV system results from the chain-scission dominating over the post-curing effect of vulcanisates.

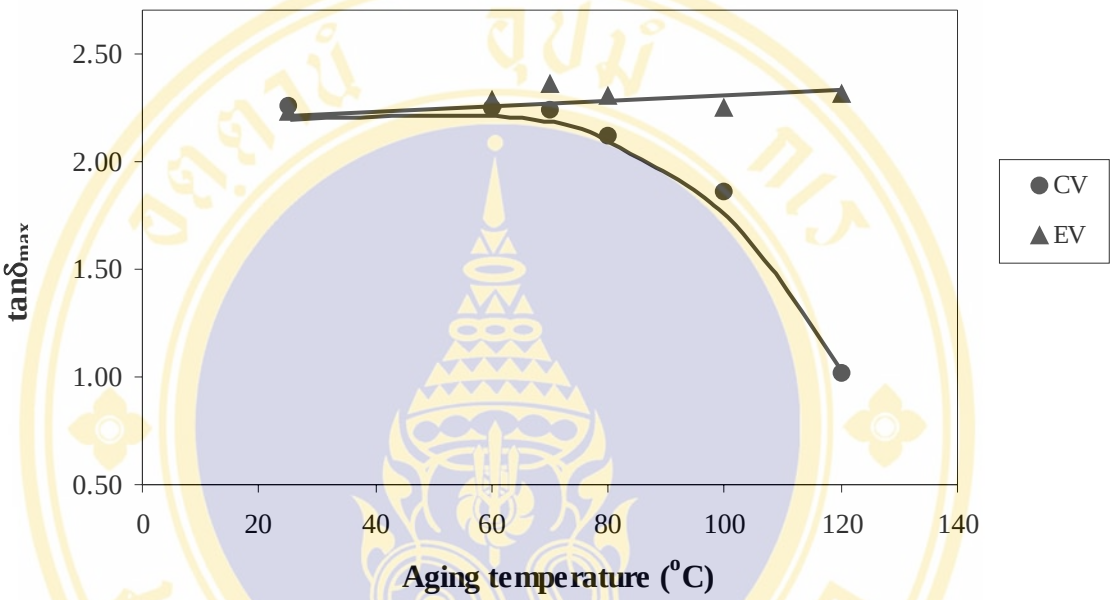


Figure 5.6 Effect of ageing temperature on $tan\delta_{max}$ of NR cured with CV and EV systems

Figure 5.6 demonstrates the effect of ageing temperature on $tan\delta_{max}$ of NR cured with CV and EV systems. Normally, $tan\delta_{max}$ depends on crosslink density, i.e., $tan\delta_{max}$ decreases with increasing crosslink density due to the increases in molecular restriction via intermolecular linkages. It is evident that $tan\delta_{max}$ of the vulcanisates cured with CV system decreases as ageing temperature increases, clearly supporting the increase in crosslink density by post-curing effect. On the contrary, the increase in $tan\delta_{max}$ of the vulcanisates cured with EV system with ageing temperature is attributed to the increase in molecular mobility via the chain-scission of rubber vulcanisates.

Copyright by Mahidol University

5.1.2 Effect of ageing time on properties of NR vulcanisates

In some cases, the products of NR vulcanisates are subjected to high temperature, which may change the properties of NR vulcanisates. Therefore, it is necessary to study the effect of ageing time on ageing properties of NR vulcanisates. Figure 5.7 illustrates the influence of ageing time on tensile strength of NR cured with CV and EV systems. Referred to the results of ageing time effect on tensile strength, the test temperatures of 70 and 100^{o}C are selected for the ageing time test of specimens cured with CV and EV systems, respectively. It is evident that the onset of sharp drops of tensile strength in vulcanisates with CV system is observed at ageing time of 4 days while tensile of vulcanisates with EV system drops progressively with increasing ageing time. The change in tensile strength at ageing time beyond 4 days illustrates the greater thermal stability of the monosulfidic linkages in the vulcanisates cured with EV system. The change in tensile strength can be explained by the alteration in crosslink density, as mentioned previously. With CV system, the post-curing effect would increase the crosslink density and therefore the excessive crosslink density would decrease the tensile strength (see also Figure 5.3). Evidence of an increase in crosslink density as a function of ageing time is shown in Figure 5.8 in terms of %swelling. It can be seen that %swelling of the vulcanisates cured with CV system decreases with increasing ageing time because of the post-curing effect. In the case of the vulcanisates cured with EV system, there is a slight increase in %swelling as ageing time increases, indicating the decrease in crosslink density and/or the increase in chain-scission of the vulcanisates. The disruption of carbon-carbon NR molecules leads to a main chain-scission while that of intermolecular scission causes the scission of carbon-sulphur bond. Because the bond energy of carbon-carbon bond is higher than that of carbon-sulphur bond, as demonstrated in Table 5.1, the degradation of NR vulcanisates should dominantly occur at the carbon-sulphur linkages. As a consequence, the progressive decrease in tensile strength with ageing time as illustrated in Figure 5.7 is believed to be due mainly to the thermal degradation at sulphur linkages rather than the chain-scission of NR main-chain.

Copyright by Mahidol University

Table 5.1 Sulphur versus peroxides bond strength [24]

Bond types	Cure system	Bond strength (kJ / mol)
C-C	Peroxide	350
C-S	Low sulphur	285
S-S	Traditional sulphur cure	115 to 270

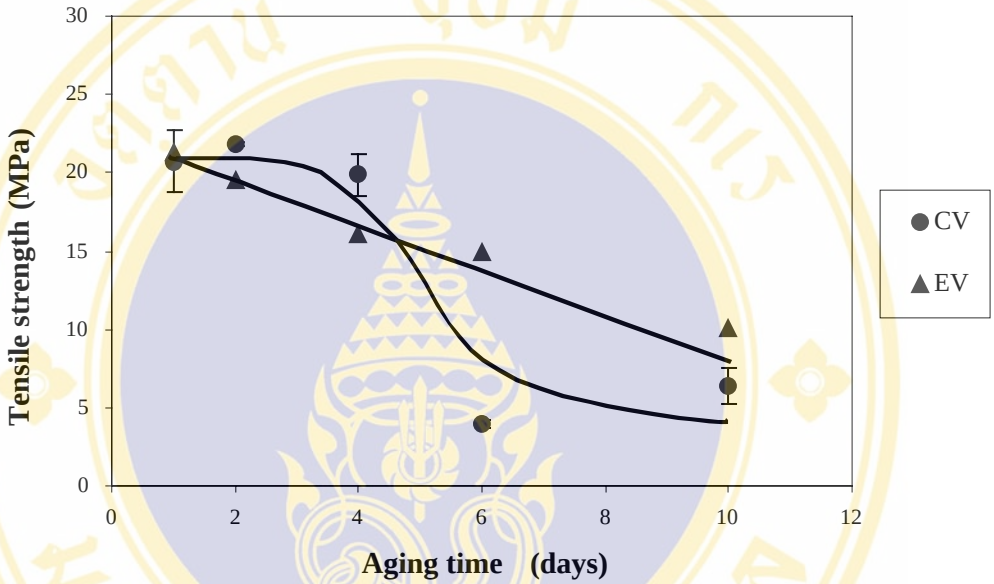


Figure 5.7 Effect of ageing time on tensile strength of NR cured with CV and EV systems

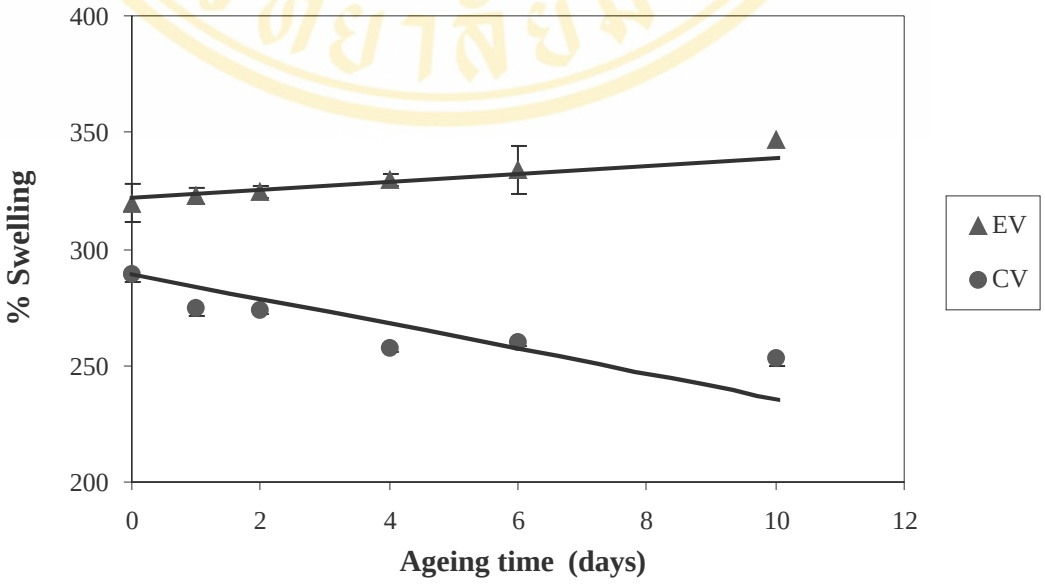


Figure 5.8 Effect of ageing time on %swelling of NR cured with CV and EV systems

Copyright by Mahidol University

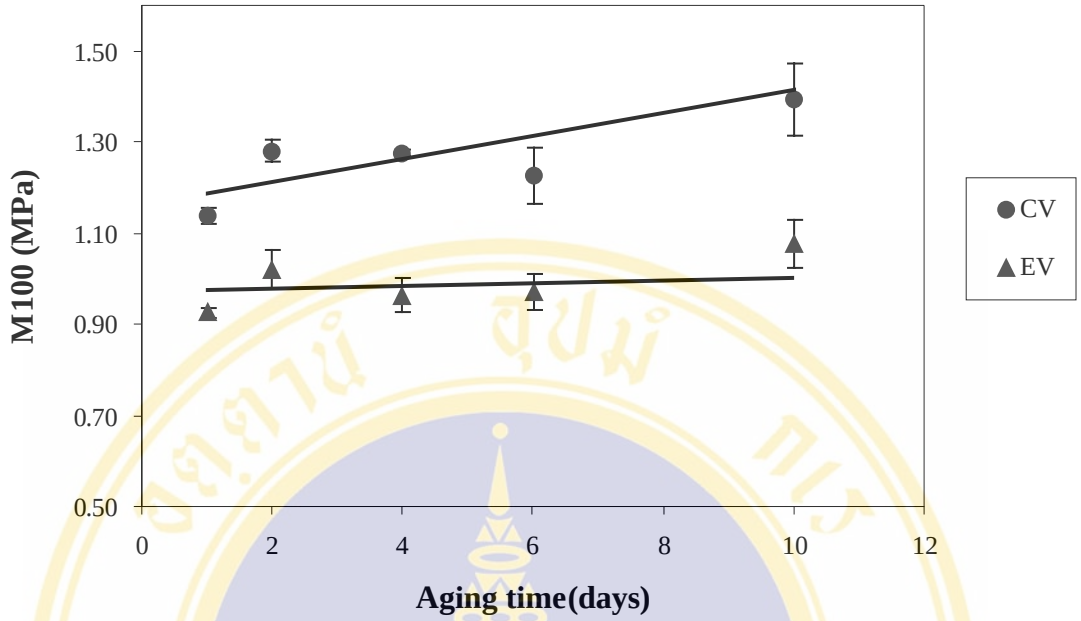


Figure 5.9 Effect of ageing time on M100 of NR cured with CV and EV system

Figure 5.9 represents M100 of NR vulcanisates cured with CV and EV systems as a function of ageing time. It is evident that M100 of the vulcanisates cured with CV system increases as ageing time increases while the M100 of the specimens cured with EV system does not significantly change with increasing ageing time. This phenomenon agrees with the change in crosslink density, the higher the crosslink density, the greater the M100, as mentioned previously. However, the unchange in the M100 in the vulcanisates cured with EV system might be due to the change in crosslink density is insufficient to influence the M100 as previously mentioned in Figure 5.4.

Figure 5.10 demonstrates the effect of ageing time on E' at 15^{o}C determined from dynamic mechanical properties of NR cured with CV and EV systems. It is evident that E' of the specimens cured with CV system increases while that of the specimens cured with EV system decreases as ageing temperature increases. The change in E' could be explained by the post-curing and linkages scission for vulcanisates cured with CV and EV systems, respectively, as discussed earlier.

Copyright by Mahidol University

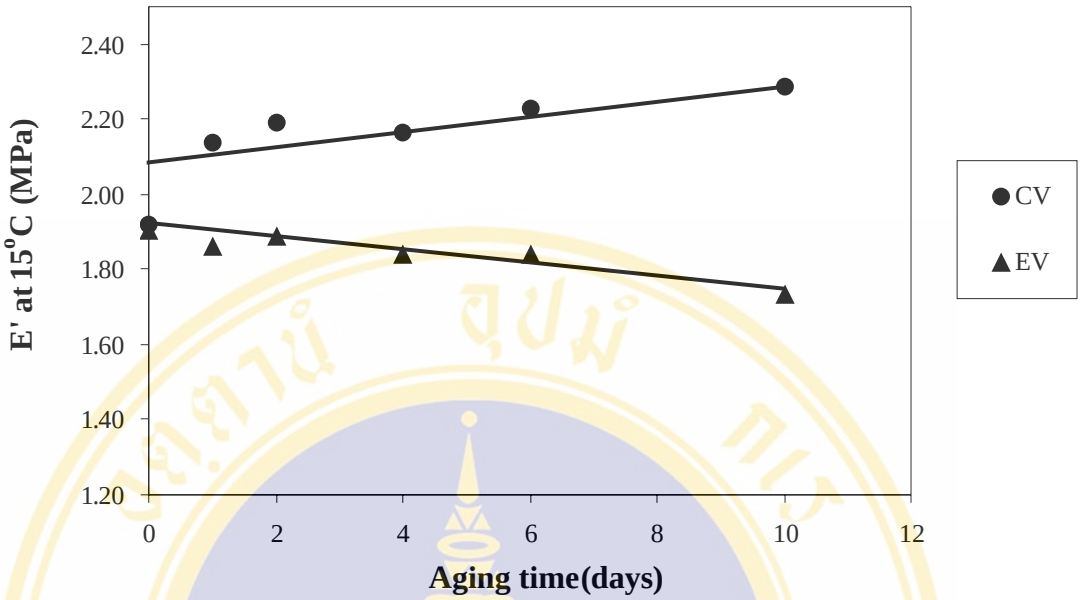


Figure 5.10 Effect of ageing time on E' at 15°C of NR cured with CV and EV systems

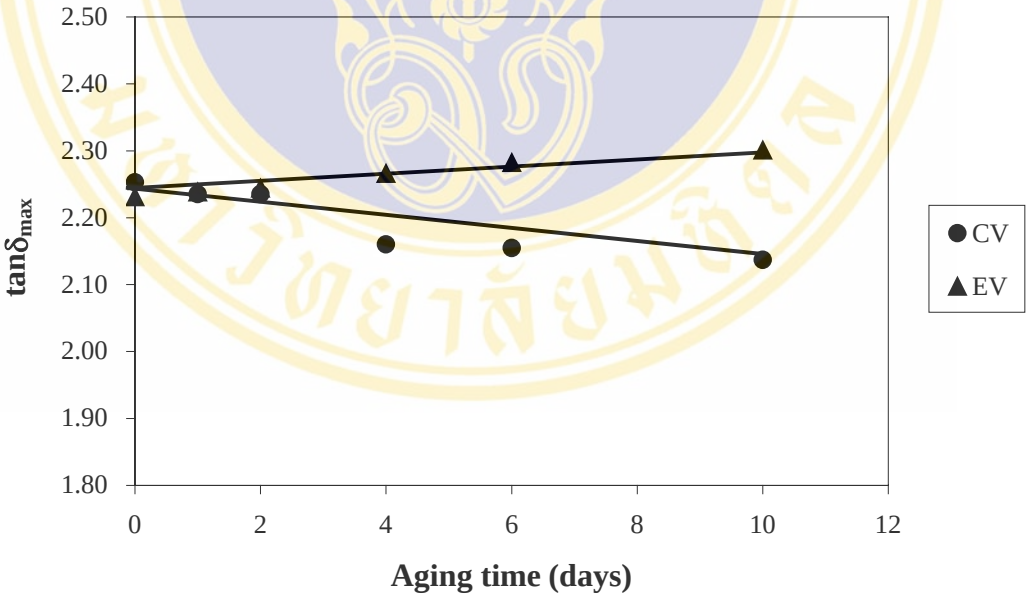


Figure 5.11 Effect of ageing time on $\tan\delta_{max}$ of NR cured with CV and EV systems

Figure 5.11 illustrates the effect of ageing time on $\tan\delta_{max}$ of NR cured with CV and EV systems. It is evident that $\tan\delta_{max}$ of the vulcanisates cured with CV system decreases as ageing time increases, which supports the post-curing effect. Likewise, the increase in $\tan\delta_{max}$ with ageing time of the specimens cured with EV system is in

Copyright by Mahidol University

good agreement with the proposed explanation based on a linkages scission as mentioned earlier.

Copyright by Mahidol University

5.2 Effect of antioxidant on ageing properties of NR vulcanisates

5.2.1 Effect of types of antioxidant

Usually, there are several kinds of commercial antioxidants used in the rubber industries, and different antioxidants have different efficiencies in degradation protection, depending mainly on their functional groups. Therefore, the effect of types and amount of antioxidant on ageing properties of NR vulcanisates is necessary to be investigated. In some cases, a simple antioxidant is sufficient to resist ageing, but sometimes a combination of several kinds of antioxidants is required, usually known as the synergistic system. In this work, 6-PPD, TMQ, BHT and the combined system of 6-PPD and TMQ were investigated on their ageing protection. The results are demonstrated in terms of tensile properties, dynamic mechanical properties and also crosslink density. Based on tensile strength results, the suitable antioxidant is then selected and used for subsequent study for the reinforcing filler effect on ageing properties. Each of the prepared vulcanisates is abbreviated using the codenames, which are represented in Table 5.2.

Copyright by Mahidol University

Table 5.2 Sample codename of specimens used in the study of antioxidant effect

Sample codename	Curing system	Antioxidant concentration (phr)		
		TMQ	6-PPD	BHT
A	CV	-	-	-
B	CV	2	-	-
C	CV	-	2	-
D	CV	-	-	2
E	CV	1	1	-
F	CV	2	2	-
G	EV	-	-	-
H	EV	2	-	-
I	EV	-	2	-
J	EV	-	-	2
K	EV	1	1	-
L	EV	2	2	-

Copyright by Mahidol University

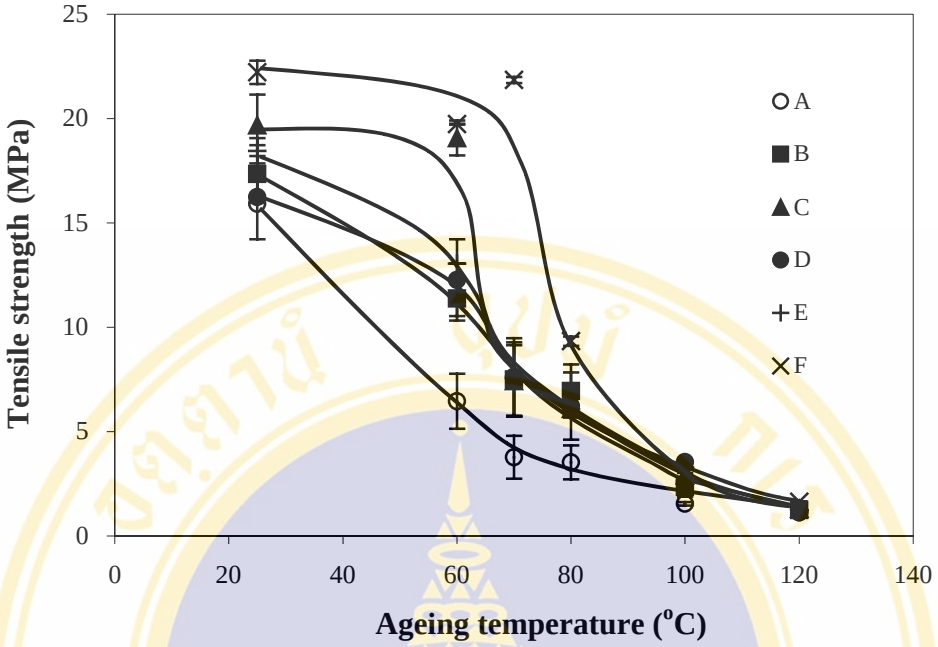


Figure 5.12 Effect of ageing temperature on tensile strength of NR vulcanisates cured with CV system filled with various antioxidants

Figure 5.12 shows the effect of ageing temperature on tensile strength of the vulcanisates cured with CV system filled with various antioxidants. It is clear that antioxidant affects strongly the tensile strength of NR vulcanisates. At any given ageing temperature, tensile strength of vulcanisates with antioxidants is much higher than the control vulcanisate (sample A). As for the mechanism of antioxidant action, the antioxidant can inhibit the polymer degradation process by scavenging the free-radical intermediate, i.e., polymer chain and hydroperoxide, in the system via hydrogen abstraction followed with chain transfer reaction. Then, a new stable radical product, which could not initiate further oxidation of polymer chain, is generated [65]. Moreover, the tensile strength of sample F is highest, followed by that of samples C, E, B and D, respectively. This is due to sample F has the largest concentration of antioxidant used (4 phr). The decreases in tensile strength with increasing ageing temperature are observed in all vulcanisates. The sharp drop at ageing temperature higher than 60^{o}C can be explained by the change in crosslink density as shown in Figure 5.13.

Copyright by Mahidol University

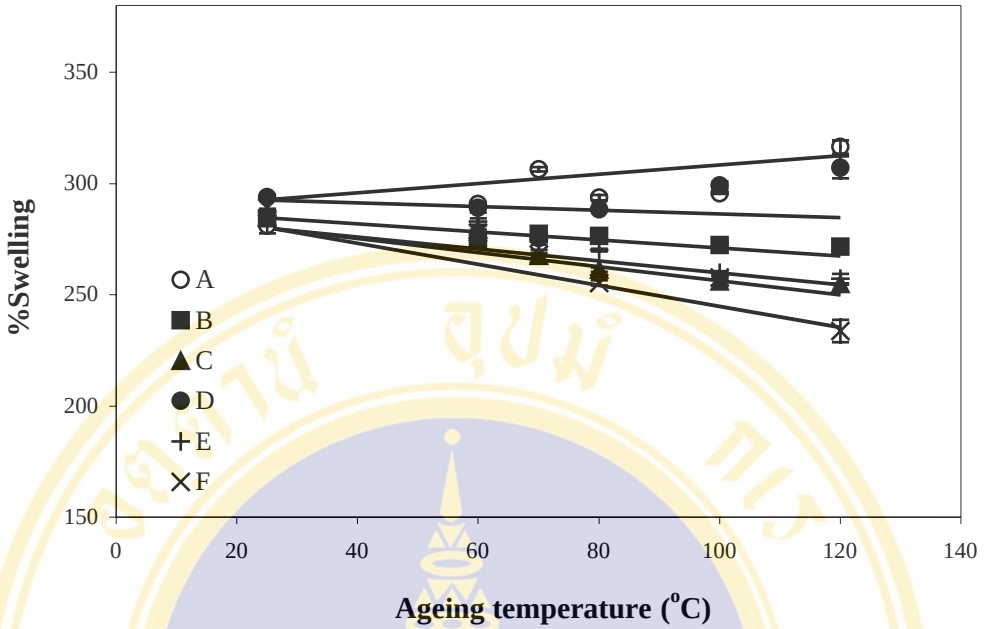
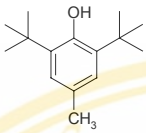
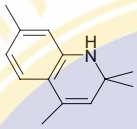
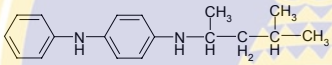


Figure 5.13 Effect of ageing temperature on %swelling of NR vulcanisates cured with CV system filled with various antioxidants

It is found from Figure 5.13 that %swelling of the specimens with antioxidant is lower than that without antioxidant, implying a reduction in chain-scission of NR vulcanisates provided by the antioxidant during thermal oxidative ageing. In addition, it is observed that %swelling of sample A slightly increases as ageing temperature increases while vulcanisates with antioxidants decreases with increasing ageing temperature. As mentioned previously, thermal oxidative ageing leads to the occurrence of two competitive phenomena, which are post-curing and molecular chain-scission. The addition of antioxidant tends to override the molecular chain-scission by the post-curing effect. In other words, the decrease of %swelling of the vulcanisates with antioxidant is believed to be caused by the post-curing effect. On the other hands, the increase in %swelling of sample A can be explained by the molecular chain-scission effect dominating over the post-curing effect. Moreover, %swelling of sample D is higher than that of samples B, E, C and F, respectively.

Copyright by Mahidol University

Table 5.3 Structure and reactivity of antioxidants used in the study

Antioxidant name	Structure	Chemical structure	Relative reactivity
BHT (phenolic)		Phenol	Low
TMQ (amine)		Conjugated benzene ring	Medium
6-PPD (diamine)		Linear and conjugated benzene ring	High

The results can be explained by the difference in chemical structure and reactivity of each antioxidant as shown in Table 5.3. Then, it can be deduced that the efficiency of 6-PPD to protect molecular chain-scission is higher than that of TMQ and BHT, respectively. This is due to the fact that the 6-PPD with linear structure and conjugated benzene ring possesses higher reactivity to react with free radicals than TMQ and BHT, respectively [66]. In addition, %swelling of sample E is higher than that of sample C indicating the lower efficiency to protect the molecular chain-scission of the combined system of TMQ and 6-PPD. In other words, the combination of 6-PPD and TMQ does not show any synergistic effect on thermal stabilisation. The decrease in protection degradation efficiency can be explained that the dilution of 6-PPD with high efficiency of thermal stabilisation by TMQ with low thermal stabilisation efficiency. By contrast, %swelling of sample F is lowest, which might be due to the highest concentration of antioxidant used. The results from %swelling, as shown in Figure 5.13, are harmonized with tensile strength illustrated in Figure 5.12. Tensile strength of sample F is highest due to the largest of total antioxidant concentration. The sharp drop of tensile strength of vulcanisates with antioxidant is attributed to the excess of crosslink density occurring during thermal oxidative ageing,

Copyright by Mahidol University

which reduces the energy dissipation process. On the other hand, the sharp drop of tensile strength found in sample A can be explained by the occurrence of molecular chain-scission, which tends to reduce the crosslink density of such vulcanisates.

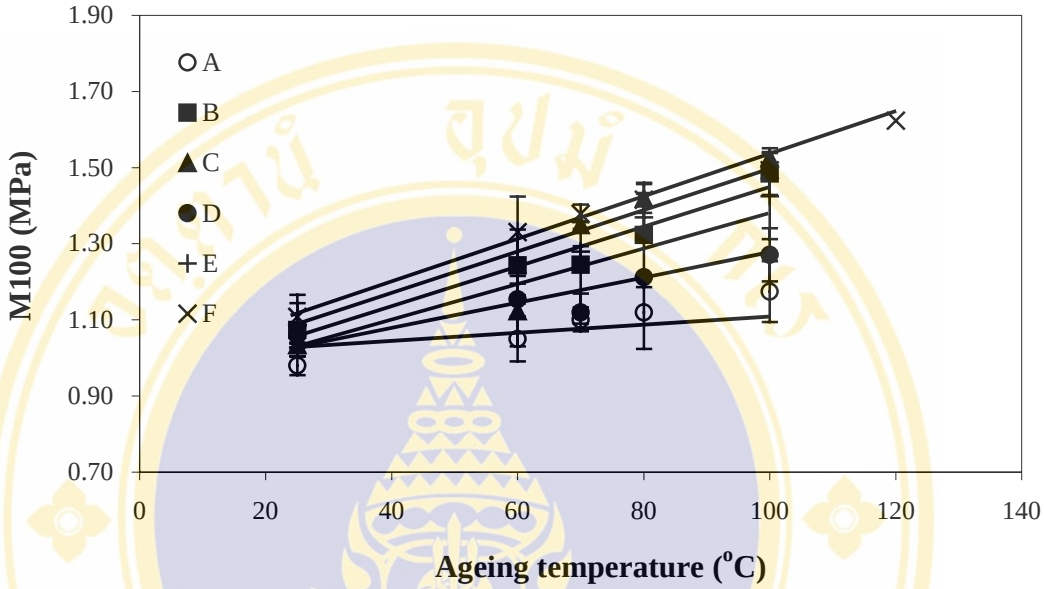


Figure 5.14 Effect of ageing temperature on M100 of NR vulcanisates cured with CV system filled with various antioxidants

Figure 5.14 shows the effect of ageing temperature on M100 of NR vulcanisates cured with CV system filled with various antioxidants. It is evident that M100 increases as ageing temperature increases for specimens with antioxidant. This result can be explained by the increase in crosslink density via the post-curing during thermal oxidative ageing as discussed in the result of %swelling as demonstrated in Figure 5.13. M100 of sample A is found to be lower than those with antioxidant due to a molecular chain-scission override the post-curing effect. Also, M100 of sample F appears to be higher than those with samples C, E, B and D, respectively, which can be explained by the highest degree of crosslink density of such vulcanisates, as shown previously in Figure 5.13.

Copyright by Mahidol University

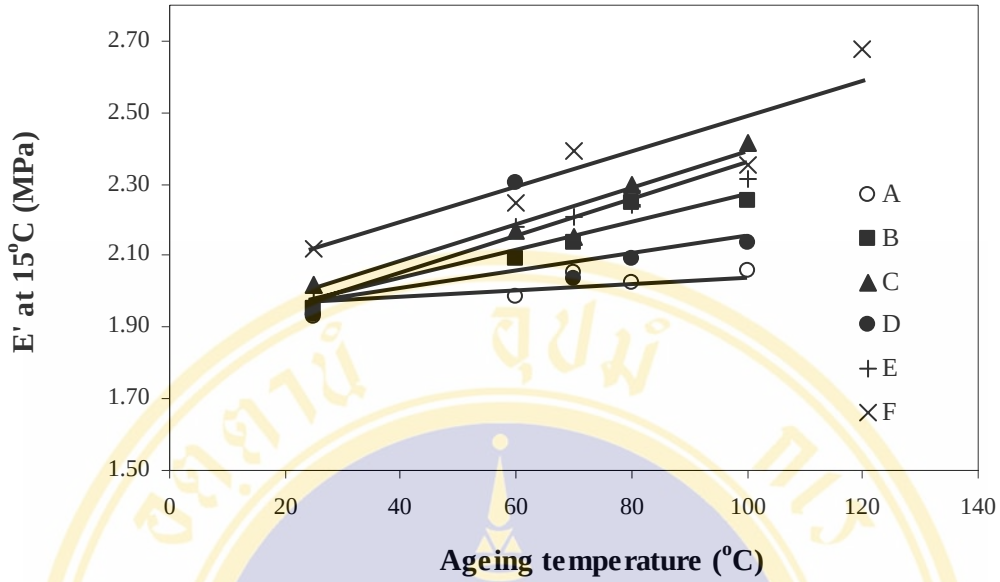


Figure 5.15 Effect of ageing temperature on E' at 15°C of NR vulcanisates cured with CV system filled with various antioxidants

In order to determine the effect of crosslink density on modulus more precisely, the storage modulus (E') and $\tan\delta_{max}$ determined from DMTA were measured, and the results are shown in Figures 5.15 and 5.16, respectively. Figure 5.15 shows that E' increases as ageing temperature increases, supporting the occurrence of the post-curing effect during thermal oxidative ageing, as mentioned previously in Figure 5.13. In the case of sample A, it is observed that E' is the lowest due to the greater extent of molecular chain-scission during thermal oxidative ageing. Moreover, it is found that E' of sample F is the highest because of the greatest crosslink density.

Copyright by Mahidol University

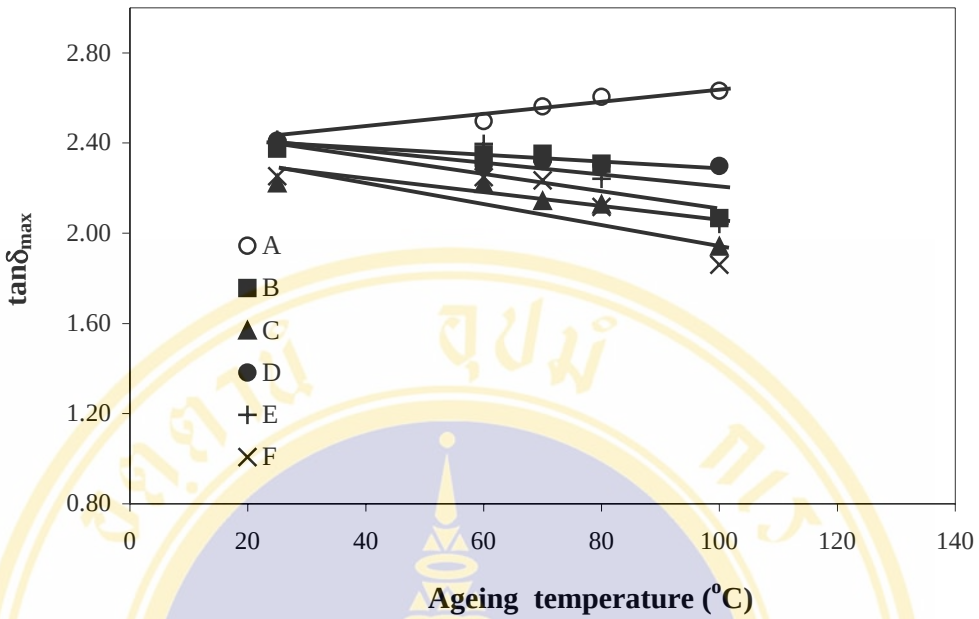


Figure 5.16 Effect of ageing temperature on $tan\delta_{max}$ of NR vulcanisates cured with CV system filled with various antioxidants

Figure 5.16 exhibits a change in $tan\delta_{max}$ of vulcanisates with and without antioxidant as a function of ageing temperature. It is clear that $tan\delta_{max}$ of vulcanisates with antioxidant tends to decrease as ageing temperature increases, supporting the post-curing effect. In the case of sample A, $tan\delta_{max}$ increases as ageing temperature increases, which implies the dominant molecular chain-scission over the post-curing effects.

Copyright by Mahidol University

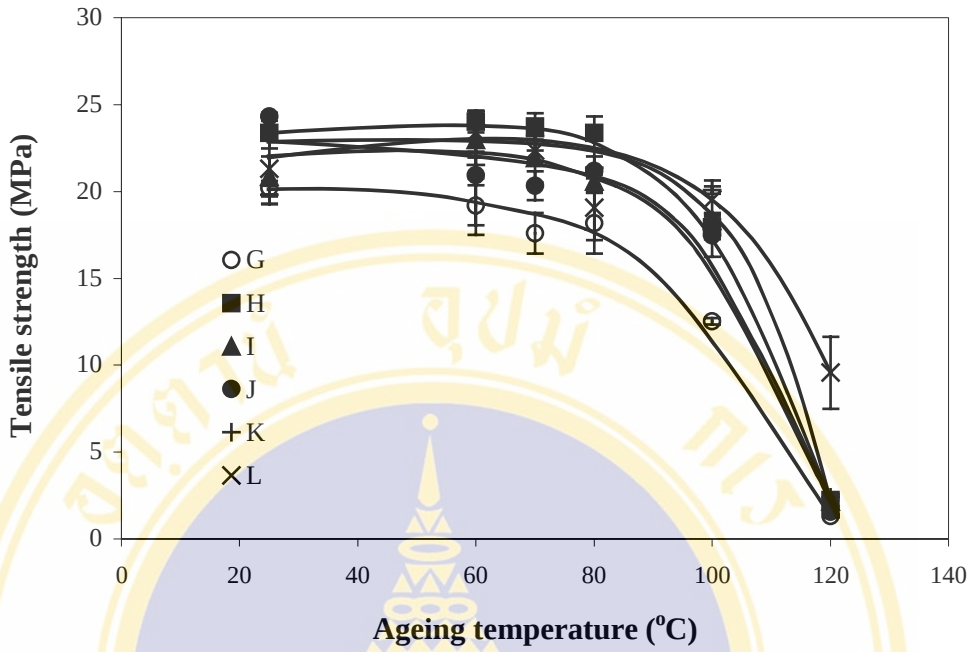


Figure 5.17 Effect of ageing temperature on tensile properties of NR vulcanisates cured with EV system filled with various antioxidants

In the case of antioxidant effect on tensile strength in NR vulcanisates cured with EV system, it is observed from Figure 5.17 that the tensile strength of specimens with antioxidants is significantly higher than that of sample G (i.e., vulcanisates without antioxidant), which in similar to the case of CV system. Also, tensile strength of vulcanisates with various types of antioxidant is not significantly different. Notably, tensile strength of vulcanisates cured with EV system shows sharp drop at ageing temperature higher than 80°C and 100°C for vulcanisates without and with antioxidant, respectively. The result implies that the thermal stabilization via tensile strength provided by antioxidant in the vulcanisates with EV system is independent of antioxidant types. To explain the result, a determination of crosslink density is carried out via a measurement of %swelling, and the result is shown in Figure 5.18.

Copyright by Mahidol University

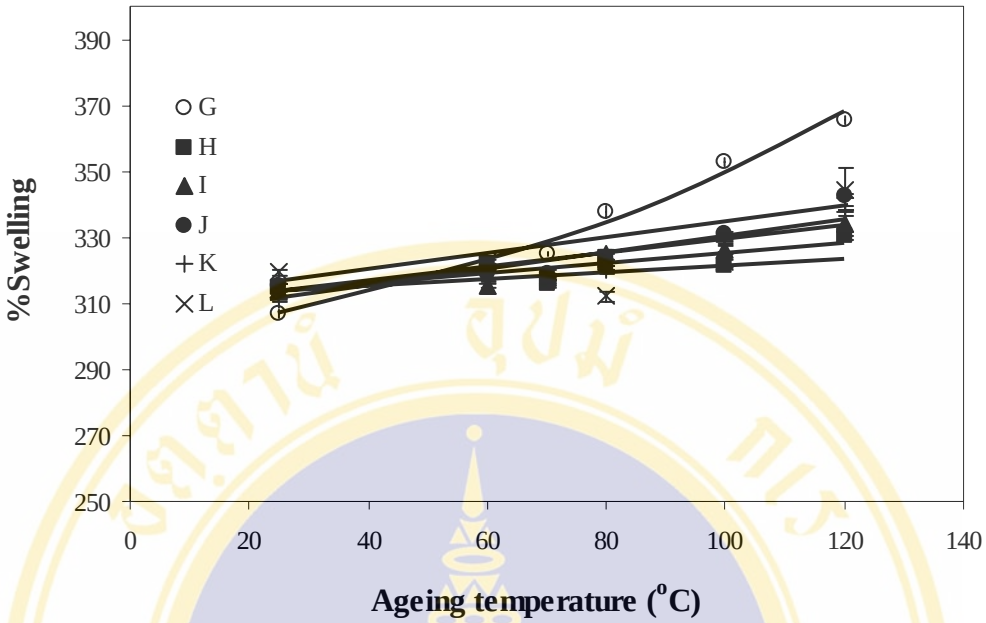


Figure 5.18 Effect of ageing temperature on %swelling of NR vulcanisates cured with EV system with various antioxidants

It is evident from Figure 5.18 that %swelling as an indicator for crosslink density of all specimens increases as ageing temperature increases due to the chain-scission dominated over the post-curing effect, as mentioned previously in the part of ageing conditions effect (section 5.1). The %swelling of sample G is higher than that of the other samples implying an antidegrading effect provided by an antioxidant, as mentioned previously. Clearly, the %swelling of vulcanisates with different types of antioxidants is not obviously different, supporting the independence of antioxidant on tensile strength shown earlier in Figure 5.17. Additionally, the %swelling of sample G tends to increase with increasing ageing temperature, particularly at the ageing temperature beyond 80°C, which agrees with the result of tensile strength as illustrated in Figure 5.17.

Copyright by Mahidol University

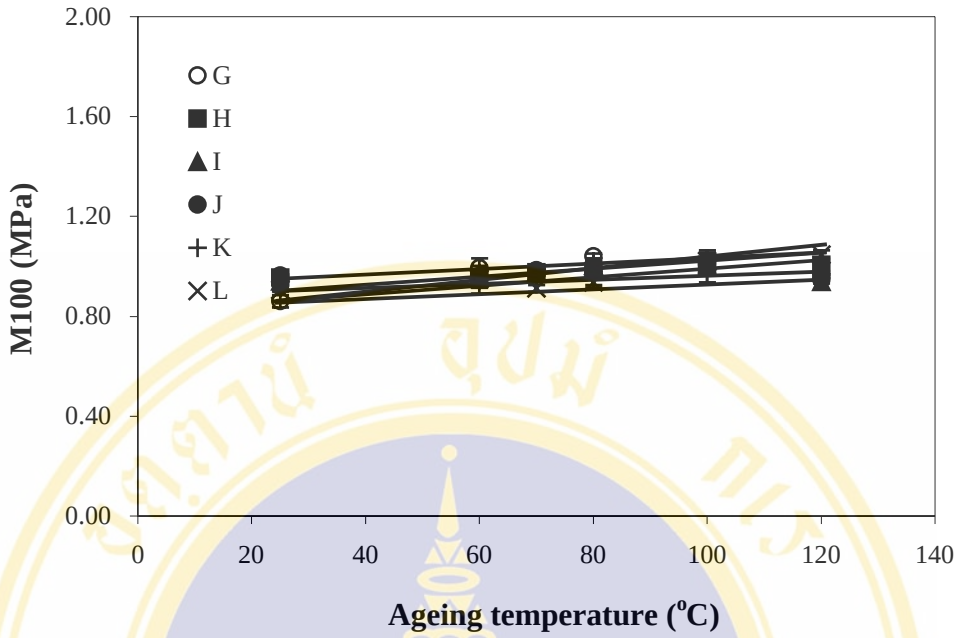


Figure 5.19 Effect of ageing temperature on M100 of NR vulcanisates cured with EV system filled with various antioxidants

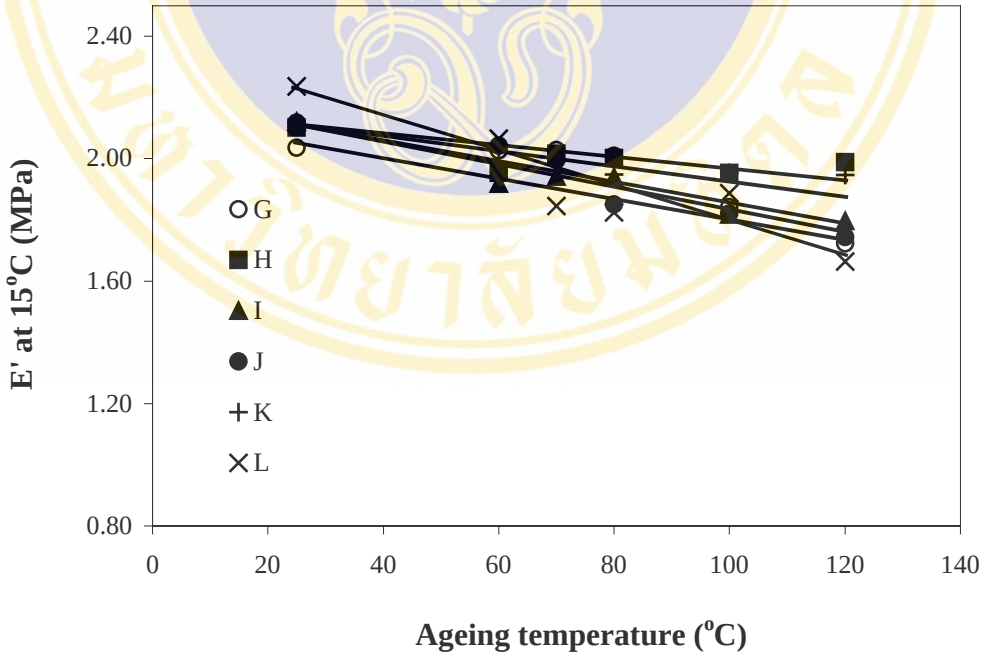


Figure 5.20 Effect of ageing temperature on E' at 15°C of NR vulcanisates cured with EV system filled with various antioxidants

Copyright by Mahidol University

Figure 5.19 illustrates that M100 of vulcanisates cured with EV system at any given ageing temperature are not significantly different. This result suggests that, in the EV system, M100 is not sufficiently sensitive to the change of crosslink density.

Figure 5.20 illustrates the effect of ageing temperature on E' of NR vulcanisates with various antioxidants in the EV system. It is obvious that E' supports the occurrence of the linkages scission of the vulcanisates, i.e., E' decreases with increasing ageing temperature, as mentioned previously in Figure 5.18. Furthermore, it is impossible to draw a clear relationship between antioxidant types, E' and crosslink density at any given ageing temperature.

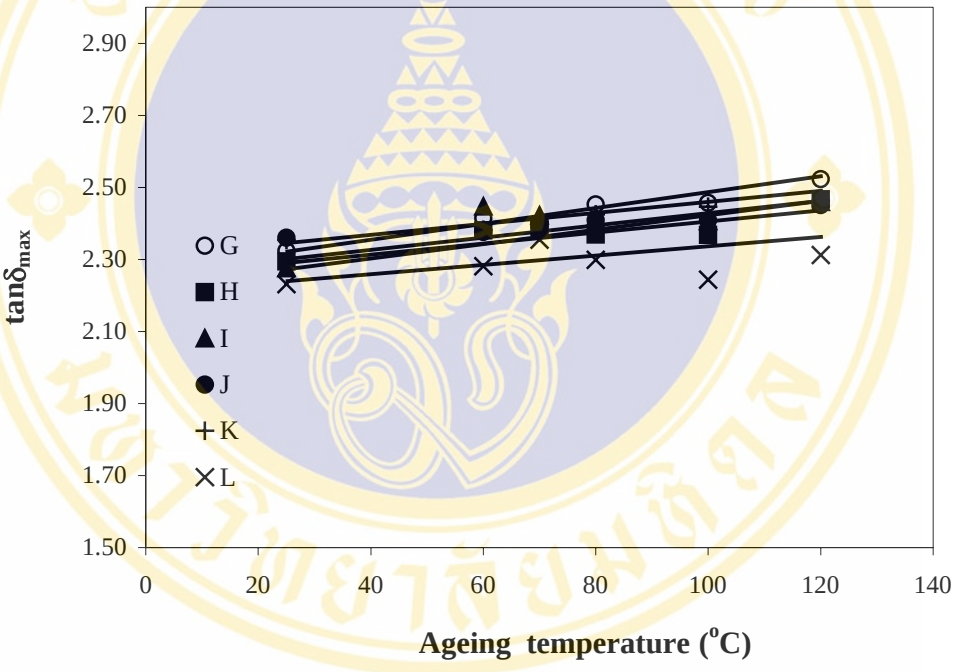


Figure 5.21 Effect of ageing temperature on $\tan\delta_{max}$ of NR vulcanisates cured with EV system filled with various antioxidants

Figure 5.21 demonstrates the $\tan\delta_{max}$ results of NR vulcanisates cured with EV system filled with various antioxidants. It is evident that $\tan\delta_{max}$ tend to increase as ageing temperature increases, which agrees with the occurrences of the linkages scission leading to the increase in molecular mobility. Moreover, $\tan\delta_{max}$ of all vulcanisates with antioxidant except for the sample L is not significantly different owing to a similar order of crosslink density, as shown previously in Figure 5.18. The

Copyright by Mahidol University

lowest $\tan\delta_{max}$ of sample L is believed to be due to the highest thermal oxidation resistance caused by the largest amount of antioxidant.

Copyright by Mahidol University

5.2.2 Effect of antioxidant concentration

From the results of antioxidant effect, it is evident that 6-PPD is an efficient antioxidant to protect NR from the molecular chain-scission. Therefore, the 6-PPD will be used as an antioxidant in this section by varying its concentration from 0.5 to 4 phr.

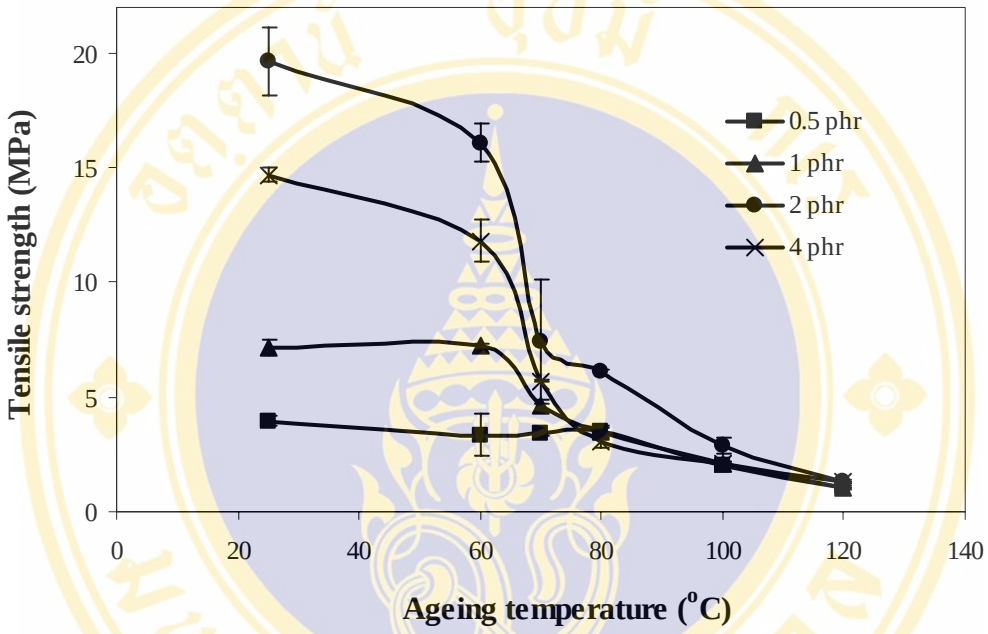


Figure 5.22 Effect of 6-PPD concentration on tensile strength of aged NR vulcanisates cured with CV system

Figure 5.22 demonstrates an effect of 6-PPD concentration on tensile strength of the vulcanisates cured with CV system. It is obvious that, at ageing temperature upto 60°C, tensile strength of NR vulcanisates cured with CV system depends strongly on 6-PPD concentration, i.e., tensile strength markedly increases with increasing concentration of 6-PPD content upto 2 phr. This implies the protection of rubber molecules from molecular chain-scission by antioxidant. Above 2 phr of 6-PPD, a drop in tensile strength could be observed, which might be explained by the cure retardation provided by an excess of 6-PPD [67]. When 6-PPD concentrations are over 2 phr, the excessive 6-PPD may interfere the crosslinking process by scavenging the free radicals, which are required to crosslink rubber molecules, yielding in a reduction

Copyright by Mahidol University

in crosslink efficiency. Thus, the optimum amounts of 6-PPD used for stabilising the rubber vulcanisates cured with CV system is 2 phr. In addition, the tensile strength of aged specimens shows sharp drops at ageing temperature higher than 60°C. This is due to the over crosslink density obtaining from the post-curing effect and thus a reduction in energy dissipation via molecular mobility. Nevertheless, a clear evidence of crosslink density increasing as a function of ageing time is shown in Figure 5.23.

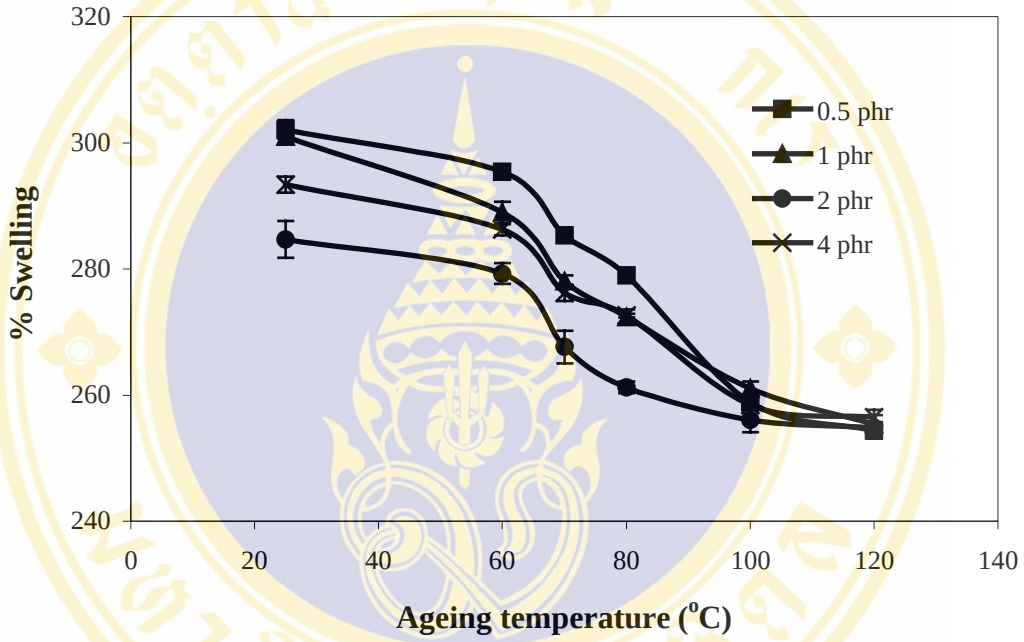


Figure 5.23 Effect of 6-PPD concentration on %swelling of aged NR vulcanisates cured with CV system

It is evident from Figure 5.23 that the %swelling of aged NR vulcanisates cured with CV system decreases with increasing 6-PPD concentration upto 2 phr due to the increase in antioxidant effect. Beyond 2 phr of antioxidant concentration, the %swelling appears to increase. In other words, the decrease in %swelling is due to an increase in crosslink density leading to greater retention of tensile strength as shown in Figure 5.22. The increase in %swelling at high antioxidant concentration of 4 phr indicates a decrease in crosslink density, which might be explained by the cure retardation effect by an excess of 6-PPD, as mentioned previously. The sharp drop of tensile strength at the ageing temperature of about 60°C is in good agreement with the drop in %swelling. Alternatively, an excessive crosslink density caused by the post-

Copyright by Mahidol University

curing effect is responsible for the drop in tensile strength at ageing temperature beyond 60°C. Moreover, if the increase in crosslink density is carefully considered, there are 2 main possible pathways. The first one is a further vulcanisation during thermal oxidative ageing by the excessive sulphur, remaining from the curing process. The other one is the conversion of sulphur linkages from polysulfidic to mono- or disulfidic linkages leading to the rise in crosslink density.

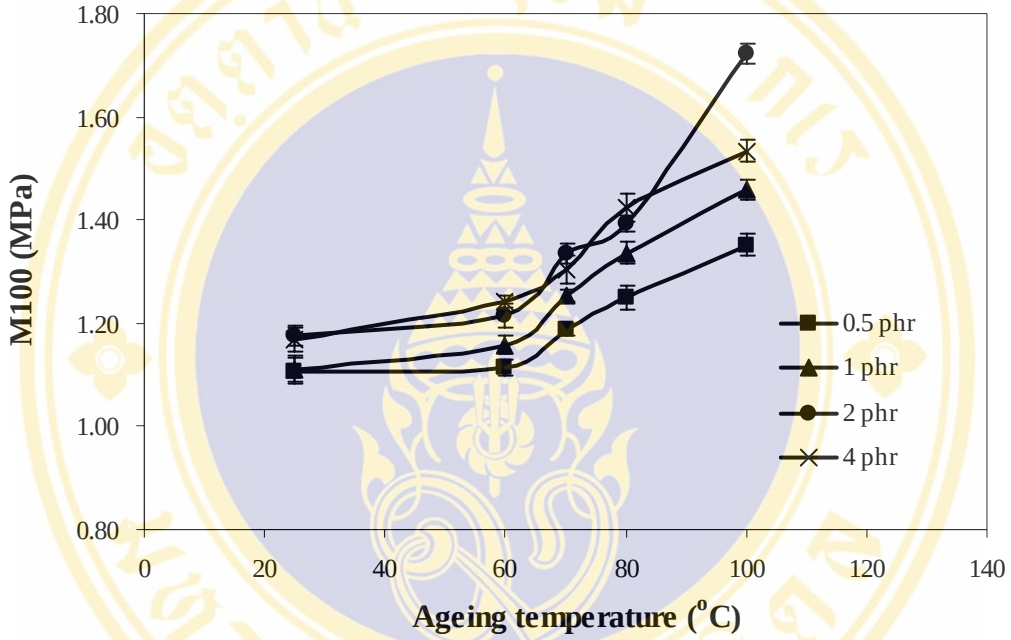


Figure 5.24 Effect of 6-PPD concentration on M100 of aged NR vulcanisates cured with CV system

Figure 5.24 shows the effect of 6-PPD content on M100 of aged NR vulcanisates cured with CV system. M100 appears to increase as 6-PPD concentration increases upto 2 phr because of the increase in crosslink density via the post-curing effect, according to the %swelling result. The drop in M100 at antioxidant concentration greater than 2 phr is certainly caused by a decrease in crosslink density as mentioned previously in Figure 5.23. Also, a sharp rise in M100 at the ageing temperature of about 60°C is in good agreement with an abrupt increase in crosslink density, as discussed in %swelling result.

Copyright by Mahidol University

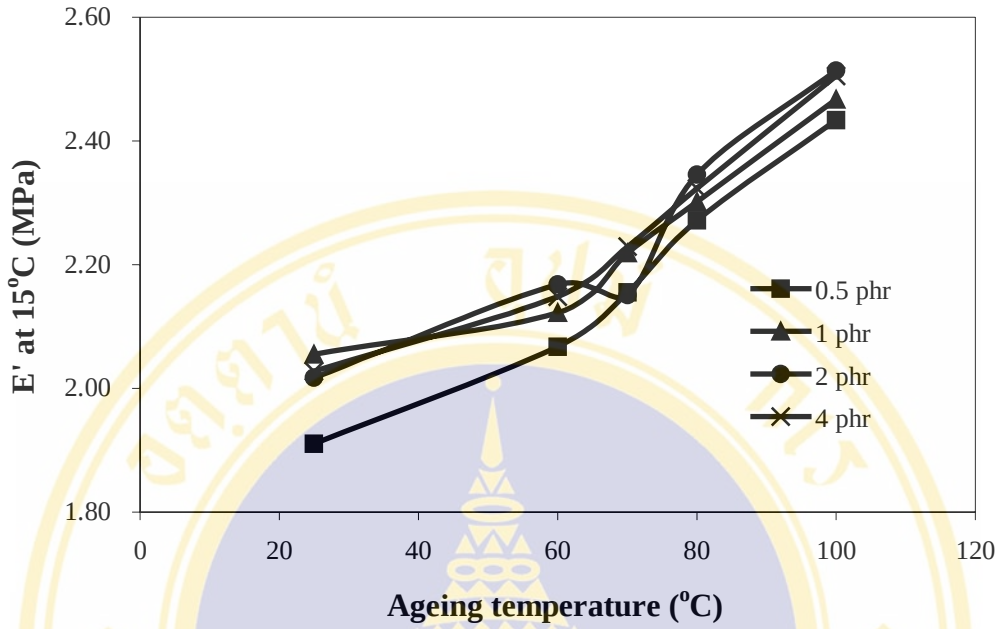


Figure 5.25 Effect of 6-PPD concentration on E' at 15°C of aged NR vulcanisates cured with CV system

In the case of E' influenced by an antioxidant concentration, Figure 5.25 shows that, similar to M100 result shown in Figure 5.24, E' of the vulcanisates cured with CV system increases as 6-PPD concentration increases. Moreover, it is observed that E' increases as ageing temperature increases, which is attributed to the increase in crosslink density via the post-curing effect, as mentioned previously. Unexpectedly, the sensitivity of E' towards antioxidant concentration is lower than that of M100. The explanation is unclear at present.

Copyright by Mahidol University

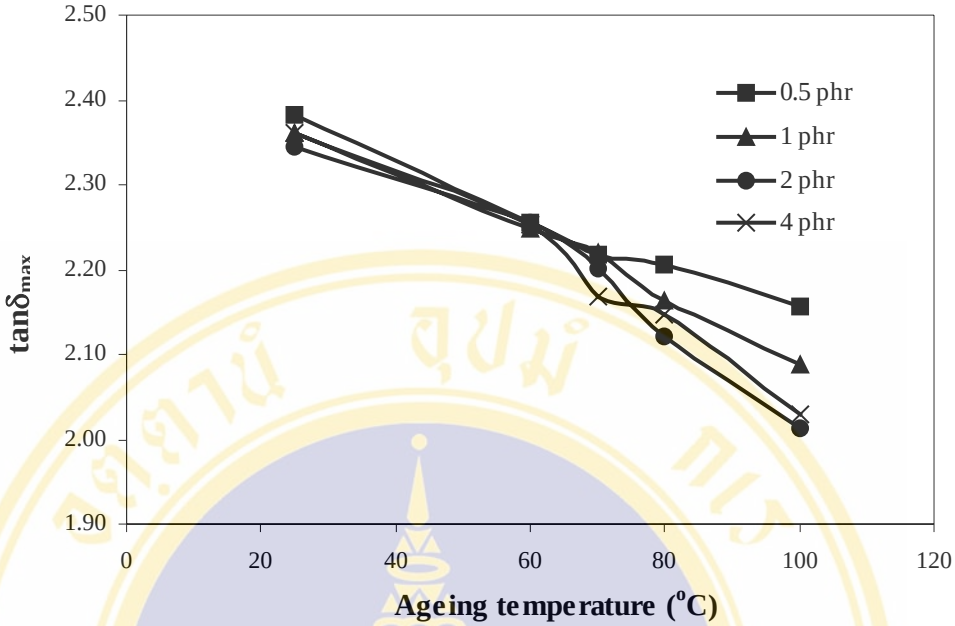


Figure 5.26 Effect of 6-PPD concentration on $\tan\delta_{max}$ of aged NR vulcanisates cured with CV system

For the elasticity changed by increasing antioxidant concentration, it is evident from Figure 5.26 that $\tan\delta_{max}$ of the vulcanisates cured with CV system decreases as 6-PPD concentration increases upto 2 phr. This is due to the increase in crosslink density of vulcanisates leading to a reduction in molecular motion. Also, it is clear that $\tan\delta_{max}$ decreases with increasing ageing temperature, which correlates to the increase in crosslink density via the post-curing effect, as discussed previously in Figure 5.23.

Copyright by Mahidol University

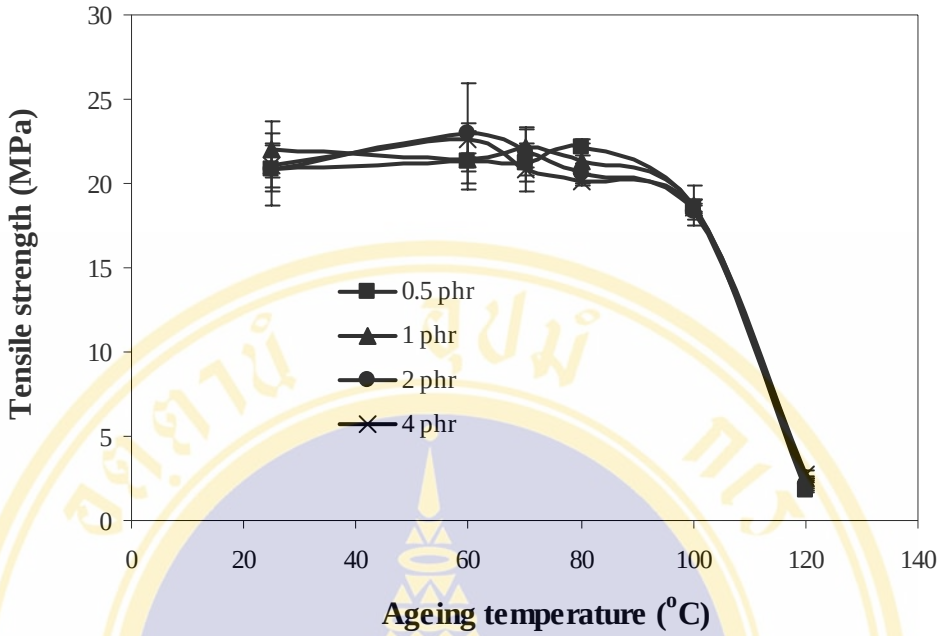


Figure 5.27 Effect of 6-PPD concentration on tensile strength of aged NR vulcanisates cured with EV system

In the case of the vulcanisates cured with EV system, Figure 5.27 illustrates that an antioxidant concentration does not give any significant difference in tensile strength. Moreover, it is found that there are sharp drops in tensile strength at a similar ageing temperature of about 100°C. The tensile strength results agree very well with that of %swelling shown in Figure 5.28. In other words, tensile strength results of vulcanisates cured with EV system depend strongly on crosslink density.

Copyright by Mahidol University

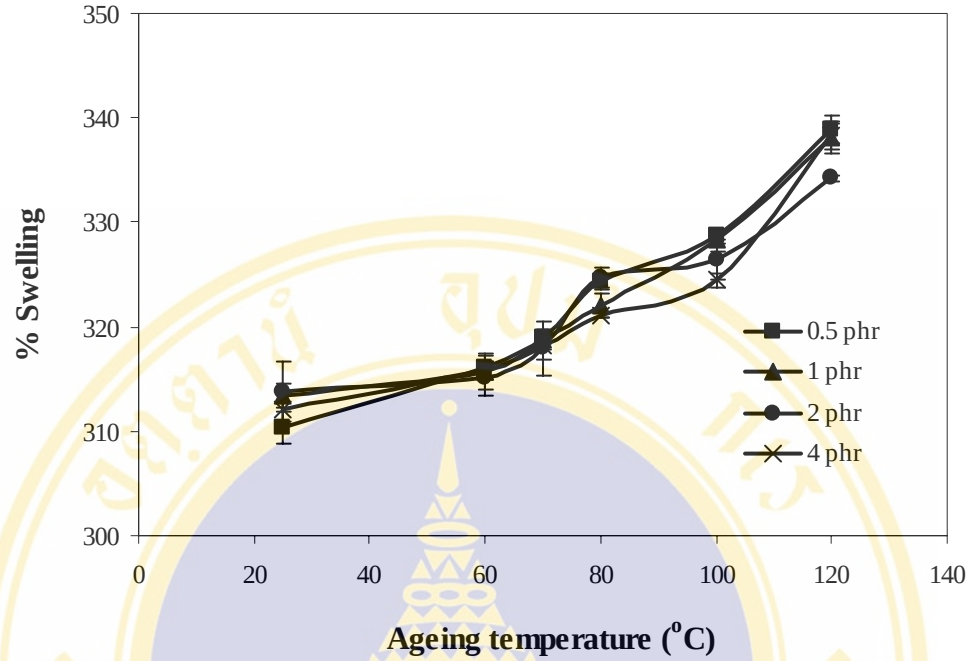


Figure 5.28 Effect of 6-PPD concentration on %swelling of aged NR vulcanisates cured with EV system

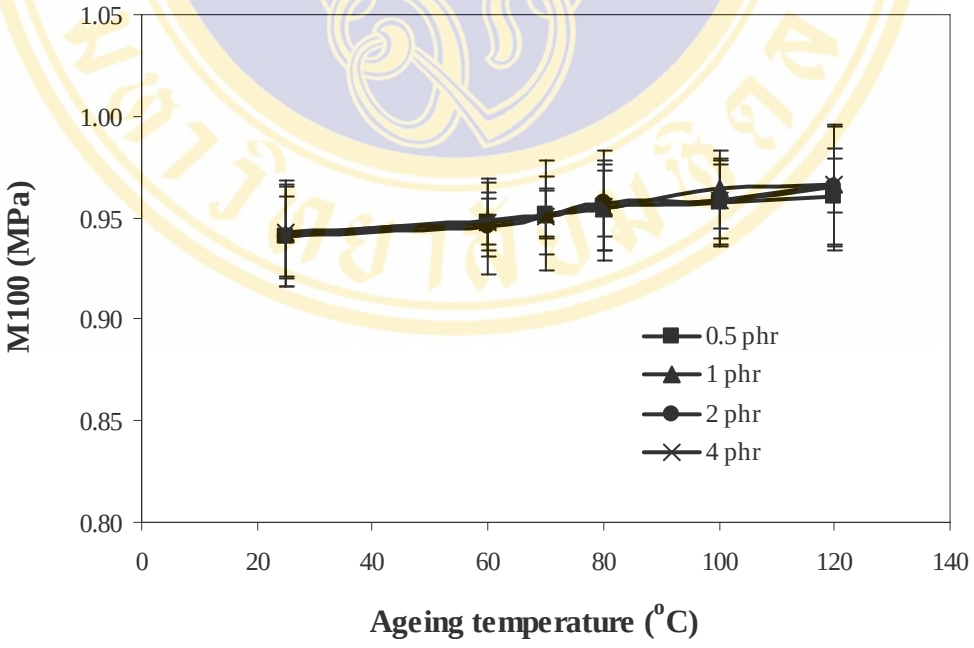


Figure 5.29 Effect of 6-PPD concentration on M100 of aged NR vulcanisates cured with EV system

Copyright by Mahidol University

Evidently, %swelling of the vulcanisates cured with EV system falls in the same line, regardless of the antioxidant concentration, which supports the results of tensile strength as discussed previously. In addition, it is observed that the %swelling starts to increase at the ageing temperature higher than 100°C, which is in good accordance with the tensile strength result illustrated earlier in Figure 5.27.

Similar to tensile strength, Figure 5.29 shows M100 of the aged NR vulcanisates cured with EV system influenced by antioxidant concentration. It is evident that M100 of the vulcanisates cured with EV system is not significantly dependent on antioxidant concentration. Again, the unchange in M100 with increasing ageing temperature is believed to be the result of insufficient sensitivity of M100 to change in crosslink density. Thus, the storage modulus (E′) was measured, and the result is revealed in Figure 5.30.

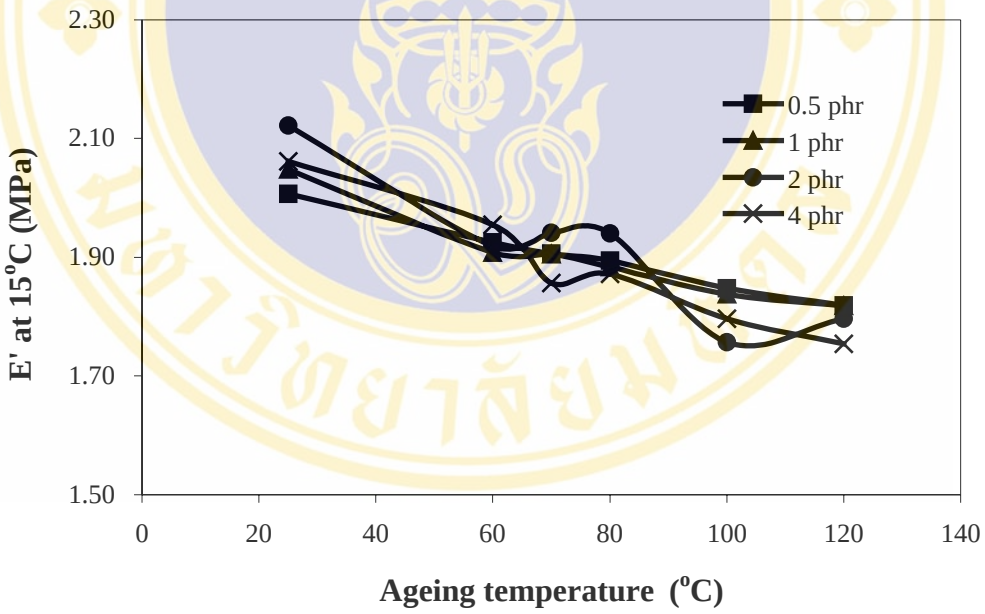


Figure 5.30 Effect of 6-PPD concentration on E' at 15°C of aged NR vulcanisates cured with EV system

Copyright by Mahidol University

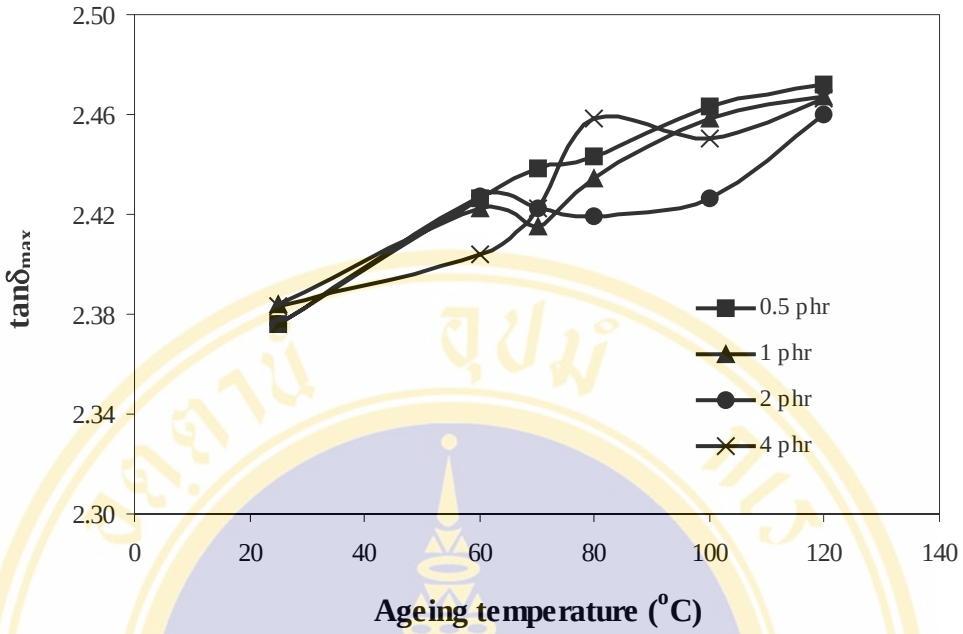


Figure 5.31 Effect of 6-PPD concentration on $tan\delta_{max}$ of aged NR vulcanisates cured with EV system

It can be observed from Figure 5.30 that E' of vulcanisates with EV system also shows no significant change with antioxidant concentration, similar to the M100 result, which is attributed to the indifference in crosslink density (see Figure 5.28). However, E' result as a function of ageing temperature reveals a significant reduction in E' with increasing ageing temperature, which support the linkages scission over post-curing effect. The result of E' is in good agreement with that of $tan\delta_{max}$ as shown in Figure 5.31. Regardless of the antioxidant concentration, $tan\delta_{max}$ increases with increasing ageing temperature indicating an increase in viscous responses and thus the dominant occurrance of linkages scission over the post-curing effect.

Copyright by Mahidol University

5.3 Effect of reinforcing fillers on ageing properties of NR vulcanisates

The final part of this thesis is an investigation of types and amount of reinforcing filler influencing ageing properties of NR vulcanisates. Generally, fillers are used to reinforce or enhance properties of elastomers and to reduce cost of the compound. In black filled compound, carbon blacks are usually used. For non-black compounds, silica, clay, calcium carbonate can be used. From the previous work, it was found that carbon black has a significant impact on ageing properties of NR vulcanisates due to the difference of thermal conductivity between NR and carbon black [68]. Therefore, other fillers, which have different thermal conductivity from NR, may also affects to the ageing properties of NR vulcanisates. The present work aims to study the effects of carbon black and silica on ageing properties of NR vulcanisates. Three different grades of carbon black (N330, N550 and N660) were used and their effects on ageing properties were monitored at the ageing temperature of 60^{o}C and 100^{o}C for the vulcanisates cured with CV and EV system, respectively. The ageing time was mainly focused in the range of 0-4 days. The results are illustrated in the terms of tensile properties, dynamic mechanical properties and crosslink density. Instead of % swelling, the crosslink density is reported as a molecular weight between crosslink (M_c), which is calculated from the Flory-Rehner equation, due to the dilution effect of reinforcing fillers, which would interfere the %swelling result.

Copyright by Mahidol University

Table 5.4 Effects of types and loading of filler and ageing time on tensile strength of the vulcanisates cured with CV system

Sample codename	Filler loading (phr)	Tensile strength (MPa)		
		0 day	2 days	4 days
CV CB N330	10	23.74 ± 0.04	23.19 ± 0.19	22.85 ± 0.16
	20	24.07 ± 0.27	23.54 ± 0.48	23.34 ± 0.28
	30	24.78 ± 0.16	24.40 ± 0.10	24.15 ± 0.11
CV CB N550	10	20.24 ± 0.03	19.14 ± 0.34	18.40 ± 0.55
	20	20.55 ± 0.38	19.73 ± 0.33	19.78 ± 0.26
	30	21.12 ± 0.76	20.63 ± 0.29	19.55 ± 0.71
CV CB N660	10	19.54 ± 0.78	18.95 ± 0.25	19.11 ± 0.67
	20	20.42 ± 0.10	19.57 ± 0.21	19.01 ± 0.05
	30	21.59 ± 0.85	21.32 ± 0.57	21.37 ± 0.47
CV silica	10	25.51 ± 0.18	25.09 ± 0.46	26.53 ± 0.51
	20	25.86 ± 0.22	26.68 ± 0.17	26.39 ± 0.48
	30	23.28 ± 0.13	23.18 ± 0.17	24.08 ± 0.12
Unfilled CV 6-PPD	-	19.676 ± 0.48	19.072 ± 0.23	19.244 ± 0.36

The vulcanisates cured with CV system and various types and filler loading are named as shown in Table 5.4. It is evident from Table 5.4 that tensile strength of carbon black-filled NR vulcanisates cured with CV system increases as carbon black loading increases for all grades of carbon black, which can be explained by the 2 main reason. The first one is the strong interaction between the surfaces of carbon black and rubber, usually known as a bound rubber, leading to the improving of tensile strength of vulcanisates, as shown in Figure 5.32 [69].

Copyright by Mahidol University

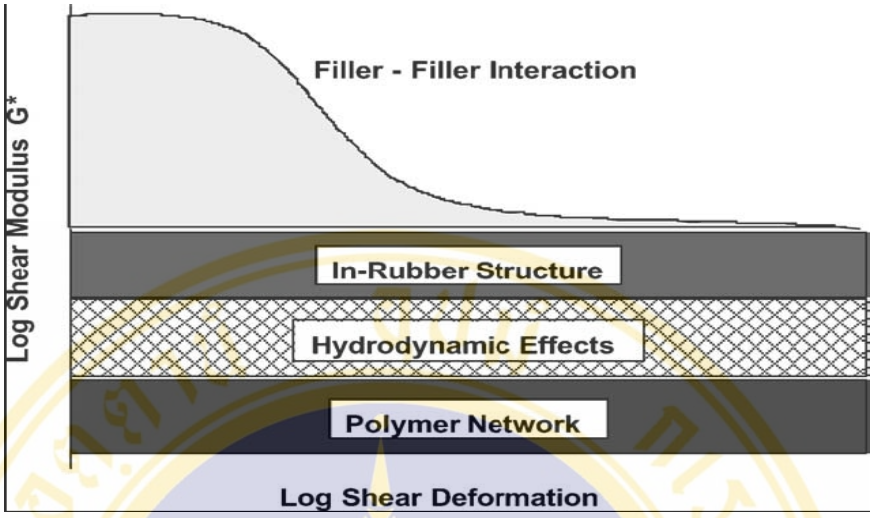


Figure 5.32 Idealised form of a typical elastic modulus curve [70]

This strong interaction increases the energy dissipation through molecular restriction. The other one is the increase in crosslink density from the cure promotion of carbon black provided by a good thermal diffusivity and the functional group of carbon black surface. Moreover, it is found that tensile strength tends to decrease with increasing ageing time because of the occurrence of the post-curing process taking place during thermal oxidative ageing. In the case of silica-filled vulcanisates, it is observed that tensile strength increases with silica loading upto 20 phr, compared to unfilled vulcanisates. The reduction of tensile strength at higher silica loading could be attributed to poor silica dispersion and/or a cure retardation provided by silanol functional groups of silica. It is known that a polar silanol on silica surfaces could form a strong inter-aggregate or clusters via H-bonding and also could adsorb the cure activator [71]. Therefore, the degree of silica dispersion in non-polar NR is considerably low, compared to carbon black. Moreover, it is found that tensile strength of silica-filled vulcanisates increases as ageing time increases. The increase of tensile strength is believed to result from the post-curing effect, as discussed previously. Compared to N550 and N660, N330 gives the highest reinforcing effect due to the highest specific surface area giving rise to the largest amount of bound rubber. Evidently, when the tensile strength of vulcanisates filled with carbon black and silica is compared, it is found that tensile strength of silica-filled vulcanisates is higher than

Copyright by Mahidol University

that of black filled vulcanisates. This phenomenon might be explained by a larger specific surfaces area of silica compared to carbon black (i.e., 80 m^2/g versus 148 m^2/g for carbon black and silica, respectively) leading to the higher degree of reinforcement in silica-filled vulcanisates.

Table 5.5 Effects of types and loading of filler and ageing time on M_c of the vulcanisates cured with CV system

Sample codename	Filler loading (phr)	Mc (x 10^3)		
		0 day	2 days	4 days
CV CB N330	10	2.75 ± 0.02	2.62 ± 0.01	2.62 ± 0.02
	20	2.57 ± 0.02	2.44 ± 0.02	2.40 ± 0.03
	30	2.53 ± 0.02	2.37 ± 0.02	2.31 ± 0.02
CV CB N550	10	2.74 ± 0.02	2.62 ± 19.21	2.62 ± 0.02
	20	2.56 ± 0.03	2.48 ± 0.03	2.38 ± 0.02
	30	2.39 ± 0.02	2.26 ± 0.01	2.21 ± 0.01
CV CB N660	10	2.78 ± 0.01	2.69 ± 0.01	2.64 ± 0.01
	20	2.65 ± 0.01	2.48 ± 0.01	2.42 ± 0.01
	30	2.60 ± 0.02	2.43 ± 0.02	2.40 ± 0.01
CV silica	10	3.51 ± 0.04	3.29 ± 0.03	3.27 ± 0.04
	20	4.50 ± 0.02	4.20 ± 0.03	4.10 ± 0.04
	30	6.00 ± 0.03	5.84 ± 0.04	5.73 ± 0.06
Unfilled CV 6-PPD	-	3.14 ± 0.07	3.01 ± 0.04	2.86 ± 0.04

Generally, M_c is used as an indicator for determining the crosslink density of both unfilled and filled vulcanisates. The effects of types and filler loading and ageing time on M_c of the vulcanisates cured with CV system are illustrated in Table 5.5. It is evident that M_c of carbon black-filled vulcanisates decreases as carbon black loading increases for any given carbon black grade. This phenomenon can be explained by a

Copyright by Mahidol University

good thermal diffusivity and/or the crosslinking promotion of functional group of carbon black surface causes the increase in state-of-cure [72]. In addition, the dilution of viscoelastic phase by the undeformable carbon black leads to the increase in concentration of sulphurating agent reacting with NR resulting the increase of crosslink density. Moreover, it is evident that M_c of carbon black-filled vulcanisates decreases (i.e., crosslink density increases) as ageing time increases, which clearly supports the occurrence of post-curing during thermal oxidative ageing, as mentioned previously. By contrast, M_c of silica-filled vulcanisates increases as silica loading increases, supporting an adsorption of cure activator (ZnO and stearic acid) and cure accelerator by silanol groups of silica leading to a reduction in state-of-cure [67]. Also, silica-filled vulcanisates shows a post-curing effect, which can be observed from a reduction in M_c with increasing ageing time. Additionally, M_c of vulcanisates filled with various carbon blacks demonstrates that M_c is independent of grades of carbon black. Compared to M_c of carbon black-filled vulcanisates, M_c of silica-filled vulcanisates is higher that means the crosslink density of silica-filled vulcanisates is lower. Referred to Figure 5.3, by thermal oxidative ageing, the crosslink density of silica-filled vulcanisates might be in zone 1 while that of carbon black-filled vulcanisates stays in zone 3. Notably, zone 1 is the range, where tensile strength increases as crosslink density increases. By contrast, tensile strength of zone 3 decreases as crosslink density increases.

Copyright by Mahidol University

Table 5.6 Effects of types and filler loading and ageing time on M100 of the vulcanisates cured with CV system

Sample codename	Filler loading (phr)	M100 (MPa)		
		0 day	2 days	4 days
CV CB N330	10	1.62 ± 0.01	1.64 ± 0.02	1.62 ± 0.01
	20	2.07 ± 0.03	2.50 ± 0.02	2.54 ± 0.02
	30	3.01 ± 0.08	3.53 ± 1.01	3.68 ± 0.08
CV CB N550	10	1.82 ± 0.02	1.93 ± 0.02	2.07 ± 0.03
	20	2.15 ± 0.02	2.53 ± 0.05	2.54 ± 0.06
	30	3.12 ± 0.21	3.45 ± 0.05	3.59 ± 0.19
CV CB N660	10	1.68 ± 0.01	1.75 ± 0.04	1.80 ± 0.06
	20	2.10 ± 0.01	2.43 ± 0.04	2.51 ± 0.08
	30	3.13 ± 0.06	3.47 ± 0.06	3.57 ± 0.10
CV silica	10	1.39 ± 0.04	1.44 ± 0.02	1.57 ± 0.02
	20	1.37 ± 0.02	1.38 ± 0.02	1.46 ± 0.03
	30	1.33 ± 0.05	1.34 ± 0.05	1.38 ± 0.01
Unfilled CV 6-PPD	-	1.11 ± 0.01	1.16 ± 0.09	1.18 ± 0.04

It is evident from Table 5.6 that M100 of carbon black-filled vulcanisates cured with CV system increases as carbon black loading increases, regardless of the carbon black grade, due to the increase of reinforcement and/or cure efficiency. In addition, M100 tends to increase as ageing time increases. This result supports the occurrence of the post-curing effect. M100 of silica-filled vulcanisates appears to decrease slightly by increasing silica loading due to the decrease in crosslink density by the depletion of cure activators and cure accelerators. M100 of silica-filled vulcanisates also increases with ageing time increases due to the post-curing effect, as discussed previously. Compared to M100 of unfilled vulcanisates, M100 of filled vulcanisates is higher due to the reinforcing effect and/or the cure promotion (in the case of carbon black)

Copyright by Mahidol University

leading to the increase of the energy dissipation through molecular retriction. Moreover, the addition of undeformable reinforcing filler to viscoelastic phase is the once reason, which used to explain the increase in modulus. In addition, grades of carbon black have no significant effect on the M100 of vulcanisates cured with CV system.

Table 5.7 Effects of types and filler loading and ageing time on E′ at 15°C of the vulcanisates cured with CV system

Sample codename	Filler loading (phr)	E′ at 15°C (MPa)		
		0 day	2 days	4 days
CV CB N330	10	2.59	2.70	2.75
	20	3.42	3.60	3.76
	30	4.78	5.00	5.08
CV CB N550	10	2.62	2.71	2.73
	20	3.55	3.66	3.75
	30	4.76	5.01	5.08
CV CB N660	10	2.51	2.59	2.60
	20	3.32	3.65	3.77
	30	4.77	4.99	5.09
CV silica	10	4.60	4.88	5.16
	20	2.86	2.89	2.91
	30	2.30	2.30	2.31
Unfilled CV-6PPD	-	2.02	2.17	2.19

Table 5.7 demonstrates E′ of the vulcanisates filled with various types and filler loadings cured with CV system. It is evident that E′ of carbon black-filled vulcanisates increases with black loading because of the higher reinforcement and crossink density, as mentioned previously. Also, E′ of carbon black-filled vulcanisates increases with increaseing ageing time, which is attributed to the post-curing effect. In the case of

Copyright by Mahidol University

silica-filled vulcanisates, E′ of silica-filled vulcanisates decreases as silica loading increases. This supports the adsorption of curing agent (e.g., activators and accelerators), which causes the decrease in curing efficiency. Additionally, the increase of ageing time leads to the increase of E′ of silica-filled vulcanisates. It could be explained by the post-curing effect, as discussed previously. Moreover, E′ of filled vulcanisates is higher than unfilled vulcanisates due to the reinforcing effect and/or the higher crosslink density. The result of E′ agrees very well with M_c and M100.

Table 5.8 Effects of types and filler loading and ageing time on $tan\delta_{max}$ of the vulcanisates cured with CV system

Sample codename	Filler loading (phr)	$tan\delta_{max}$		
		0 day	2 days	4 days
CV CB N330	10	2.14	2.09	2.08
	20	1.98	1.96	1.89
	30	1.77	1.74	1.70
CV CB N550	10	2.12	2.11	2.10
	20	1.91	1.86	1.85
	30	1.68	1.63	1.61
CV CB N660	10	2.22	2.19	2.15
	20	1.99	1.96	1.95
	30	1.78	1.77	1.75
CV silica	10	1.68	1.63	1.59
	20	2.01	2.00	1.99
	30	2.21	2.18	2.15
Unfilled CV 6-PPD	-	2.42	2.40	2.39

It is evident from Table 5.8 that $tan\delta_{max}$ of carbon black-filled vulcanisates decreases with increasing carbon black loading because of the increase in crosslink

Copyright by Mahidol University

density provided by the cure acceleration of carbon black as well as the dilution of viscoelastic phase by the undeformable carbon black. Moreover, the post-curing effect causes the decrease in $\tan\delta_{max}$ of carbon black-filled vulcanisates, as discussed previously. In the case of silica-filled vulcanisates, $\tan\delta_{max}$ increases as silica loading increases supporting the cure retardation provided by silanol groups of silica while the post-curing leads to the reduction of $\tan\delta_{max}$ with increasing ageing time. From the result of Tables 5.4-5.8, it is indicated that ageing properties depends strongly on the crosslink density, which changes during thermal oxidative ageing. The particle size of carbon black does not affect strongly the ageing properties, which illustrates in the terms of M_c, M100, E' and $\tan\delta_{max}$.

Copyright by Mahidol University

Table 5.9 Effects of types and filler loading and ageing time on tensile strength of the vulcanisates cured with EV system

Sample name	Filler loading (phr)	Tensile strength (MPa)		
		0 day	2 days	4 days
EV CB N330	10	27.97 ± 0.15	23.41 ± 0.58	19.29 ± 0.81
	20	29.52 ± 0.11	24.00 ± 0.12	22.06 ± 0.47
	30	29.56 ± 0.43	27.05 ± 0.84	22.66 ± 0.61
EV CB N550	10	25.67 ± 0.55	22.45 ± 0.40	18.04 ± 0.53
	20	25.82 ± 0.52	22.75 ± 0.17	17.53 ± 0.58
	30	27.21 ± 0.51	24.86 ± 0.49	22.09 ± 0.68
EV CB N660	10	24.86 ± 0.31	21.98 ± 1.05	17.41 ± 0.21
	20	26.20 ± 0.54	20.44 ± 0.13	16.42 ± 0.64
	30	26.83 ± 0.05	24.54 ± 0.41	21.57 ± 0.37
EV silica	10	23.59 ± 0.13	22.68 ± 0.62	20.93 ± 0.07
	20	26.37 ± 0.44	22.32 ± 0.54	22.61 ± 0.51
	30	29.40 ± 0.31	25.22 ± 0.61	25.70 ± 0.60
Unfilled EV 6-PPD	-	20.86 ± 2.15	18.30 ± 0.46	16.91 ± 0.49

Table 5.9 shows effects of types and filler loading and ageing time on tensile strength of the vulcanisates cured with EV system. Similar to the case of CV system, it is found that tensile strength of carbon black-filled vulcanisates cured with EV system increases as carbon black loading increases. This is attributed to the reinforcing effect and the cure acceleration provided by carbon black leading to the increase in strength of vulcanisates. In addition, tensile strength decreases as ageing time increases, which is believed to be due to the occurrence of the linkages scission during thermal oxidative ageing leading to the decrease in crosslink density. In the case of silica-filled vulcanisates cured with EV system, it is evident that tensile strength increases as silica loading increases. Surprisingly, the result from silica-filled vulcanisates cured with EV

Copyright by Mahidol University

system is opposite way from that of cured with CV system. In fact, tensile strength of silica filled-vulcanisates shall decrease as silica loading increases due to the poor dispersion and/or the cure retardation provided by silanol functional groups of silica. The undoubted result might be explained that the tensile strength is mainly controlled by crosslink density and reinforcing effect. Then, the interaction between rubber and reinforcing filler is the complicate process and difficult to clear understanding. Therefore, in some case, tensile strength cannot explain by the reinforcing effect only. Evidently, it is observed that tensile strength decreases as ageing time increases due to the linkages scission, as discussed previously. Compared to N550 and N660, it is observed that the N330 gives the highest tensile strength because the highest specific surface area. Also, tensile strength of silica-filled vulcanisates is higher than that filled with carbon blacks due to the higher reinforcement obtaining from the higher specific surface area of silica. Results also reveal that tensile strength of filled vulcanisates is higher than unfilled vulcanisates. This indicates that carbon black and precipitated silica improve the tensile strength of vulcanisates because such filler increase the energy dissipation via molecular mobility restriction.

Copyright by Mahidol University

Table 5.10 Effects of types and filler loading and ageing time on M_c of the vulcanisates cured with EV system and various

Sample codename	Filler loading (phr)	Mc (x 10^3)		
		0 day	2 days	4 days
EV CB N330	10	3.33 ± 0.03	3.75 ± 0.02	3.80 ± 0.01
	20	3.19 ± 0.02	3.42 ± 0.03	3.51 ± 0.04
	30	3.00 ± 0.02	3.25 ± 0.01	3.40 ± 0.02
EV CB N550	10	3.31± 0.02	3.66 ± 0.03	3.75 ± 0.02
	20	3.20 ± 0.02	3.35 ± 0.03	3.46 ± 0.03
	30	2.97 ± 0.02	3.24 ± 0.02	3.39 ± 0.02
EV CB N660	10	3.34 ± 0.03	3.80 ± 0.03	3.81 ± 0.03
	20	3.21 ± 0.02	3.46 ± 0.02	3.57 ± 0.03
	30	3.03 ± 0.04	3.32 ± 0.02	3.41 ± 0.03
EV silica	10	3.30 ± 0.03	3.49 ± 0.03	3.93 ± 0.02
	20	4.50 ± 0.02	4.69 ± 0.03	5.02 ± 0.03
	30	6.12 ± 0.02	6.80 ± 0.03	7.04 ± 0.03
Unfilled EV 6-PPD	-	3.85 ± 0.06	3.91 ± 0.02	4.10 ± 0.06

The results from Table 5.10 show that M_c of carbon black-filled vulcanisates cured with EV system decreases with increasing carbon black loading for any black particle size. This can be explained by the cure acceleration provided by a good thermal diffusivity and functional groups of carbon black, which helps to promote the crosslinking, as mentioned previously. In addition, M_c increases as ageing time increases due to the occurrence of the linkages scission, which takes place during thermal oxidative ageing. In the case of silica-filled vulcanisates, it is evident that M_c increases as silica loading increases because of the cure retardation caused by the adsorption of curing agents (activators and accelerators) by the silanol groups of silica leading to the decrease of state-of-cure. Additionally, M_c increases with increasing

Copyright by Mahidol University

ageing time because of the linkages scission, as discussed previously. It is found that M_c of the vulcanisates is independent carbon black grade, which is similar to the case of vulcanisates cure with CV system. Moreover, M_c of silica-filled vulcanisates is higher than that of carbon black-filled vulcanisates due to the cure retardation given by silanol groups of silica. However, M_c of carbon black-filled vulcanisates is lower than unfilled vulcanisates that means crosslink density of carbon black-filled vulcanisates is higher. This supports the cure acceleration and good thermal diffusivity of carbon black leading to the increase in state-of-cure. Therefore, it is clear that the M_c result agrees very well with tensile strength results, i.e., the tensile strength depends strongly on crosslink density.

Copyright by Mahidol University

Table 5.11 Effects of types and filler loading and ageing time on M100 of the vulcanisates cured with EV system and various

Sample codename	Filler loading (phr)	M100 (MPa)		
		0 day	2 days	4 days
EV CB N330	10	1.42 ± 0.04	1.45 ± 0.04	1.49 ± 0.07
	20	1.77 ± 0.09	1.75 ± 0.01	1.79 ± 0.03
	30	2.89 ± 0.02	2.92 ± 0.11	2.97 ± 0.08
EV CB N550	10	1.72 ± 0.05	1.71 ± 0.06	1.72 ± 0.03
	20	2.00 ± 0.03	2.09 ± 0.04	2.08 ± 0.02
	30	2.98 ± 0.04	3.01 ± 0.07	3.08 ± 0.22
EV CB N660	10	1.56 ± 0.04	1.56 ± 0.05	1.59 ± 0.06
	20	2.19 ± 0.50	2.13 ± 0.50	2.23 ± 0.11
	30	2.97 ± 0.04	2.92 ± 0.06	2.93 ± 0.02
EV silica	10	1.80 ± 0.02	1.81 ± 0.50	1.82 ± 0.01
	20	1.67 ± 0.01	1.67 ± 0.03	1.623 ± 0.06
	30	1.28 ± 0.02	1.26 ± 0.03	1.33 ± 0.05
Unfilled EV 6-PPD	-	1.04 ± 0.04	1.02 ± 0.02	1.03 ± 0.01

Table 5.11 illustrates the effect of types and filler loading and ageing time on the vulcanisates cured with EV system. It is observed that M100 of carbon black-filled vulcanisates increases with increasing carbon black loading for any given grade of carbon black. This can be explained by the increase of reinforcing effect and dilution effect and/or the cure acceleration provided by carbon black. It is evident that M100 does not significantly change as ageing time increases. This indicates the insufficient sensitivity of M100 to the crosslink density of the vulcanisates cured with EV system. In the case of silica-filled vulcanisates, it is found that M100 decreases as silica loading increases. This phenomenon can be explained by the cure retardation given by silanol groups of silica dominated over the poor dispersion. Also, M100 of the silica-

Copyright by Mahidol University

filled vulcanisates marginally decreases as ageing time increases due to the insufficient sensitivity of M100 to the crosslink density. M100 of filled vulcanisates is higher than that of unfilled vulcanisates. This result reveals the reinforcing effect of carbon black and precipitated silica, which helps to improve properties of NR vulcanisates. In addition, M100 of silica-filled vulcanisates is lower than that of carbon black-filled vulcanisates because of the cure retardation of silica associated with the effect of poor rubber-filler interaction.

Table 5.12 Effects of types and filler loading and ageing time on E′ at 15°C of the vulcanisates cured with EV system and various

Sample codename	Filler loading (phr)	E′ at 15°C (MPa)		
		0 day	2 days	4 days
EV CB N330	10	2.54	2.53	2.49
	20	3.82	3.58	3.53
	30	5.97	5.76	5.62
EV CB N550	10	2.53	2.52	2.45
	20	3.83	3.59	3.50
	30	5.86	5.70	5.54
EV CB N660	10	2.52	2.49	2.44
	20	3.58	3.56	3.45
	30	5.87	5.79	5.59
EV silica	10	5.83	5.82	5.74
	20	3.20	3.18	3.02
	30	2.24	2.22	2.10
Unfilled EV 6-PPD	-	2.12	1.72	1.72

Table 5.12 demonstrates that E′ of carbon black-filled vulcanisates cured with EV system increases as carbon black loading increases for any grade of carbon black due to the increase in reinforcing effect. In addition, E′ decreases as ageing time increases.

Copyright by Mahidol University

This can be explained that the linkage scission, which appears to be more pronounced during the thermal oxidative ageing. Evidently, E′ of silica-filled vulcanisates decreases as silica loading increases due to the cure retardation of the silanol groups on silica surface. Also, E′ of silica-filled vulcanisates decreases as ageing time increases because of the linkages scission, as mentioned previously. The reinforcing effect of carbon black and silica makes E′ of the filled vulcanisates higher than that of the unfilled vulcanisates. The result of E′ agrees very well with M_c and M100.

Table 5.13 Effects of types and filler loading and ageing time on $tan\delta_{max}$ of the vulcanisates cured with EV system

Sample codename	Filler loading (phr)	Ageing time (days)		
		0 day	2 days	4 days
EV CB N330	10	1.98	2.01	2.14
	20	1.64	1.75	1.82
	30	1.35	1.40	1.46
EV CB N550	10	2.01	2.11	2.19
	20	1.65	1.74	1.85
	30	1.34	1.48	1.50
EV CB N660	10	2.07	2.12	2.20
	20	1.70	1.72	1.88
	30	1.33	1.46	1.55
EV silica	10	1.57	1.58	1.66
	20	1.95	1.97	2.04
	30	2.12	2.24	2.32
Unfilled EV 6-PPD	-	2.29	2.38	2.41

It is evident from Table 5.13 that $tan\delta_{max}$ of carbon black-filled vulcanisates cured with EV system decreases as carbon black loading increases due to the cure

Copyright by Mahidol University

acceleration provided by carbon black and/or the dilution of viscoelastic phase by undeformable carbon balck. While $\tan\delta_{max}$ increases as ageing time increases. This result supports the linkages scission, which dominates the crosslinking during thermal oxidative ageing. In the case of silica-filled vulcanisates, $\tan\delta_{max}$ increases with increasing silica loading because the cure retardation provided by the silanol groups on silica surface leading to the decrease in crosslink density. The $\tan\delta_{max}$ of silica-filled vulcanisates is tend to increase with increasing agein gtime. The explanation is given by the linkages scission taking place during thermal oxidative ageing process. Evidently, $\tan\delta_{max}$ of the filled vulcanisates is lower than that of unfilled vulcanisates due to the decrease in rubber phase by dilution effect provided by carbon black and silica.

From the result of Tables 5.9-5.13, it is evident that ageing properties depends strongly on the crosslink density, which changes during thermal oxidative ageing. M_c and M100 are independent of grades of carbon black.

Copyright by Mahidol University

CHAPTER 6
CONCLUSIONS

The aim of this thesis is to investigate the effects of thermal ageing conditions and some compounding ingredients on properties, including tensile and dynamic properties as well as a crosslink density, of NR vulcanisates. In the first part, the effects of thermal oxidative ageing, i.e., ageing temperature and ageing time, on tensile and dynamic mechanical properties were investigated. Thereafter, the effects of antioxidant and reinforcing filler on properties of aged NR vulcanisates were focused in the second and third parts, respectively. The results can be summarised as follows:

1. Effect of thermal oxidative ageing conditions on ageing properties of the NR vulcanisates

When sulphur-cured NR compounds are exposed to a thermal oxidative ageing environment, significant changes in physical and dynamic mechanical properties are observed.

1. Ageing properties of NR vulcanisates depend strongly on crosslink density, which changes during thermal oxidative ageing.

2. Increases in ageing temperature and time cause dominantly the post-curing and linkages scission for vulcanisates cured with CV and EV systems, respectively.

3. With increasing ageing temperature, tensile strength shows sharp drop at ageing temperature higher than 70^{o}C and 100^{o}C for the specimens cured with CV and EV systems, respectively. The sharp drop of tensile strength of vulcanisates cured with CV system is due to the too-high crosslinking, which is caused by the post-curing effect. In the case of the vulcanisates cured with EV system, linkage scission causes the sharp drop of tensile strength.

Copyright by Mahidol University

2. Effects of antioxidants on ageing properties of the NR vulcanisates

The addition of antioxidant to rubber mixes can protect the rubber from thermal oxidative ageing. However, each antioxidant has different efficiency, which depends greatly on its chemical structures and reactivity, to protect vulcanisates from thermal oxidative ageing.

1. Ageing properties of the vulcanisates cured with CV system are strongly controlled by type of antioxidant. By contrast, ageing properties of these cured with EV system is independent of type of antioxidant.

2. For NR vulcanisates cured with CV system, 6-PPD has the highest protection followed by TMQ and BHT, respectively.

3. The optimum concentration of 6-PPD to protect the rubber from thermal degradation is 2 phr (based on the ageing properties).

3. Effect of reinforcing fillers on ageing properties of the NR vulcanisates

Generally, fillers are used to reinforce or enhance properties of elastomers and to reduce cost of the compound. Three different grades of carbon black (N330, N550 and N660) and precipitated silica were used, and their effects on ageing properties were monitored at ageing temperature of 60^{o}C and 100^{o}C for vulcanisates cured with CV and EV systems, respectively. The addition of carbon black and precipitated silica can change the ageing properties of sulphur-cured vulcanisates via the changes in crosslink density. Carbon black and precipitated silica strongly affect cure behaviour; carbon black accelerates cure whereas precipitated silica retards cure.

Copyright by Mahidol University

REFERENCES

1. A. Subramaniam, *Rubber Chemistry and Technology*, 1993, 19
2. K. Nagdi, editor. Rubber as an engineering material: Guideline for users. 1st ed. Newyork: Hanser; 1993
3. E. Hwee, S. Ejisi, S. Kawahara and Y. Tanaka, *Rubber Chemistry and Technology*, 1993, 386
4. Encyclopedia in polymer science and technology. vol 14. Newyork: Interscience; 1970
5. R.L. Fan, Y. Zhang, C. Huang, Y.X. Zhang, K. Sun and Y.Z. Fan, *Polymer Testing*, **20**, 2001, 925
6. J.P. Berry, W.F. Watson, *Journal of Polymer Science*, **18**, 1995, 201
7. J.L. Cunneen, *Rubber Chemistry and Technology*, **41**, 1968, 182
8. J.L. Morand, *Rubber Chemistry and Technology*, **50**, 1977, 370
9. R.W. Keller, *Rubber Chemistry and Technology*, **58**, 1985, 637
10. J. Frohlich, W. Niedermeier and H.D. Luginsland, The effect of filler-filler and filler-elastomer interaction on rubber reinforcement. Composite: Part A, **36**, 2005, 449
11. D.J. Schuring, S. Futamura, *Rubber Chemistry and Technology*, **63**, 1990, 315
12. W.J. Kern and S. Futamura, *Polymer*, **29**, 1988, 1081
13. H.E. Trexler and M.C.H. Lee, *Journal of Appl Polym Sci*, **32(3)**, 1986, 3899
14. J.D. Ulmer, V.E. Chirio, *American Chemical Society*, *Division of Rubber Chemistry Papers*, **4,** 1973, 61
15. M.J. Wang, *Rubber Chemistry and Technology*, **71(3)**, 1998, 520
16. A.I. Medalia, *Rubber Chemistry and Technology*, **51**, 1978, 437
17. M.L. Studebacher and J.R. Beatty, *Rubber Chemistry and Technology*, **47**, 1994, 803
18. G.R. Taylor and S.R. Darin, *Journal of Polym Sci*, **17**, 1955, 51
19. R.F. Dunbrook, Rubber. Colliers Encycopedia CD-ROM February, **28**, 1996, 20
20. Y. Tanaka, *Rubber Chemistry and Technology*, **74**, 2001, 355

Copyright by Mahidol University

21. A.D. Roberts, in “Natural Rubber Science and Technology”, B.G. Crowther, P. M. Lewis, and C. Metherell, Eds., Oxford University Press, Oxford, 1988, Chapter 6
22. C.D. Trivette Jr., E. Motita and E.J. Young, *Rubber Chemical and Technology*, **35**, 1962, 1370
23. R.P. Quirk, *Rubber Plast Technol*, **4 (1)**, 1988, 31
24. J. Sanchez and T.N. Myers, in “Organic Peroxides”, Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, **18**, 1996, 203
25. J. Sanchez and T.N. Myers, in “Polymeric Materials Encyclopedia”, Peroxide Initiators (Overiew), 4927-4938, (1996)
26. V.R. Kamath and L.H. Palys, Polyethylene Melt Flow Modification, SPE Regional Technical Conference (RETEC), Plastics Waste Management, Paper No. 6, October (1990)
27. G.A. Harpell and D.H. Walrod, *Rubber Chemistry and Technology*, **46(4)**, 1973, 1007
28. Bremmer, Tim., Rudin and Alfred, Modification of High Density Polyethylene by Reaction with Dicumyl Peroxide, Guelph-Waterloo Centre for Graduate Work in Chemistry and Department of Chemistry, University of Waterloo, Waterloo, Ontario. Canada, (1990)
29. C.D. Trivette Jr., E. Morita and O.W. Maender, *Rubber Chemistry and Technology*, **50(3)**, 1977, 570
30. www. google.com / acid retarder and cure curve / concepts
31. A.Y. Coran, in “Science and Technology of Rubber”, E.M. James, B. Erman, and F.R. Eirich, Eds., Academic Press, New york, 1978, Chapter 7
32. W. Hoffman, in “Vulcanisation and Vulcanising Agents”, Palmerton Publishing Co. Inc., New York, 1967
33. G. Alliger and I.J. Sjothun, in “Vulcanisation of Elastomers”, Reinhold Publishing Corp., New York, 1964
34. A.Y. Coran, in “Encyclopedia of Polymer Science and Technology of Rubber”, Vol. 14, J.R. Wolfe Jr., Eds., John Wiley & Sons, Inc., New York, 1989, p. 666

Copyright by Mahidol University

35. C.B. Krishna and L.S. Howard, in “Basic Elastomer Technology”, P.R. Charles, Eds., Akron university , USA, 2001, Chapter 7

36. A.D. Roberts, in “Natural Rubber Science and Technology”, B.G. Crowther, P. M. Lewis, and C. Metherell, Eds., Oxford University Press, Oxford, 1988, Chapter 6
37. M. Akiba and A.S. Hashim, Polym Sci, **22,** 1997, 475-521
38. F. Roberts and R.T. Ohm, *Rubber world*, **219(1),** 1998, 26, 30, 32
39. C. Hooker and R. Vara, *Rubber world*, **225(5),** 2002, 36, 46
40. I. Klaric, N.V. Stipanelov and U. Roje, *Jounal of Appl Polym Sci*, **78**, 2000, 166
41. E.J. Blackman and E.B. Mccall, *Rubber Chemical and Technology*, **43(3)**, 1970, 651
42. M.R. Krejsa and J.L. Koenig, *Rubber Chemistry and Tecnology*, **66**, 1993, 376
43. R. Ding and A.I. Leonov, *Jounal of Appl Polym Sci*, **61**, 1996, 455
44. L.O. Amberg, in “Vulcnaisation of Elastomers”, G. Alliger and I.J. Sjothun, Eds., Reinhold Publishing Corporation, New York, 1964, p. 286
45. JR. Fried, Polymer Science and Technology, London: Prentice-Hall International; 1995
46. C.M. Blow and C. Hephun, Rubber Technology and Manufacture, 2nd ed. The plastic and rubber insitute: 1982
47. A.N. Gent, Engineering material: Guideline for users, 1st ed. New York: Hanser; 1993
48. R.A. Mazzeo, *Rubber world*, **211(5)**, 1995, 22
49. L. Bateman and H K.R. Argrave, Oxidation of organic sulphides. Proc. R. Soc. A., 1954, 224, 389
50. D. Barnard, *Journal of Chem Soc*, 1956, 489
51. Scott G., Peroxidolytic antioxidants: sulphur antioxidants and auto-synergistic stabilisers based on alkyl and aryl sulphides. In developments in polymer stabilisation-6 (ed. G. Scott) Chap. 2. Applied Science Publishers, London, 1983

Copyright by Mahidol University

52. E.J. Percy, A radiochemical study of the oxidation of thiosulphinates, and of their effect on free radical chain processes. PhD. Thesis, London University, 1964

53. A.D. Roberts, in “Natural Rubber Science and Technology”, B.G. Crowther, P.M. Lewis, and C. Metherell, Eds., Oxford University Press, Oxford, 1988, Chapter 10

54. D. Barnard, M.E. Cain, J.I. Cunneen and T.H. Houseman, *Rubber Chemistry and Technology*, **42**, 1972, 381

55. G. Arrey, D. Barnard, and T.H. Houseman, The use of redioisotropically labeled analytical reagents in organic chemistry. *Chem. Rev*., **71**, 371

56. P. Boochathum and W. Prajudtake, *European Polymer Journal*, **37(3)**, 2001, 417

57. E.J. Blackman and E.B. Mccall, *Rubber Chemical and Technology*, **43(3)**, 1970, 651

58. J. Heiner, B. Stenberg and M. Persson, *Polymer Testing*, **22**, 2003, 253

59. C. Sirisinha, and W. Sittichokchuchai, *Journal of Appl Polym Sci*, **80**, 2001, 2474

60. M. Nasir and G.K. Teh, *European Polymer Journal*, **24(8)**, 1988, 733

61. G.M. Bristow, R.F. Tiller, *Kautschuk Und Gummi Kunststoffe*, **23(2)**, 1970, 55

62. A.I. Medalia, *Rubber Chemistry and Technology*, **64**, 1991, 481

63. J.A.C. Harwood, A.R. Pyne and J.F. Smith, *Rubber Chemistry and Technology*, **43**, 1970, 687

64. E. Meinecke, *Rubber Chemistry and Technology*, **64**, 1990, 269

65. Y. Ohkatsu, T. Matsuura and M. Yamato, *Polymer Degradation and Stability*, **81**, 2003, 181

66. P. Gijsman and M. Gitton-Chevalier, *Polymer Degradation and Stability*, **81**, 2003, 483

67. S.A. Pushpa and P. Goonetilleke, *Rubber Chemistry and Technology*, **68(5)**, 1995, 705

68. www. google.com / thermal conductivity of carbon black / MACSFR-Report on thermal diffusivity of tire bales

69. S.S. Choi and I.S. Kim, *European Polymer Journal*, **38**, 2002, 1265

70. P. Sae-Oui, U. Thepsuwan and K. Hutthapanit, *Polymer Testing*, **23**, 2004, 397

Copyright by Mahidol University

71. A. Ansarifara, A. Azharb, N. Ibrahima, S.F. Shiaha and J.M.D. Lawtonc, International Journal of Adhesion and Adhesives, **25**, 2005, 77

72. C.H. Chent, J.L. Koenig, J.R. Shelton and E.A. Collins, *Rubber Chemistry and Technology*, **55(1)**, 1982, 103

Copyright by Mahidol University

APPENDIX

Copyright by Mahidol University

Appendix A

Influences of ageing temperature and time on ageing properties of NR vulcanisates

Table A1 Tensile strength of NR vulcanisates after thermal oxidative ageing at various temperatures

Ageing temperature (^{o}C)	Tensile strength (MPa)	
	CV	EV
25 (control)	22.22 ± 0.56	21.32 ± 2.02
60	19.73 ± 0.03	23.41 ± 1.19
70	21.85 ± 0.14	22.35 ± 0.61
80	9.34 ± 0.22	19.08 ± 1.88
100	2.92 ± 0.10	19.53 ± 1.09
120	1.64 ± 0.01	9.57 ± 2.08

Table A2 %swelling of NR vulcanisates after thermal oxidative ageing at various temperatures

Ageing temperature (^{o}C)	%swelling	
	CV	EV
25 (control)	289.18 ± 3.28	319.33 ± 0.92
60	277.77 ± 1.41	322.64 ± 0.61
70	267.98 ± 0.75	318.47 ± 0.68
80	255.31 ± 1.17	312.09 ± 1.39
100	257.80 ± 0.92	322.38 ± 0.89
120	233.72 ± 5.01	344.63 ± 6.25

Copyright by Mahidol University

Table A3 M100 of NR vulcanisates after thermal oxidative ageing at various temperatures

Ageing temperature (^{o}C)	M100 (MPa)	
	CV	EV
25 (control)	1.10 ± 0.06	0.91 ± 0.01
60	1.13 ± 0.19	0.85 ± 0.03
70	1.28 ± 0.03	0.91 ± 0.02
80	1.32 ± 0.02	0.94 ± 0.02
100	1.39 ± 0.01	1.02 ± 0.04
120	1.62 ± 0.01	1.05 ± 0.02

Table A4 E' at 15^{o}C of NR vulcanisates after thermal oxidative ageing at various temperatures

Ageing temperature (^{o}C)	E' at 15^{o}C (MPa)	
	CV	EV
25 (control)	2.12	2.14
60	2.25	1.97
70	2.39	1.85
80	2.26	1.83
100	2.36	1.89
120	2.68	1.67

Copyright by Mahidol University

Table A5 $tan\delta_{max}$ of NR vulcanisates after thermal oxidative ageing at various temperatures

Ageing temperature (^{o}C)	$tan\delta_{max}$	
	CV	EV
25 (control)	2.25	2.23
60	2.25	2.28
70	2.24	2.36
80	2.12	2.30
100	1.86	2.25
120	1.02	2.31

Table A6 Tensile strength of NR vulcanisates after thermal oxidative ageing at various times

Ageing time (days)	Tensile strength (MPa)	
	CV	EV
0	22.22 ± 0.56	21.32 ± 2.02
1	20.72 ± 1.98	21.36 ± 2.99
2	21.85 ± 0.14	19.53 ± 1.09
4	19.87 ± 1.34	16.06 ± 2.62
6	3.99 ± 0.25	14.89 ± 2.13
10	6.33 ± 1.15	10.03 ± 2.50

Copyright by Mahidol University

Table A7 %swelling of NR vulcanisates after thermal oxidative ageing at various times

Ageing time (days)	%swelling	
	CV	EV
0	289.18 ± 3.28	319.33 ± 0.92
1	274.74 ± 3.39	322.61 ± 8.17
2	273.70 ± 1.93	324.37 ± 3.25
4	257.37 ± 1.55	329.51 ± 2.45
6	260.47 ± 1.70	334.13 ± 2.67
10	252.92 ± 2.94	346.81 ± 10.31

Table A8 M100 of NR vulcanisates after thermal oxidative ageing at various times

Ageing time (days)	M100 (MPa)	
	CV	EV
0	1.11 ± 0.06	0.91 ± 0.01
1	1.14 ± 0.02	0.93 ± 0.01
2	1.28 ± 0.02	1.02 ± 0.04
4	1.28 ± 0.01	0.96 ± 0.04
6	1.23 ± 0.06	0.97 ± 0.04
10	1.39 ± 0.08	1.08 ± 0.05

Copyright by Mahidol University

Table A9 E' at 15°C of NR vulcanisates after thermal oxidative ageing at various times

Ageing time (days)	E' at 15°C (MPa)	
	CV	EV
0	1.92	1.91
1	2.14	1.86
2	2.19	1.89
4	2.17	1.84
6	2.23	1.84
10	2.29	1.74

Table A10 $\tan\delta_{max}$ of NR vulcanisates after thermal oxidative ageing at various times

Ageing time (days)	$\tan\delta_{max}$	
	CV	EV
0	2.25	2.23
1	2.24	2.24
2	2.24	2.25
4	2.16	2.27
6	2.16	2.28
10	2.14	2.30

Copyright by Mahidol University

Appendix B

Influences of antioxidants on ageing properties of NR vulcanisates

Table B1 Sample codename of specimens used in the study of antioxidant effect

Sample codename	Curing system	Antioxidant concentration (phr)		
		TMQ	6-PPD	BHT
A	CV	-	-	-
B	CV	2	-	-
C	CV	-	2	-
D	CV	-	-	2
E	CV	1	1	-
F	CV	2	2	-
G	EV	-	-	-
H	EV	2	-	-
I	EV	-	2	-
J	EV	-	-	2
K	EV	1	1	-
L	EV	2	2	-

Copyright by Mahidol University

Table B2 Tensile strength of NR vulcanisates cured with CV system filled with various antioxidants after thermal oxidative ageing at various temperatures

Sample codename	Tensile strength (MPa)					
	25°C	60°C	70°C	80°C	100°C	120°C
A	15.92 ± 1.71	6.46 ± 1.32	3.77 ± 1.02	3.53 ± 0.81	1.55 ± 0.09	1.13 ± 0.14
B	17.34 ± 1.38	11.38 ± 0.84	7.49 ± 1.78	6.95 ± 1.28	2.34 ± 0.46	1.24 ± 0.06
C	19.68 ± 1.48	19.07 ± 0.83	7.43 ± 1.71	6.09 ± 0.15	2.89 ± 0.37	1.31 ± 0.04
D	16.24 ± 0.06	12.27 ± 1.95	7.62 ± 1.85	6.23 ± 1.61	3.55 ± 0.08	1.13 ± 0.09
E	18.46 ± 0.61	13.06 ± 0.01	7.56 ± 0.10	6.08 ± 0.06	2.63 ± 0.13	1.23 ± 0.05
F	22.22 ± 0.56	19.73 ± 0.03	21.85 ± 0.14	9.34 ± 0.22	2.92 ± 0.10	1.64 ± 0.01

Table B3 %swelling of NR vulcanisates cured with CV system filled with various antioxidants after thermal oxidative ageing at various temperatures

Sample codename	%swelling					
	25°C	60°C	70°C	80°C	100°C	120°C
A	281.14 ± 3.48	290.74 ± 0.70	306.30 ± 0.95	293.76 ± 1.19	295.61 ± 0.29	316.33 ± 2.98
B	284.30 ± 0.59	274.39 ± 1.16	277.24 ± 0.83	276.49 ± 0.38	272.20 ± 0.96	271.60 ± 0.51
C	284.69 ± 2.91	279.28 ± 1.65	267.63 ± 2.57	261.23 ± 0.92	256.04 ± 1.93	254.78 ± 0.29
D	293.82 ± 1.34	289.16 ± 2.25	275.39 ± 2.80	288.37 ± 0.79	299.26 ± 1.63	307.10 ± 4.91
E	287.25 ± 1.30	282.85 ± 1.35	274.66 ± 0.43	270.06 ± 0.62	259.86 ± 0.60	257.20 ± 2.13
F	289.18 ± 3.28	277.77 ± 1.41	267.98 ± 0.75	255.31 ± 1.17	257.80 ± 0.92	233.72 ± 5.00

Copyright by Mahidol University

Table B4 M100 of vulcanisates cured with CV system filled with various antioxidants after thermal oxidative ageing at various temperatures

Sample codename	M100 (MPa)					
	25°C	60°C	70°C	80°C	100°C	120°C
A	0.95 ± 0.03	1.05 ± 0.06	1.10 ± 0.01	1.15 ± 0.10	1.28 ± 0.08	-
B	1.08 ± 0.07	1.24 ± 0.09	1.25 ± 0.01	1.32 ± 0.14	1.49 ± 0.06	-
C	1.03 ± 0.01	1.12 ± 0.09	1.35 ± 0.01	1.42 ± 0.04	1.53 ± 0.03	-
D	1.06 ± 0.02	1.16 ± 0.01	1.12 ± 0.05	1.21 ± 0.01	1.27 ± 0.07	-
E	1.09 ± 0.01	1.22 ± 0.03	1.28 ± 0.02	1.37 ± 0.06	1.43 ± 0.01	-
F	1.11 ± 0.06	1.33 ± 0.09	1.38 ± 0.02	1.42 ± 0.02	1.49 ± 0.01	1.62 ± 0.01

Table B5 E' at 15°C of vulcanisates cured with CV system filled with various antioxidants after thermal oxidative ageing at various temperatures

Sample codename	E' at 15°C (MPa)					
	25°C	60°C	70°C	80°C	100°C	120°C
A	1.901	2.038	2.053	2.134	2.159	-
B	1.954	2.089	2.138	2.247	2.254	-
C	2.017	2.168	2.151	2.296	2.414	-
D	1.903	2.301	2.035	2.140	2.135	-
E	1.998	2.181	2.210	2.242	2.315	-
F	2.119	2.247	2.390	2.260	2.356	2.675

Copyright by Mahidol University

Table B6 $tan\delta_{max}$ of vulcanisates cured with CV system filled with various antioxidants after thermal oxidative ageing at various temperatures

Sample codename	$tan\delta_{max}$					
	25°C	60°C	70°C	80°C	100°C	120°C
A	2.410	2.497	2.563	2.605	2.632	-
B	2.375	2.350	2.352	2.309	2.067	-
C	2.222	2.219	2.143	2.128	1.942	-
D	2.408	2.302	2.319	2.301	2.299	-
E	2.415	2.396	2.321	2.242	2.042	-
F	2.253	2.248	2.235	2.117	1.861	-

Table B7 Tensile strength of vulcanisates cured with EV system filled with various antioxidants after thermal oxidative ageing at various temperatures

Sample codename	Tensile strength (MPa)					
	25°C	60°C	70°C	80°C	100°C	120°C
A	20.21 ± 0.38	19.20 ± 1.15	17.59 ± 1.16	18.18 ± 1.76	12.53 ± 0.18	1.325 ± 0.11
B	23.37 ± 0.88	24.03 ± 0.63	23.74 ± 0.76	23.36 ± 0.98	17.93 ± 0.68	2.26 ± 0.37
C	20.862 ± 1.15	22.95 ± 1.01	21.93 ± 1.41	20.58 ± 0.59	18.30 ± 0.46	2.15 ± 0.32
D	24.313 ± 0.23	20.95 ± 3.44	20.33 ± 0.82	21.18 ± 1.24	17.482 ± 1.15	1.55 ± 0.13
E	19.80 ± 0.52	21.53 ± 0.76	23.18 ± 0.82	21.38 ± 0.64	20.08 ± 0.22	2.39 ± 0.17
F	21.32 ± 2.02	23.41 ± 1.91	22.35 ± 0.61	19.08 ± 1.88	19.53 ± 1.09	9.57 ± 2.08

Copyright by Mahidol University

Table B8 %swelling of vulcanisates cured with EV system filled with various antioxidants after thermal oxidative ageing at various temperatures

Sample codename	%swelling					
	25°C	60°C	70°C	80°C	100°C	120°C
A	306.85 ± 1.09	319.70 ± 1.45	325.16 ± 0.53	337.74 ± 1.60	353.02 ± 1.23	365.60 ± 1.13
B	314.49 ± 1.21	322.12 ± 2.48	315.70 ± 0.70	323.90 ± 0.94	321.20 ± 0.37	330.30 ± 1.11
C	313.84 ± 1.95	315.09 ± 2.18	317.94 ± 0.81	324.76 ± 1.41	326.47 ± 1.11	334.23 ± 3.84
D	315.08 ± 0.94	318.81 ± 1.19	319.17 ± 0.70	320.81 ± 0.79	330.78 ± 0.87	342.67 ± 0.47
E	311.31 ± 1.05	315.76 ± 0.86	318.12 ± 0.97	320.24 ± 1.07	328.58 ± 0.74	337.98 ± 1.36
F	319.33 ± 0.92	322.64 ± 0.61	318.47 ± 0.68	312.09 ± 1.39	322.38 ± 0.89	344.63 ± 6.25

Table B9 M100 of vulcanisates cured with EV system filled with various antioxidants after thermal oxidative ageing at various temperatures

Sample codename	M100 (MPa)					
	25°C	60°C	70°C	80°C	100°C	120°C
A	0.86 ± 0.01	0.99 ± 0.01	0.98 ± 0.06	1.04 ± 0.01	1.02 ± 0.01	0.86 ± 0.02
B	0.96 ± 0.01	0.96 ± 0.03	0.98 ± 0.01	0.98 ± 0.03	1.01 ± 0.03	1.11 ± 0.03
C	0.94 ± 0.04	0.96 ± 0.03	0.97 ± 0.02	1.00 ± 0.02	1.02 ± 0.03	0.94 ± 0.01
D	0.96 ± 0.02	0.96 ± 0.07	0.99 ± 0.01	0.99 ± 0.02	1.01 ± 0.03	0.85 ± 0.02
E	0.95 ± 0.03	0.95 ± 0.04	0.97 ± 0.03	0.98 ± 0.05	0.97 ± 0.04	0.97 ± 0.02
F	0.91 ± 0.01	0.85 ± 0.03	0.91 ± 0.02	0.94 ± 0.02	1.02 ± 0.02	1.05 ± 0.02

Copyright by Mahidol University

Table B10 E' at 15°C of vulcanisates cured with EV system filled with various antioxidants after thermal oxidative ageing at various temperatures

Sample codename	E' at 15°C (MPa)					
	25°C	60°C	70°C	80°C	100°C	120°C
A	2.04	2.03	2.03	2.01	1.84	1.73
B	2.10	1.96	2.02	2.00	1.96	1.99
C	2.12	1.92	1.94	1.94	1.82	1.80
D	2.12	2.04	2.00	1.85	1.82	1.75
E	2.10	2.02	1.96	1.95	1.95	1.95
F	2.14	1.97	1.85	1.83	1.89	1.67

Table B11 $\tan\delta_{max}$ of vulcanisates cured with EV system filled with various antioxidants after thermal oxidative ageing at various temperatures

Sample codename	$\tan\delta_{max}$					
	25°C	60°C	70°C	80°C	100°C	120°C
A	2.324	2.414	2.399	2.453	2.457	2.523
B	2.294	2.381	2.390	2.369	2.368	2.467
C	2.276	2.447	2.422	2.419	2.406	2.460
D	2.360	2.376	2.391	2.409	2.408	2.451
E	2.354	2.382	2.404	2.425	2.446	2.463
F	2.231	2.281	2.355	2.299	2.244	2.312

Copyright by Mahidol University

Table B12 Tensile strength of aged NR vulcanisates cured with CV system at various 6-PPD concentration after thermal oxidative ageing at various temperatures

6-PPD concentration (phr)	Tensile strength (MPa)					
	25°C	60°C	70°C	80°C	100°C	120°C
0.5	3.97 ± 0.24	3.35 ± 0.92	3.42 ± 0.09	3.47 ± 0.28	2.03 ± 0.09	1.09 ± 0.66
1.0	7.13 ± 0.35	7.25 ± 0.08	4.65 ± 0.23	3.53 ± 0.12	2.13 ± 0.08	1.01 ± 0.07
2.0	19.68 ± 1.48	19.07 ± 0.83	7.43 ± 1.71	6.09 ± 0.15	2.89 ± 0.37	1.31 ± 0.04
4.0	14.70 ± 0.32	11.83 ± 0.94	5.71 ± 0.07	3.05 ± 0.30	2.12 ± 0.07	1.33 ± 0.07

Table B13 %swelling of aged NR vulcanisates cured with CV system at various 6-PPD concentration after thermal oxidative ageing at various temperatures

6-PPD concentration (phr)	%swelling					
	25°C	60°C	70°C	80°C	100°C	120°C
0.5	302.11 ± 1.49	295.38 ± 1.22	285.32 ± 0.52	279.00 ± 0.83	258.86 ± 0.71	254.41 ± 1.31
1.0	300.98 ± 1.10	288.98 ± 1.71	278.06 ± 0.95	272.42 ± 1.12	261.09 ± 1.11	255.39 ± 1.48
2.0	284.69 ± 2.91	279.28 ± 1.65	267.63 ± 2.57	261.23 ± 0.92	256.04 ± 1.93	254.78 ± 0.29
4.0	293.38 ± 1.27	286.23 ± 0.91	276.22 ± 1.28	272.62 ± 0.31	258.41 ± 0.67	256.45 ± 1.26

Copyright by Mahidol University

Table B14 M100 of aged NR vulcanisates cured with CV system at various 6-PPD concentration after thermal oxidative ageing at various temperatures

6-PPD concentration (phr)	M100 (MPa)					
	25°C	60°C	70°C	80°C	100°C	120°C
0.5	1.11 ± 0.05	1.12 ± 0.12	1.19 ± 0.04	1.25 ± 0.03	1.35 ± 0.04	-
1.0	1.11 ± 0.08	1.16 ± 0.06	1.25 ± 0.02	1.34 ± 0.02	1.46 ± 0.09	-
2.0	1.03 ± 0.01	1.12 ± 0.09	1.35 ± 0.01	1.42 ± 0.04	1.53 ± 0.03	-
4.0	1.17 ± 0.03	1.24 ± 0.04	1.31 ± 0.03	1.42 ± 0.02	1.53 ± 0.03	-

Table B15 E' at 15°C of aged NR vulcanisates cured with CV system at various 6-PPD concentration after thermal oxidative ageing at various temperatures

6-PPD concentration (phr)	E' at 15°C (MPa)					
	25°C	60°C	70°C	80°C	100°C	120°C
0.5	1.910	2.067	2.155	2.272	2.434	-
1.0	2.055	2.122	2.219	2.302	2.467	-
2.0	2.017	2.168	2.151	2.346	2.514	-
4.0	2.028	2.148	2.229	2.323	2.515	-

Copyright by Mahidol University

Table B16 $tan\delta_{max}$ of aged NR vulcanisates cured with CV system at various 6-PPD concentration after thermal oxidative ageing at various temperatures

6-PPD concentration (phr)	$tan\delta_{max}$					
	25°C	60°C	70°C	80°C	100°C	120°C
0.5	2.38	2.26	2.22	2.21	2.16	-
1.0	2.36	2.25	2.22	2.16	2.09	-
2.0	2.35	2.26	2.20	2.12	2.01	-
4.0	2.36	2.25	2.17	2.15	2.03	-

Table B17 Tensile strength of aged NR vulcanisates cured with EV system at various 6-PPD concentration after thermal oxidative ageing at various temperatures

6-PPD concentration (phr)	Tensile strength (MPa)					
	25°C	60°C	70°C	80°C	100°C	120°C
0.5	20.89 ± 1.37	21.26 ± 0.50	21.23 ± 1.10	22.14 ± 0.52	18.55 ± 0.48	1.83 ± 0.11
1.0	22.02 ± 1.68	21.40 ± 1.74	22.10 ± 1.13	21.29 ± 1.15	18.66 ± 1.21	2.53 ± 0.14
2.0	20.86 ± 1.15	22.95 ± 1.01	21.93 ± 1.41	20.58 ± 0.59	18.30 ± 0.46	2.15 ± 0.32
4.0	21.05 ± 1.30	22.59 ± 1.03	20.82 ± 1.28	20.17 ± 0.29	18.56 ± 0.19	2.72 ± 0.28

Copyright by Mahidol University

Table B18 %swelling of aged NR vulcanisates cured with EV system at various 6-PPD concentration after thermal oxidative ageing at various temperatures

6-PPD concentration (phr)	%swelling					
	25°C	60°C	70°C	80°C	100°C	120°C
0.5	310.30 ± 0.90	316.09 ± 0.89	318.95 ± 0.64	324.34 ± 0.58	328.65 ± 1.09	338.84 ± 1.19
1.0	313.39 ± 0.22	315.75 ± 0.36	318.77 ± 0.78	321.99 ± 0.66	328.29 ± 1.10	338.10 ± 0.71
2.0	313.84 ± 1.95	315.09 ± 2.18	317.94 ± 0.81	324.76 ± 1.41	326.47 ± 1.11	334.23 ± 3.84
4.0	312.08 ± 0.88	315.85 ± 0.50	318.19 ± 0.65	321.15 ± 0.78	324.44 ± 0.85	338.22 ± 0.75

Table B19 M100 of aged NR vulcanisates cured with EV system at various 6-PPD concentration after thermal oxidative ageing at various temperatures

6-PPD concentration (phr)	M100 (MPa)					
	25°C	60°C	70°C	80°C	100°C	120°C
0.5	0.94 ± 0.03	0.95 ± 0.02	0.95 ± 0.01	0.96 ± 0.02	0.96 ± 0.02	0.96 ± 0.03
1.0	0.94 ± 0.03	0.95 ± 0.02	0.95 ± 0.01	0.96 ± 0.02	0.97 ± 0.02	0.97 ± 0.03
2.0	0.94 ± 0.02	0.95 ± 0.03	0.95 ± 0.02	0.96 ± 0.02	0.96 ± 0.02	0.97 ± 0.03
4.0	0.94 ± 0.02	0.95 ± 0.01	0.95 ± 0.03	0.96 ± 0.03	0.96 ± 0.02	0.97 ± 0.01

Copyright by Mahidol University

Table B20 E' at 15°C of aged NR vulcanisates cured with EV system at various 6-PPD concentration after thermal oxidative ageing at various temperatures

6-PPD concentration (phr)	E' at 15°C (MPa)					
	25°C	60°C	70°C	80°C	100°C	120°C
0.5	2.01	1.93	1.91	1.90	1.85	1.82
1.0	2.05	1.91	1.91	1.89	1.84	1.82
2.0	2.12	1.92	1.94	1.94	1.76	1.80
4.0	2.06	1.96	1.86	1.87	1.98	1.76

Table B21 $\tan\delta_{max}$ of aged NR vulcanisates cured with EV system at various 6-PPD concentration after thermal oxidative ageing at various temperatures

6-PPD concentration (phr)	$\tan\delta_{max}$					
	25°C	60°C	70°C	80°C	100°C	120°C
0.5	2.38	2.47	2.44	2.44	2.46	2.47
1.0	2.39	2.42	2.42	2.44	2.46	2.47
2.0	2.38	2.43	2.42	2.42	2.43	2.46
4.0	2.38	2.41	2.42	2.46	2.45	2.47

Copyright by Mahidol University

BIOGRAPHY

NAME	Mr. Vorapong Pimolsiriphol
DATE OF BIRTH	Feb 14, 1980
PLACE OF BIRTH	Bangkok, Thailand
INSTITUTIONS ATTENDED	Mahidol University, 1998-2002: Bachelor of Science (Chemistry) Mahidol University, 2002-2005: Master of Science (Polymer Science and Technology)
HOME ADDRESS	65/6 Soi Happyland 1 Ladphrao khongjun Bangkapi Bangkok Thailand, 10240 Tel. 0-2734-0611, Mobile 0-6536-8565

Copyright by Mahidol University