

**PREPARATION, CHARACTERIZATION AND PROPERTIES OF WASTE
FERRITE FILLED RUBBER COMPOSITES**

by

SAM SUNG TING

**Thesis submitted in fulfilment of the
requirements for the degree
of Master of Science**

April 2007

**PREPARATION, CHARACTERIZATION AND PROPERTIES OF WASTE
FERRITE FILLED RUBBER COMPOSITES**

SAM SUNG TING

UNIVERSITI SAINS MALAYSIA

2007

ACKNOWLEDGEMENT

I would like to express my deepest and sincere gratitude to my supervisor, Prof. Dr. Hanafi Ismail. His wide knowledge and logical thinking have been of great value for me. His understanding, encouragement and personal guidance have provided a good basis for the present thesis. I wish to express my warm and sincere thanks to my co-supervisor Associate Prof. Dr. Ahmad Fauzi Mohd. Noor and Dr. Azhar Abu Bakar. Their comments and suggestions on my thesis have been useful to my research.

I would also like to thank the technician and staff in School of Materials and Mineral Resources Engineering especially Mr. Segaran a/l N.B. Dorai, Mr. Md. Zandar bin Md. Saman, Mr. Mohammad bin Hassan and Mr. Rashid Selamat, Mr. Mohd Rokman Mat Nasir and Mr. Mohd. Faizal Mohd. Kassim. They are willing to help students in conducting experiment in lab. They had also taught me a lot of technical knowledge. I wish to extend my warmest thanks to ACME Ferrite Products Sdn. Bhd for providing raw material in my research.

I owe my loving thanks to my parents, brother, sister and my special friend, Teoh Wan Yeong. Without their encouragement and understanding it would have been impossible for me to finish this work. My special gratitude is due to my postgraduate friends around. They let me own a happy life in USM.

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	vii
LIST OF FIGURES	ix
LIST OF SYMBOLS	xvi
LIST OF ABBREVIATION	xvii
LIST OF PUBLICATIONS	xix
ABSTRAK	xx
ABSTRACT	xxii
CHAPTER ONE : INTRODUCTION	
1.0 Introduction	1
1.1 Research Objectives	5
CHAPTER TWO : LITERATURE REVIEW	
2.0 Natural Rubber	7
2.1 SMR L	10
2.2 Styrene Butadiene Rubber (SBR)	11
2.3 Rubber Compounding	15
2.3.1 Definition of Rubber Compounding	15
2.3.2 Rubber Compounding Process	16
2.3.3 Vulcanization System	18
2.3.3(a) Sulfur Crosslinking Agent	18
2.3.3(b) Crosslinking Agent without Sulfur	21
2.4 Filler	24
2.4.1 Definition and Classification of Filler	24
2.4.2 Fillers Reinforcement Principles	25
2.5 Ferrites	28

2.5.1	Introduction to Ferrites	28
2.5.2	Classification of Ferrites	30
	2.5.2(a) Hard Ferrites	30
	2.6.2(b) Soft Ferrites	31
2.5.3	The Use of Ferrites in Rubber and Thermoplastic Elastomer (TPE)	34
2.5.4	Magnetic Properties of RFCs	36
2.6	Carbon Blacks	36
2.6.1	Classification of Carbon Blacks	37
2.6.2	Morphology and Properties of Carbon Blacks	39
	2.6.2(a) Particle size and surface area	39
	2.6.2(b) Structure	39
	2.6.2(c) Chemical properties and surface activity	40
	2.6.2(d) Electrical conductivity	41
2.6.3	The Effect of Carbon Blacks on Rubber Vulcanizate	41

CHAPTER THREE : EXPERIMENTS

3.0	Raw Materials	43
3.1	Instruments	44
3.2	Formulation of Rubber Compounds	44
3.3	Mixing and Rubber Compounding	46
3.4	Cure Characteristics Test	50
3.5	Vulcanization	50
3.6	Mechanical Test	51
	3.7.1 Tensile Test	51
	3.7.2 Hardness Test	52
3.7	Swelling Test	53
3.8	Morphology Test	54
3.9	Thermogravimetric Analysis	54
3.10	Aging Test	54
3.11	Magnetic Test	55

CHAPTER FOUR : RESULTS AND DISCUSSION

4.0	Filler Morphology	56
4.1	The Effect of Ferrite Loading on the Ferrite Filled SMR L Composites	57
4.1.1	Cure Characteristics	57
4.1.2	Mechanical Properties	59
4.1.3	Swelling Behavior	66
4.1.4	Thermogravimetric Analysis	67
4.1.5	Aging Properties	68
4.1.6	Magnetic Properties	71
4.2	Comparison between Ferrite Filled SMR L Composites and Ferrite Filled SBR Composites	74
4.2.1	Cure Characteristics	74
4.2.2	Mechanical Properties	78
4.2.3	Swelling Behavior	84
4.2.4	Thermogravimetric Analysis	85
4.2.5	Aging Properties	87
4.2.6	Magnetic Properties	92
4.3	The Effect of Type and Loading of Carbon Black on the Ferrite Filled SMR L Composites	95
4.3.1	Cure Characteristics	95
4.3.2	Mechanical Properties	98
4.3.3	Swelling Behavior	105
4.3.4	Thermogravimetric Analysis	106
4.3.5	Aging Properties	107
4.3.6	Magnetic Properties	113
4.4	The Effect of Ferrite Loading on Properties of SMR L/SBR Blends	116

4.4.1	Cure Characteristics	116
4.4.2	Mechanical Properties	119
4.4.3	Swelling Behavior	124
4.4.4	Thermogravimetric Analysis	125
4.4.5	Aging Properties	126
4.4.6	Magnetic Properties	130

CHAPTER FIVE : CONCLUSIONS AND RECOMMENDATION FOR FUTURE RESEARCH

5.1	Conclusions	135
5.2	Recommendation for Future Research	138
	REFERENCES	139
	PUBLICATIONS	147

LIST OF TABLES

		Page
Table 2.1	Typical content in NR	7
Table 2.2	Specification of SMR L	10
Table 2.3	The rubber ingredients and their function in rubber compounds	15
Table 2.4	Type of vulcanization system and its characteristics	19
Table 2.5	Relationship between particle size and reinforcement effect on rubber	25
Table 2.6	Properties of some popular carbon blacks	38
Table 3.1	List of raw material used	43
Table 3.2	Physical properties of waste ferrite and carbon black	43
Table 3.3	List of instruments and tests/processes involved in this research work	44
Table 3.4	Formulation of ferrite loading on SMR L composites	45
Table 3.5	Formulation of ferrite loading on SBR composites	45
Table 3.6	Formulation of types and loading of carbon black in hybrid with ferrite on NR compounds	45
Table 3.7	Formulation of ferrite loading on different compositions of SMR L/ SBR blends	46
Table 3.8	Mixing cycle of gum vulcanizate	48
Table 3.9	Mixing cycle of filled vulcanizate	49
Table 4.1	TGA data for RFCs with different loading of ferrite	68
Table 4.2	TGA data for RFCs with different loading of ferrite	87

Table 4.3	TGA data for RFCs with different loadings of carbon black	107
Table 4.4	TGA data for RFCs 40 phr ferrite filled SMR L/SBR blends	126

LIST OF FIGURES

		Page
Figure 2.1	Structure of cis 1,4- polyisoprene	8
Figure 2.2	Chemical structure of tri-block L-SBR	13
Figure 2.3	The rubber compounding steps from raw rubber to vulcanizate	17
Figure 2.4	The sulfur crosslinking process of polyisoprene	19
Figure 2.5	Interaction between XNBR and carbon black	27
Figure 2.6	The trend of stress-strain curve of Mullin Effect	27
Figure 2.7	Locations of the oxygen and the metal ions in two adjacent octants of a single cell of ferrites	28
Figure 2.8	The B-H curve of hard ferrite and soft ferrite	29
Figure 2.9	Simplified Process Flow Diagram	30
Figure 2.10	Various active groups at carbon black surface	41
Figure 3.1	Dimensions of rubber thin sheets	51
Figure 3.2	The shape and the dimensions of the mould used in hardness test	51
Figure 3.3	The shape and dimensions of tensile test specimen	52
Figure 4.1	SEM micrograph of waste nickel zinc ferrite (1000x magnification)	56
Figure 4.2	Variation of scorch time and cure time with ferrite loading of RFCs	58
Figure 4.3	Relationship between maximum torque and ferrite loading of RFCs	58

Figure 4.4	Relationship between torque difference and ferrite loading of RFCs	59
Figure 4.5	The effect of ferrite loading on elongation at break and tensile strength RFCs	60
Figure 4.6	SEM micrograph of the RFCs of ferrite distribution at loadings (a) 40 phr (b) 80 phr and (c) 120 phr at magnification 1000X	62
Figure 4.7	SEM micrograph of the RFCs after tensile fracture at various filler loadings (a) 0 phr (control) (b) 40 phr (c) 80 phr (d) 120 phr at magnification 100X	64
Figure 4.8	The effect of filler loading on M100 (modulus at 100% elongation) and M300 (modulus at 300% elongation) in SMR L matrix	65
Figure 4.9	The effect of filler loading on hardness Shore A of RFCs	65
Figure 4.10	The effect of ferrite loading on swelling percentage of RFCs	66
Figure 4.11	Thermogravimetric analysis of RFCs containing different ferrite loading	68
Figure 4.12	Variation in tensile strength of ferrite filled SMR L composites after aging at 70 °C	70
Figure 4.13	Variation in elongation at break (E_b) of ferrite filled SMR L composites after aging at 70 °C	70
Figure 4.14	Variation in modulus at 300% elongation (M300) ferrite filled SMR L composites after aging at 70 °C.	71
Figure 4.15	Variation of initial permeability with frequency for different ferrite loading of RFCs	73
Figure 4.16	Variation of quality factor (Q factor) with frequency for different ferrite loading of RFCs	73
Figure 4.17	Variation of relative loss factor with frequency for different ferrite loading of RFCs	74

Figure 4.18	Variation of scorch time with ferrite loadings in different rubber Matrix	76
Figure 4.19	Variation of cure time with ferrite loadings in different rubber matrix	76
Figure 4.20	Relationship of maximum torque between SMR L and SBR composites with various ferrite loadings	77
Figure 4.21	Relationship of torque difference between SMR L and SBR composites with various ferrite loadings	77
Figure 4.22	Comparison of tensile strength between SMR L and SBR composites with various ferrite loading	79
Figure 4.23	SEM micrograph of ferrite distribution of the SBR composites at loadings (a) 40 phr (b) 80 phr and (c) 120 phr at 500X magnification	82
Figure 4.24	Comparison of elongation at break (E_b) between SMR L and SBR composites with various ferrite loading	82
Figure 4.25	Comparison of M100 between SMR L and SBR composites with various ferrite loading	83
Figure 4.26	Comparison of M300 between SMR L and SBR composites with various ferrite loading	83
Figure 4.27	Comparison of hardness between SMR L and SBR composites with various ferrite loading	84
Figure 4.28	Comparison of swelling percentage between SMR L and SBR composites with various ferrite loading	85
Figure 4.29	Thermogravimetric analysis of SMR L composites and SBR composites with various ferrite loading	87
Figure 4.30	Variation in tensile strength of ferrite filled SMR L composites and SBR composites after 7 days aging	89
Figure 4.31	Variation in tensile strength of ferrite filled SMR L composites and SBR composites after 14 days aging	89

Figure 4.32	Variation in elongation at break of ferrite filled SMR L composites and SBR composites after 7 days aging	90
Figure 4.33	Variation in elongation at break of ferrite filled SMR L composites and SBR composites after 14 days aging	90
Figure 4.34	Variation in M100 of ferrite filled SMR L composites and SBR composites after 7 days aging	91
Figure 4.35	Variation in M100 of ferrite filled SMR L composites and SBR composites after 14 days aging	91
Figure 4.36	Variation of initial permeability with frequency for ferrite filled SMR L composites and SBR composites	93
Figure 4.37	Variation of quality factor with frequency for ferrite filled SMR L composites and SBR composites	94
Figure 4.38	Variation of RLF with frequency for ferrite filled SMR L composites and SBR composites	94
Figure 4.39	Variation of scorch time with carbon black loading in RFCs	96
Figure 4.40	Variation of cure time with carbon black loading in RFCs	97
Figure 4.41	Variation of maximum torque with carbon black loading in RFCs	97
Figure 4.42	Variation of torque difference with carbon black loading in RFCs	98
Figure 4.43	Variation of tensile strength with carbon blacks loading for SMR L	100
Figure 4.44	SEM micrograph of the tensile fracture surface of RFCs with carbon black N330 loading (a) 10 phr (b) 30 phr and (c) 50 phr at 500X magnification	101
Figure 4.45	SEM micrograph of the tensile fracture surface of RFCs with carbon black N660 loading (a) 10 phr (b) 30 phr and (c) 50 phr at 500X magnification	102
Figure 4.46	Variation of E_b with carbon blacks loading for SMR L	103

Figure 4.47	Variation of M100 with carbon blacks loading for SMR L	103
Figure 4.48	Variation of M300 with carbon blacks loading for SMR L	104
Figure 4.49	Variation of hardness with carbon blacks loading for SMR L	104
Figure 4.50	Relationship between weight of toluene uptake per gram of RFC and carbon blacks loading	105
Figure 4.51	Thermograph of RFCs with different type and loading of carbon black	107
Figure 4.52	Variation in tensile strength of carbon black N330 filled SMR L composites after aging	109
Figure 4.53	Variation in tensile strength of carbon black N660 filled SMR L composites after aging	109
Figure 4.54	Comparison of tensile strength between carbon black N330 and carbon black N660 filled SMR L composites after 14 days aging	110
Figure 4.55	Variation in E_b of carbon black N330 filled SMR L composites after aging	110
Figure 4.56	Variation in E_b of carbon black N660 filled SMR L composites after aging	111
Figure 4.57	Comparison of E_b between carbon black N330 and carbon black N660 filled SMR L composites after 14 days aging	111
Figure 4.58	Variation in M100 of carbon black N330 filled SMR L composites after aging	112
Figure 4.59	Variation in M100 of carbon black N660 filled SMR L composites after aging	112
Figure 4.60	Comparison of M100 between carbon black N330 and carbon black N660 filled SMR L composites after 14 days aging	113
Figure 4.61	Variation of initial permeability with frequency for different type and loading of carbon blacks	114

Figure 4.62	Variation of quality factor with frequency for different type and loading of carbon blacks	115
Figure 4.63	Variation of relative loss factor with frequency for different type and loading of carbon blacks	115
Figure 4.64	Dependence of scorch time (t_{s2}) on blend composition of SMR L and SBR for ferrite filled rubber blends	117
Figure 4.65	Dependence of cure time (t_{90}) on blend composition of SMR L and SBR for ferrite filled rubber blends	117
Figure 4.66	Dependence of maximum torque (M_H) on blend composition of SMR L and SBR for ferrite filled rubber blends	118
Figure 4.67	Dependence of torque difference ($M_H - M_L$) on blend composition of SMR L and SBR for ferrite filled rubber blends	118
Figure 4.68	Variation of tensile strength with blends composition of ferrite filled SMR L/SBR blends	120
Figure 4.69	SEM micrograph of 40 phr ferrite filled SMR L/SBR blends with blends composition (a) 50:50 (b) 75:25 at 500X magnification	121
Figure 4.70	SEM micrograph of 100 phr ferrite filled SMR L/SBR blends with blends composition (a) 50:50 (b) 75:25 at 500X magnification	122
Figure 4.71	Variation of E_b with blends composition of ferrite filled SMR L/SBR blends	123
Figure 4.72	Variation of M300 with blends composition of ferrite filled SMR L/SBR blends	123
Figure 4.73	Variation of hardness with blends composition of ferrite filled SMR L/SBR blends	124
Figure 4.74	Variation of swelling percentage with blends composition of ferrite filled SMR L/SBR blends	125
Figure 4.75	Thermograph of 40 phr ferrite filled SMR L/SBR blends	126

Figure 4.76	Variation in tensile strength of 40 phr ferrite filled SMR L/SBR blends after aging	128
Figure 4.77	Variation in tensile strength of 100 phr ferrite filled SMR L/SBR blends after aging	128
Figure 4.78	Variation in E_b of 40 phr ferrite filled SMR L/SBR blends after Aging	129
Figure 4.79	Variation in E_b of 100 phr ferrite filled SMR L/SBR blends after aging	129
Figure 4.80	Variation in M100 of 100 phr ferrite filled SMR L/SBR blends after aging	130
Figure 4.81	Variations in μ_i for 40 phr ferrite filled SMR L/SBR rubber blends as function of frequency	131
Figure 4.82	Variations in μ_i for 100 phr ferrite filled SMR L/SBR rubber blends as function of frequency	132
Figure 4.83	Variations in Q factor for 40 phr ferrite filled SMR L/SBR rubber blends as function of frequency	132
Figure 4.84	Variations in Q factor for 100 phr ferrite filled SMR L/SBR rubber blends as function of frequency	133
Figure 4.85	Variations in relative loss factor for 40 phr ferrite filled SMR L/SBR rubber blends as function of frequency	133
Figure 4.86	Variations in relative loss factor for 100 phr ferrite filled SMR L/SBR rubber blends as function of frequency	134

LIST OF SYMBOLS

M_H	Maximum Torque
M_H-M_L	Torque difference
T_{s2}	Scorch time
T_{90}	Cure time
$T_{-5\%}$	Temperature at 5% degradation
$T_{-30\%}$	Temperature at 30% degradation
μ_i	Initial permeability
Q	Quality factor
M100	Modulus at 100% elongation
M300	Modulus at 300% elongation

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
B	Magnetic induction
CBS	N-Cyclohexyl-2-Benzothiazole Sulfenamide
CDO	p-Benzoquinonedioxime
CM	Chlorinated polyethylene
CR	Chloroprene rubber
CV	Conventional vulcanization
DC	Direct current
EMI	Electro-magnetic interference
ENR	Epoxidised natural rubber
EPM	Ethylene propylene copolymer
E-SBR	Emulsion styrene butadiene rubber
ETU	Ethylene thiourea
EV	Efficient vulcanization
EVM	Ethylene vinyl acetate
H	Magnetizing force
HDPE	High density polyethylene
L-SBR	Solution styrene butadiene rubber
MBTS	Dibenzothiazole disulfide
MRPRA	Malaysia Rubber Producers Research Association
MWD	Molecular weight distribution

NKF	Sterically hindered bisphenol
nm	nanometer
NR	Natural rubber
PRI	Plasticity retention index
RFCs	Rubber ferrite composites
RFI	Radio frequency interference
RLF	Relative loss factor
SBR	Styrene butadiene rubber
SEM	Scanning Electron Microscope
SMR	Standard Malaysia Rubber
TGA	Thermogravimetric Analysis
TPE	Thermoplastic elastomer
TPNR	Thermoplastic natural rubber
TPU	Thermoplastic polyurethane
TSR	Technically specified rubber

LIST OF PUBLICATIONS

	Page
Publication A Properties of Ferrite Filled Natural Rubber Composites	147
Publication B The Effect of Carbon Black on the Properties of Magnetic Ferrite Filled Natural Rubber Composites	148
Publication C The Effect of Carbon Black on Ferrite Filled Natural Rubber Composites	149
Publication D The Effect of Ferrite Loading on Natural Rubber Composites	150
Publication E Tensile and Magnetic Properties of Waste Ferrite Filled SMR L/SBR Blends Rubber Composites	151
Publication F Effect of Waste Ferrite Loading on Tensile and Magnetic Properties of SMR L and SBR Composites	152

PREPARATION, CHARACTERIZATION AND PROPERTIES OF WASTE FERRITE FILLED RUBBER COMPOSITES

ABSTRACT

Ferrite is a type of magnetic material that is widely used in electrical and electronic industry. This type of material is normally available in ceramic form which is hard and brittle. During grinding process, some waste ferrite would be produced. This type of waste cannot be reused and re-sintered. Therefore, the incorporation of the waste ferrite in rubber is a way to transform this material into useful application. Average particle size of the waste ferrite used in this project is about 6 μm . The compounding process was conducted by using two roll mills and conventional vulcanization system was selected in this system. The scorch time (t_{s2}), cure time (t_{90}), maximum torque (M_H) and torque difference (M_H-M_L) were determined by using a Monsanto rheometer. The determination of rubber vulcanizate's properties includes tensile test, hardness test, swelling test, aging test, thermogravimetric analysis and magnetic test. The magnetic test involved the measurement of initial permeability (μ_i), quality factor (Q) and relative loss factor of ferrite filled rubber composites. Results showed that the thermal resistance of both natural rubber (NR) and styrene butadiene rubber (SBR) composites was improved by the incorporation of waste ferrite. The enhancement of thermal resistance was further improved by the incorporation of carbon blacks in NR. However, the incorporation of carbon blacks with waste ferrite in NR reduced the tensile strength of the composites. The waste ferrite could act as semi-reinforcing filler. Furthermore, the addition of waste ferrite in NR, SBR and NR/SBR blends could improve the swelling

resistance of the composites. Generally, the curing and mechanical properties of ferrite filled NR composites were better than ferrite filled SBR composites. However, the thermal resistance of SBR composites was slightly better than NR composites. The initial permeability (μ_i) of ferrite filled SMR L composites was higher than ferrite filled SBR composites at 40 phr ferrite loading. However, at higher ferrite loading the opposite trend was observed. At the similar ferrite loading, ferrite filled NR composites showed higher Q factor compared to ferrite filled SBR composites. This was due to the better ferrite-NR matrix interaction compared to ferrite-SBR matrix.

CHAPTER 1 INTRODUCTION

1.0 Introduction

In recent years, the soft ferrite cores have been widely used in electronics industry. This is because the soft ferrite has important characteristic over other magnetic material, i.e high volume resistivity in monolithic form. Ferrites are magnetic oxides of iron with other metal such as barium, strontium, manganese, nickel and zinc (Solomon *et al.*, 2005). The ferrite cores are produced by ceramic process. Thus, they are hard and brittle. The application of the ferrite core can be found in our daily life usage such as televisions, telephone system and computer. For example, the hard disk in our computer is coated with a layer of ferrite (Lloyd, 1996). However, the ferrite in ceramic form has inherent drawback because it is not mouldable or flexible to form complex shapes of products. Thus the incorporation of ferrite filler in rubber composites is utmost important because it has several advantages such as flexibility, easy machinability, and mouldability. Therefore, this type of flexible magnet which is called rubber ferrite composites (RFCs) can be tailored in various form of potential application in electrical and electronic industry (Sindhu *et al.*, 2002, Solomon *et al.*, 2005).

There are other type of ferrites that were employed in rubber matrix in order to impart magnetic properties and microwave absorbing properties in the composites. The nickel-zinc ferrite used in this research is a type of soft ferrite. Anantharaman *et al.* (1999) reported that this type of ferrite has high electric resistivity and low eddy current lost. Other researchers have also studied other type of soft ferrite such as manganese-zinc and nickel-cobalt-zinc (NiCoZn) ferrite in natural rubber composites (Anantharaman *et al.*, 2001, Puryanti *et al.*, 2006). Puryanti *et al.* (2006) has revealed the effect of NiCoZn ferrite on mechanical and electrical properties of thermoplastic elastomers. The tensile strength, elongation at break and the resistivity decreased but the dielectric constant increased. Meanwhile, the effect of hard ferrites in rubber

composites was discussed by Solomon *et al.* (2005). Cure characteristic and dielectric properties of strontium ferrite in natural rubber matrix have been investigated in the research. From the dielectric measurement, they found that the appropriate dielectric strength can be tailored by the appropriate amount of strontium ferrite.

Most of the previous researches focused their study by using virgin ferrite powder in rubber composites (Sindhu *et al.*, 2002, Puryati *et al.*, 2006, Sláma *et al.*, 1994, Anantharaman *et al.*, 1999 & 2001, Makled *et al.*, 2005). The electrical, magnetic and mechanical properties of the ferrite filled rubber composites were improved by using virgin ferrite. The electrical and magnetic properties imparted by the ferrite in natural rubber composites encouraged further research. This research was carried out by using by-product from ferrite cores industry and was incorporated in rubber matrix. The by-product which is a waste from the industry is believed to be able to reduce the compounding cost of rubber composites. Basically, the ferrite powder can be collected in the grinding process in ferrite core process. The abrasion mechanism in the grinding process produces ferrite powder with different particle size. The ferrite by-product cannot be recycled to form ceramic ferrite core and can only be sent to landfill. Thus, the employment of the waste ferrite as filler in rubber composites can save the cost of landfill and even earn benefit from the use of the by-product.

Fillers are important in rubber industry due to their special characteristic of them. Basically fillers can be divided in two major category, i.e reinforcing effect and non-reinforcing effect fillers. The reinforcing fillers normally refer to carbon blacks. Many researches have work on carbon black filled rubber matrix. The curing properties, mechanical properties, electrical properties and thermal properties were found to be improved with the addition of carbon black in rubber matrix (Flandin *et al.*, 2001, Tricás *et al.*, 2003, Kim and Jeong, 2005, Schwartz *et al.*, 2003, Guriya *et al.*, 1998). Besides that, carbon black is an important filler in the study of microwave absorbing properties.

A lot of researches focus on the incorporation of carbon black in RFCs in order to produce an enhanced microwave shielding material (Ganchev *et al.*, 1994, Annadurai *et al.*, 2002, Solomon *et al.*, 2003). Therefore, carbon black not only can improve the mechanical properties of the rubber composites but the dielectric and microwave absorbing properties. The hybrid of carbon black and ferrite in rubber matrix may be able to improve some magnetic properties such as initial permeability or quality factor. However, the research on this type of hybrid fillers is not developed.

Nevertheless, the production of the carbon blacks causes a lot of environmental problem. Thus, a substitution of carbon black is required in order to overcome the problem. In rubber industry the most notable carbon black replacement filler is silica. The utilization of silica in rubber industry can improve the performance of the rubber products due to the good rubber-filler interaction (Arroyo *et al.*, 2003). Hence, the environmental factor becomes an important factor for the rubber product manufacturer in choosing filler in their products. Other than the reinforcing filler, there are other types of fillers that can be used to impart the white or light-colored, certain unique properties like thermal conductivity, electrical properties and magnetic properties, and save the production cost (Pongdhorn *et al.*, 2005). Ferrites are filler with 0.05-14 μm with good chemical resistant (Wypych, 2000). It can be used as semi- reinforcing filler because of the particle size range between 1-5 μm (Ismail and Hashim, 1998). Besides the magnetic properties imparted, the ferrites can be used to reduce the production cost. Hence, the potential of the waste ferrite used as filler in rubber matrix is encouraging.

In order to achieve the desired properties of rubber composites, the blends between rubbers is sometimes required. The properties that obtained from the blends are superior to those individual constituent. Besides the properties imparted, the blends of elastomers can reduce the compounding cost and ease of shape fabrication. Several researches have been done by using various types of rubber blend (De *et al.*, 2006,

Phewthongin *et al.*, 2006, Jurkowska *et al.*, 2006, Wootthikanokkhan *et al.*, 2006). They found that the miscibility and compatibility of the rubber blends are important in tailoring some properties. The blends of natural rubber (NR) and styrene butadiene rubber (SBR) have been developed due to the cost and processing factor (Poh *et al.*, 2001). One of the significant effects of the NR/SBR blends is the improvement of mechanical properties because the NR can be crystallized upon stretching (Poh *et al.*, 2001). Poh *et al.* (2001) have reported the mechanical properties of NR blended with SBR. They suggested that the carbon black and silica were able to improve the tensile properties and hardness of rubber blends. Therefore, the incorporation of fillers in this polymer system are very popular for the industry for both cost and performance objectives. An advantage of using SBR in the blends is the preferential to take up more fillers compare with NR (Bhowmick and Stephens, 2001). This is because the addition of ferrite in rubber composites is normally in a very high volume (Mohammed *et al.*, 2002) and can achieve 120 parts per hundred rubber (phr). Thus, SBR in blends with natural rubber can improve the ferrite uptake.

The latest development found is the incorporation of the nanosized ferrite powder in rubber composites (Kolev *et al.*, 2006). The research was carried out by comparing the conventional micron-sized magnetite filler with nanosized filler in silicon rubber matrix. In the research, they found that the nanosized filler is suitable to be used in high frequency application because the resonance magnetic losses of the RFCs was shifted to the higher frequencies compared to the micron-sized ferrite filler. Furthermore, the addition of nanosized ferrite in polymer composites was proven to be able to improve some mechanical properties such as the modulus in polymer due to the well dispersed system (Bhaskar *et al.*, 2004). Therefore, nanosized ferrite not only can impart magnetic properties but enhanced the mechanical properties of rubber composites.

In this project, the addition of the waste ferrite as a filler in rubber matrix is relatively new research. Initially, the research was focused on the effect of ferrite loading in natural rubber. The result obtained was compared with the result of synthetic rubber, i.e SBR. Furthermore, the effect of the incorporation of carbon black in RFCs was investigated. Finally, the effect of ferrite loading in the rubber blends was examined, i.e natural rubber and SBR.

1.1 Research Objectives

The aim of this research was to obtain a magnetic rubber with the incorporation of waste ferrite in natural rubber and synthetic rubber. The potential of the waste ferrite as a filler in rubber composites need to be studied in order to resolve the environmental problem. Hence, the research was divided in 4 phases:

1. The effect of the waste ferrite loading on properties of SMR L composites was investigated.
2. The comparison effect of waste ferrite loading on properties of SBR composites and SMR L composites.
3. The effect of the carbon black loading in hybrid with waste ferrite on properties of SMR L composites.
4. The effect of waste ferrite loading on properties of SMR L/SBR blends.

The testing involved from part 1 to part 4 were cure characteristics, mechanical tests, swelling test, thermal stability tests, magnetic tests and morphology. The cure characteristics parameter measured includes scorch time (t_{s2}), cure time (t_{90}), maximum torque (M_H) and torque difference ($M_H - M_L$). The cure time is important to determine the time needed to produce a rubber vulcanizate. The mechanical tests include tensile strength, modulus at 100% and 300% elongation, elongation at break and hardness. Swelling test was conducted by measuring the swelling percentage of the rubber composites. Thermal tests were focused on the thermogravimetric analysis (TGA) and

aging test. The magnetic tests were initial permeability (μ_i), quality factor (Q) and relative loss factor (RLF). All of the tests are important to be conducted so that the effect of the waste ferrite as a filler in rubber matrix can be known.

CHAPTER 2 LITERATURE REVIEW

2.0 Natural Rubber

Natural rubber (NR) was discovered around 400 hundred years ago. It was found in the sap of a tree named *Hevea brasiliensis*. The basic polymer appears in the sap called polyisoprene. The *Hevea brasiliensis* produces 99.99% *cis*-1,4-polyisoprene and remains the most widely used products nowadays. The typical content of natural rubber is shown in Table 2.1. The analysis was conducted by using acetone extract method (Barlow and Fred, 1988). The word “rubber” normally refers to natural rubber and the vendors normally assume the customer was specifically asking for natural rubber (Ciesielski, 1999). In the mid of 20-century, some chemists had discovered the use of Ziegler-Natta catalyst for the production of synthetic *cis*-polyisoprene (Bhowmick and Stephens, 2001). However, the synthetic *cis*-polyisoprene still cannot replace the natural rubber to become the most widely used rubber in the world. Due to the toxic waste generated from synthetic rubber industry, the natural rubber becomes more important because it is a sustainable raw material.

Table 2.1: Typical content of NR

Component	%
Moisture	0.6
Acetone extract	2.9
Protein (calculated from nitrogen)	2.8
Ash	0.4
Rubber hydrocarbon	93.3

The chemical structure of *cis*-polyisoprene is shown in Figure 2.1. The average molecular weight of this homopolymer in NR ranges from 200,000 to 400,000 with broad molecular weight distribution (MWD). The molecular weight could be broken down to facilitate the processability of rubber by mastication process. The broad MWD

resulted in good processing behavior of NR (Hoffman, 1989). However, the determination of the molecular weight of natural rubber is difficult because the long chain of the rubber would degrade in gas permeation chromatography unless some parameters such as solvent and interstitial gaps are well maintained (Bhowmick and Stephens, 2001). Thus, light scattering measurement conducted is more effective in determining the molecular weight. The MWD of NR depends on the tapping frequency, the more frequency of tapping the lesser the gel content. The rubber tapped for the first time contains around 80% gel (Sekhar, 1962).

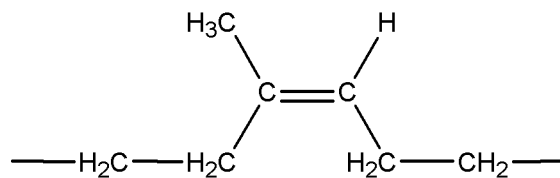


Figure 2.1: Structure of cis 1,4- polyisoprene

The double bond of polyisoprene in NR is important for sulphur vulcanization process. However these double bonds are easily attacked by oxygen or ozone consequently degrading the rubber. Thus, antioxidant is normally added into the rubber compounds in order to prevent it from reacting with oxygen. Some of the antioxidant such as lignin (Gregorová *et al.*, 2006) and alkylated phenolic resins (Malshe *et al.*, 2006) are quite effective in reducing the degradation of rubber vulcanizate. The raw NR has less resistance to the organic solvent or liquid such as benzene, toluene, gasoline, vegetable oil and mineral oil. These liquid would swell the unvulcanized rubber to viscous liquid because the polymer chains has broken. Therefore, the chemical crosslinking in NR is important to reduce the swelling effect of NR. The employment of the filler in NR vulcanizate can also decrease the swelling percentage. Ismail *et al.* (1999) reported the swelling effect of diamine salt of fatty acid in NR. They found that the incorporation of the filler can reduce the swelling effect. According to Da Costa *et*

al. (2001), the addition of rice husk ash in natural rubber can also decrease the swelling effect of the rubber to organic solvent (Da Costa *et al.*, 2001)

The raw NR has the specific gravity of 0.934 at 20°C. It increases when the rubber is frozen or stretched. The specific heat of NR is 0.502 at 20°C. The refraction index after acetone extraction ranges between 1.5215 and 1.5238. Besides that, the specific resistivity of rubber sheets and crepe is 1×10^{15} and 2×10^{15} ohms-cm respectively (Hoffman, 1989). The NR can undergo cold crystallization at temperature around -25°C. The rate of the crystallization of the synthetic cis-1,4-polyisoprene containing stearic acid is lower compared to NR (Burfield, 1984). The stereoregularity of the polymer chain of NR can undergo stress induced crystallization. The phenomenon can be seen from the tensile tests of the NR vulcanizate. Several researches indicate that tensile modulus is greatly increased while the stress applied on the vulcanizate. The tensile strength is even higher than the semi-reinforcing filler filled vulcanizate (Poh *et al.*, 2002, Anantharaman *et al.*, 2001). There are some unique thermal effects with the elongation of the rubber. When the rubber is elongated at small extent, the temperature would drop. However, the temperature increased at greater elongation (Stern and Jacob, 1967).

The NR grades plantation rubbers are very hard to process, thus the mastication is required to break down the molecular weight of the polymer chains for the eased of processing. NR also has excellent extrudability and calendability. The high cure rate of NR is also important for the rubber processability. The double bonds present in the polyisoprene contribute to this property (Hoffman, 1989). In the process of producing rubber products, the rubber undergoes creep, stress relaxation, recovery and flow. These phenomena could influence the processability of the rubber. For instance, the elastic properties of rubbers could influence the die swell, nerve, green strength, shrinkage, etc. The stress relaxation of the viscoelastic materials always

brings the bad impact of the rubber springs in engineering. There are 2 phases of stress relaxation i.e the short term physical relaxation and long term chemical relaxation. The physical relaxation refers to the molecular rearrangement and orientation whereas the chemical relaxation is molecular chain scission and reformation.

2.1 SMR L

The classification of the standard of the smoked sheet and pale crepe from different plantation is needed because the cure rate and processability can vary. SMR (Standard Malaysia Rubber) is a scheme produced by Malaysia to classify the grades of rubber for dirt content, ash content, nitrogen content, plasticity Retention Index (PRI), Mooney viscosity and others related specification. This scheme is widely recognized by some rubber producing countries. This type of Technically Specified Rubber (TSR) is supplied in compact, pressed bales or sheets. The marketing successes of the natural rubber graded by SMR bring about the grading of other countries such as SIR from Indonesia, SLR from Sri Lanka, TTR from Thailand etc (Hofmann, 1989). The production of the SMR L is focused on its color. The light colored SMR is produced by adding sodium metabisulfite at 0.04% dry rubber content (DRC). Table 2.2 shows the SMR L specification. (Bhowmick and Stephens, 2001).

Table 2.2: Specification of SMR L

Parameter	SMR L
Dirt retained on 44 μ aperture (max, % wt)	0.03
Ash content (max, % wt)	0.5
Nitrogen content (max, % wt)	0.60
Volatile matter (max, % wt)	0.80
Wallace Rapid Plasticity-minimum initial value (P_0)	30
Plasticity Retention Index, PRI (min, %)	60
Color limit (Lovibond Scale, max)	6.0

2.2 Styrene Butadiene Rubber (SBR)

SBR was first discovered by E. Tchunkur and A. Bock by an emulsion polymerization process in 1929. These emulsion SBR (E-SBR) called Buna S, is easier for processing compare to other Buna grades SBR (Hofmann, 1989). There are two types E-SBR in the market. One of them is the hot rubber which is produced at 50°C, whereby the molecular weight is high and depolymerization can occur at high temperature. Another type of E-SBR, cold rubber is using a redox initiator to lower the polymerization temperature to 5°C and the chain modifier is applied to control the molecular weight.

The World War II which occurred in 1939 has brought about the large scale production of SBR in some western countries. United States and Canada had produced SBR for the use in military and civilian requirement. The purpose of producing this synthetic rubber is to lessen the dependence on natural rubber which is mostly produced in third world countries (Barlow and Fred, 1988). In 1953, about 62% of the SBR production is cold rubbers and the hot rubber become relatively unimportant (Hofmann, 1989). Some of the cold rubber was marketed as oil extended rubbers (OE-SBR). The usage of the catalyst based organic metallic compounds in the solution process made L-SBR. But, the E-SBR is still the major marketed rubber.

The mixture of sodium salt emulsifier is normally used as emulsifier for the dispersion in polymerization (Hoffman, 1989). The other chemicals used in the process are free radicals in initiation step, redox activator as chelating agent and chain modifier in controlling the molecular weight. The Mooney viscosity (ML 1+4) of the commercial E-SBR ranges from 30 to around 120. The average molecular weight is 250,000 to 800,000. The viscosity of SBR is particularly important because it cannot be masticated readily. The viscosity would affect the processibility of the rubber as the lower viscosity grade of E-SBR would accept the filler and oil more easily. However the higher

viscosity grade E-SBR has better mechanical properties such as tensile strength and compression set. The styrene content in SBR has great influence to its properties. The higher the styrene content increases the T_g and decrease the resilience. Nevertheless, it improves the processibility such as extrusion rate and green strength. Besides the molecular structure of the SBR, the types and amount of stabilizer and emulsifier added in the E-SBR processing would affect the processibility (Hoffman, 1989).

L- SBR has different properties depending on its content and the orientation of the styrene and butadiene block in SBR. The SBR products can be tailored in different properties by using the particular polymerization conditions. There are different types of L-SBR such as L-SBR with higher 1,2- butadiene content, random L-SBR, segmented L-SBR and triblock L-SBR. The vinyl unit present in the side group contributes the same properties as styrene which would lower the T_g . Another similar type of L-SBR is the random L-SBR. The difference of random L-SBR from high 1,2-butadiene content L SBR is the higher content of cis1, 4- butadiene. It also has narrower molecular weight distribution. Another type of L-SBR is segmented L-SBR. The processibility of this type of L-SBR is good because the polystyrene blocks behave like thermoplastic. Furthermore, it has good abrasion resistance. There is a type of the L-SBR which can be acted as elastomer without vulcanization is called tri-block L-SBR. The SBS structure of the tri-block L-SBR is shown in Figure 2.2. The two phases of the rubber are contributed to the physical properties, i.e the styrene phase and the butadiene blocks (Hoffman, 1989).

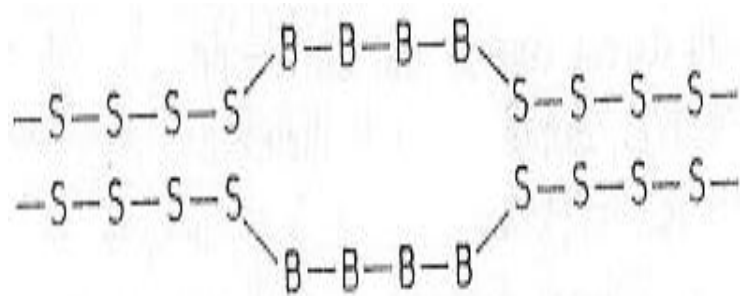


Figure 2.2: Chemical structure of tri-block L-SBR

SBR is usually used to produce masterbatches with oil and carbon black. The masterbatches with the addition of oil called OE-SBR. The processibility of the rubber can be improved by using the oil and this would reduce the production cost in high loading (Barlow and Fred, 1988). The oils used in the OE-SBR are made from petroleum oil which is cheaper than other oils. Basically the oils applied in OE-SBR are highly aromatic and naphthetic. However, the high aromatic oil is toxic. Bowman *et al.* (2004) used the non-toxic extender to replace the high aromatic oil. The OE-SBR is important in tyre industry because it produce good traction and low tire noise (Hoffman, 1989). SBR masterbatches with oil and carbon black can be produced by latex process method. The first step is stir the carbon black in high speed with water dispersion process, then adding the dispersion agent and stabilizer, the oil is added before coagulation and finally dried and baled.

The vulcanizate of the SBR strongly depends on the filler in the matrix. The gum vulcanizate of SBR has far poorer tensile strength compared to natural rubber vulcanizate. Thus, reinforcing filler is required to enhance the tensile properties and physical properties. Carbon black and silica are among the common reinforcing filler applied in SBR to improve the tensile strength. Recent development has used starch, carbon nanofiber and mica as reinforcing filler in SBR (Gauthier *et al.*, 2005, Qi *et al.*, 2006, Furtado *et al.*, 1999). Although the filler can improve the SBR vulcanizate comparable to NR, however the tear resistance is poorer than NR (Hoffman, 1989).

The SBR has superior dynamic fatigue resistance, aging resistance and heat resistance over NR vulcanizate. The service temperature of the SBR is higher than NR for about 20°C. However, the service temperature is varying with the vulcanization system used. Basfar *et al.* (2002) reported that the peroxide cured SBR has superior aging resistance compared to sulfur and radiation curing. The present of reinforcing filler in SBR can produce abrasion resistance which is comparable with NR due to its good abrasion resistance and aging properties. SBR replaces NR in some application such as passenger tire treads. However in the dynamic application the high heat build up of the SBR can lead to the excess temperature of the tyre treads. Thus, the SBR is usually blended with other type of rubber such as NR or polybutadiene (BR) for lowering the heat build up. Pham *et al* (2001) investigated the different types of SBR in blends with NR in tyre treads compound. The research found that the tensile, tear strength, aging index and abrasion resistance are strongly dependant on the styrene and butadiene content in SBR. The SBR also has poor conductivity as NR because it is non-polar material. However, the electrical properties of the SBR depend on the residual emulsifier and electrolyte present. In comparison with NR, SBR has greater shrinkage in calendaring process and greater die swell in the of extrusion process (Stern and Jacob, 1967).

The different process of the SBR produces different properties. Thus, it can be used in variety applications. The E-SBR is applied mostly in heavy truck and high speed tires and sometimes blended with L-SBR to improve some properties such as extrudability, surface smoothes, and heat resistance. The different grade of SBR can be applied in variety of industry purpose. For example, the grade 1500 is normally used in tire treads and technical rubber, grade 1502 is used in light colour technical rubber goods and grade 1509 is used in cable and electrical industry (Hoffman, 1989).

2.3 Rubber Compounding

2.3.1 Definition of Rubber Compounding

In principles, the basic properties of the elastomers come from its nature. However the incorporation of other ingredient into the matrix can modify the properties (Hofmann, 1989). The process of the introducing the chemicals or additives into the rubber to modify its properties is called rubber compounding. A good compounding needs to consider many aspects such as environmentally safe, good processability, satisfactory service life and minimum production cost (Barlow, 1988). The different types of additives and chemical contribute to the above factors. Table 2.3 shows some ingredients and their function in rubber compounds (Barlow, 1988).

Table 2.3: The rubber ingredients and their function in rubber compounds

Ingredients	Function
Elastomer	The main characteristics of the rubber compounds
Vulcanizing agent	To produce chemical reaction with rubber matrix to form crosslinking
Accelerators	Materials used in quickening the speed of the vulcanization
Activator	A substance that increase the effect of accelerators
Fillers	It divided into black and non-black filler to reinforce the rubbers
Age resistor	Material used to prolong the service life of rubber products

2.3.2 Rubber Compounding Process

The overall compounding process is shown in Figure 2.3. The early stage of the rubber compounding is the softening process of raw rubber by mastication. Sometimes the peptisers will be added. In rubber industry, the widely used equipment to masticate rubber is two roll mills. The mastication is normally applied to NR. The synthetic rubber seldom needs prior mastication because they are tailored made and can be processed directly. The mastication time of NR is longer than synthetic rubber because the NR is normally supplied in high Mooney Viscosity. Mastication time of NR is normally controlled within 15 minutes whereas the synthetic rubber is just only 2 minutes (SBP Board of Consultants & Engineers, 1900). Mastication process is also important to produce a homogenous dispersion of filler into the rubber matrix. The filler can be only dispersed well in rubber matrix when certain viscosity is achieved. The proper viscosity can improve the processibility of rubber compounds.

Basically, there are two categories of mastication process, i.e mastication without peptisers and mastication with peptisers. The mastication without peptisers requires high shear force of two roll mills or internal mixer to break down the polymer chain and consequently reduce the molecular weight. The mastication process depends on the temperature. As the temperature increase, the elastomers soften and consequently absorb less mechanical energy. This is due to the polymer molecules can flow more easily. The high temperature can cause oxidative attack and increase the rate of chain scission consequently reducing the viscosity. The mechanical degradation will then occur and lead to the excessive softening.

After mastication process, the ingredients will be added in the raw rubber by using two roll mills or internal mixer. A typical recipe and mixing schedule was designed by Committee D-11 for the reference of rubber compounder in rubber mixing process. For example, the mixing procedure of carbon black in NR can be found in ASTM Designation D 3192-82. In the finishing step of the compounding, the mass of the

compounds needs to be checked. If the mass difference of the batch is more than 0.5% compared to theoretical mass, the batch has to be rejected (Morton, 1987).

The finishing step of the rubber compounding is the shaping of products. During the vulcanization process, the long chain of the rubber molecules forms crosslinks with the reaction of vulcanization agent into 3 dimensional structures. Therefore, the rubber transforms from soft to stronger elastic material. Besides that, the rubber would have better resistance to heat, light and some solvents. The details features and benefit of the vulcanization process will be discussed in next section.

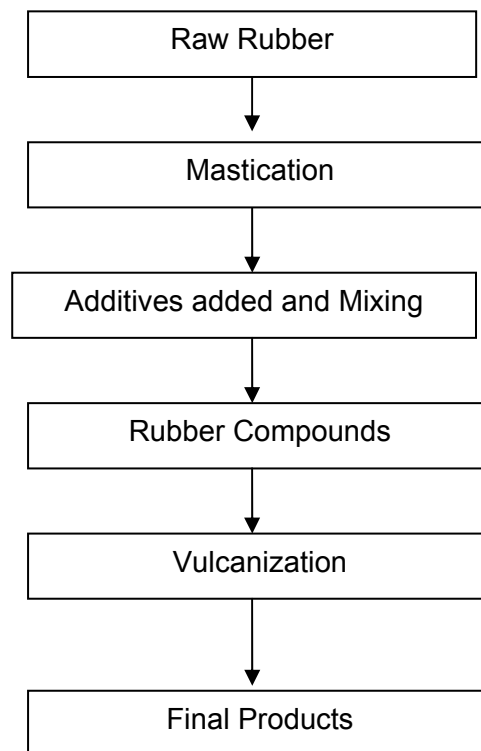


Figure 2.3: The rubber processing steps from raw rubber to vulcanizate (Ismail and Hasim, 1998)

2.3.3 Vulcanization System

2.3.3(a) Sulfur Crosslinking Agent

Vulcanization is a process that increases the overall elasticity of rubber by locking the chains to each other through chemical crosslinks. The slippage behavior of the plastic-like material would change to more dimensional stable material (Ciesielski, 1999). The most common use of crosslink agent in rubber is sulfur because it is inexpensive and plentiful. This crosslinker can link the double bonds of the rubber chains together. NR and SBR are always crosslinked by this type of vulcanization process due to the only small amount of sulfur to be used.

Generally, there are a number of sites which are attractive to sulfur atoms along the rubber molecules called cure sites. In the vulcanization reaction, the eight-membered ring of sulfur breaks down in smaller parts with varying numbers of sulfur atoms. Figure 2.4 represents the sulfur crosslinking process of polyisoprene. One or more sulfur atoms can attach itself to the double bond, and then the sulfur can grow until it reaches the other cure sites of double bonds. The sulfur bridge can vary from two to ten atoms. The length of the sulfur chain can affect the physical properties of the vulcanizate. The shorter the sulfur crosslink give the better heat resistance to rubber vulcanizate. Thus, the EV vulcanization system which has lower polysulfide crosslinks gives better heat and aging resistance. However, the high crosslink in the rubber vulcanizate produce very good dynamic properties. The dynamic properties are important in tyre side wall industry. Good flexing properties can reduce the formation of cracks and consequently minimize the failure of the rubber products.

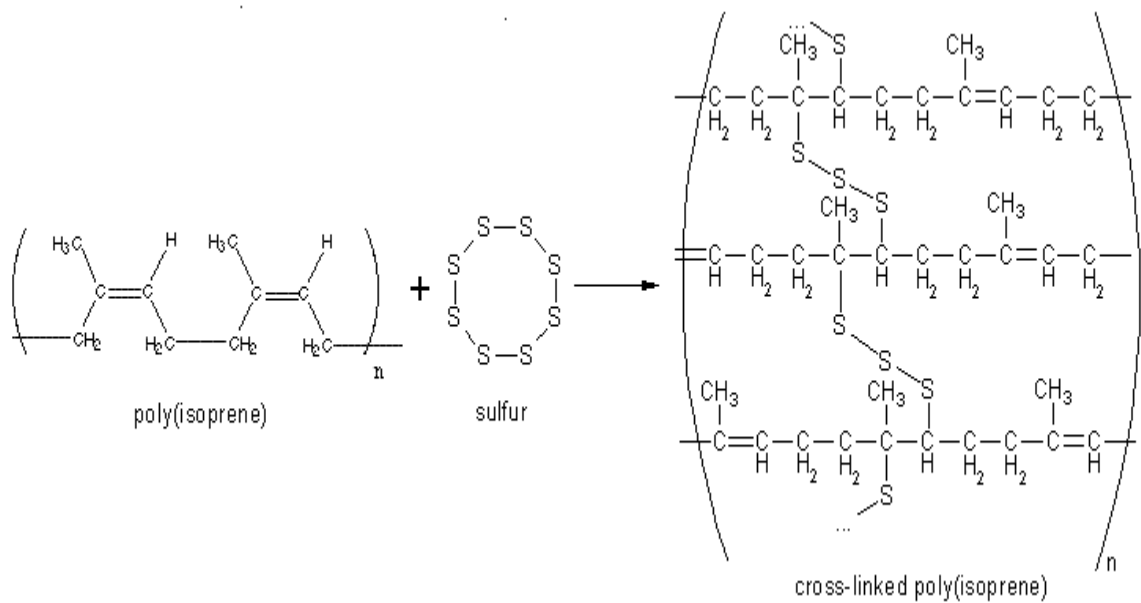


Figure 2.4: The sulfur crosslinking process of polyisoprene

Three categories of sulfur vulcanization system are used in rubber technology, i.e conventional vulcanization (CV), semi-efficient vulcanization (semi-EV) and efficient vulcanization (EV). The difference between these systems is the ratio of sulfur and accelerator added into the rubber compounds. Different properties of the vulcanizate can be obtained by varying the sulfur to accelerator ratio in recipe. Table 2.4 represents the type of vulcanization system and its characteristics.

Table 2.4: Type of vulcanization system and its characteristics (Ismail & Hashim, 1998)

Properties	CV	Semi-EV	EV
E* value	8-25	4-8	1.5-4
di- and polysulfidic crosslinks	95	50	20
monosulfidic crosslinks	5	50	80
Cyclic sulfidic concentration	High	Medium	Low
Heat aging resistance	Low	Medium	High
Resilience	Low	Medium	High
Compression set (%) at 70°C for 220 hours	30	20	10

The sulfur content in CV ranges from 2 to 3 phr and the accelerator is 0.5-1 phr. This curing system produces multiple sulfurs in the crosslink called polysulfidic crosslinks. The EV system contains the sulfur about 0.3-0.8 phr and accelerator 2-5 phr. More monosulfidic crosslinks were produced by using this system compared to CV. Semi-EV system is compromise between CV and EV system. The sulfur used in semi-EV is 1-2 phr and the accelerator is 1-2.5 phr. The sulfur to accelerator ratio of different vulcanization system represents the different cure rates of the system. As well known, the EV system with highest accelerator to sulfur ratio has highest cure rate. However, as the temperature increased the effect of the accelerator to sulfur ratio becomes not significant (Sadequ et al., 1998). In term of fatigue life, CV system is better compared to semi-EV and EV. However, the heat aging resistance of CV is poorer than semi-EV and EV due to the presence of polysulfidic crosslinks in CV system. The sulfur-sulfur bonds are weaker than sulfur-carbon bonds, which eventually leads to the thermally unstable in CV system. Rattanasom *et al.* (2005) investigated the heat aging resistance of natural rubber tyre tread reclaimed rubber blends in different vulcanization system. They found that the heat aging resistance of vulcanizate with EV system was greater than CV system. Nevertheless, the mechanical properties of the CV vulcanizate were greater than EV system. The type of rubber and additives used would affect the properties of vulcanization system. Ismail and Chia (1998) reported the effect of multifunctional additive and vulcanization system on silica filled epoxidized natural rubber (ENR). The result showed that the semi-EV system exhibited greater tensile strength and tear strength followed by EV and CV system. The research carried out also indicated the crosslink density of the CV in ENR was the greatest as it showed higher hardness and maximum torque compared to semi-EV and EV system.

Sometimes, the sulfur cure system is used in conjunction with urethane crosslinkers. The urethane crosslinker was discovered by researchers of Malaysia Rubber Producers Research Association (MRPRA). The urethane crosslinker was

commercialized under the trade name Novor 924. The crosslinker is an adduct of p-nitrosophenol and diisocyanate which is called quinine oxime urethane. The rubber vulcanizate formed with this crosslinker would have better heat aging resistance (Barlow, 1988).

2.3.3(b) Non- Sulfur Crosslinking Agent

(a) Peroxide curing system

Peroxide crosslinking was discovered in the early 1950s. It becomes more important with the development of saturated synthetic rubber such as Ethylene vinylacetate (EVM), Ethylene propylene copolymer (EPM), Chlorinated polyethylene (CM) and silicone rubber. There are several advantages of using peroxide curing system such as scorch free storage of compounds, rapid vulcanization at high temperatures, low compression set, no discoloration and stable at high temperature. Moreover, this curing agent is easy in handling and not hazardous (Hofmann, 1989).

Peroxide curing agent can be divided in two categories, i.e peroxides with carboxyl groups such as diacetylperoxide and peroxides without carboxyl groups such as di-terbutylperoxide. In comparison, the carboxyl group peroxides have lower sensitivity to acids, lower decomposition temperature and higher sensitivity to oxygen. The curing reaction starts when the peroxides start to decompose. The decomposition of the peroxides is influenced by heat, light or high energy radiation and reactions with other materials (Hofmann, 1989). All these factors need to be considered in choosing the correct peroxides curing agents. In peroxide curing system, some disadvantages found such as limited compounding due to the easy reaction with antioxidant and plasticizer, sensitive to oxygen and difficult in adjusting scorch time/plateau relation.

In term of vulcanizate, the products normally have lower tear resistance, lower elasticity and poorer dynamic properties compared to sulfur vulcanizate. Nakason *et al.*

(2006) reported the effect on curing system on dynamic vulcanization of NR/high density polyethylene (HDPE) blends. The researches cured the blends through three vulcanization system, i.e sulfur, peroxide and mixed of both systems. The peroxide cured products showed higher tensile strength, tension set and hardness compared to sulfur cured vulcanizates. Nevertheless, the elongation at break of peroxide cured products was inferior. This is however depending on the type of rubber or the blends involved in the system. For example, the ENR/Polypropylene blends which were cured by peroxide curing system exhibits higher tensile strength and hardness compared to sulfur cured products (Nakason *et al.*, 2006). Peroxide cured products generally give lower swelling resistance compared to sulfur cured system. However, the heat stability and compression set is better than the sulfur system.

(b) Metallic Oxide

Generally, metallic oxides are used as curing agent in chloroprene rubber (CR). The metal oxides used include zinc oxide, magnesium oxide and lead oxide. The addition of the metallic oxide can also improve the water resistance of the vulcanizate. The metal oxide is always used to control the scorch time of CR.

The most commonly used metallic oxide is zinc oxide. It can be produced by either American process or French process. The American process produces the zinc oxide from zinc sulfide ore whereas the raw material of French process is zinc metal. The zinc sulfide is oxidized and then reduced with carbon to zinc vapor in American process. However, the zinc vapors of the French process produced by direct vaporization of zinc metal. In the both process, the zinc vapor will be drawn in combustion zone and oxidized at the final stage. Zinc oxide produced by French process has more nearly spherical shape and narrower particle size compared to American process. The purity of the zinc oxide of French process is higher. Moreover it has finer particle size and bigger surface area (Barlow, 1988). This characteristic is

preferred for the curing of CR. The zinc oxide is normally added late in the mix cycle to avoid scorch and also insure a good particle distribution. The incomplete dispersion would cause localized overcure and consequently affecting the physical properties of vulcanizate. Due to the economic factor, the use of predispersed form of metallic oxide in compounding can reduce the mix cycle (Morton, 1987).

In order to reduce the moisture contamination, magnesia would sometimes be added. The suitable ratio of zinc oxide to magnesium oxide is 5 parts to 4 parts. Ismail *et al.* (2003) had used the combination of zinc oxide and magnesium oxide together with ethylene thiourea (ETU) as curative system to compare with a type of quaternary ammonium salt in CR. The metallic oxide combination system still shows superior tensile strength, hardness and resilience compared to the newer system.

(c) Miscellaneous

For crosslinking of butyl rubber (IIR), several curing agent have been used, the most suitable one is p-Benzoquinonedioxime (CDO). However, CDO is not suitable for the usage of classic diene rubber. It is seldom used in conjunction with sulfur because the addition of sulfur would reduce the heat stability and compression set of the vulcanizates. The combination with MBTS in curing system is recommended as it gives the optimum tensile strength, elongation at break, age resistance and compression set. Another comparable curing agent applied in IIR is polymetholphenolic resins. This type of curing agent is normally use together with SnCl_2 activator. Nevertheless, this activator is difficult to mix in rubber and corrosive (Hofmann, 1989). Besides that, electron beam curing agent can be used in vulcanization throughout the tire industry. About 4 megarads of radiation dosage is needed in tire production. This curing agent has improved the ozone resistance and crack initiation in rubber of SBR vulcanizate (Ciesielski, 1999).

2.4 Filler

2.4.1 Definition and Classification of Filler

Filler is a material that can be added in sufficiently large quantities to reduce the polymer matrix used in compounding (SBP Consultants & Engineers, 1900). It is also defined as the substance that is inert and not poisonous in processing (Bakar, 1995). The purpose of adding filler into the rubber matrix is to reduce the production cost, and sometimes to give reinforcement. The reinforcing filler would increase the mechanical properties such as tensile strength, elongation at break, and tear resistance to the rubber vulcanizate. Examples of reinforcing filler are carbon black, precipitated silica, fumed silica, calcium silicate and zinc oxide etc. On the other hand, the non-reinforcing fillers are used to impart the white or light color, reducing cost and produce certain unique properties of vulcanizate such as thermal conductivity (Barlow & Fred, 1988). Besides that, some of the fillers are added into rubber to impart the color of the vulcanizate such as titanium dioxide and litoton.

Fillers should not be contaminated with manganese, copper and moisture. The metallic substance would deteriorate the rubber and the moisture can cause air trap which consequently form porous during curing process. Thus, the filler should be dried before being incorporated into the rubber matrix. On the other hand, the specific gravity is important in choosing the filler. The example of fillers categorized as heavy fillers are Litharge and zinc oxide whereas the light fillers are carbon black and magnesia (SBP Board of Consultants and Engineers, 1900).

The reinforcement effect of the filler depends on its particle size, shape and surface area. Table 2.5 shows the relation between particles size and its reinforcing effect. The particle size of the filler is important for the rubber compounder in tailoring the mechanical properties of the vulcanizate.