

**THE CURING CHARACTERISTICS, THERMAL AND
MECHANICAL PROPERTIES OF RECYCLED
POLY(ETHYLENE TEREPHTHALATE) AND HYBRID
RECYCLED POLY(ETHYLENE TEREPHTHALATE)
FILLED NATURAL RUBBER COMPOUNDS**

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UNIVERSITI SAINS MALAYSIA

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AND HYBRID RECYCLED POLY(ETHYLENE TEREPHTHALATE)
FILLED NATURAL RUBBER COMPOUNDS**

by

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**Thesis submitted in fulfillment of the requirement
for the degree of
Master of Science
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April 2011

DECLARATION

I declare that the content presented in this dissertation is my own work which was done at Universiti Sains Malaysia unless informed otherwise. The dissertation has not been previously submitted for any other degree.

Saya isytiharkan bahawa kandungan yang dibentangkan di dalam disertasi ini adalah hasil kerja saya sendiri dan telah dijalankan di Universiti Sains Malaysia kecuali dimaklumkan sebaliknya. Disertasi ini juga tidak pernah disertakan untuk ijazah yang lain sebelum ini.

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In the Name of Allah, the Most Gracious, the Most Merciful.

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TABLE OF CONTENTS

ACKNOWLEDGEMENTS	i
TABLES OF CONTENTS	ii
LIST OF TABLES	vii
LIST OF FIGURES	ix
LIST OF ABBREVIATIONS	xiv
LIST OF SYMBOLS	xviii
ABSTRAK	xix
ABSTRACT	xx
CHAPTER 1: INTRODUCTION	
1.1 Introduction	1
1.2 Problem Statement	2
1.3 Research Objectives	3
CHAPTER 2: LITERATURE REVIEW	
2.1 Natural Rubber	5
2.1.1 Standard Malaysian Rubber (SMR L)	6
2.1.2 Epoxidized Natural Rubber (ENR 50)	6
2.2 Poly(ethylene terephthalate), (PET)	7
2.2.1 PET Waste Management	9
2.2.2 The Utilization of Recycled Poly(ethylene terephthalate)	10
a) Modification of R-PET	11
b) Durability of R-PET	12
c) R-PET Composites	13

2.3 Fillers	14
2.3.1 Carbon Black	15
2.3.2 Halloysite Nanotubes (HNTs)	18
2.3.3 Precipitated Silica	20
2.3.4 Hybrid Composites	22
a) Carbon Black Hybrid Composites	23
b) Halloysite Nanotubes Hybrid Composites	24
c) Natural Fibers Hybrid Composites	25
2.3.5 The Reinforcing Mechanism of Filler in Rubber Matrix	27
2.3.6 Mechanical Properties of Filled Rubber Matrix	30
2.4 Rubber Compounding	32
2.5 Compounding Ingredients	36
2.5.1 Activators	36
2.5.2 Accelerators	37
2.5.3 Vulcanizing agent	38
2.5.4 Antidegradant	40

CHAPTER 3: RESEARCH METHODOLOGY

3.1 Raw Materials	41
3.2 Equipments	42
3.3 Formulations	43
3.4 Preparation of Recycled(polyethylene terephthalate) Powder	44
3.5 Compounding and Curing Characteristics	44
3.6 Sample Preparation	44
3.7 Measurement of Tensile Properties	45

3.8 Measurement of Crosslink Density	45
3.9 Measurement of Fatigue to Failure Test	46
3.10 Thermo gravimetric Analysis	47
3.11 Scanning Electron Microscopy	47
CHAPTER 4: RESULTS AND DISCUSSION	
4.1 Effect of Recycled Poly(ethylene terephthalate) Loading on the Properties of Natural Rubber Compounds (SMR L and ENR 50)	48
4.1.1 Curing Characteristics	48
4.1.2 Tensile Properties	50
4.1.3 Crosslink Density	53
4.1.4 Fatigue Life	54
4.1.5 Morphological Studies of Tensile and Fatigue Fractured Surfaces	56
4.1.6 Thermo Gravimetric Analysis	61
4.2 Effect of Carbon Black (N550)/Recycled Poly(ethylene terephthalate) Hybrid Filler on the Properties of Natural Rubber Compounds	63
4.2.1 Curing Characteristics	63
4.2.2 Tensile Properties	64
4.2.3 Crosslink Density	66
4.2.4 Fatigue Life	67
4.2.5 Morphological Studies of Tensile and Fatigue Fractured Surfaces	68
4.2.6 Thermo Gravimetric Analysis	71

4.3 Effect of Halloysite Nanotubes (HNTs)/Recycled Poly(ethylene terephthalate)	
Hybrid Filler on the Properties of Natural Rubber Compounds	73
4.3.1 Curing Characteristics	73
4.3.2 Tensile Properties	74
4.3.3 Crosslink Density	76
4.3.4 Fatigue Life	78
4.3.5 Morphological Studies of Tensile and Fatigue	
Fractured Surfaces	79
4.3.6 Thermo Gravimetric Analysis	83
4.4 Effect of Precipitated Silica/Recycled Poly(ethylene terephthalate)	
Hybrid Filler on the Properties of Natural Rubber Compounds	85
4.4.1 Curing Characteristics	85
4.4.2 Tensile Properties	86
4.4.3 Crosslink Density	88
4.4.4 Fatigue Life	89
4.4.5 Morphological Studies of Tensile and Fatigue	
Fractured Surfaces	90
4.4.6 Thermo Gravimetric Analysis	93
4.5 Comparative Study of Commercial Fillers/Recycled Poly(ethylene terephthalate)	
Hybrid Filled Natural Rubber Compounds	95
4.5.1 Curing Characteristics	95
4.5.2 Tensile Properties	98
4.5.3 Crosslink Density	104

4.5.4 Fatigue Life	106
4.5.5 Morphological Studies of Tensile and Fatigue Fractured Surfaces	109
4.5.6 Thermo Gravimetric Analysis	116
CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS	
5.1 Conclusions	121
5.2 Recommendations	122
REFERENCES	124
PUBLICATIONS	134

LIST OF TABLES

	Page	
Table 2.1:	General relationship between particle size and properties of rubber reinforcement.	15
Table 2.2:	Types of carbon blacks.	17
Table 2.3:	Forms and properties of silica used in rubber compounding.	21
Table 2.4:	Classifications of the accelerators used in rubber compounding.	38
Table 3.1:	List of raw materials, their functions and suppliers.	41
Table 3.2:	List of equipments, their model and involved processes/tests.	42
Table 3.2:	The compounding formulations of natural rubber at different loading of R-PET (SMR L and ENR 50).	43
Table 3.3:	The compounding formulation of N550/R-PET, HNTs/R-PET and Silica/R-PET hybrid filled natural rubber compounds.	43
Table 4.1:	Curing characteristics of R-PET filled SMR L and ENR 50 compounds.	49
Table 4.2:	The thermal stability parameters of R-PET filled SMR L and ENR 50 compounds.	61
Table 4.3:	Curing characteristics of NR/N550/R-PET hybrid filled natural rubber compounds.	63
Table 4.4:	The thermal stability parameters of NR/N550/R-PET hybrid filled natural rubber compounds.	72
Table 4.5:	Curing characteristics of NR/HNTs/R-PET hybrid filled natural rubber compounds.	73
Table 4.6:	The thermal stability parameters of NR/HNTs/R-PET hybrid filled natural rubber compounds.	84
Table 4.7:	Curing characteristics of NR/Silica/R-PET hybrid filled natural rubber compounds.	85
Table 4.8:	The thermal stability parameters of NR/Silica/R-PET hybrid filled natural rubber compounds.	94

		Page
Table 4.9:	The comparison of curing characteristics of NR/N550/R-PET, NR/HNTs/R-PET, and NR/Silica/R-PET hybrid filled natural rubber compounds.	96
Table 4.10:	The Comparison of tensile properties of NR/N550/R-PET, NR/HNTs/R-PET, and NR/Silica/R-PET to the previous studies.	102
Table 4.11:	The comparison of the thermal stability parameters of NR/N550/R-PET, NR/HNTs/R-PET, and NR/Silica/R-PET hybrid filled natural rubber compounds.	120

LIST OF FIGURES

	Page
Figure 2.1: Cis and trans isomers of polyisoprene.	6
Figure 2.2: The structure of epoxidized natural rubber (ENR 50).	7
Figure 2.3: Schematic of the formation of PET.	8
Figure 2.4: Illustration of carbon black aggregates in rubber matrix: (A) carbon black aggregate, (B) sulphur crosslinking, (C) chain entanglement, (D) tight loop, (E) loose loop, (F) free tail, and (G) zone of smaller chain mobility.	16
Figure 2.5: Effect of carbon black level on compound properties.	18
Figure 2.6: Schematic structure of a halloysite nanotubes.	19
Figure 2.7: Silica surface groups: siloxane (-Si-O-Si-) and isolated, vicinal and germinal silanols (-Si-O-H-).	20
Figure 2.8: Idealized form of a typical elastic modulus curve.	29
Figure 2.9: Flow chart of rubber compounding.	33
Figure 2.10: Network formation of sulfur cure system.	36
Figure 2.11: Chemical structure of N-cyclohexyl-2-benzothiazole sulfonamide (CBS).	38
Figure 2.12: Chemical structure of N-Isopropyl-N'-phenyl-p-phenylenediamine (IPPD).	40
Figure 4.1: Stress at 100% elongation of R-PET filled SMR L and ENR 50 compounds.	50
Figure 4.2: Stress at 300% elongation of R-PET filled SMR L and ENR 50 compounds.	51
Figure 4.3: Tensile strength of R-PET filled SMR L and ENR 50 compounds.	52
Figure 4.4: Elongation at break of R-PET filled SMR L and ENR 50 compounds.	52
Figure 4.5: Crosslink density of R-PET filled SMR L and ENR 50 compounds.	54

	Page
Figure 4.6: Fatigue life of R-PET filled SMR L and ENR 50 compounds.	55
Figure 4.7: SEM micrographs show tensile fracture surface of R-PET filled SMR L compounds at 0 phr (a) and 5 phr (b); ENR 50 compounds at 0 phr (c) and 5 phr (d) (magnification 100X).	57
Figure 4.8: SEM micrographs show tensile fracture surface of R-PET filled SMR L compounds at 20 phr (a) and 40 phr (b); ENR 50 compounds at 20 phr (c) and 40 phr (d) (magnification 100X).	58
Figure 4.9: SEM micrographs show fatigue fracture surface of R-PET filled SMR L compounds at 0 phr (a), 20 phr (b) and 40 phr (c); ENR 50 compounds at 0 phr (d), 20 phr (e) and 40 phr (f) (magnification 100X).	60
Figure 4.10: TGA curves of R-PET filled SMR L and ENR 50 compounds.	62
Figure 4.11: Stress at 100% and 300% elongation of NR/N550/R-PET hybrid filled natural rubber compounds.	65
Figure 4.12: Tensile strength and elongation at break of NR/N550/R-PET hybrid filled natural rubber compounds.	65
Figure 4.13: Crosslink density of NR/N550/R-PET hybrid filled natural rubber compounds.	67
Figure 4.14: Fatigue life of NR/N550/R-PET hybrid filled natural rubber compounds.	68
Figure 4.15: SEM micrographs show tensile fractured surfaces of NR/N550/R-PET hybrid filled natural rubber compounds at N550:R-PET loading ratio of (a) 20:0 phr, (b) 15:5 phr, (c) 5:15 phr and (d) 0:20 phr at magnification (100×).	69
Figure 4.16: SEM micrographs show fatigue fractured surfaces of NR/N550/R-PET hybrid filled natural rubber compounds at N550:R-PET loading ratio of (a) 20:0 phr, (b) 15:5 phr, (c) 5:15 phr and (d) 0:20 phr at magnification (100×).	70
Figure 4.17: TGA curves of NR/N550/R-PET hybrid filled natural rubber compounds.	71

	Page
Figure 4.18: Stress at 100% and 300% elongation of NR/HNTs/R-PET hybrid filled natural rubber compounds.	75
Figure 4.19: Tensile strength and elongation at break of NR/HNTs/R-PET hybrid filled natural rubber compounds.	76
Figure 4.20: Crosslink density of NR/HNTs/R-PET hybrid filled natural rubber compounds.	77
Figure 4.21: Fatigue life of NR/HNTs/R-PET hybrid filled natural rubber compounds.	78
Figure 4.22 SEM micrographs show tensile fractured surfaces of HNTs/R-PET hybrid filled natural rubber compounds at HNTs:R-PET loading ratio of (a) 20:0 phr, (b) 15:5 phr, (c) 5:15 phr and (d) 0:20 phr at magnification (100×).	80
Figure 4.23: SEM micrographs show tensile fractured surfaces of HNTs/R-PET hybrid filled natural rubber compounds at HNTs:R-PET loading ratio of (a) 15:5 phr, (b) 5:15 phr and (c) 0:20 phr at magnification (5.00 Kx).	81
Figure 4.24: SEM micrographs show fatigue fractured surfaces of HNTs/R-PET hybrid filled natural rubber compounds at HNTs:R-PET loading ratio of (a) 20:0 phr, (b) 10:10 phr, (c) 0:20 phr at magnification (100×).	82
Figure 4.25: TGA curves of NR/HNTs/R-PET hybrid filled natural rubber compounds.	84
Figure 4.26: Stress at 100% and 300% elongation of NR/Silica/R-PET hybrid filled natural rubber compounds.	87
Figure 4.27: Tensile strength and elongation at break of NR/Silica/R-PET hybrid filled natural rubber compounds.	88
Figure 4.28: Crosslink density of NR/Silica/R-PET hybrid filled natural rubber compounds.	89
Figure 4.29: Fatigue life of NR/Silica/R-PET hybrid filled natural rubber compounds.	90
Figure 4.30: SEM micrographs show tensile fractured surfaces of Silica/R-PET hybrid filled natural rubber compounds at Silica:R-PET loading ratio of (a) 20:0 phr, (b) 15:5 phr, (c) 5:15 phr and (d) 0:20 phr at magnification (100×).	91

	Page
Figure 4.31: SEM micrographs show fatigue fractured surfaces of Silica/R-PET hybrid filled natural rubber compounds at Silica:R-PET loading ratio of (a) 20:0 phr, (b) 10:10 phr, (c) 0:20 phr at magnification (100×).	93
Figure 4.32: TGA curves of NR/Silica/R-PET hybrid filled natural rubber compounds.	95
Figure 4.33: The comparison of stress at 300% elongation of NR/N550/R-PET, NR/HNTs/R-PET, and NR/Silica/R-PET hybrid filled natural rubber compounds.	99
Figure 4.34: The comparison of tensile strength of NR/N550/R-PET, NR/HNTs/R-PET, and NR/Silica/R-PET hybrid filled natural rubber compounds.	100
Figure 4.35: The comparison of elongation at break of NR/N550/R-PET, NR/HNTs/R-PET, and NR/Silica/R-PET hybrid filled natural rubber compounds.	101
Figure 4.36: The comparison of crosslink density of NR/N550/R-PET, NR/HNTs/R-PET, and NR/Silica/R-PET hybrid filled natural rubber compounds.	106
Figure 4.37: The comparison of fatigue life of NR/N550/R-PET, NR/HNTs/R-PET, and NR/Silica/R-PET hybrid filled natural rubber compounds.	108
Figure 4.38: SEM micrographs show tensile fractured surfaces of N550, HNTs, and silica filled natural rubber compounds at 20 phr; (a) N550, (b) HNTs, (c) Silica (magnification 100×).	110
Figure 4.39: SEM micrographs show tensile fractured surfaces of NR/N550/R-PET, NR/HNTs/R-PET, and NR/Silica/R-PET hybrid filled natural rubber compounds at 10:10 (phr:phr) loading ratio; (a) N550, (b) HNTs, (c) Silica (magnification 100×).	111
Figure 4.40: SEM micrograph shows tensile fractured surfaces of R-PET filled natural rubber compounds at 20 phr (magnification 100×).	112
Figure 4.41: SEM micrographs showing fatigue fractured surfaces of N550, HNTs, and silica filled natural rubber compounds at 20 phr; (a) N550, (b) HNTs, (c) Silica (magnification 100×).	113

	Page
Figure 4.42: SEM micrographs show fatigue fractured surfaces of NR/N550/R-PET, NR/HNTs/R-PET, and NR/Silica/R-PET hybrid filled natural rubber compounds at 10:10 (phr:phr) loading ratio; (a) N550, (b) HNTs, (c) Silica (magnification 100×).	114
Figure 4.43: SEM micrograph shows fatigue fractured surfaces of R-PET filled natural rubber compounds at 20 phr (magnification 100×).	115
Figure 4.44: The comparison of TGA curves of natural rubber filled with R-PET, carbon black, HNTs and Silica at 20 phr.	117
Figure 4.45: The comparison of TGA curves of NR/N550/R-PET, NR/HNTs/R-PET, and NR/Silica/R-PET at loading ratio of 15:5 (phr:phr).	118
Figure 4.46: The comparison of TGA curves of NR/N550/R-PET, NR/HNTs/R-PET, and NR/Silica/R-PET at loading ratio of 10:10 (phr:phr).	118

LIST OF ABBREVIATIONS

Al ₂ O ₃	Aluminium Oxide
Al ₂ Si ₂ O ₅ (OH) ₄ H ₂ O	Aluminosilicate
ASTM	American Standard of Testing Materials
CaCO ₃	Calcium Carbonate
CBS	N-cyclohexyl-2-benzothiazylsulfenamide
CNTs	Carbon Nanotubes
CH ₃	Methyl Group
C ₅ H ₈	Cis-1,4-Polyisoprene
C ₈ H ₆ O ₄	Terephthalic Acid
DCBS	N, N-Dicyclohexyl-2-benzothiazolesulfenamide
DOTG	Diorthotolyl Guanidine
DPG	Diphenylguanidine
DSC	Differential Scanning Calorimeter
EB	Elongation at Break
EBGMA	Ethylene/n-Butyl-Acrylate/Glycidyl-Methacrylate
ENR 25	Epoxidized Natural Rubber with 25 mol% Epoxy Group
ENR 50	Epoxidized Natural Rubber with 50 mol% Epoxy Group
EMA	Ethylene-Methyl-Acrylate
EPDM	Ethylene Propylene Diene Monomer
EVA	Ethylene Vinyl Acetate Copolymer

FEF	Fast Extrusion Furnace
FF	Fine Furnace
Fe ₂ O ₃	Ferum Oxide
GPF	General Purpose Furnace
HAF	High Abrasion Furnace
HDPE	High Density Poly(ethylene)
HNTs	Halloysite Nanotubes
IPPD	N-isopropyl-N'-phenyl-p-phenylenediamine
IRP	Industrial Rubber Product
ISAF	Intermediate Super Abrasion Furnace
LLDPE	Linear Low Density Poly(ethylene)
LOI	Limiting Oxygen Index
MDR	Monsanto Moving Die Rheometer
MBS	N-oxydiethylene-2-benzothiazylsulfenamide
MBT	2-mercaptobenzothiazole
MBTS	2,2'-dithiobisbenzothiazole
M100	Stress at 100% Elongation
M300	Stress at 300% Elongation
NBR	Acrylonitrile Butadiene Rubber
NR	Natural Rubber
N550	550 Grade Carbon Black
PCr	Recycled Polycarbonate
PET	Poly(ethylene terephthalate)
PETr	Recycled Poly(ethylene terephthalate)

POM	Polarized Optical Microscope
PP	Poly(propylene)
PP-g-MA	Maleic anhydride grafted Polypropylene
PP-g-GMA	Glycidyl-Methacrylate-grafted Polypropylene
PVC	Poly(vinyl chloride)
R-PET	Recycled Poly(ethylene terephthalate)
RRIM	Rubber Research Institute of Malaysia
SAF	Super Abrasion Furnace)
SBR	Styrene Butadiene Rubber
SEBS-g-MA	Maleic Anhydride-grafted Poly(styrene-ethylene-butadiene-styrene)
SEBS	Poly(styrene-ethylene-butadiene-styrene)
SEM	Scanning Electron Microscope
SiO ₂	Silicon Dioxide
SMR L	L Grade Standard Malaysia Rubber
SRF	Semi Reinforcing Furnace
SWCNT	Single Walled Carbon Nanotubes
(-Si-O-Si-)	Siloxane Faunctionality
(-Si-O-H-)	Silanol Functionality
TBBS	N-tert-butyl-2-benzothiazolesulfenamide
TBZTD	Tetrabenzylthiuram disulfide
TETD	Tetraethyl thiuram disulfide
TGA	Thermo Gravimetric Analysis
TiO ₂	Titanium Dioxide
TSR	Technical Specified Rubber

TMTD	Tetramethyl thiuram disulfide
TMTM	Tetramethyl thiuram monosulfide
UV	Ultra Violet
ZBPD	Zinc O,O-dibutylphosphorodithioate
ZDBC	Zinc dibutyldithiocarbamate
ZDMC	Zinc dimethyldithiocarbamate
ZnO	Zinc Oxide

LIST OF SYMBOLS

cm^3	Cubic Centimeter
dN.m	Deci Newton Meter
M_H	Maximum Torque
M_L	Minimum Torque
M_n	Number Average Molecular Weight
nm	Nanometer
phr	Part per Hundred Rubber
Q	Swelling Ratio
t_{c90}	Cure Time
t_{s2}	Scorch Time
$T_{-x\%}$	Temperature at Various Percentage of Weight Losses
V_e	Crosslink Density
V_s	Molar Volume of the Solvent
Wd	Dried Weight
Ws	Swollen Weight
W_{\max}	Maximum Weight Loss
W1	Weight Fraction of the Polymer
W2	Weight Fraction of the Solvent
ρ	Density
μm	Micrometer
χ	Interaction Parameter of the Rubber Network-Solvent
$\Delta S = M_H - M_L$	Torque Difference

**SIFAT – SIFAT PEMATANGAN, TERMA DAN MEKANIK SEBATIAN
GETAH ASLI TERISI POLIETILENA TEREFTALAT KITAR SEMULA
DAN HIBRID POLIETILENA TEREFTALAT KITAR SEMULA**

ABSTRAK

Kesan pengisian serbuk polietilena tereftalat kitar semula, (R-PET) dalam sebatian getah asli telah dikaji. Sebatian disediakan dengan menggunakan pengiling bergulung dua bersaiz makmal pada suhu bilik. Dua kajian yang berbeza telah dilakukan; i) kesan pembebanan R-PET sehingga 40 bsg terhadap sifat-sifat getah asli (SMR L) dan getah asli terepoksida (ENR 50), dan ii) kesan penghibridan R-PET dengan pengisi-pengisi komersil terhadap sifat-sifat sebatian getah asli. Kajian menunjukkan bahawa penambahan R-PET ke dalam matriks getah asli meningkatkan tork maksima, perbezaan tork, masa skorj dan masa pematangan. Manakala kesan pembebanan di dalam sebatian getah asli terepoksida (ENR 50) menunjukkan pengurangan masa skorj dan masa pematangan. Penambahan R-PET juga meningkatkan ketumpatan sambung silang dan modulus tensil sebatian, namun kekuatan tensil, pemanjangan pada takat putus dan hayat fatig kedua-dua sebatian menunjukkan pola menurun. Kajian morfologi menunjukkan nyah lekatan dan penggumpalan R-PET dalam matriks kedua-dua sebatian dengan peningkatan komposisi R-PET. Penghibridan pengisi-pengisi komersil dengan R-PET menunjukkan penggantian karbon hitam (N550), HNTs dan silika oleh R-PET mengurangkan kekuatan tensil, dan modulus tensil. Komposit hibrid NR/N550/R-PET juga menunjukkan sifat mekanik tertinggi diikuti oleh komposit NR/HNTs/R-PET dan NR/Silika/R-PET. Selain itu, kajian morfologi menunjukkan hibrid N550/R-PET membantu penyebaran partikel R-PET dalam matriks getah asli berbanding hibrid HNTs/R-PET dan Silika/R-PET.

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FILLED NATURAL RUBBER COMPOUNDS**

ABSTRACT

The effects of recycled poly(ethylene terephthalate) (R-PET) powder filled natural rubber compounds were investigated. The compounds were prepared on a laboratory size two-roll-mill at room temperature. Two different studies have been carried out; i) effect of R-PET loading up to 40 phr on the properties of natural rubber and epoxidized natural rubber, and ii) the hybridization of R-PET with commercial fillers on the properties of natural rubber compounds. Results indicated that the maximum torque, torque difference, scorch time and cure time of SMR L compounds increased with increasing R-PET loading, whereas ENR 50 compounds showed the decreasing trend in scorch time and cure time. Increment in R-PET loading increased the crosslink density and tensile modulus of both natural rubber compounds. Tensile strength, elongation at break and fatigue life of both natural rubber compounds showed the decreased trend with increasing R-PET loading. The morphological study exhibited the detachment of R-PET and more agglomeration when increasing R-PET loading in both natural rubber compounds. Hybridization of commercial fillers with R-PET indicated that the replacement of carbon black (N550), HNTs and silica by R-PET decreased the tensile strength, and tensile modulus, where NR/N550/R-PET compounds showed the highest mechanical properties followed by NR/HNTs/R-PET and NR/Silica/R-PET compounds. Moreover, the morphological study confirmed that the co-incorporation of N550/R-PET improved the dispersion of R-PET in NR matrix than R-PET and Silica/R-PET hybrid fillers.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Since the development of plastic, it has become a popular material used in a wide variety of applications. The growth in plastics is due to its various beneficial properties. These include; extreme versatility and ability to be tailored to meet very specific technical needs, extreme durability, lighter weight than other materials, reducing fuel consumption during transportation, resistance to chemicals, good safety and hygienic properties for food packaging and soft drink bottles as well as relatively inexpensive to produce and excellent thermal and electrical insulation properties.

Nowadays, the amount of plastics in municipal plastics waste has been increasing because of the expansion in production and consumption. There are about 50 different groups of plastics which can be recyclable. For easier recycling, the American Society of Plastic Industry has developed a standard marking code to help consumers identify and sort different types of plastics. Poly(ethylene terephthalate), or PET has been coded as number 1. PET is a thermoplastics resin that belongs to the family of polyester produced from condensation polymerization between terephthalic acid and ethylene glycol (Lachenal, 1997). PET was first produced in 1946, which was commercially available in 1953 as a textile fiber. There was significant development of PET especially in the manufacturing sector for soft drink bottles replacing the heavier and easily breakable glass. The main reasons for the popularity of PET are the properties of glass-like transparency, high toughness coupled with adequate gas barrier properties for retention of carbonation (Karayannidis and Achilias, 2007; Mousa, 2008)

Unfortunately, in spite of the usefulness of PET, it contributes to huge pollution problem. In 2007, over 4.53 million tonnes of PET bottles were collected worldwide and the trend has been growing up due to the polymer's superiority over glass for bottling beverage. Especially, in Europe alone, 1.36 million tonnes of waste PET bottles were faced in 2009 (http://en.wikipedia.org/wiki/PET_bottle/recycling, 10th October 2009). Due to its high resistance to atmospheric and biological agents, PET bottles have become noxious materials of concern in relatively recent environmental protection issues. The necessity to find a simple economic route for recycling waste PET bottles is an important practice for sustainable recycling and contributes to the conservation of raw petrochemical products and energy (Karayannidis and Achilias, 2007).

1.2 Problem Statement

Natural rubber technology has been developed rapidly and filler becomes the most important additive as the second largest component following the base polymer in rubber compounding (Blow and Hepburn, 1982). They are incorporated into rubber compound to improve processability and physico-mechanical properties. Among commercial fillers, carbon black and precipitated silica are the most important reinforcing fillers and extensively used when high strength is required. However, for some applications where cost and processability are concern, the use of non or semi-reinforcing fillers such as clay, talc, and calcium carbonate (CaCO₃) as well as other fillers from renewable resources and wasted materials, i.e. wood waste (Ichazo et al., 2005), seed shells (Osabohien and Egboh, 2010), paper sludge (Ismail et al., 2007) and oil palm wood flour (Zaini et al., 1996) were used as fillers for rubber and plastics, which are low cost, renewable and environment friendly.

Due to legislative pressure to recycle and reduce scrap in the environment, the disposal of plastic waste products is significant concern. Landfill disposal and transportation costs are expected to increase. The recycling of thermoplastic materials is carried out widely, with some limitations in terms of the possible selection of a material to achieve a particular purpose in the recycling of thermoplastic materials. As a consequence of this, to eliminate or reduce waste PET from the environment and to reduce costs of some manufacturing products, a relatively new area of interest is the use of recycle poly(ethylene terephthalate), (R-PET) bottling powder as filler for natural rubber. Since over the years, utilization of R-PET are applicable in polymer concrete (Choi et al., 2009), blending with virgin PET and commercial plastics (Burillo et al., 2002; Zhang et al., 2007), and use of R-PET as a matrix in filled composites (Pegoretti and Penati, 2004; Pegoretti et al., 2004), but no attempts were carried out to use R-PET bottles as filler in natural rubber compound reported by any researcher. Therefore, the purpose of this work is to study the potential and the reinforcing effect of R-PET powder, as well as to reduce the overall compounding cost and reduce PET waste from the environment. If R-PET can exhibit an acceptable properties like as that of commercial filler used, thus this new invention would bring many benefits as mentioned above.

1.3 Research Objectives

This research involved the utilization of recycled poly(ethylene terephthalate) as a filler in natural rubber compounds. The main purpose of this present work is to investigate the potential of R-PET as a filler to enhance the properties of natural rubber compounds. The work was carried out to achieve the following objectives;

1. To investigate the effect of recycled poly(ethylene terephthalate), (R-PET) loading on the properties of natural rubber and epoxidized natural rubber compounds.
2. To investigate the effect of carbon black/recycled poly(ethylene terephthalate) hybrid filler on the properties of natural rubber compounds.
3. To investigate the effect of halloysite nanotubes (HNTs)/recycled poly(ethylene terephthalate) hybrid filler on the properties of natural rubber compounds.
4. To investigate the effect of precipitated silica/recycled poly(ethylene terephthalate) hybrid filler on the properties of natural rubber compounds.
5. To study the comparative properties of commercial fillers/recycled poly(ethylene terephthalate) hybrid filled natural rubber compounds

This research project was carried out to produce samples from rubber compounds according to their respective compounding formulations and the testing was done as follows;

- Curing characteristics
- Mechanical properties; Tensile Properties and Fatigue Life
- Crosslink density
- Thermo gravimetric Analysis
- Morphological observation of tensile and fatigue to failure fractured surfaces

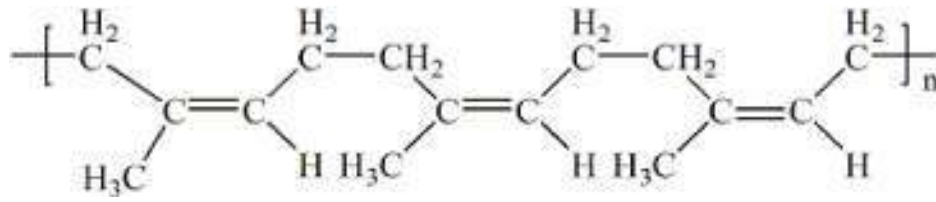
CHAPTER 2

LITERATURE REVIEWS

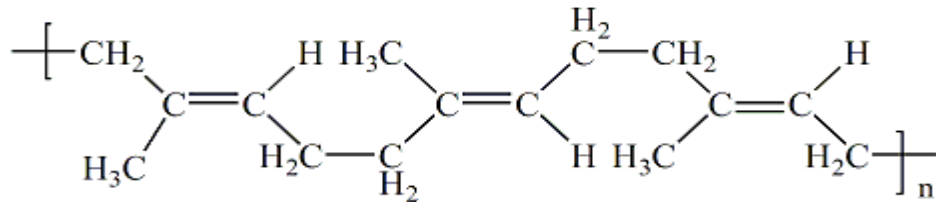
2.1 Natural Rubber

Natural rubber is a hydrocarbon with the formula of isoprene $(C_5H_8)_n$, which is built up in the form of a continuous chain with an number average molecular weight (M_n) of natural rubber in the range of 0.25×10^6 to 2.71×10^6 . The succession of isoprene units in the chain is perfectly regular, with every fourth carbon atom in the chain carrying the methyl (CH_3) side group (Figure 2.1). The presence of the double bond is very significant, since it largely determines the chemical reactivity of the molecule and its ability to react with sulfur or other reagents in the vulcanization process (Treloar, 2005). The double bond is also responsible for the susceptibility of the rubber molecules to oxidation or other degradative reactions leading to a deterioration of physical properties.

The other natural polymer of isoprene is gutta-percha, which differs slightly from that of rubber. In natural rubber, the single bonds lie on the same side of the double bond, forming the cis-configuration (Figure 2.1), whereas in gutta-percha, they lie on opposite sides of the double bond, giving the trans-configuration. One consequence of this difference is that gutta-percha crystallizes more readily than rubber. It is in fact crystalline at room temperature, becoming rubber-like only when heated above the crystal melting point (Rodgers, 2004; Treloar, 2005).



cis-polyisoprene



trans-polyisoprene

Figure 2.1: Cis and trans isomers of polyisoprene (Rodgers, 2004).

2.1.1 Standard Malaysian Rubber (SMR L)

L Grade Standard Malaysia Rubber (SMR L) is one of the natural rubbers including the technical specified rubber (TSR) for light-colored rubber produced from high quality latex. It has ash content less than 0.50% and dirt content is less than 0.02%, it is packed and presented in the same way as CV grade SMR. Technologically, SMR L shows high tensile strength, modulus, and ultimate elongation at break for all compounds. It can be used for light-colored and transparent products such as surgical or pressure-sensitive tape, textiles, rubber bands, hot water bottles, pharmaceutical products, large industrial rollers for the paper printing industry, sportswear, bicycle tubes, chewing gum, cable sheaths, gaskets, and adhesive solutions (Rodgers, 2004).

2.1.2 Epoxidized Natural Rubber (ENR)

Epoxidized natural rubber (ENR) is a derivative of natural rubber produced by chemical modification (Figure 2.2). ENR also known as epoxyrene comes in two grades, ENR 25 and ENR 50 which are double bonds in the backbone be epoxidized

to 25 mol% and 50 mol% respectively. Epoxy groups are randomly distributed along the polymer chain of ENR. It shows better oil resistance, damping and low gas permeability compared to natural rubber. The increment in polarity also increased the compatibility with polar polymer such as polyvinyl chloride (PVC), Acrylonitrile Butadiene Rubber (NBR) (Dick and Annicelli, 2001).

Epoxydation changes several physical properties, including increasing the glass transition temperature but still can undergo strain crystallization. On the other hand, beyond 50 mol% of epoxy group caused a rapid reduction in strain crystallization. ENR are beneficial where these properties are required in combination with high tensile, fatigue or tear strengths, particularly when the use of reinforcing fillers is not practical (Baker et al., 1985).

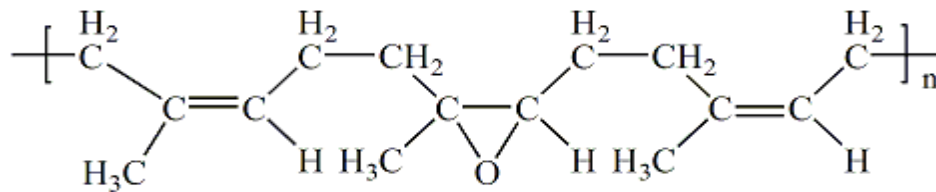


Figure 2.2: The structure of epoxidized natural rubber (ENR 50) (Baker et al., 1985).

2.2 Poly(ethylene terephthalate), (PET)

Poly(ethylene terephthalate) or PET is a thermoplastic resin belongs to the family of polyester which is produced from condensation polymerization between terephthalic acid (C₈H₆O₄) and ethylene glycol (C₂H₆O₂). The reaction to form PET obtains in the presence of catalysts including salts of manganese, cobalt, cadmium, calcium and germanium with removing of water or methanol (Figure 2.3). The basic raw

materials for PET production are crude oil and natural gas liquids (ethane, propane and butane) (Ehrig, 1992).

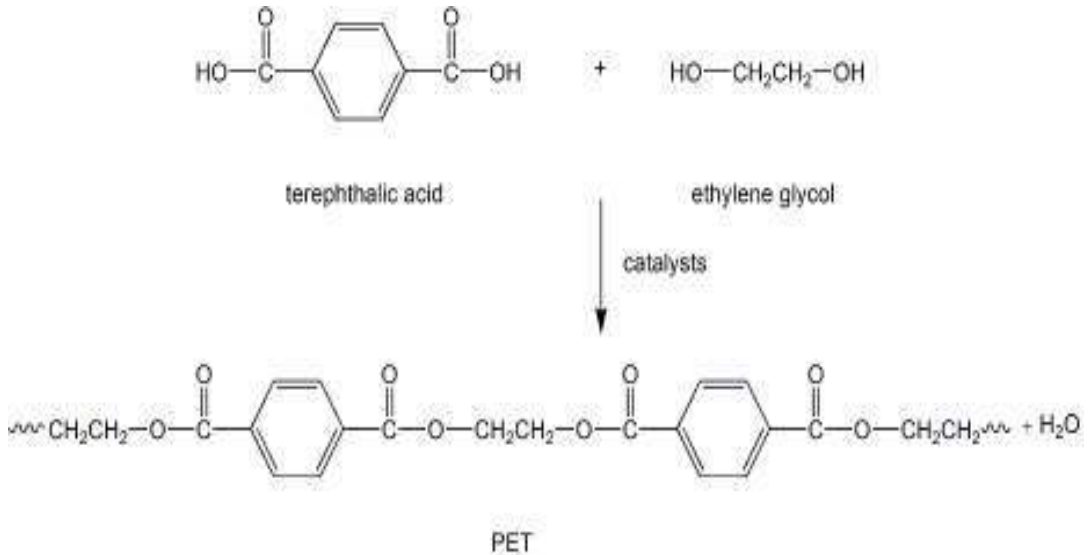


Figure 2.3: Schematic of the formation of PET (Ehrig, 1992).

PET can be classified as a semi-crystalline polymer which exhibits a transition from a rigid glass like state to a rubbery elastic form when heat was applied at 70 – 80°C (Paszun and Sychaj, 1997). At this point, the polymer molecular chains can be stretched and aligned in either one direction to form fibers, or two directions to form films and bottles. This material melts in a temperature range of 250–260°C. After melting, if the melt is quickly cooled while held in a stretched state, the material turns out to be very tough and can be formed into bottles that are used for storage purposes. If the PET is held in the stretched form at temperatures above 72°C, it slowly crystallizes and the material starts to become opaque, more rigid and less flexible. At this stage PET can withstand high temperature and can be used to make containers that can carry on with moderate oven temperatures (Sinha et al., 2010).

PET also known as poly(oxyethylene oxyterephthalate) (Harper, 2006). It is a versatile engineering plastic material with excellent thermal, chemical resistance and mechanical performance. It is extensively used in producing engineering components due to its high melting temperature (around 250°C) and glass transition temperature (around 80°C). PET has good properties at temperatures up to 175-180°C. Its crystallinity varies from amorphous to fairly high crystalline. It can be highly transparent and colorless, but thicker samples are usually opaque and off white. PET is a hard, stiff, strong, dimensionally stable material that absorbs very little water (Vedula, 2005).

Because of this wide spread application the PET waste disposal poses a serious problem to maintain a clean environment. It should be pointed out, that PET does not create a direct hazard to the environment, but due to its substantial fraction by volume in the waste stream and its high resistance to the atmospheric and biological agents, it is seen as a noxious material. Therefore, the recycling of PET does not only serve as a partial solution to the solid waste problem but also contributes to the conservation of raw petrochemical.

2.2.1 PET Waste Management

A very important feature of PET is that it does not have any side effects directly on the human beings, thus influencing the choice of its wide application in the manufacture of packaging for the food industries. Recycling of PET bottles is the activity whereby bottles made out of PET plastic are collected and processed in order to reuse the material out of which they are made. In the United States, PET is coded with the number 1 which is found inside the universal recycling symbol, usually

located on the bottom of the container. The empty PET packaging is discarded by the consumer after use and becomes PET waste. In the recycling industry, this is referred as "post-consumer PET". Many local governments and waste collection agencies have started to collect post-consumer PET separately from other household waste (Kosmidis et al., 2001).

Post-consumer PET is sometimes also sorted into different color fractions: transparent or uncolored PET, blue and green colored PET, and the remainder into a mixed colors fraction. For decades, the technology for recycling PET soft drink bottles has been advancing. The disappearance of the base caps and change from aluminum to PP closures has greatly facilitated the recycling process. Aluminum, in particular, was difficult to remove and caused serious performance problems in the recycled material. Metal caps are still used on a few PET containers, but nearly all now use plastic caps and lids. Change of the labels from paper to plastic has also facilitated recycling. In current processes, the PP label fragments that are not removed during previous process steps will be removed with the PP caps in the hydro cyclone resulting in pure PET fragments or PET flakes (López-Fonseca et al., 2010).

2.2.2 The Utilization of Recycled Poly(ethylene terephthalate)

Poly(ethylene terephthalate) (PET) is widely used in packaging materials especially in beverage packages, owing to its good mechanical properties and excellent barrier properties. Most of these beverage bottles are used only once, which surely creates serious resource waste and pollution. Therefore, with the increased awareness of the environmental protection, governments pay more attention to the issue of recycling

waste PET. Compared to other post-consumed plastics, the source of recycled PET (R-PET) is more stable, and R-PET bottles are easier to separate and purified. As a consequence of this, in order to eliminate or reduce waste PET from the environment as well as to reduce costs of some manufacturing products, the study of the potentials of R-PET have been done so far in many research areas.

a) Modification of R-PET

R-PET undergoes a series of degradation problems such as thermal, hydrolytic, mechanical and oxidative degradation during melt processing. This leads to a reduction in molecular weight and intrinsic viscosity, which in turn decreases the mechanical properties of recycled materials (Buxbaum, 1968; Torres et al., 2000). Chain extension has been employed in order to improve the mechanical properties and melt strength of R-PET. It is very useful to apply chain extension in the reprocessing of R-PET, because the reduction of molecular weight of PET can be compensated for by introducing the chain extender. Chain extenders are general poly-functional compounds with thermal stability and have the ability of fast reaction with the hydroxyl or carboxyl end groups of PET (Bikiaris and Karayannidis, 1996; Incarnato et al., 2000).

Zhang et al. (2007) investigated the structure and mechanical properties, thermal properties, and crystallization behavior of compatibilized blends of recycled PET (R-PET) from PET beverage bottles, and LLDPE were prepared by low temperature solid state extrusion. They used poly(styrene-ethylene/butyldiene-styrene) (SEBS) and maleic anhydride-grafted poly(styrene-ethylene/butyldiene-styrene) (SEBS-g-MA) as compatibilizers. Meanwhile, Tao and Mai (2007) also studied the binary

blends of PP/R-PET, R-PET/grafted PP and ternary blends of PP/R-PET compatibilized with various contents of maleic anhydride grafted polypropylene (PP-g-MA) or glycidyl methacrylate grafted polypropylene (PP-g-GMA), which were prepared by melt extrusion. They observed the influences of blends compositions, pre-melting temperature and cooling rates on the non-isothermal crystallization and subsequent melting behavior of the blends using differential scanning calorimetry (DSC) and crystallization morphology by polarized optical microscope (POM). Both of these studied found that with using compatibilizers give better interfacial adhesion between the components of the blends, and together with better properties.

b) Durability of R-PET

The recycling process of PET leads to the thermal and hydrolytic degradation, which occur more easily in the presence of contaminants, such as poly(vinyl chloride) (PVC), ethylene-vinyl acetate copolymer (EVA), adhesives, moisture, etc. It is well known that the recycling of waste PET is to recover the performance of R-PET. Torres et al. (2000) studied thermal and mechanical properties of virgin and recycled poly(ethylene terephthalate) before and after injection molding. The study is focused on the mechanical recycling of post-consumer PET bottles. They studied two types of scraps of PET bottles: the first one arising from homogeneous deposits and the second one coming from heterogeneous deposits soiled by PVC because a complementary sorting to separate colors and to reduce the rate of PVC would increase the cost of recycled PET.

Swoboda et al. (2007) used the recycle PET as engineering applications with enhanced flame retardancy from the blends of recycled polycarbonate (PCr) and

recycled poly(ethylene terephthalate) (PETr). If used virgin PC, it will have limitation in oxygen index (LOI) of 28 and produces a large fraction of char during combustion, whereas PET has an LOI of 22, that contribute huge dripping during combustion. When they are mixed, at lower PCr weight content, the fire reaction upgrades gradually from pure PETr low performance to pure PCr behavior, except for the flammability which increases with PCr content.

c) R-PET Composites

The natural fiber is used as additives for composite materials and presents a great potential for improving performance and technological application. This is because of the low cost, abundance, biodegradability and high specific strength of natural fiber. Sugar cane bagasse fiber is a kind of natural fiber, which is widely produced recently, as a by-product of the sugar and bio-ethanol industry (Ripoli et al., 2000). Corradini et al. (2009) produced environmentally friendly products by studied the potential of recycled PET/sugarcane bagasse fiber composites and their interfacial behavior using ethylene/n-butyl-acrylate/glycidyl-methacrylate (EBGMA) and ethylene-methyl-acrylate (EMA) as compatibilizing agents. They found that by using the compatibilizer indicated that EBGMA increased the interaction between the constituents more effectively than EMA. The addition of bagasse sugar cane fiber did not affect the tensile modulus but reduced the tensile strength and elongation of PETr, as is normally observed in these types of composites.

Some of the previous works that have been carried out using the recycled poly(ethylene terephthalate) are; new epoxy resins based on R-PET (Atta et al., 2007), polymer concrete (Choi et al., 2009), blending with virgin PET and

commercial plastics (Burillo et al., 2002; Zhang et al., 2007). However, the utilization of R-PET is very popular in many current research areas in progress.

2.3 Fillers

Filler is one of the major additives used in natural rubber and has marked effect and influence on rubber compounds. It actually functions to modify the physical and chemical properties of vulcanizates. Fillers are incorporated into rubber matrices mainly to achieve improvement of service properties or reduce material cost and impart the white or light color (Simpson, 2002). In rubber compounding, filler can be classified based on their criteria of reinforcement inside rubber. Generally, rubber reinforcement is defined as modification of rubber viscoelastic and failure properties so that one or more rubber vulcanizate properties can be improved without change in its deformability. Therefore, based on the definition of filler usage inside rubber compounding (Mark et al., 2005). Fillers can be classified into two groups;

a) Reinforcing filler; Filler can be classified as reinforcing filler if it has smaller particle size (larger surface area) and is referred to that filler that is able to increase the modulus and improve failure properties of rubber vulcanizate such as tensile strength, tear strength, abrasion resistance and tensile modulus. The addition of reinforcing filler also increases the required energy to fail the rubber. Reinforcing fillers that are commonly used are carbon black and silica.

b) Non reinforcing filler; Non reinforcing filler is used to increase the hardness, modulus or to produce rubber product with cheaper price. The example for non reinforcing filler is mineral filler, silicate, calcium carbonate, clay and talc (Dick and Annicelli, 2001).

General relationship between particle size and properties of rubber reinforcement is shown in Table 2.1:

Table 2.1: General relationship between particle size and properties of rubber reinforcement (Ismail, 2000).

Particle size	Reinforcement level
Particle > 5000 nm	Rubber weaken
Particle between 1000 nm – 5000 nm	Larger quantity is required for small filler reinforcement
Particle < 1000 nm	Rubber become stronger
Particle < 100 nm	The actual reinforcing agent

2.3.1 Carbon Black

Carbon black consists about 30% used in rubber industries. The addition of carbon black can affect virtually all phases of a rubber factory's operation as well as the performance characteristics of the end product due to its unique properties which can produce strong interaction with the any rubbers (Figure 2.4), whether it is a tire component or an industrial rubber product (IRP).

Because carbon black is so important to rubber compounds, tracking the total quality cost is essential. The total quality cost of using a particular grade of carbon black, from a given source, at a specific loading, can be quite different from the cost of carbon black alone. To obtain the maximum value from purchased carbon black, the total cost of this significant filler should be considered (Dick and Annicelli, 2001). The term carbon black refers to materials that are essentially elemental carbon and

that can be made by one of several processes. The most general statement that can be made about carbon black is that it is made by partial combustion or thermal decomposition of hydrocarbon in the vapor phase (Mark et al., 2005).

The loading of carbon black can vary between 30-70 parts per hundred parts of rubber (phr). Furnace blacks are mostly used for rubber reinforcement. They can be roughly classed into reinforcing (< 35 nm) and semi-reinforcing (> 45 nm) grades by their particles size. The anti-abrasion property of carbon black increases with the decrease in particle size (Donnet et al., 1993).

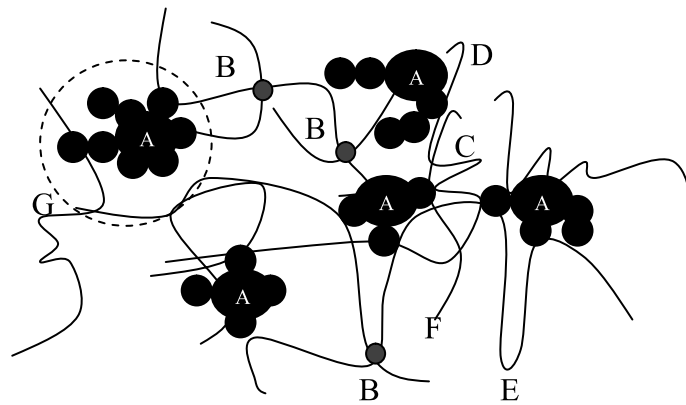


Figure 2.4: Illustration of carbon black aggregates in rubber matrix: (A) carbon black aggregate, (B) sulphur crosslinking, (C) chain entanglement, (D) tight loop, (E) loose loop, (F) free tail, and (G) zone of smaller chain mobility (Donnet et al., 1993).

Standard classification system for carbon black can be obtained in ASTM D 1765. Generally, grade introduction refers to one letter followed by three number digits. The first digit is a letter indicating the relative curing rate, N (normal) or S (slow); the next digit (1-9) is a measure of particle size range and the final two digits are designated by the supplier (Rodgers, 2004).

In this research, carbon black N550 is used as hybrid filler with PET powder. Table 2.2 below displays the general classes of rubber-grade carbon blacks as defined in ASTM Standard D1765-04.

Table 2.2: Types of carbon blacks (Rodgers, 2004).

Type	ASTM designation	Particle size (nm)	General use
SRF (Semi Reinforcing Furnace)	N762	61-100	Nontread Components
GPF (General Purpose Furnace)	N660	49-60	Nontread Components
FEF (Fast Extrusion Furnace)	N550	40-48	Nontread Components
FF (Fine Furnace)	N475	31-39	Nontread Components
HAF (High Abrasion Furnace)	N330	26-30	Tread and other Components
ISAF (Intermediate Super Abrasion Furnace)	N220	20-25	Tread
SAF (Super Abrasion Furnace)	N110	11-19	Tread

As an empirical guide, an increase in a carbon black aggregate size or structure will result in an improvement in cut growth and fatigue resistance. A decrease in particle size results in an increase in abrasion resistance and tear strength, a drop in resilience and an increase in hysteresis and heat buildup. Figure 2.5 illustrates the general trends for tread-grade carbon black loading and the effect on compound physical properties.

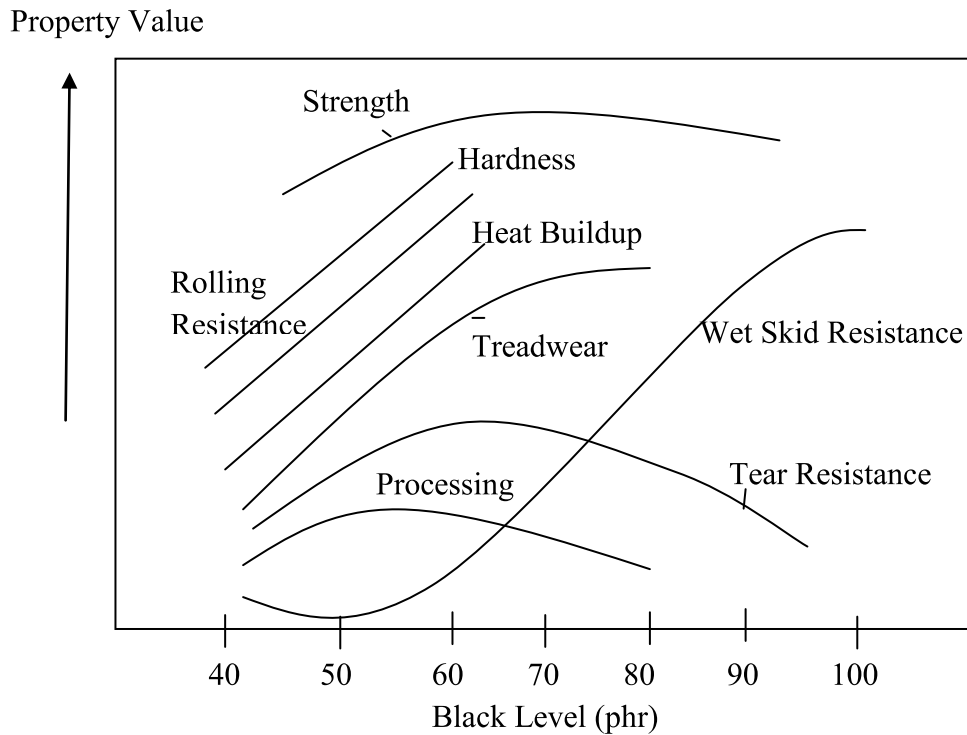


Figure 2.5: Effect of carbon black level on compound properties (Rodgers, 2004)

2.3.2 Halloysite Nanotubes (HNTs)

Halloysite nanotubes are unique and versatile nanomaterials that are formed by surface weathering of aluminosilicate minerals and are composed of aluminum, silicon, hydrogen and oxygen. Halloysite nanotubes are ultra-tiny hollow tubes with diameters typically smaller than 100 nanometers, with lengths typically ranging from about 500 nanometers to over 1.2 microns. Halloysite is a superfine clay material, often occurs as an ultramicroscopic hollow tube with a multilayer wall in nature (Zhang et al., 2008). Figure 2.6 shows the schematic structure of halloysite nanotubes. HNTs have two different interlayer surfaces; the AL-OH group is located inside the tubes while the outer surface of HNTs is covered by the siloxane group (Joussein et al., 2005; Liu et al., 2007). The lumen space inside the halloysite tubes can be intercalated and interacts with vulcanization ingredients and other materials (Pasbakhsh et al., 2010).

As a kaolinite mineral, halloysite has the same theoretical chemical composition as kaolinite except that it contains higher water content that is interlayered between its unit layers. The elemental compositions are SiO_2 ; 49.5, Al_2O_3 ; 35.5, Fe_2O_3 ; 0.29, TiO_2 ; 0.09 (http://www.imerys-ceramics.com/Upload/Fichiers/Halloysite_table1.pdf, 9th September 2009). The particles of halloysite can adopt a variety of morphology, the most dominant morphology of which is the fine, elongated tubule. The tubule may be long and thin, short and stubby or emerging from other tubes (Hedicke-Höchstötter et al., 2009; Joussein et al., 2005).

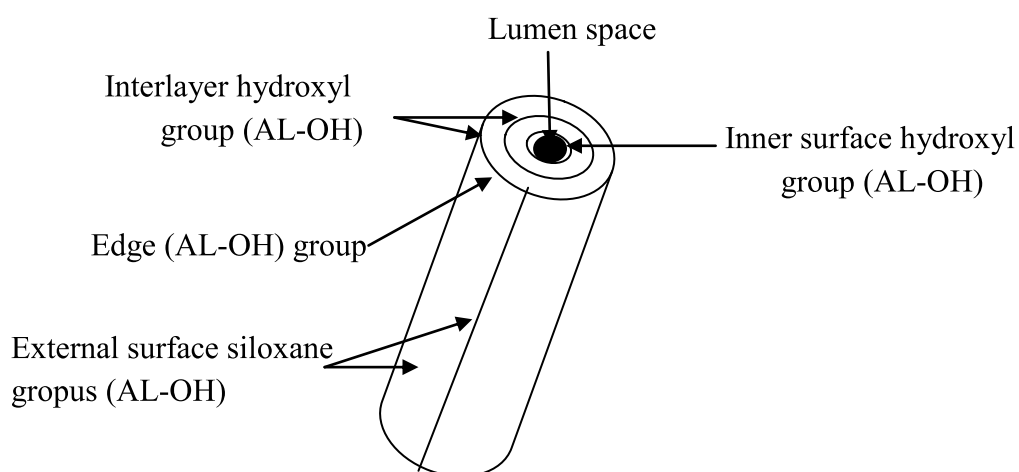


Figure 2.6: Schematic structure of a halloysite nanotubes (Pasbakhsh et al., 2010).

The presence of water molecules between the tetrahedral and octahedral sheets disrupts the hydrogen bonds across the interlayers creating a misfit between the tetrahedral and octahedral sheets that resulted in a rolling of the layers to acquire the tubular shape. Halloysite Nanotubes (HNTs) as reported by Guo et al. (2008) are multi-walled kaolinite nanotubes which have the outer diameters smaller than 100

nm, the length ranges from 500 nm to 1600 nm and wall thickness around 20 nm of which all concluded that there are tens of layers in the wall (Singh, 1996).

2.3.3 Precipitated Silica

Silica consists of ultimate particles of the inorganic polymer (SiO_2), where a silicon atom is covalently bonded in a tetrahedral arrangement to four oxygen atoms. Each of the four oxygen atoms is covalently bonded to at least one silicon atom to form either a siloxane ($-\text{Si}-\text{O}-\text{Si}-$) or silanol ($-\text{Si}-\text{O}-\text{H}-$) functionality. Surface silanol groups can be isolated from one another such that hydrogen bonding between the silanols cannot occur, vicinal to one another, promoting the formation of intramolecular hydrogen bonding, or geminal to one another, where two silanol groups are bonded to same silicon atom (Figure 2.7) (Waddell et al., 1995).

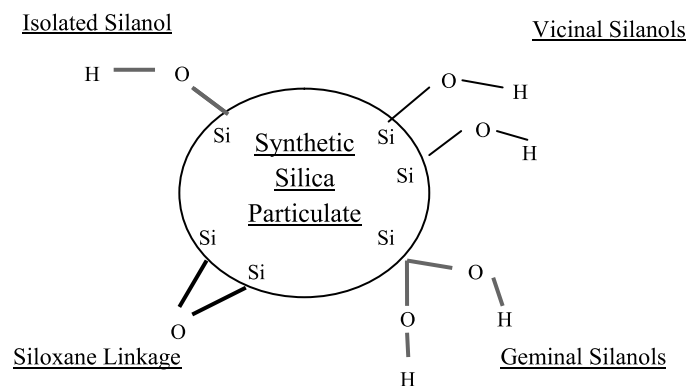


Figure 2.7: Silica surface groups: siloxane ($-\text{Si}-\text{O}-\text{Si}-$) and isolated, vicinal and geminal silanols ($-\text{Si}-\text{O}-\text{H}-$) (Waddell et al., 1995).

In this research, reinforcing precipitated silica is used as hybrid filler with PET powder. The position in the family of silica relies on a classification of commercial silicon dioxide and based on origin and primary particle size. Table 2.3 shows a partial listing of the many varieties used of silica in rubber compounding.

Table 2.3: Forms and properties of silica used in rubber compounding (Hewitt, 2007).

Natural (Crystalline)	Primary Size, μm	Function in Rubber
Ground quartz	1 – 10	Extending
Diatomite	1 - 5	Processing; Extending
Neuberg silica	1 – 5	Extending
Synthetic (Amorphous)	Primary Size, μm	Function in Rubber
Fumed	0.005 – 0.02	Reinforcing
Precipitated	0.01 – 0.03	Reinforcing
Precipitated	0.04	Semi-reinforcing
Precipitated	0.08	Processing; Color
Ferro-silicon by-product	0.10	Extending

The two major classes based on origin, are natural and synthetic. This distinction translates to a division between crystalline and amorphous forms and of equal importance to a substantial division between coarse and fine primary particles. Among the natural, it is defined in respect to their geographic and geologic origin whereas the synthetic group is defined in terms of enhanced abrasion resistance, tear and tensile strength.

Particulate silicas are made by precipitation from aqueous solution. The physical and chemical properties of precipitated silica can vary according to the manufacturing process. Reinforcement and control of suspension pH, temperature, and salt content can change the particle and aggregate sizes of silicas precipitated from solution. Adsorption is a function of the ultimate particle size which are three-dimensional clusters of ultimate particles, covalently bonded to one another via siloxane bonds. Aggregates can physically agglomerate through intermolecular hydrogen bonding of

surface silanol groups of one aggregate to a silanol group of another aggregate (Hewitt, 2007).

The small particle size and complex aggregate structure, precipitated silica imparts high degree of reinforcement to elastomer compounds. This superior reinforcement is employed in a variety of rubber compounds for shoe soles, industrial rubber goods, and tires. It has been used in shoe soles for its resistance to wear and to tearing, its non-scuffing characteristics with light color, or even transparent materials (Waddell et al., 1995).

2.3.4 Hybrid Composites

The most effective use of polymer composite materials is their life durability. The diverse and contradictory requirement for modern composites materials has brought forefront the very complex problem of developing new types of composite materials. In recent years, hybrid composites have been developed by using more than one type, shape, or size of reinforcement. These composites have been developed to provide synergistic properties of the chosen fillers and matrix.

The successful use of hybrid composite is determined by the chemical, mechanical and physical stability of the hybrid system. The matrix provides the solidity of hybrid composite, its resistance to the action of environmental factors, the required level of operating temperature and chemical resistance. The mechanical properties of the matrix mainly determine the level of shear and compressing strength of the hybrid composites. Finally, the processability of the hybrid composite depends only on the matrix composition where processing parameters of the composites depends on the

matrix properties (Perov and Khoroshilova, 1995). There are many types of hybrid fillers which have been used previously.

a) Carbon Black Hybrid Composites

In the past two decades, research was aimed to develop other reinforcing agents to replace carbon black in rubber compounds such as sepiolite, kaolin, and precipitated silica (Donnet et al., 1993). These fillers are inorganic in nature and incompatible with organic polymer matrices. Thus, the reinforcing effect of these fillers was much lower than that of carbon black. However, the layered silicate nanofillers have already been developed. In those nanofillers, the silicate layer surfaces have been effectively modified to render them organophilic so that the organically modified nanofillers can significantly enhance the critical performance properties of polymer clay nanocomposites. The unique properties imparted by nanoclay to rubber composites have opened up a new prospect in developing carbon black/nanoclay hybrid nanocomposites via facilitating the possible partial replacement of carbon black with nanoclay in rubber products without affecting the critical performance properties. Earlier studies have reported the properties of carbon black filled rubber vulcanizates. It has been amply demonstrated that the structure, particle size and functional groups on the surface influence the critical performance properties (Cataldo, 2001). Jia et al. (2005) reported a very high reinforcement and stiffening effect of nanoclay in carbon black filled rubber composites having 10, 20, 30 phr of total filler loading. Combined effect of nanoclay and carbon black on properties of natural rubber nanocomposites was evaluated. It was found that the nanoclay/carbon black natural rubber nanocomposites retained advantages from both fillers. Zhu and Narh (2004) executed the numerical simulation of the tensile modulus corresponding

to nanoclay filled polymer composites having three phases: polymer matrix, interlayer, and clay platelet.

Ratanasom et al. (2007) studied the reinforcing effect of silica and carbon black hybrid filled natural rubber compounds. Since silica has its own unique properties, it provides a unique combination of tear strength, abrasion resistance and adhesion properties. In tire treads, silica yields a lower rolling resistance at equal wear resistance and wet grip than carbon black. Since carbon black and silica possess their own advantages, the utilization of hybrid filler or blends of silica have been interesting fields in recent years.

c) Halloysite Nanotubes Hybrid Composites

Pasbakhsh et al. (2009a) studied the synergistic effect of silica with halloysite nanotubes (HNTs) on the properties of ethylene propylene diene monomer (EPDM). They found that with the hybridization of HNTs using the commercial filler used could give the optimum properties of silica/HNTs at loading ratio of 25/5 (phr/phr). The mixing of 5 phr of HNT and 25 phr of silica could make a synergistic effect on reinforcement of EPDM matrix. Adding 5 phr of HNT improved dispersion of silica inside the EPDM because of special charge distribution, unusual crystal shape, and good dispersion of HNTs inside the EPDM and nanotubular shapes of the HNTs. Similar observation of Yu et al. (2007) who had reported the mixing of two materials with different shapes may enhance the reinforcement effect of the composite because of synergistic effect and new reinforcement mechanism.

Ismail and Shaari (2010) investigated the effects of palm ash/halloysite nanotube weight ratio on the curing characteristics, tensile properties and morphology of Palm Ash (PA)/Halloysite Nanotubes (HNTs) hybrid filled Ethylene-Propylene-Diene Monomer (EPDM). They found that with increasing halloysite nanotube content, the overall properties such as curing time, scorch time, maximum torque, tensile strength and tensile modulus were increased except the elongation at break which showed the opposite trend. Morphological studies of tensile fracture surfaces of PA/HNTs hybrid composites also indicated that HNTs has better adhesion to the EPDM matrix as compared to palm ash. Furthermore, it was observed that some peaks which obtained from FTIR spectra were shifted or absent due to the formation of hydrogen bonding between the functional group of these two fillers. The shift in adsorption peaks of -OH groups in palm ash from 3388 cm^{-1} to 3393 cm^{-1} , the shift of adsorption peaks of Si-O stretching in HNT at 1016 cm^{-1} to 1028 cm^{-1} and 1068 cm^{-1} to 1014 cm^{-1} , 1032 cm^{-1} and 1081 cm^{-1} and the small shift of Al-OH vibrations adsorption peaks at 911 cm^{-1} and 931 cm^{-1} to 912 cm^{-1} and 934 cm^{-1} which form with the absence of Si-O stretching bands of palm ash at 860 cm^{-1} .

d) Natural Fibers Hybrid Composites

Fiber reinforced rubber composites are most important both in end-use applications and the area of research and development. These composites exhibit the combined behavior of the soft, elastic rubber matrix and the stiff, strong fibrous reinforcement. Sisal fiber is one of the strongest fibers, which can be used for several applications (Iannace et al., 2001), whilst oil palm fiber is one of the hard and tough fibers and it has found to be a potential reinforcement in phenol-formaldehyde resin (Sreekala et al., 1997). Due to the different natural fibers sisal and oil palm fibers appear to be