

ACKNOWLEDGEMENTS

I owe my deepest gratitude to my supervisor, Professor Dr. Hanafi Ismail, whose endless patience, encouragement, supervision and support from the preliminary to the concluding level enabled me to develop an understanding of the subject. It would have been next to impossible to write this thesis without his help, guidance, and endless patience and encouragement. My second supervisor, Associate Professor Dr. Nadras Othman, I would like to express my appreciation for her endless motivation, encouragements and ideas. I would not have made it through to this point without the financial support of USM Fellowship Scheme and I take the opportunity to thank Universiti Sains Malaysia for the financial support which made my dream come true.

I would also like to extend my gratitude to my beloved parents, and family for their endless understanding, support and encouragement from day one of my postgraduate studies. Lastly, I offer my regards and blessings to all of those who have supported me in any aspect during the completion of the project. It has been an amazing journey filled with ups and downs that I am thus thankful to everyone.

Shazlin Mohamed Shaari

“Writing is easy. All you do is stare at a blank sheet of paper until drops of blood form on your forehead” – Gene Fowler

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	xi
LIST OF FIGURES	xiii
LIST OF ABBREVIATIONS	xxx
LIST OF SYMBOLS	xxxii
ABSTRAK	xxxiii
ABSTRACT	xxxv

CHAPTER ONE: INTRODUCTION

1.1	Introduction	1
1.2	Problem Statement	2
1.3	Background of Research	4
1.4	Research Objectives	5
1.5	Outline of Thesis	6

CHAPTER TWO: LITERATURE REVIEW

2.1	Introduction to Rubber	9
2.2	Natural Rubber	9
2.3	Epoxidised Natural Rubber	11
2.4	Styrene-butadiene Rubber	13
2.5	Fillers as Reinforcements in Rubber Compounds	14
2.5.1	Renewable Resources Based Fillers	16

2.5.1.1	Chitin	16
2.5.1.2	Chitosan	18
2.6	Vulcanization of Rubber Compounds	23
2.6.1	Sulphur Vulcanization	24
2.6.2	Peroxide Based Vulcanization	26
2.6.3	Influence of Vulcanization Systems on The Properties of Vulcanizates	29
2.7	Rubber – Filler Interactions	31
2.7.1	Coupling agents in rubber compounds	33
2.7.2	Silane Based Coupling Agents	33
 CHAPTER THREE: METHODOLOGY		
3.1	Raw Materials	38
3.1.1	Rubber Materials	38
3.1.2	Filler Materials	38
3.1.3	Compounding Additive Materials	38
3.2	Equipments and Apparatus	39
3.2.1	Two roll mill	39
3.2.2	Moulding Machine	39
3.3	Formulations of Chitosan-Filled Natural Rubber Compounds	39
3.3.1	Chitosan-filled natural rubber compounds with different chitosan loading	39
3.3.2	Chitosan-Filled Epoxidized Natural Rubber (ENR) and Chitosan-Filled Styrene-Butadiene Rubber (SBR) Compounds	40
3.3.3	Chitosan-Filled Natural Rubber Compounds With Different Curing System	41

3.3.4	Chitosan-Filled Natural Rubber with The Addition of Silane Coupling Agent	41
3.4	Measurement of Curing Characteristics	42
3.5	Preparation of Moulded Sheets of Rubber Compounds	42
3.6	Characterization and Properties of Rubber Compounds	43
3.6.1	Measurement of Mechanical and Physical Properties	43
3.6.1.1	Measurement of Tensile Properties	43
3.6.1.2	Measurement of Hardness	43
3.6.1.3	Measurement of Fatigue Properties	44
3.6.1.4	Measurement of Rubber – Filler Interactions	46
3.6.2	Scanning Electron Microscopy (SEM) Micrographs of Tensile Fracture Surface	47
3.6.3	Fourier-Transform Infrared (FTIR) Analyses	47
3.6.4	Degradation Study	48
3.6.4.1	Weathering Test	50
3.6.4.2	Soil Burial Test	51
3.7	Flow Charts	53

CHAPTER FOUR: CHARACTERIZATION OF CHITOSAN-FILLED NATURAL RUBBER COMPOUNDS

4.1	Characterization of Chitosan	55
4.1.1	Particle Size Distribution Analysis	55
4.1.2	Scanning Electron Microscopy (SEM) Observation	56
4.1.3	Fourier Transform Infrared (FTIR) Analysis	57
4.2	The Effect of Chitosan Loading on the Properties and Degradation Behaviour of Chitosan-Filled Natural Rubber Compounds.	59
4.2.1	Fourier Transform Infrared Spectrometry Analyses	59
4.2.2	Determination of Curing Characteristics	61

4.2.3	Determination of Mechanical and Physical Properties	65
4.2.3.1	Tensile Properties	65
4.2.3.2	Hardness Properties	69
4.2.3.3	Fatigue Life	69
4.2.3.4	Determination of Rubber – Filler Interactions	71
4.2.4	Morphological Studies of Tensile Fractured Surfaces and Fatigue Fractured Surfaces.	72
4.2.4.1	Tensile Fractured Surfaces	72
4.2.4.2	Fatigue Failure Surfaces	74
4.2.5	Influence of Natural Weathering on the Tensile Properties of Chitosan-Filled Natural Rubber Compounds	77
4.2.5.1	Fourier Transform Infrared Spectroscopy Analysis	77
4.2.5.2	Determination of Weight Loss	81
4.2.5.3	Determination of Tensile Properties	82
4.2.5.4	Morphological Studies of Exposed Surfaces	86
4.2.6	Influence of Soil Burial on the Properties of Chitosan-Filled Natural Rubber Compounds	90
4.2.6.1	Fourier Transform Infrared Spectrometry Analysis	91
4.2.6.2	Determination of Weight Loss	95
4.2.6.3	Determination of Tensile Properties	97
4.2.6.4	Morphological Studies of Buried Surfaces	100

CHAPTER FIVE: COMPARATIVE STUDY OF CHITOSAN-FILLED EPOXIDISED NATURAL RUBBER (ENR) AND CHITOSAN-FILLED STYRENE-BUTADIENE RUBBER (SBR) WITH CHITOSAN-FILLED NATURAL RUBBER (NR) COMPOUNDS.

5.1	Fourier Transform Infrared Spectroscopy Analysis	104
5.2	Determination of Curing Characteristics	109
5.3	Determination of Mechanical and Physical Properties	113
5.3.1	Tensile Properties	113

5.3.2	Hardness Properties	118
5.3.3	Determination of Rubber-Filler Interactions	119
5.4	Morphological Studies of Tensile Fractured Surfaces	120
5.5	Influence of Cyclic Deformation on the Properties of Chitosan-filled Natural Rubber (NR), Epoxidised Natural Rubber (ENR) and Styrene-Butadiene Rubber (SBR) Compounds	122
5.5.1	Stress-strain Behaviour	122
5.5.2	Fatigue and Hysteresis Behaviour	124
5.5.3	Morphological Studies of Fatigue Fractured Surfaces	128
5.6	Influence of Natural Weathering on the Tensile Properties of Chitosan-Filled Epoxidised Natural Rubber (ENR) and Styrene-Butadiene Rubber (SBR) in Comparison to Chitosan-Filled Natural Rubber (NR) Compounds	130
5.6.1	Fourier Transform Infrared Spectrometry Analysis	130
5.6.2	Determination of Weight Loss	137
5.6.3	Tensile Properties	139
5.6.4	Morphological Studies of Exposed Surfaces	143
5.7	Influence of Soil Burial on the Properties of Chitosan-Filled Epoxidised Natural Rubber (ENR) and Styrene-Butadiene Rubber (SBR) Compounds.	146
5.7.1	Fourier Transform Infrared Spectroscopy Analysis	146
5.7.2	Determination of Weight Loss	152
5.7.3	Determination of Tensile Properties	153
5.7.4	Morphological Studies of Buried Surfaces	157

CHAPTER SIX: COMPARATIVE STUDY OF CHITOSAN-FILLED NATURAL RUBBER WITH DIFFERENT CURING SYSTEMS

6.1	Fourier Transform Infrared Spectrometry Analysis (FTIR)	161
6.2	Determination of Cure Characteristics	165
6.3	Determination of Mechanical Properties	168
6.3.1	Tensile Properties	168
6.3.2	Hardness Properties	173
6.3.3	Fatigue Life	174
6.4	Determination of Swelling Index	175
6.5	Morphological Studies of Tensile Fractured and Fatigue Failure Surfaces	177
6.5.1	Tensile Fractured Surfaces	177
6.5.2	Fatigue Failure Surfaces	180
6.6	Influence of Natural Weathering on the Tensile Properties of Chitosan-Filled Natural Rubber Compounds with Different Curing System	184
6.6.1	Fourier Transform Infrared Spectrometry Analysis	184
6.6.2	Determination of Weight Loss	189
6.6.3	Determination of Tensile Properties	191
6.6.4	Morphological Studies on Exposed Surfaces	197

CHAPTER SEVEN: COMPARATIVE STUDY OF CHITOSAN-FILLED NATURAL RUBBER COMPOUNDS WITH THE ADDITION OF SILANE COUPLING AGENT

7.1	Fourier Transform Infrared (FTIR) Spectrometry Analysis	201
7.2	Determination of Cure Characteristics	204

7.3	Determination of Mechanical Properties	207
7.3.1	Tensile Properties	207
7.3.2	Hardness Properties	211
7.3.3	Fatigue Life	211
7.4	Determination of Rubber-Filler Interactions	213
7.5	Morphological Studies of Tensile Fractured and Fatigue Failure Surfaces	214
7.5.1	Tensile Fractured Surfaces	214
7.5.2	Fatigue Failure Surfaces	216
7.6	Influence of Natural Weathering on the Tensile Properties of Chitosan-Filled Natural Rubber Compounds with the Addition of Silane Coupling Agent	217
7.6.1	Fourier Transform Infrared Spectrometry Analysis	217
7.6.2	Determination of Tensile Properties	221
7.6.3	Morphological Studies of Exposed Surfaces	225
7.7	Influence of Soil Burial on the Tensile Properties of Chitosan-Filled NR Compounds with the Addition of Silane Coupling Agent	226
7.7.1	Fourier Transform Infrared Spectrometry Analysis	226
7.7.2	Determination of Tensile Properties	229
7.7.3	Morphological Studies of Buried Surfaces	232
 CHAPTER EIGHT: CONCLUSION AND RECOMMENDATIONS		
8.1	Conclusion	234
8.2	Recommendation for Future Research	236

LIST OF TABLES

	Page
Table 2.1 Typical compounding formulation for natural rubber (Dick et al., 2009)	11
Table 2.2 Vulcanizing system and their relative sulphur–accelerator amount (Coran, 2013)	25
Table 2.3 Vulcanizing systems and its vulcanizate properties (Coran, 2013)	25
Table 2.4 The Relationship between the number of completed half- life and amount of decomposed peroxide (Rajan et al., 2012)	28
Table 3.1 Formulations of chitosan-filled rubber compounds	40
Table 3.2 Formulations of chitosan-filled natural rubber with different vulcanising systems	41
Table 3.3 Formulation of chitosan-filled natural rubber compounds with the addition of silane coupling agent	42
Table 3.4 Sample batch and degradation study periods	48
Table 3.5 Garden soil composition	52
Table 3.6 Details of experimental procedure in “A” phase	53
Table 5.1 Strain exponent values (n) of chitosan-filled NR, ENR and BR vulcanizates at different loading of chitosan.	127
Table 7.1 Characteristic peaks of 3-Aminopropyltriethoxysilane (APTES)	201

Table 7.2	Cure characteristics of chitosan-filled NR/CV and NR/CV/APTES compounds	205
-----------	---	-----

LIST OF FIGURES

	Page
Figure 2.1 Linear chains of cis-1,4-polyisoprene (Billmeyer, 1984).	10
Figure 2.2 The general chemical structure for epoxidised natural rubber (ENR) (Gelling, 1991).	12
Figure 2.3 Structural formula for styrene-butadiene rubber (Brandt et al., 2011)	14
Figure 2.4 Chemical structure of chitin (Atkins, 1985).	17
Figure 2.5 Chemical structure of chitosan (Roberts, 1992).	18
Figure 2.6 A typical crosslinking mechanism of peroxide vulcanization (Loan, 1967).	27
Figure 3.1 Average rainfall and mean temperature during 1 st and 2 nd batch degradation period (June 2010 to May 2011).	49
Figure 3.2 Average rainfall and mean temperature during 3 rd and 4 th batch degradation period (June 2011 to May 2012).	49
Figure 3.3 Average rainfall and mean temperature during 5 th batch degradation period (June 2012 to May 2013).	50
Figure 4.1 Particle size distribution of chitosan powder	56
Figure 4.2 SEM micrograph of chitosan particles taken at a magnification of 50x	57
Figure 4.3 SEM Micrograph of chitosan particles taken at magnification of 300x	57

Figure 4.4	Fourier transform infrared (FTIR) spectrum of chitosan particles	58
Figure 4.5	FTIR characteristic spectra of chitosan-filled natural rubber compounds with (a) 0 phr; (b) 10 phr; and (c) 40 phr chitosan loading	60
Figure 4.6	Proposed hydrogen bonding in a chitosan polymer	61
Figure 4.7	Proposed hydrogen bonding between chitosan particles	61
Figure 4.8	Influence of chitosan loading on the scorch time (t_{s2}) of chitosan-filled natural rubber compounds	63
Figure 4.9	Influence of chitosan loading on the cure time (t_{90}) of chitosan-filled natural rubber compounds	63
Figure 4.10	Influence of chitosan loading on the cure rate index (CRI) of chitosan-filled natural rubber compounds	64
Figure 4.11	Influence of chitosan loading on the maximum torque (M_H) of chitosan-filled natural rubber compounds	65
Figure 4.12	Influence of chitosan loading on the tensile strength of chitosan-filled NR vulcanizates	66
Figure 4.13	Influence of chitosan loading on the elongation at break of chitosan-filled NR vulcanizates	68
Figure 4.14	Influence of chitosan loading on the tensile modulus (M_{100} and M_{300}) of chitosan-filled NR vulcanizates	68
Figure 4.15	Influence of chitosan loading on the hardness values of chitosan-filled NR vulcanizates	69

Figure 4.16	Influence of chitosan loading on the fatigue life of chitosan-filled NR vulcanizates	70
Figure 4.17	Influence of chitosan loading on the rubber-filler interactions of chitosan-filled NR vulcanizates	71
Figure 4.18	SEM micrograph of unfilled NR vulcanizate taken at magnification of 300 x	72
Figure 4.19	SEM micrographs of chitosan-filled NR vulcanizate at (a) 10 phr chitosan and (b) 40 phr chitosan taken at magnification of 150 x.	74
Figure 4.20	SEM micrograph of a typical fatigue failure surface of chitosan-filled NR vulcanizate	75
Figure 4.21	SEM micrographs of fatigue failure surfaces of chitosan-filled NR vulcanizates taken at a magnification of 100 x; (a) 10 phr chitosan loading and (b) 40 phr chitosan loading.	76
Figure 4.22a	Representative FTIR spectra of chitosan-filled NR vulcanizates before and after exposure to natural weathering for a period of 3, 6 and 12 months.	79
Figure 4.22b	Close examination of FTIR spectra in the carbonyl region of 1500 – 1900 cm ⁻¹ .	79
Figure 4.23	Influence of chitosan loading on the carbonyl index (C.I) values of chitosan-filled NR vulcanizates subjected to natural weathering for exposure period of 3, 6 and 12 months	80

Figure 4.24	Influence of chitosan loading and exposure period on the percentage of weight loss of chitosan-filled NR vulcanizates	82
Figure 4.25	Influence of chitosan loading and exposure period on the tensile strength of chitosan-filled NR vulcanizates.	83
Figure 4.26	Influence of chitosan loading and exposure period on the elongation at break retention (%) of chitosan-filled NR vulcanizates.	84
Figure 4.27	Influence of chitosan loading and exposure period on the tensile modulus of chitosan-filled NR vulcanizates	86
Figure 4.28	SEM micrographs of chitosan-filled NR vulcanizates weathered for 3 months with (a) 0 phr (unfilled); (b) 10 phr and (c) 40 phr chitosan loading taken at a magnification of 50 x.	87
Figure 4.29	SEM micrographs of chitosan-filled NR vulcanizates exposed to natural weathering for a period of 6 and 12 months with different chitosan loading (a) 0phr/6months; (b) 0phr/12months; (c) 10phr/6months; (d) 10phr/12months; (e) 40 phr/6months and (f) 40phr/12months taken at magnification of 50 x.	89
Figure 4.30	SEM micrographs of chitosan-filled NR vulcanizates with 10 phr chitosan loading exposed to natural weathering for (a) 6 months and (b) 12 months taken at magnification of 300 x.	90

Figure 4.31	Representative FTIR spectra of (a) chitosan-filled NR vulcanizates before and after soil burial for 3, 6 and 12 months and (b) a close examination of IR spectra in the carbonyl region of 1600 – 1900 cm ⁻¹	93
Figure 4.32	Influence of chitosan loading and soil burial period on the carbonyl index (C.I) values of chitosan-filled NR vulcanizates	95
Figure 4.33	Influence of chitosan loading and burial period on the weight loss of the chitosan-filled NR vulcanizates	96
Figure 4.34	Influence of chitosan loading and burial period on the retention values of tensile strength (%) of chitosan-filled NR vulcanizates.	98
Figure 4.35	Influence of chitosan loading and burial period on the retention values of elongation at break (%) of chitosan-filled NR vulcanizates.	98
Figure 4.36	Influence of chitosan loading and burial period on the retention values of M100 of chitosan-filled NR vulcanizates.	99
Figure 4.37	SEM micrographs of surfaces of chitosan-filled NR vulcanizates incorporated with (a) 0 phr; (b) 10 phr and (c) 40 phr chitosan loading after 3 months of soil burial, taken at a magnification of 100 x.	101
Figure 4.38	SEM micrographs of chitosan-filled NR vulcanizates exposed to soil burial for 6 and 12 months with different chitosan content (a) 0phr/6months; (b) 0phr/12months; (c) 10phr/6months; (d) 10phr/12months; (e) 40 phr/6months and (f) 40phr/12months taken at magnification of 50 x.	102

Figure 5.1	FTIR spectra of chitosan-filled ENR vulcanizates incorporated with varied chitosan loading; (a) 0 phr; (b) 10 phr; and (c) 40 phr.	106
Figure 5.2	FTIR spectra of (a) chitosan-filled SBR vulcanizates incorporated with 0, 10 and 40 phr chitosan loading and (b) close examination of FTIR spectra in the region of 1400 – 1900 cm ⁻¹ .	108
Figure 5.3	Influence of chitosan loading on the scorch time (t_{s2}) of chitosan-filled natural rubber (NR), epoxidised natural rubber (ENR) and styrene-butadiene rubber (SBR) compounds.	109
Figure 5.4	Influence of chitosan loading on the cure time (t_{90}) of chitosan-filled natural rubber (NR), epoxidised natural rubber (ENR) and styrene-butadiene rubber (SBR) compounds.	110
Figure 5.5	Influence of chitosan loading on the cure rate index (CRI) of chitosan-filled natural rubber (NR), epoxidised natural rubber (ENR) and styrene-butadiene rubber (SBR) compounds.	112
Figure 5.6	Influence of chitosan loading on the maximum torque (MH) of chitosan-filled natural rubber (NR), epoxidised natural rubber (ENR) and styrene-butadiene rubber (SBR) compounds.	113
Figure 5.7	Influence of chitosan loading on the tensile strength of chitosan-filled natural rubber (NR), epoxidised natural rubber (ENR) and styrene-butadiene rubber (SBR) vulcanizates.	114

Figure 5.8	Influence of chitosan loading on the tensile modulus at 100% elongation (M100) of chitosan-filled natural rubber (NR), epoxidised natural rubber (ENR) and styrene-butadiene rubber (SBR) vulcanizates	115
Figure 5.9	Influence of chitosan loading on the tensile modulus at 300% elongation (M300) of chitosan-filled natural rubber (NR), epoxidised natural rubber (ENR) and styrene-butadiene rubber (SBR) vulcanizates	116
Figure 5.10	Influence of chitosan loading on the elongation at break (Eb) of chitosan-filled natural rubber (NR), epoxidised natural rubber (ENR) and styrene-butadiene rubber (SBR) vulcanizates	117
Figure 5.11	Influence of chitosan loading on the hardness properties of chitosan-filled natural rubber (NR), epoxidised natural rubber (ENR) and styrene-butadiene rubber (SBR) vulcanizates	118
Figure 5.12	Influence of chitosan loading on the rubber-filler interactions of chitosan-filled natural rubber (NR), epoxidised natural rubber (ENR) and styrene-butadiene rubber (SBR) vulcanizates.	119
Figure 5.13	SEM micrographs of chitosan-filled rubber vulcanizates of (a) NR at 10 phr chitosan loading; (b) ENR at 10 phr chitosan loading; (c) SBR at 10 phr chitosan loading; (d) NR at 40 phr chitosan loading; (e) ENR at 40 phr chitosan loading and (f) SBR at 40 phr chitosan loading taken at magnification of 150-x.	121
Figure 5.14	Relationship between stress and strain of NR, ENR and SBR vulcanizates filled with different loading of chitosan.	123

Figure 5.15	Relationship between accumulated strain energy and extension ratio of NR, ENR and SBR rubber vulcanizates filled with different loading of chitosan.	124
Figure 5.16	Influence of extension ratio on the fatigue life of chitosan-filled NR, ENR and SBR vulcanizates at different chitosan loading.	125
Figure 5.17	Influence of strain energy on the fatigue life of chitosan-filled NR, ENR and SBR vulcanizates at different loading of chitosan.	126
Figure 5.18	SEM micrographs of fatigue life surfaces of (a) NR; (b) ENR and (c) SBR vulcanizates filled with 10 phr chitosan loading taken at a magnification of 100-x.	128
Figure 5.19	SEM micrographs of fatigue life surfaces of (a) NR; (b) ENR and (c) SBR vulcanizates filled with 40 phr chitosan loading taken at a magnification of 100-x.	129
Figure 5.20	Representative FTIR spectra of chitosan-filled ENR vulcanizates before and after exposure to natural weathering for 3, 6 and 12 months.	132
Figure 5.21	Representative FTIR spectra of chitosan-filled SBR vulcanizates before and after exposure to natural weathering for 3, 6 and 12 months.	134
Figure 5.22	Influence of chitosan loading on the carbonyl index (CI) values of chitosan-filled NR, ENR and SBR vulcanizates subjected to natural weathering for exposure period of 3, 6 and 12 months.	137

Figure 5.23	Influence of chitosan loading and exposure period on the percentage of weight loss of chitosan-filled NR, ENR and SBR vulcanizates.	138
Figure 5.24	Influence of chitosan loading and exposure period on the retention values of tensile strength of chitosan-filled NR, ENR and SBR vulcanizates.	140
Figure 5.25	Influence of chitosan loading and exposure period on the retention values of EB (%) of chitosan-filled NR, ENR and SBR vulcanizates.	141
Figure 5.26	Influence of chitosan loading and exposure period on the retention values of M100 (%) of chitosan-filled NR, ENR and SBR vulcanizates.	143
Figure 5.27	SEM micrograph of chitosan-filled compounds of (a) ENR at 10 phr chitosan loading; (b) ENR at 40 phr chitosan loading; (c) SBR at 10 phr chitosan loading and (d) SBR at 40 phr chitosan loading after 3 months of natural weathering.	144
Figure 5.28	SEM micrograph of chitosan-filled vulcanizates of (a) ENR at 10 phr chitosan loading; (b) ENR at 40 phr chitosan loading; (c) SBR at 10 phr chitosan loading and (d) SBR at 40 phr chitosan loading after 6 months of natural weathering.	145
Figure 5.29	Representative FTIR spectra of chitosan-filled ENR before and after soil burial for 3, 6 and 12 months.	146
Figure 5.30	Representative FTIR spectra of chitosan-filled SBR vulcanizates before and after soil burial for 3, 6 and 12 months.	149

Figure 5.31	Influence of chitosan loading and soil burial on the carbonyl index (C.I) values of chitosan-filled NR, ENR and SBR vulcanizates.	151
Figure 5.32	Influence of chitosan loading and soil burial period on the percentage of weight loss of chitosan-filled NR, ENR and SBR vulcanizates.	153
Figure 5.33	Influence of chitosan loading and burial period on the tensile strength retention (%) of chitosan-filled NR, ENR and SBR vulcanizates.	154
Figure 5.34	Influence of chitosan loading and burial period on the elongation at break retention (%) chitosan-filled NR, ENR and SBR vulcanizates.	155
Figure 5.35	Influence of chitosan loading and burial period on the M100 Retention (%) of chitosan-filled NR, ENR and SBR vulcanizates.	156
Figure 5.36	SEM micrographs of chitosan-filled rubber vulcanizates exposed to soil burial for 3 months with different chitosan content (a) 10 phr chitosan-filled ENR; (b) 40 phr chitosan-filled ENR; (c) 10 phr chitosan-filled SBR and (d) 40 phr chitosan-filled SBR, taken at a magnification of 50 x	158
Figure 5.37	SEM micrographs of chitosan-filled rubber vulcanizates exposed to soil burial for 6 and 12 months with different chitosan loading (a) 10 phr/ENR/6 months; (b) 10 phr/ENR/12 months; (c) 40 phr/ENR/6 months; (d) 40 phr/ENR/12 months; (e) 10 phr/SBR/6 months; (f) 10 phr/SBR/12 months; (g) 40 phr/SBR/6 months and (h) 40 phr/SBR/12 months.	159

Figure 6.1	Representative FTIR spectra of chitosan-filled NR/semiEV vulcanizates incorporated with 0, 10 and 40 phr chitosan loading.	163
Figure 6.2	FTIR characteristic spectra of chitosan-filled NR/DCP vulcanizates incorporated with 0, 10 and 40 phr chitosan loading.	164
Figure 6.3	Decomposition of dicumyl peroxide (Dick et al., 2009)	165
Figure 6.4	Influence of chitosan loading and vulcanizing systems on the scorch time of chitosan-filled NR compounds.	166
Figure 6.5	Influence of chitosan loading and vulcanising system on the cure time of chitosan-filled NR compounds	167
Figure 6.6	Influence of chitosan loading and vulcanising system on the maximum torque of chitosan-filled NR compounds.	168
Figure 6.7	Influence of chitosan loading and vulcanising systems on the tensile strength of chitosan-filled NR vulcanizates.	170
Figure 6.8	Influence of chitosan loading and vulcanizing systems on the elongation at break of chitosan-filled NR vulcanizates.	171
Figure 6.9	Influence of chitosan loading and vulcanising systems on the tensile modulus at 100% elongation (M100) of chitosan-filled NR vulcanizates	172
Figure 6.10	Influence of chitosan loading and vulcanizing systems on the hardness of the chitosan-filled NR vulcanizates.	174
Figure 6.11	Influence of chitosan loading and vulcanizing systems on the fatigue life of chitosan-filled NR vulcanizates.	175

Figure 6.12	Influence of chitosan loading and vulcanising systems on the swelling index of chitosan-filled natural rubber compounds	177
Figure 6.13	SEM micrographs of unfilled NR vulcanizates of (a) NR/CV; (b) NR/SemiEV and (c) NR/DCP system	178
Figure 6.14	SEM micrographs of chitosan-filled NR vulcanizates of (a) CV cure system with 10 phr chitosan; (b) SemiEV cure system with 10 phr chitosan; (c) DCP cure system with 10 phr chitosan; (d) CV cure system with 40 phr chitosan; (e) SemiEV cure system with 40 phr chitosan; (f) DCP cure system with 40 phr chitosan;	179
Figure 6.15	SEM micrographs of fatigue life surfaces of (a) chitosan-filled NR/CV; (b) chitosan-filled NR/semiEV and (c) chitosan-filled NR/DCP vulcanizates with 10 phr chitosan loading taken at a magnification of 100-x.	181
Figure 6.16	SEM micrographs of fatigue life surfaces of (a) chitosan-filled NR/CV; (b) chitosan-filled NR/semiEV and (c) chitosan-filled NR/DCP vulcanizates with 40 phr chitosan loading taken at a magnification of 100-x.	183
Figure 6.17	Representative FTIR spectra of chitosan-filled NR/semiEV vulcanizates before and after natural weathering for 3, 6 and 12 months.	185
Figure 6.18	Representative FTIR spectra of chitosan-filled natural rubber compounds cured using peroxide based vulcanising system (DCP) before and after natural weathering for 3 and 6 months.	187

Figure 6.19	Influence of chitosan loading and exposure period on the carbonyl index (C.I) values of chitosan-filled NR vulcanizates cured using different vulcanising system.	188
Figure 6.20	Influence of chitosan loading and exposure period on the percentage of weight loss of chitosan-filled NR vulcanizates cured using different types of vulcanising system.	190
Figure 6.21	Influence of chitosan loading on the tensile retention of the chitosan-filled NR/CV, NR/semiEV and NR/DCP vulcanizates subjected to natural weathering for a period of 3, 6 and 12 months.	192
Figure 6.22	Influence of chitosan loading on the EB retention values of chitosan-filled NR/CV, NR/semiEV dan NR/DCP vulcanizates subjected to natural weathering for 3, 6 and 12 months.	195
Figure 6.23	Influence of chitosan loading on the M100 retention values of the chitosan-filled NR/CV, NR/semiEV and NR/DCP vulcanizates subjected to natural weathering for 3, 6 and 12 months.	196
Figure 6.24	SEM micrographs of chitosan-filled NR vulcanizates of (a) NR/semiEV at 10 phr chitosan loading; (b) NR/semiEV at 40 phr chitosan loading; (c) NR/DCP at 10 phr chitosan loading and (d) NR/DCP at 40 phr chitosan loading after 3 months of natural weathering.	198