

REACTIONS BETWEEN PALM STEARIN ALKYDS WITH
HIGH CARBOXYLIC ACID CONTENT AND
EPOXIDISED NATURAL RUBBER

KHONG YOKE KUM

THESIS SUBMITTED IN FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
UNIVERSITY OF MALAYA
KUALA LUMPUR

2014

UNIVERSITI MALAYA

ORIGINAL LITERARY WORK DECLARATION

Name of Candidate: **KHONG YOKE KUM** I/C/Passport No: **861122-38-6736**

Registration/Matric No.: **SHC090041**

Name of Degree: **DOCTOR OF PHILOSOPHY**

Title of Project Paper/Research Report/Dissertation/Thesis ("this Work"):

"REACTIONS BETWEEN PALM STEARIN ALKYDS WITH HIGH CARBOXYLIC ACID CONTENT AND EPOXIDISED NATURAL RUBBER"

Field of Study: **POLYMER CHEMISTRY**

I do solemnly and sincerely declare that:

- (1) I am the sole author/writer of this Work,
- (2) This Work is original,
- (3) Any use of any work in which copyright exists was done by way of fair dealing and for permitted purposes and any excerpt or extract from, or reference to or reproduction of any copyright work has been disclosed expressly and sufficiently and the title of the Work and its authorship have been acknowledged in this Work,
- (4) I do not have any actual knowledge nor do I ought reasonably to know that the making of this work constitutes an infringement of any copyright work,
- (5) I hereby assign all and every rights in the copyright to this Work to the University of Malaya ("UM"), who henceforth shall be owner of the copyright in this Work and that any reproduction or use in any form or by any means whatsoever is prohibited without the written consent of UM having been first had and obtained,
- (6) I am fully aware that if in the course of making this Work I have infringed any copyright whether intentionally or otherwise, I may be subject to legal action or any other action as may be determined by UM.

(Candidate Signature)

Date:

Subscribed and solemnly declared before,

Witness's Signature

Date:

Name **PROFESSOR DR GAN SENG NEON**

Designation

ABSTRACT

Vulcanisation serves as a chemical process to transform weak and permanently deformable rubber into vulcanised rubber with ultimate elastic performance. Crosslinking of rubber using environment friendly crosslinker without any toxic additive offers a wide range of potential applications. In this work, self-vulcanisable rubber blend that utilises reaction between epoxidised natural rubber with 50 mol % of epoxidation (ENR50) and palm stearin alkyd at ambient temperature has been developed. Palm stearin alkyds were used as green crosslinkers in epoxidised natural rubber. The first alkyd (AlkydCO) was formulated with excess hydroxyl groups and low level of carboxyl groups, reflected from its hydroxyl value (148.5 mg KOH/g alkyd), and acid value (16.7 mg KOH/ g alkyd). AlkydCO was then utilised to produce modified alkyds with higher amounts of carboxyl groups. AlkydMA1 and AlkydMA2 were prepared through half ester formation between hydroxyl groups in AlkydCO with maleic anhydride (MA) at controlled reaction temperature, while AlkydPA1 was prepared from phthalic anhydride (PA). Incorporation of acid anhydride into AlkydCO has resulted in the increase in acid values of AlkydMA1 and AlkydMA2 to 44.0 and 68.7 mg KOH/ g alkyd respectively, while AlkydPA1 recorded acid value of 46.0 mg KOH/ g alkyd. These alkyds were then blended with ENR50 through solvent casting technique and thin films of the blend were analysed by FTIR, ¹H-NMR, DSC and TGA. The occurrence of crosslinking in the rubber is in good agreement with the gel content results, where ENR50/Alkyd blends able to resist dissolution and appear as gel in toluene. Individually, ENR50 and alkyd is completely soluble in toluene.

The carboxylic acid side chain in alkyd is responsible for the crosslinking with epoxide group in ENR50. AlkydMA2 which has higher density of carboxyl group produces blend with higher percentage of gel, higher crosslink density and higher T_g

than ENR50/AlkydMA1 blend. At equivalent level of carboxyl content, the structure of the pendant $-\text{COOH}$ groups at the alkyd was found to affect the crosslinking reaction as well. AlkydMA1 with pendant $-\text{OOC}-\text{CH}=\text{CH}-\text{COOH}$ groups are able to produce blend with higher amount of gel insoluble in toluene and better thermal resistance as compared to ENR50/AlkydPA1 blend where the acid side chain of carboxylic acid in the alkyd comprised of $-\text{OOC}-\text{Ph}-\text{COOH}$ (where Ph = aromatic ring).

In the later part of this work, extent of crosslinking in the ENR50/Alkyd blend was enhanced via incorporation of ultraviolet (UV) curing technology. Benzophenone which acts as UV photoinitiator was introduced into the system, followed by irradiating the blend using UV light. UV irradiation has induced formation of crosslinked structure involving $-\text{C}=\text{C}-$ in the system. FTIR peak absorbance at 835 cm^{-1} which corresponds to $-\text{C}=\text{C}-$ group of the isoprene unit in ENR50 has reduced significantly upon UV irradiation. Further approach was taken to enhance crosslinking in the system by incorporating trimethylolpropanetriacrylate (TMPTA). Likewise, crosslink density in the blend has improved where the product is able to better resist dissolution when immersed in toluene.

ABSTRAK

Pemvulkanan merupakan satu proses kimia untuk menukar getah yang bersifat lemah dan berubah bentuk kekal kepada getah tervulkan yang berprestasi elastik tinggi. Penggunaan agen penyilangan mesra alam tanpa bahan tambahan toksik dalam perangkaian getah menyumbang kepada pelbagai aplikasi berpotensi. Dalam kajian ini, adunan getah memvulkan sendiri telah dihasilkan melalui penggabungan getah asli terepoksida dengan 50 mol % epoksida (ENR50) dan alkid stearin kelapa sawit pada suhu bilik. Alkid stearin kelapa sawit merupakan agen penyilangan hijau di dalam getah asli terepoksida. Alkid pertama (AlkidCO) diformulasikan dengan kandungan kumpulan hidroksil yang berlebihan dan kumpulan karboksil yang rendah seperti yang ditunjukkan pada nilai hidroksil (148.5 mg KOH/ g alkid) dan nilai asid (16.7 mg KOH/ g alkid). AlkidCO seterusnya digunakan untuk menghasilkan alkid yang mempunyai kandungan kumpulan karboksil yang tinggi. AlkidMA1 dan AlkidMA2 telah dihasilkan melalui pembentukan ester separa antara kumpulan hidroksil dalam AlkidCO dengan maleik anhidrida (MA) pada suhu terkawal, sementara AlkidPA1 disediakan dengan menggunakan flatik anhidrida (PA). Penggabungan asid anhidrida pada AlkidCO telah menyebabkan peningkatan dalam nilai asid pada AlkidMA1 dan AlkidMA2, masing-masing kepada 44.0 dan 68.7 mg KOH/ g alkid. AlkidPA1 pula melaporkan nilai asid sebanyak 46.0 mg KOH/ g alkid. Alkid yang terhasil kemudian diadunkan dengan ENR50 melalui teknik pelarut acuan dan salutan nipis daripada adunan dianalisa melalui FTIR, ¹H-NMR, DSC dan TGA. Pembentukan rangkai silang di dalam getah adalah sejajar dengan keputusan daripada kandungan gel, di mana adunan ENR50/Alkid berupaya untuk menentang pelarutan dan muncul sebagai gel di dalam toluena. Secara berasingan, ENR50 dan alkid adalah terlarut sepenuhnya di dalam toluena.

Rantai cabang asid karboksilik dalam alkid bertanggungjawab dalam pembentukan rangkaian silang dengan kumpulan epoksida dalam ENR50. AlkidMA2 yang mempunyai ketumpatan kumpulan karboksilik yang tinggi menghasilkan adunan yang mempunyai peratusan gel, ketumpatan rangkaian silang dan T_g yang tinggi berbanding dengan adunan ENR50/AlkidMA1. Pada tahap kandungan karboksil yang sama, struktur rantai cabang asid karboksilik pada alkid juga mempengaruhi kadar pembentukan rangkaian silang. AlkidMA1 dengan struktur rantai cabang $-OOC-CH=CH-COOH$ berupaya membentuk adunan yang mempunyai kandungan gel tak terlarut dalam toluena dan rintangan terma yang tinggi berbanding dengan adunan ENR50/AlkidPA1 yang terdiri daripada rantai cabang asid karboksilik yang berstruktur $OOC-Ph-COOH$ (Ph= gelang aromatic) di dalam alkid.

Bahagian selanjutnya di dalam disertasi ini melaporkan peningkatan kadar rangkaian silang di dalam adunan ENR50/Alkid melalui penerapan teknologi pemvulkanan menggunakan sinaran ultraungu (UV). Benzofenon yang berfungsi sebagai UV fotopemula telah disertakan di dalam sistem, dan adunan divulkankan dengan menggunakan sinaran UV. Rangkaian silang melibatkan kumpulan $-C=C-$ di dalam sistem terbentuk hasil daripada penyinaran UV. Puncak serapan FTIR pada panjang gelombang 835 cm^{-1} yang disebabkan oleh kumpulan $C=C$ daripada unit isoprena di dalam ENR50 menurun dengan nyata sekali selepas penyinaran UV. Adunan ENR50/Alkid juga digabungkan dengan trimethylolpropane triacrylate (TMPTA) untuk meningkatkan lagi kadar rangkaian silang di dalam sistem. Ketumpatan rangkaian silang didapati meningkat dan sebahagian besar adunan yang terbentuk tidak terlarut di dalam toluena.

ACKNOWLEDGEMENT

I would like to express my deepest appreciation to my supervisor, Professor Dr. Gan Seng Neon for his continuous support throughout my PhD study and his brilliant suggestions and guidance in writing academic journals and this dissertation. I am indebted to my many colleagues and friends from the Chemistry Department, University of Malaya who had generously offering helps in many ways. A special thanks to my family members, especially my mother, Mdm. Loke Fong Yin for her endless love and support. Last but not least, I would like to thank University of Malaya for the financial support given to me through UM scholarship scheme. Research grant IPPP353/2010A from Institute of Graduate Study UM has helped making this project a success.

TABLE OF CONTENTS

	Page	
TITLE PAGE		
ORIGINAL LITERARY WORK DECLARATION		
ABSTRACT	iii	
ABSTRAK	v	
ACKNOWLEDGEMENTS	vii	
TABLE OF CONTENTS	viii	
LIST OF FIGURES	xv	
LIST OF TABLES	xx	
LIST OF SYMBOLS AND ABBREVIATIONS	xxiii	
CHAPTER 1: INTRODUCTION		
1.1	Polymer blends	1
1.1.1	Preparations of polymer blends	3
	(a) Solution blending	3
	(b) Latex blending	4
	(c) Melt mixing	5
	(d) Freeze drying	6
1.1.2	Miscibility of polymer blends	6
1.1.3	Properties of blends	8
1.1.4	Commercial polymer blends	9
1.1.5	Self-crosslinking polymer blends	11
1.2	Epoxidised natural rubber (ENR)	13
1.2.1	Background	13
1.2.2	Preparation of ENR	13

1.2.3	Properties of ENR	15
1.2.4	Application	15
1.2.5	Vulcanisation and crosslinking in ENR	16
	(a) Sulfur vulcanisation	17
	(b) Crosslinking involving epoxide groups of ENR	19
1.3	Alkyd	20
1.3.1	Background	20
1.3.2	Alkyd raw materials	21
	(a) Oils and fatty acids	21
	(b) Polyols	22
	(c) Polyacids	24
1.3.3	Preparation of alkyd	26
	(a) Monoglyceride process	26
	(b) Fatty acid process	28
	(c) Acidolysis process	28
1.3.4	Alkyd polyesterification process	29
1.3.5	Classification of alkyds	30
	(a) Drying properties of alkyd resins	30
	(b) Oil length of alkyd resins	30
1.3.6	Modification of alkyds	32
	(a) Modification by reaction of double bonds of alkyd	33
	(b) Modification by reaction of functional groups of alkyd	33

CHAPTER 2: LITERATURE REVIEWS

2.1	Known/ published works on ENR reactions and their applications	34
2.2	Various alkyds (short, medium & long oil lengths) and their modification reactions	40
2.3	Scopes of study	43

CHAPTER 3: EXPERIMENTAL

3.1	Materials	45
3.2	Characterisation of palm stearin	45
3.2.1	Determination of acid value	45
3.2.2	Determination of iodine value: ASTM D5768	46
3.2.3	Determination of non-volatile content	48
3.2.4	Fourier transform infrared (FTIR) spectroscopy	48
3.2.5	Proton nuclear magnetic ($^1\text{H-NMR}$) spectroscopy	48
3.3	Characterisation of ENR50	49
3.3.1	FTIR spectroscopy	49
3.3.2	$^1\text{H-NMR}$ spectroscopy	49
3.3.3	Differential scanning calorimetry (DSC)	49
3.4	Alkyd synthesis	50
3.4.1	Theoretical design of AlkydCO formulation	51
	(a) Initial acid value	53
	(b) Excess $-\text{OH}$ groups or equivalents	54
	(c) Patton gel point	54
3.4.2	AlkydCO formulation	55

3.4.3	Theoretical design of modified alkyd formulation	56
	(a) Initial acid value	57
	(b) Expected final acid value	58
3.4.4	AlkydMA1 formulation	58
3.4.5	AlkydMA2 formulation	59
3.4.6	AlkydPA1 formulation	60
3.4.7	Preparation of AlkydCO	61
3.4.8	Preparation of MA-modified alkyds, AlkydMA1 and AlkydMA2	64
3.4.9	Preparation of PA-modified alkyd, AlkydPA1	64
3.5	Characterisation of alkyds	65
3.5.1	Final acid value and amount of –COOH groups in alkyds	65
3.5.2	Hydroxyl value	65
3.5.3	FTIR analysis	66
3.5.4	¹ H-NMR analysis	66
3.5.5	DSC analysis	67
3.6	Preparation of ENR and alkyd solutions	67
3.6.1	Preparation of 10 % w/w ENR50 solution	67
3.6.2	Preparation of 60 % w/w alkyd solution	67
3.7	Preparation of ENR50/Alkyd blend	68
3.7.1	Effect of –COOH content in MA-modified alkyds on reaction between ENR50 and alkyd	68
3.7.2	Effect of type of anhydride modification in alkyd on reaction between ENR50 and alkyd: Comparison between AlkydPA1 and AlkydMA1	69

3.8	Characterisation of ENR50/Alkyd blends	69
3.8.1	FTIR analysis	69
3.8.2	Determination of gel content	69
3.8.3	DSC analysis	70
3.8.4	TGA analysis	70
3.8.5	Gel permeation chromatography (GPC) analysis	71
3.9	Development of UV-curable ENR50/Palm stearin alkyd blend	71
3.9.1	Preparation of UV-curable ENR50/Palm stearin alkyd blend	71
3.9.2	Characterisation of UV-curable ENR50/Palm stearin alkyd blend	73
	(a) FTIR analysis	73
	(b) Thermal analysis	73
	(c) Swelling test and crosslink density calculation	74

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1	Characterisation of palm stearin	78
4.1.1	Properties of palm stearin	78
4.1.2	FTIR spectroscopy	80
4.1.3	¹ H-NMR spectroscopy	81
4.2	Characterisation of ENR50	83
4.2.1	FTIR spectroscopy	83
4.2.2	¹ H-NMR analysis	85
4.2.3	DSC analysis	87

4.3	AlkydCO synthesis	88
4.3.1	Acid value of reaction mixture during AlkydCO cook	88
4.3.2	¹ H-NMR spectroscopy of AlkydCO	89
4.3.3	FTIR spectroscopy of AlkydCO	92
4.4	Characterisation of alkyds	95
4.4.1	Final acid value and hydroxyl value of alkyds	95
4.4.2	FTIR spectroscopy of alkyds	98
4.4.3	¹ H-NMR spectroscopy of alkyds	100
4.4.4	DSC analysis	102
4.5	Characterisation and properties of ENR50/Alkyd blends: Effect of – COOH content in MA-modified alkyds	104
4.5.1	Reactions during blending	104
4.5.2	Comparisons between blends from alkyds with different – COOH content (AlkydMA1 and AlkydMA2)	109
	(a) FTIR analysis	109
	(b) Gel content	110
	(c) DSC analysis	112
4.5.3	Analysis on sol portion of ENR50/AlkydMA2 blend	116
4.6	Characterisation and properties of ENR50/Alkyd blends: Comparison of reaction between PA-modified alkyd and MA-modified alkyd with ENR50	119
4.6.1	FTIR analysis	119
4.6.2	Gel content	121
4.6.3	Thermal analysis	122
	(a) Activation energy of degradation (E_d) using Kissinger equation	125

	(b) Activation energy of degradation (E_d) using Flynn-Wall-Ozawa method	132
4.7	Development of UV-induced crosslinking in ENR50/AlkydMA1 blend	137
4.7.1	Reactions during UV irradiation	137
4.7.2	Swelling percentage and crosslink density	145
4.7.3	DSC analysis	149
4.8	Enhancing UV-induced crosslinking in ENR50/AlkydMA1 blend via incorporation of TMPTA	152
4.8.1	Gel fraction	152
4.8.2	Thermal analysis	156
4.8.3	FTIR analysis	162
CHAPTER 5: CONCLUSIONS AND SUGGESTION FOR FURTHER RESEARCH		
5.1	Conclusions	165
5.1.1	Modification of palm stearin alkyd	165
5.1.2	Reactions of palm stearin alkyds with epoxidised natural rubber (ENR50)	166
5.1.3	Enhancing crosslinking in ENR50/AlkydMA1 blend via UV irradiation	167
5.2	Suggestion for further research	168
	REFERENCES	169
	LIST OF PUBLICATIONS AND PAPERS PRESENTED	183
	APPENDICES	185

LIST OF FIGURES

Figure 1.1	Idealised behavioural patterns of polymer blend as blend composition changes	9
Figure 1.2	Classification of thermoplastic polymers	10
Figure 1.3	General structure of ENR	13
Figure 1.4	Formation of monoglyceride	27
Figure 1.5	Relationship of oil length with the general properties of alkyd resin	32
Figure 2.1	Proposed crosslinking of ENR via sulfur vulcanisation	35
Figure 2.2	Probable crosslinking mechanism in (a) XNBR/ENR blends, (b) CSM/ENR blends, (c) CR/ENR blends, and (d) PVC/ENR blends	39
Figure 3.1	Mettler Toledo DSC (Model: DSC822e): (a) Temperature controller; (b) Intercooler	50
Figure 3.2	Apparatus set-up for (a) Alcoholysis process, and (b) Esterification process	63
Figure 3.3	Perkin Elmer TGA 6 instrument: (a) Furnace (b) Intercooler	71
Figure 3.4	DYMAX Light Curing System 5000E (a) Power supply, (b) Roller belt and (c) Reflector housing with a 400W UV light bulb	73
Figure 4.1	FTIR spectrum of palm stearin	80
Figure 4.2	¹ H-NMR spectrum of palm stearin	82
Figure 4.3	FTIR spectrum of ENR50	84
Figure 4.4	¹ H-NMR spectrum of ENR50	86

Figure 4.5	DSC thermogram of ENR50	87
Figure 4.6	Changes in acid value against esterification time during AlkydCO synthesis	88
Figure 4.7	¹ H-NMR spectra of (a) palm stearin and (b) AlkydCO	90
Figure 4.8	Plausible structure of AlkydCO	92
Figure 4.9	FTIR spectrum of AlkydCO	94
Figure 4.10	Plausible synthesis route of AlkydCO	95
Figure 4.11	Incorporation of anhydrides into AlkydCO	97
Figure 4.12	FTIR spectra of (a) AlkydCO, (b) AlkydPA1, (c) AlkydMA1, and (d) AlkydMA2	99
Figure 4.13	¹ H-NMR spectra of (a) AlkydCO, (b) AlkydPA1, and (c) AlkydMA1	101
Figure 4.14	DSC thermograms of (a) AlkydCO, (b) AlkydPA1, (c) AlkydMA1, and (d) AlkydMA2	103
Figure 4.15	DSC thermograms of AlkydCO obtained from repeated heating and cooling	103
Figure 4.16	FTIR spectra of (a) AlkydMA1, (b) ENR50, and (c) ENR50/AlkydMA1 blend (blended for 12 hours)	105
Figure 4.17	Normalised FTIR spectra of ENR50/AlkydMA1 blend series	107
Figure 4.18	Plausible reaction between ENR50 and AlkydMA1 during blending	108
Figure 4.19	Variation of gel content with blending time in ENR50/AlkydCO, ENR50/AlkydMA1 and ENR50/AlkydMA2 blend series	111

Figure 4.20	DSC thermograms of ENR50/Alkyd blend series: (i) ENR50/AlkydCO blend, blended for 5 minutes, (ii) ENR50/AlkydCO blend, blended for 12 hours, (iii) ENR50/AlkydMA1 blend, blended for 5 minutes, (iv) ENR50/AlkydMA1 blend, blended for 12 hours, (v) ENR50/AlkydMA2 blend, blended for 5 minutes, and (vi) ENR50/AlkydMA2 blend, blended for 12 hours	114
Figure 4.21	FTIR spectrum of sol portion of ENR50/AlkydMA2 blend (blending time = 7 hours)	116
Figure 4.22	Molecular weight distribution curves of (a) Dissolved ENR50, (b) AlkydMA2, and (c) sol fraction of ENR50/AlkydMA2 blend (blending time= 7 hours)	118
Figure 4.23	Normalised FTIR spectra of ENR50/AlkydMA1 and ENR50/AlkydPA1 blend series	120
Figure 4.24	Variation of gel content in ENR50/AlkydMA1 and ENR50/AlkydPA1 blend series at different blending time	122
Figure 4.25	Overlay TG curve of ENR50/AlkydMA1 and ENR50/AlkydPA1 blends, blended for 12 hours at heating rate of 30 °C/min	124
Figure 4.26	DTG curves of (a) ENR50/AlkydMA1 and, (b) ENR50/AlkydPA1 blends, blended for 7 hours	128
Figure 4.27	Dependence of $-\ln(\beta/T_m^2)$ on $1/T_m$ for non-isothermal degradation of (a) ENR50/AlkydMA1 blend series and (b) ENR50/AlkydPA1 blend series (Kissinger equation).	129

Figure 4.28	Flynn-Wall-Ozawa plots of (a) ENR50, (b) ENR50/AlkydMA1 blends, blended for 7 hours and (c) ENR50/AlkydPA1 blend, blended for 7 hours at varying degree of conversion, α .	134
Figure 4.29	Plots of activation energy at various degree of conversion for ENR50, ENR50/AlkydMA1 and ENR50/AlkydPA1 blends	137
Figure 4.30	FTIR spectra of (a) EA-B0T0 blend and, (b) EA-B5T0 blend, before irradiated with UV light	139
Figure 4.31	Normalised FTIR spectra of EA-B0T0 blend, before (0 s) and after (240 s) UV irradiation	140
Figure 4.32	Normalised FTIR spectra of EA-B5T0 blend, before (0 s) and after (240 s) UV irradiation	141
Figure 4.33	Proposed reactions that took place during UV irradiation of ENR50/AlkydMA1 blend	144
Figure 4.34	Variation of swelling % in EA-B0T0 and EA-B5T0 blends at different UV irradiation time	146
Figure 4.35	DSC thermograms of EA-B0T0 blends after irradiated with UV light for different duration of time: (i) 0 s, (ii) 60 s, (iii) 120 s, (iv) 180 s, and (v) 240 s.	150
Figure 4.36	DSC thermograms of EA-B5T0 blends after irradiated with UV light for different duration of time: (i) 0 s, (ii) 60 s, (iii) 120 s, (iv) 180 s, and (v) 240 s.	151
Figure 4.37	Effect of adding TMPTA on the gel content of UV-induced crosslinking in ENR50/AlkydMA1 blends	153

Figure 4.38	TGA thermograms of (a) EA-B5T0 blend, (b) EA-B5T1 blend, (c) EA-B5T3 blend, and (d) EA-B5T5 blend	157
Figure 4.39	DSC thermograms of EA-B5T1 blends after irradiated with UV light for different duration of time: (i) 0 s, (ii) 60 s, (iii) 120 s, (iv) 180 s, and (v) 240 s	159
Figure 4.40	DSC thermograms of EA-B5T3 blends after irradiated with UV light for different duration of time: (i) 0 s, (ii) 60 s, (iii) 120 s, (iv) 180 s, and (v) 240 s	160
Figure 4.41	DSC thermograms of EA-B5T5 blends after irradiated with UV light for different duration of time: (i) 0 s, (ii) 60 s, (iii) 120 s, (iv) 180 s, and (v) 240 s.	161
Figure 4.42	(a) Normalised FTIR spectra, and (b) Plot of peak absorbance A_{838}/A_{1448} of EA-B5T3 blend series after irradiated with UV light for different intervals of time	163
Figure 4.43	Proposed structure of UV-cured EA-B5T3 blend	164

LIST OF TABLES

Table 1.1	Formulations for accelerated sulfur vulcanisation of ENR	18
Table 1.2	Some common polyalcohols used in alkyd synthesis	23
Table 1.3	Some common dicarboxylic acids and anhydrides used in alkyd synthesis	25
Table 1.4	Alkyd resin polyesterification process	29
Table 3.1	Recommended specimen weight for iodine value test based on estimated iodine value	47
Table 3.2	Descriptions of symbols used in alkyd formulation	51
Table 3.3	Theoretical design of AlkydCO formulation	52
Table 3.4	AlkydCO formulation	55
Table 3.5	Theoretical design of modified alkyd formulation	57
Table 3.6	AlkydMA1 formulation	59
Table 3.7	AlkydMA2 formulation	60
Table 3.8	AlkydPA1 formulation	61
Table 3.9	Compositions of UV-curable ENR50/Palm stearin alkyd blend	72
Table 4.1	Properties of palm stearin	79
Table 4.2	Type of fatty acids in palm stearin with its proportions	79
Table 4.3	Peak assignments for ¹ H-NMR spectrum of palm stearin	81
Table 4.4	Peak assignments for ¹ H-NMR spectrum of AlkydCO	91
Table 4.5	FTIR peak assignments of AlkydCO	93
Table 4.6	Hydroxyl value, initial acid value, final acid value, and amount of -COOH groups of alkyds	97

Table 4.7	FTIR peak absorbance at 3472 cm^{-1} (A_{3472}), 1457 cm^{-1} (A_{1457}) and A_{3472} / A_{1457} of alkyds	100
Table 4.8	Peak assignments for FTIR spectrum of ENR50/AlkydMA1 blend	106
Table 4.9	FTIR peak absorbance A_{875}/A_{835} of ENR50/Alkyd blend series and % reduction in A_{875}/A_{835}	109
Table 4.10	Glass transition temperature of ENR50, alkyds and ENR50/Alkyd blend series	113
Table 4.11	T_i of ENR50/AlkydMA1 and ENR50/AlkydPA1 blend series at different blending times	124
Table 4.12	Values of kinetic parameters for non-isothermal degradation of ENR50/AlkydMA1 blends (composition: 10 parts of AlkydMA1 per 100 parts of ENR50) determined by Kissinger method	130
Table 4.13	Values of kinetic parameters for non-isothermal degradation of ENR50/AlkydPA1 blends (composition: 10 parts of AlkydPA1 per 100 parts of ENR50) determined by Kissinger method	131
Table 4.14	Percentage of swelling in toluene, crosslink density and average molecular weight between crosslink of UV-cured EA-B0T0 blends	147
Table 4.15	Percentage of swelling in toluene, crosslink density and average molecular weight between crosslink of UV-cured EA-B5T0 blends	148

Table 4.16	Percentage of swelling in toluene, crosslink density and average molecular weight between crosslink of UV-cured EA-B5T1 blends	154
Table 4.17	Percentage of swelling in toluene, crosslink density and average molecular weight between crosslink of UV-cured EA-B5T3 blends	155
Table 4.18	Percentage of swelling in toluene, crosslink density and average molecular weight between crosslink of UV-cured EA-B5T5 blends	156

LIST OF SYMBOLS AND ABBREVIATIONS

ASTM	American Society for Testing and Materials
CR	Polychloroprene
CSM	Chlorosulphonated polyethylene rubber
DA	Dodecanedioic acid
DMI	Dimethylimidazole
DSC	Differential Scanning Calorimetry
ENR25	Epoxidised natural rubber with 25 % mol of epoxidation
ENR50	Epoxidised natural rubber with 50 % mol of epoxidation
FTIR	Fourier Transform Infrared
GPC	Gel Permeation Chromatography
IPPP	Institute of Research Management and Consultancy
MA	Maleic anhydride
NR	Natural rubber
PA	Phthalic anhydride
PAA	Poly(acrylic acid)
PS	Palm stearin
PVC	Poly(vinyl chloride)
¹ H-NMR	Proton nuclear magnetic resonance
R.B.D	Refined, Bleached and Deodorised
RRIM	Rubber Research Institute Malaysia
TMPTA	Trimethylolpropanetriacrylate
XNBR	Carboxylated nitrile butadiene rubber
Zn-SEPDM	Zinc salt sulphonated ethylene propylene diene monomer rubber