# FUNCTIONALIZED NATURAL RUBBER: RUBBER PARTS FOR GASOHOL RESISTANCE



#### Khantharat Phothiphon

A Thesis Submitted in Partial Fulfilment of the Requirements for the Degree of Master of Science The Petroleum and Petrochemical College, Chulalongkorn University in Academic Partnership with The University of Michigan, The University of Oklahoma, and Case Western Reserve University

2010

# 530037

Thesis Title:	Functionalized Natural Rubber: Rubber Parts for Gasohol
	Resistance
By:	Khantharat Phothiphon
Program:	Polymer Science
Thesis Advisors:	Assoc. Prof. Rathanawan Magaraphan

Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfillment of the requirements for the Degree of Master of Science.

... College Dean

(Asst. Prof. Pomthong Malakul)

**Thesis Committee:** 

R. Mayoup

(Assoc. Prof. Rathanawan Magaraphan)

Thanyald Chais-. . . . . . .

(Dr. Thanyalak Chaisuwan)

Gasa bijen

(Dr. Orasa Onjun)

#### ABSTRACT

5172014063: Polymer Science Program Khantharat Phothiphon: Functionalized Natural Rubber: Rubber Parts for Gasohol Resistance.

Thesis Advisors: Assoc. Prof. Rathanawan Magaraphan 116 pp.

Keywords: Dynamic vulcanization/ Thermoplastic vulcanizate (TPV)/ Natural Rubber (NR)/ Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)/ Poly(vinylidene fluoride) (PVDF)/ Conventional vulcanization system (CV system)/ Efficient vulcanization system (EV system)/ 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane (DBPH)/ Epoxidized soybean oil (ESO)

Nowadays, the global warming and the increasing of oil price lead to use petroleum resources carefully and reduce the use of petroleum by using other alternative energy resources. Gasohol is the one of those alternative energy which important for automobile and has a widely use in Thailand. It is a kind of the combination between gasoline and ethanol or hydrocarbon and polar solvent. The material which can resist deteriorating from gasohol is limited. NR and PHBV do not dissolve in ethanol which can be developed to be a thermoplastic vulcanizate (TPV) incorporated with PVDF, the high chemical resistant. The TPV is derived from dynamic vulcanization process which has a melt mixing of polymers and vulcanization reaction by peroxide, DBPH, is occur at the same time. The results found that the increasing amount of DBPH provides the high mechanical properties and reduce the degree of swelling in gasohol. The addition of ESO can improve the mechanical properties and the resistance to swell from gasohol with the swelling percentage lower 50 and 150 % at the temperatures of 25 and 100 °C, respectively. The morphology of TPV was also improved. The rubber phase was deformed into particles with the sized of 1 micron and had well dispersed in thermoplastic phase.

۰.

.....

• :

# บทคัดย่อ

คันธารัตน์ โพธิผล : การปรับปรุงยางธรรมชาติเพื่อใช้งานด้านชิ้นส่วนยางทนน้ำมัน แก๊สโซฮอล (Functionalized Natural Rubber: Rubber Parts for Gasohol Resistance) อ.ที่ปรึกษา : รองศาสตราจารย์ คร.รัตนวรรณ มกรพันธุ์ 116 หน้า

จากสภาวะ โลกร้อนในปัจจุบันประกอบกับราคาน้ำมันที่พุ่งสูงขึ้นทำให้มีการใช้พลังงาน จากปีโตรเลียมลดน้อยลงและทดแทนโดยการใช้พลังงานทางเลือกอื่นๆ เพิ่มมากขึ้น น้ำมันแก๊ส ์ โซฮอลเป็นหนึ่งในพลังงานทางเลือกที่จำเป็นสำหรับยานพาหนะที่ใช้น้ำมันเป็นเชื้อเพลิง ซึ่งใช้กัน อข่างแพร่หลายในประเทศไทย แก๊สโซฮอลได้จากการผสมน้ำมันเบนซินกับเอทานอลที่สัดส่วน ต่างๆ ซึ่งก็คือของผสมระหว่างไฮโครการ์บอนที่ไม่มีขั้วกับตัวทำละลายมีขั้ว ดังนั้นวัสดุที่สามารถ ทนทานได้ทั้งสารละลายมีขั้วและไม่มีขั้วจึงค่อนข้างมีจำกัดและมีราคาแพง ด้วยสมบัติของยาง ธรรมชาติซึ่งมีมากมายในประเทศไทยและพลาสติกชีวภาพอย่าง PHBV ที่ไม่ละลายในเอทานอล นั้น สามารถนำมาพัฒนาเป็นวัสดุที่สามารถทนแก๊สโซฮอลร่วมกับพลาสติกทนสารเคมีสูงอย่าง กลายเป็นวัสดุใหม่ที่เรียกว่า เทอร์โมพลาสติกยางวัลคาในซ์ (Thermoplastic ได้ PVDF vulcanizate: TPV) วัสคุเทอร์โมพลาสติกยางวัลกาไนซ์นี้เตรียมได้จากเทกนิกการกงรูปแบบพลวัต (dynamic vulcanization) ซึ่งเป็นการผสมพลาสติกในสภาวะหลอมเหลวไปพร้อมๆกับการคงรูป ยางด้วยสารคงรูปเปอร์ออกไซด์อย่าง DBPH ผลการศึกษาพบว่า เมื่อเพิ่มปริมาณสารคงรูป DBPH สมบัติทางกลและสมบัติการต้านทานต่อการบวมพองในน้ำมันแก๊สโซฮอลจะเพิ่มขึ้นด้วย เมื่อใส่ ้ น้ำมันถั่วเหลืองอิพ๊อกซิไคซ์ซึ่งเป็นสารช่วยผสมชีวภาพลงไปในของผสมที่มีส่วนผสมของวัส**ดุทั้ง** สามในสัคส่วน NR/PVDF/PHBV เท่ากับ 50/40/10 พบว่า สารช่วยผสมมีบทบาทสำคัญในการลด ความหนืดและปรับปรุงความเข้ากันได้ของวัสดุทั้งสาม รวมทั้งปรับปรุงสมบัติทางกล สมบัติการ ้ด้านทานต่อการบวมในน้ำมันแก๊สโซฮอลที่ดีขึ้น โดยมีเปอร์เซ็นต์การบวมพองไม่เกิน 50 และ 150 % ที่อุณหภูมิ 25 และ 100 องศาเซลเซียส ตามลำดับ สารช่วยผสม ESO ยังช่วยปรับปรุง โครงสร้างสัณฐานวิทยาของวัสดุเทอร์โมพลาสติกยางวัลกาในซ์โดยทำให้ยางกระจายตัวเป็น อนุภาคขนาดเล็กประมาณ 1 ไมครอน อยู่ในเฟสของเทอร์ โมพลาสติกด้วย

#### ACKNOWLEDGEMENT

This work would not have been possible without the assistance of the following individuals:

First of all, the author would like to gratefully give special thanks to her advisor Assoc. Prof. Rathanawan Magaraphan, the Petroleum and Petrochemical College, Chulalongkorn University for her constructive criticism, very useful suggestions, valuable guidance, and vital help throughout this research work with warmth and proximity.

The author would also like to thank Dr. Orasa Onjun, and Dr. Thanyalak Chaisuwan for being on the thesis committee, giving very kind help and suggestions, and proof-reading this thesis book.

The author gratefully appreciates to thank Mr. Robert Wright for his invaluable suggestion and criticism.

The author would like to acknowledge the Petroleum and Petrochemical College; the National Excellence Center for Petroleum, Petrochemicals, and Advanced Materials, Thailand; the National Research Council of Thailand; and, the Polymer Processing and Polymer Nanomaterials Research Unit for the financial support of this project.

Finally, the author would like to take the opportunity to thank all of her friends and the staff at this college for their friendly assistance, creative suggestions, and strong encouragement. The author is also greatly indebted to her parents for their love, support, understanding, and encouragement during this pursuit.

## **TABLE OF CONTENTS**

PAGE

-	Title Page	i
1	Abstract (in English)	iii
1	Abstract (in Thai)	iv
1	Acknowledgements	v
-	Table of Contents	vi
l	List of Tables	viii
I	List of Figures	x
CHA	PTER	
]	I INTRODUCTION	1
J	II LITERATURE REVIEW	3
J	III EXPERIMENTAL	43
J	IV PRELIMINARY STUDY THE EFFECT OF	
	VULCANIZATION SYSTEM AND QUANTITY OF	
	VULCANIZING AGENT ON MECHANICAL AND	
	SWELLING PROPERTIES OF NATURAL RUBBER	53
	4.1 Abstract	53
	4.2 Introduction	53
	4.3 Experimental	54
	4.4 Results and discussion	56
	4.5 Conclusion	68
	4.6 Acknowledgements	69
	4.7 References	69

.

V	EFFECT OF VULCANIZING AGENT OF NR/F	VDF
	THERMOPLASTIC VULCANIZATE ON PRO	PERTIES
	OF RUBBER USED IN FUEL SYSTEM	72
	5.1 Abstract	72
	5.2 Introduction	72
	5.3 Experimental	73
	5.4 Results and discussion	75
	5.5 Conclusion	87
	5.6 Acknowledgements	87
	5.7 References	88
VI	EFFECT OF EPOXIDIZED SOYBEAN OIL IN	
	PEROXIDE CURED NR/PVDF/PHBV	
	THERMOPLASTIC VULCANIZATE ON	
	PROPERTIES OF RUBBER USED IN FUEL SY	( <b>STEM</b> 90
	6.1 Abstract	90
	6.2 Introduction	90
	6.3 Experimental	- 91
	6.4 Results and discussion	95
	6.5 Conclusion	108
	6.6 Acknowledgements	109
	6.7 References	109
VII	CONCLUSION AND RECOMMENDATIONS	113
	REFERENCES	115
	APPENDICES	120
	Appendix A Cure Characteristic Data	120
	Appendix B Calculations of Crystallinity Percen	tage 123
	CURRICULUM VITAE	127

### LIST OF TABLES

TABI	JE		PAGE
	CHAPTER II		
2.1	Structures of vulcanized rubber and properties of differen	t	16
	curing systems		
2.2	Half-life of peroxides		16
2.3	Relative crosslinking efficiencies of various rubbers with		19
	DCP		
	CHAPTER III		
	4		

3.1	Compounding formulae and mixing schedule	46
3.2	Compounding formulae and mixing schedule	47
3.3	Formula and mixing schedule for compounding NR	49
3.4	Schedule for mixing compounded NR and thermoplastic	49
	blend	

### **CHAPTER IV**

4.1 Compounding formula	e and mixing schedule	55
-------------------------	-----------------------	----

#### **CHAPTER V**

5.1	Compounding formulae and mixing schedule	74
-----	--	----

## **CHAPTER VI**

6.1	Formula and mixing schedule for compounding NR	93
6.2	Schedule for mixing compounded NR and thermoplastic	93
	blend	
6.3	Melting temperature, crystallization temperature, and percent	95
	crystallinity of PVDF, PHBV, and the blend	

TABLE		

6.4	The thermal properties of TPVs at various amount of ESO	101
	CHAPTER VII	
7.1	Comparison of raw material costs for producing rubber part	114
	between the TPV and the commercial	
	APPENDICES	
Al	Parameter results of compounded NR with EV system at	120
	Acc:S ratio of 12	
Ă2	Parameter results of the compounded NR by DCP system at	120
	DCP content of 3 phr	
A3	Parameter results of the compounded NR by DBPH system	121
	at DBPH content of 3 phr	
A4	Parameter results of the compounded NR by CV and EV	121
	systems	
A5	Parameter results of the thermoplastic vulcanizates with the	122
	NR/PVDF composition of 50/50 vulcanized by peroxide	
	system at 180 °C	

## **LIST OF FIGURES**

### **FIGURE**

х

## **CHAPTER II**

2.1	Classification of TPE	3
2.2	Schematic structures of TPE: (a) block copolymers, and (b)	
	polymer blends	
2.3	Schematic of extruder profile for dynamic vulcanization	5
2.4	Schematic of morphology development of dynamic	5
	vulcanizates during the crosslinking	
2.5	Abdou-Sabet et al., (1996) result indicates the effect of	6
	rubber particle size on stress-strain properties of TPV	
2.6	Abdou-Sabet et al., (1996) result indicate the effect of curing	7
	on mechanical properties and oil swell of TPV	
2.7	Divisions of application fields for TPV in Germany through	8
	the years 2000-2003	
2.8	Chemical structures of polyisoprene, NR and polyisoprene	9
	isomers	
2.9	The stress-strain curves of peroxide-crosslinked NR samples	11
2.10	Rheographs of themixes indicating the curing of NR to a	13
	common torque of 33.8 dNm. (A) Dicumyl peroxide, (B)	
	CV, (C) EV, and (D) mixed	
2.11	The crosslink structures of natural rubber by sulfur	14
	vulcanizing agent	
2.12	The crosslinking reaction of the peroxide vulcanization	17
	system	
2.13	The radical formation of polydiene and NR	18
2.14	The possible crosslink structures present in peroxide	18
	crosslinked natural rubber (P = Polymer chain)	

## FIGURE

· · ·

•

# PAGE

2.15	The plot between crosslink density and peroxide content in	20
	NR shows modulus values, stress-strain values, and swelling	
	values	
2.16	The chemical structure of PVDF	21
2.17	Variation of the $T_g$ of PVDF/PHBV blends ( $\Box$ ) and the $T_m$	22
	of $PVDF(O)$ as a function of the PHBV composition	
2.18	DSC curves of melt-quenched samples of PVDF, PHB, and	23
	PVDF/PHB blends during the heating process at 10 K/min	
2.19	DSC thermogram of PVDF, PHB, and PVDF/PHB blends	24
	during the cooling process from the molten state at 10 K/min	
2.20	Spherulitic morphologies of PVDF in 40/60 (wt/wt)	25
	PVDF/PHB blends crystallized isothermally at various	
	crystallization temperatures of PVDF: (a) 140 °C, (b)	
	145 °C, (c) and (d) 150 °C, (e) 158 °C, and (f) as (d) but	
	additional PHB crystallized at the crystallization of PHB =	
	60 °C	
2.21	(a) spherulitic morphology of PVDF crystallized at the	26
	temperature = 148 °C in a blend PVDF/PHB = $40/60$	
	(wt/wt). (b)-(f) PHB spherulite nucleated inside a PVDF	
	spherulite and grown radially at 60 °C for: (b) 3 min, (c) 15	
	min, (d) 21 min, (e) 30 min, and (f) crystallized completely	
2.22	The chemical structures of PHB, PHV, and PHBV	30
2.23	The weight remaining of PHBV and PHBV/OMMT	31
	nanocomposites in soil suspension	

1

2.24	The appearances of sample surface before and after (30 days)	32
	of the environmental degradation test by optical microscopy	
	(A) PDLLA (before), (a) PDLLA (after); and (E)	
	PDLLA/PHBV/PEG (70/30/20) (before), (e) PDLLA/PHBV/	
	PEG (70/30/20) (after)	
2.25	The weight-loss curves of PDLLA/PHBV/PEG blends	33
2.26	The DSC traces of PHBV/PES blends after melt-quenching	34
	at a heating rate of 20 °C/min	
2.27	The summary of the results of $T_g$ and $T_m$ of PHBV/PES	34
	blends after melt-quenching at a heating rate of 20 °C/min;	
	$\Box$ ,O: T <sub>g</sub> s of PES and PHBV, respectively; $\triangle$ : Tm of PES;	
	$\nabla$ , $\diamond$ : T <sub>m</sub> s of PHBV, respectively	
2.28	The Mechanical properties of PHBV/PES blends: (a) tensile	35
	strength, (b) elongation at break and (c) Young's modulus	
2.29	The schematic of ESO synthesis	36
2.30	The plasticizer production from plant oils and petrochemical	37
	feedstocks in the U.S., millions of pounds per year	
2.31	The $T_{gs}$ of PHBV blend as a function of additive (SO and	38
	ESO) content	
2.32	The impact strength of PHBV blend as a function of additive	38
	(SO and ESO) content	
2.33	The mechanical properties of PHBV/plasticizer blends	39
2.34	The Scanning electron micrographs of PHBV/plasticizer	40
	blends: (a) SO, (b) ESO, (c) TEC, and (d) DBP	
2.35	The tan $\delta$ of neat PLA and PLA/ESO blends as a function of	41
	temperature	
2.36	The stress-strain curves of neat PLA and PLA/ESO blends	41

PAGE

xiii

2.37	The SEM micrographs of fracture surfaces of PLA/ESO	42
	blends: (a) 100/10 (b) 100/20	

## **CHAPTER IV**

4.1	The torque curve and the appearance of compounded NR	
	after compounding in EV system at room temperature	57
4.2	The torque curve and the appearance of compounded NR	
	after compounding in DCP system at room temperature	57
4.3	The torque curve and the appearance of compounded NR	
	after compounding in DBPH system at room temperature	58
4.4	The cure characteristic and parameter curves for vulcanizing	
	compounded NR in EV system	59
4.5	The cure characteristic and parameter curves for vulcanizing	
	compounded NR in DCP system	60
4.6	The cure characteristic and parameter curves for vulcanizing	
	compounded NR in DBPH system	61
4.7	The appearance of vulcanized NR: (a) EV system, (b) DCP,	
	(c) DBPH 3 phr, (d) DBPH 5 phr, and (e) DBPH 7 phr	62
4.8	The tensile strength of vulcanized NR at various	
	vulcanization systems	64
4.9	The percent elongation at break of vulcanized NR at various	
	vulcanization systems	64
4.10	The Young's modulus of vulcanized NR at various	
	vulcanization systems	65
4.11	The percent swelling of vulcanized NR at 25 °C in different	
	oil types	66
4.12	The percent swelling of vulcanized NR at 100 °C in different	
	oil types	66

FIGU	FIGURE		PAGE
4.13	The swelling index of vulcanized NR at 25 °C in different		
	oil types		67
4.14	The percent swelling of vulcanized NR at 100 °C in different		
	oil types		67
	CHAPTER V	x	
5.1 :	The cure characteristics of compounded NR by CV and EV		
***	systems		76
5.2	The cure characteristic of compounded NR by peroxide		
	DBPH of 3 phr		77
5.3	The cure characteristics at 180 °C of TPV with various		
•	amounts of DBPH		78
5.4	The appearance of fully vulcanized TPV after compression:		
	(a) CV system, (b) EV system, (c) 1 DBPH system, (d) 3	···	
•	DBPH system, (e) 5 DBPH system, (f) 7 DBPH system	а *.	79
5.5	The tensile strength of TPVs before and after aging at	÷.	
	various vulcanization systems		80
5.6	The percent elongation at break of TPVs before and after		
	aging at various vulcanization systems		81
5.7	The tear strength of TPVs before and after aging at various		
	vulcanization systems		82
5.8	The drawing of crack propagation in TPV at different		
	vulcanization systems: (a) sulfur system, and (b) peroxide		
	systems		83
5.9	The percent swelling of TPVs at 25 °C in various oil types		84
5.10	The swelling index of TPVs at 25 °C in various oil types		84

3.

5.11 Immersed Samples of oils at various vulcanization system which were CV, EV, 1 DBPH, 3 DBPH, 5 DBPH, and 7 DBPH from left to right, respectively. The immersion was done at 25 °C for 24 h: (a) gasohol 91, (b) gasohol 95, (c) gasohol E20, (d) gasohol E85, and (e) biodiesel.

#### **CHAPTER VI**

6.1	The heating curves of DSC thermogram	96
6.2	The cooling curves of DSC thermogram	96
6.3	The cure characteristic and parameter curves for vulcanizing	
	TPV at 180 °C in different amount of ESO	98
6.4	The appearance of fully vulcanized TPVs at various amount	
	of ESO: (a) 0 phr, (b) 1 phr, (c) 2 phr, (d) 5 phr, (e) 7 phr,	
	and (f) 10 phr	99
6.5	The heating curves of DSC thermogram from TPVs at	
	various amount of ESO	100
6.6	The cooling curves of DSC thermogram from TPVs at	
	various amount of ESO	101
6.7	The tensile strength of TPVs at various amount of ESO	102
6.8	The Young's modulus of TPVs at various amount of ESO	103
6.9	The hardness of TPVs at various amount of ESO	103
6.10	The percent elongation at break of TPVs at various amount	
	of ESO	104
6.11	The morphology of TPVs at various amount of ESO: (a)	
	ESO 0 phr, (b) ESO 10 phr with 700x magnification; (A)	
	ESO 0 phr, (B) ESO 10 phr with 1,500x magnification	105
6.12	The percent swelling of TPVs at various amount of ESO at	
	25 °C in different oil types for 1 day	106

.

PAGE

۰.

. . . . .

6.13	The percent swelling of TPVs at various amount of ESO at	
	25 °C in different oil types for 7 days	106
6.14	The percent swelling of TPVs at various amount of ESO at	
	100 °C in different oil types for 1 day	107
6.15	The percent swelling of TPVs at various amount of ESO at	
	100 °C in different oil types for 7 days	107
		: