# PREPARATION OF GRAPHENE/NATURAL RUBBER COMPOSITE FOR COMPLIANT ELECTRODE APPLICATIONS

Sasithorn Korattanawittaya

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

2014

**Thesis Title:** Preparation of Graphenen/Natural Rubber Composite for

Compliant Electrode Applications

By: Sasithorn Korattanawittaya

Program: Polymer Science

**Thesis Advisor:** Prof. Anuvat Sirivat

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

College Dean

(Asst. Prof. Pomthong Malakul)

**Thesis Committee:** 

(Prof. Anuvat Sirivat)

(Assoc. Prof. Sujitra Wongkasemjit)

(Dr. Karnthidaporn Wattanakul)

#### **ABSTRACT**

5572021063: Polymer Science Program

Sasithorn Korattanawittaya: Preparation of Graphenen/Natural Rubber

Composite for Compliant Electrode Applications.

Thesis Advisor: Prof. Anuvat Sirivat 162 pp.

Keywords: Natural rubber/ Graphene/ Compliant electrode/ Flexible material

A compliant electrode is a stretchable electronic device that retains good conductivity under stretching. It has been used in various electro-actuating applications that require large deformations under electrical activated energy. The purpose of this work was to fabricate the compliant electrode possessing high electrical conductivity and good mechanical properties. Due to the excellent mechanical properties of natural rubber (NR), it was used as a matrix for preparing a compliant electrode. Graphene is one of many innovative new conductive fillers that provides excellence electrical conductivity. In order to investigate its mechanical properties and electrical conductivity, an experiment was carried out by using a melt rheometer in tension mode. Both mechanical and electrical properties were improved by introducing graphene into the matrix. Despite the strain of NR films reaching 80%, the films were able to maintain electrical conductivity values with very low drop offs. The highest electrical conductivity was obtained from the 35.0 %v/v graphene/NR composite which was greater than the DANFOSS commercial compliant electrode. In conclusion, a graphene /NR composite was shown as a promising material for using as a compliant electrode.

## บทคัดย่อ

ศศิธร ก่อรัตนวิทยา: การเตรียมขั้วไฟฟ้าแปรรูปจากแผ่นฟิล์มคอมโพสิทระหว่างกราฟิน และยางธรรมชาติ (Preparation of Graphene/Natural Rubber Composite for Compliant Electrode Application) อ. ที่ปรึกษา: ศ. อนุวัฒน์ ศิริวัฒน์ 162 หน้า

ขั้วไฟฟ้า แปรรูป (Compliant electrode) เป็นขั้วไฟฟ้าที่คงความสามารถในการนำไฟฟ้า ได้ดีในขณะที่ขั้วไฟฟ้าถูกดึงชืด ขั้วไฟฟ้าชนิดนี้เหมาะสำหรับการนำไปใช้ในงานแอคชูเอเตอร์ (Actuators) ซึ่งเป็นวัสดุที่มีการเปลี่ยนแปลงขนาดเมื่อได้รับกระแสไฟฟ้า จุดประสงค์ของงานวิจัยนี้ คือ เพื่อเตรียมขั้วไฟฟ้าแปรรูปที่มีความสามารถในการนำไฟฟ้าสูงและมีคุณสมบัติเชิงกลที่ดี ใน งานวิจัยนี้จึงเลือกใช้ยางธรรมชาติเป็นวัสดุหลักสำหรับการเตรียมขั้วไฟฟ้าแปรรูป เนื่องจากเป็นวัสดุที่ มีคุณสมบัติเชิงกลที่ดี แต่เนื่องจากขางธรรมชาติเป็นวัสดุที่มีคุณสมบัติเป็นฉนวนไฟฟ้า จึงจำเป็นต้องมี การเติมสารเติมแต่งเพื่อปรับปรุงคุณสมบัติการนำไฟฟ้าให้เหมาะสำหรับการนำไปใช้เป็นขั้วไฟฟ้า กราฟืนเป็นวัสดุคาร์บอนที่มีความสารมารถในการนำไฟฟ้าสูงจึงถูกเลือกมาใช้ในงานวิจัยเพื่อเสริม ความสามารถในการนำไฟฟ้าของขั้วไฟฟ้าแปรรูป

คุณสมบัติเชิงกลและคุณสมบัติการนำไฟฟ้าของแผ่นฟิล์มคอมโพสิท ได้รับการศึกษาด้วย เครื่องเมลรีโอมิเตอร์ (Melt Rheometer) ผลการศึกษาพบว่า เมื่อใช้กราฟืนเป็นสารเติมแต่ง คุณสมบัติเชิงกลและการนำไฟฟ้าของแผ่นฟิล์มคอมโพสิทมีค่าเพิ่มขึ้น แม้ว่าถูกคึงยืดถึง 80 % แต่ แผ่นฟิล์มคอมโพสิทยังคงคุณสมบัติการนำไฟฟ้าที่ดี แผ่นฟิล์มคอมโพสิทที่เตรียมโดยเติมกราฟิน 35.0 % โดยปริมาตร ให้ค่าการนำไฟฟ้าที่สูงสุด ซึ่งมีค่าการนำไฟฟ้าสูงกว่าขั้วไฟฟ้าแปรรูปทางการค้า จาก บริษัท DANFOSS จากผลการวิจัยสามารถสรุปได้ว่า แผ่นฟิล์มคอมโพสิทระหว่างกราฟินและยาง ธรรมชาติ เหมาะสำหรับการใช้เป็นวัสคุขั้วไฟฟ้าแปรรูป

#### **ACKNOWLEDGEMENTS**

I would like to express my sincere gratitude to all those who gave the possibility to complete this thesis work.

First of all, I am grateful for the scholarship and funding of the thesis work provided by The Petroleum and Petrochemical College. The Center of Excellence on Petrochemical, Thailand Research Fund, and Materials Technology, Thailand.

I am deeply indebted to my thesis advisors, Prof. Anuvat Sirivat who gave admirable guidance, encouragement, stimulating suggestions and helped me in all the time of my research.

My sincere thank are due to the official committees. Assoc. Prof. Sujitra Wongkasemjit and Dr. Karnthidaporn Wattanakol, for their detailed review, constructive criticism and excellent advices.

Lastly, this special thesis would not have been possible without the knowledge received from all the lecturers and staffs at The Petroleum and Petrochemical College, plus love and constant support from my family and friends.

### TABLE OF CONTENTS

			PAGE
	Title	Page	i
	Abst	ract (in English)	iii
	Abst	ract (in Thai)	iv
	Ackr	V	
	Table	vi	
	List	X	
	List	of Figures	xii
Cŀ	HAPTE!	R	
	1	INTRODUCTION	1
	П	THEORETICAL BACKGROUND AND LITERATUR	RE
		REVIEW	3
		2.1 Compliant Electrode	3
		2.2 Graphene	8
		2.3 Natural Rubber	15
		2.4 Vulcanization of Rubber	19
		2.5 Polymer/Carbon Filler Composite	22
	Ш	METHODOLOGY	25
		3.1 Materials	25
		3.1.1 Chemical: Natural Rubber Latex	25
		3.1.2 Fillers	25
		3.1.3 Chemicals and Solvents	25
		3.2 Equipments	25
		3.3 Experimental	26

CHAPTER			PAGE
		3.3.1 Preparation of Graphene/NR Composite	26
	3.4	Characterizations	26
		3.4.1 Raman Spectrometer (NT-MDT, NTEGRA Spectra)	26
		3.4.2 X-ray Diffraction Spectrometer, XRD	
		(Rigaku, DMAX 2200)	26
		3.4.3 Fourier Transform Infrared Spectrometer, FT-IR	
		(Nicolet, Nexus 670)	27
		3.4.4 Thermogravimetric Analyzer, TGA	
		(Thermo, TGA Q 50)	27
		3.4.5 Determination of Crosslink density)	27
		3.4.6 Melt Rheometer (Rheometric Scientific, Ares)	28
		3.4.7 Scanning Electron Microscope (FE-SEM, JSM-7001F)	29
		3.4.8 Atomic Force Microscope	
		(AFM, Park System, XE-100)	30
		3.4.9 Scanning Electron Microscope (FE-SEM, JSM-7001F)	30
IV	PRI	E PARATION OF GRAPHENE/NATURAL RUBBER	
	CO	MPOSITE FOR COMPLIANT ELECTRODE	
	API	PLICATION	31
	4.1	Abstract	31
	4.2	Introduction	32
	4.3	Experimental	33
	4.4	Result and Discussion	37
	4.5	Conclusions	43
	4.6	Acknowledgements	43
	4.7	References	43

CHAPTER		PAGE
V	CONCLUSIONS AND RECOMMENDATIONS	63
	5.1 Conclusions	63
	5.2 Recommendations	64
	REFERENCES	66
	APPENDICES	72
	<b>Appendix A</b> Raman spectra of The Synthesized Graphene	72
	Appendix B XRD Pattern of The Synthesized Graphene	75
	<b>Appendix C</b> FT-IR Spectra of The Synthesized Graphene	
	and Natural Rubber (NR)	77
	Appendix D TGA Themogram of The Natural Rubber Film	1
	and The Composites	82
	Appendix E Mole Percent Uptake of Solvent, Weight Loss	•
	and Crosslink Density Determined by Swelling	2
	Method	87
	Appendix F Mechanical Properties of Natural Rubber Film	98
	Appendix G Mechanical Properties of Natural Rubber and	
	Graphene Composite Film under The Effect o	f
	Commercial Graphene multilayers with UV	
	Irradiation time of 7 min. and Concentration of	of
	Crosslinker 5.0 %v/v	108

**CHAPTER** PAGE

Appendix H Mechanical Properties and Electrical Conductivity		
of Natural Rubber and Graphene Composite Film		
under The Effect of Graphene Multilayers with UV		
Irradiation Time of 7 min. and concentration of		
Crosslinker of 5.0 %v/v with Applied Electric Field		
of 5 Volt	113	
Appendix I FE-SEM Images of The Graphene/NR Composite		
Film	140	
Appendix J AFM Images of The Graphene/NR Composite Film	143	
Appendix K Electrical Conductivity Measurement of		
The Graphene Multilayers	149	
Appendix L Synthesized Graphene	151	
CURRICULUM VITAE	162	

## LIST OF TABLES

ΓABLE		PAGE
	CHAPTER II	
2.1	Comparisons of compliant electrode properties	4
2.2	Comparative chart on the mechanical, thermal and electrical	
	properties of graphene with CNT, steel, plastic, rubber, fiber	11
2.3	Physical properties of different carbon materials	15
2.4	The composition and functions of components in NR latex	16
2.5	Conductivities of NR-PTh films	17
	CHAPTER IV	
4.1	Mechanical properties of NR films at various UV-irradiation	
	times, a fixed concentration of crosslinker of 2.0 %v/v, by	
	using the melt rheometer in the tension mode with a strain	
	rate $0.01 \text{ s}^{-1}$ and temperature of 300 K	48
4.2	Mechanical properties of NR films at various concentrations	
	of crosslinker, a fixed UV-irradiation time of 7 min., by	
	using the melt rheometer in the tension mode with a strain	
	rate 0.01 s <sup>-1</sup> and temperature of 300 K	48
4.3	FE-SEM images of the 5.0%v/v graphene/NR composite and	
	the 20.0%v/v graphene/NR composite at different	
	magnifications	49
4.4	Mechanical properties of graphene/NR composites at various	
	concentrations of the graphene multilayers as measured by	
	the melt rheometer in the tension mode with a strain rate of	
	0.01 s <sup>-1</sup> , temperature of 300 K, and applied electric field of 5	
	volt	50

51

TABLE PAGE

4.5 Electrical conductivity of graphene/NR composites at various concentrations of the graphene multilayers was measured by the melt rheometer in the tension mode with a strain rate of 0.01 s<sup>-1</sup>, temperature of 300 K, and applied electric field of 5 volt

## LIST OF FIGURES

FIGU	RE	PAGE
	CHAPTER II	
2.1	Application of compliant electrode, it provides current to	
	dielectric actuator then material is squeezed out	3
2.2	Graphene (top left) is a honeycomb lattice of carbon atoms.	
	Graphite (top right) can be viewed as a stack of graphene	
	layers. Carbon nanotubes are rolled-up cylinders of graphene	
	(bottom left). Fullerenes (C60) are molecules consisting of a	
	wrapped graphene through the introduction of pentagons on	
	the hexagonal lattice	10
2.3	Molecular chemical structure of natural rubber, cis-1,4-	
	polyisoprene	17
2.4	The three main types of carbon-based electrodes: a) Loose	
	carbon powders particles directly applied on the elastomer	
	membrane; b) Carbon grease consists of carbon particles	
	dispersed in a viscous oil; and c) Conductive rubber consists	
	of carbon particles dispersed into a crosslinked elastomer	22
	CHAPTER IV	
4.1	Raman spectra of graphene multilayers	52
4.2	XRD pattern of the graphene multilayers	53
4.3	Crosslinking density of crossliked NR film at various	
	crosslinking times, a fixed crosslink concentration of	
	2.0 %v/v	54
4.4	Crosslink density of crossliked NR film at various	
	concentrations of crosslinker, and at a fixed UV-irradiation	
	time of 7 min.	55

FIGUI	RE	PAGE
4.5	Stress-strain curve of NR film with various UV-irradiation	
	times, a fixed concentration of crosslinker of 2.0 %v/v, by	
	using the melt rheometer in the tension mode with a strain	
	rate 0.01 s <sup>-1</sup> and temperature of 300 K	56
4.6	Stress-strain curve of NR film at various concentrations of	
	crosslinker, a fixed UV-irradiation time of 7 min, by using	
	the melt rheometer in the tension mode with a strain rate	
	0.01 s <sup>-1</sup> and temperature of 300 K	57
4.7	Distribution in micro-scale of composite in the area of 2	
	$\mu\text{m}^2$ : (a) 1.0%v/v graphene/NR composite; (b) 5.0%v/v	
	graphene/NR composite: (c) 10.0%v/v graphene/NR	
	composite; (d) 20.0%v/v graphene/NR composite; and	
	(e) DANFOSS commercial compliant electrode	58
4.8	Stress-strain curve of graphene/NR composites at various	
	concentrations of the graphene multilayers as measured by	
	the melt rheometer in the tension mode with a strain rate of	
	0.01s <sup>-1</sup> , temperature of 300 K, and applied electric field of 5	
	volt	59
4.9	Conductivity of graphene/NR composites at various	
	concentrations of the graphene multilayers as measured by	
	the melt rheometer in the tension mode with a strain rate of	
	0.01 s <sup>-1</sup> , temperature of 300 K, and applied electric field of 5	
	volt	60

FIGURE		
4.10	Conductivity of the graphene/NR composites as a function of stretching cycles at fixed strain 1% as measured by the	
	melt rheometer in the tension mode with a strain rate of	
	0.01s <sup>-1</sup> , temperature of 300 K, and applied electric field of 5	
	volt	61
4.11	Conductivity of 5.0 %v/v graphene/NR composites as a	
	function of strain rate as measured by the melt rheometer in	
	the tension mode with a strain rate of 0.01s <sup>-1</sup> , temperature of	
	300 K, and applied electric field of 5 volt	62