

**MODIFICATION OF CLAY SURFACE FOR RUBBER NANOCOMPOSITE
USING A CONTINUOUS ADMICELLAR POLYMERIZATION SYSTEM**

Sanchuta Senasuttipan

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,
Case Western Reserve University and Institut Français du Pétrole

2005

ISBN 974-9937-21-x

I 22243197

Thesis Title: Modification of Clay Surface for Rubber Nanocomposite
Using a Continuous Admicellar Polymerization System
By: Sanchuta Senasuttiapan
Program: Polymer Science
Thesis Advisors: Asst. Prof. Pitt Supaphol
Assoc. Prof. Sumaeth Chavadej
Dr. Nuchanat Na-Ranong
Dr. Sarintorn Limpanart

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

Nantaya Yanumet.
..... College Director
(Assoc. Prof. Nantaya Yanumet)

Thesis Committee:

Pitt Supaphol.
.....
(Asst. Prof. Pitt Supaphol)

Sumaeth Chavadej.
.....
(Assoc. Prof. Sumaeth Chavadej)

Nantaya Yanumet.
.....
(Assoc. Prof. Nantaya Yanumet)

Nuchanat Na-Ranong.
.....
(Dr. Nuchanat Na-Ranong)

Sarintorn Limpanart.
.....
(Dr. Sarintorn Limpanart)

Manit Nithitanakul.
.....
(Asst. Prof. Manit Nithitanakul)

ABSTRACT

4672022063: Polymer Science Program
Sanchuta Senasuttipan: Modification of Clay Surface for Rubber Nanocomposites Using Continuous Admicellar Polymerization System.
Thesis Advisors: Asst. Prof. Pttt Supaphol, Assoc. Prof. Sumaeth Chavadej, Dr. Nuchanat Na-Ranong, Dr. Sarintorn Limpanart, 110 pp. ISBN 974-9937-21-x
Keywords: Clay/ Admicellar Polymerization/ Natural Rubber nanocomposite/ Continuous Stirred Tank Reactor/ Mixed Surfactant

Clay mineral represents a new alternative to conventionally (macroscopically) reinforcing fillers in natural rubber. Dispersing only 10% of its delaminated structure may replace a three to four time greater amount of traditional fillers without deterioration in mechanical properties. Due to its nonpolar nature, modification by in situ polymerization of organic monomers in surfactant layer adsorbed onto the clay surface was carried out in a continuously stirred tank reactor (CSTR). Teric X10 was used as a nonionic surfactant for reducing the amount of cationic surfactant (ARQUAD[®]) required. The adsorption isotherms of various molar ratios of ARQUAD[®] to Teric X10 were studied. The organoclay with different molar ratios of were used as controls to evaluate these clays after modification by using either thermogravimetric analysis or X-ray diffraction technique. Natural rubber (NR)/clay nanocomposites were subsequently prepared by melt technique. The effects of molar ratio of ARQUAD[®] to Teric X10 on some physico-chemical properties of the modified clay and rubber compounds were also investigated. The results indicated that the mechanical property improvements caused by various molar ratios of ARQUAD[®] to Teric X10 were ranged as follow: 3:1>1:0> 1:1 > 1:3.

บทคัดย่อ

สัณหจจุทา เสนะสุททิจพันธุ : การปรับสภาพผิวดินขาวโดยกระบวนการแอคไมเซลลาร์โพลีเมอไรเซชันสำหรับวัสดุนาโนคอมโพสิตของยางธรรมชาติในเครื่องปฏิกรณ์แบบต่อเนื่อง (Modification of clay surface for rubber nanocomposite using a continuous admicellar polymerization system) อ.ที่ปรึกษา: ผศ. ดร.พิชญ์ สุภผล รศ.ดร.สุเมธ ชวเดช ดร.นุชนาฏ ณ ระนอง และ ดร.สรินทร ลีมนานาท 110 หน้า ISBN 974-9937-21-x

ดินขาวเป็นอีกทางเลือกหนึ่งของสารตัวเติมที่มีคุณสมบัติช่วยเสริมแรงในเนื้อยางธรรมชาติ เนื่องจากการกระจายตัวของดินขาวที่มีโครงสร้างแบบคิลาไมเนตในเนื้อยางเพียง 10 เปอร์เซ็นต์ สามารถทดแทนการใช้สารตัวเติมชนิดอื่นซึ่งปกติจะเติมลงไปมากกว่าสามถึงสี่เท่าของปริมาณดินขาว อย่างไรก็ตาม ปัญหาหลักในการใช้ดินขาวเป็นสารเติมแต่งคือ ความเป็นขั้วของผิวดินที่เกิดขึ้นเองตามธรรมชาติ ในงานวิจัยนี้จึงทำการปรับสภาพผิวดินด้วยวิธีใหม่ซึ่งเป็นวิธีที่มีพื้นฐานจากการพอลิเมอไรซ์โมโนเมอร์ในชั้นของสารลดแรงตึงผิวที่ถูกดูดซับบนผิวของดินขาวในเครื่องปฏิกรณ์แบบต่อเนื่อง และใช้เทอร์ริกเอ็กซ์10 ซึ่งเป็นสารลดแรงตึงผิวชนิดไม่มีขั้วเพื่อลดปริมาณการใช้สารลดแรงตึงผิวชนิดที่มีขั้วบวก (เอควาร์ด) และศึกษาผลของโดยโมลของเอควาร์ด ต่อเทอร์ริกเอ็กซ์10 เปรียบเทียบกับ ออร์กาโนเคลย์ที่เตรียมจากอัตราส่วนต่างๆ โดยโมลของเอควาร์ด ต่อเทอร์ริกเอ็กซ์10 หลังการปรับสภาพผิวของดินขาวแล้ว จะนำไปเตรียมเป็นวัสดุนาโนคอมโพสิตของยางธรรมชาติและทดสอบสมบัติเชิงกล ผลการทดลองพบว่าสมบัติของยางดีขึ้นตามลำดับเมื่ออัตราส่วน โดยโมลของเอควาร์ด ต่อเทอร์ริกเอ็กซ์10 เป็น 1:3, 1:1, 1:0 และ 3:1 ตามลำดับ

ACKNOWLEDGEMENTS

I would like to express my deepest sincere gratitude to the following individuals and organizations that are, always, my inspiration to complete this work.

I would like to give my special thank to Asst. Prof. Pitt Supaphol for his invaluable suggestions, useful recommendation, encouragement and for proofreading. Moreover, I am most obliged to Assoc. Prof. Sumaeth Chavadej for his guidance, creative discussion and for the opportunity throughout of my thesis work.

I would like to thank Dr. Nuchanart Na-Ranong and Dr. Sarintorn Limpanart for their kindness, invaluable advices in rubber compound physical properties part and also their encouragement.

Furthermore, I would like to extend my sincere thank to Assoc. Prof. Nantaya Yanumet and Dr. Manit Nithitanakul for being my committee.

To all faculty and staff at the Petroleum and Petrochemical College for their helpful advices during my two years here.

I would like to thank all staffs at The Postharvest and Processing Research and Development office, Department of Agriculture, Thailand for their helpful assistance to success of my work.

To Huntsman Co.,Ltd. for providing Octyl phenol ethoxylate during my experimental work.

I am grateful for the partially funded by Postgraduate Education and Research Programs in Petroleum and Petrochemical Technology (PPT Consortium and The Research Unit: Applied Surfactant for Separation and Pollution Control from Ratchadapisak Sompote Fund, Chulalongkorn University for research funding).

A special thanks to all my colleagues for their friendship, cheerfulness and mindfulness along two years here, as well as the enjoyable work environment.

Most of all, I would like express my deepest gratitude to my family for their forever love, understanding, endless encouragement, being a constant source of inspiration and the greatest role in my success.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vii
List of Tables	ix
List of Figures	x
 CHAPTER	
I INTRODUCTION	1
II BACKGROUND AND LITERATURE SURVEY	3
2.1 Natural Rubber	3
2.2 Clay and Clay Mineral	5
2.3 Montmorillonite	9
2.4 Polymer Nanacomposite	10
2.5 Surfactant Structure	15
2.6 Surfactant Adsorption	19
2.7 Solubilization	24
2.8 Adsolubilization	25
2.9 Ultra-Thin Film Formation	26
2.10 Mixture of Surfactant	28
III EXPERIMENTAL	
3.1 Materials	30
3.2 Experimental Set-up	30
3.3 Experimental Procedures	31
3.1.1 Adsorption Isotherm of Surfactants onto Bentonite	31

3.3.2	Surface Modification procedure	32
3.3.3	Testing Procedure	33
IV	MODIFICATION OF CALY SURFACE FOR RUBBER NANOCOMPOSITE USING A CONTINUOUS ADMICELLAR POLYMERIZATION	36
4.1	Abstract	36
4.2	Introduction	37
4.3	Experimental	38
4.4	Results and Discussion	40
4.5	Conclusions	46
4.6	Acknowledgements	47
4.7	References	47
V	CONCLUSIONS AND RECOMMENDATIONS	95
5.1	Conclusions	95
5.2	Recommendations	95
	REFERENCES	97
	APPENDICES	101
	Appendix A Adsorption isotherm	102
	Appendix B Continuous stirred tank reactor	109
	CURRICULUM VITAE	110

LIST OF TABLES

TABLE		PAGE
CHAPTER II		
2.1	Classification of phyllosilicates, emphasis on clay mineral	6
2.2	Chemical fomula of clay in 2:1 phyllosilicates types	7
CHAPTER III		
3.1	Properties tested and equipment used for clay analysis	33
3.2	Rubber compound formula	34
3.3	Rubber compound test methods	35
CHAPTER IV		
4.1	Adsorption ratio of ARQUAD [®] : Teric X10 on clay (1:1 the initial ratio of ARQUAD [®] : Teric X10	50
4.2	Adsorption ratio of ARQUAD [®] : Teric X10 on clay (1:3 the initial ratio of ARQUAD [®] : Teric X10	51
4.3	Adsorption ratio of ARQUAD [®] : Teric X10 on clay (3:1 the initial ratio of ARQUAD [®] : Teric X10	52
4.4	XRD data for studied materials	63
4.5	Physical properties of modified clay /NR nanocomposites	83
4.6	Physical properties of organoclay/ NR nanocomposites	84

LIST OF FIGURES

FIGURE		PAGE
CHAPTER II		
2.1	Chemical structure of NR (cis-1,4-polyisoprene)	3
2.2	Structure of 2:1 phyllosilicates	8
2.3	Microstructure of montmorillonite	9
2.4	Different types of composite arising from the interaction of layered silicates and polymer	11
2.5	Surfactant structure	16
2.6	Cetyltrimethylammoniumbromide	17
2.7	Fatty amine salts	18
2.8	Octyl phenol ethylene oxide	19
2.9	Surfactant molecules lean to adsorb to surface of oil droplets.	20
2.10	Adsorption isotherm for an ionic surfactant on oppositely charged substrate	21
2.11	Surfactant bilayer	22
2.12	Structure of micelle	23
2.13	Phenomena of solubilization and adsolubilization	24
2.14	Admicellar polymerization process for the formation of a thin polymer film	26
CHAPTER III		
3.1	Continuous admicellar polymerization system	31
CHAPTER IV		
4.1	Adsorption isotherms of surfactants onto Bentonite H at 30 °C at various of ARQUAD [®] : Teric X10 molar ratios	49

4.2	FTIR spectrum of Bentonite H	53
4.3	FTIR spectrum of AQUARD [®]	54
4.4	FTIR spectrum of Teric X10	55
4.5	FTIR spectrum of standard polyisoprene.	56
4.6	FTIR spectra of extracted material from admicellar polymerization modified clay with 1:0 the initial ratio of ARQUAD [®] :Teric X10	57
4.7	FTIR spectra of extracted material from admicellar polymerization modified clay with 3:1 the initial ratio of ARQUAD [®] :Teric X10	58
4.8	FTIR spectra of extracted material from admicellar polymerization modified clay with 1:1 the initial ratio of ARQUAD [®] :Teric X10	59
4.9	FTIR spectra of extracted material from admicellar polymerization modified clay with 1:3 the initial ratio of ARQUAD [®] :Teric X10	60
4.10	Transmission FTIR for extracted material from admicellar polymerization modified clay with different molar ratios of AQUARD [®] : Teric X10	61
4.11	Overlay plots of transmission FTIR for extracted material from admicellar polymerization modified clay with different molar ratios of AQUARD [®] : Teric X10	62
4.12	X-ray diffraction patterns for untreated clay and admicellar polymerization modified clay with different molar ratios of AQUARD [®] : Teric X10	64
4.13	X-ray diffraction patterns for untreated clay and organoclay with different molar ratios of AQUARD [®] : Teric X10	65
4.14	X-ray diffraction patterns for compounds with untreated clay, admicellar polymerization modified clay with different molar ratios of AQUARD [®] : Teric X10 and organoclay with	

	different molar ratios of AQUARD [®] : Teric X10	66
4.15	TGA result of ARQUAD [®]	67
4.16	TGA result of Teric X10	68
4.16	TGA result of standard polyisoprene	69
4.16	TGA result of untreated clay	70
4.19	TGA result of organoclay with 1:0 molar ratio ARQUAD [®] :Teric X10	71
4.20	TGA result of admicellar modified clay with 1:0 molar ratio ARQUAD [®] :Teric X10	72
4.21	TGA result of organoclay with 3:1 molar ratio ARQUAD [®] :Teric X10	73
4.22	TGA result of admicellar modified clay with 3:1 molar ratio ARQUAD [®] :Teric X10	74
4.23	TGA result of organoclay with 1:1 molar ratio ARQUAD [®] :Teric X10	75
4.24	TGA result of admicellar modified clay with 1:1 molar ratio ARQUAD [®] :Teric X10	76
4.25	TGA result of organoclay with 1:3 molar ratio ARQUAD [®] :Teric X10	77
4.26	TGA result of admicellar modified clay with 1:3 molar ratio ARQUAD [®] :Teric X10	78
4.27	TGA result of organoclay with 0:1 molar ratio ARQUAD [®] :Teric X10	79
4.28	TGA result of admicellar modified clay with 1:3 molar ratio ARQUAD [®] :Teric X10	80
4.29	TGA plots of admicellar modified clay at different molar ratios of ARQUAD [®] :Teric X10	81
4.30	The lots of DTG of admicellar modified clay at different molar ratios of ARQUAD [®] :Teric X10	82
4.31	Cure time of rubber compounds with different admicellar	

	polymerization modified clay	85
4.32	100 % moldulus @ before aging of rubber compounds with different of ARQUAD [®] :Teric X10 molar ratios.	86
4.33	200 % moldulus @ before aging of rubber compounds with different of ARQUAD [®] :Teric X10 molar ratios.	87
4.34	300 % moldulus @ before aging of rubber compounds with different of ARQUAD [®] :Teric X10 molar ratios.	88
4.35	Tensile strength @ before aging of rubber compounds with different of ARQUAD [®] :Teric X10 molar ratios.	89
4.36	Hardness @ before aging of rubber compounds with different of ARQUAD [®] :Teric X10 molar ratios	90
4.37	Tear strength @ before aging of rubber compounds with different of ARQUAD [®] :Teric X10 molar ratio	91
4.38	Resilience of rubber compounds with different of ARQUAD [®] :Teric X10 molar ratios	92
4.39	Heat build up @ before aging of rubber compounds with different of ARQUAD [®] :Teric X10 molar ratios	93
4.40	Specific gravity @ before aging of rubber compounds with different of ARQUAD [®] :Teric X10 molar ratios	94