

CHITIN-CHITOSAN FOR RUBBER APPLICATIONS



Tipparat Lertwattanaseri

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

2009

522105

Thesis Title: Chitin-Chitosan for Rubber Applications
By: Tipparat Lertwattanaseri
Program: Polymer Science
Thesis Advisors: Assoc. Prof. Suwabun Chirachanchai
Prof. Yasuyuki Tanaka

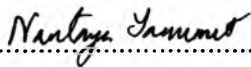
Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.



..... Dean

Asst. Prof. Pomthong Malakul

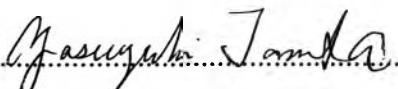
Thesis Committee:



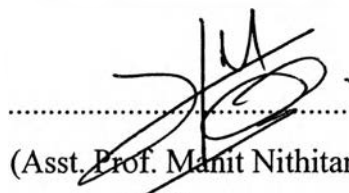
.....
(Assoc. Prof. Nantaya Yanumet)



.....
(Assoc. Prof. Suwabun Chirachanchai)



.....
(Prof. Yasuyuki Tanaka)



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



.....
(Assoc. Prof. Jitladda Sakdapipanich)



.....
(Dr. Lucksanaporn Tarachiwin)

บทคัดย่อ

ทิพรัตน์ เลิศวัฒนาเสรี : ไคติน-ไคโตซานสำหรับการประยุกต์ใช้กับยาง (Chitin-Chitosan for Rubber Applications) อ. ที่ปรึกษา : รองศาสตราจารย์ ดร. สุวบุญ จิรชาญชัย และ ศาสตราจารย์ ดร. ยาชุกี ทานากะ 95 หน้า

วิทยานิพนธ์ฉบับนี้เสนอการนำอนุพันธ์ไคติน-ไคโตซานที่สามารถละลายน้ำได้ไปประยุกต์ใช้เป็นสารที่ช่วยในการจับอนุภาคของยางให้รวมตัวเป็นกลุ่ม ความสามารถของสารที่ช่วยในการจับอนุภาคศึกษาได้โดยการหาปริมาณของยางที่จับตัวได้ และศึกษาความบริสุทธิ์ของยางที่ได้เปรียบเทียบกับยางที่ได้จากการตกตะกอนด้วยการใช้กรดอะซิติก งานนี้ยังได้ทำการศึกษาฟิวเลอร์ชีวภาพที่มีขนาดระดับนาโนเมตรเช่นไคโตซานที่ได้จากการตกตะกอน และไคโตซานนาโนสแกฟโฟลด์ สำหรับนำไปใช้ในยาง การใช้ไมโครเวฟเทคนิคในการเตรียมไคโตซานนาโนสแกฟโฟลด์ได้ถูกนำเสนอขึ้นเพื่อเป็นวิธีในการเตรียมวัสดุที่มีขนาดระดับนาโนเมตรอย่างมีประสิทธิภาพ การพัฒนา วัสดุให้มีขนาดระดับนาโนเมตรเป็นนาโนวิสเกอร์ อนุภาคนาโนสแกฟโฟลด์ไปใช้เป็นฟิวเลอร์ชีวภาพสำหรับยาง การวิเคราะห์ด้วยเทคนิคอิเล็กตรอนแบบส่องผ่านพิสูจน์ให้ทราบถึงการเกิดเป็นคอมโพสิตชีวภาพในระดับนาโนเมตรระหว่างยางกับไคโตซานที่มีขนาดในระดับนาโน

ABSTRACT

4682009063: Polymer Science Program

Tipparat Lertwattanaseri : Chitin-Chitosan for Rubber Applications

Thesis Advisors: Assoc. Prof. Suwabun Chirachanchai and Prof.

Yasuyuki Tanaka 95 pp.

Keywords: Chitin-Chitosan/ Rubber/ Flocculants/ Coagulant/ Nanomaterial/
Microwave Technique/ Nanocomposites/ Chitin Whisker/ Chitosan
Nanoscaffold

A series of water-soluble chitin-chitosan derivatives is proposed as a bio-flocculants. The evaluation of flocculants ability is based on the amount of rubber obtained and the purity of rubber as compared to acetic acid coagulant ability. The work extends to the study on nano-biofillers, i.e., reprecipitated chitosan (RCS) and chitosan nanoscaffold (CSN) for rubber. Nanoscaffold chitosan prepared by microwave technique is proposed as an effective way to obtain nano-scaled material. Nanomaterization nanowhisker and nanoscaffold particles use as biofiller for rubber. The transmission electron micrograph confirms the bio-nanocomposites formation between rubber and nano-scaled chitosan.

ACKNOWLEDGEMENTS

The present dissertation would not have been accomplished without her Thai supervisor, Associate Professor Suwabun Chirachanchai, who not only originated this work, but also provide her with intensive suggestions and discussion, invaluable guidance, constructive criticisms, constant encouragement, inspiration and vital assistance throughout this research.

The author would also like to express her thanks to her overseas advisor, Professor Yasuyuki Tanaka (Institute of Science and Technology for Research and Development, Mahidol University, Thailand) for the value suggestions and helpful guidance. She is grateful to Ichikawa Naoya for fruitful discussion, worth advice, and concern during her staying in SRI R&D Ltd., Kobe, Japan. She would like to give sincere thanks to all members in SRI R&D Ltd. for their help and good discussions.

The author is also owing to Associate Professor Jitladda Sakdapipahich (Department of Chemistry, Faculty of Science, Mahidol University) for her comment and help in rubber processing and Associate Professor Buncha Pulpoka (Department of Chemistry, Faculty of Science, Chulalongkorn University) for his help in the NMR measurement. She extends her appreciation to Seafresh Chitosan (Lab) Company Limited, Thailand, for their support with the chitosan materials, Unimac Rubber Co., Ltd., Thailand, for natural rubber latex, and Sumirubber Malaysia SDN. BHD., Malaysia, for epoxidized natural rubber latex. She would also like to thanks members in Research and Development Center for Thai Rubber Industry, Thailand, for the guidance and help in rubber processing.

This thesis work is partially funded by the Petroleum and Petrochemical College, the National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Thailand, and Sumitomo Rubber Industries, Ltd., Japan.

The author is also thankful to the dissertation committee for their suggestions and comments in the reading of the thesis book. She greatly appreciates all professors who have tendered invaluable knowledge to her at the Petroleum and Petrochemical College, Chulalongkorn University.

Special thanks are given to her senior, Dr. Rangrong Yoksan, Dr. Suttinun Phontamrug, Dr. Sasiphapa Phongying and Dr. Wanvimol Pasanphan, and to her junior in her laboratory for their help, invaluable guidance, suggestions and encouragement throughout this research. She would also like to thank all friends and the college staff members at the Petroleum and Petrochemical College. She is also thankful to her friends at Faculty of Science, Chulalongkorn University and at Sainumpueng School.

Last but not least, she would like to express her gratitude to her family for their love, understanding, encouragement, limitless sacrifice, and for being a constant source of their inspiration throughout her study.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vii
List of Schemes	x
List of Tables	xi
List of Figures	xii
 CHAPTER	
I INTRODUCTION	1
 II LITERATURE REVIEW	
2.1 Natural Rubber	6
2.2 Coagulation	7
2.3 Flocculation	8
2.4 Compounding of Natural Rubber	9
2.5 Modified Natural Rubber	10
2.6 Chitin-Chitosan: the Structure and Unique Properties	11
2.7 Modifications of Chitin-Chitosan	13
2.7.1 Water-Soluble Chitosan	14
2.7.2 Nanometerization	15
2.7.2.1 Nanomaterizations via Physical Treatments	15
2.7.2.2 Nanomaterizations via Chemical Treatments	15
2.8 Development of Chitin-Chitosan as Flocculant	16
2.9 Development of Chitin-Chitosan as Biofillers	17
2.10 Points of the Present Work	18

CHAPTER	PAGE
III WATER-SOLUBLE CHITIN-CHITOSAN DERIVATIVES AND THEIR APPLICATIONS ON A RUBBER FLOCCULANT	19
3.1 Abstract	19
3.2 Introduction	19
3.3 Experimental	22
3.4 Results and discussion	26
3.5 Conclusions	38
3.6 Acknowledgements	38
3.7 References	39
IV MICROWAVE TECHNIQUE FOR EFFICIENT DEACETYLATION OF CHITIN NANOWHISKER TO CHITOSAN NANOSCAFFOLD	41
4.1 Abstract	41
4.2 Introduction	41
4.3 Experimental	43
4.4 Results and discussion	45
4.5 Conclusions	52
4.6 Acknowledgements	52
4.7 References	53
V BIO-NANOCOMPOSITE SYSTEM OF NANO-CHITOSAN IN EPOXIDIZED NATURAL RUBBER	55
5.1 Abstract	55
5.2 Introduction	55
5.3 Experimental	57
5.4 Results and discussion	59

CHAPTER	PAGE
5.5 Conclusions	76
5.6 Acknowledgements	77
5.7 References and notes	77
VI EPOXIDIZED NATURAL RUBBER BIO-NANOCOMPOSITE: A MODEL CASE OF BIO-NANOCOMPOSITE USING NANOFIBROUS CHITOSAN AND ITS CONSEQUENT METAL ION ABSORPTIVITY	80
6.1 Abstract	80
6.2 Introduction	80
6.3 Experimental	81
6.4 Results and discussion	81
6.5 Conclusions	84
6.6 Acknowledgements	85
6.7 References	85
VII CONCLUSIONS AND RECOMMENDATIONS	86
REFERENCES	87
CURRICULUM VITAE	93

LIST OF SCHEMES

SCHEME		PAGE
CHAPTER II		
1.1	(A) Presumed coagulation and (B) flocculation processes	2
1.2	Structure of chitin-chitosan	3
CHAPTER II		
2.1	Chemical repeating unit of natural rubber	7
2.2	Chemical repeating unit of ENR	10
2.3	Chemical structures of (a) cellulose, (b) chitin, and (c) chitosan	12
CHAPTER III		
3.1	Preparation of (a) CS-HOBt, (b) CM-CS, (c) CS-Acetate, and (d) Iodo-CS	25

LIST OF TABLES

TABLE		PAGE
CHAPTER III		
3.1	Degradation temperature (T_d) of chitosan and its derivatives	29
3.2	Zeta potential and contact angle value of water-soluble chitosan derivatives	31
3.3	Flocculation capability of water-soluble chitosan derivatives	33
3.4	% Content in rubber obtained from flocculation by TG-DTA	36
CHAPTER IV		
4.1	Degradation temperature (T_d) of 2 and 3	51
CHAPTER V		
5.1	Crosslink density (η_{phys}) of ENR nanocomposites	71

LIST OF FIGURES

FIGURE	PAGE
CHAPTER III	
3.1 FT-IR spectra of (a) chitosan, (b) CS-HOBt, (c) CM-CS, (d) CS-Acetate, and (e) Iodo-CS.	27
3.2 ¹ H-NMR spectra of (a) CS-HOBt, (b) CM-CS, (c) CS-Acetate, and (d) Iodo-CS	28
3.3 WAXD patterns of (a) chitosan, (b) CS-HOBt, (c) CM-CS, (d) CS-Acetate, and (e) Iodo-CS	30
3.4 (A) Particle size of NR (—) and that of NR mixing with CM-CS at various concentrations of 0.0125M (---), 0.025M (- - -), 0.0375 (- · ·), 0.05 (—), and 0.075M (—) and (B) Particle size of NR and that of NR mixing with CM-CS at various concentrations in the range of 0.2-1.5 (□), 1.6-26.7 (■), and 26.8-148.7 μm (■)	34
3.5 Particle size of NR and that of NR mixing with (A) CS-HOBt, (B) CS-Acetate, and (C) Iodo-CS at various concentrations in the range of 0.2-1.5 (□), 1.6-26.7 (■), and 26.8-148.7 μm (■).	35
3.6 % Recovered rubber efficiency of acetic acid (■), CS-HOBt (▲), CM-CS (●), CS-Acetate (□), and Iodo-CS (△) with various concentrations	37
CHAPTER IV	
4.1 FTIR spectra of (a) 1 , (b) 2 and (c) 3 under 60% alkaline solution for 6 h treating time	45
4.2 ¹ H-NMR spectrum of 3 under 60% alkaline solution treating for 6 h	46

FIGURE	PAGE
4.3 (A) FTIR spectra and curve fitting of 3 under 60% alkaline solution for (a) 1 h, (b) 3 h, and (c) 6 h and (B) quantitative analysis based on (A) for (●) 2 , and 3 under various treating time and alkaline concentrations in (■) 40%, (▲) 50%, and (○) 60% for 1, 3, and 6 h treating time	47
4.4 % DD of 3 under various alkaline concentrations in (■) 40%, (▲) 50%, and (○) 60% for 1, 3, and 6 h treating time	48
4.5 WAXD patterns of (a) 1 , (b) 2 , and 3 under various alkaline concentrations in (c) 40%, (d) 50%, and (e) 60% for 6 h treating time	49
4.6 (A) SEM micrographs and (B) TEM micrographs of (a) 2 and 3 under various alkaline concentrations in (b) 40%, (c) 50%, and (d) 60% for 6 h treating time	50

CHAPTER V

5.1 TEM micrographs of (a) CSN and (b) RCS	60
5.2 TEM micrographs of (a) ENR and ENR nanocomposites with CSN (b) and RCS (c) at 20 phr	61
5.3 (A) Topographic images and (B) topographic profiles of ENR (a) and ENR incorporating with CSN at 2.5 (b), 5 (c), 10 (d), and 20 phr (e) in the size of 20 μm^2	63
5.4 (A) FMM amplitude images and (B) FMM amplitude profiles of ENR (a) and ENR incorporating with CSN at 2.5 (b), 5 (c), 10 (d), and 20 phr (e) in the size of 20 μm^2	64
5.5 (A) Phase images and (B) phase profiles of ENR (a) and ENR incorporating with CSN at 2.5 (b), 5 (c), 10 (d), and 20 phr (e) in the size of 20 μm^2	65

FIGURE	PAGE
5.6 Relative FMM amplitude (solid) and normalization of FMM phase (blank) of ENR (●) and ENR nanocomposites with CSN (■) and RCS (▲) at various biofillers contents	66
5.7 (A) Lateral force images (forward), (B) Lateral force images (backward), and (C) lateral force loop of ENR (a) and ENR incorporating with CSN at 2.5 (b), 5 (c), 10 (d), and 20 phr (e) in the size of 20 μm^2	67
5.8 Relative FMM lateral force of ENR (●) and ENR nanocomposites with CSN (■) and RCS (▲) at various biofillers contents	68
5.9 FE-SEM surface micrographs of (a) ENR and ENR incorporating with (b) CSN and (c) RCS at 20 phr, after immersing in copper solution of (d) ENR and ENR incorporating with (e) CSN and (f) RCS at 20 phr and copper mapping mode of (g) ENR and ENR incorporating with (h) CSN and (i) RCS at 20 phr	69
5.10 Torque maximum (M_H , ■), torque minimum (M_L , □), and torque difference ($M_H - M_L$, ■) of ENR and ENR nanocomposites	71
5.11 (A) Hardness properties of ENR (●) and ENR incorporating with CSN (■), and RCS (▲) and (B) swelling percentage in toluene (solid) and methanol (blank) 24 h of ENR (●) and ENR incorporating with CSN (■) and RCS (▲)	73
5.12 (A) Modulus at 100 % elongation (M_{100}) of ENR (●) and ENR nanocomposites with CSN (■) and RCS (▲), and modulus at 300 % elongation (M_{300}) of ENR (○) and ENR nanocomposites with CSN (□) and RCS (Δ) and (B) tensile strength of ENR (●) and ENR incorporating with either CSN (■) or RCS (▲)	75
5.13 FE-SEM micrographs of tensile fracture surface of (a) ENR and ENR nanocomposites with (b) CSN and (c) RCS at 20 phr	76

FIGURE	PAGE
CHAPTER VI	
6.1 Chemical structures of (a) chitosan, and (c) ENR rubber, (d) possible ENR-nanofibrous chitosan bio-nanocomposite structure, and (b) TEM micrograph of reprecipitated showing nanofibrous form	81
6.2 (A) FTIR spectra of (a) nanofibrous chitosan, (b) ENR, and (c) ENR-nanofibrous chitosan bio-nanocomposite (10 phr), (B) curve fitting of ENR-nanofibrous chitosan bio-nanocomposite (10 phr), and (C) quantitative analysis based on (B) at various chitosan contents	82
6.3 (A) Topographic AFM images, (B) FMM amplitude AFM images ($20 \mu\text{m}^2$), (C) FMM amplitude profiles of; (a) ENR and (b) ENR-nanofibrous chitosan bio-nanocomposite (20 phr), (D) relative FMM amplitude (●) and tensile strength (○) of ENR-nanofibrous chitosan bio-nanocomposite with various chitosan contents, and (E) FE-SEM micrographs of ENR-nanofibrous chitosan bio-nanocomposite (20 phr) after immersing in copper sulfate solution: (a) surface and (b) mapping mode (Note: For (A), (B), and (C), a reference NR was shown in the left area)	83