EXTRUSION OF ADMICELLED NATURAL RUBBER FILLED WITH NANOMAGNETIC PARTICLES



Nuttida Srirachya

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

2009

522053

Thesis Title:	Extrusion of Admicelled Natural Rubber Filled with
	Nanomagnetic Particles
By:	Nuttida Srirachya
Program:	Polymer Science
Thesis advisors:	Dr.Thanyalak Chaisuwan
	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:

Thanyalch Chaise

(Dr. Thanyalak Chaisuwan)

R. Magazz

(Assoc. Prof. Rathanawan Magaraphan)

(Asst.Prof. Manit Nithitanakul)

N Heart

(Asst.Prof. Wirunya Keawwattana)

ABSTRACT

5072009063 : Polymer Science Program
 Nuttida Srirachya: Extrusion of Admicelled Natural Rubber Filled
 with Nanomagnetic Particles.
 Thesis Advisors: Dr. Thanyalak Chaisuwan, and Assoc. Prof.
 Rathanawan Magaraphan 100 pp.

Keywords : Admicellar polymerization/ Natural rubber/ Polystyrene/ Polymethyl methacrylate/ Nanomagnetic particles

Thin layers of polystyrene (PS) and poly(methyl methacrylate) (PMMA) are coated on natural rubber (NR) particles via admicellar polymerization using bilayers of cethyltrimethylammnonium bromide (CTAB) as a reaction template. The obtained admicelled PS-NR and PMMA-NR are characterized by FTIR, SEM, OM, and TGA. From the FTIR study, the admicelled rubbers showed the characteristic peaks of polystyrene and poly(methyl methacrylate), which confirmed the existence of PS and PMMA after the polymerization. The OM and SEM micrographs revealed the even coating of PS and PMMA over latex particles and they showed the coreshell structure of PS, PMMA and NR. As seen in the result of TGA, the admicelled rubbers began to lose weight at higher temperature, compared to that of NR, and they also showed the shift of major decomposition of pure PS and PMMA to higher temperature. The DTG curves also demonstrated an increase of char yields of the admicelled rubbers. As PS and PMMA content increased, the residual content also increased. The admicelled magnetite showed the characteristic peaks of polystyrene, poly(methyl methacrylate) which confirmed the existence of PS and PMMA after the polymerization. The OM micrographs revealed the even coating of PS and PMMA over magnetite particles and they showed the core-shell structure of PS, PMMA and Magnetite particles.

บทคัดย่อ

ณัฐธิดา ศรีราชยา: กระบวนการพอลิเมอร์ไรเซชั่นแบบแอ๊ดไมเซลล์ของยางธรรมชาติ ผสมกับอนุภาคแม่เหล็กขนาดนาโน (Extrusion of Admicelled Natural Rubber Filled with Nanomagnetic Particles) อ. ที่ปรึกษา: ดร.ธัญญลักษณ์ ฉายสุวรรณ์, รศ. ดร. รัตนวรรณ มกร พันธุ์ 100 หน้า

ฟิล์มบางของพอลิเมอร์ชนิดพอลิสไตรีน และพอลิเมทิลเมทาคริเลต เคลือบบนอนุภาค ของขางธรรมชาติด้วยกระบวนการพอลิเมอร์ไรเซชั่นแบบแอ๊คไมเซลล่าโดยใช้ชั้นของสารลดแรง ดึงผิวชนิดประจุบวก CTAB เป็นตัวช่วย โดยการทดลองนี้ได้ใช้เทคนิด FTIR, SEM, OM และ TGA ในการตรวจสอบความสมบูรณ์ของฟิล์มบางของพอลิเมอร์ที่เคลือบบนอนุภาคขาง ธรรมชาติ ผลการวิเคราะห์ด้วยเทคนิค FTIR ยืนยันการสังเคราะห์ได้จริงของกระบวนการแอ๊คไม เซลล่าด้วยเทคนิคนี้ จากการตรวจสอบค้วยกล้องจุลทรรศน์ชนิดส่องผ่านและชนิดมองด้วยตาเปล่า พบว่า อนุภาคขางธรรมชาติแต่ละอนุภาคถูกล้อมด้วยฟิล์มบางของพอลิสไตรีน และพอลิเมทิลเม ทาคริเลต เช่นเดียวกับการวิเคราะห์ด้วยเทคนิค TGA พบว่าอุณหภูมิการสลายตัวของยาง ธรรมชาติที่สังเคราะห์ได้จะเพิ่มขึ้นตามความเข้มข้นของสไตรีนมอนอเมอร์ และเมทิลเมทาคริเลต มอนอเมอร์ที่ใช้ในการสังเคราะห์ และจากการการเคลือบอนุภาคแม่เหล็กขนาดนาโนด้วยฟิล์ม บางของพอลิสไตรีน และพอลิเมทิลเมทาคริเลต ยืนยันการทดสอบด้วยกล้องจุลทรรศน์ชนิดมอง ด้วยตาเปล่า เห็นฟิล์มบางของพอลิเมอร์เคลือบบนแต่ละอนุภาคแม่เหล็กขนาดนาโนด้วยฟิล์ม นามารถสังเคราะห์แผ่นฟิล์มบางของพอลิเมอร์เคลือบบนแต่ละอนุภาคแม่เหล็กขนาดนาโนจึงยืนอันได้ว่า สามารถสังเคราะห์แผ่นฟิล์มบางของพอลิเมอร์เคลือบบนเต่ละอนุภาคแม่เหล็กขนาดนาโนจึงยินอนได้ว่า สามารถสังเคราะห์แผ่นฟิล์มบางของพอลิเมอร์เคลือบบนเต่ละอนุภาคแม่เหล็กขาดจาโนจึงยินอนได้ว่า สามารถสังเคราะห์แผ่นฟิล์มบางของพอลิเมอร์เคลือบบนเต่วของอนุภาคขางธรรมชาติ และอนุกาค แม่เหล็กขนาดนาโนได้

ACKNOWLEDGEMENTS

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 advisors Assoc. Prof. Rathanawan Magaraphan, and Dr. Thanyalak Chaisuwan the Petroleum and Petrochemical College, Chulalongkorn University for their constructive criticism, very useful suggestions, valuable guidance and vital help throughout this research work.

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

The author would also like to thank Asst. Prof. Manit Nithitanakul and Asst. Prof. Wirunya Keawwattana for proof-reading this thesis book and for being on the thesis committee.

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	e Page	i
Abst	tract (in English)	iii
Abst	tract (in Thai)	iv
Ack	nowledgements	v
Tabl	e of Contents	vi
List	of Tables	ix
List	of Figures	x
СНАРТЕ	CR	
Ι	INTRODUCTION	1
II	LITERATURE REVIEW	3
Ш	EXPERIMENTAL	32
IV	SURFACTANT AID IN ADMICELLAR	
	POLYMERIZATION OF STYRENE ON	
	NATURAL RUBBER LATEX	38
	4.1 Abstract	38
	4.2 Introduction	38
	4.3 Experiment	39
	4.4 Results and discussion	41
	4.5 Conclusion	48
	4.6 Acknowledgement	49
	4.7 References	49

V	POLYSTYRNE COATED ON NATURAL RUBBE	R
	LATEX AND NANOMAGNATIC PARTICLES BY	
	ADMICELLAR POLYMERIZATION	51
	5.1 Abstract	51
	5.2 Introduction	51
	5.3 Experiment	52
	5.4 Results and discussion	54
	5.5 Conclusion	68
	5.6 Acknowledgement	69
	5.7 References	69

VI	POLY (METHYL METHACRYLATE) COATED ON	
	NATURAL RUBBER LATEX AND NANOMAGNATIC	
	PARTICLES BY ADMICELLAR POLYMERIZATION	72
	6.1 Abstract	72
	6.2 Introduction	72
	6.3 Experiment	73
	6.4 Results and discussion	75
	6.5 Conclusion	85
	6.6 Acknowledgement	86
	6.7 References	86
VП	CONCLUSION AND RECOMMENDATIONS	88
	REFERENCES	89

APPENDICES

Appendix A Calculation of percent weight polystyrene	
and poly(methyl methacrylate) in admicellar	
modified natural rubber	

CHAPTER	
Appendix B Data of Rheology	94
Appendix C Data of Gel Permeation Chromatogra	aphy 98
CURRICULUM VITAE	99

LIST OF TABLES

TABLE

PAGE

CHAPTER II

2.1	World production of natural rubber (2004)	4
2.2	Different types of rubber in Thailand (2004)	5
2.3	Composition of fresh latex and dry rubbers	5

CHAPTER IV

4.1	Parameters to be measured for admicelled rubber properties	39
4.2	Experimental condition of the natural rubber, styrene monomer	40
	and CTAB concentration	

CHAPTER V

5.1	Parameters to be measured for admicelled PS-NR properties	52
5.2	Decomposition temperatures of admicelled PS-NR	56
5.3	The molecular weight of 50 PS-NR	67

CHAPTER VI

6.1	Parameters to be measured for admicelled PMMA-NR	73
	properties	
6.2	Decomposition temperatures of admicelled PMMA-NR	77
6.3	The molecular weight of 50 PMMA-NR	84

LIST OF FIGURES

FIGURE

CHAPTER II

2.1	Structure of the NR latex particles.	7
2.2	Schematic representation of the structure of a NR latex	8
	particle.	
2.3	Schematic representing the structure isomerism with both cis-	8
	and <i>trans</i> - isoprene, repeating units.	
2.4	Unit cell structure of the natural rubber molecule.	9
2.5	Effects of the stretched rubber molecule.	9
2.6	Typical structure of NR latex from Hevea brasiliensis.	10
2.7	Schematic representation of the structure of cis-polymer : cis-	10
	1,4-polyisoprene (~97%), cis-1,2- polyisoprene(~2.7) and cis-	
	3,4- polyisoprene(<0.3%).	
2.8	Formation of a sodium dodecyl sulfate admicelle on an	15
	alumina surface.	
2.9	a) Admicelle formation of polymerization process.	15
	b-1) Admicelle Adsolubilization of polymerization process.	16
	b-2) Phenomena of solubilization and adsolubilization.	16
	c) Polymer formation of polymerization process.	17
	d) Surfactant removal of polymerization process.	17
2.10	A surfactant molecule.	19
2.11	Molecular structure of a surfactant.	19
2.12	Surfactant aggregates.	20
2.13	Typical adsorption isotherm of a surfactant in solution (S-	23
	shaped curve).	
2.14	Point of zero charge on a natural rubber surface.	25
2.15	Adsorption isotherm of a surfactant from aqueous solution	26
	onto nonpolar, hydrophobic adsorbents.(L-shaped curve).	

FIGURE

CHAPTER IV

4.1	The appearance of modified natural rubber at different %wt of	41
	natural rubber, styrene monomer, and surfactant.	
4.2	FTIR spectra of admicelled PS-NR with and without CTAB at	44
	different styrene concentration.	
4.3	TGA results of admicelled PS-NR with and without CTAB at	45
	different styrene concentration.	
4.4	DTG results of admicelled PS-NR with and without CTAB.	46
4.5	The SEM of admicelled 100PS-5NR with CTAB.	47
4.6	The SEM of admicelled 100PS-5NR without CTAB.	48

CHAPTER V

Appearance of admicelled PS-NR with 20 – 300 mM styrene	54
concentration.	
FTIR spectra of admicelled PS-NR at various styrene	55
monomer concentration.	
TGA results of admicelled PS-NR at various styrene	56
monomer concentration.	
DTG results of admicelled PS-NR at various styrene	57
monomer concentration.	
The phase morphology of pure natural rubber.	58
The phase morphology of admicellar modified natural rubber	58
with polystyrene.	
The phase morphology of admicellar modified natural rubber	59
with polystyrene after heating to 300 °C.	
The SEM of of admicellar modified natural rubber with	59
polystyrene.	
Infrared spectra of admicelled PS-Mag and pure magnetite	60
particles.	
	 Appearance of admicelled PS-NR with 20 – 300 mM styrene concentration. FTIR spectra of admicelled PS-NR at various styrene monomer concentration. TGA results of admicelled PS-NR at various styrene monomer concentration. DTG results of admicelled PS-NR at various styrene monomer concentration. The phase of admicelled PS-NR at various styrene monomer concentration. The phase morphology of pure natural rubber. The phase morphology of admicellar modified natural rubber with polystyrene. The phase morphology of admicellar modified natural rubber with polystyrene after heating to 300 °C. The SEM of of admicellar modified natural rubber with polystyrene. Infrared spectra of admicelled PS-Mag and pure magnetite particles.

FIGURE

5.10	The phase morphology of pure magnetite particles.	61
5.11	The phase morphology of admicellar modified magnetite	61
	particle with polystyrene.	
5.12	Logarithmic plots of apparent shear stress versus apparent	62
	shear rate of NR blend PS and NR blend magnetic and PS at	
	150 °C.	
5.13	Plots of die swell versus apparent shear rate of NR blend PS	63
	and NR blend magnetic and PS at 150 °C.	
5.14	The phase morphology of natural rubber blended with PS-NR,	64
	PS-Mag and PS by using scanning electron microscope at	
	magnification.	
5.15	Logarithmic plots of apparent shear stress versus apparent	65
	shear rate of PS-NR and PS-NR-0.5%Mag at 150 °C.	
5.16	Logarithmic plots of apparent shear viscosity versus apparent	66
	shear rate of PS-NR and PS-NR-0.5%Mag at 150 °C.	
5.17	Plots of die swell versus apparent shear rate of PS-NR and	67
	PS-NR-0.5%Mag at 150 °C.	
5.18	The molecular weight result of 50 PS-NR.	68
5.19	Chromatogram of 50 PS-NR.	68

CHAPTER VI

6.1	Appearance of admicelled PMMA-NR with 20 – 300 mM	75
	methyl methacrylate concentration.	
6.2	FTIR spectra of admicelled PMMA-NR at various methyl	76
	methacrylate monomer concentration.	
6.3	TGA results of admicelled PMMA-NR.	78
6.4	DTG results of admicelled PMMA-NR at various methyl	79
	methacrylate monomer concentration.	
6.5	The phase morphology of 50 mM PS - 5 %wt. NR.	80

FIGURE

6.6	The SEM of of admicellar modified natural rubber with	80
	poly(methyl methacrylate).	
6.7	Infrared spectra of admicelled PMMA-Mag and pure	81
	magnetite particles.	
6.8	The phase morphology of admicellar modified magnetite	82
	particle with poly(methyl methacrylate).	
6.9	Logarithmic plots of apparent shear stress versus apparent	83
	shear rate of PMMA-NR and PMMA-NR-0.5%Mag at 150	
	°C.	
6.10	Logarithmic plots of apparent shear viscosity versus apparent	83
	shear rate of PMMA-NR and PMMA-NR-0.5%Mag at 150	
	°C.	
6.11	Plots of die swell versus apparent shear rate of PMMA-NR	84
	and PMMA-NR-0.5%Mag at 150 °C.	
6.12	The molecular weight result of 50 PMMA-NR.	85
6.13	Chromatogram of 50 PMMA-NR.	85

1410