Rheological Behavior for Unfilled & Filled Natural Rubber (NR) and Linear Low Density Polyethylene (LLDPE) Blends with Maleic Anhydride (MA) as a Compatibilizer



Ms. Kunjana Intharuksa

A Thesis Submitted in Partial Fulfillment 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

1999

ISBN 974-331-923-9

Thesis Title : Rheological Behavior for Unfilled & Filled Natural rubber

(NR) and Linear Low Density Polyethylene (LLDPE) Blends

with Maleic anhydride (MA) as a Compatibilizer

By : Ms. Kunjana Intharuksa

Program : Polymer Science

Thesis Advisors: Professor Ica Manas-Zloczower

Dr. Rathanawan Magaraphan

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

College Director

(Prof. Somchai Osuwan)

Thesis Committee:

(Prof. Ica Manas-Zloczower)

R Magaryon

(Dr. Rathanawan Magaraphan)

(Assoc. Prof. Anuvat Sirivat)

Aniwathowal 28/4/99

ABSTRACT

##94XXX : POLYMER SCIENCE PROGRAM

KEY WORDS : Rheological Behavior/Polymer Blends/Linear Low

Density Polyethylene/Natural Rubber/Compatibilizer

Ms. Kunjana Intharuksa: Rheological Behavior for Unfilled & Filled Natural Rubber (NR) and Linear Low Density Polyethylene (LLDPE) Blends with Maleic anhydride (MA) as a Compatibilizer. Thesis Advisors: Prof. Ica Manas-Zloczower and Dr. Rattanawan Magaraphan, 81 pp ISBN 974-331-923-9

The rheological behavior of linear low density polyethylene (LLDPE), natural rubber (NR) and their blends were studied by a cone-and-plate rheometer in dynamic mode at a frequency ranges from 0.1-100 rad/sec and a capillary rheometer in steady mode at high shear rates. Maleic anhydride (MA) was added to the blends as a compatibilizer. The presence of a single $\tan \delta$; i.e. a single glass transition temperature, indicated that the compatibility of LLDPE/NR blends was improved by the addition of maleic anhydride. The results illustrated the effects of blend ratio, maleic anhydride concentration, shear stress/shear rate and temperature on melt viscosity and melt elasticity of the blends. Addition of NR caused the increase in viscosity and modulus. But blend viscosity reduced at high shear rate while the storage modulus increased. SEM analysis of the fracture surfaces of the compatibilized blends showed that the addition of a small percentage of the compatibilizer was enough to decrease and stabilize the domain size of dispersed NR phase. Without MA, the morphology was altered by shear rate due to the change of viscosity with shear rate. Dynamic mechanical properties of the blends were also investigated. Master curves of G' and G" for the blend system were constructed by using the time-temperature superposition principle.

observed that the master curves of the blends did not fall on the same curve due to morphological changes induced by the viscosity difference and the drop-coalescence mechanism. Fine calcium carbonate was used as a filler in the blends. It was found that viscosity of the filled blends increased significantly with amount of filler at low frequency.

บทคัดย่อ

นางสาวกัญจนา อินทร์รักษา : ชื่อหัวข้อวิทยานิพนธ์ การศึกษาพฤติกรรมการใหลของ พอลิเอททิลีนชนิดความหนาแน่นต่ำเชิงเส้นตรง (LLDPE) ซึ่งผสมกับยางธรรมชาติ (NR) โดยมีมา เลอิกแอนไฮไดร์ (MA) เป็นตัวประสาน (Compatibilizer) (ภาษาอังกฤษ) (Rheological Behavior for Unfilled & Filled Natural Rubber (NR) and Linear Low Density Polyethylene (LLDPE) Blends with Maleic Anhydride (MA) as a Compatibilizer) อ. ที่ปรึกษา : ศ. ไอก้า มานาส-สล็อคโซเวอร์ และ คร. รัตนวรรณ มกรพันธุ์ 81 หน้า ISBN 974-331-939-5

การวิจัยนี้เป็นการศึกษาพฤติกรรมการใหลของพอลิเอททิลีนชนิดความหนาแน่นต่ำเชิง เส้นตรง, ยางธรรมชาติ และสารผสมระหว่างสารทั้งสองชนิดนี้ซึ่งมีมาเลอิกแอนไฮไดร์เป็นตัวช่วย ประสานโดยใช้เครื่องมือวัดการใหลแบบโคนและเพลทที่ความถี่ต่ำ และเครื่องมือวัดการใหลแบบ แคปปิลารีที่อัตราแรงเฉือนสูง จากผลของการทดสอบทางเชิงกลแบบไดนามิกส์พบว่ามาเลอิกแอน ใฮไดร์ช่วยให้พอลิเอททิลีนชนิดความหนาแน่นต่ำเชิงเส้นตรงและยางธรรมชาติผสมเข้ากันได้ดีซึ่ง เห็นได้จากพีกของแทนเดลตาเกิดขึ้นเพียงเส้นเดียวที่ -64 องสาเซลเซียส นอกจากนี้การศึกษาโครง สร้างของสารผสมโดยใช้เครื่องมือแสกนนิ่งอิเล็กตรอนไมโครสโคป (SEM) พบว่าขนาดอนุภาค ของยางลคลงเมื่อเติมมาเลอิกแอนไฮไดร์ลงไปในสารผสมนี้ ซึ่งบ่งบอกถึงการเพิ่มขึ้นของแรง กระทำระหว่างสารทั้งสอง จากการศึกษาคุณสมบัติการใหลของสารผสมเมื่อมีและไม่มีมาเลอิก แอนไฮไดร์พบว่าความหนืดและความยืดหยุ่นของสารผสมเพิ่มขึ้นเมื่อปริมาณมาเลอิกแอนไฮไดร์ เพิ่มมากขึ้นจนถึงจุดอิ่มตัว หลังจากนั้นคุณสมบัติทั้งสองนี้จะลดลง

ACKNOWLEDGEMENTS

The author wishes to express the appreciation to Dr. Ratanawan Magaraphan and Prof. Ica Manas-Zloczower, who gave the inspiration to conduct this project and their valuable suggestion for the lab planning and problem solving of the instruments. The appreciation is extended to Assoc. Prof. Anuvat Sirivat for being a thesis committee member and his useful suggestions in cone and plate rheometer. Besides, I would like to thanks Mr. John W. Ellis for his kind suggestion on capillary rheometer.

The author would like to mention that this work can not be accomplished without the support from Ratchadaphisaek Sompoch Reserch Fund.

The author wishes to express her thanks to all of her friends who have given her encouragement and also to all of college staff for providing the use of research facilities.

Finally, the author is deeply indebted to her parents for their love, understanding encouragement and for being a constant source of her inspiration.

TABLE OF CONTENTS

		PAGE
	Title Page	i
	Abstract (in English)	iii
	Abstract (in Thai)	v
	Acknowledgements	vi
	Table of Contents	vii
	List of Tables	ix
	List of Figures	x
CHAPTER		
I	INTRODUCTION	1
	1.1 Polymer blends	1
	1.2 Rheology	2
П	LITERATURE SURVEY	3
	2.1 Polymer blends	3
	2.2 Rheology	8
	2.3 Research Objectives	17
III	EXPERIMENTAL SECTION	18
***	3.1 Materials	18
	3.2 Instruments	18
	3.3 Procedures	20
	3.3.1 Sample Preparation	20
	3.3.2 Rheological Measurements	21
	3.3.3 Time-Temperature Superposition	27
	I IIIIO I DIIIDOLULUI DUDULDUULUI	- ·

CHAPTER			PAGE
IV	RESULT	S AND DISCUSSION29	29
	4.1 Dynai	mic mechanical analysis	29
	4.1.1	Effect of compatibilizer on the glass	
		transition temperature of 70/30 LLDPE/NR	
		blends	34
	4.2 Morph	hology study	35
	4.2.1	Effect of maleic anhydride concentration on	
		morphology	35
	4.2.2	Effect of shear force on the morphology of	
		uncompatibilized blends	38
	4.2.3	Effect of shear force on the morphology of	
		compatibilized blends	44
	4.3 Rheol	ogical study	48
	4.3.1	Cone-and-plate Rheometer study	48
	4.3.2	Capillary Rheometer study	61
	4.3.3	Time-Temperature Superposition	67
V	CONCLU	JSIONS	71
	REFERE	NCES	73
	APPEND	IX	80
	CURRIC	ULUM VITAE	81

LIST OF TABLES

TABLE		
1	Characteristics of the raw materials	19
2	The velocity profile schedule used in capillary rheometer	22

LIST OF FIGURES

FIGUR	RE	PAGE
3.1	Variation of entrance-exit pressure drop ΔP with L/R ratio	
211	of capillary at constant shear rate	24
3.2	Schematic plot of shear stress versus shear rate for	
	Newtonian and non-Newtonian fluids	25
3.3	The dynamic mechanical behavior of an ideal polymer	27
4.1	Effect of temperature on damping (tanδ) of pure	
	natural rubber and pure linear low-density polyethylene	29
4.2	Effect of temperature on loss modulus (G") of pure natural	
	rubber and pure linear low-density polyethylene	30
4.3	Effect of temperature on storage modulus (G') of pure	
	natural rubber and pure linear low-density polyethylene	30
4.4	Effect of temperature on damping $(\tan\delta)$ of 70/30	
	LLDPE/NR blend without maleic anhydride	32
4.5	Effect of temperature on damping ($tan\delta$) of 70/30	
	LLDPE/NR blend with different % maleic anhydride	
	(a) 3% MA, (b) 5% MA and (c) 7% MA	33
4.6	SEM micrographs of 70/30 LLDPE/NR blends	
	with different % maleic anhydride: (a) 0% MA	
	(b) 1% MA, (c) 3% MA, (d) 5% MA and (e) 7% MA	36
4.7	Effect of compatibilizer loading on the dispersed phase	
	size of 70/30 LLDPE/NR blends	37
4.8	SEM micrograph of 90/10/0 LLDPE/NR/MA blends	
	at different frequency: (a) 0.1 rad/sec, (b) 1 rad/sec,	
	(c) 10 rad/sec and (d) 100 rad/sec at 180° C	40

FIGURE		PAGE	
	4.9	Plot of viscosity ratio for LLDPE/NR blend	
		system as a function of frequency at 180°C	41
	4.10	SEM micrograph of 70/30/0 LLDPE/NR/MA blends	
		at different frequency: (a) 0.1 rad/sec, (b) 1 rad/sec,	
		(c) 10 rad/sec and (d) 100 rad/sec at 180°C	42
	4.11	SEM micrograph of 70/30/0 LLDPE/NR/MA blends	
		at different shear rates: (a) 45 1/sec, (b) 130 1/sec	
		at 180°C (M. Pornpirom, 1999)	43
	4.12	SEM micrograph of 90/10/3 LLDPE/NR/MA blends	
		at different frequency: (a) 0.1 rad/sec, (b) 1 rad/sec,	
		(c) 10 rad/sec and (d) 100 rad/sec at 180°C	45
	4.13	SEM micrograph of 70/30/5 LLDPE/NR/MA blends	
		at different frequency: (a) 0.1 rad/sec, (b) 1 rad/sec,	
		(c) 10 rad/sec and (d) 100 rad/sec at 180°C	46
	4.14	SEM micrograph of 70/30/5 LLDPE/NR/MA blends	
		at different shear rates: (a) 42 1/sec, (b) 127 1/sec	
		at 180°C (M. Pornpirom, 1999)	47
	4.15	Strain sweep at 180°C for NR, LLDPE and 80/20 LLDPE/NR	
		blend. The arrows indicate the maximum value of % strain	
		for the linear viscoelastic response	49
	4.16	The complex viscosity as a function of frequency for pure	
		LLDPE, NR and LLDPE/NR blends at 180°C	50
	4.17	Effect of NR content on the complex viscosity of LLDPE/NR	
		blend at various frequencies and 180°C	51
	4.18	The complex viscosity as a function of frequency for 70/30	
		LLDPE/NR blends with various %maleic anhydride at 180°C	52

FIGUR	E	PAGE
4.19	Effect of % MA on the complex viscosity of 70/30 LLDPE/NR	
	blends as a function of frequency at 180°C	53
4.20	Effect of % MA on the complex viscosity of 90/10 LLDPE/NR	
	blends as a function of frequency at 180°C	53
4.21	Effect of % MA on the complex viscosity of 80/20 LLDPE/NR	
	blends as a function of frequency at 180°C	54
4.22	The complex viscosity as a function of frequency for 70/30	
	LLDPE/NR blends without maleic anhydride at different	
	temperature	55
4.23	Effect of temperature on the complex viscosity of 70/30	
	LLDPE/NR blends with various % MA	
	at frequency 0.1 rad/sec	55
4.24	Effect of CaCO ₃ content on the complex viscosity of 70/30	
	LLDPE/NR blend compare with pure components at 180°C	56
4.25	The storage modulus as a function of frequency for pure	
	LLDPE, NR and LLDPE/NR blends at 180°C	58
4.26	The loss modulus as a function of frequency for pure	
	LLDPE, NR and LLDPE/NR blends at 180°C	58
4.27	The effect of NR concentration on the storage, loss and	
	complex modulus for LLDPE/NR blends at 180°C and	
	frequency of 0.1 rad/sec	59
4.28	Effect of MA content on the storage modulus of 70/30	
	LLDPE/NR blend as a function of frequency at 180°C	59
4.29	Variation of viscosity with shear stress at 180°C for	
	LLDPE/NR blend at various compositions	62
4.30	Variation of viscosity with shear rate at 180°C for	
	LI DPF/NR blend at various compositions	62

FIGUR	E	PAGE
4.31	Variation of viscosity with shear stress at 180°C for	
	70/30 LLDPE/NR blends with various percent	
	maleic anhydride	63
4.32	Variation of viscosity with shear rate at 180°C for	
	70/30 LLDPE/NR blends with various percentage	
	of maleic anhydrides	63
4.33	Variation of viscosity as a function of MA content for	
	70/30 LLDPE/NR blends at 180°C with various shear rates	64
4.34	Effect of maleic anhydride concentration and temperature	
	on the extrudate swell of 70/30 LLDPE/NR at the	
	shear rate 45 sec-1	66
4.35	Effect of shear rate on the extrudate swell of LLDPE/NR	
	blends with and without maleic anhydride at 180°C	66
4.36	Effect of NR content on the extrudate swell of LLDPE/NR	
	blends without MA at 180°C and shear rate 45 sec-1	67
4.37	Storage and loss modulus master curve of pure LLDPE	
	at the reference temperature 180 °C	68
4.38	Shift factors a _T from master curves of pure LLDPE	
	at the reference temperature 180 °C	68
4.39	Storage and loss modulus master curve of 70/30 LLDPE/NR	
	blend at reference temperature 180 °C	69
4.40	Storage and loss modulus master curve of 70/30/5	
	LLDPE/NR/MA blend at the reference temperature 180 °C	69

80

FIGURE	PAGE

A The complex viscosity as a function of frequency at different temperature for 70/30 LLDPE/NR blends at various %MA: (a) 1%MA, (b) 3%MA(c) 5%MA and (d) 7%MA