# INFLUENCE OF COMPATIBILIZER ON MOPHOLOGY AND MECHANICAL PROPERTIES OF LLDPE/NR BLENDS PRODUCED BY BLOWN FILM AND CHILL ROLL CAST FILM EXTRUSION



Mr. Pornpirom Moteplay

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 974-331-935-2

Thesis Title : Influence of Compatibilizer on Morphology and Mechanical

Properties of LLDPE/NR Blends Produced by Blown Film

and Chill Roll Cast Film Extrusion

By : Mr. Pornpirom Moteplay

**Program** : Polymer Science

Thesis Advisors: Prof. 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 Master of Science.

**Thesis Committee:** 

(Prof. Ica Manas-Zloczower)

(Dr. Rathanawan Magaraphan)

R. Magnapin

(Dr. Suwabun Chirachanchai)

#### **ABSTRACT**

##972018 : POLYMER SCIENCE PROGRAM

KEY WORDS : Blown Film Extrusion/ Chill Roll Cast Film Extrusion/

Molecular Orientation

(Mr. Pronpirom Moteplay): (Influence of Compatibilizer on

Morphology and Mechanical Properties of LLDPE/NR Blends Produced by Blown Film and Chill Roll Cast Film Extrusion). Thesis Advisors: Prof. Ica Manas-Zloczower and Dr. Rathanawan Magaraphan, 90 pp. ISBN 974-331-935-2

The addition of Natural Rubber (NR) into Linear Low Density Polyethylene (LLDPE) significantly improved processability of LLDPE resins as evidenced by the increase of draw ratio (DR) and blow up ratio (BUR) which directly relate to the *ultimate melt strength* of LLDPE. Maleic anhydride (MA) was added in 1-5 wt% to *in-situ* compatibilize the blend. By using this technique the melt viscosity, morphology and mechanical properties of LLDPE/NR blends were affected. The biaxial orientation in blown film and uniaxial orientation in chill roll cast film processes were investigated by infrared dichoism. The crystalline orientation ( $f_c$ ) was higher than amorphous orientation ( $f_{am}$ ). Moreover, the molecular orientation strongly affected the mechanical properties of the film; such as tear resistance, tensile strength, impact strength. Tear resistance and impact strength also increased as NR loading increased; whereas, the tensile strength of films decreased.

## บทคัดย่อ

นาย พรภิรมย์ โหมคพลาย: ชื่อหัวข้อวิทยานิพนธ์ (ภาษาไทย) อิทธิพลของตัวประสาน ต่อ โครงสร้างสัณฐานและสมบัติเชิงกลของของผสมพอลิเอทิลีนชนิดความหนาแน่นต่ำเชิงเส้น และยางธรรมชาติโดยการขึ้นรูปแบบเป่าฟิล์มและรีด (ภาษาอังกฤษ) (Influence of Compatibilizer on Morphology and Mechanical Properties of LLDPE/NR Blends Produced by Blown Film and Chill Roll Cast Film Extrusion) อ. ที่ ปรึกษา : ศ. ไอกา มานาส ซลอคโซเวอ และ อ. คร. รัตนวรรณ มกรพันธุ์ 90 หน้า ISBN 974-331-935-2

การขึ้นรูปของพอลิเอทิลีนชนิดความหนาแน่นต่ำเชิงเส้นสามารถทำได้ง่ายขึ้นอย่างเห็นได้ ชัดจากการเพิ่มขึ้นของอัตราส่วนการดึงและอัตราส่วนการเบ่ง โดยวิธีการขึ้นรูปแบบเป่าฟิล์มและ รีด ภายหลังจากการผสมยางธรรมชาติและตัวประสานที่พอเหมาะ ปัจจัยที่มีความสำคัญต่อขบวน การขึ้นรูปแบบเป่าฟิล์มและแบบรีด คือสมบัติความแข็งแรงของพอลิเมอร์หลอมต่อแรงดึงระหว่าง การขึ้นรูป การเดิมยางธรรมชาติและตัวประสาน มาเลอิกแอนไฮไดร์ จำนวน 1-5 กรับ/น้ำหนัก พบ ว่ามีผลอย่างมากต่อความหนืด สัณฐานวิทยาของของผสม และสมบัติเชิงกลของฟิล์ม การขึ้นรูป แบบเป่าฟิล์มและแบบรีดส่งผลให้การเรียงตัวของโมเลกุลแบบทิสทางเดียวและสองทิสทาง สามารถตรวจสอบโดยเทคนิคการดูดกลืนรังสีอินฟราเรด ส่วนที่เป็นโครงสร้างผลึกจะเรียงตัวดี กว่าส่วนโครงสร้างอสัณฐาน การเรียงตัวของส่วนที่เป็นโครงสร้างผลึกและส่วนที่เป็นโครงสร้าง อสัณฐานส่งผลอย่างมากต่อสมบัติเชิงกลของฟิล์ม เช่น สมบัติการทนแรงฉีกขาด ความแข็งแรง และความสามารถทนแรงกระแทกของฟิล์ม สมบัติการทนแรงฉีกขาดและสมบัติความสามารถ ทนแรงกระแทกเพิ่มมากขึ้นเมื่อเพิ่มปริมาณยางธรรมชาติในของผสม ส่วนความแข็งแรงของฟิล์ม ลดลงเมื่อเพิ่มปริมาณยางธรรมชาติ

#### **ACKNOWLEDGEMENTS**

The work was supported by Ratchadaphisaek Sompoch Research Fund in the year of 1998.

The author wishes to express the appreciation to Dr. Rathanawan Magarphan and Prof. Ica Manas Zloczower, who gave the inspiration to conduct this project and their valuable suggestions for the lab planning and problem solving of the instruments. Besides, his special thank was offered to Prof. I. R. Harrison (Pensylvania State University), Dr. Wannee Chinsirikul (National Metal and Material Center (MTEC) and Dr. Sanong Ekgasit for their kind suggestion on valuable documents and comment on his work for optical polarizing microscope and FTIR-dichroism.

The author also thanks all of his friends and the staff at the PPC who encouraged him in carrying out the experiment and this thesis writing. Finally, the author is also deeply indebted to his mother and father: Sumruay and Jumlong Moteplay for greatest love, encouragement and financial support.

### **TABLE OF CONTENTS**

		PAGE
	Title Page	i
	Abstract (in English)	iii
	Abstract (in Thai)	iv
	Acknowledgements	v
	Table of Contents	vi
	List of Tables	xi
	List of Figures	xii
СНАРТЕ	.R	
I	INTRODUCTION	1
II	LITERATURE SURVEY	3
	History and Background	
	2.1 Polymer Blends	3
	2.2 Polyethylene Film	4
	2.3 Natural Rubber (NR)	6
	2.4 Compatibilizer for Polymer Blends	8
	2.5 Role of Compatibilizer in Polymer Blends	8
	2.6 Morphology of Polymer Blends	10
	2.7 Thermal Properties	10
	2.8 Processing of Polyethylene	11
	2.8.1 Blown Film Extrusion	11
	2.8.2 Chill Roll Cast Film Extrusion	14
	2.9 Mechanical Properties	15
	2.9.1 Tensile Properties	15
	2.9.2 Impact Strength	16
	2.9.3 Tear Resistance	17
	2.10 Molecular Orientation	18

CHAPTER	P	AGE
	2.10.1 Infrared Dichroism	18
	2.10.2 Birefringence	20
Ш	EXPERIMENTAL	23
	3.1 Materials	23
	3.1.1 Linear Low Density Polyethylene (LLDPE)	23
	3.1.2 Natural Rubber (NR)	24
	3.1.3 Maleic Anhydride (MA)	25
	3.2 Experimental	26
	3.2.1 Characterization of the Materials	25
	3.2.2 Preparation the Materials	26
	3.2.3 Testing the Properties of the Blends	28
	3.2.4 Mechanical Properties	29
	3.2.5 Molecular Orientation	31
IV	RESULTS AND DISCUSSION	32
	4.1 Characterization of Polymer Properties	
	Weight Average Molecular Weight (Mw),	
	Number Average Molecular Weight (M <sub>n</sub> )	
	and Molecular Weight Distribution (MWD)	32
	4.2 Processability and Rheological Characteristics	36
	4.3 Morphology of LLDPE/NR Blends	39
	4.3.1 Effect of Compatibilizer on Morphology	
	of LLDPE/NR Blends	39
	4.3.2 Effect of Shear Rate on Morphology of	
	LLDPE/NR Blends	41
	4.4 Thermal Properties of LLDPE, NR and	
	LLDPE/NR Blends	47

1.4

CHAPTER	P	AGE
	4.4.1 Effect of NR on Melting Temperature (T <sub>m</sub> )	
	and Degree Crystallinity of LLDPE	47
	4.4.2 Effect of MA on Glass Transition	
	Temperature (Tg) of LLDPE/NR Blends	48
	4.5 Molecular Orientation	50
	4.5.1 Infrared Dichroism	50
	4.5.1.1 Effect of Process Variables BUR and	
	DR for LLDPE and LLDPE/NR Blends	
	Produced by Blown Film Process.	50
	4.5.1.2 Molecular Orientation of Film Produced	
	from Chill Roll Cast Film Process.	55
	4.5.1.3 Effect of NR and MA Content on	
	Crystalline (f <sub>c</sub> ) and Amorphous	
	Orientation (f <sub>am</sub> ) of LLDPE Phase in	
	LLDPE/NR Blends	58
	4.5.1.4 Comparing Biaxial and Uniaxial	
	Molecular Orientation between Blown Fi	ilm
	and Chill Roll Cast Film Processes	60
	4.5.2 Effect of Process Variables on LLDPE Blow	wn
	Film Determined by Birefringence.	62
	4.6 Mechanical Properties	68
	4.6.1 Tensile Strength at Break	70
	4.6.1.1 Effect of Process Variables BUR and	
	DR in Blown Film Process on Tensile	
	Strength at Break of LLDPE and	
	LLDPE/NR Blend Films	70
	4.6.1.2 Tensile Strength at Break for LLDPE	
	and LLDPE/NR Blend Films Produced	

CHAPTER	PA	GE
	from Chill Roll Cast Film Process.	74
	4.6.1.3 Effect of MA and NR Content on Tensile	
	Strength of LLDPE and LLDPE/NR	
	Blend Films Produced from Blown Film	
	and Chill Roll Cast Film Processes.	78
	4.6.1.4 Effect of Biaxial and Uniaxial	
	Orientation in Blown Film and Cast	
	Film Processes on Tensile Strength	
	of LLDPE and LLDPE/NR Blend Films	79
	4.6.2 Impact Strength	81
	4.6.2.1 Effect of Process Variables BUR and	
	DR in Blown Film Process on Impact	
	Strength of LLDPE and	
	LLDPE/NR Blend Films	81
	4.6.2.2 Impact Strength of LLDPE	
	and LLDPE/NR Blend Films Produced	
	from Chill Roll Cast Film Process.	84
	4.6.2.3 Effect of MA and NR Content on Impact	
	Strength of LLDPE and LLDPE/NR	
	Blend Films Produced from Blown Film	
	and Chill Roll Cast Film Processes.	86
	4.6.2.4 Effect of Biaxial and Uniaxial	
	Orientation in Blown Film and Cast	
	Film Processes on Impact Strength	
	of LLDPE and LLDPE/NR Blend Films	87
	4.6.3 Tear Resistance	88
	4.6.3.1 1 Effect of Process Variables BUR and	
	DR in Blown Film Process on Tear	

CHAPTER	P	AGE
	Resistance of LLDPE and	
	LLDPE/NR Blend Films	89
	4.6.3.2 Tear Resistance of LLDPE	
	and LLDPE/NR Blend Films Produced	
	from Chill Roll Cast Film Process.	91
	4.6.3.3 Effect of MA and NR Content on Tear	
	Resistance of LLDPE and LLDPE/NR	
	Blend Films Produced from Blown Film	
	and Chill Roll Cast Film Processes	94
	4.6.3.4 Effect of Biaxial and Uniaxial	
	Orientation in Blown Film and Cast	
	Film Processes on Tear Resistance	
	of LLDPE and LLDPE/NR Blend Films	95
V	CONCLUSIONS	96
	REFERENCES	97
	APPENDIX	105
	CURRICULUM VITAE	165

## LIST OF TABLES

TAE	BLE		PAGE
3.	.1	Physical properties of LLDPE films	23
3.	.2	Specification for standard Thai rubber (STR 5L)	24
3.	.3	Test condition for tensile testing	29
4.	. 1	Characteristics of LLDPE	33
4.	.2	Characteristics of NR	33
4.	.3	Characteristics of LLDPE/NR blends	34
4.	.4	Melt viscosity of LLDPE, NR and LLDPE/NR blends	36
4.	.5	Degree of crystallinity of LLDPE and LLDPE/NR blends	47
4.	.6	Glass transition temperature (Tg) of LLDPE,	
		NR and LLDPE/NR blends	49
4.	.7	Birefringence of LLDPE films from blown film at BUR 3	65
4.	8	Birefringence of LLDPE films from blown film at BUR 5	65
4.	9	Thickness of LLDPE and LLDPE/NR blend films from	
		blown film process at BUR 3	68
4.	10	Thickness of LLDPE and LLDPE/NR blend films from	
		blown film process at BUR 5	69
4.	11	Thickness of LLDPE and LLDPE/NR blend films from chill	
		roll cast film process	70

## LIST OF FIGURES

FIGURE		PAGE
2.1	Schematic describing film blowing process.	12
2.2	Schematic describing chill roll cast film process.	14
3.1	Twin screw extruder.	26
3.2	Constant-radius specimens for tear resistance test.	30
4.1	Blow instability of LLDPE at BUR 6.	37
4.2	Blow stability of LLDPE after introducing 10 % NR	
	at BUR 6.	38
4.3	Morphology of LLDPE/NR/MA at composition 70/30; a) 0% N	MА
	b) 1% MA, c) 3% MA and d) 5% MA (magnification 2000X).	40
4.4	Morphology of LLDPE/NR/MA at 70/30/0%; a) shear rate 46.:	54 s <sup>-1</sup> ,
	b) shear rate 139.6 $s^{-1}$ and d) shear rate 232.7 $s^{-1}$	
	(magnification 2000X).	42
4.5	Morphology of LLDPE/NR/MA at 70/30/1%; a) shear rate 40.7	70 s <sup>-1</sup> ,
	b) shear rate 122.10 s <sup>-1</sup> and d) shear rate 203.60 s <sup>-1</sup>	
	(magnification 2000X).	43
4.6	Morphology of LLDPE/NR/MA at 70/30/3%; a) shear rate 43.	12 s <sup>-1</sup> ,
	b) shear rate 129.40 s <sup>-1</sup> and c) shear rate 215.60 s <sup>-1</sup>	
	(magnification 2000X).	44
4.7	Morphology of LLDPE/NR/MA at 70/30/5%; a) shear rate 42	.40 s <sup>-1</sup> ,
	b) shear rate $127.20 \text{ s}^{-1}$ and d) shear rate $210.00 \text{ s}^{-1}$	
	(magnification 2000X).	45
4.8	Crystalline (f <sub>c</sub> ) and amorphous (f <sub>am</sub> ) orientation functions	
	of LLDPE blown films at BUR 3, DR 1, 3 and 5.	51
4.9	Crystalline (f <sub>c</sub> ) and amorphous (f <sub>am</sub> ) orientation functions	
	of LLDPE blown films at BUR 5, DR 1, 3 and 5.	51
4 10	Crystalline (f.) and amorphous (f.,,) orientation functions	

FIGURE	PAGE
of LLDPE /NR blown films at composition 90/10 wt% at BUF	₹3
and DR 1, 3 and 5.	52
4.11 Crystalline (f <sub>c</sub> ) and amorphous (f <sub>am</sub> ) orientation functions	
of LLDPE /NR blown films at composition 90/10 wt%	
at BUR 5, DR 1, 3 and 5.	52
4.12 Crystalline ( $f_c$ ) and amorphous ( $f_{am}$ ) orientation functions	
of LLDPE /NR blown films at composition 80/20 wt%	
at BUR 3 and DR 1, 3 and 5.	53
4.13 Crystalline ( $f_c$ ) and amorphous ( $f_{am}$ ) orientation functions	
of LLDPE /NR blown films at composition 80/20 wt%	
at BUR 5 and DR 1, 3 and 5.	54
4.14 Crystalline ( $f_c$ ) and amorphous ( $f_{am}$ ) orientation functions	
of LLDPE cast films at DR 1, 3 and 5.5.	55
4.15 Crystalline ( $f_c$ ) and amorphous ( $f_{am}$ ) orientation functions	
of LLDPE /NR cast films at composition 90/10 wt%	
at DR 1, 3 and 5.5.	56
4.16 Crystalline ( $f_c$ ) and amorphous ( $f_{am}$ ) orientation functions	
of LLDPE /NR cast films at composition 80/20 wt%	
at DR 1, 3 and 5.5.	56
4.17 Crystalline ( $f_c$ ) and amorphous ( $f_{am}$ ) orientation functions	
of LLDPE /NR cast films at composition 70/30 wt%	
at DR 1, 3 and 5.5.	57
4.18 Sketch of basic semicrystalline structure, the	
crystalline lamellae connected with amorphous segments	
by tie chains.	59
4.19 Crystalline ( $f_c$ ) and amorphous ( $f_{am}$ ) orientation function	
of LLDPE blown films at BUR 3 and	
chill roll cast film processes.	60

FIGURE	PAGE
4.20 Optical polarizing microscope of fully extended chains	
(a) cross polar (H) and b) $\lambda$ (magnification 400X).	63
4.21 Optical polarizing microscope for fully extended chains, c) $\lambda/4$	. 64
4.22 Optical polarizing microscope of LLDPE blown films	
at BUR 3.	66
4.23 Tensile strength at break for LLDPE blown films in MD and T	D
at BUR 3, DR 1, 3 and 5.	71
4.24 Tensile strength at break for LLDPE blown films in MD and T	CD
at BUR 5, DR 1, 3 and 5.	71
4.25 Tensile strength at break for LLDPE/NR blown films at	
composition 90/10 wt% in MD and TD at BUR 3,	
DR 1, 3 and 5.	72
4.26 Tensile strength at break for LLDPE/NR blown films at	
composition 90/10 wt% in MD and TD at BUR 5,	
DR 1, 3 and 5.	72
4.27 Tensile strength at break for LLDPE/NR blown films at	
composition 80/20 wt% in MD and TD at BUR 3,	
DR 1, 3 and 5.	73
4.28 Tensile strength at break for LLDPE/NR blown films at	
composition 80/20 wt% in MD and TD at BUR 5,	
DR 1, 3 and 5.	73
4.29 Tensile strength at break for LLDPE cast films at DR 1, 3	
and 5.5.	75
4.30 Tensile strength at break for LLDPE/NR cast films at	
composition 90/10 wt% in MD and TD at DR 1, 3 and 5.5.	76
4.31 Tensile strength at break for LLDPE/NR cast films at	
composition 80/20 wt% in MD and TD at DR 1, 3 and 5.5.	76
4.32 Tensile strength at break for LLDPE/NR cast films at	

FIGURE	PAGE
composition 70/30 wt% in MD and TD at DR 1, 3 and 5.5.	77
4.33 Tensile strength at break for LLDPE blown films	
at BUR 3 and films from chill roll cast film process.	79
4.34 Impact strength of LLDPE and LLDPE/NR blown films	
at composition 90/10 wt% at BUR 3.	81
4.35 Impact strength of LLDPE and LLDPE/NR blown films	
at composition 90/10 wt% at BUR 5.	82
4.36 Impact strength of LLDPE/NR blown films at	
composition 80/20 wt% at BUR 3.	82
4.37 Impact strength of LLDPE/NR blown films at	
composition 80/20 wt% at BUR 5.	83
4.38 Impact strength of LLDPE and LLDPE/NR cast films at	
composition 90/10 wt%.	85
4.39 Impact strength of LLDPE/NR cast films at	
composition 80/20 wt%.	85
4.40 Impact strength of LLDPE/NR cast films at	
composition 70/30 wt%.	86
4.41 Impact strength of LLDPE films produced by blown film at	
BUR 3 and chill roll cast film processes.	87
4.42 Tear resistance of LLDPE and LLDPE/NR blown films at	
composition 90/10 wt% at BUR 3.	89
4.43 Tear resistance of LLDPE/NR blown films at	
composition 90/10 wt% at BUR 5.	89
4.44 Tear resistance of LLDPE/NR blown films at	
composition 80/20 wt% at BUR 3.	90
4.45 Tear resistance of LLDPE/NR blown films at	
composition 80/20 wt% at BUR 5.	90
4.46 Tear resistance of LLDPE/NR cast films at	

FIGURE	PAGE
composition 90/10 wt%.	92
4.47 Tear resistance of LLDPE/NR cast films at	
composition 80/20 wt%.	92
4.48 Tear resistance of LLDPE/NR cast films at	
composition 70/30 wt%.	93
4.49 Tear resistance of film from blown film at BUR 3 and chill roll	
cast film processes.	95