

การเสริมการรับแรงของพอลิเมอร์ผสมพอลิเอทธิลีนและพอลิโพรพิลีน
โดยการเติมสารควบคู่ที่สังเคราะห์มาจากไดไอโซไซยานต



นางสาวเลิศลักษณ์ อุดมสุข

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี

คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2548

ISBN 974-53-2886-3

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

REINFORCEMENT OF POLYETHYLENE-POLYPROPYLENE MIXTURES
BY ADDING SYNTHESIZED DIISOCYANATE COMPATIBILIZERS

Miss Lerdlaksana Ubonnut

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering

Department of Chemical Engineering

Faculty of Engineering

Chulalongkorn University


Academic Year 2005

ISBN 974-53-2886-3


481637


Thesis Title REINFORCEMENT OF POLYETHYLENE-
POLYPROPYLENE MIXTURES BY ADDING
SYNTHESIZED DIISOCYANATE COMPATIBILIZERS
By Lerdlaksana Ubonnut
Field of Study Chemical Engineering
Thesis Advisor Associate Professor ML. Supakanok Thongyai, Ph.D.


Accepted by the Faculty of Engineering, Chulalongkorn University in
Partial Fulfillment of the Requirements for the Master's Degree

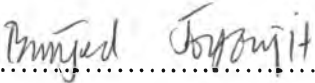

.....Dean of the Faculty of Engineering
(Professor Direk Lavansiri, Ph.D.)

THESIS COMMITTEE


..... Chairman
(Associate Professor Suttichai Assabumrungrat, Ph.D.)


..... Thesis Advisor
(Associate Professor ML. Supakanok Thongyai, Ph.D.)


..... Member
(Assistant Professor Seeroong Prichanont, Ph.D.)


..... Member
(Assistant Professor Bunjerd Jongsomjit, Ph.D.)

เลิศลักษณ์ อุบลนุช: การเสริมการรับแรงของพอลิเมอร์ผสมพอลิเอทิลีนและพอลิโพรพิลีนโดยการเติมสารควบคู่ที่สังเคราะห์มาจากไดไอโซไซยานาต (REINFORCEMENT OF POLYETHYLENE-POLYPROPYLENE MIXTURES BY ADDING SYNTHESIZED DIISOCYANATE COMPATIBILIZERS) อ. ที่ปรึกษา: รศ. ดร. มล. ศุภกนก ทองใหญ่, 112 หน้า, ISBN 974-23-2886-3

งานวิจัยนี้ มุ่งเน้นที่จะศึกษาเกี่ยวกับการเสริมการรับแรงของพอลิเมอร์ผสมพอลิเอทิลีนและพอลิโพรพิลีน เนื่องจากพอลิเมอร์ทั้งสองชนิดดังกล่าวไม่สามารถเข้ากันได้ทำให้คุณสมบัติทางกลลดลง จึงมีการสังเคราะห์สารควบคู่เพื่อเสริมการรับแรงให้กับพอลิเมอร์ผสมพอลิโพรพิลีนและพอลิเอทิลีนเพื่อเพิ่มการยึดติดระหว่างผิวสัมผัสระหว่างพอลิเมอร์ โดยสารควบคู่สังเคราะห์ได้จากตัวเร่งปฏิกิริยาซีเกลอร์-เนตดา โดยมีตัวเชื่อมระหว่างสายโซ่พอลิเอทิลีนและพอลิโพรพิลีนเป็นหมู่ไดไอโซไซยานาต พอลิเอทิลีน-บล็อก-พอลิโพรพิลีนที่ได้สามารถตรวจสอบได้ด้วยการวิเคราะห์โดยเครื่องมือ FTIR เมื่อเติมสารควบคู่ที่สังเคราะห์ได้ลงในพอลิเมอร์ผสมและวิเคราะห์โดยการศึกษากลศาสตร์ คุณสมบัติทางความร้อน และคุณสมบัติทางกล พบว่า คุณสมบัติทางกลของพอลิเมอร์ผสมพอลิเอทิลีนและพอลิโพรพิลีน (อัตราส่วน 50:50) ดีขึ้นเมื่อเติมสารควบคู่

ภาควิชา.....วิศวกรรมเคมี.....

สาขาวิชา.....วิศวกรรมเคมี.....

ปีการศึกษา..... 2548.....

ลายมือชื่อนิสิต.....เลิศลักษณ์ อุบลนุช.....

ลายมือชื่ออาจารย์ที่ปรึกษา..........

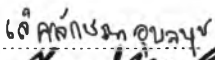
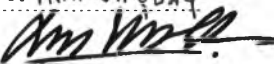
4770432721: MAJOR CHEMICAL ENGINEERING

KEY WORD: PE/PP BLEND, POLYETHYLENE-POLYPROPYLENE BLOCK
COPOLYMER, REINFORCE

LERDLAKSANA UBONNUT : REINFORCEMENT OF
POLYETHYLENE-POLYPROPYLENE MIXTURES BY ADDING
SYNTHESIZED DIISOCYANATE COMPATIBILIZERS. THESIS
ADVISOR: ASSOC. PROF. ML. SUPAKANOK THONGYAI, Ph.D., 112 pp.
ISBN 974-53-2886-3

Immiscible and incompatible binary blends of commercial polypropylene/polyethylene display poor mechanical properties. The addition of compatibilizer to reinforce and enhance an adhesion at the interfaces between polyethylene-polypropylene mixtures has been conducted. The compatibilizer chosen was in the group of Ziegler-Natta's polyethylene-polypropylene block copolymer with diisocyanate linkage. The effects of adding the compatibilizers were assessed by morphology studies, thermal analysis and mechanical testing. DSC curves of crystallization and FTIR provided evidences to support the formation of PP/PE block copolymer. Significant improvements in the mechanical properties of 50/ 50 PE/PP blends containing compatibilizer have been noted.

Department.....Chemical Engineering
Field of study.....Chemical Engineering
Academic Year.....2005.....

Student's signature.....
Advisor's signature.....

ACKNOWLEDGEMENTS

I would like to express my deeply gratitude to my advisor, Associate Professor Dr. ML. Supakanok Thongyai, Ph.D. to his continuous guidance, enormous number of invaluable discussions, helpful suggestions, warm encouragement, patience to correct my writing and all supporting. I am grateful to Associate Professor Suttichai Assabumrungrat, Ph.D., Assistant Professor Seeroong Prichanont, Ph.D. and Associate Professor Bunjerd Jongsomjit, Ph.D. for serving as chairman and thesis committees, respectively, whose comments were constructively and especially helpful.

This thesis would not be possible without the kind assistance from Associate Professor Takeshi Shiono, Bangkok Polyethylene Co., Ltd. For chemical supply and polymer characterization with GPC, Ms. Rujiporn, Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University, for SEM characterization and Department of Science Service for ^{13}C NMR and FTIR characterization by Ms. Nongnaphat Duangdee, and National Petrochemical (NPC) for chemical supply.

Sincere thanks are made to Mektec Manufacturing Corporation for using Differential Scanning Calorimetry (DSC), Universal Testing Machine, Dynamic Mechanical Analysis (DMA) and digital hot-plate stirrer, Polymer Engineering Research Laboratory (PEL), Chulalongkorn University for using and Hot Press.

Sincere thanks to all my friends and all members of the Center of Excellent on Catalysis & Catalytic Reaction Engineering (Petrochemical Engineering Research Laboratory), Department of Chemical Engineering, Chulalongkorn University for their assistance and friendly encouragement.

Finally, I would like to dedicate this thesis to my parents and my families, who generously supported and encouraged me through the year spent on this study.

CONTENTS

	Page
ABSTRACT(IN THAI).....	iv
ABSTRACT(IN ENGLISH).....	v
ACKNOWLEDGEMENTS.....	vi
CONTENTS.....	vii
LIST OF FIGURES.....	x
LIST OF TABLES.....	xiii
CHAPTERS	
I INTRODUCTION.....	1
1.1 The Objective of This Thesis.....	3
1.2 The Scope of This Thesis.....	3
II LITERATURE REVIEWS.....	4
2.1 Synthesize PE-b-PP copolymer.....	4
2.2 Blending and Mechanical Properties.....	6
III THEORY.....	9
3.1 Polyethylene.....	9
3.2 Polypropylene.....	10
3.2.1 General features.....	10
3.2.2 PP properties.....	12
3.3 Ziegler-Natta Catalyst.....	14
3.3.1 Stereospecificity.....	15
3.4 The molecular architecture of block copolymers.....	17
3.5 Polymer blends.....	18
3.5.1 Blends of block copolymer with two homopolymers.....	20
3.5.2 Methods of blending.....	22
3.6 Reinforecd Polymer Blends.....	24

	Page
3.7 Isocyanates.....	26
3.7.1 Reactions of isocyanates.....	27
3.8 Mechanical Properties.....	28
3.8.1 Stress-Strain Diagram.....	29
3.8.2 Type of Stress-Strain Curve.....	32
3.8.3 Tensile Test.....	33
3.9 Dynamic Mechanical Analysis.....	37
3.11.1 Introduction to dynamic mechanical analysis.....	34
3.11.2 Basic Principle.....	34
3.11.3 Time-Temperature Scans.....	37
IV EXPERIMENT.....	41
4.1 Equipments and Chemicals.....	41
4.1.1 Chemicals.....	41
4.1.2 Equipments.....	42
4.2 Preparation of Ziegler-Natta Precursor.....	46
4.3 Polymerization Procedure.....	47
4.4 Blocking Copolymerization.....	47
4.5 Blending Preparation.....	48
4.6 Molding Preparation.....	48
4.7 Characterization Instruments.....	48
4.7.1 Scanning Electron Microscope (SEM).....	48
4.7.2 Gel Permeation Chromatography (GPC).....	49
4.7.3 Infrared Spectroscopy (FTIR).....	49
4.7.4 ¹³ C-Nuclear Magnetic Resonance (13C-NMR).....	49
4.7.5 Differential Scanning Calorimetry (DSC).....	49
4.7.6 Dynamic Mechanical Analysis (DMA).....	50
4.7.7 Tensile testing machine.....	52

	Page
V RESULTS AND DISCUSSION.....	54
5.1 Functionalization of PP and PE by hydroxyl group.....	54
5.1.1 Chain structure of PE/PP block copolymer.....	54
5.2 Mechanical Properties.....	61
5.2.1 Tensile mechanical properties.....	61
5.2.2 Dynamic mechanical properties.....	65
5.3 Morphology.....	69
VI CONCLUSIONS AND SUGGESTIONS.....	73
6.1 Conclusions.....	73
6.2 Recommendations.....	74
REFERENCES.....	75
APPENDICES.....	78
APPENDIX A.....	79
APPENDIX B.....	81
APPENDIX C.....	84
APPENDIX D.....	88
APPENDIX E.....	90
APPENDIX F.....	106
VITA.....	112

LIST OF FIGURES

Figure	Page
3.2.1 Polymerization of propylene.....	10
3.2.2 Schematic illustration of chains organization in PP spherulites.....	11
3.4.1 Molecular architecture of block copolymers.....	18
3.5.1 The different morphologies exhibited by immiscible blends of polymers.....	20
3.5.2 Schematic diagram showing location of block and graft copolymers at phase interfaces.....	21
3.7.1 Structure of Diisocyanates.....	27
3.7.2 Polyurethane addition reaction.....	27
3.8.1 A typical stress-strain curve.....	28
3.8.2 Extension types (a) bond bending (b) uncoiling (c) slippage.....	31
3.8.3 Types of stress-strain curve.....	32
3.8.4 Diagram illustrating stress-strain curve form which modulus and elongation values are derived.....	33
3.9.1 How a DMA works.....	35
3.9.2 Stress-strain curves relate force to deformation.....	35
3.9.3 DMA relationships.....	36
3.9.4 Storage and loss.....	36
3.9.5 Time-temperature studies in the DMA (a) Vary temperature (b) Hold temperature constant.....	37
3.9.6 Ideallized temperature scan of a polymer.....	39
3.9.7 Operating range by DMA (a) Polycarbonate (b) Epoxy and (c) Polypropylene.....	40
4.1.1 (a) Glove box.....	43
4.1.2 (b) Schlenk line.....	44
4.1.3 (c) Schlenk tube.....	44

Figure	Page
4.1.4 (d) Inert gas supply system.....	45
4.1.5 (e) Vacuum pump.....	45
4.3 Polymerization line.....	47
4.4 Blocking copolymerization.....	48
4.7.1 Differential Scanning Calorimetry (DSC) Equipment.....	50
4.7.2 Dynamic Mechanical Analysis (DMA) Equipment.....	51
4.7.3 Universal Testing Machine equipment.....	52
4.8 Flow diagram of research methodology.....	53
5.1.1 The block copolymerization.....	54
5.1.2 IR-spectra of PE-b-PP at 25 °C.....	56
5.1.3 DSC curve of the addition of PE-b-PP 6% to PE/PP blend.....	60
5.1.4 DSC endotherms of PP/PE blend , PE-b-PE and addition of PE-b-PP to PE/PP blend after thermal segregation treatment.....	60
5.2.1 Tensile strength of PE/PP blend.....	61
5.2.2 Tensile strength of 3% PE-b-PP in PE/PP blend.....	62
5.2.3 Tensile strength of 6% PE-b-PP in PE/PP blend.....	62
5.2.4 Tensile strength of 12% PE-b-PP and 20% PE-b-PP in PE/PP blend.....	63
5.2.5 Additive effect of PE-b-PP to PE/PP blend on stress -strain behavior at 25 °C.....	64
5.2.6 DMA curves (storage modulus (E') and temperature) for PE/PP and compatibilised PE/PP.....	67
5.2.7 DMA curves (loss modulus (E'') and temperature) for PE/PP and compatibilised PE/PP.....	67
5.2.8 DMA curves (tanδ and temperature) for PE/PP and compatibilised PE/PP.....	68
5.3.1 SEM of tensile fracture surface of a)PP b) PE/PP blend c) PE/PP + PEbPP3% d) PE/PP+ PEbPP6% e) PE/PP+ PEbPP12% f) PE/PP+ PEbPP20%.....	71
5.3.2 SEM of cryogenic fracture surface of a) PE b) PP c) PE/PP blend d) PE/PP+ PEbPP3% e) PE/PP+ PEbPP6% f) PE/PP+ PEbPP12% g) PE/PP+ PEbPP20%.....	72

Figure	Page
A.1 C ¹³ NMR spectrum of PE-b-PE	79
A.2 C ¹³ NMR spectrum of PP-b-PP	79
A.3 C ¹³ NMR spectrum of PP-b-PP	80
A.4 C ¹³ NMR spectrum of PE-b-PP	80
A.5 C ¹³ NMR spectrum of PE-b-PP	80
B.1 GPC curve of PEOH	81
B.2 GPC curve of PPOH	81
B.3 GPC curve of PE-b-PE01	81
B.4 GPC curve of PE-b-PE02	82
B.5 GPC curve of PE-b-PE03	82
B.6 GPC curve of PE-b-PP01	82
B.7 GPC curve of PE-b-PP02	83
B.8 GPC curve of PE-b-PP03	83
C.1 DSC curve of PEOH	84
C.2 DSC curve of PPOH	84
C.3 DSC curve of PE-b-PE	84
C.4 DSC curve of PP-b-PP	85
C.5 DSC curve of PE/PP blend	85
C.6 DSC curve of PE-b-PP	85
C.7 DSC curve of PE/PP blended with 3%PE-b-PP	86
C.8 DSC curve of PE/PP blended with 6%PE-b-PP	86
C.9 DSC curve of PE/PP blended with 12%PE-b-PP	86
C.10 DSC curve of PE/PP blended with 20%PE-b-PP	87
D.1 DMA curve of PE	88
D.2 DMA curve of PE/PP blend	88
D.3 DMA curve of PE/PP blended with 3% PE-b-PP	88
D.4 DMA curve of PE/PP blended with 6% PE-b-PP	89
D.5 DMA curve of PE/PP blended with 12% PE-b-PP	89
D.6 DMA curve of PE/PP blended with 20% PE-b-PP	89

LIST OF TABLES

Table	Page
3.1.1 Types of Polyethylene.....	10
3.2.1 Properties of Commodity Polyolefins.....	13
3.8.1 Characteristic features of stress-strain curve as they relate to the polymer properties.....	32
4.7.1 Conditions and parameter for running DMA.....	51
5.1.1 The molecular weight of all synthesized PE-b-PP.....	57
5.1.2 Characterization of polymers.....	59
5.2.1 Prediction of T _g , T _m from DMA experiment.....	68