โพลิเมอร์ผสมระหว่างโพลิแอไมค์กับโพลิสไตรีนชนิคทนแรงกระแทกสูง

นาย ศรมิษฐ์ หอบุญมาสุทธิ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

ภาควิชาวิศวกรรมเคมี

บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

พ.ศ. 2539

ISBN 974-634-528-1

ลิขสิทธิ์ของบัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

A POLYMER BLEND OF POLYAMIDE AND HIGH IMPACT POLYSTYRENE

Mr. Sorramit Horboonmasuth

A Thesis Submitted in Partial Fulfillment of the Requirements for the

Degree of Master of Engineering

Department of Chemical Engineering

Graduate School

Chulalongkorn University

1996

ISBN 974-634-528-1

Thesis Title

A POLYMER BLEND OF POLYAMIDE AND

HIGH IMPACT POLYSTYRENE

By

Mr. Sorramit Horboonmasuth

Department

Chemical Engineering

Thesis Advisor

Dr. Sirijutaratana Covavisaruch

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

(Associate Professor Santi Thoongsuwan, Ph.D.)

Thesis Committee

Wibrit Vanthypanichakon. Chairman

(Professor Wiwut Tanthapanichakoon, Ph.D.)

(Sirijutaratana Covavisaruch, Ph.D.)

Assistant Professor Sasithorn Boon-Long, Dr. 3 ieme Cycle)

พิมพ์ต้นฉบับบทคัดย่อวิทยานิพนธ์ภายในกรอบสีเขียวนี้เพียงแผ่นเดียว

ศรมิษฐ์ หอบุญมาสุทธิ์: โพลิเมอร์ผสมระหว่างโพลิแอไมด์กับโพลิสไตรีน (A POLYMER BLEND OF POLYAMIDE AND HIGH IMPACT POLYSTYRENE) อาจารย์ที่ปรึกษา : อ.คร. สิริจุฑารัตน์ โควาวิสารัช, 152หน้า. ISBN 974-634-528-1

การวิจัยนี้ศึกษาโพลิเมอร์ผสมระหว่าง โพลิแอไมด์ 6 (PA6) และโพลิสไตรีนชนิดทนแรง กระแทกสูง (HiPS) ที่อัตราส่วน 20/80 40/60 60/40 และ 80/20 PA6/HiPS ตามลำดับ นอกจากนี้ ยังศึกษา การปรับปรุงสมบัติโพลิเมอร์ผสมโดยเติมโคโพลิเมอร์ของสไตรีนเอทิลีนบิวทิลีนที่ต่อแขนงกับมาลิอิค แอนไฮไดรด์ (SEBS-g-MA) เป็นตัวช่วยให้เข้ากันที่ปริมาณ 2.5, 5, 7.5 และ 10 ส่วนในร้อยส่วนของโพลิ เมอร์ผสม การศึกษาด้านสมบัติเชิงกล โดยการดึง การกระแทก และ อุณหภูมิที่ทำให้โค้งผิดรูป พบว่าเมื่อ ใส่ SEBS-g-MA โพถิเมอร์ผสมที่อัตราส่วน 20/80 60/40 และ 80/20 PA6/HiPS มีความเหนียวดีขึ้น ยกเว้น ที่อัตราส่วน 40/60 PA6/HiPS ซึ่งความเหนียวด้อยลง อย่างไรก็ตาม สมบัติด้านเชิงกลของโพลิเมอร์ผสมที่ ได้ยังคงต่ำกว่าโพลิเมอร์พื้นฐานทั้งสอง การศึกษาสมบัติเชิงความร้อน จากอุณหภูมิสภาพคล้ายแก้ว พบว่า โพลิเมอร์ผสมทั้งที่เติมและไม่เติม SEBS-g-MA เป็นโพลิเมอร์ผสมประเภทมีการเข้ากันได้บางส่วน การ ศึกษาระดับจลภาค พบว่าการเติม SEBS-g-MA ช่วยให้การกระจายตัวและการแพร่ของวักภาคดีขึ้น สำหรับกรณี 40/60 PA6/HiPS มีการเปลี่ยนลักษณะของวัฏภาคกระจายตัวจากเดิมที่เป็นเส้นใยในกรณีไม่ เติม SEBS-g-MA เป็นอนุภาคกระจายตัวในกรณีที่เติม SEBS-g-MA ซึ่งสอดคล้องกับการลดลงของความ เหนียวที่อัตราส่วนนี้ และแสดงให้เห็นว่าสัณฐานของโพลิเมอร์ผสมมีผลต่อสมบัติด้านเชิงกลของโพลิเมอร์ ผสมที่ได้

ภาควิชา	วิศวกรรมเคมี	
สาขาวิชา	วิศวกรรมเคมี	
ปีการศึกษา	2538	

ลายมือชื่อนิสิต	Post	mann N	
ลายมือชื่ออาจารย์		0 // 1 A	m
ลายมือชื่ออาจารย์	ที่ปรึกษาร่วม	•	

a distributed in the state of t

C516957 : MAJOR CHEMICAL ENGINEERING

KEY WORD: POLYMER BLEND/ POLYAMIDE/ HIPS/ INCOMPATIBILITY/ PARTIAL MISCIBILITY SORRAMIT HORBOONMASUTH: A POLYMER BLEND OF POLYAMIDE AND HIGH IMPACT POLYSTYRENE.

THESIS ADVISOR: SIRIJUTARATANA COVAVISARUCH, Ph.D.

152 pp. ISBN 974-634-528-1

This research aims to study a polymer blend between polyamide 6 (PA6) and high impact polystyrene at a blend ratios of 20/80, 40/60, 60/40 and 80/20 PA6/HiPS respectively. Maleated styrene-ethylene/butylene-styrene block copolymer (SEBS-g-MA) is added as a compatibilizer for the blend systems. The mechanical properties in terms of tensile properties, impact properties and the heat distortion temperature were investigated. The study shows that the addition of the SEBS-g-MA compatibilizer improves the toughness of almost all the polymer blends except the 40/60 PA6/HiPS. At such composition, the addition of the SEBS-g-MA shows an adverse effect in toughness. However, most of the mechanical properties of the polymer blends are still lower than both parent polymers. The thermal properties in terms of the glass transition and the melting point temperature were also studied. The results imply that uncompatibilized and compatibilized polymer blends are partially miscible. Microscopic study of the polymer blends shows that the addition of the compatibilizer improves the distribution and the dispersion of domain phase in the matrix. For 40/60 PA6/HiPS, the addition of the SEBS-g-MA compatibilizer changes from the fibril domain phase observed when SEBS-g-MA is not applied to a particle domain phase when SEBS-g-MA is applied. This change explains the reduction of the toughness at the 40/60 ratio. In addition, it shows the influence of the polymer blend morphology on the mechanical properties of the blends.

ภาควิชา	วิศวกรรมเคมี
สาขาวิชา	วิศวกรรมเคมี
รีไการศึกษา	2538

ACKNOWLEDGEMENTS

With the assistance and collaboration of many people, this research work and thesis is completed. I wish to extend my heart-felt thanks to Dr. Sirijutaratana Covavisaruch, my thesis advisor, for her help which is first and foremost contributed to me. I also thank members of my thesis committee, Assistant Professors Dr.Sasithorn Boon-Long and Professor Wiwut Tanthapanichakoon of the Chemical Engineering Department, Faculty of Engineering, who have kindly given their valuable time to comments on my thesis. Thanks are also extended to Bangkok Polyethylene Co., Ltd. (BPE) for their kind permission in allowing me to enjoy all facilities in their factory with the best co-operation from Mr. Anusorn Pumchusak and Ms. Nuchanan Utairatana who have given me best help; Ms. Sutathip Tangrotanasophan of Pacific Plastics (Thailand) Ltd., Mrs. Nutha Chiralak and Ms. Wannaporn Chongpiyarat of The Shell Co., Ltd. of Thailand; Mr. Verasak Krudthaphan and other students in the polymer laboratory. I thank all members of my family for their unfailing support and encouragement.

CONTENTS

PAGE

ABSTRACT (THAI) iv ABSTRACT (ENGLISH) v ACKNOWLEDGEMENTS vi CONTENTS -----vii LIST OF TABLES xii **CHAPTER** INTRODUCTION — 1 1.1 General Introduction _____1 1.2 The Purpose of the Present Study 3 II 2.1 Polymer Blends 4 2.2.1 Glass-transition Temperature — 9 2.2.2 Scattering 2.2.3 Microscopy — 14 2.3 The Methods of Blending 14 2.3.1 Melt mixing 14

PAGE

2.3.1.1 Mechanical mixing	14
2.3.1.2 Mechano-chemical mixing	
(Reactive mixing):	15
2.3.2 In situ polymerization	16
2.3.3 Solution blending	16
2.4 Properties of polymer blends	19
2.4.1 Miscible blends	19
2.4.1.1 Thermal properties	19
2.4.1.2 Mechanical properties	22
2.4.2 Immiscible Blends	23
2.4.2.1 Thermal property	23
2.4.2.2 Mechanical properties	24
2.4.2.3 Interfacial adhesion	25
2.4.2.4 Morphology	26
2.4.3 Partially miscible or Compatibilized blends	27
2.4.3.1 Thermal property	27
2.4.3.2 Mechanical properties	28
2.4.3.3 Interface adhesion	29
2.4.3.4 Morphology	31
2.5 Phase inversion	32
2.6 Blend morphology	
2.6.1 Morphology generation and control	38
2.7 Process	

PAGE

	2.8 Compatibilization	41
	2.8.1 Types and characteristics of compatibilizing	
	reaction	44
	2.8.2 Routes to reactive compatibilization	46
	2.8.2.1 Functionalized blend components	46
	2.8.2.2 Polymeric compatibilizers	48
	2.8.2.3 Low MW. compatibilizing compounds	49
	2.9 Literature survey	51
Ш	EXPERIMENTAL WORK	54
	3.1 Materials	54
	3.1.1 Polyamide6	54
	3.1.2 High Impact Polystyrene	54
	3.1.3 Maleated Styrene-Ethylene/Butylene-Styrene	
	Block Copolymer	56
	3.2 Mixing and sample preparation	57
	3.2.1 Mixing ————————————————————————————————————	57
	3.2.2 Mechanical blending	58
	3.2.3 Molding and specimens preparation	60
	3.3 Mechanical Test	
	3.3.1 Tension test	61
	3.3.2 Impact test	62
	3.3.2.1 Izod impact test	62
	3.3.2.2 Falling weight test	63

PAGE

	3.3.3 Heat-distortion temperature (HDT)	64
	3.4 Characterization	65
	3.4.1 Density measurement	65
	3.4.2 Dynamic mechanical test	65
	3.4.3 Differential Scanning Calorimeter (DSC)	67
	3.4.4 Fractography	67
IV	RESULTS AND DISCUSSIONS	68
	4.1 Mixer test	68
	4.2 Mechanical Properties	72
	4.2.1 Effect of compatibilizer content on parent	72
	4.2.1.1 Tensile properties	73
	4.2.1.2 Izod impact test	85
	4.2.1.3 Falling-weight test	87
	4.2.1.4 Heat-distortion temperature; HDT	89
	4.2.2 PA6/HiPS blends	90
	4.2.2.1 Tensile properties	90
	4.2.2.2 Izod impact strength	114
	4.2.2.3 Falling-weight test.	118
	4.2.2.4 Heat-distortion temperature; HDT	122
	4.3 Characterization	125
	4.3.1 Density	125
	4.3.2 Dynamic Mechanical Thermal Analysis	
	(DMTA)	127
	4.3.3 Differential Scanning Colorimeter (DSC)	131

		PAGE
	4.3.4 Fractography	-136
V	CONCLUSION —	- 142
	5.1 Conclusion	- 142
	5.2 Recommendation for further studies	- 144

REFERENCES — 145

LIST OF TABLE

TABLE		PAGE
2.1	The advantages and disadvantages of various	
	blending or alloying equipments.	15
2.2	The advantage and disadvantage of each blending	
	method.	18
2.3	Molecular and morphological parameters that	
	influence technical properties.	29
2.4	Compatibilization through the reaction	
	functionalized blend components.	47
2.5	Compatibilization through reactive copolymers	
	functionlized polymers added separately.	48
2.6	Compatibilization through Low MW reactive	
	compounds promoting copolymer formation.	49
2.7	Compatibilization through Low MW reactive	
	compounds promoting copolymer formation and	
	cross-linking reactions.	50
3.1	Formulation of the PA6/HiPS blend in the mixer.	57
3.2	Formulations of PA6/HiPS blends by Twin screw	
	extruder.	59
4.1	Torque and Relative melt viscosity of parent polymer	
	in each condition	60

LIST OF FIGURES

FIGURE	PAGE
2.1	Morphologies of a blend of polymer-A and
	polymer-B.——5
2.2	Interrelations in polymer blend nomenclature. 7
2.3	Approximate ranges of experimental techniques to
	study blend morphology.——9
2.4	Effects of composition on the temperature
	dependence of the modulus or the stiffness.——————————————————10
2.5	DSC thermogram of a miscible one-phase 50:50
	blend of polycarbonate (PC) and poly(cyclohexane-
	1,4-dimethanol-co-terephthalate)(PCTD).——11
2.6	DSC thermogram of an immiscible one-phase 50:50
	blend of polycarbonate(PC) and polystyrene(PS).——12
2.7	Transparency plotted against composition for blends of
	PC with PCTD and PC with PETG or poly(ethylene
	glycol-co-cyclohexane-1,4-dimethanal terephthalate)
	(PETG).————————————————————————————————————
2.8	The polymer mixtures are classified in terms of
	preparation.method.
2.9	Typical property of a polymer blend against the
	composition for miscible blends of polymers-A
	and -B20

FIGURE	PAGE
2.10	Mechanical property against the composition
	profiles of immiscible and miscible blends.————25
2.11	Modulus-temperature behavior of blends of
	polystyrene with a 30/70 butadiene/styrene
	copolymer. 27
2.12	Phase dispersion and distribution. 28
2.13	Composition profiles at a polymer-polymer
	interface and interface thickness.
2.14	An idealized phase continuity diagram for
	mechanical blends.
2.15	Different types of dispersion of a polymer in the
	matrix of an immiscible polymer. 36
2.16	Various possibilities for morphological phase
	arrangement in polymer composites and blends.——37
2.17	Conceptual illustration of interpenetrating network
	of phases by showing the two interlocking material
	separated from one another.————————————————————————————————————
2.18	Molecular interaction on the phase contact surface.—41
2.19	Schematic of phase size in miscible, immiscible and
	compatibilized polymer blends.————————————————————————————————————
2.20	Examples of common compatibililizing reactions
	between functionalized blend constituents.——45
3.1	The chemical structure of polyamide 654
3.2	Morphology of the conventional HiPS.

FIGURE	P	AGE
3.3	The chemical structure of SEBS block copolymers.	-56
3.4	Maleic anhydride reaction with saturated	
	hydrocarbon elastomers.	57
3.5	The dimension of the dumbell specimens of type	
	IV.	61
3.6	The dimension of Izod test specimen.	63
3.7	Apparatus for deflection temperature test.	64
4.1	The sequence of the breakup of droplets in a simple	
	shear field.	69
4.2	The torque time diagram of mixing	
	uncompatibilized PA6/HiPS blends.	71
4.3	The load-deformation diagram from tensile test of	
	compatibilized PA6 and HiPS.	73
4.4	The tensile elastic modulus of compatibilized PA6	
	and HiPS plotted against the SEBS-g-MA	
	concentrations.	74
4.5	The 0.2% offset tensile yield stress of	
	compatibilized PA6 and HiPS plotted against the	
	SEBS-g-MA concentrations.	75
4.6	The 0.2% offset tensile yield strain of	
	compatibilized PA6 and HiPS plotted against the	
	SFBS-g-MA concentrations.	77

FIGURE	DACE
FIGURE	PAGE

4.7	The tensile stress at break of compatibilized PA6	
	and HiPS plotted against the SEBS-g-MA	
	concentrations.	··· 78
4.8	The tensile strain at break of compatibilized PA6	
	and HiPS plotted against the SEBS-g-MA	
	concentrations.	79
4.9	The tensile work done of compatibilized PA6 and	
	HiPS plotted against the SEBS-g-MA	
	concentrations.	··· 81
4.10	Schematic diagram for the deformation mechanism	
	of an idealized morphology under uniaxial tensile	
	test: (a) before and (b) after deformation.	84
4.11	The Izod impact strength of compatibilized PA6	
	and HiPS plotted against the SEBS-g-MA	
	concentrations.	85
4.12	The of Falling-weight impact energy compatibilized	
	PA6 and HiPS plotted against the SEBS-g-MA	
	concentrations.	87
4.13	The heat-distortion temperature of compatibilized	
	PA6 and HiPS plotted against the SEBS-g-MA	
	concentrations.	89
4.14	The load-deformation diagram from tensile test of	
	uncompatibilized PA6/HiPS blends.	- 91
4.15	The load-deformation diagram from tensile test of	
	compatibilized PA6/HiPS blends.	92

FIGURE		PAGE
4.16	The tensile elastic modulus of uncompatibilized an	d
	compatibilized PA6/HiPS blends plotted against th	e
	PA6 concentrations.	93
4.17	The tensile elastic modulus of compatibilized	
	PA6/HiPS blends plotted against the compatibilize	r
	concentrations.	94
4.18	The 0.2% offset tensile yield stress of	
	uncompatibilized and compatibilized PA6/HiPS	
	blends plotted against the PA6 concentrations.	96
4.19	The 0.2% offset tensile yield stress of	
	compatibilized PA6/HiPS blends plotted against th	e
	compatibilizer concentrations.	98
4.20	The 0.2% offset tensile yield strain of	
	uncompatibilized and compatibilized PA6/HiPS	
	blends plotted against the PA6 concentrations.	100
4.21	The 0.2% offset tensile yield strain of	
	compatibilized PA6/HiPS blends plotted against th	e
	compatibilizer concentrations.	101
4.22	The tensile stress at break of uncompatibilized and	
	compatibilized PA6/HiPS blends plotted against the	e
	PA6 concentrations.	103
4.23	The tensile stress at break of compatibilized	
	PA6/HiPS blends plotted against the compatibilizer	
	concentrations.	105

FIGURE		PAGE
4.24	The tensile strain at break of uncompatibilized and compatibilized PA6/HiPS blends plotted against the	
4.25	PA6 concentrations. The tensile strain at break of compatibilized PA6/HiPS blends plotted against the compatibilizer	·· 107
4.26	The tensile work done of uncompatibilized and compatibilized PA6/HiPS blends plotted against the	
4.27	PA6 concentrations. The tensile work done of compatibilized PA6/HiPS blends plotted against the compatibilizer	111
4.28	concentrations. The Izod impact strength of uncompatibilized and compatibilized PA6/HiPS blends plotted against the	
4.29	PA6 concentrations. The Izod impact strength of compatibilized PA6/HiPS blends plotted against the compatibilizer	114
4.30	The Falling-weight energy of uncompatibilized and compatibilized PA6/HiPS blends plotted against the	
4.31	PA6 concentrations. The Falling-weight impact energy of compatibilized PA6/HiPS blends plotted against the compatibilizer	··· 118

concentrations.

FIGURE	-	PAGE
4.32	The Heat-distortion temperature of	
	uncompatibilized and compatibilized PA6/HiPS	100
	blends plotted against the PA6 concentrations.	122
4.33	The heat-distortion temperature of compatibilized	
	PA6/HiPS blends plotted against the compatibilizer	
	concentrations.	123
4.34	The density of blend against the percentage of	
	polyamide 6.	125
4.35	The glass transition temperature (Tg) of each	
	component for the uncompatibilized PA6/HiPS	
	blends and the compatibilized PA6/HiPS blends	
	against the percentage of Polyamide 6.	128
4.36	The glass transition temperature of PS in HiPS	
	against the percentage of Polyamide 6.	131
4.37	The melting point of Polyamide 6 in blend against	
	the percentage of Polyamide 6.	132
4.38	The heat of fusion against the percentage of	
	Polyamide 6.	··· 134
4.39	Crystallinity of the polyamide 6 against the	
	percentage of Polyamide 6.	135
4.40	The morphology of incompatible blend at different	
	composition of PA6 and HiPS.	137
4.41	The morphology of compatible blend plotted	

against the 2.5 phr of SEBS-g-MA.

FIGURE		PAGE
4.42	The morphology of compatible blend of	
	composition of PA6/HiPS 80/20 with 2.5 to 7.5 ph	r
	of SEBS-g-MA.	139
4.43	The morphology of compatibilized blends when	
	using high magnification.	141

NOMENCLATURES

ΔG_{m}	Gibbs' free energy of mixing
ΔH_2	Heat of fusion of 100% Crystalline part
ΔH_{m}	Enthalpy of mixing
χ12	Interaction Parameter of the blends
χ_{AB}	Flory-Huggins interaction parameter
δ	Phase angle
δ_1 , $\delta 2$	Solubility parameters of two homopolymers; 1, 2
ф	Phase volume fraction
ϕ_2	Volume Fraction of Crystalline Part
γ	Shear rate
γ_1, γ_2	Degree of Polymerization
η	Melt viscosity
η_{d}	Viscosity of the matrix
η_{m}	Viscosity of the droplet
σ	Interfacial tension
а	Characteristic interfacial thickness;
В	The minor axis of the ellipsoidal deformed droplet in
	the shear field
B_{12}	Interaction energy density
D	Deformation of a droplet in the shear field
	Glass transition temperature of the mixture

The major axis of the ellipsoidal deformed droplet in the shear field

P Viscosity ratio

R Radius of the droplet

T_g Glass-transition temperature

T_{g,i} Glass transition temperature of the *i*th component

T_m Equilibrium melting temperature

T_m° Equilibrium temperature of Pure Component

V₁, V₂ Molar Volume of amorphous and Crystalline

components in the shear field

We Weber number

Wi Weight fraction of the ith component