# MISCIBLE BLENDS OF ESCOR $^{TM}$ ACID TERPOLYMER AND EAA COPOLYMERS

Ms. Nathaporn Somrang

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

2003
ISBN 974-17-2331-8

Thesis Title:

Miscible Blends of ESCOR<sup>TM</sup> Acid Terpolymers

and Ethylene Acrylic Acid Copolymers

By:

Nathaporn Somrang

Program:

Polymer Science

**Thesis Advisors:** 

Dr. Manit Nithitanakul

Assoc. Prof. Brian. Grady

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

K. Bunyahint - College Director

(Assoc. Prof. Kunchana Bunyakiat)

**Thesis Committee:** 

(Dr. Manit Nithitanakul)

(Assoc. Prof. Brian. Grady)

(Asst. Prof. Rathanawan Magaraphan)

(Asst. Prof. Pitt Supaphol)

#### **ABSTRACT**

4472011063 : POLYMER SCIENCE PROGRAM

Nathaporn Somrang: Miscible Blend of ESCOR<sup>TM</sup> Acid

Terpolymer and EAA Copolymers

Thesis Advisor: Dr. Manit Nithitanakul and Assoc. Prof. Brian

Grady, 114 pp. ISBN 974-17-2331-8

Keywords : Miscible blend/ ESCOR<sup>TM</sup> terpolymer/ Ethylene acrylic acid

copolymer/ Nonisothermal crystallization/ Crystallization kinetics

Ethylene-methyl acrylate-acrylic acid terpolymers (ESCOR<sup>TM</sup>) Ethylene-acrylic acid copolymers (EAA) were studied crystallization kinetics in nonisothermal conditions using Differential Scanning Calorimetry (DSC). nonisothermal crystallization of ethylene-methyl acrylate-acrylic acid terpolymers (ESCOR<sup>TM</sup>) and Ethylene-acrylic acid copolymers (EAA) data were analyzed for their kinetic parameters using Avrami, Ozawa, Ziabicki and Friedman models. In addition, the blends of ESCOR<sup>TM</sup> 325 terpolymers and four different grades of EAA copolymers containing different amount of acrylic acid at various blend compositions were prepared by melt mixing on a twin-screw extruder. The miscibility of blends was investigated by dynamic mechanical measurements. Rheological, thermal, mechanical, and dynamic mechanical properties of the ESCOR<sup>TM</sup> 325/EAAs blends were also studied. The results showed that the rheological properties such as the storage and loss modulus of the blends were slightly increased with increased EAA contents, but the complex viscosity of the blend decreased with increased EAA contents. In addition, most blends exhibited improvement in tensile strength at break, Young's modulus, hardness (shore-D), and a reduction in elongation at break with the increase in EAA content. Escor<sup>TM</sup>/EAA5 blends consisted EAA5 content from 80 to 95%wt in blends showed synergestic behavior (tensile strength, young's modulus and hardness) due to higher percent crystallinity, whereas most of blends at low EAA contents showed property values below a linear relationship because of phase separation.

## บทคัดย่อ

ณัฐพร สมร่าง: การศึกษาการผสมเข้าเป็นเนื้อเดียวกันระหว่าง ESCOR™ เทอร์พอลิเมอร์ และ EAAโคพอลิเมอร์ (Miscible Blend of ESCOR<sup>™</sup> Acid Terpolymer and EAA Copolymers) อ.ที่ปรึกษา: คร. มานิตย์ นิธิธนากุล และ รศ. ไบรอัน แกรคี้ 114 หน้า ISBN 974-17-2331-8

งานวิจัยนี้มุ่งถึงการศึกษาจลศาสตร์การตกผลึกแบบอุณหภูมิไม่คงที่ของเอทิลีนเมททิล อะคริเลทอะคริลิกเอซิดและเอทิลีนอะคริลิกเอซิดโดยใช้เทคนิค DSC ข้อมูลการทดลองจากการ ตกผลึกแบบอุณหภูมิแบบไม่คงที่ถูกวิเคราะห์โดยการเปรียบเทียบค่าที่ได้จากการทดลองกับค่าที่ ได้จากแบบจำลองของ Avarami Ozawa Ziabicki และ Friedman นอกจากนั้นคุณสมบัติต่างๆ และการผสมเข้าเป็นเนื้อเดียวกัน ได้แก่ คุณสมบัติเชิงกล (Mechanical properties) คุณสมบัติ เชิงความร้อน (Thermal analysis) คุณสมบัติใดนามิกส์เชิงกล (Dynamic mechanical properties) และคุณสมบัติการใหล (Rheological properties) ของพอลิเมอร์ผสมระหว่าง ESCOR™ เทอร์พอลิเมอร์และ EAAโคพอลิเมอร์ ค่าคุณสมบัติเชิงกล ได้แก่ ความต้านทานต่อ การดึงยึด (Tensile strength) ความแข็ง (Hardness) ค่าความใส (Gloss) และค่าโมคูลัส (Young's modulus) พบว่ามีค่าเพิ่มขึ้นเมื่อเพิ่มอัตราส่วนของ EAAโคพอถิเมอร์ ขณะที่บาง อัตราส่วนมีค่าสูงกว่าความสัมพันธ์นี้ เนื่องจากเกิดปริมาณผลึกเพิ่มขึ้น อย่างไรก็ตามบางอัตราส่วน ได้มีค่าต่ำกว่าความสัมพันธ์นี้ เพราะว่าการแยกเฟสของพอลิเมอร์ผสม ค่าความด้านทานต่อการดึง ยืดตามความยาว (Elongation at break) ของพอถิเมอร์ผสมนี้มีค่าลคลงเมื่อเพิ่มอัตราส่วนของ EAAโคพอลิเมอร์ แสดงว่าพอลิเมอร์ผสมมีความเปราะเพิ่มขึ้นเมื่ออัตราส่วนของ EAAโคพอลิ เมอร์เพิ่มขึ้น ส่วนค่าคุณสมบัติเชิงความร้อน (Thermal analysis) และคุณสมบัติการใหล (Rheological properties) ของของพอลิเมอร์ผสมมีคุณสมบัติดีขึ้นเมื่ออัตราส่วนของ EAAโค พอลิเมอร์เพิ่มขึ้น นอกจากนั้นคณสมบัติการแสดงการเข้าเป็นเนื้อเดียวกัน ได้อย่างดี จากงานวิจัยนี้ สามารถสรุปว่าพอลิเมอร์ผสมระหว่าง ESCOR<sup>TM</sup> กับ EAA1 และ EAA5 ที่อัตราส่วนระหว่าง 80 ถึง 90 เปอร์เซ็นต์โดยน้ำหนัก EAA แสดงค่าคุณสมบัติเชิงกลค่อนข้างสูง เนื่องจากมีความเป็น ผลึกสูงขึ้น

#### **ACKNOWLEDGEMENTS**

The author would like for express my deepest appreciation to Dr. Manit Nithitanakul, my Thai advisor, for his continuous advice, valuable suggestions, inspiring guidance, motivation, support, his willpower and vital help throughout the research work, and my U.S. advisor, Assco. Prof. Brian Grady of Oklahoma University, Oklahoma, U.S.A. who gave recommendations and suggestions for the lab planning and problems solving.

The author grateful to Asst Prof Dr. Pitt Supapol, Asst Prof Dr. Ratthanawan Magaraphan and Mr. John W. Ellis for providing technical knowledge and some very helpful suggestions

The author wishes to thank Exxon Chemical Company to supply of ethyleneacrylic acid copolymers and ethylene-methyl acrylic-acid terpolymers used in this research. This thesis work is partially funded by Postgraduate Education and Research Programs in Petroleum and petrochemical Technology (PPT Consortium).

The author also wishes to give a sincere thanks to all of my friends and staff of the Petroleum and Petrochemical College for giving the permission to freely use the research facilities.

Most of all, this work is dedicated to my parents for their tender love and care, generous encouragement, understanding and moral support during this study.

## **TABLE OF CONTENTS**

			PAGE
		Title Page	i
		Abstract (in English)	ii
		Abstract (in Thai)	iii
		Acknowledgements	V
		Table of Contents	vi
		List of Tables	ix
		List of Figures	xiii
CE	IAPTE	.R	
	I	INTRODUCTION	1
	П	LITERATURE REVIEW	3
		2.1 Miscibility of Polymer Blends having Acrylic Acid	3
		2.2 Vibration Damping	6
		2.3 Crystallization Characteristic in Other Polymers	6
	III	EXPERIMENTAL	8
		3.1 Materials	8
		3.1.1 ESCOR <sup>TM</sup> Acid Terpoymer	8
		3.1.2 EAA Copolymer	9
		3.2 Experimental Procedure	10
		3.2.1 Polymer Blend Preparation	10
		3.2.1.1 Blending	10
		3.2.2 Specimen Preparation	11
		3.3 Characterization of Polymer-Polymer blends	11
		3.3.1 Mechanical Properties	11
		3.3.1.1 Tensile Properties	11
		3.3.1.2 Hardness	12

СНАРТЕ	CR	PAGE
	3.3.1.3 Gloss	12
	3.3.2 Thermal Properties	12
	3.3.2.1 Thermal Properties of Polymer Blend	12
	3.3.3 Crystallization	12
	3.3.3.1 Crystallization Structure	12
	3.3.3.2 Crystallization Behavior	13
	3.3.4 Rheological Measurement	13
	3.3.5 Dynamic Mechanical Properties	14
IV	STUDIES ON MISCIBLE BLEND OF ESCOR <sup>TM</sup>	
	TERPOLYMERS AND EAA COPOLYMERS:	
	RHEOLOGICAL, THERMAL AND	
	MECHANICAL PROPERTIES	
	Abstract	15
	Introduction	16
	Experimental	17
	Results and Discussion	19
	Conclusions	24
	Acknowledgements	25
	References	25
V	NON-ISOTHERMAL MELT CRYSTALLIZATION	
	KINETICS FOR ETHYLENE-ACRYLIC ACID	
	COPOLYMERS AND ETHYLENE METHYL	
	ACRYLATE-ACRYLIC ACID TERPOLYMERS	
	Abstract	46
	Introduction	47
	Experimental	50
	Results and Discussion	51
	Conclusions	57

СНАРТЕ	CHAPTER	
	Acknowledgements	58
	References	59
VI	CONCLUSIONS	77
	REFERENCES	80
	APPENDICES	82
	<b>Appendix A</b> Mean value of mechanical properties of ESCOR <sup>TM</sup> 325/EAAs blends	82
	<b>Appendix B</b> Rheological properties of Escor <sup>TM</sup> 325/EAAs blends	87
	<b>Appendix C</b> Melting and crystalline temperature of ESCOR <sup>TM</sup> 325/EAAs blends measured by DSC	97
	Appendix D X-ray diffraction measurement	104
	Appendix E Non-isothermal crystallization kinetic	110
	CURRICULUMVILAE	114

## LIST OF TABLES

TABLE		PAGI	
	CHAPTER III		
3.1	The characteristic of ESCOR <sup>TM</sup> 325 terpolymers	9	
3.2	The composition of EAA copolymers	10	
	CHAPTER IV		
1	Copolymer and terpolymer compositions (all values are in mole fractions)	28	
2	The melting and crystallization temperature of pure components	29	
3	The melting temperature and % crystallinity of ESCOR <sup>TM</sup> 325 with EAA1, EAA2, EAA4 and EAA5 blends.	30	
	CHAPTER V		
1	Compositions in mole fractions for EAA copolymers and E-MA-AA terpolymers studied	61	
2	Characteristic data of non-isothermal melt crystallization exotherms for EAA copolymers studied	62	
3	Characteristic data of non-isothermal melt crystallization63 exotherms for E-MA-AA terpolymers studied		
4	Enthalpy of crystallization and characteristic data of subsequent melting endotherms for EAA copolymers studied	64	
5	Enthalpy of crystallization and characteristic data of subsequent melting endotherms for E-MA-AA terpolymers studied	65	

TABLE		PAGE
6	Non-isothermal crystallization kinetics for EAA	66
	copolymers based on Ozawa analysis.	
7	Non-isothermal crystallization kinetics for E-MA-AA	67
	terpolymers based on Ozawa analysis	
8	Non-isothermal crystallization kinetics for EAA	68
	copolymers based on Ziabicki analysis	
9	Non-isothermal crystallization kinetics for E-MA-AA	69
	terpolymers based on Ziabicki analysis	
10	Effective energy barrier describing the overall non-	71
	isothermal melt crystallization of EAA copolymers	
	based on Friedman method.	
11	Effective energy barrier describing the overall	72
	non-isothermal melt crystallization of E-MA-AA	
	terpolymers based on Friedman method	
	APPENDICES	
Al	Young's modulus of ESCOR <sup>TM</sup> 325/EAAs blends	82
A2	Tensile strength at break of ESCOR <sup>TM</sup> 325/EAAs blends	83
A3	Elongation at break of ESCOR <sup>TM</sup> 325/EAAs blends	84
A4	Hardness of ESCOR <sup>TM</sup> 325/EAAs blends	85
A5	Gloss value at 20° of ESCOR <sup>TM</sup> 325/EAAs blends	86
<b>A</b> 6	Gloss value at 60° of ESCOR <sup>TM</sup> 325/EAAs blends	86
B1	The complex viscosity (η*, Pa s) of ESCOR <sup>TM</sup> 325/EAA1	87
	blends	
B2	The complex viscosity (η*, Pa s) of ESCOR <sup>TM</sup> 325/EAA2	88
	blends	
В3	The complex viscosity (η*, Pa s) of ESCOR <sup>TM</sup> 325/EAA4	89
	blends	

ΓABLE		PAGE
B4	The complex viscosity $(\eta^*, Pa s)$ of ESCOR <sup>TM</sup> 325/EAA5	90
	blends	
B5	Rheological properties (G', dyn/cm <sup>2</sup> ) of ESCOR <sup>TM</sup> 325/EAA1	91
	blends	
B6	Rheological properties (G', dyn/cm <sup>2</sup> ) of ESCOR <sup>TM</sup> 325/EAA2	92
	blends	
B7	Rheological properties (G', dyn/cm <sup>2</sup> ) of ESCOR <sup>TM</sup> 325/EAA4	93
	blends	
B8	Rheological properties (G', dyn/cm <sup>2</sup> ) of ESCOR <sup>TM</sup> 325/EAA5	94
	Blends	
B9	Rheological properties (G", dyn/cm <sup>2</sup> ) of ESCOR <sup>TM</sup> 325/EAA1	95
	blends	
B10	Rheological properties (G", dyn/cm <sup>2</sup> ) of ESCOR <sup>TM</sup> 325/EAA2	96
	blends	
B11	Rheological properties (G", dyn/cm <sup>2</sup> ) of ESCOR <sup>TM</sup> 325/EAA4	97
	blends	
B12	Rheological properties (G", dyn/cm <sup>2</sup> ) of ESCOR <sup>TM</sup> 325/EAA5	98
	blends	
Cl	Melting, crystallization temperature, and percent	99
	crystallinity of ESCOR <sup>TM</sup> 325/EAA1 blends measured by	
	DSC	
C2	Melting, crystallization temperature, and percent	100
	crystallinity of ESCOR <sup>TM</sup> 325/EAA2 blends measured by	
	DSC	
C3	Melting, crystallization temperature, and percent	101
	crystallinity of ESCOR <sup>TM</sup> 325/EAA4 blends measured by	
	DSC	

TABLE		PAGE
C4	Melting, crystallization temperature, and percent	102
	crystallinity of ESCOR <sup>TM</sup> 325/EAA5 blends measured by	
	DSC	
Dl	Crystal lattice structure and percent crystallinity of	106
	ESCOR <sup>TM</sup> 325 and EAA1 blends from	
	X-ray measurement	
D2	Crystal lattice structure and percent crystallinity of	107
	ESCOR <sup>TM</sup> 325 and EAA2 blends from	
	X-ray measurement	
D3	Crystal lattice structure and percent crystallinity of	108
	ESCOR <sup>TM</sup> 325 and EAA4 blends from	
	X-ray measurement	
D4	Crystal lattice structure and percent crystallinity of	109
	ESCOR <sup>TM</sup> 325 and EAA5 blends from	
	X-ray measurement	
El	Non-isothermal crystallization kinetic based on Avrami	110
	and Tobin approach of EAA1	
E2	Non-isothermal crystallization kinetic based on Avrami	110
	and Tobin approach of EAA2	
E3	Non-isothermal crystallization kinetic based on Avrami	111
	and Tobin approach of EAA4	
E4	Non-isothermal crystallization kinetic based on Avrami	111
	and Tobin approach of EAA5	
E5	Non-isothermal crystallization kinetic based on Avrami	112
	and Tobin approach of ESCOR <sup>TM</sup> 310	
<b>E</b> 6	Non-isothermal crystallization kinetic based on Avrami	112
	and Tobin approach of ESCOR <sup>TM</sup> 320	
E7	Non-isothermal crystallization kinetic based on Avrami	113
	and Tobin approach of ESCOR <sup>TM</sup> 325	

## LIST OF FIGURES

FIGURE		PAGE	
	CHAPTER III		
3.1	Processing condition	10	
	CHAPTER IV		
la	Complex viscosity, $\eta^*$ , as a function of frequency for	31	
	pure EAA1, pure ESCOR <sup>TM</sup> 325 and ESCOR <sup>TM</sup> 325/EAA1 blends		
16	Complex viscosity, η*, as a function of frequency for	31	
	pure EAA2, pure ESCOR <sup>TM</sup> 325 and ESCOR <sup>TM</sup> 325/EAA2 blends.		
lc	Complex viscosity, η*, as a function of frequency for	32	
	pure EAA4, pure ESCOR <sup>TM</sup> 325 and ESCOR <sup>TM</sup> 325/EAA4 blends		
1 d	Complex viscosity, $\eta^*$ , as a function of frequency for	32	
	pure EAA5, pure ESCOR <sup>TM</sup> 325 and ESCOR <sup>TM</sup> 325/EAA5		
_	blends	22	
2a	Storage moduli, G', as a function of frequency for pure	33	
	EAA1, pure ESCOR <sup>TM</sup> 325 and ESCOR <sup>TM</sup> 325/EAA1 blends		
2b	Storage moduli, G', as a function of frequency for pure	33	
	EAA2, pure ESCOR <sup>TM</sup> 325 and ESCOR <sup>TM</sup> 325/EAA2		
	blends		
2c	Storage moduli, G', as a function of frequency for pure	34	
	EAA4, pure ESCOR <sup>TM</sup> 325 and ESCOR <sup>TM</sup> 325/EAA4		
	blends		
2d	Storage moduli, G', as a function of frequency for pure	34	
	EAA5, pure ESCOR <sup>TM</sup> 325 and ESCOR <sup>TM</sup> 325/EAA5		
	Blends		

FIGURE		PAGE
3a	Storage moduli, G" as a function of frequency for pure EAA1, pure ESCOR <sup>TM</sup> 325 and ESCOR <sup>TM</sup> 325/EAA1	35
	blends	
3b	Storage moduli, G" as a function of frequency for pure	35
50	EAA2, pure ESCOR <sup>TM</sup> 325 and ESCOR <sup>TM</sup> 325/EAA2	33
	blends	
3c	Storage moduli, G" as a function of frequency for pure	36
	EAA4, pure ESCOR <sup>TM</sup> 325 and ESCOR <sup>TM</sup> 325/EAA4	
	blends	
3d	Storage moduli, G" as a function of frequency for pure	36
	EAA5, pure ESCOR <sup>TM</sup> 325 and ESCOR <sup>TM</sup> 325/EAA5	
	blends	
4a	DSC crystallization peaks of pure EAA1, ESCOR <sup>TM</sup> 325	37
	and ESCOR <sup>TM</sup> 325/EAA1 blends containing 20, 40, 50, 60	
	and 80%wt EAA1	
4b	DSC crystallization peaks of pure EAA2, ESCOR <sup>™</sup> 325	37
	and ESCOR <sup>TM</sup> 325/EAA2 blends containing 20, 40, 50, 60	
	and 80%wt EAA2	
4c	DSC crystallization peaks of pure EAA4, ESCOR <sup>TM</sup> 325	38
	and ESCOR <sup>TM</sup> 325/EAA4 blends containing 20, 40, 50, 60	
	and 80%wt EAA4	
4d	DSC crystallization peaks of pure EAA4, ESCOR <sup>TM</sup> 325	38
	and ESCOR <sup>TM</sup> 325/EAA5 blends containing 20, 40, 50, 60	
	and 80%wt EAA5	
5a	DSC melting peaks of pure EAA1, ESCOR <sup>TM</sup> 325 and	39
	ESCOR <sup>TM</sup> 325/EAA1 blends containing 20, 40, 50, 60 and	
	80%wt EAA1	
5b	DSC melting peaks of pure EAA2, ESCOR <sup>TM</sup> 325 and	39
	ESCOR <sup>TM</sup> 325/EAA2 blends containing 20, 40, 50, 60 and	
	80%wt EAA2	

FIGURE		PAGE
5c	DSC melting peaks of pure EAA4, ESCOR <sup>TM</sup> 325 and ESCOR <sup>TM</sup> 325/EAA4 blends containing 20, 40, 50, 60 and	40
	80%wt EAA4	
5d	DSC melting peaks of pure EAA5, ESCOR <sup>TM</sup> 325 and	40
Ju	ESCOR <sup>TM</sup> 325/EAA4 blends containing 20, 40, 50, 60 and	40
	80%wt EAA5	
6	X-ray diffraction patterns of ESCOR <sup>TM</sup> 325/EAA1 blends:	41
	(a) pure ESCOR <sup>TM</sup> 325, (b) 20% EAA1, (c) 40% EAA1,	
	(d) 50% EAA1, (e) 60% EAA1, (f) 80%EAA1, and	
	(g) pure EAA1	
7a	Young modulus of ESCOR <sup>TM</sup> 325/EAAs blends	42
7b	Tensile strength at break of ESCOR <sup>TM</sup> 325/EAAs blends	42
7c	Elongation at break of ESCOR <sup>TM</sup> 325/EAAs blends	43
8	Hardness of ESCOR <sup>™</sup> 325/EAAs blends	44
9	Complex viscosity, $\eta*(\omega)$ as a function of blend	45
	composition for ESCOR <sup>TM</sup> 325/EAA5 blends at	
	various frequencies	
	CHAPTER V	
1a	Non-isothermal crystallization exotherms for EAA4	72
	at various cooling rates.	
1b	Non-isothermal crystallization exotherms for	72
	E-MA-AA310 at various cooling rates.	
2a	Non-isothermal crystallization exotherms for four	73
	grades of EAA at the cooling rate of 10°C·min <sup>-1</sup> .	
2b	Non-isothermal crystallization exotherms for three grades	73
	of E-MA-AA at the cooling rate of 10°C·min <sup>-1</sup> .	
3a	Subsequent melting endotherms of EAA4 for EAA4	74
	after non-isothermally crystallized at various cooling rates.	

FIGU	PAGE	
3b	Subsequent melting endotherms of EAA4 for	74
	E-MA-AA310 after non-isothermally crystallized	
	at various cooling rates	
4a	The relative crystallinity function of temperature for	75
	EAA4 at various cooling rates	
4b	The relative crystallinity function of temperature for	75
	E-MA-AA310 at various cooling rates	
5a	Typical Ozawa analysis based on the non-isothermal	76
	crystallization data of EAA4	
5b	Typical Ozawa analysis based on the non-isothermal	76
	crystallization data of E-MA-AA310	
	APPENDICES	
D1	X-ray diffraction pattern of ESCOR <sup>TM</sup> 325/EAA1 blends	103
D2	X-ray diffraction pattern of ESCOR <sup>TM</sup> 325/EAA2 blends	104
D3	X-ray diffraction pattern of ESCOR <sup>TM</sup> 325/EAA4 blends	104
D4	X-ray diffraction pattern of ESCOR <sup>TM</sup> 325/EAA5 blends	105