

**SHEAR INDUCED DROP BREAKUP AND COALESCENCE IN
PS/PP, PS/HDPE, AND PMMA/HDPE BLENDS**

Ms. Thanaporn Insuan

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

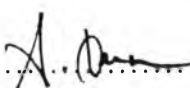
1999

ISBN 974-331-940-9


I19337954

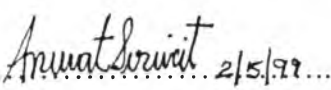
Thesis Title : Shear Induced Drop Breakup and Coalescence in PS/PP,
PS/HDPE, and PMMA/HDPE Blends
By : Ms. Thanaporn Insuan
Program : Polymer Science
Thesis Advisors : Professor Ronald G. Larson
Associate Professor Anuvat Sirivat

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


..... College Director
(Professor Somchai Osuwan)

Thesis Committee :


.....
(Professor Ronald G. Larson)


.....
(Associate Professor Anuvat Sirivat)


.....
(Dr. Mani Nithitanakul)

บทคัดย่อ

นางสาวธนาภรณ์ อินสวน : การแตกตัวของอนุภาคทรงกลมและการรวมตัวของอนุภาคทรงกลมที่เกิดขึ้นจากการเฉือน ในสารผสมพอลิเมอร์ระหว่าง พอลิสไตรีน/พอลิโพรพิลีน พอลิสไตรีน/พอลิเอทิลีนความหนาแน่นสูง และ พอลิเมททิลเมทาไคลเลท/พอลิเอทิลีนความหนาแน่นสูง (Shear Induced Drop Breakup and Coalescence in PS/PP, PS/HDPE, and PMMA/HDPE Blends) อ. ที่ปรึกษา : ศ. ดร. รอนาล ลาสัน และ รศ. ดร. อนุวัฒน์ ศิริวัฒน์ 83 หน้า ISBN 974-331-940-9

งานวิจัยนี้ศึกษาและค้นคว้าผลของแรงเฉือนและระยะเวลาของการเฉือนต่อโครงสร้างภายในของสารพอลิเมอร์ผสมที่ไม่สามารถรวมตัวเป็นเนื้อเดียวกันได้ อันได้แก่ พอลิสไตรีน/พอลิโพรพิลีน พอลิสไตรีน/พอลิเอทิลีนความหนาแน่นสูง และ พอลิเมททิลเมทาไคลเลท/พอลิเอทิลีนความหนาแน่นสูง เราพบว่า มีการรวมตัวของอนุภาคของสารพอลิเมอร์ที่มีสัดส่วนน้อยกว่า (พอลิสไตรีนและพอลิเมททิลเมทาไคลเลท) อันส่งผลให้ขนาดของอนุภาคมีขนาดใหญ่ขึ้น ขนาดของอนุภาคเหล่านี้มีขนาดเล็กที่สุดเมื่อทำการเฉือนด้วยอัตรา 200 ต่อวินาที ที่อัตราการเฉือนมากกว่าหรือน้อยกว่านี้ เราพบว่า ขนาดของอนุภาคของสารพอลิเมอร์ที่มีสัดส่วนน้อยกว่ามีขนาดใหญ่ขึ้น จากการศึกษาถึงความสัมพันธ์ระหว่างโครงสร้างภายในและคุณสมบัติ viscoelastic ของสารผสมพอลิเมอร์ พบว่า อัตราแรงเฉือนต่อแรงผุดตัวของอนุภาค (Capillary Number) แสดงความสัมพันธ์ที่ดีกับอัตราส่วนระหว่างความยืดหยุ่นของสารพอลิเมอร์ทั้งสอง และพบว่า (ก) เมื่ออัตราส่วนระหว่างความยืดหยุ่นของสารพอลิเมอร์ทั้งสองมากกว่า 3 อัตราการรวมตัวสูงกว่าอัตราการแตกตัวทำให้อนุภาคมีขนาดใหญ่ขึ้น เนื่องจากอัตราการเฉือนที่เร็วและอัตราการไหลออกเร็วของสารพอลิเมอร์รอบอนุภาค และ(ข) ที่อัตราส่วนระหว่างความยืดหยุ่นของสารพอลิเมอร์ทั้งสองน้อยกว่า 3 (ซึ่งพบที่อัตราการเฉือนต่ำ) อนุภาคมีขนาดใหญ่ขึ้นเช่นกัน นอกจากนี้ที่ถฤษฎีของพาลีเยน (Palierne) ยังถูกนำมาทดสอบในการทำนายโครงสร้างภายในของสารพอลิเมอร์

ABSTRACT

972022 : POLYMER SCIENCE PROGRAM

KEY WORDS : Immiscible blends/ Drop breakup/ Coalescence/ Normal stress difference/ Capillary number

Ms. Thanaporn Insuan : Shear Induced Drop Breakup and Coalescence in PS/PP, PS/HDPE, and PMMA/HDPE Blends. Thesis Advisors: Prof. Ronald G. Larson and Assoc. Prof. Anuvat Sirivat, 83 pp. ISBN 974-331-940-9

Morphology of immiscible blends, PS/PP, PS/HDPE, and PMMA/HDPE, was investigated in terms of shear strain rate and shearing time. The coalescence process was observed. The minimum dispersed sizes of all blend systems were found at the shear strain rate of 200 s^{-1} . Above and below this shear strain rate value, the rate of coalescence overcame the rate of drop breakup resulting in larger droplet size. The correlation between viscoelasticity and morphology can be expressed by two dimensionless parameters, capillary number (Ca) and the first normal stress difference ratio (N_r). At $N_r > 3$, coalescence was promoted due to high collision rate and fast matrix drainage during collision. At $N_r < 3$, coalescence also occurred due to low shear stress. Palierne's theory was tested and it can be used to predict the complex modulus of the immiscible blends.

ACKNOWLEDGEMENTS

The author greatly appreciates the efforts of her research advisors, Professor Ronald G. Larson and Associate Professor Anuvat Sirivat for their constructive criticism, suggestions and proof-reading of this manuscript. The author would like to give sincere thanks to Dr. Manit Nithitanakul for being a thesis committee member.

The author would like to gratefully acknowledge all professors who taught her at the Petroleum and Petrochemical College, Chulalongkorn University, especially those in the Polymer Science Program. Another thank is to Assist. Prof. Ranoo Thavarorhit, the Botany Department, Chulalongkorn University, for microtome technique.

The author wishes to express her thanks to Ms. Khine Yi Mya who has given her suggestions and encouragements and also to all of college staffs for providing the use of research facilities.

Finally, the author is deeply indebted to her family for their love, financial support and encouragements, all of which contributed greatly in her work.

TABLE OF CONTENTS

	PAGE
Title Page	ii
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	x
List of Figures	xi
List of Symbols	xiv
CHAPTER	
I INTRODUCTION	1
1.1 Physical Properties of Polymer Blends	1
1.2 Controlling the Morphology of Immiscible Blends	2
1.2.1 Drop Breakup	3
1.2.2 Coalescence	5
1.3 Literature Survey	6
1.4 Objectives	12
II EXPERIMENT	13
2.1 Materials	
2.1.1 Polymers	13
2.1.2 Paraffin	14
2.2 Instruments	14
2.2.1 Brabender Mixer	14
2.2.2 Rheometer	14
2.2.3 Microtome Sector	15

CHAPTER	PAGE
2.2.4 Optical Microscope	15
2.3 Methodology	
2.3.1 Sample Preparation	15
2.3.1.1 Blending	15
2.3.1.2 Shearing by the Cone and Plate Rheometer	17
2.3.1.3 Sectioning by Microtome Sector	17
2.3.2 Rheological Measurements	18
2.3.2.1 Shear Viscosity (η)	18
2.3.2.2 The first Normal Stress Difference (N_1)	18
2.3.2.3 Dynamic Modulus (G' , G'' , and G^*)	19
2.3.3 Morphology Investigation	21
2.4 Calculation of Interfacial Tension of Polymer Blends	21
III RESULTS AND DISCUSSION	24
3.1 Rheological Characterizations	24
3.1.1 Molecular Weight Characterization	24
3.1.2 Shear Viscosity (η)	25
3.1.3 The First Normal Stress Difference (N_1)	27
3.1.4 The Viscosity Ratio and Normal Stress Ratio of the Blends	30
3.1.5 The Complex Moduli $G^*(\omega)$ of PP and PS	31
3.2 Effect of Shearing Time on Morphology of the PS/PP Blends	33

CHAPTER	PAGE
3.2.1 Droplet Size versus Dimensionless of Time	33
3.2.2 Distribution Function of Droplet Size as a Function of Shearing Time	35
3.3 Effect of Shear Strain Rate on Equilibrium Morphology of the Blends	40
3.3.1 Equilibrium Droplet Size as a Function of Shear Strain rate	40
3.3.2 Distribution Function of of Droplet Size as a Function of Shear Strain Rate on Equilibrium Morphology of the Blends	41
3.4 Effect of Initial Conditions on Equilibrium Morphology of the Blends	45
3.5 The Correlation between Viscoelastic properties and Morphology of the Immiscible Blends	46
3.5.1 The Capillary Number (Ca) and Viscosity Ratio (η_r) Correlation	46
3.5.2 The Capillary Number (Ca) and Normal Stress Ratio (N_r) Correlation	47
3.5.3 The Capillary Number (Ca) and Normal Stress Ratio Correction (N_r') Correlation	49
3.6 Palierne's Theory	51
3.6.1 Effect of Shear History on Complex Modulus of PS/PP Blends	52
3.6.2 Comparison of the Experimental Complex Modulus of the PS/PP Blend with the Prediction of Palierne's Theory	53

CHAPTER	PAGE
3.6.3 Effect of % Strain on Complex Modulus of the PS/PP Blends	55
IV CONCLUSIONS	57
REFERENCES	58
APPENDIX	62
CURRICULUM VITAE	83

LIST OF TABLES

TABLE	PAGE
2.1 The material properties of the five polymers	13
2.2 The weight of polymer for mixing in the brabender mixer	16
2.3 The conditions of mixing for the blend systems	17
2.4 The conditions of shearing for equilibrium morphology	17
2.5 The conditions of shear viscosity and the first normal force stress difference measurement	19
2.6 The strain sweep testing conditions of homopolymers and polymer blends	20
2.7 The conditions of pre-shearing for dynamic modulus testing	20
2.8 The frequency sweep testing conditions of homopolymers and polymer blends at 200 °C	21
2.9 Surface tension of homopolymers	22
2.10 Interfacial tension of polymer blends	23
3.1 The molecular weights of the five polymers characterized by the cone and plate rheometer	24
3.2 The zero shear viscosity of homopolymers at 200 °C	25
3.3 The ensemble averages of droplet size of the PS/PP blend at	
(a) shear strain rate of 1 s ⁻¹	38
(b) shear strain rate of 10 s ⁻¹	38
(c) shear strain rate of 100 s ⁻¹	39
(d) shear strain rate of 800 s ⁻¹	39
3.4 The ensemble averages of equilibrium droplet size of the blends as a function of shear strain rate	
(a) the PS/PP blends	44
(b) the PS/HDPE(2) blends	44
(c) the PMMA/HDPE(1) blends	44

LIST OF FIGURES

FIGURE	PAGE
3.1 Shear viscosities of homopolymers as a function of shear strain rate at 200 °C	
(a) PP(P640J) and PS	26
(b) HDPE(H5418J) and PS	26
(c) HDPE(H5840B) and PMMA	27
3.2 The first normal stress differences of homopolymers as a function of shear strain rate at 200 °C	
(a) PP(P640J) and PS	28
(b) HDPE(H5418J) and PS	28
(c) HDPE(H5840B) and PMMA	29
3.3 The viscosity ratio of the blends as a function of shear strain rate at 200 °C	30
3.4 The normal stress ratio of the blends as a function of shear strain rate at 200 °C	31
3.5 The Complex modulus $G^*(\omega)$ of polypropylene as a function of frequency after pre-shearing at 1, 10, and 100 s ⁻¹ , at 200 °C	32
3.6 The Complex modulus $G^*(\omega)$ of polystyrene as a function of frequency after pre-shearing at 1, 10, and 100 s ⁻¹ , at 200 °C	32
3.7 The number average diameter of minor phase PS versus product of shear strain rate multiplied by shearing time at shear strain rates of 1, 10, and 100 s ⁻¹ , at 200 °C	34

FIGURE	PAGE
3.8 The Plot of $(D_n/D_{\text{equilibrium}})$ versus $(\gamma \times t)$ of the PS/PP blends at the shear strain rates of 1, 10, 100, and 800 s^{-1} , at 200°C	34
3.9 Distribution function of droplet size for the PS/PP blend as a function of shearing time at the shear strain rate of 1 s^{-1}	36
3.10 Distribution function of droplet size for the PS/PP blends as a function of shearing time at the shear strain rate of 10 s^{-1}	36
3.11 Distribution function of droplet size for the PS/PP blends as a function of shearing time at the shear strain rate of 100 s^{-1}	37
3.12 Distribution function of droplet size for the PS/PP blends as a function of shearing time at the shear strain rate of 800 s^{-1}	37
3.13 The equilibrium droplet size as a function of shear strain rate of the PS/PP blends, PS/HDPE(2) blends, and the PMMA/HDPE(1) blends at 200°C	40
3.14 Distribution function of droplet size of the PS/PP blends as a function of shear strain rate at 200°C	42
3.15 Distribution function of droplet size of the PS/HDPE(2) blends as functions of shear strain rate at 200°C	42
3.16 Distribution function of droplet size of the PMMA/HDPE(1) blends as a function of shear strain rate at 200°C	43
3.17 Droplet size distribution as a function of shear strain rate	43
3.18 The equilibrium droplet size of minor phase PS of the PS/PP blends as functions of shear strain rate and mixing speed at 200°C	45
3.19 The correlation between a capillary number (Ca) and viscosity ratio (η_d/η_m) of the PS/PP blends, the PS/HDPE(2) blends, and the PMMA/HDPE(1) blends at 200°C	47

FIGURE	PAGE
3.20 The correlation between a capillary number (Ca) and viscosity ratio (N_d/N_m) by means of shear strain rate of the PS/PP blends, the PS/HDPE(2) blends, and the PMMA/HDPE(1) blends at 200 °C	48
3.21 The schematic explanation for the meanings of normal stress ratio of the immiscible blends	49
3.22 The correlation between a capillary number (Ca) and viscosity ratio (N'_d/N_m) by means of shear stress of the PS/PP blends, the PS/HDPE(2) blends, and the PMMA/HDPE(1) blends at 200 °C	50
3.23 The complex modulus $G^*(\omega)$ as a function of frequency for the PS/PP blends after shearing at 1, 10, 100, and 200 s^{-1} , at 200 °C	52
3.24 The comparison between experimental data and the predicted values by Palierne's theory of complex modulus $G^*(\omega)$ for the PS/PP blends at 200 °C	
(a) at pre-shearing of 1 s^{-1}	54
(b) at pre-shearing of 10 s^{-1}	54
(c) at pre-shearing of 100 s^{-1}	55
3.25 The effect of % strain on complex modulus $G^*(\omega)$ of the PS/PP blends after pre-shearing at 100 s^{-1} , at 200 °C	56

LIST OF SYMBOLS

SYMBOL

Subscript-d	dispersed phase
Superscript-m	matrix phase
$\dot{\gamma}$	shear strain rate (1/s)
τ	shear stress (dyn/cm ²)
η_d	shear viscosity of dispersed phase (dyn/cm ² .s)
η_m	shear viscosity of matrix phase (dyn/cm ² .s)
η_r	viscosity ratio (η_d / η_m)
N_1	the first normal stress difference (dyn/cm ²)
N_d	the first normal stress of dispersed phase by means of shear strain rate (dyn/cm ²)
N'_d	the first normal stress of dispersed phase by means of shear stress (dyn/cm ²)
N_m	the first normal stress of matrix phase by means of shear strain rate (dyn/cm ²)
N_r	the normal stress ratio (N_d / N_m)
Ca	Capillary number
D_n	number average diameter of dispersed phase (μm)
D_e	equilibrium number average diameter of dispersed phase (μm)
d	diameter of dispersed phase (μm)
R_1	number average radius of dispersed phase (μm)
Γ	interfacial tension (dyn/cm)
$G^*(\omega)$	complex modulus (dyn/cm ²)
ω	frequency (rad/s)