

9

**DROP BREAKUP AND RHEOLOGICAL PROPERTIES OF
POLYSTYRENE/POLYPROPYLENE BLENDS**

Ms. Chatriya Suamsung

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

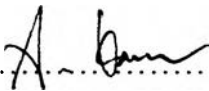
2000

ISBN 974-334-167-6

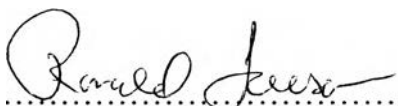
I 193 132 76


Thesis Title : Drop Breakup and Rheological Properties of
Polystyrene/Polypropylene Blends
By : Ms. Chatriya Suamsung
Program : Polymer Science
Thesis Advisors : Professor Ronald G. Larson
Associate Professor Anuvat Sirivat

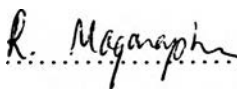
Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfillment of the requirements for the Degree of Master of Science.


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

Thesis Committee:

 9/5/2000
.....
(Prof. Ronald G. Larson)

 28/4/2000
.....
(Assoc. Prof. Anuvat Sirivat)


.....
(Dr. Rathanawan Magaraphan)

ABSTRACT

4172005063 : POLYMER SCIENCE PROGRAM

KEYWORD : Drop breakup/ Coalescence/ Capillary number/ viscosity ratio/ The first normal stress difference ratio

Chatriya Suamsung: Drop Breakup, Coalescence and Rheological Properties of Polystyrene/Polypropylene Blends. Thesis Advisors: Prof. Ronald G. Larson, Assoc. Prof. Anuvat Sirivat, 81 pp. ISBN 974-334-167-6

In order to control the polymer blend rheological properties, a better understanding of mechanisms of drop breakup and coalescence during processing is very important. In this work, the morphology of dispersed phase in terms of number average droplet size was investigated as a function of shearing time and shear strain rate. The number average droplet sizes were found to reach the statistical equilibrium morphology with monomodal size distributions at the shear strain unit about 10,000 for PS/PP blends at high and low viscosity ratios. Only drop breakup process was observed in our investigation. For the effect of elasticity, the correlation between two dimensionless parameters, capillary number (Ca) and the first normal stress difference ratio ($N_{1,r}$) was observed. Ca was found to increase linearly with the first normal stress difference ratio at any given value of viscosity ratio. For a given the first normal stress difference ratio, Ca was found to be surprisingly higher for a lower viscosity ratio. The capillary number of the viscoelastic systems was higher than that of a Newtonian system due to the effect of elasticity in the immiscible polymer blends investigated.

บทคัดย่อ

นางสาวฉัตรจิรา สวมสูง : การแตกตัวของอนุภาคทรงกลมและคุณสมบัติการไหลที่เกิดจากการเชื่อมของสารผสมพอลิเมอร์ระหว่าง พอลิสไตรีน/พอลิโพรพิลีน (Drop Breakup and Rheological Properties of Polystyrene/Polypropylene Blends) อ. ที่ปรึกษา : ศ. ดร. รอนาล ลาสัน และ รศ. ดร. อนุวัฒน์ ศิริวัฒน์ 81 หน้า ISBN 974-334-167-6

งานวิจัยนี้ศึกษาและค้นคว้าผลของแรงเฉือนและระยะเวลาของการเชื่อมต่อโครงสร้างภายในของสารผสมพอลิเมอร์ที่ไม่สามารถรวมตัวเป็นเนื้อเดียวกัน ซึ่งได้แก่ พอลิสไตรีน/พอลิโพรพิลีน ขนาดโดยเฉลี่ยจากจำนวนของอนุภาคทรงกลมถูกศึกษาโดยขึ้นอยู่กับเวลาในการเชื่อมและอัตราเร็วของการเชื่อม จากผลการทดลองพบว่าขนาดโดยเฉลี่ยจากจำนวนของอนุภาคทรงกลมทั้งอัตราส่วนความหนืดสูงและความหนืดต่ำ เข้าสู่สภาวะสมดุลโดยมีการกระจายตัวแบบเอกภาพ เมื่อความเครียดเฉือนมีค่า 10000 ที่สภาวะการทดลองนี้ มีเพียงปรากฏการณ์การแตกตัวของอนุภาคทรงกลมเกิดขึ้นเท่านั้น

สำหรับการศึกษาผลกระทบจากความยืดหยุ่นนั้น ได้ทำการศึกษาจากความสัมพันธ์ระหว่างอัตราส่วนระหว่างแรงเฉือนต่อแรงพุงตัวของอนุภาคทรงกลม (Capillary Number) กับอัตราส่วนระหว่างความยืดหยุ่นของสารพอลิเมอร์ทั้งสอง พบว่า อัตราส่วนระหว่างแรงเฉือนต่อแรงพุงตัวของอนุภาคทรงกลม ณ อัตราส่วนของความหนืดต่างๆ มีค่าเพิ่มขึ้นโดยตรงกับอัตราส่วนระหว่างความยืดหยุ่นของสารสองชนิด โดยอัตราส่วนระหว่างแรงเฉือนต่อแรงพุงตัวเพิ่มขึ้นเมื่ออัตราส่วนของความหนืดสูงขึ้น นอกจากนี้ผลที่ได้จากการทดลองทั้งหมดมีค่าสูงกว่า ระบบที่ไม่มี ความยืดหยุ่น (Newtonian system)

ACKNOWLEDGEMENTS

The author gratefully gives special thanks to her U.S. advisor, Prof. Ronald G. Larson for his recommendations on the research. She is also deeply indebted to her Thai advisors, Assoc. Prof. Anuvat Sirivat, who not only originated the thesis work, but also gave the intensive suggestion, invaluable guidance, constructive advices and vital help throughout this research work.

She greatly appreciates all professors for invaluable knowledge to hers at the Petroleum and Petrochemical College, Chulalongkorn University.

She would like to express her thanks to HMC Polymer Company and Dow Chemical for supporting polypropylenes and polystyrenes.

Finally, the sincerest appreciation is for her family for the love, understanding, 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	x
List of Figures	xi
Abbreviation	xiii
 CHAPTER	
I	INTRODUCTION 1
1.1	Theoretical Background 3
1.1.1	Drop Breakup for Newtonian Fluids and Polymer Blends 3
1.1.2	Coalescence for Newtonian Fluids and Polymer Blends 4
II	LITERATURE SURVEY 7
2.1	Immiscible Polymer Blends in Newtonian System 7
2.2	Immiscible Polymer Blend in Non-Newtonian System 8
III	EXPERIMENTAL 14
3.1	Materials 14

CHAPTER	PAGE
4.1.4 Polymer Degradation	26
4.2 Effect of Shearing Time	30
4.2.1 Droplet Size	30
4.2.2 Distribution Function of Droplet Size	32
4.3 Effect of Shear Strain Rate	35
4.3.1 Droplet Size	35
4.3.2 Distribution Function of droplet Size	36
4.4 The Correlation between Viscoelastic Properties and Morphology of Immiscible Polymer Blends	38
4.4.1 The Viscosity Ratio and the First Normal stress Difference Ratio of the Blends	38
4.4.2 The Capillary Number (Ca) and the First Normal Stress Difference Ratio ($N_{1,r}$) Correlation	42
V CONCLUSIONS	45
REFERENCES	46
APPENDIX A	50
APPENDIX B	52
APPENDIX C	59

CHAPTER	PAGE
APPENDIX D	72
APPENDIX E	75
APPENDIX F	79
CURRICULUM VITAE	82

LIST OF TABLES

TABLE	PAGE
3.1 The Polymer Properties of Polypropylene and Polystyrene	14
3.2 The Conditions of Shearing Time Required for the Ensemble Mean Equilibrium and the Statistical Equilibrium of the Blend System at 220 °C	19
4.1 The Molecular Weights and Molecular Weight Dispersities of PP and PS Characterized by the Cone and Plate Rheometer	21
4.2 The Zero Shear Viscosities of All Homopolymers at 220 °C	22
4.3 The Initial Zero Shear Viscosity and the Final Zero Shear Viscosity of PP After Shearing at 220 °C	29
4.4 (a) The First Normal Stress Difference Ratio of PS/PP Blends at the Shear Viscosity of 0.5	39
(b) The First Normal Stress Difference Ratio of PS/PP Blends at the Shear Viscosity of 1	39
(c) The First Normal Stress Difference Ratio of PS/PP Blends at the Shear Viscosity of 2	40
(d) The First Normal Stress Difference Ratio of PS/PP Blends at the Shear Viscosity of 3	40
4.5 The Shear Viscosity Ratios and the First Normal Stress Difference Ratio for Pre and Post Shearing at 220 °C	41

LIST OF FIGURES

FIGURE	PAGE
1.1 Idealized Depiction of Shear-Induced Coalescence of Dispersed Newtonian Droplets	5
4.1 (a) The Shear Viscosities of Polystyrene as a Function of Shear Strain Rate at 220 °C	23
(b) The Shear Viscosities of Polypropylene as a Function of Shear Strain Rate at 220 °C	24
4.2 (a) The First Normal Stress Difference of Polystyrene as a Function of Shear Strain Rate at 220 °C	25
(b) The First Normal Stress Difference of Polypropylene as a Function of Shear Strain Rate at 220 °C	25
4.3 The Degradation Mechanism of Polypropylene in the presence of O ₂	26
4.4 Pre-Processing and Post-Processing Shear Viscosity of PP as a Function of Shear Strain Rate at 220 °C	28
4.5 The Number Average Diameter of Dispersed Phase PS Versus Shear Strain Unit at 220 °C	31
4.6 The plot of ($D_n/D_{equilibrium}$) versus shear strain rate unit of dispersed phase PS at 220 °C	31
4.7 Distribution Function of Droplet Size for PS(1)/PP(4) Blends as a Function of Shear Strain Unit at Shear Strain Rate of 10 s ⁻¹	33

FIGURE	PAGE
4.8 Distribution Function of Droplet Size for PS(1)/PP(4) Blends as a Function of Shear Strain Unit at Shear Strain Rate of 100 s^{-1}	33
4.9 Distribution Function of Droplet Size for PS(2)/PP(3) Blends as a Function of Shear Strain Unit at Shear Strain Rate of 10 s^{-1}	34
4.10 Distribution Function of droplet Size for PS(2)/PP(3) Blends as a Function of Shear Strain Unit at Shear Strain Rate of 100 s^{-1}	34
4.11 The Equilibrium Droplet Size as a Function of Shear Strain Rate of PS(1)/PP(4) and PS(2)/PP(3) Blends at $220 \text{ }^{\circ}\text{C}$	35
4.12 Distribution Function of Droplet Size of PS(1)/PP(4) as a Function of Shear Strain Rate at $220 \text{ }^{\circ}\text{C}$	37
4.13 Distribution Function of Droplet Size of PS(1)/PP(4) as a Function of Shear Strain Rate at $220 \text{ }^{\circ}\text{C}$	37
4.14 The Correlation between a Capillary Number (Ca) and The First Normal Stress Difference Ratio ($N_{1,r}$) with Various Shear Viscosity Ratios at Pre-Shearing and at $220 \text{ }^{\circ}\text{C}$	42
4.15 The Correlation between a Capillary Number (Ca) and The First Normal Stress Difference Ratio ($N_{1,r}$) with Various Shear Viscosity Ratios after Shearing for 5000 Strain Unit and at $220 \text{ }^{\circ}\text{C}$	43

LIST OF SYMBOLS

SYMBOL

Subscript-d	dispersed phase
Subscript-m	matrix phase
η_d	shear viscosity of dispersed phase (dyn/cm ² .s)
η_m	shear viscosity of matrix phase (dyn/cm ² .s)
η_r	shear viscosity ratio
$N_{1,d}$	the first normal stress difference of dispersed phase (dyn/cm ²)
$N_{1,m}$	the first normal stress difference of matrix phase (dyn/cm ²)
$N_{1,r}$	the first normal stress difference ratio
Ca	Capillary number
D	drop diameter (μm)
D_n	number average diameter of dispersed phase (μm)
Γ	interfacial tension (dyn/cm)
γ	shear strain rate (s ⁻¹)