

**A STABILITY DIAGRAM FOR THE ONSET OF HDPE, MDPE AND
LLDPE SHARKSKIN EXTRUDATES**

Ms. Jeerawan Banyam



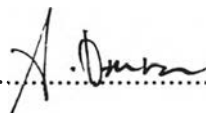
A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma
and Case Western Reserve University

1998


ISBN 974-638-479-1

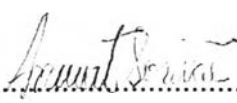
Thesis Title : A Stability Diagram for the Onset of HDPE and LLDPE
Sharkskin Extrudates
By : Ms. Jeerawan Banyam
Program : Polymer Science
Thesis Advisors : Prof. Ronald G. Larson
Assoc. Prof. Anuvat Sirivat


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


..... Director of the College
(Prof. Somchai Osuwan)

Thesis Committee


.....
(Prof. Ronald G. Larson)


.....
(Assoc. Prof. Anuvat Sirivat)


.....
(Dr. Rathanawan Magaraphan)

ABSTRACT

962002 : POLYMER SCIENCE PROGRAM

KEY WORDS : Sharkskin Defect/ Flow Instability / Critical Wall Shear Stress/ Stability Diagram/ Unique Line

Jeerawan Banyam: A Stability Diagram for the Onset of HDPE, MDPE and LLDPE Sharkskin Extrudates. Thesis Advisors: Prof. Ronald G. Larson and Assoc. Prof. Anuvat Sirivat, 173 pp. ISBN 974-638-479-1

Sharkskin defect and flow instability of HDPE, MDPE, and LLDPE polymer melts were studied by capillary and parallel plates rheometers. The onset conditions of HDPE, MDPE, and LLDPE sharkskin were investigated in terms of molecular weight, melt temperature, and die geometry. The recoverable shear (S_R), obtained by normalizing the critical wall shear stress with the liquidlike entanglement storage modulus, was found to depend only on material type. Stability diagram of sharkskin defects can be constructed by using the normalized length scale ratio of the sharkskin wavelength (λ_S) and amplitude (ϵ_S) and the recoverable shear (S_R). There are two sharkskin boundaries depending on the material type: one unique line for HDPE, and one unique line for LLDPE and MDPE.

บทคัดย่อ

จิราวรรณ บานแย้ม : การสร้างแผนภาพของเสถียรภาพการไหลสำหรับผิวหนังปลาฉลาม (sharkskin) ของพอลิเอทิลีนชนิดความหนาแน่นเชิงเส้นสูง กลาง และ ต่ำ (A Stability Diagram for the Onset of HDPE, MDPE and LLDPE sharkskin Extrudates) อ.ที่ปรึกษา : Prof. Ronald G. Larson และ รศ. ดร. อนุวัฒน์ สิริวัฒน์ 173 หน้า ISBN 974-638-479-1

การสร้างแผนภาพของเสถียรภาพการไหลสำหรับผิวหนังปลาฉลาม (sharkskin) ของพอลิเอทิลีนชนิดความหนาแน่นเชิงเส้นสูง, กลาง และ ต่ำ ของพลาสติกที่หลอมเหลวโดยเครื่อง Capillary and Parallellates Rheometer การเกิดผิว sharkskin ของพอลิเอทิลีนชนิดความหนาแน่นเชิงเส้นสูง กลาง และ ต่ำ ศึกษาในเทอมของ มวลโมเลกุล อุณหภูมิ และ ขนาดของไดต์ (die geometry)

เราสามารถสร้างแผนภาพของเสถียรภาพการไหลสำหรับผิวหนังปลาฉลาม (sharkskin) ได้โดยการปรับอัตราส่วนค่าความสูงครีปของผิว (λ_c) และความยาวระหว่างครีปของผิว (E_c) sharkskin และ recoverable shear (S_R) โดยพบว่า แผนภาพของเสถียรภาพการไหลจะแบ่งเป็นสองบริเวณ ขึ้นกับสารที่นำมาทดลอง โดย เส้นหนึ่งจะเป็นของพอลิเอทิลีนชนิดความหนาแน่นเชิงเส้นสูง (HDPE) และอีกเส้นหนึ่งจะเป็นของพอลิเอทิลีนชนิดความหนาแน่นเชิงเส้นกลาง และ ต่ำ (MDPE and LLDPE)

ACKNOWLEDGMENTS



The author would like to gratefully acknowledge all professors who have taught her at the Petroleum and Petrochemical College, Chulalongkorn University, especially those in the Polymer Science Program.

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

The author would like to thank the Siam Chemical Trading Co., Ltd. and Thai Polyethylene Co., Ltd. for the raw materials of HDPE, LDPE, LLDPE, MDPE and PP and performing characterization measurements.

She wishes to express her thanks to all of her friends who have given her encouragements and also College staff for providing the use of research facilities.

Finally, she is deeply indebted to her presents for their love, understanding, encouragements, and for being a constant source of her inspiration.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract	iii
Acknowledgments	v
List of Tables	viii
List of Figures	ix
 CHAPTER	
I INTRODUCTION	
1.1 Extrudates Distortion and Sharkskin Texture	2
1.2 Previous Studies	4
1.3 Research Objectives	8
 II EXPERIMENTAL SECTION	
2.1 Materials	10
2.2 Characterizations	10
2.2.1 Melt Flow Index (MFI : g/10 min)	11
2.2.2 Density (ρ : g/cm ³)	11
2.2.3 Weight Average Molecular Weight (M_w : g/mol)	12
2.3 Capillary Rheometer	12
2.3.1 Instrument	12
2.3.2 Procedure	13
2.3.2 Calculations	13

CHAPTER	PAGE
2.4 Parallel Plates Rheometer	15
2.4.1 Instrument	15
2.4.2 Procedure	15
2.4.3 Normalizations	16
2.5 The Extrudates surface and Sharkskin Studies	19
2.5.1 Zoom Stereo Microscopy	19
2.5.2 Optical Microscopy	19
2.5.3 Scanning Electron Microscopy (SEM)	21
III RESULTS AND DISCUSSION	
3.1 Regime Identification of HDPE, LLDPE and MDPE	22
3.1.1 Flow curves	24
3.1.2 Surface Textures of L2009F	29
3.1.3 Critical Values	31
3.2 Rheological Characterizations	34
3.2.1 G' vs. ω and G'' vs. ω	35
CHAPTER	PAGE
3.2.2 Master Curves of HDPE, LLDPE and MDPE	37
3.2.3 Cox-Merz Rule of HDPE (H5690S) and LLDPE (L2020F)	43
3.3 Effect of M_w on the sharkskin characteristic (λ_s/ϵ_s) of HDPE and LLDPE	48
3.4 Effect of temperature on (λ_s/ϵ_s) of (HDPE) H5690S and (LLDPE) L2020F	55

CHAPTER	PAGE
3.5 Effect of Die Geometry on (λ_S/ϵ_S) of H5690S and L2020F	59
3.6 Stability Diagram of HDPE, LLDPE and MDPE	63
3.6.1 λ_S/ϵ_S vs. S_R - Stability Diagram	63
IV COCLUSIONS	65
REFERENCES	66
APPENDICES	68
CURRICULUM VITAE	170

LIST OF TABLES

TABLE	PAGE	
2.1	Physical properties of LLDPE, MDPE and HDPE	11
2.2	Characteristics of the three dies	12
3.1	Molecular weight of HDPE, LDPE, LLDPE, MDPE and PP studies	22
3.2	The critical wall shear stress ($\tau_{w,c}$) and strain rates ($\dot{\gamma}_a$) of LLDPE, MDPE and HDPE's at the onsets of flow regimes	31
3.3	The critical wall shear stress ($\tau_{w,c}$) and strain rates ($\dot{\gamma}_a$) of HDPE (H5690S) and LLDPE (L2020F) at the onset of sharkskin regimes function of melt temperature	32
3.4	The critical wall shear stress ($\tau_{w,c}$) and strain rates ($\dot{\gamma}_a$) of HDPE (H5690S) and LLDPE (L2020F) at the onset of sharkskin regimes function of die geometry	33
3.5	G^0_N of LLDPE, MDPE and HDPE melts at 190 °C	41
3.6	G^0_N of LLDPE (L2020F) and HDPE (H5690S) melts as functions of the melt temperature.	42
3.7	Skin parameter and normalization of sharkskin defect of HDPE (N3260, H5690S and R1760) and LLDPE (L2009F, L2020F) and MDPE (M3204RU) at 190 °C, die no. 614	50
3.8	Skin parameter and normalization of sharkskin defect of HDPE (H5690S) and LLDPE (L2020F) at various temperatures die no. 614	55

TABLE	PAGE
3.9 Skin parameter and normalization of sharkskin defect of LLDPE (L2020F) and HDPE (H5690S) at various diameters used	59

LIST OF FIGURES

FIGURE		PAGE
1.1	Capillary Rheometer (Instron 3213)	13
3.1	Flow curves at 190 °C: a) LLDPE (L2009F); b) LLDPE (L2020F); c) MDPE (M3204RU); d) HDPE (N3260); e) HDPE (H5690S); f) HDPE (R1760)	25
3.2	Skin textures of L2009F at 190 °C: a) smooth; b) sharkskin; c) slip-stick; d) melt fracture	29
3.3	G vs. ω of LLDPE (L2009F) at 190 °C: a) G' vs. ω ; b) G'' vs. ω	36
3.4	Master curves at 190 °C: a) LLDPE (L2009F); b) LLDPE (L2020F); c) MDPE (M3204RU); d) HDPE (N3260); e) HDPE (H5690S); f) HDPE (R1760)	38
3.5	Cox-Merz rule at 190 °C: a) HDPE (H5690S); b) LLDPE (L2020F)	44
3.6	LLDPE (L2020F) at 190 °C: a) η^*_0 vs. ω ; b) η'_0 vs. ω	46
3.7	Sharkskin textures of HDPE (N3260, H5690S, R1760) and LLDPE (L2009F, L2020F), MDPE (M3204RU) at 190 °C	48
3.8	Sharkskin surface of HDPE (N3260) from SEM (200 \times magnification) and the measured wavelength (λ_S) and amplitude (ϵ_S) at 190 °C	49
3.9	HDPE (N3260, H5690S, R1760) and LLDPE (L2009F, L2020F) and MDPE (M3204RU) at 190 °C: a) λ_S vs. M_W ; b) ϵ_S vs. M_W ; c) λ_S/ϵ_S vs. M_W	51

FIGURE	PAGE
3.10 Stability diagram between S_R vs. λ_S/ϵ_S of HDPE (H5690S) and LLDPE (L2020F) at 190 °C	53
3.11 HDPE (H5690S) various temperatures (160 °C - 200 °C); a) λ_S vs. temperature; b) ϵ_S vs. temperature; c) λ_S/ϵ_S vs. temperature	56
3.12 Stability diagram of HDPE (H5690S) various temperatures (210 °C - 150 °C) and LLDPE (L2020F) various temperatures (200 °C - 160 °C)	58
3.13 HDPE (H5690S) various dies (214, 614 and 1860) and LLDPE (L2020F) various dies (214, 614 and 1860): a) λ_S vs. l_C/d_C ; b) ϵ_S vs. vs. l_C/d_C ; c) λ_S/ϵ_S vs. l_C/d_C	60
3.14 Stability diagram of HDPE (H5690S) various dies (214, 614 and 1860) and LLDPE (L2020F) various dies (214, 614 and 1860)	62
3.15 Stability diagram of HDPE, LLDPE and MDPE various materials, melt temperature and die geometry	64