

การสลายตัวของฟิล์ม โพลีเอทิลีนด้วยสารไวแสง



นาย วรวิทย์ จันทร์วัฒนากุล

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาเทคโนโลยีปิโตรเคมี

บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

พ.ศ. 2534

ISBN 974-578-838-4

ลิขสิทธิ์ของบัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

017544 117843210

DEGRADATION OF PHOTSENSITIZED POLYETHYLENE FILM

Mr. Voravit Janwattanakul

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering
Program of Petrochemical Technology
Graduate School
Chulalongkorn University

1991

ISBN 974-578-838-4



Thesis Title Degradation of Photosensitized Polyethylene Film
By Mr. Voravit Janwattanakul
Department Petro - Polymer Interprogram
Thesis Advisor Associate Professor Pattarapan Prasassarakich, Ph.D.

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

Thavorn Vajrabhaya

..... Dean of Graduate School
(Professor Thavorn Vajrabhaya, Ph.D.)

Thesis Committee

Suda Kiatkamjornwong

..... Chairman
(Associate Professor Suda Kiatkamjornwong, Ph.D.)

Pattarapan Prasassarakich

..... Thesis Advisor
(Associate Professor Pattarapan Prasassarakich, Ph.D.)

Supawan Tantanon

..... Member
(Associate Professor Supawan Tantanon, Ph.D.)

Kanchana Trakulcoo

..... Member
(Associate Professor Kanchana Trakulcoo, D.Eng.)

VORAVIT JANWATTANAKUL : DEGRADATION OF PHOTSENSITIZED
 POLYETHYLENE FILMS. THESIS ADVISOR : ASSOC.PROF.PATTARAPAN
 PRASASSARAKICH, Ph.D. : 132 PP. ISBN 974-578-838-4

Low density polyethylene and high density polyethylene films sensitized with aromatic ketones or aromatic diketones were exposed outdoor for six months. The degradation of sensitized polyethylene films were also studied by irradiation with medium pressure mercury lamp. The effect of photosensitizers and the progress of degradation were studied by measuring the changes in tensile strength, elongation at break, gel formation, molecular weight and fourier transform infrared absorption. The relative infrared absorbance of the carbonyl and vinyl groups increased regularly during the whole exposure time. The elongation at break and molecular weight decreased with exposure time. An accelerating factors for outdoor exposure and irradiation with medium pressure mercury lamp were calculated.

From the results, it was found that the photosensitizers accelerated the degradation. Regarding to the type of photosensitizers, polyethylene films sensitized with thioxanthone, derivatives of benzophenone and of anthraquinone show a higher degradation rate than ones sensitized with benzophenone and anthraquinone. In addition to this, the degradation of high density polyethylene is faster than that of low density polyethylene.

ภาควิชา ศาสตร์เคมี - โพลีเมอร์
 สาขาวิชา เทคโนโลยีโพลีเมอร์
 ปีการศึกษา 2533

ลายมือชื่อนิสิต A
 ลายมือชื่ออาจารย์ที่ปรึกษา
 ลายมือชื่ออาจารย์ที่ปรึกษาร่วม



ACKNOWLEDGEMENTS

I would like to express my sincere appreciation and gratitude to my advisor, Associate Professor Dr.Pattarapan Prasassarakich , for providing valuable advice and encouragement throughout this study as well as for the criticism during the course of this study and for kindly reviewing this thesis.

I am very grateful to the Department of Chemical Technology and the Department of Material Science, Faculty of Science, and Petroleum and Petrochemical College, Chulalongkorn University, to the Thai Packaging Center, Thailand Institute of Scientific and Technological Research for the use of their laboratories, equipment, and their excellent facilities. The great gratitude also go to the Thai Petrochemical Industry Co.,Ltd. for the starting materials. Thanks are also extended to the senior and junior students, my good friends and family for their assistance and good encouragements.

The financial support for this research from The Scientific and Technology Development Board (STDB) is gratefully acknowledged. Finally, I wish to thank the thesis committee for their comments. Thanks are also due to everyone who has contributed suggestions and give me support for this thesis.



CONTENTS

	Page
ABSTRACT IN THAI.....	iv
ABSTRACT IN ENGLISH.....	v
ACKNOWLEDGEMENTS.....	vi
CONTENTS.....	vii
LIST OF TABLES.....	x
LIST OF FIGURES.....	xii
CHAPTER	
1. INTRODUCTION.....	1
2. THEORETICAL CONSIDERATION AND LITERATURE REVIEW	
2.1 Polyethylene.....	3
2.1.1 Physical and chemical properties.....	3
2.1.2 Production.....	4
2.1.3 Low density polyethylene.....	5
2.1.4 High density polyethylene.....	5
2.1.5 Application.....	6
2.2 Processing.....	6
2.2.1 Extrusion.....	7
2.2.2 Tubular blown film.....	8
2.3 Theory of photodegradation.....	10
2.4 Photophysical processes.....	11
2.5 Photochemical processes.....	15
2.6 Photooxidation.....	18
2.7 Sensitized photodegradation.....	20
2.8 Ultraviolet light.....	23
2.9 Identification and selection of degradation sensitizing additive.....	24
2.10 Literature review.....	25
3. APPARATUS AND EXPERIMENTAL METHOD	
3.1 Reagent and materials.....	29
3.2 Apparatus.....	32
3.3 Sample preparation.....	33

	Page
3.4 Sample irradiation.....	33
3.4.1 Natural exposures.....	33
3.4.2 Irradiation using medium pressure mercury vapour lamp.....	33
3.5 Mechanical measurements.....	39
3.6 FTIR measurements.....	39
3.7 Gel content measurements.....	40
3.8 Molecular weight measurements.....	40
4. RESULTS	
4.1 Natural weathering test.....	43
4.1.1 Tensile properties measurements.....	43
4.1.2 Gel measurements.....	61
4.1.3 Molecular weight measurements.....	65
4.1.4 Fourier transform infrared absorption measurements.....	70
4.2 Irradiation using medium pressure mercury lamp.....	80
4.2.1 Tensile properties measurements.....	80
4.2.2 Gel measurements.....	89
4.2.3 Molecular weight measurements.....	91
4.2.4 Fourier transform infrared absorption measurements.....	93
4.3 Results of visual inspection for outdoor exposure polyethylene films.....	100
5. DISCUSSION	
5.1 Environmental degradation of polyethylene..	102
5.2 Irradiation using medium pressure mercury lamp.....	108
5.3 Indoor test of sensitized polyethylene films	109
5.4 Comparison of the degradation tendencies between outdoor exposure and irradiation using medium pressure mercury lamp.....	112
6. CONCLUSION.....	114

	Page
REFERENCES.....	116
APPENDIX	
A. SAMPLE OF CALCULATION.....	118
B. FTIR DATA.....	123
C. YELLOWNESS INDEX.....	131
VITA.....	132

LIST OF TABLES

Table	Page
2.1 Wavelength of UV radiation at which various polymers have maximum sensitivity.....	12
3.1 Physical properties of Polene JJ4324 and A3355.....	30
3.2 The characterization and properties of photosensitizers.....	31
3.3 Absolute spectral power distribution.....	32
3.4 Temperatures at zones in the extruder.....	33
3.5 Meteorological data.....	36
3.6 Temperature and % R.H. for polyethylene in testing period.....	36
3.7 Constants for viscosity molecular weight calculation	40
4.1 Tensile properties of outdoor exposure LDPE films..	48
4.2 Tensile properties of outdoor exposure HDPE films..	51
4.3 Tensile properties of indoor exposure LDPE films...	55
4.4 Tensile properties of indoor exposure HDPE films...	58
4.5 Gel content of outdoor exposure LDPE films.....	62
4.6 Gel content of outdoor exposure HDPE films.....	62
4.7 Intrinsic viscosity and molecular weight of outdoor exposure LDPE films.....	66
4.8 Intrinsic viscosity and molecular weight of outdoor exposure HDPE films.....	68
4.9 Changes in carbonyl and vinyl index of outdoor exposure LDPE films.....	76
4.10 Changes in carbonyl and vinyl index of outdoor exposure HDPE films.....	78
4.11 Tensile properties of irradiated LDPE films.....	83
4.12 Tensile properties of irradiated HDPE films.....	86
4.13 Gel content of irradiated LDPE films.....	90
4.14 Gel content of irradiated HDPE films.....	90

LIST OF TABLES (continued)

Table	Page
4.15 Viscosity and molecular weight of irradiated LDPE films.....	92
4.16 Viscosity and molecular weight of irradiated HDPE films.....	92
4.17 Changes in carbonyl and vinyl index of irradiated LDPE films.....	98
4.18 Changes in carbonyl and vinyl index of irradiated HDPE films.....	99
5.1 Changes in tensile properties, molecular weight and relative absorbance I_{CO} and I_{vinyl} for outdoor exposure.....	104
5.2 Changes in tensile properties, molecular weight and relative absorbance I_{CO} and I_{vinyl} for irradiation with HPK 125 W.....	110
5.3 Time period when the failure criterion of 50 % loss of elongation is reached.....	113
5.4 Accelerating factors of outdoor exposure and irradiation polyethylene films.....	113
B.1 Changes in the relative infrared absorbance peaks of LDPE films.....	123
B.2 Changes in the relative infrared absorbance peaks of HDPE films.....	127
C Yellowness index of polyethylene films.....	131

LIST OF FIGURES

Figure	Page
2.1 Main features of a single screw extruder.....	9
2.2 Diagram of blown film process.....	9
2.3 Potential energy curves of a molecule.....	14
2.4 Potential energy curves of a molecule.....	14
2.5 Photodissociation of a molecule.....	16
2.6 Photodissociation of a molecule after intersystem crossing.....	16
2.7 Average number of chain scissions in one original macromolecule as a function of time.....	20
2.8 Carbonyl index as a function of time during UV irradiation of low density polyethylene samples....	23
3.1 Medium pressure mercury vapour lamp.....	32
3.2 Exposure equipment.....	35
3.3 Irradiated cabinet with medium pressure mercury lamp	35
3.4 Average monthly temperature and relative humidity at Bangkok, Thailand.....	37
3.5 Total monthly rainfall and radiation at Bangkok, Thailand.....	37
3.6 Average hourly temperature and relative humidity for LDPE during irradiation with HPK 125 W.....	38
3.7 Average hourly temperature and relative humidity for HDPE during irradiation with HPK 125 W.....	38
3.8 Ubbelohbe viscometer.....	42
4.1 Stress-strain traces for LDPE samples at various exposure times.....	46
4.2 Stress-strain traces for HDPE samples at various exposure times.....	47
4.3 Changes in tensile strength and elongation at break of LDPE films during natural weathering.....	49
4.4 Changes in tensile strength and elongation at break of HDPE films during natural weathering.....	53

LIST OF FIGURES (continued)

Figure	Page
4.5 Changes in tensile strength and elongation at break of LDPE films during indoor exposure.....	56
4.6 Changes in tensile strength and elongation at break of HDPE films during indoor exposure.....	59
4.7 Changes in the gel content of unsensitized and sensitized LDPE films during natural weathering....	63
4.8 Changes in the gel content of unsensitized and sensitized HDPE films during natural weathering....	64
4.9 Changes in the molecular weight of unsensitized and sensitized LDPE films during natural weathering....	67
4.10 Changes in the molecular weight of unsensitized and sensitized HDPE films during natural weathering...	69
4.11 FT-IR spectra of outdoor exposure LDPE samples....	72
4.12 FT-IR spectra of outdoor exposure HDPE samples....	74
4.13 Changes in carbonyl and vinyl index of LDPE films during natural weathering.....	77
4.14 Changes in carbonyl and vinyl index of HDPE films during natural weathering.....	79
4.15 Stress-strain traces for LDPE samples at various irradiation times.....	81
4.16 Stress-strain traces for HDPE samples at various irradiation times.....	82
4.17 Changes in tensile strength and elongation at break of LDPE films during irradiation with HPK 125 W...	84
4.18 Changes in tensile strength and elongation at break of HDPE films during irradiation with HPK 125 W...	87
4.19 FT-IR spectra of irradiated LDPE samples.....	94
4.20 FT-IR spectra of irradiated HDPE samples.....	96
4.21 Photographs of exposed LDPE films after 6 months..	100
4.22 Photographs of exposed HDPE films after 3 months..	101
5.1 Scheme of degradation reaction of polyethylene films	106

LIST OF FIGURES (continued)

Figure	Page
5.2 Scheme of degradation reaction of sensitized polyethylene films.....	107
A.1 Intrinsic viscosity of original LDPE.....	121
A.2 Intrinsic viscosity of original HDPE.....	122