ผลของส่วนผสมและปริมาณสารเติมแต่งต่อสมบัติกายภาพและเชิงกล ของโฟมพอลิเมอร์ผสมพอลิเอทิลีนชนิดความหนาแน่นต่ำ/เอทิลีนไวนิลอะซิเตต

นางสาวพรรณศิริ สุขท่า

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2552

EFFECTS OF BLEND COMPOSITIONS AND ADDITIVES ON PHYSICAL AND MECHANICAL PROPERTIES OF LDPE/EVA BLEND FOAMS

Miss Phansiri Suktha

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2009

Thesis Title	EFFECTS OF BLEND COMPOSITIONS AND ADDITIVES ON PHYSICAL AND MECHANICAL PROPERTIES OF LDPE/EVA BLEND FOAMS
By	Miss Phansiri Suktha
Field of Study	Chemical Engineering
Thesis Advisor	Varun Taepaisitphongse, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

....Dean of the Faculty of Engineering
(Associate Professor Boonsom Lerdhirunwong, Dr. Ing.)

THESIS COMMITTEE

.... Chairman
(Professor Suttichai Assabumrungrat, Ph.D.)

.... Thesis Advisor
(Varun Taepaisitphongse, Ph.D.)

.... Examiner
(Assistant Professor Anongnat Somwangthanaroj, Ph.D.)

S. Petchuay
.... External Examiner
(Sawitree Petchuay, Ph.D.)

พรรณศิริ สุขท่า : ผลของส่วนผสมและปริมาณสารเติมแต่งต่อสมบัติกายภาพและเชิงกลของโฟมพอลิเมอร์ผสมพอลิเอทิลีนชนิดความหนาแน่นต่ำ/เอทิลีนไวนิลอะซิเตต. (EFFECTS OF BLEND COMPOSITIONS AND ADDITIVES ON PHYSICAL AND MECHANICAL PROPERTIES OF LDPE/EVA BLEND FOAMS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: อ.ดร.วรัญ แต้ไพสิฐพงษ์, 107 หน้า.

งานวิจัยนี้มุ่งศึกษาผลของปริมาณของสารเชื่อมโยงสายโซ่ไดคิวมิลเปอร์ออกไซด์และสารเร่งฟูอาโซไดคาร์โบนาไมด์ที่มีการปรับสมบัติด้วยซิงค์ออกไซด์ ผลของอัตราส่วนระหว่างพอลิเอทิลีนชนิดความหนาแน่นต่ำกับเอทิลีนไวนิลอะซิเตตที่ 70/30 และ 80/20 โดยน้ำหนัก และผลของปริมาณไวนิลอะซิเตตในเอทิลีนไวนิลอะซิเตตที่ 18% และ 28% โดยน้ำหนักไวนิลอะซิเตตต่อสมบัติกายภาพและเชิงกลของโฟมพอลิเมอร์ผสมพอลิเอทิลีนชนิดความหนาแน่นต่ำ/เอทิลีนไวนิลอะซิเตต พอลิเอทิลีนชนิดความหนาแน่นต่ำถูกผสมกับเอทิลีนไวนิลอะซิเตตและสารเติมต่าง ๆ แบบหลอมเหลวในเครื่องอัดรีดแบบเกลียวคู่ หลังจากนั้นนำมาขึ้นรูปเป็นโฟมด้วยวิธีสองขั้นตอน โดยขั้นแรกแผ่นพรีโฟมถูกเตรียมด้วยเครื่องอัดขึ้นรูปและถูกนำมาพองตัวเป็นโฟมในเตาอบลมร้อน

ผลการทดลองพบว่า การเพิ่มปริมาณไดคิวมิลเปอร์ออกไซด์ทำให้ระดับการเชื่อมโยงสายโซ่เพิ่มขึ้นซึ่งทำให้ความหนาแน่นของโฟมที่ได้ลดลง แต่การเพิ่มสารเชื่อโยงสายโซ่ไปพร้อมกับการเพิ่มสารเร่งฟูกลับทำให้ระดับการเชื่อมโยงสายโซ่เพิ่มขึ้นสูงมากกเกินไปสำหรับปริมาณสารเร่งฟูที่ใช้ ทำให้ได้โฟมที่มีความหนาแน่นสูงขึ้น โดยรวมสมบัติเชิงกลของโฟมที่เตรียมได้มีค่าเพิ่มขึ้นตามความหนาแน่นของโฟมที่เพิ่มขึ้น ถ้าความหนาแน่นของโฟมมีค่าลดลง โฟมจะมีความนิ่มและความยืดหยุ่นมากขึ้น

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต
สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก
ปีการศึกษา 2552

4970458221 : MAJOR CHEMICAL ENGINEERING
KEYWORDS : FOAM/LOW DENSITY POLYETHYLENE/ETHYLENE VINYL ACETATE COPOLYMER/FLEXIBILITY

PHANSIRI SUKTHA : EFFECTS OF BLEND COMPOSITIONS AND ADDITIVES ON PHYSICAL AND MECHANICAL PROPERTIES OF LDPE/EVA BLEND FOAMS THESIS ADVISOR: VARUN TAEPAISITPHONGSE, Ph.D. 107 pp.

The effects of dicumylperoxide crosslinking agent loading and modifiled azodicarbonamide with zinc oxide chemical blowing agent loading, ratio of LDPE/EVA at 70/30 and 80/20 wt/wt and vinyl acetate content in ethylene vinyl acetate copolymer at 18%wtVA and 28%wtVA on the physical and mechanical properties of LDPE/EVA blend foams were studied. LDPE were mixed with EVA and additives using twin-screw extruder. Polymer blend foam were produced by two-stage process; pre-foamed sheet were made by compression molder and expanded in hot air oven.

The experimental results showed that increasing of crosslinking agent loading led to higher degree of crosslinking and lower foam density. However, the increasing of crosslinking agent loading together with increasing of chemical blowing agent loading led to higher foam density due to too high degree of crossling for the amount of chemical blowing agent used. Overall, the mechanical properties of obtained foams increased with increasing foam densities. Lower the foam density, softer and more flexible the foams became.

Department : Chemical Engineering
Field of Study : Chemical Engineering
Academic Year : 2009

Student's Signature Phansiri Suktha
Advisor's Signature

ACKNOWLEDGMENTS

The author would like to express sincere gratitude to my advisor, Dr. Varun Taepaisitphongse, for his vision, intelligence, guidance and kindness throughout the course of this research. In addition, I would like to thank members of my thesis committee, Prof. Suttichai Assabumrungrat, Asst. Prof. Anongnat Somwangthanaroj and Dr. Sawitree Petchuay for their comments and many helpful recommendations for completing my thesis.

Gratefully, thanks to TPI Polene Public Company Limited for providing polymer resin and Chulalongkorn University Graduate School Thesis Grant, Chulalongkorn University, for partial financial supports.

I wish to thanks all my friends and everyone in the Polymer Engineering Laboratory, Chulalongkorn University, for their discussion and friendly encouragement. I feel so fortunate having a chance to learn here.

Finally, I would like to dedicate this paragraph to my parents who give their unfailing love, understanding, and generous encouragement during my studies.

CONTENTS

PAGE

ABSTRACT (THAI) iv

ABSTRACT (ENGLISH) v

ACKNOWLEDGEMENTS.. vi

CONTENTS.. vii

LIST OF TABLES.. xi

LIST OF FIGURES.. xiii

CHAPTER

I INTRODUCTION.. 1

1.1 Background.. 1

1.2 Objectives.. 2

1.3 Scopes of Work.. 3

1.4 Expected Benefits.. 3

II THEORY.. 4

2.1 Foam Fundamentals 4

2.1.1 Principle of Foam Formation 4

2.1.2 Structure of polymer foam 5

2.1.3 Characterization of Cellular Structure.. 6

2.2 Foam properties 7

2.2.1 Compression properties 7

2.2.2 Energy Absorption Properties.. 8

2.2.3 Creep and Gas Diffusion.. 9

2.2.4 Thermal Properties.. 9

2.2.5 Tensile Properties.. 10

2.3 Manufacturing Process.. 12

2.3.1 Extruded Crosslinked Foam 12

PAGE

CHAPTER

2.3.1.1 Irradiation Crosslinked Extruded Sheet 13

2.3.1.2 Chemically Crosslinked Extruded Sheet........................ 13

2.3.2 Press Moulded Crosslinked Foam Process............................... 14

2.3.2.1 Single Stage Process.. 14

2.3.2.2 Two Stage Process 14

2.3.3 Injection Moulded Foam Process.. 15

2.4 Improvements of Formulations.. 15

2.4.1 Polymers.. 15

2.4.2 Blowing Agents... 16

2.4.2.1 Chemical Blowing Agents... 16

2.4.2.2 Physical Blowing Agents... 20

2.4.3 Crosslinking Agent.. 20

2.5 Low Density Polyethylene.. 24

2.6 Ethylene Vinyl Acetate Copolymer.. 26

2.6.1 Weight% Vinyl Acetate... 27

2.6.2 Molecular Weight and Distribution... 28

2.6.3 Molecular Branching.. 29

III LITERATURE REVIEWS.. 30

IV EXPERIMENTALS... 35

4.1 Materials... 35

4.2 Formulations of LDPE/EVA Blend foam 36

4.3 Preparation of LDPE/EVA Blend foam... 36

4.4 Preparation of LDPE/EVA Blend Foam Specimens.................................. 38

4.5 Foam Characterizations 41

4.5.1 Density Test.. 41

4.5.2 Gel Content Test.. 41

PAGE

CHAPTER

4.5.3 Morphology………………………………………………….................. 42
4.5.4 Tensile Properties……………………………………………………......... 42
4.5.5 Compressive Strength…………………………………………………..... 42
4.5.6 Compression Set Test..………………………………………………… 42
4.5.7 Thermal Properties of Chemical Blowing Agent………..…………….. 43

V RESULT AND DISCUSSION…..…………………………………………………... 44
5.1 Effect of ZnO on the Decomposition Behaviors of Azodicarbonamide Blowing Agent……..………………………………………………………… 44
5.2 Effect of Crosslinking Agent Loading on Properties of LDPE/EVA Blend Foam……………………………………………………………………….…...... 46
5.3 Effect of Blend Compositions on Properties of LDPE/EVA Blend Foam……………………………………………………………………….….. 57
5.3.1 Effect of Ratio of LDPE/EVA on Properties of LDPE/EVA Blend Foam 57
5.3.2 Effect of %Vinyl Acetate in Ethylene Vinyl Acetate Copolymer on Properties of LDPE/EVA Blend Foam………………………………... 67
5.4 Effect of Chemical Blowing Loading on Properties of LDPE/EVA Blend Foam……………………………………………………………………….….. 73
5.5 Discussion of Effects of Blend Compositions and Additives on Properties of LDPE/EVA Blend Foam………………………………………………….. 79

VI CONCLUSIONS…..……………………………………………………………… 81

REFERENCES…………………………………………………………………........... 83

APPENDICES…………………………………………………………………............ 86

PAGE

CHAPTER

Appendix A Quantity of polymers and additives for LDPE/EVA blend foams………………………………………………………………… 87
Appendix B Calculation of the foam density………………………………… 89
Appendix C Calculation of the gel content ………………………………… 90
Appendix D Calculation of the Young’s modulus………..………………….. 91
Appendix E Calculation of Compression set……………………………..… 92
Appendix F The data of foam density……………………………………… 93
Appendix G The data of gel content……………………………….……… 99
Appendix H The data of mechanical properties……………….………… 101
Appendix I List of publications……………………………………………… 106

VITA…………………………………………………………………................................ 107

LIST OF TABLES

TABLE PAGE

2.1 Characteristic feature of stress-strain curves as related to polymer properties.. 11

2.2 Properties of chemical blowing agents... 18

2.3 Densities and degree of crystallinity of polyethylene............................. 24

2.4 Changes in physical properties of EVA as a function of decreased crystallinity due to increasing vinyl acetate content.............................. 27

2.5 Changes in physical properties of EVA as a function of increasing molecular weigh... 28

4.1 The properties of LDPE, EVA18wt%VA and EVA28wt%VA..................... 35

4.2 Proportion of LDPE, EVA and additive in mixtures................................. 37

4.3 The temperature profile of twin screw extruder..................................... 37

5.1 The values of foam density of LDPE/EVA blend foam with different of %vinyl acetate and crosslinking agent loading……………………………. 68

A.1 Quantity of polymers and additives for LDPE/EVA blend foams……….. 87

A.2 Quantity of polymers and additives for LDPE/EVA blend foams (cont.).. 88

F.1 Raw data for determining foam density of LDPE/EVA blend foam with ratio of LDPE/EVA 70/30 wt/wt, EVA 18wt%VA, ADC 17 phr and DCP 0.6-1.2 phr………………………………………………………………….. 93

F.2 Raw data for determining foam density of LDPE/EVA blend foam with ratio of LDPE/EVA 70/30 wt/wt, EVA 18wt%VA, ADC 17 phr and DCP 0.6-1.2 phr(cont.)…..…………………………………………………….. 94

F.3 Raw data for determining foam density of LDPE/EVA blend foam with ratio of LDPE/EVA 70/30 wt/wt, EVA 28wt%VA, ADC 17 phr and DCP 0.6-1.2 phr………………………………………………………………….. 95

F.4 Raw data for determining foam density of LDPE/EVA blend foam with ratio of LDPE/EVA 80/20 wt/wt, EVA 18wt%VA, ADC 17 phr and DCP 0.6-1.2 phr………………………………………………………………….. 96

TABLE PAGE

F.5 Raw data for determining foam density of LDPE/EVA blend foam with ratio of LDPE/EVA 80/20 wt/wt, EVA 28wt%VA, ADC 17 phr and DCP 0.6-1.2 phr………………………………………………………………….. 97

F.6 Raw data for determining foam density of LDPE/EVA blend foam with ratio of LDPE/EVA 70/30 wt/wt, EVA 18wt%VA, ADC 20 phr and DCP 0.6-1.2 phr………………………………………………………………….. 98

G.1 Raw data for determining gel content of LDPE/EVA blend foam……….. 99

G.2 Raw data for determining gel content of LDPE/EVA blend foam (cont.).. 100

H.1 Mechanical properties data of LDPE/EVA blend foam with ratio of LDPE/EVA 70/30 wt/wt, EVA 18wt%VA, ADC17phr and DCP 0.6-1.2phr 101

H.2 Mechanical properties data of LDPE/EVA blend foam with ratio of LDPE/EVA 70/30 wt/wt, EVA 28wt%VA, ADC17phr and DCP0.6-1.2phr 102

H.3 Mechanical properties data of LDPE/EVA blend foam with ratio of LDPE/EVA 80/20 wt/wt, EVA 18wt%VA, ADC17phr and DCP0.6-1.2phr 103

H.4 Mechanical properties data of LDPE/EVA blend foam with ratio of LDPE/EVA 80/20 wt/wt, EVA 28wt%VA, ADC17phr and DCP0.6-1.2phr 104

H.5 Mechanical properties data of LDPE/EVA blend foam with ratio of LDPE/EVA 70/30 wt/wt, EVA 18wt%VA, ADC20phr and DCP 0.6-1.2phr 105

LIST OF FIGURES

FIGURE PAGE

2.1 Model of the foam's microstructure…………………………………… 4

2.2 Foam Structure of Polymer ………………..…………………………… 5

2.3 Schematic compression stress-strain curve for foam………………….. 7

2.4 Generalized stress-strain curve for plastics 10

2.5 Tensile stress-strain curves for several types of polymeric material 11

2.6 Decomposition of azodicarbonamide pathway one….………………… 19

2.7 Decomposition of azodicarbonamide pathway two………..…………… 19

2.8 Radiation crosslinking of polyethylene………………………………… 21

2.9 Peroxide crosslinking of polyethylene…………………………………. 22

2.10 Chemical structure of polyethylene……………………………………. 24

2.11 Principal variants of polyethylene...............…………………………… 25

2.12 Chemical structure of ethylene vinyl acetate copolymer………………. 26

4.1 Dimension of specimen for density test……………………………… 38

4.2 Density specimen of LDPE/EVA Blend Foam………………………… 38

4.3 Dimension of dogbone-shaped specimens for tensile test…………… 39

4.4 Tensile specimen of LDPE/EVA Blend Foam…………………………. 39

4.5 Dimension of circle-shaped specimens for compressive strength test 39

4.6 Compressive strength specimen of LDPE/EVA Blend Foam………….. 40

4.7 Dimension of specimen for compression set test……………………… 40

4.8 Compression set specimen of LDPE/EVA Blend Foam………………... 40

4.9 Gel content test of LDPE/EVA Blend Foam…………………………… 41

5.1 The effect of ZnO on the decomposition of ADC……………………… 45

5.2 The initial decomposition temperature of ADC/ZnO mixture………….. 45

5.3 Densities of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 18wt%VA, ADC 17 phr with different crosslinking agent loading………………………………………….......................... 47

FIGURE PAGE

5.4 Densities of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 28wt%VA, ADC 17 phr with different crosslinking agent loading.. 47

5.5 Gel contents of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 18wt%VA, ADC 17 phr with different crosslinking agent loading.. 48

5.6 Gel contents of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 28wt%VA, ADC 17 phr with different crosslinking agent loading.. 49

5.7 SEM images of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 18wt%VA and ADC 17 phr DCP 0.6, 0.9 and 1.2 phr 50

5.8 SEM images of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 28wt%VA and ADC 17 phr DCP 0.6, 0.9 and 1.2 phr......... 51

5.9 Stress at break of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 18wt%VA, ADC 17 phr with different crosslinking agent loading.. 53

5.10 Stress at break of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 28wt%VA, ADC 17 phr with different crosslinking agent loading.. 53

5.11 Young’s modulus of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 18wt%VA, ADC 17 phr with different crosslinking agent loading.. 54

5.12 Young’s modulus of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 28wt%VA, ADC 17 phr with different crosslinking agent loading.. 54

5.13 Compressive strength of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 18wt%VA, ADC 17 phr with different crosslinking agent loading... 55

FIGURE PAGE

5.14 Compressive strength of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 28wt%VA, ADC 17 phr with different crosslinking agent loading…………………………………………………… 55
5.15 Compression set of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 18wt%VA, ADC 17 phr with different crosslinking agent loading………………………………………………………………… 56
5.16 Compression set of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 28wt%VA, ADC 17 phr with different crosslinking agent loading………………………………………………………………… 57
5.17 Densities of LDPE/EVA blend foams at LDPE/EVA 70/30 and 80/20wt/wt, EVA with 18 wt%VA, ADC 17 phr at different crosslinking agent loadings…………………………………………………………… 58
5.18 Densities of LDPE/EVA blend foams at LDPE/EVA 70/30 and 80/20wt/wt, EVA with 28 wt%VA, ADC 17 phr at different crosslinking agent loadings…………………………………………………………… 58
5.19 Gel contents of LDPE/EVA blend foams at LDPE/EVA 70/30 and 80/20wt/wt, EVA with 18wt%VA, ADC 17 phr at different crosslinking agent loadings…………………………………………………………… 59
5.20 Gel contents of LDPE/EVA blend foams at LDPE/EVA 70/30 and 80/20wt/wt, EVA with 28wt%VA, ADC 17 phr at different crosslinking agent loadings…………………………………………………………… 59
5.21 SEM images of LDPE/EVA blend foams which LDPE/EVA 80/20wt/wt, EVA with 18wt%VA and ADC 17 and 20 phr DCP 0.60, 0.90 and 1.20 phr………………………………………………………………………… 60
5.22 SEM images of LDPE/EVA blend foams which LDPE/EVA 80/20wt/wt, EVA with 28wt%VA and ADC 17 and 20 phr DCP 0.60, 0.90 and 1.20 phr………………………………………………………………………… 61

FIGURE PAGE

5.23 Stress at break of LDPE/EVA blend foams at LDPE/EVA 70/30 and 80/20wt/wt, EVA with 18wt%VA, ADC 17 phr at different crosslinking agent loadings………………………………………………………………….. 62
5.24 Stress at break of LDPE/EVA blend foams at LDPE/EVA 70/30 and 80/20wt/wt, EVA with 28wt%VA, ADC 17 phr at different crosslinking agent loadings………………………………………………………………….. 63
5.25 Young’s modulus of LDPE/EVA blend foams at LDPE/EVA 70/30 and 80/20wt/wt, EVA with 18wt%VA, ADC 17 phr at different crosslinking agent loadings………………………………………………………………….. 63
5.26 Young’s modulus of LDPE/EVA blend foams at LDPE/EVA 70/30 and 80/20wt/wt, EVA with 28wt%VA, ADC 17 phr at different crosslinking agent loadings………………………………………………………………….. 64
5.27 Compressive strength of LDPE/EVA blend foams at LDPE/EVA 70/30 and 80/20wt/wt, EVA with 18wt%VA, ADC 17 phr at different crosslinking agent loadings…………………………………………………… 65
5.28 Compressive strength of LDPE/EVA blend foams at LDPE/EVA 70/30 and 80/20wt/wt, EVA with 28wt%VA, ADC 17 phr at different crosslinking agent loadings…………………………………………………… 65
5.29 Compression set of LDPE/EVA blend foams at LDPE/EVA 70/30 and 80/20wt/wt, EVA with 18wt%VA, ADC 17 phr at different crosslinking agent loadings………………………………………………………………….. 66
5.30 Compression set of LDPE/EVA blend foams at LDPE/EVA 70/30 and 80/20wt/wt, EVA with 28wt%VA, ADC 17 phr at different crosslinking agent loadings………………………………………………………………….. 66
5.31 Foam densities of all formulations of LDPE/EVA blend foams………… 67
5.32 The relation between stress at break for LDPE/EVA18wt%VA and LDPE/EVA28wt%VA blend foams as function of foam density………... 69
5.33 The relation between Young’s modulus for LDPE/EVA18wt%VA and LDPE/EVA28wt%VA blend foams as function of foam density………… 70

FIGURE PAGE

5.34 The relation between compressive strength for LDPE/EVA18wt%VA and LDPE/EVA28wt%VA blend foams at same of foam density………. 71

5.35 The relation between compression set for LDPE/EVA18wt%VA and LDPE/EVA28wt%VA blend foams at same of foam density.................. 72

5.36 Densities of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 18wt%VA, ADC 17 and 20 phr at different crosslinking agent loadings…………………………………………….............................. 73

5.37 Gel contents of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 18wt%VA, ADC 17 and 20 phr at different crosslinking agent loadings………………………………….................................. 74

5.38 SEM images of LDPE/EVA blend at LDPE/EVA 70/30wt/wt, EVA with 18wt%VA and ADC 17 and 20 phr DCP 0.60, 0.90 and 1.20 phr….. 75

5.39 Stress at break of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 18wt%VA, ADC 17 and 20 phr at different crosslinking agent loadings…………………………………………........................ 76

5.40 Young’s modulus of LDPE/EVA blend foams, LDPE/EVA 70/30wt/wt, EVA with 18wt%VA, ADC 17 and 20 phr at different crosslinking agent loadings…………………………………………........................ 77

5.41 Compressive strength of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 18wt%VA, ADC 17 and 20 phr at different crosslinking agent loadings………………………......................... 77

5.42 Compression set of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 18wt%VA, ADC 17 and 20 phr at different crosslinking agent loadings…………………………………………..................... 78

D.1 The Tensile stress-strain curve of LDPE/EVA blend foam with ratio of LDPE/EVA 70/30 wt/wt, EVA 18wt%, ADC 17 phr and DCP 0.6 phr….. 91

CHAPTER I

INTRODUCTION

1.1 Background

Polymer foam is two-phase material in which gas is dispersed in solid polymer matrix. The foam is called polyolefin foams when produced by olefins. The commercial materials used to produce polyolefin foams are low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP) and ethylene vinyl acetate copolymer (EVA). Areas of polyolefin foam application include packaging, sports and leisure, insulation, automotive, buoyancy, cushioning and others [1]. These applications are usually determined from which properties from hard and tough to soft and resilient and range of foam densities to use. Generally, high density rigid foams are for load bearing whilst low density flexible foams are used in furniture and automotive seats. Polyolefin rigid foams are normally produced from polypropylene or high density polyethylene and flexible foams are produced from ethylene copolymer such as ethylene vinyl acetate [1-2].

Properties of polyolefin foam are dependent on several parameters such as the type of polymer, chemical composition, foam density, and foam structure (open-cell content, cell size, cell shape, cell wall thickness). Nowadays, properties of polyolefin foams have been improved by creating structural inhomogeneity in polymer matrix, consisting of hard and soft regions. Hard region is created by crosslinking and is the main overall cellular structure of foam. Soft region is non-crosslinked section and is open-cell structure due to the thinning of cell walls during cell growth to create interconnections between cells [3].

Low density polyethylene is usually used to produce crosslinked polyethylene foam because of its excellent properties such as softness, elasticity, processibility and insulation. Crosslinking improves the thermal and mechanical properties by creating the three dimensional network. There are many crosslinking methods for polyolefin foam such as using organic peroxide such as diculmyl peroxide, or crosslinking by electron beam or gamma ray radiation, or by silane-moisture curing [6]. Crosslinking by organic peroxide is easy method and the degree of crosslinking can be controlled by the level of crosslinking agent content [4, 6].

Ethylene vinyl acetate copolymer foams are in the range of low density polyolefin foam. They have good flexibility and compression recovery [2]. Properties of ethylene vinyl acetate copolymer depend on the vinyl acetate (VA) content in the copolymer. Ethylene vinyl acetate copolymer is available as a thermoplastic elastomer which contains 28wt%VA and rubber which contains 50wt%VA [7]. Ethylene vinyl acetate foam is used when greater flexibility than that of low density polyethylene foam is required.

Although the low density polyethylene has good mechanical properties and low price, the low density polyethylene foam market is still only a small part of the total low density polyethylene market [8]. Hence, this research aimed to study the effects of amount of ethylene vinyl acetate copolymer and vinyl acetate content in copolymer, blowing agent and crosslinking agent loadings on physical properties such as foam density and morphology and mechanical properties such as tensile strength, elastic modulus, compressive strength, compression set in LDPE/EVA blend foams in order to improve the proportion of LDPE/EVA blend foams and increase their application.

1.2 Objectives

To study the effects of crosslinking agent loading, chemical blowing agent loading, LDPE/EVA weight ratio, VA weight content in EVA on physical and mechanical properties of LDPE/EVA blend foams.

1.3 Scope of Work

1.3.1 Use the weight ratio between LDPE and EVA at 70/30and 80/20 wt/wt.

1.3.2 Use the vinyl acetates content in EVA copolymer at 18 and 28 wt%VA.

1.3.3 Use the crosslinking agent loading in LDPE/EVA blend foam at 0.6, 0.9, and 1.2 phr.

1.3.4 Use the chemical blowing agent loading in LDPE/EVA blend foam at 17 and 20 phr.

1.3.5 Characterization LDPE/EVA blend foams in term foam density, degree of crosslinking and the mechanical properties, i.e. tensile strength at break, Young's modulus, compressive strength, compression set.

1.4 Expected Benefits

1.4.1 To understand the influences of LDPE/EVA ratio, vinyl acetate content in EVA copolymer, blowing agent loading and crosslinking agent loading on physical and mechanical properties of LDPE/EVA blend foams.

1.4.2 Obtaining guidelinse for changing the physical and mechanical properties of LDPE/EVA blend foams and increasing the usage of these materials in the cushioning application.

CHAPTER II

THEORY

2.1 Foam Fundamentals

2.1.1 Principle of Foam Formation

Polymer foam is two-phase material in which gas is dispersed in solid polymer matrix. Foam prepared by the dispersion process has three steps including bubble formation, bubble growth, and stabilization [1].

Bubble formation is formed by process involving nucleation and growth of gas bubble in polymer matrix. There are two processes in bubble formation; self–nucleation process is when bubbles are formed in an initially homogeneous liquid whilst nucleation process is when bubbles are formed at the liquid-solid interface in which the solid particles are called nucleating agents. In the nucleation process, well-dispersed solid particles decrease the surface tension of liquid. Surface tension is important factor for bubble formation. Bubble formation is easier when the surface tension of the liquid is lower. Nucleating agent will reduce surface tension at the interface between the liquid and solid particles to produce voids at this interface. The foaming gas comes out of the liquid into the void and can easily grow a larger bubble [1].

Bubble growth results primary from the diffusion of gas from the solution into the microvoids or foam bubbles. When the gas volume is small, bubbles are spherical in shape. As the bubble volumes grow, the fluid phase becomes insufficient to maintain the spherical shape, so the bubbles take on polyhedral shapes, with the fluid is distributed in thin membranes between two close bubbles. When bubbles grow large enough to give low density foam, cell shapes are dodecahedrons [1].

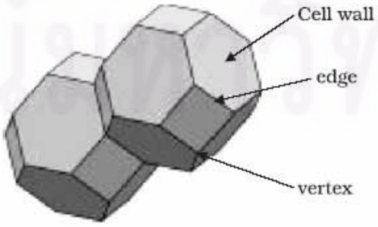
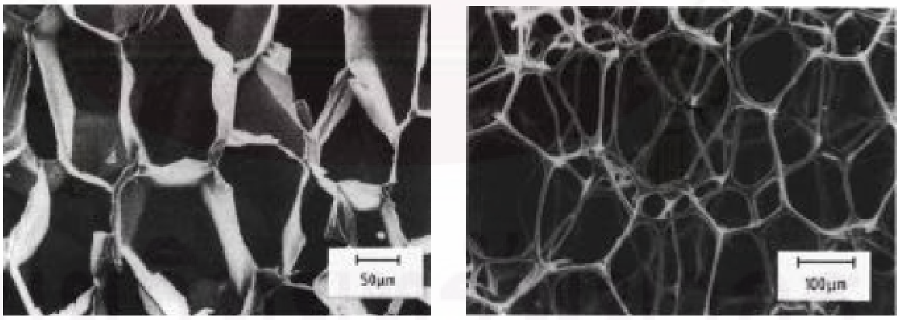


Figure 2.1 Model of microstructure of foam [9]

Stabilization is the step when bubble growth stops and the foam maintain its final structure. The stabilization of bubbles is affected by 2 factors. These factors are surface tension and viscosity of polymer melt, which affect how materials flow towards the intersecting cell elements to form junctions of tricuspid cross-section. In addition, temperature of foam affects both factors. Increasing in temperature reduces viscosity and surface tension, which cause the thinning of membranes and leading to the rupture of membranes to result in the open-cell foam [1,2].

2.1.2 Structure of Polymer Foam

Plastic foams or Cellular plastics are plastics containing many cells or bubbles. Plastic foam is commonly used for describing a two-phase system of a gas dispersed in a solid polymer matrix. Gaseous phase is derived from a blowing agent and solid phase is from blend or alloy of polymers [1]. Generally, the cell structures of plastics foam can be classified into a closed-cell structure and an open-cell (porous) structure. For a closed-cell structure, large proportions of the cells are independent of each other and are easily produced during foaming. However, for an open-cell structure, a large proportion of the cells are connected to other cells by open passage and are very difficult to produce during foaming [12].



(a) Closed-cell foam (b) Open-cell foam

Figure 2.2 Foam Structure of Polymer [12]

Structure of Polymer foam depends on the degree of expansion and the formulation. Physical Characterizations of foam include foam density, cell size, open-cell/close cell ratio, anisotropy and cell shape.

Foam density is an important property of polymer foam. The classifications of foam density of polymer foam are divided into five classes including very light (3-50 kg/m^3), light (50-200 kg/m^3), medium (200-500 kg/m^3), heavy (500-700kg/m^3) and super heavy (more than 700 kg/m^3) [1].

The other important measurement is relative density (ϕ), which is the ratio between density of foam (ρ_f) and density of original polymer (ρ_s). It is calculated from

$$\phi = \frac{\rho_f}{\rho_s} \tag{2.1}$$

Relative density indicates the volume fraction of polymer in foam. For example, low density foams have volume fraction of polymer less than 0.1 [2].

Cell size or average cell size and cell shape are measured by inspection of foam cross-section. Most measurement is done by Scanning Electron Microscopy (SEM) technique. The production of cell of different sizes is caused partly by random cell nucleation in space and partly by large cell growth by diffusion of gas from small cells. The cell shape of polymeric foams that are formed by the growth of nucleated gas bubbles are often considered to be in the pentagonal dodecahedron [2].

Open-cell/closed-cell ratio is important in determining properties such as density and flexibility of foam.

Anisotropy means property of foam depends on direction. Generally, foams are made by expansion in three dimensions and are anisotropic. But foams that are produced by extrusion process are anisotropic when cells have some lateral distortion [2].

2.1.3 Characterization of Cellular Structure

The most characterized parameter is cell size, which can be determined using various methods such as scanning electron microscopy. The other characterization parameters of the cellular structure include mean cell wall thicknesses which are measured directly in the micrographs, cell shape, and anisotropy.

It should be noted that the polymer in the walls and edges of foam could have different morphological characteristics than that of continuous polymers produced by extrusion or injection molding. Several reasons support this hypothesis [9].

1. The cell wall thickness of very low density foams could be less than 1 micron. These sizes are smaller than the typical spherulite dimension of a LDPE. As a consequence, a possible influence of cellular structure on the way in which the foam crystallizes could be expected.
2. The polymer in the foam is crosslinked.
3. The polymer is stretched during foaming.

2.2 Foam Properties

2.2.1 Compression Properties

All foams show a compression stress-strain curve, which splits into three regions as shown in Figure 2.3.

Figure 2.3 Schematic compression stress-strain curve for foam [2]

Region 1, linear Hookian behavior which is linear elastic behavior, is controlled by cell wall bending. For closed-cell foam, it is controlled by cell wall stretching due to the contained gas pressure. In region 2, collapse plateau, the cells collapse through cell wall buckling or in brittle foams by cell crushing and cell wall fracture. In region 3, densification occurs. Overall, as foam density increases, Young's modulus increases in region 1, the plateau stress value increases and the strain at which densification starts reduces. The compression of gas in the cells also contributes more in regions 2 and 3 than 1 [2].

In a compression test, Region 1 is a linear region where the material follows Hooke's Law,

$$\sigma = E\varepsilon \tag{2.2}$$

where *E* is the Young's modulus for compression, σ is stress and ε is strain. This linear region terminates at what is known as the yield point. Above this point the material behaves plastically and will not return to its original length once the load is removed.

At large compressive strain, the stress-strain curve increases sharply due to densification and tends towards a limiting slope at a limiting strain. This limiting strain is lower than the point that can be calculated by assuming it is the point at which all porosity has been eliminated, as the cell walls join together at a somewhat lower strain [2].

Using idealized cell structures, equations have been derived relating foam properties to the foam structure, the matrix polymer properties and relative density of foam. Initial compression modulus, shear modulus, elastic collapse stress and Poisson’s ratio have all been considered. However, for the practical purposes and because in many foams the initial polymer properties are modified by reactions during foam manufacturing such as crosslinking, foam properties are always measured directly and given by manufacturer in table or figures [2].

2.2.2 Energy Absorption Properties

Many foam applications make use of the energy absorption capability of foam structures which is better than the solid polymers from which they are made [2]. Energy is absorbed essentially in the plateau region of the stress-strain curve where cells deform by elastic buckling, plastic yielding or brittle crushing. In elastomeric foams, the plateau stress is determined by elastic buckling of cells and much of the external work is stored during impact deformation and released after impact. However, some energy is dissipated by hysteresis effects due to viscous flow of the contained fluid in open cell foams and hysteresis in polymer deformation. In plastic foams, the energy is absorbed by plastic flow of cells. Brittle foams also absorb energy with little recovery, energy absorption occurring by cell fracture and crushing. Closed-cell polyethylene foams are an example of a material which absorbs energy mainly by plastic deformation of the cells.

Various methods have been used to characterize the packaging or cushioning ability of foams to be characterized. Most manufacturers of foams intended for cushion packaging applications publish cushioning curves which are generated by measuring the peak deceleration of series of falling weights dropped onto the foam from a given height [2].

2.2.3 Creep and Gas Diffusion

Creep is dominated by the viscoelasticity if the stress is less than the collapse stress. But at higher stresses, gas compression takes an increasing proportion of the load. Gas diffusion is a creep mechanism operating on a time scale that depends on the size of the foam block. Sample of EVA foam (20x20x20 mm^3) with density of 275 kg/m^3 has 50% air loss on the time scale of 10 h [9].

Recovery after creep is a slow process. For LDPE, EVA and PP foams, subjected to creep for 10^6 s, it appears that 100% recovery from the high creep strains will eventually occur, but this will take longer than 10^6 s. If a significant percentage of the cell air has diffused out of the foam during creep, the recovery will be slow, because there will be a weak viscoelastic recovery, hindered by the slow reentry of the air to the foam [9].

2.2.4 Thermal Properties

A major application for polymer foams is thermal insulation in areas including building and construction, transportation, appliances. The thermal conductivity of foam is governed by four factors including conduction of heat through the solid polymer, conduction of heat through the gas, convection of heat through the cells and radiation through cell walls and across voids. As the foam density reduces, the amount of thermal conduction through the solid polymer reduces corresponding by and conductivity of foam falls to a minimum at relative density of around 0.05. The general method of reducing conductivity is to replace air with a contained gas of lower conductivity.

Furthermore, the effect of cell size on thermal conductivity of foam with cell diameter less than 2 mm is relatively small, but the tendency is for conductivity to reduce as the cell size decreases. The melting point or softening point of foam is essentially that of the solid polymer. The thermal properties such as specific heat are essentially that of the solid polymer. The closed-cell plastic or elastic foams of low density have higher thermal expansion coefficient due to pressure exerted on the foam by contained gas as temperature increases [2].

2.2.5 Tensile Properties

Tensile properties are determined by the stress-strain curve of material under tension. This is usually done by measuring continuously the force developed as the sample is elongated at constant rate of extension.

The generalized stress-strain curve for plastics is shown in Figure 2.4. It is used to define several useful quantities, such as modulus or stiffness (the slope of the curve), yield stress, and strength and elongation at break. Figure 2.5 shows typical stress-strain curves of some other classes of polymeric materials. The properties of these polymers are related to the characteristics of their stress-strain curves in Table 2.1 [13].

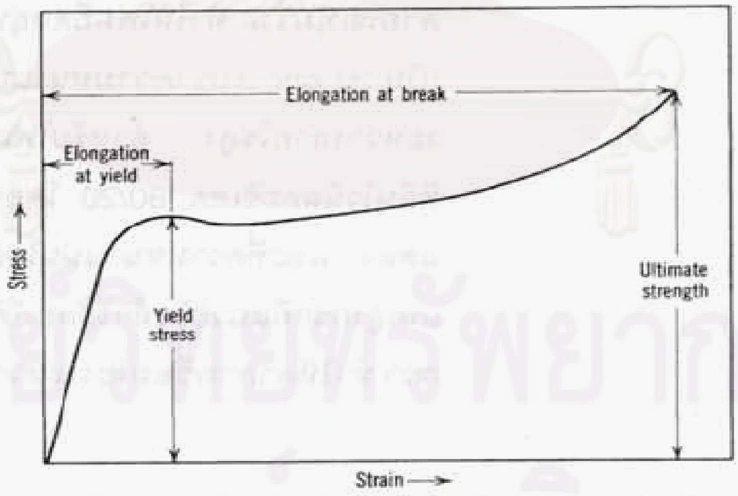


Figure 2.4 Generalized stress-strain curve for plastics [13]

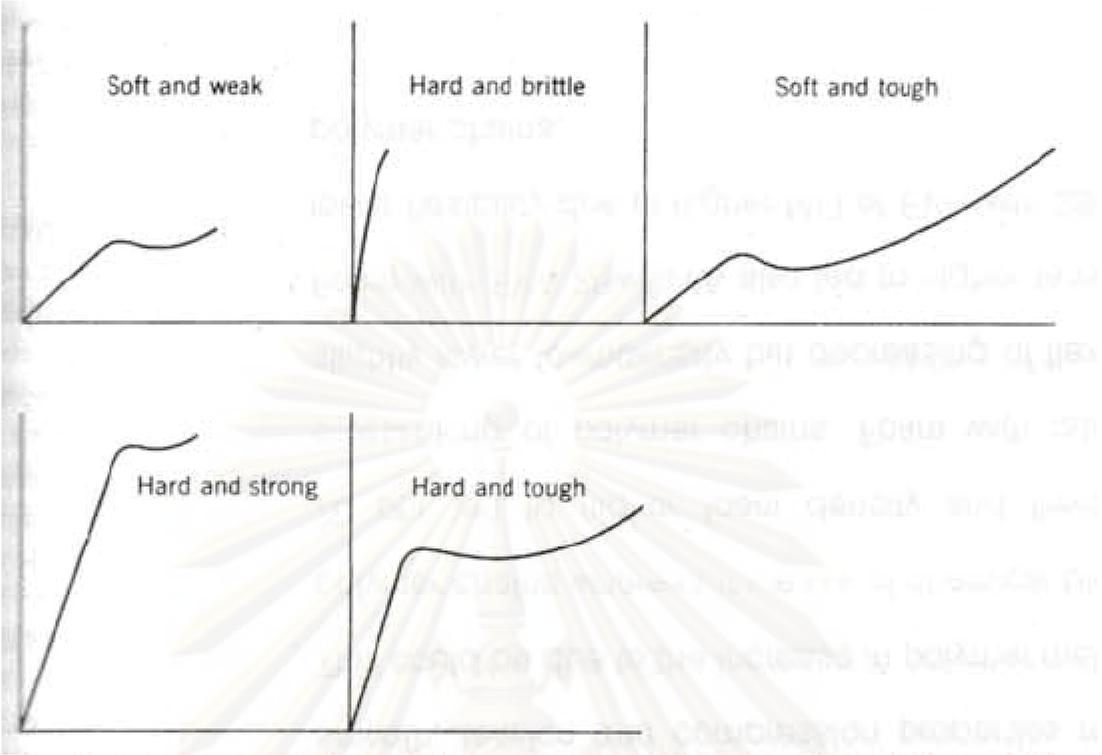


Figure 2.5 Tensile stress-strain curves for several types of polymeric material [13]

Table 2.1 Characteristic feature of stress-strain curves as related to polymer properties [13]

Description of polymer	Characteristics of stress-strain curve			
	Modulus	Yield stress	Ultimate strength	Elongation at break
Soft, weak	Low	Low	Low	Moderate
Soft, tough	Low	Low	Yield stress	High
Hard, brittle	High	None	Moderate	Low
Hard, strong	High	High	High	Moderate
Hard, tough	High	High	High	High

2.3 Manufacturing Process

2.3.1 Extruded Crosslinked Foam

There are two processes for manufacture of crosslinked polyolefin foam by extrusion. Both use a chemical blowing agent but are distinguished by the crosslinking method.

Irradiation crosslinking, in which crosslinking and expansion are separate, makes it easier to balance the two stages of reaction.

Chemical crosslinking, in which crosslinking chemicals are compounded into the mix at an early stage, has the crosslinking taking place at the same stage as expansion. This process is more sensitive to operate owing to the additional heat input at the compounding stage and the requirement to balance crosslinking and blowing agent decomposition at the expansion stage [2].

2.3.1.1 Irradiation Crosslinked Extruded Sheet

The process involves three stages: sheet extrusion, irradiation crosslinking and expansion [2].

Typically, sheet extrusion stage, powder grade of LDPE or EVA copolymers or blends are fed into a high length:diameter ratio (L/D) extruder (such as 30:1), together with a chemical blowing agent and activators and lubricants. A powder polymer feed must be thoroughly mixed with chemical blowing agent, which is added at typical levels of 10-20 phr. An essential requirement is to keep the melt temperature below the decomposition point of the blowing agent to prevent premature expansion in the extruder, and melt temperatures normally are maintained at 130-145 ^{o}C which is adequate for melt fluidity without pre-decomposition. The extruder is designed to provide good mixing whilst giving good temperature control, and is fitted with a sheet die providing extruded sheet up to 1.5m wide and 4mm thick [2].

After extrusion, the sheet is exposed to radiation. Technically radiation could be from a gamma ray source, but in practice electron beam radiation is used owing to the greater control, freedom from gradual decay, and no requirement for permanent heavy shielding [2].

Although the process is generally thought of as continuous, in practice the crosslinked sheet is stored in take-up roll until needed and then expanded as required. Extrusion crosslinking stages do not then have to match the linear throughput rate of the expansion stage and storage space requirements are reduced [2].

Expansion is carried out in an infrared hot air oven generally arranged vertically so as to minimize the degree of contact of the hot expanding sheet with guidance bars which have to cope with the three dimensional expansion of sheet. Temperatures are in the range 220-230 ^{o}C. The expanded sheet is taken up on rolls. It has a fine cell structure and good surface quality, although the surface quality can deteriorate owing to degradation from high irradiation dose with thicker sheet. This therefore is another factor limiting sheet thickness [2].

2.3.1.2 Chemically Crosslinked Extruded Sheet

This process includes stage involves melt compounding a peroxide crosslinking agent and a chemical blowing agent with chosen polymer. Since both the crosslinking agent and the blowing agent will decompose or react if compounding temperatures reach critical levels for any length of time, temperatures at this stage are closely controlled and the crosslinker and blowing agent system are selected so as to give safe operating window[2].

Compounding methods include both internal Banbury type mixer feeding a pelletising line, and twin screw compounding extruders. Good dispersion is essential in achieving high quality expanded sheet with uniform cell structure. Crosslinking agent and blowing agent may be compounded together [2].

It is noted that the semi-continuous nature of the crosslinked sheet foam process gives good production efficiency but both the radiation and chemical crosslink routes have a limitation on the maximum thickness of foam that can be produced. In the radiation process it is the inability of the electron beam to achieve uniform crosslinking with thick extrusions, whilst in chemically crosslinked foam the limitation is heat transfer at the crosslinking or expansion stage. Normal maximum thickness of extrude crosslinked sheet foam is about 15 mm whilst thicker foams can be produced from thin sheet by heat lamination [2].

2.3.2 Press Moulded Crosslinked Foam Process

This process can be divided into two types, single stage process and two stage process.

2.3.2.1 Single Stage Process

The process involves firstly compounding the polymer with crosslinker, blowing agent and any required additives. Banbury batch mixers and twin screw compounding extruders are both used. A defined weight of compound is then placed in a mould and press cured, typically for 45 minutes at 150-170 °C. Under these conditions curing is complete and the blowing agent is fully decomposed. When the mould is opened the product expands directly, literally jumping out of the mould. Moulds are designed to facilitate this. Mould design is critical to avoid generation of internal stresses with the likelihood of foam defects during expansion [2].

2.3.2.2 Two Stage Process

Compounding is carried out the as same as single stage process, but at the press curing stage crosslinking and gas evolution are controlled to ensure no or only partial expansion occurs on release from the mould. Full expansion is carried out in a later second stage. Several difficult presses curing stage can be used as the following [2].

(a) Press curing for 40 minutes at 130 °C. The product is essentially fully crosslinked but there is only partial decomposition of the blowing agent and therefore only limited expansion in the mould. The expansion is completed by transferring the product to a hot air oven, typically for 50 minutes at 170 °C [2].

(b) Press curing for some 20 minutes at 130 °C, resulting in partial curing but no significant decomposition of blowing agent. The product is taken from the mould and transferred to a hot air oven as before to complete curing and enable expansion, typically 60 minutes at 165 °C [2].

Furthermore, highly expansion crosslinked polyolefin foam. The composition was pressed under the pressure applied to sheet have to the least degree of crosslinking which foamed product have open cell structure. Temperature range preferably from 120-140 °C Low density polyolefin foam usually produced by two stage foam process, in first step, the crosslinked sheet is heated in atmosphere or nitrogen at temperature range in 145-180 °C for 10-45 minute. In second step, foam product is heated in at temperature range in 170-210 °C for 15-40 minute [14].

(c) Press curing at 170 °C followed by chilling. Curing is complete and most of the blowing agent is decomposed. Chilling the product gives the material sufficient strength to prevent significant expansion after removal from the mould. Whilst immediate transfer to an expansion oven is not necessary, there is a slow loss of the blowing agent trapped at high pressure within the solid product, and final expansion is generally carried out shortly after press curing, again in a hot air oven. This process has timing longer than single-stage process but foamed product with an expansion ratio is more of up to 15 times the original volume can be obtained. Therefore, highly expansion ratio is produced by two-stage process [15].

2.3.3 Injection Moulded Foam Process

Formulations are similar to those used for press curing. Polymers are selected to have high melt fluidity in temperature range of 100-200 °C so as to permit good mixing without predecomposition. Screws with high L/D ratio (25-30:1) are used for mixing prior to injection. During moulding, similar constraints apply as for the single stage process of the press mouled crosslinked from process since the product expands directly inside the mould. The mould design is important in preventing undue internal stress during expansion. Mould temperatures are about 200 °C and insulation is needed to maintain temperature uniformity. Foam densities are normally in the range 100-300 kg/m^3 [2].

2.4 Improvements of Formulations

2.4.1 Polymers

Normally, polyolefin foam are produced by high density polyethylene, low density polyethylene, linear low density polyethylene and ethylene vinyl acetate. Properties of polymer such as density and melt flow index (MFI) are significant factor for polymer foam. When the density of resin is more than 0.953 g/cm^3, the foamed product is hard and has low expansion ratio. Conversely, when density of resin is less than 0.860 g/cm^3 or melt flow index of resin is more than 100 g/10min (low viscosity), heat resistance of foam is deteriorated. In case the melt flow index is less than 0.1 g/10min (high viscosity), the additives such as crosslinking agent, blowing agent, filler and other additives are poor dispersion because high melt viscosity in compound [14].

2.4.2 Blowing Agents

The various compounds can be used as blowing agents for foaming of the polymers. The general classification scheme is based on mechanism by which gas is liberated.

2.4.2.1 Chemical Blowing Agents

Chemical blowing agents are individual compounds that liberate gas as a result of chemical reaction, including thermal decomposition or as a result of chemical reaction of chemical blowing agents or interactions of chemical blowing agents with other components of the formulation.

There are two advantages in using the chemical blowing agent. It is easy to mix them into the composition to be foamed and they are easily processed with ordinary equipment. A number of factors must be considered when selecting the chemical blowing agents [1].

1. The temperature of decomposition of chemical blowing agent must be close to melting point and hardening of the polymer.
2. Gas must be liberated within a certain narrow temperature range.
3. The rate of gas liberated must be adequately high and must be controllable by temperature, pressure and the decomposition of activator.
4. The gas liberated and the products of its decomposition must be non-corrosive, nontoxic and nonflammable.
5. The chemical blowing agent and the gas liberated must readily disperse or dissolve in polymer composition.
6. The decomposition of chemical blowing agent must not be accompanied by release of so much heat that the polymer matrix is thermally destroyed.
7. The chemical blowing agent and products of its decomposition must not affect the rate of polymerization or cause destruction of the matrix.

8. The rate of liberation of gas must not decease appreciably during the process of thermal decomposition of the chemical blowing agent as the internal pressure in the system increases.
9. Under normal conditions, the gases liberated during decomposition of the chemical blowing agent must have a low rate of diffusion in the polymer, that is, they must stay in the mass being foamed for a rather long time.

When selecting a chemical blowing agent, it is important that the reaction products and residue of chemical blowing agent must be compatible with the material to be foamed and have little or no detrimental effect on properties or colour of the end product. The chemical blowing agents are generally subdivided into two major categories; exothermic and endothermic. The proportion of the some chemical blowing agents are listed Table 2.2 [2].

Azodicarbonamide (ADC) or azodicarbonic acid diamide or 1,1’-azobisformamide is the most commonly used chemical blowing agent [2,9]. Azodicarbonamide is fine yellow powder with a range of particle diameters of 3-30 micron corresponding to specific surface areas from 3 to 0.5×10^6 m^2/m^3 and apparent densities of 300-700 kg/m^3. It decomposes at temperatures of 205-215 ^{o}C, releasing about 220×10^{-3} m^3/kg of gas, primarily N_2, with lesser amounts of CO, CO_2 and NH_3. Its decomposition temperature can be reduced to as low as about 150 ^{o}C through the addition of activator or kickers, to match the desired processing method and polymer to be foamed. Typical activators include metal oxide, zinc oxide, lead oxide, zinc stearate, salicylic acid, stearic acid [2, 9]. Azodicarbonamide is also available as formulated material in powder form, or basic modified material in pre-dispersion or masterbatch form. Modifications of azodicarbonamide include flow conditioned grades which disperse more easily, damped grades to reduce dust. The decomposition reactions of azodicarbonamide are shown in Figure 2.6 and 2.7. The solid decomposition products of azodicarbonamide include biurea, cyamelide, cyanuric acid and urazol [2].

Table 2.2 Properties of chemical blowing agents [2]

Description	Type*	Decomposition Temperature (^{o}C)	Gas Yiled @STPx10^{-3} (m^3/kg)	Gases
Azodicarbonamide(Azo)	Exo	200-230	220-245	N_2, CO, NH_3, O_2
4,4-Oxybis (benzenesulfonyl-hydrazide) (OBSH)	Exo	150-160	120-125	N_2, H_2O
p-Toluenesulfonyl-hydrazide (TSH)	Exo	110-120	110-115	N_2, H_2O
p-Toluenesulfonyl-semicarbazide (TSS)	Exo	110-120	110-115	N_2, CO_2
Dinitrosopenta-methlenetetramine	Exo	195	190-200	N_2, NH_3, HCHO
Polyphenylene sulfoxide (PPSO)	Exo	300-340	80-100	SO_2, CO, CO_2
Sodium bicarbonate	Endo	120-150	130-170	CO_2, H_2O
Zinc carbonate	Endo	-	-	CO_2
Citric acid derivatives	Endo	200-220	110-150	CO_2, H_2O
5-Phenyltetrazole	Endo	240-250	190-210	N_2

*Exo = Exothermic

Endo= Endothermic

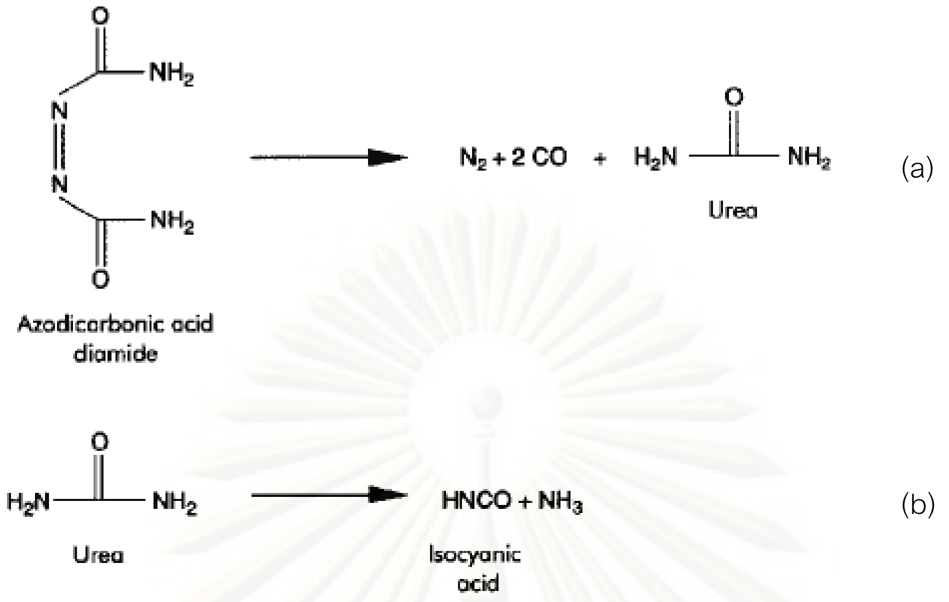


Figure 2.6 Decomposition of azodicarbonamide pathway one [16]

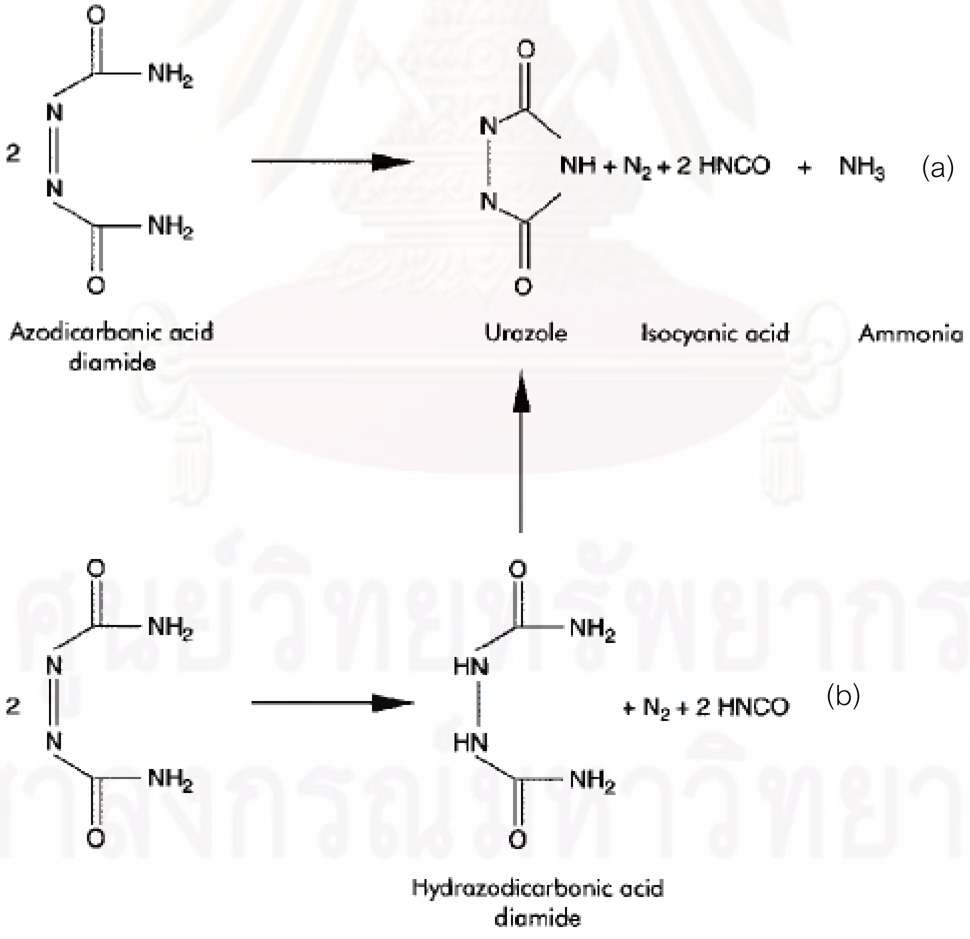


Figure 2.7 Decomposition of azodicarbonamide pathway two [16]

2.4.2.2 Physical Blowing Agents

Physical blowing agents are compounds that give out gases as a result of physical processes. Blowing agents of this type are low-boiling volatile liquids, such as aliphatic, low-boiling alcohols, ethers, ketones, aromatic hydrocarbons and solid adsorbents saturated with gases or low-boiling liquids [1].

Inert gases, especially carbon dioxide and nitrogen, are among the widely used blowing agents. CO_2 and N_2 are widely used as blowing agents because their relatively moderate critical temperature and pressure. Inert gas is in a supercritical fluid state when it is maintained at a temperature and pressure exceeding its critical temperature and pressure. In the supercritical state, the material is dense like a liquid yet maintains a gas-like ability to flow with almost no viscosity or surface tension. Its solubility in a polymer increases significantly and this lowers the glass transition temperature of most polymers. When polymer melt saturated with supercritical fluid is depressurized rapidly, the polymer becomes supercritical with the gas, nucleation of cells occur at a very high concentration and growth of these cells continues until the polymer solidities. This phenomena is used to make cellular (typical cell size is more than 70 micron), microcellular (cell size between 1-70 micron) and super-microcellular (cell size below 1 micron) with a variety of polymers using CO_2 and N_2 [2].

2.4.3 Crosslinking Agents

The crosslinking process consists the formation of chemical bonds (crosslinks) between adjacent molecular chains to form a three-dimensional network. Polymer crosslinking provides beneficial effect on the mechanical properties (even for long periods of time) leading to harder, stiffer, stronger and tougher products [17]. The crosslinking agent is required to remain inactive during compounding and extrusion, with rapid crosslinking triggered subsequently at higher temperature before any substantial decomposition of blowing agent [2]. There are usually three crosslinking techniques of polyolefins such peroxides crosslinking, silane-moisture curing and radiation by electron beam or gamma ray [11].

Direct crosslinking can be brought about by irradiation of solid product with gamma radiation or high energy electrons. The radiation splits carbon hydrogen bonds to produce free radicals, as shown in Figure 2.8(a). The free radicals can migrate along the length of a chain by the process of hydrogen exchange shown in Figure 2.8(b). When two free radicals meet, they combine to form a covalent bond between the carbon atoms creating a crosslink between adjacent chains, as illustrated in Figure 2.8(c) [18].

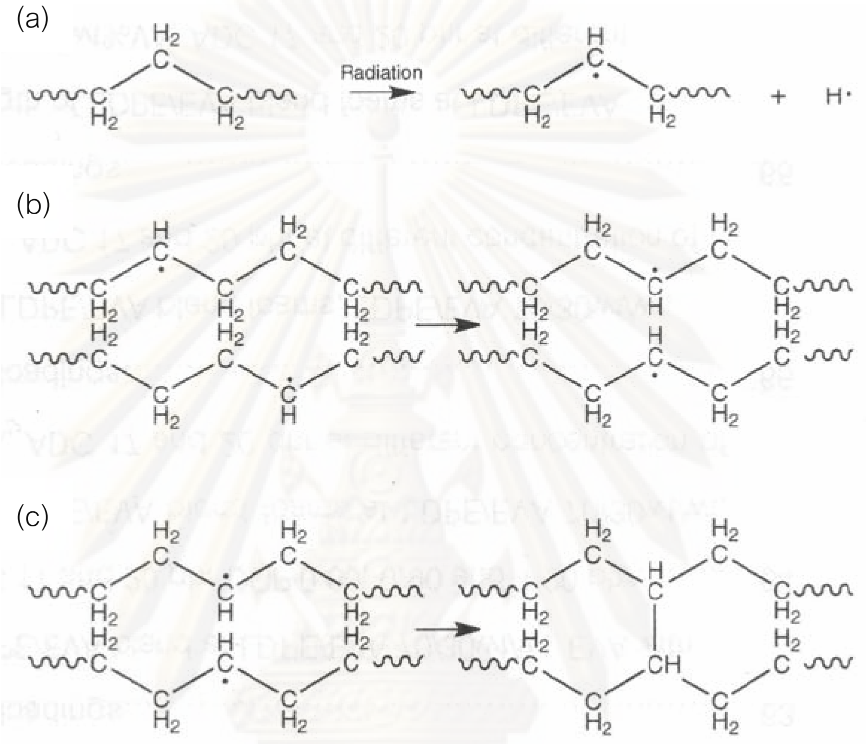


Figure 2.8 Radiation crosslinking of polyethylene [18]
(a) scission of C-H bond,
(b) migration of radicals and
(c) formation of covalent C-C crosslink

The crosslinking method via organic peroxide is the action of peroxy radicals as shown in Figure 2.9. For example, dicumyl peroxide is blended into molten polyethylene at below the decomposing temperature which of peroxide. When temperature is increased, the peroxide decomposes into peroxy radical, as shown in Figure 2.9(a). The peroxy radicals abstract hydrogen atoms from polyethylene chains to create free radicals of polyethylene chains, as shown in Figure 2.9(b). Crosslinking takes place when two radical react to form a covalent bond, as shown in Figure 2.9(c) [18].

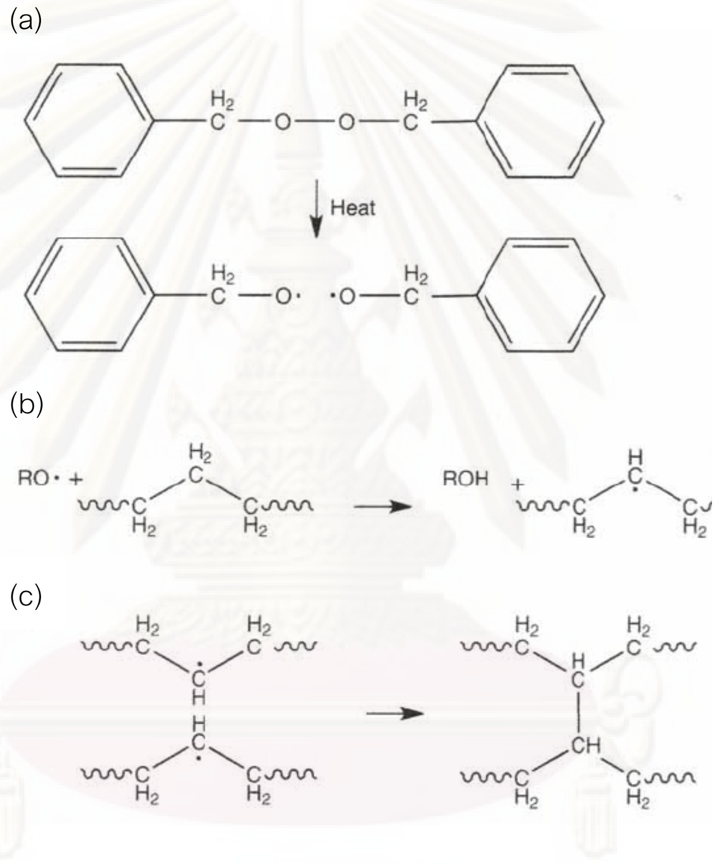


Figure 2.9 Peroxide crosslinking of polyethylene [18]

(a) decomposition of dicumyl peroxide

(b) abstraction of hydrogen from polyethylene chain, and

(c) formation of covalent C-C crosslink

Alkyl peroxides are most commonly used as chemical crosslinking agent. Dicumyl peroxide has half life of 1 minute at 171 °C. 1,3-(bis(*t*-butyl peroxy isopropyl) benzene which has half life of 1 minute at 182 °C. It is used for higher decomposition temperature [2].

The gel content analysis is used as crosslinking analysis method, which determines the weight fraction of crosslinked polymer that is bound into insoluble network. A known weight of crosslinked polymer is put in a stainless steel mesh basket and then is immersed in a suitable solvent. Afterward, the basket is removed from the solvent and the remaining polymer is dried and weighted [18]. The gel content is calculated as

$$\text{Gel content (\%)} = \left(\frac{\text{final mass}}{\text{original mass}}\right) \text{x } 100 \qquad (2.3)$$

Polymers have to be crosslinked before expansion in the foam process Crosslinking helps to promote the polymer melt strength which is needed to withstand the high blowing pressure and to stabilize the expanding bubbles [5]. The melt strength, by definition, as the strength of the polymer while in the molten state [10] or may be considered as a degree of resistance to the extensional flow of the cell wall during the drainage of polymer from the cell wall when volume expansion takes place. The melt strength of polymer increased by crosslinking due to enhanced branching and increased in molecular weight [11].

2.5 Low Density Polyethylene

Polyethylene molecule consists of long backbone of covalently bonded carbon atom, to each of which is attached a pair of hydrogen atom as shown in Figure 2.10. Polyethylene exhibits a range of tensile strengths and flexibilities. It is generally tough, can be readily extruded or molded, and is relatively inexpensive. Due to its large number of variant, polyethylene is used in a wider range of applications than any other polymer [13,19].

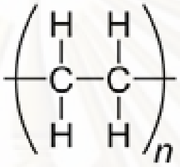


Figure 2.10 Chemical structure of polyethylene [20]

There are seven principal variants of polyethylene include high density polyethylene, low density polyethylene, linear low density polyethylene, very low density polyethylene, ethylene-vinyl ester copolymer, crosslinked polyethylene, and ethylene ionomer, which are shown in Figure 2.11 [21]. Some typical properties of polyethylene are shown in Table 2.3 [19].

Table 2.3 Densities and degree of crystallinty of polyethylene [19]

Class	Approximated density (g/cm^3)	Approximated degree of Crytallinty (%)
Very low density	0.86-0.91	5-30
Low density Linear low density	0.91-0.94	30-55
High density	0.94-0.97	10-20

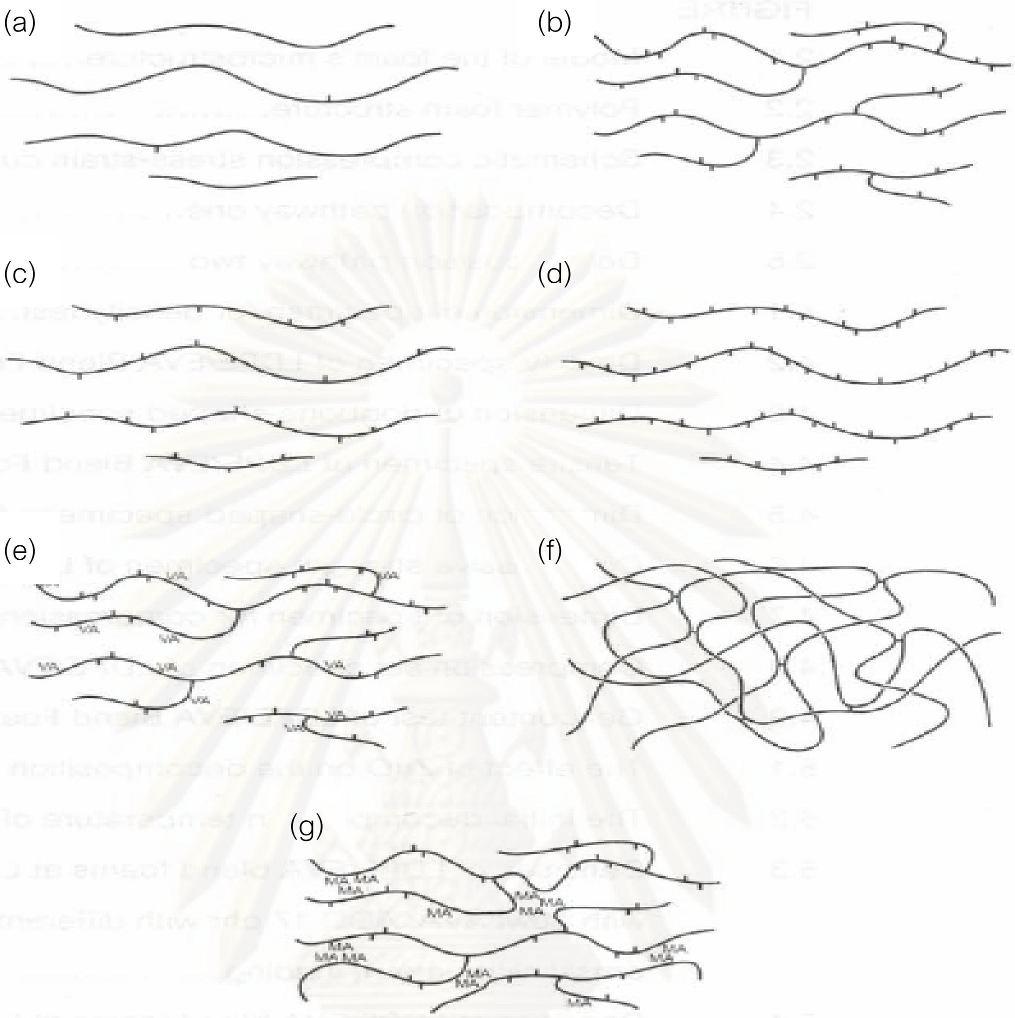


Figure 2.11 Principal variants of polyethyene [19]

(a) high density polyethylene (b) low density poly ethylene
(c) linear low density polyethylene (d) very low density polyethylene
(e) ethylene vinyl acetate copolymer (f) crosslinked polyethylene
(g) ionomer

Low density polyethylene (LDPE) contains many short and long chains. The short branches consist primarily of ethyl and butyl branches, which are often located near each other. LDPE is polydisperse in terms of its molecular weight, long chain branching length and placement and short chain branching. LDPE is a partially crystalline solid. Its density in the solid state is approximately 0.91-0.94 g/cm^3, which crytallinity levels approximately 30-55% [19]. The melting point of LDPE is at about 115°C. It is soluble in many solvents at temperature above 100 °C.

The physical properties of low density polyethylene are functions of three independent structural variables: molecular weight, molecular weight distribution or long-chain branching, and short-chain branching [13].

Short-chain branching has a predominant effect on degree of crytallinity and ,therefore, on the density of polyethylene. Properties dependent on crytallinity, such as stiffness, tear strength, hardness, chemical resistance, softening temperature and yield point, increase with increasing density or decreasing amount of short-chain branching in the polymer.

The effect of molecular weight is mainly reflected evidenced in properties of the melt and properties involving large deformation of solid. As molecular weight increases, so do tensile strength, tear strength, low temperature toughness, softening temperature, impact strength and resistance to environmental stress cracking [13].

The effect of long-chain branching on properties of polyethylene is often evaluated in term of the breadth of the molecular weight distribution. With other structural parameters held constant, increase in tensile strength, toughness and impact strength, softening temperature, and resistance to environmental stress cracking [13].

The mechanical properties of low density polyethylene are between those of rigid materials and plasticized polymers. Polyethylene has good toughness and ability over a wide temperature range [13].

2.6 Ethylene Vinyl Acetate Copolymer

Ethylene vinyl acetate copolymer (EVA) is the copolymer of ethylene and vinyl acetate (VA).The chemical structure of EVA is given in Figure 2.12.

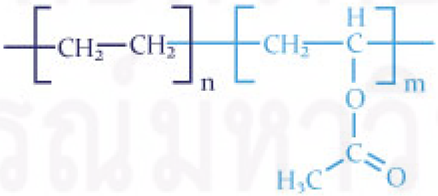


Figure 2.12 Chemical structure of ethylene vinyl acetate copolymer [21]

Three structural attributes of EVA copolymers, i.e., weight % vinyl acetate, molecular weight and distribution, and molecular branching largely determine the properties of any particular copolymer grade [22].

2.6.1 Weight % Vinyl Acetate

Vinyl acetate content has two fundamental effects on the properties of EVA copolymers. The first effect is to disrupt the crystalline regions formed by the polyethylene segments of the copolymer. Low and medium density polyethylene generally have degrees of crystallinity in the range of 40-65%. This is progressively reduced by increasing VA content until, at some point between 40 and 50 wt%VA, the material becomes completely amorphous. The physical properties of EVA copolymer as a function of increasing vinyl acetate content are shown in Table 2.4. Furthermore, as the vinyl acetate content increases, so does the polarity of the copolymer from the polar nature of the acetoxy side chain [22].

Table 2.4 Changes in physical properties of EVA as a function of decreased crystallinity due to increasing vinyl acetate content [22]

Changes in physical properties of EVA as a function of decreased crystallinity due to increasing vinyl acetate content	
Stiffness modulus	Decreases
Surface hardness	Decreases
Crystalline melting point / softening point	Decreases
Tensile yield strength	Decreases
Chemical resistance	Decreases
Impact strength (especially at low temperatures)	Increases
Optical clarity	Increases
Gas permeability	Increases
Environmental stress crack resistance	Increases

2.6.2 Molecular Weight and Distribution

As with all polymers, average molecular weight has a major influence on properties of EVA. The molecular weight is normally respect by quoting the melt index (MI) using ASTM D1238.The most important properties affected by increasing molecular weight are illustrated in Table 2.5. Increasing VA content increases chain transfer and can lead to broader molecular weight distribution (MWD). The main influence of broadening MWD on EVA is an effect on its melt flow characteristics. Typically, the long chains in broad MWD polymers tend to be entangled more than shorter chains. As a result these long chains accept a disproportionately large amount of any deformational stress and show above average elastic response. This elastic response is also delayed by viscous resistance of the smaller molecules at the same VA content and MI. Therefore, broad MWD EVA copolymers will have relatively high viscosity at very low shear stress, while at high shear stress, the flow will be significantly easier than narrow MWD EVA copolymers [22].

Table 2.5 Changes in physical properties of EVA as a function of increasing molecular weigh [22]

Changes in physical properties of EVA as a function of increasing molecular weigh	
Viscosity	Increases
Softening point	Increases
Environmental stress crack resistance	Increases
Impact strength	Increases
Tensile strength at break	Increases
Stiffness modulus	Increases (slightly)
Resistance to chemicals	Increases
Solubility (converse of chemical resistance)	Decreases
Processability (converse of viscosity)	Worsens

2.6.3 Molecular Branching

In EVA, short chain branches with less than six carbon atoms and long chain branches with six carbon atoms that become part of the crystalline network. The primary effect of short chain branches is to disrupt the crystallinity of the polyethylene (PE) segments. Thus the effect of short chain branches on EVA copolymer properties is similar to wt% VA but to a much lesser extent due to the relatively low number of short branches. The primary influence of long chain branches, formed by chain transfer by a growing polymer radical, is to increase the melt elasticity of the EVA copolymer. As mentioned in the previous section on MWD effects, the long chain branches tend to entangle and increase the elastic response of the melt [22].

CHAPTER III

LITERATURE REVIEW

Polyethylene foam is one of the important polyolefin foams. It has been developed for varieties of application because high density polyethylene and low density polyethylene have good load bearing capability [1]. Low density polyethylene (LDPE) has excellent properties such as softness, elasticity, processibility. Therefore, low density polyethylene is usually used to produce flexible polyethylene foam. Physical and mechanical properties of polyethylene foam can be modified by adjusting of chemical composition or manufacture process. The properties of foam are affected by the cellular structure. There are several variables that can affect the structure of foam such as the level of crosslinking, magnitudes of blowing pressure, and processing variables [5]. Processing variables include melt temperature, environment temperature, cooling rate, expansion pressure and pressure drop rate, rate of polymerization, and crosslinking reaction. Material variable include diffusivity and solubility of blowing gases, decomposition rate of chemical blowing agent, viscosity and elasticity of polymer matrices [5].

Blending is one of the easiest methods to modify properties of polyolefin foam. The blend foams between low density polyethylene and thermoplastic elastomers such as ethylene-propylene rubber have improved tensile and impact properties [17]. Ethylene propylene diene monomer rubber (EPDM) can be crosslinked with LDPE blend foam or ethylene vinyl acetate copolymer to improve softness because the soft polyolefin foam is commonly produced from ethylene vinyl acetate copolymer [5]. Beside, the addition of waste polyethylene in LDPE foams can increase the consumption recycled post-use polyethylene [23-24].

Accordingly, effects of main three factors including ethylene vinyl acetate content, concentration of blowing agent and level of crosslinking.on properties of LDPE foam are reviewed below.

3.1 Effects of Ethylene Vinyl Acetate Copolymer Content

Siqin Dalai and Chen Wenxin [25] studied the effect of EVA content on gel fraction of the radiation foam of the LDPE/EVA blend by varying weight ratio of LDPE/EVA at 100/0, 80/20, 75/25, 70/30 and 50/50. LDPE had melt flow index 2.0 g/10 min and EVA had melt flow index 2.0 g/10 min, vinyl acetate content of 18wt%. Azodicarbonamide was used as blowing agent. The compounds were mixed by two roll mills at 115-120 °C. Then, the result products were pressed by press machine at 120 °C to form a sheet thickness of 2.0±0.2 mm. The blend sheets were crosslinked by gamma ray radiation in air. The irradiated sheets were expanded by hot air at 200 °C. The gel fraction of the LDPE/EVA blend foam was formed to be around 25-30%. They found that at the same given dose of irradiation, gel fraction increased with increasing of EVA content. But it was observed that at ratio of LDPE/EVA higher than 70/30, gel fraction decreased.

M.A.Rodriguez-perez and co-worker [17] studied the effect of addition of EVA content with 12% vinyl acetate in copolymer in LDPE at LDPE/EVA ratio of 90/10, 70/30 and 10/90 on the thermal properties by Differential Scanning Calorimetry (DSC). The result showed that the thermal stability of LDPE/EVA blend foam with higher EVA content was less than that with lower EVA content. For morphology, it was found that most cells of LDPE/EVA blend foam are spherical shape and increasing of EVA content resulted in larger mean cell diameter. For technical properties by Dynamic Mechanical Analysis (DMA) and Creep-recovery Measurements, the results showed that the static modulus and dynamic modulus decreased while instantaneous recovery, thermal expansion and loss factor at low temperature increased with increasing of EVA content.

Hussien A. Yousself and co-worker [26] compared the properties of LDPE foam and LDPE/EVA (80/20) foam where LDPE had melt flow index 4.0 g/10 min and ethylene vinyl acetates copolymer had vinyl acetates content of 9%. Azodicarbonamide and 1,6-hexandiol diacrylate (90%) were used as blowing agent and crosslinking agent, respectively. The compounds used to obtain the foam were processed in a laboratory plastcorder mixer at 140 °C. The blend sheets with thickness of about 1 mm were prepared by compression-molding at 150 °C. Afterwards, the blend sheets were crosslinked by electron beam irradiation and were foamed by heating at 225 °C. They reported that at the same given dose of irradiation and blowing agent content, LDPE/EVA foam had the higher cell densities than LDPE foam due to higher crosslinking densities. Furthermore, the addition of EVA increased gel content and foaming degree but the tensile strength decreased.

3.2 Effects of Concentration of Blowing Agent

I-Chun Liu and co-worker [27] studied the effect of concentration of blowing agent in crosslinked polyethylene blends containing recycled polyethylene foam. First, the blend foams was prepared by mixing the LDPE, recycled polyethylene, and azodicarbonamide with varying amounts at 4, 7, 10 and 14 phr which the zinc oxide was used as activators to lower the decomposition temperature of azodicarbonamide in extruder. Continuity, the melt extrudate out of the T-die was taken up by leading rolls to form a sheet of 1.0±0.05 mm thickness. Second, the sheet was crosslinked by electron beam process. Finally, the foam was prepared by heating in hot air. They reported the decreasing of tensile strength, elongation at break and tear strength with increasing of azodicarbonamide content. They concluded that the tensile properties of closed cell foam were strongly affected by the expansion ratio.

M. Danaei and co-worker [28] studied the influence of concentration of chemical blowing agent on density, tensile properties and water absorption of radiation crosslinked polyethylene foam. Azodicarbonamide was used as blowing agent with varying amounts at 5-15 phr. Dicumyl peroxide and trimethylopropane trimethacrylate were used as crosslinking agent and crosslinking promoter, respectively. The compounds were mixed by two roll mill at 150 ^{o}C and pressed by hydraulic press at 150 ^{o}C to form a sheet thickness of 2.0 mm and exposed to gamma radiation. The foams were prepared by hot press. The result showed that the increasing of blowing agent content leading to decreasing density, tensile strength and elongation at break but increasing of water absorption due to high degree of expansion which to lower density and high contact area between polymer and water molecules.

Hussien A. Yousself and co-worker [26] studied the effect of concentration of blowing agent on LDPE/EVA (80/20) foam. Azodicarbonamide was used as blowing agent with vary amounts at 0.5-7.5 wt%. They found that increasing blowing agent content reduced stress at break of LDPE/EVA blend foam due to long cell size and thin cell walls. Besides, they reported that gel content and degree of foaming of LDPE/EVA blend foam increased with increasing the blowing agent.

3.3 Effects of Level of Crosslinking

Siqin Dalai and Chen Wenxin [25] studied the effect of dose rate of irradiation on gel fraction in the LDPE/EVA (70/30) blend foam. The result showed that there were more gel fraction in the higher dose rate foam than in the lower dose rate foam due to reaction rate of radicals was accelerated in higher dose rate. High crosslinking increased gel fraction which resulted at increased apparent density of the LDPE/EVA blend foam, decreased expansion ratio of foam and increased tensile strength.

A. Mahapatro and co-worker [29] studied the effect of crosslinking agent concentration in crosslinked polyethylene foam. Activated azodicarbonamide was used as blowing agent and 40% dicumyl peroxide on an inert clay carrier was used as crosslinking agent. It was shown that the gel content increased with increasing crosslinking agent concentration.

D.W.Kim and K.S.Kim [11] studied the effect of electron beam irradiation on the precrosslinked LDPE/EVA (80/20) blend foam with dose range of 2.8-8.0 Mrad. LDPE had melt flow index 3 g/10min and ethylene vinyl acetates copolymer had vinyl acetates content of 15wt%. Azodicarbonamide and zinc oxide-zinc stearic were used as blowing agent and activators of azodicarbonamide, respectively. The compounds were mixed by intensive mixer at 130 °C and 60 rpm rotor speed. The blend sheets with thickness of about 1.2 mm were extruded by 50 mm single screw extruder with zone temperature 110-130 °C and screw speed at 30 rpm. After irradiation, the irradiation sheet was expanded by heating in hot air oven at 190-225 °C for 150±20 seconds. The resultant foam was 6.0±0.5mm thickness. The result showed that the tensile strength initially increased with increasing radiation dose due to the formation of network structure and increasing of crystallinity. But at higher radiation dose, the tensile strength decreased due to the network structure broke down into small network structures. The tear strength increased with increasing radiation dose, but at higher radiation dose tear strength decreased because of the propagation of crack at interface and the compression set is inversely proportional to the degree of crosslinking of foam.

Hussien A. Yousself co-worker [26] studied the effect of electron beam irradiation dose in the LDPE/EVA (80/20) blend foam with irradiation dose vary at 25-100 kGy. It was found that increasing irradiation dose increased the stress at break but decreased elongation at break due to the extension of chains was hindered. For thermal stability by Thermogravimatric analysis (TGA), it was found that the thermal stability increased with increasing irradiation dose.

CHAPTER IV

EXPERIMENTALS

This chapter discussed various materials and methods employed in this research. The chapter was divided into five parts including materials, formulations of LDPE/EVA blend foam, preparation of LDPE/EVA blend foam and LDPE/EVA blend foam specimens, and characterization techniques employed.

4.1 Materials

Low density polyethylene (LDPE), ethylene vinyl acetate copolymer containing 18wt% vinyl acetate (EVA18wt%VA) and ethylene vinyl acetate copolymer containing 28wt%vinyl acetate(EVA28wt%VA) used in this work were obtained from TPI POLENE Co., Ltd., Thailand. The properties of polymer resin were shown in Table 4.1. Chemical blowing agent used in this research was azodicarbonamide (ADC) ($NH_2CON=NCONH_2$, average size 5-7 micrometer, decomposition temperature 210-220 °C) from Cosmos Chemical Co., Ltd., Thailand. Zinc Oxide (ZnO) used as activator of blowing agents and lubricant used as stearic acid ($CH_3(CH_2)_{16}COOH$) were supplied by CT Laboratory Co., Ltd., Thailand. The crosslinking agent was dicumyl peroxide (DCP) $[C_6H_5C(CH_3)_2]_2O_2$, melting point 39-41 °C, 97 %assay,) was supplied by S.M. Chemical Supplies Co., Ltd., Thailand.

Table 4.1 Properties of LDPE, EVA18wt%VA and EVA28wt%VA*

Polymer resin	Density (g/cm^3)	Melt flow index (g/10 min)
Low density polyethylene (LDPE)	0.920	5.2
Ethylene vinyl acetate copolymer containing 18wt%VA (EVA18wt%VA)	0.941	2.3
Ethylene vinyl acetate copolymer containing 28wt%VA (EVA28wt%VA)	0.953	7.8

* Technical data provided by TPI POLENE Co., Ltd., Thailand.

4.2 Formulations of LDPE/EVA Blend Foam

In previous works, ratio of LDPE/EVA at 70/30 and 80/20 wt/wt were usually used in LDPE/EVA blend foam [10, 23-24]. Hence, the same ratios were used in this work for comparison. The amounts of additives were considered by the expected foam density. Example, for 100 parts of polymer, 60 kg/m^3 foam density using 10 phr of azodicarbonamide (ADC) loading, 0.7 phr of dicumyl peroxide (DCP) loading and 30 kg/m^3 foam density using 17 phr of ADC loading, 0.9 phr of DCP loading [2]. As this work aimed to produced very light to light foam density (50-200 kg/m^3), the ADC at 17 phr and 20 phr, the DCP at 0.6, 0.9, 1.2 phr were employed.

The wt% of VA in EVA copolymer used in this work was subjected to availability from local supplier. Nevertheless, the 18wt% and 28wt%VA were the same range as often previous work [11, 25-26].

Therefore, the proportions of LDPE, EVA and additives used in this study were given in Table 4.2. The amount of stearic acid was fixed at 1 phr (phr = parts per hundred parts of polymer) for all mixture and the amount of Zinc Oxide was kept at 20 wt% of blowing agent, as determined by Thermal Gravity metric Analysis (TGA) as described in Chapter V.

4.3 Preparation of LDPE/EVA Blend Foam

For all formulations, appropriate weight of polymer and additive were processed using a twin screw extruder (ThermoHaakE Rheomex 400p PTW16/25) with rod capillary die. The processes ran at screw speed of 70 rpm. The temperature profile was set in range 85-105 ^{o}C as shown in Table 4.3. The polymer blend resin was then compressed into sheet of around 3 mm thickness in the compression molder at 100 ^{o}C and 150 kg/cm^2 for 5 minutes. The polymer blend sheet was cured by compression molding at 100 ^{o}C 50 kg/cm^2 for 30 minutes. The cured sheet was then put in a hot air oven at 160 ^{o}C for 30 minutes for the foaming to occur.

Table 4.2 Proportion of LDPE, EVA and additive in mixtures

Sample Code*	LDPE/EVA Ratio (wt/wt)	Percentage of VA in EVA (wt%)	Chemical blowing agent loading (ADC) (phr)	Crosslinking agent loading (DCP) (phr)
70/30-18-17-0.6	70/30	18	17	0.6
70/30-18-17-0.9	70/30	18	17	0.9
70/30-18-17-1.2	70/30	18	17	1.2
70/30-28-17-0.6	70/30	28	17	0.6
70/30-28-17-0.9	70/30	28	17	0.9
70/30-28-17-1.2	70/30	28	17	1.2
80/20-18-17-0.6	80/20	18	17	0.6
80/20-18-17-0.9	80/20	18	17	0.9
80/20-18-17-1.2	80/20	18	17	1.2
80/20-28-17-0.6	80/20	28	17	0.6
80/20-28-17-0.9	80/20	28	17	0.9
80/20-28-17-1.2	80/20	28	17	1.2
70/30-18-20-0.6	70/30	18	20	0.6
70/30-18-20-0.9	70/30	18	20	0.9
70/30-18-20-1.2	70/30	18	20	1.2

* a-b-c-d denoted the LDPE/EVA ratio, %VA in EVA, ADC, DCP, respectively.

Table 4.3 The temperature profile of twin screw extruder

Parameter	Setting (ºC)
Temperature 1 (TS-E1),	85
Temperature 2 (TS-E2)	90
Temperature 3 (TS-E3)	90
Temperature 4 (TS-E4)	90
Temperature 5 (TS-D1)	100
Temperature 6 (TS-D2)	105

4.4 Preparation of LDPE/EVA Blend Foam Specimens

The obtained foam was cut into several test specimens as the followings:

-square specimen (25.4x25.4x25.4 mm) for density test as shown in Figure 4.1 and 4.2 (ASTM D3575-00).

-dogbone-shaped specimens for tensile test with dimension shown in Figure 4.3 and 4.4 (ASTM D3574-05).

-cylinder specimens having a minimum cross-section surface area of 2500 mm^2 and 25mm in thickness for compressive strength as shown in Figure 4.5 and 4.6. (ASTM D3575-00).

-rectangular specimen (50×50×25.4 mm) for compression set test as shown in Figure 4.7 and 4.8. (ASTM D3575-00).

-test sample about 0.300±0.015 g for gel content test .(ASTM D2765-01).

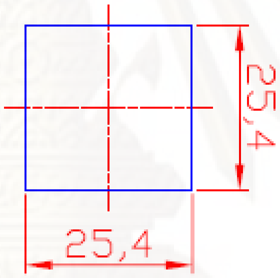


Figure 4.1 Dimension of specimen for density test

Figure 4.2 Density specimen of LDPE/EVA Blend Foam

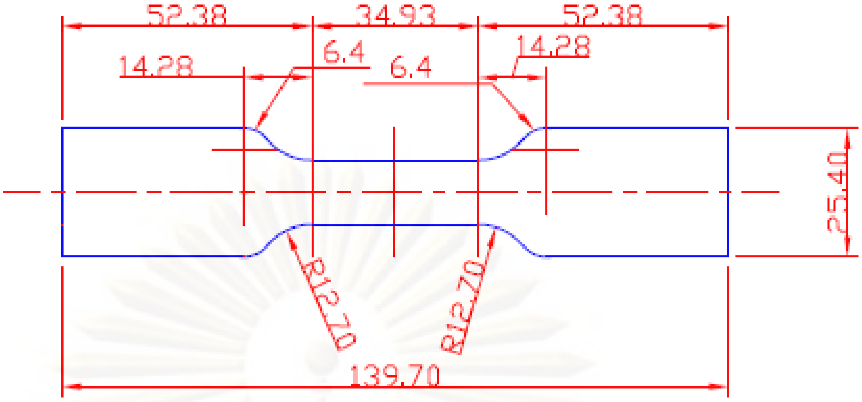


Figure 4.3 Dimension of dogbone-shaped specimen for tensile test

Figure 4.4 Tensile specimen of LDPE/EVA Blend Foam

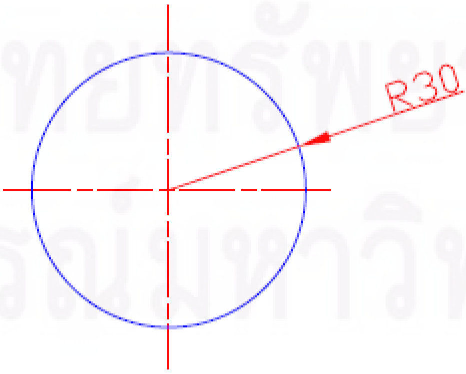


Figure 4.5 Dimension of circle-shaped specimen for compressive strength test

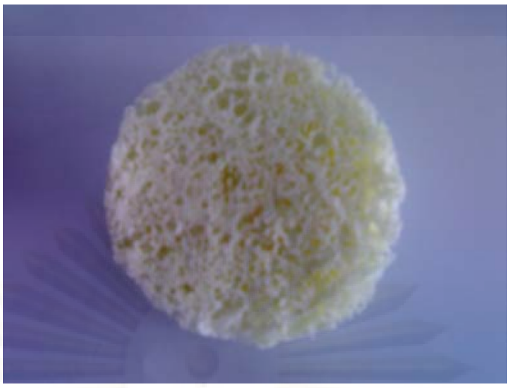


Figure 4.6 Compressive strength specimen of LDPE/EVA Blend Foam

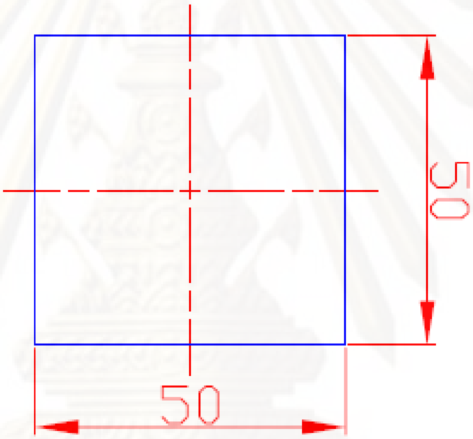


Figure 4.7 Dimension of specimen for compression set test

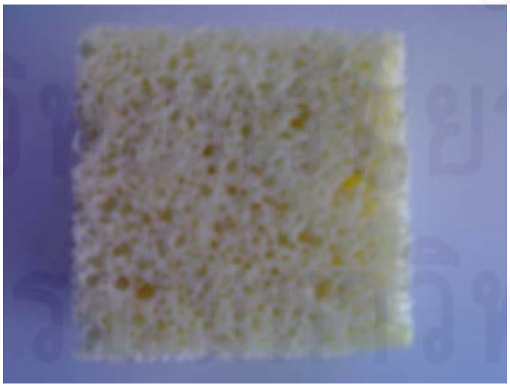


Figure 4.8 Compression set specimen of LDPE/EVA Blend Foam

4.5 Foam Characterizations

4.5.1 Density Test

Density of the foam was characterized by ASTM D 3575-00 Test method A [30], which uses the weight of the specimen from Weight or Analytical balance and the dimensions of the specimen to calculate the density.

$$D = \frac{m}{V} \tag{4.1}$$

D = Density (kg/m^3)

m = Mass (kg)

V = Volume (m^3)

4.5.2 Gel Content Test

Gel content of the foam was characterized by extracting with boiling xylene for 12 h in a reflux system according to ASTM D2765-01 Test Method A [32]. The test sample was added to a 120 mesh stainless steel pouch. After extraction, the pouch was washed by acetone and was dried in vacuum oven at 140 °C to constant weight. The reflux set up was shown in Figure 4.9 and 4.10.

$$\text{Gel content (\%)} = 100 - \left(\frac{\text{(weight lost during extraction)}}{\text{(weight of original specimen)}} \right) \tag{4.2}$$

Figure 4.9 Gel content test of LDPE/EVA Blend Foam

4.5.3 Morphology

Morphology of the foam was characterized by Scanning Electron Microscope (JEOL JSM-5410LV). The sample was immersed in liquid nitrogen and cut by knife.

4.5.4 Tensile Properties

Tensile properties of the foam was characterized by a Universal Testing Machine (Instron 5567, NY, USA) to determine the tensile strength at break and the Young's modulus of LDPE/EVA blend foams by ASTM D 3574-05 [31]. The test was done with at a minimum grip separation of 75 mm and crosshead speed of 500±50 mm/min.

4.5.5 Compressive Strength

Compressive strength was characterized by ASTM D 3575-00 [30], using Universal Testing Machine (Instron 5567, NY, USA) with a compression speed of 12.5 mm/min to determine the force required to reduce the sample thickness to 25% of original thickness.

4.5.6 Compression Set Test

Compression set was characterized by ASTM 3575-00 [30] using Compression set equipment by at 30±3 °C, 47± 2% relative humidity. First, the original thickness (t_o) was measured. Second, the sample was compressed to 50% of its original thickness for 22 h. Finally, the compression force was released and the final thickness (t_f) of sample after 24 h of recovery was measured.

$$C_d = \frac{(t_o - t_f)}{t_o} \times 100 \tag{4.3}$$

C_d = Compression set expressed as a percent of the original thickness

t_o = Original thickness (mm)

t_f = Thickness of the specimen after the specified recovery period (mm)

4.5.7 Thermal Properties of Chemical Blowing Agent

Decomposition temperature of chemical blowing agent was characterized by Thermal Gravity metric Analysis (TGA). Thermograms were performed using a SDT Analyzer Model Q600, TA Instruments, USA. The sample weights were 3-10 mg. The temperature ranges of 50-600°C at a heating rate of 10 °C/min with air purge flow rate of 100 ml/min were used.

CHAPTER V

RESULTS AND DISCUSSION

In this chapter, the experimental results and discussion were described and divided into five major parts, namely, effect of ZnO activator content on the decomposition behaviors of azodicarbonamide blowing agent, effect of crosslinking agent loading, effect of LDPE/EVA ratio and vinyl acetate content in EVA copolymer, effect of chemical blowing agent loading on the physical and mechanical properties of LDPE/EVA blend foams and discussion of effects of blend compositions and additives on properties of LDPE/EVA blend foam.

5.1 Effect of ZnO Activator Content on the Decomposition Behaviors of Azodicarbonamide Blowing Agent

In general, decomposition temperature of azodicarbonamide (ADC) blowing agent can be reduced by adding the promoter ZnO. The effect of ZnO content on the decomposition temperature of ADC had been studied by Thermal Gravity metric Analysis (TGA) (in air). In this study, the amount of ZnO was varied at 0, 10, 20 and 30 wt% of blowing agent. The results from thermal analysis were shown in Figure 5.1 and 5.2.

Figure 5.1 showed that increasing of ZnO content reduced the decomposition temperature of ADC/ZnO mixture.

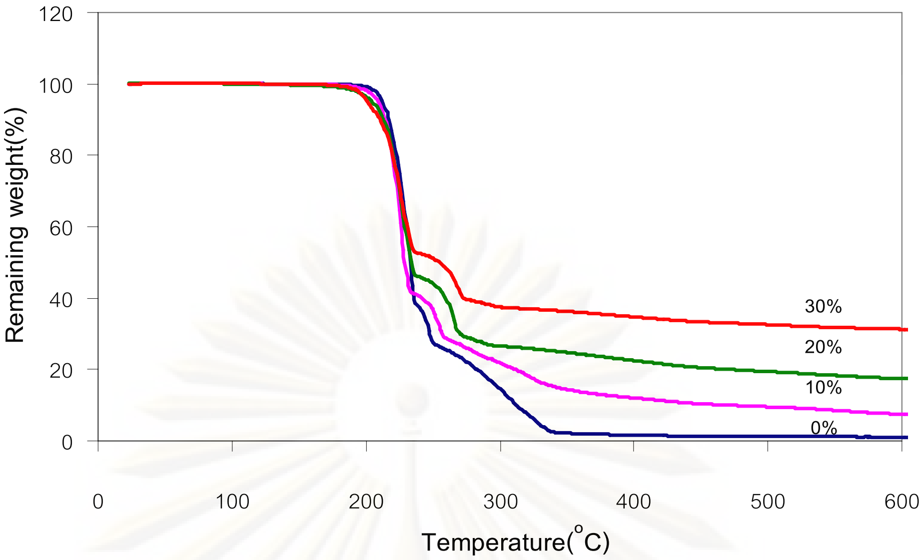


Figure 5.1 The effect of ZnO on the decomposition of ADC

At 95% of the remaining weight, the ADC/ZnO mixture containing 20wt% and 30wt% ZnO began to decompose at around 200 °C, which were lower than normal decomposition temperature of ADC (around 210-220 °C) and the ADC/ZnO mixture containing 10wt% ZnO. The results were shown in Figure 5.2.

However, the ADC/ZnO mixture containing 30wt% ZnO led to a higher residue than ADC/ZnO mixture containing 20wt% ZnO. Therefore, ADC/ZnO mixture containing 20wt% ZnO was selected for foam sheet formulation. It should be noted that the residues were from Zn and its derivatives [25].

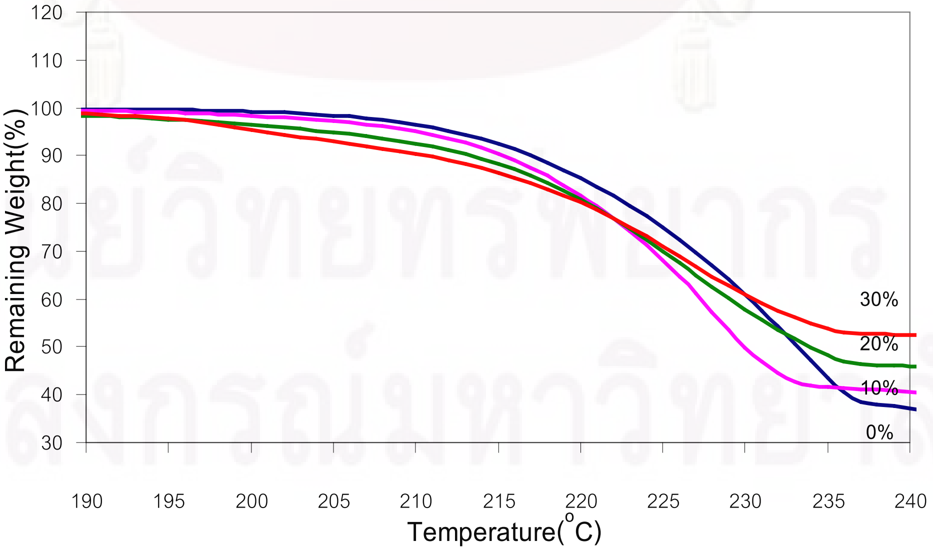


Figure 5.2 The initial decomposition temperature of ADC/ZnO mixture

5.2 Effect of Crosslinking Agent Loading on Properties of LDPE/EVA Blend Foam

LDPE/EVA blend foams were prepared by two-stage compression process, consisting of crossliking and expansion stages. In general, the degree of crosslinking affects expansion ratio of foam and the level of crosslinking is very important for development of cell structure during expanding of cell wall. In this study, the crosslinking agent loading was varied at 0.6, 0.9 and 1.2 phr.

5.2.1 Effect of Crosslinking Agent Loading on Foam Density of LDPE/EVA Blend Foam

The effect of different crosslinking agent loading on foam density of LDPE/EVA blend foams were shown in Figure 5.3 and 5.4.

For foam with LDPE/EVA ratio of 70/30 wt/wt, EVA with 18 and 28 wt%VA, and ADC loading of 17 phr, it can be seen that the foam densities of LDPE/EVA blend foam decreased with increasing the concentration of crosslinking agent loading in range 0.6-1.2 phr. The foam densities were in the light weight class (lesser than 200 kg/cm^3 [1]). Increasing of crosslinking agent loading enhances formation of polymer network or the melt strength. Increasing of polymer melt strength helps to increase extension of the cell wall during the bubble growth without cell wall rupture. Thus, low density foam is obtained by increasing of crosslinking agent loading in range 0.6-1.2 phr [10]. The results here was in general agreement with results of M. Zurina et al. [7].

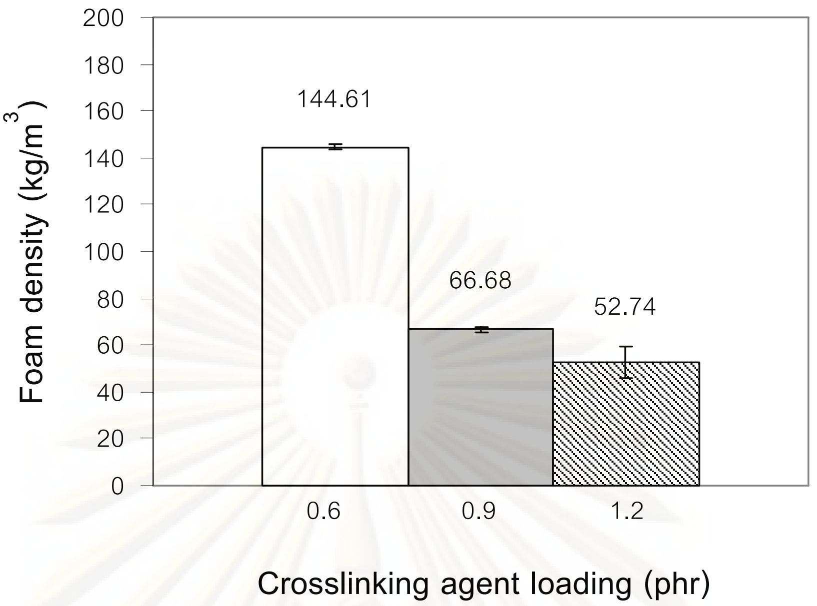


Figure 5.3 Densities of LDPE/EVA blend foams at LDPE/EVA 70/3 0wt/wt, EVA with 18wt%VA, ADC 17 phr with different crosslinking agent loading

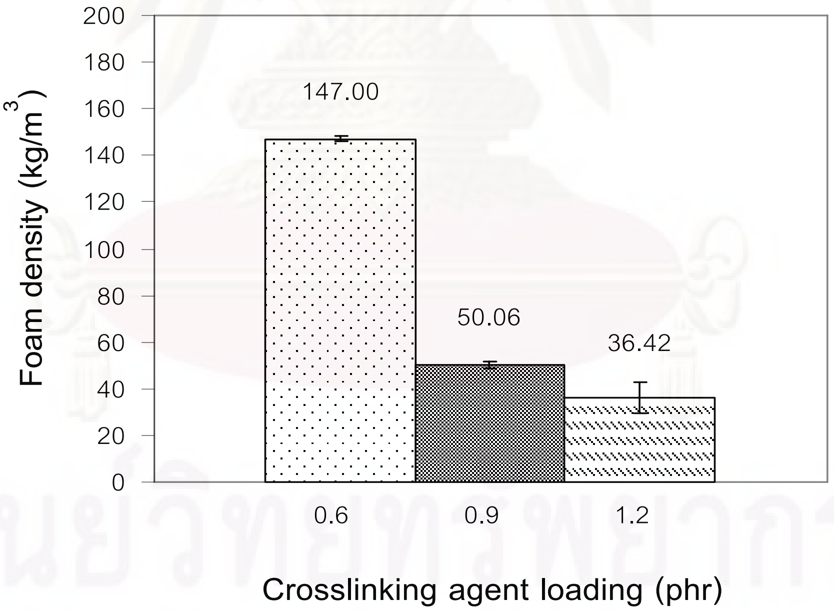


Figure 5.4 Densities of LDPE/EVA blend foams at LDPE/EVA 70/30 wt/wt, EVA with 28wt%VA, ADC 17 phr with different crosslinking agent loading

5.2.2 Effect of Crosslinking Agent Loading on Gel Content of LDPE/EVA Blend Foam

Figure 5.5 and 5.6 showed that effect of different crosslinking agent loadings on gel content of LDPE/EVA blend foam.

It found that gel content slightly increased by increasing concentration of crosslinking agent loading. Gel content indicates the degree of crosslinking, therefore, a higher gel content value means higher degree of crosslinking .Increasing of degree of crosslinking increased three-dimensional network which it can be resistance to chemical solubility. The gel content increases with increasing of insoluble content after extraction.

In this study, increasing of crosslinking agent loading led to increasing of gel content in range of DCP 0.6-1.2 phr.

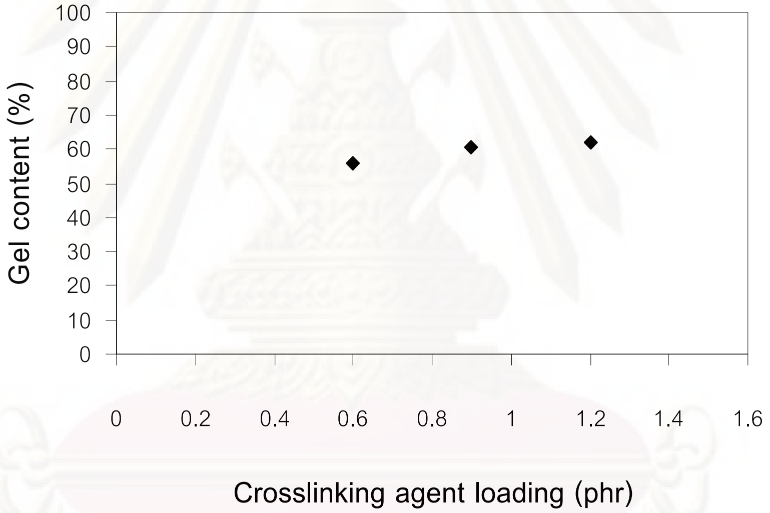


Figure 5.5 Gel contents of LDPE/EVA blend foams at LDPE/EVA 70/30 wt/wt, EVA with 18wt%VA, ADC 17 phr with different crosslinking agent loading

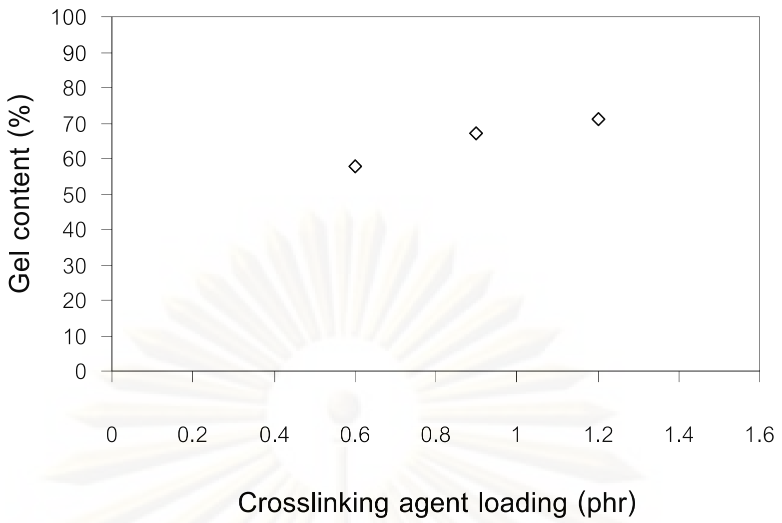


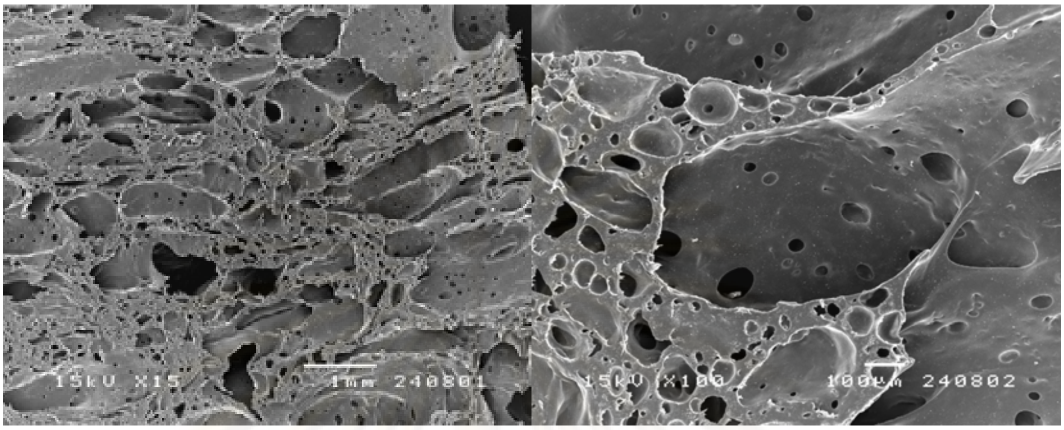
Figure 5.6 Gel contents of LDPE/EVA blend foams at LDPE/EVA 70/30 wt/wt, EVA with 28wt%VA, ADC 17 phr with different crosslinking agent loading

5.2.3 Effect of Crosslinking Agent Loading on Cell Structure of LDPE/EVA Blend Foam

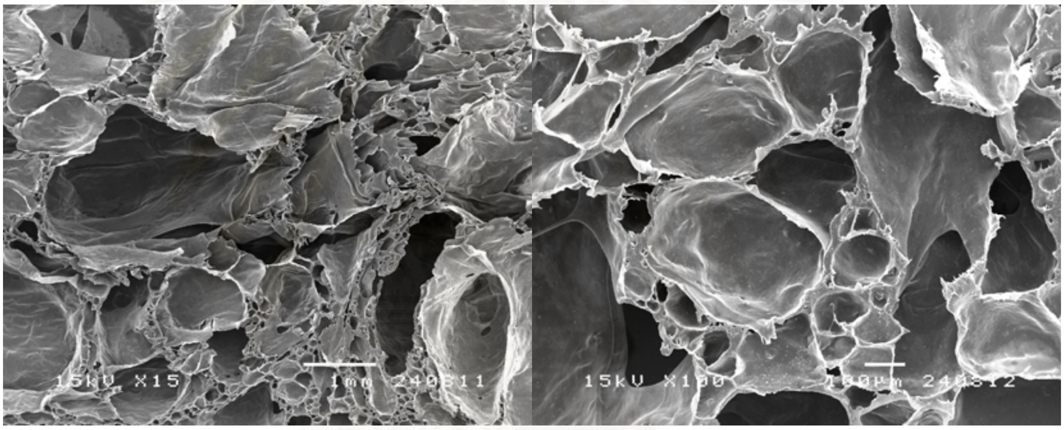
Accordingly, the effect of crosslinking agent loadings on cell structure, it is necessary to have a good balance between the resin viscosity and concentration of crosslinking agent used, led to achieve optimum foam characteristics and adding the crosslinking agent was prevent cell collapse [23]. Characterization of cell structures of LDPE/EVA blend foams with ratio of LDPE/EVA of 70/30 wt/wt, EVA with 18 and 28wt%VA and ADC loading of 17 phr were obtained by SEM. The results are shown in Figure 5.7 and 5.8.

The SEM images of LDPE/EVA blend foams showed that cell structures of LDPE/EVA blend foams were closed-cell structure which it were preferably nonuniform cells size and cells shapes may be due to free bubble expansion in the cell growth led to large cells of irregular shape.

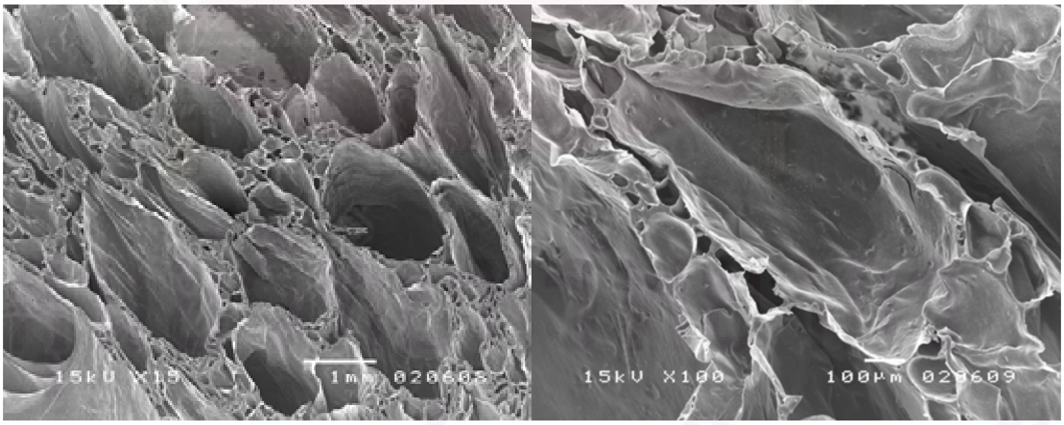
From Figure 5.7 (a) and 5.8 (a), it found that LDPE/EVA blend foams at crosslinking agent loading 0.6 phr had the holes of cell wall due to at a low degree of crosslinking affected gas lost because the polymer resin had poor withstand the high blowing pressure. Also, the expanding of cell wall ruptured. The higher crosslinking agent loading caused increasing of polymer melt strength led to increasing of resistance the bubble growth and stability of bubbles [5, 11]. Also, cell wall was smooth which affected mechanical properties of LDPE/EVA blend foams.



(a) 0.6 phr

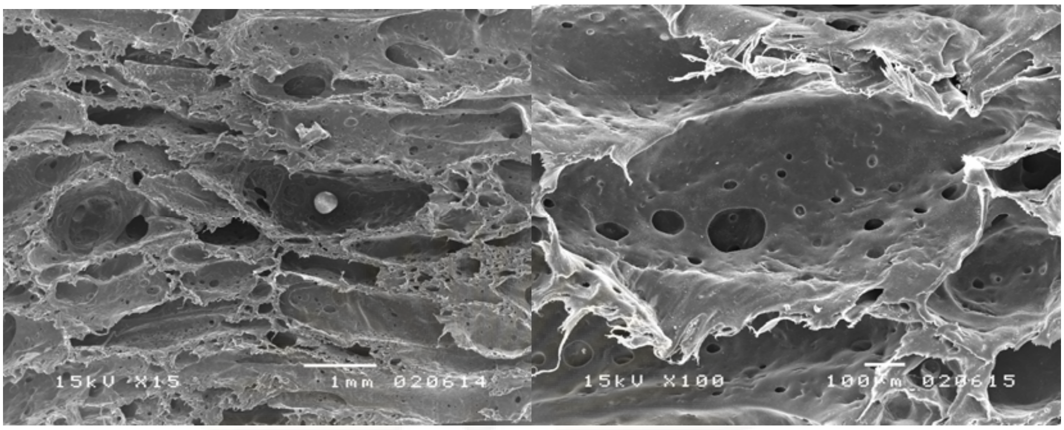


(b) 0.9 phr

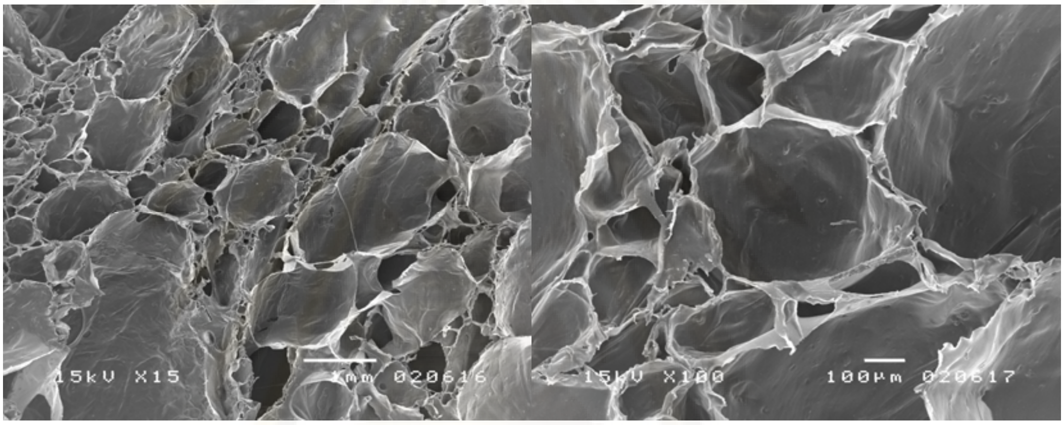


(c) 1.2 phr

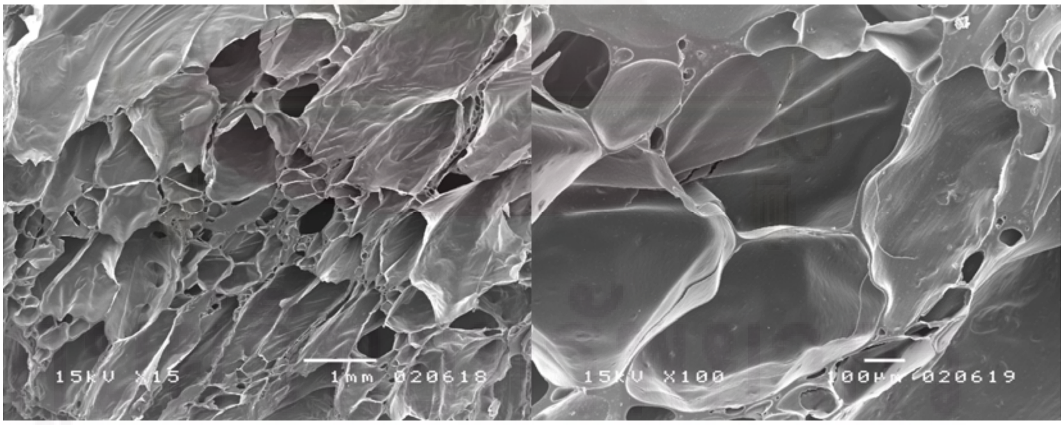
Figure 5.7 SEM images of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 18wt%VA and ADC 17 phr DCP 0.6, 0.9 and 1.2 phr



(a) 0.6 phr



(b) 0.9 phr



(c) 1.2 phr

Figure 5.8 SEM images of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 28wt%VA and ADC 17 phr DCP 0.6, 0.9 and 1.2 phr

5.2.4 Effect of Crosslinking Agent Loading on Mechanical Properties of LDPE/EVA Blend Foam

Effect of crosslinking agent loading on mechanical properties of LDPE/EVA blend foams with ratio of LDPE/EVA of 70/30 wt/wt, EVA with 18 and 28wt%VA and ADC loading of 17 phr showed in term stress at break, Young's modulus, compressive strength and compression set.

Stress at break and Young's modulus of LDPE/EVA blend foams for different crosslinking agent loadings are shown in Figure 5.9-5.12. The result showed that stress at break and Young's modulus of LDPE/EVA blend foams decreased with increasing of the crosslinking agent loading in range 0.6-1.2 phr maybe due to addition of crosslinking agent loading affect molecular weight. Increasing of molecular weight led to change the tensile properties from fragile to ductile [23].

Accordingly, Marcelo G. et al. described the addition of crosslinking agent was related to decrease in the degree of crystallinity led to the soft foam material [23] and Hussien A. et al. measured the tensile strength at break of LDPE/EVA blend foam. They found that the tensile strength of foam depended on foam density rather than cell structure or degree of crosslinking [26].

Also, these result proposed that increasing of the crosslinking agent loading in range 0.6-1.2 phr led to foam is more softness and the reduction of tensile properties corresponded to the decreasing of foam density.

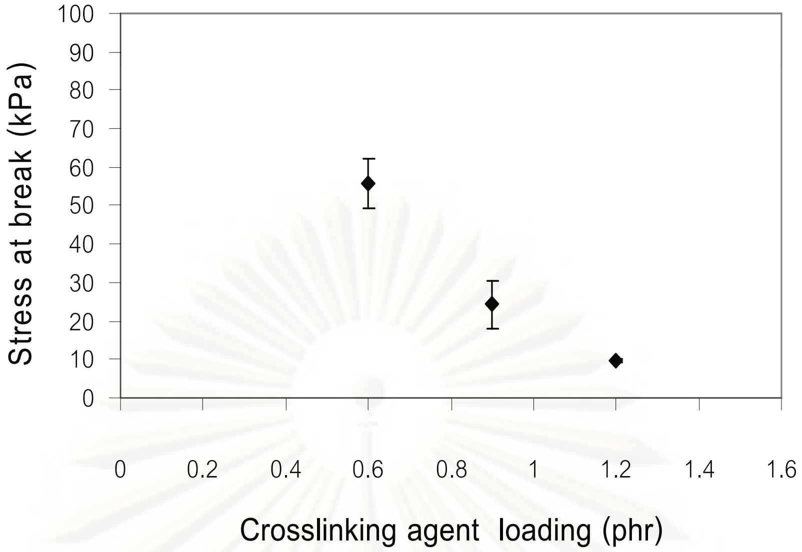


Figure 5.9 Stress at break of LDPE/EVA blend foams at LDPE/EVA 70/30 wt/wt, EVA with 18wt%VA, ADC 17 phr with different crosslinking agent loading

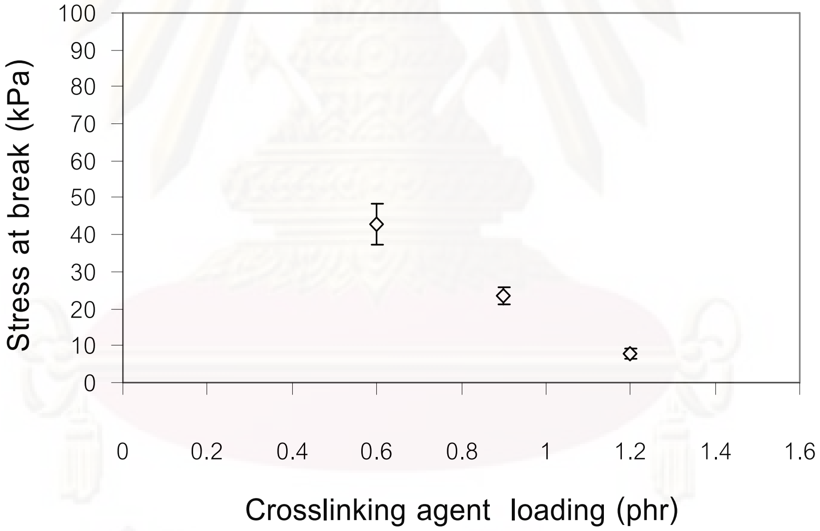


Figure 5.10 Stress at break of LDPE/EVA blend foams at LDPE/EVA 70/30 wt/wt, EVA with 28wt%VA, ADC 17 phr with different crosslinking agent loading

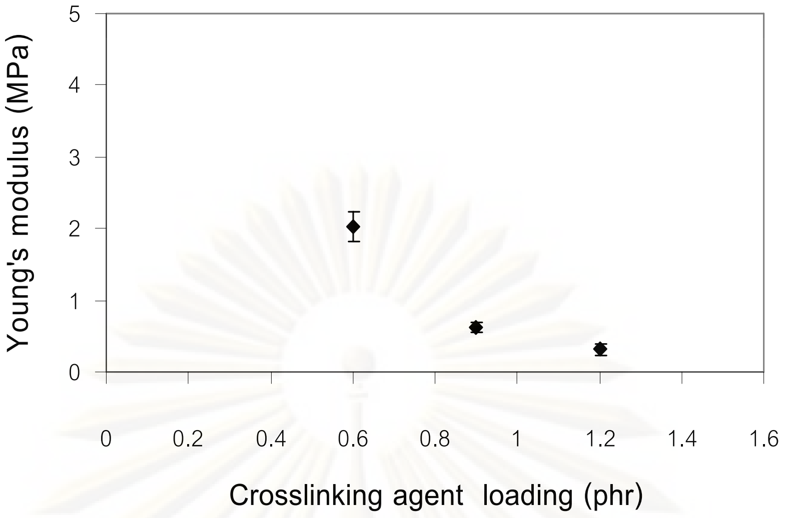


Figure 5.11 Young's modulus of LDPE/EVA blend foams at LDPE/EVA 70/30 wt/wt, EVA with 18wt%VA, ADC 17 phr with different crosslinking agent loading

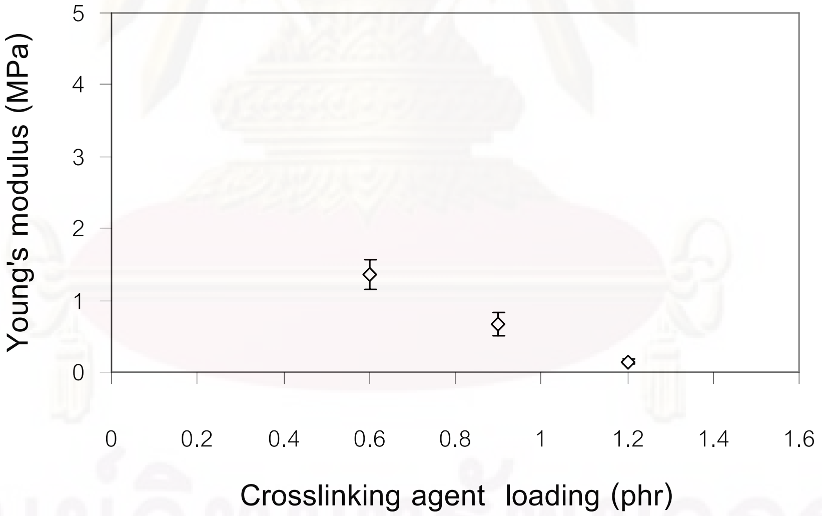


Figure 5.12 Young's modulus of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 28wt%VA, ADC 17 phr with different crosslinking agent loading

Figure 5.13 and 5.14 showed the compressive strength of LDPE/EVA blend foams with ratio of LDPE/EVA of 70/30 wt/wt, EVA with 18 and 28wt%VA and ADC loading of 17 phr at crosslinking agent loading in range 0.6-1.2 phr.

The results showed that compressive strength decreased with increasing crosslinking agent loading due to increasing of crosslinking agent loading cause it increased cell wall was smooth and decreased degree of crytallinity [23]. The compression of gas in the cells led to cell wall bending and cell face stretching when compress force to foam. Therefore, foams with higher crosslinking agent loading were better cell wall bending than lower crosslinking agent loading.

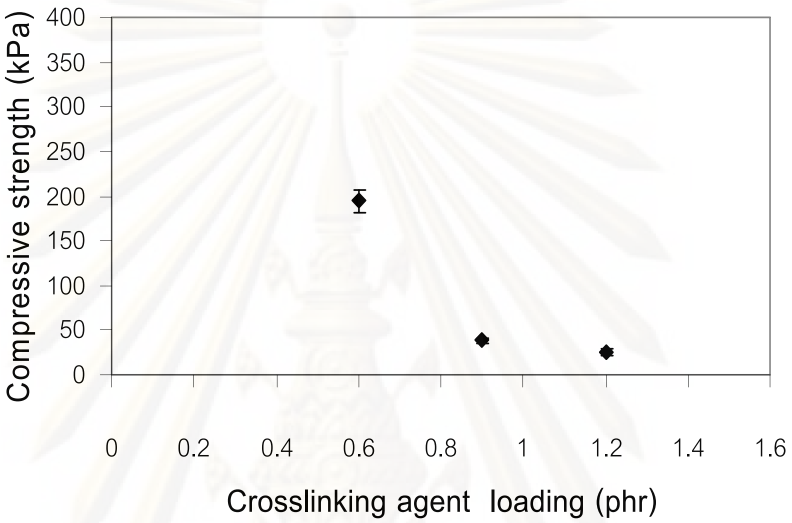


Figure 5.13 Compressive strength of LDPE/EVA blend foams at LDPE/EVA 70/30 wt/wt, EVA with 18wt%VA, ADC 17 phr with different crosslinking agent loading

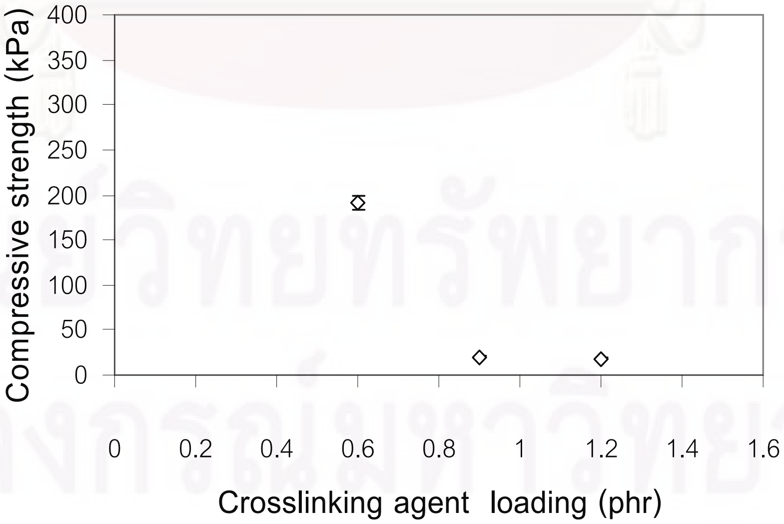


Figure 5.14 Compressive strength of LDPE/EVA blend foams at LDPE/EVA 70/30 wt/wt, EVA with 28wt%VA, ADC 17 phr with different crosslinking agent loading

In flexibility of LDPE/EVA blend foams was determined by compression set test. The compression set related to the degree of elastic recovery of foams, so that, a lower compression set value means better elastic recovery [11].

The effect of crosslinking agent loading on the foam compression set is shown in Figure 5.15 and 5.16. At higher crosslinking agent loaing (1.2 phr) in lighter foam density had compression set about 2.72% less than lower crosslinking agent loading (0.6 phr) in higher foam density was 5.10%. Therefore, the compression set was reduced by increasing of crosslinking agent content corresponded to the report of D.W.Kim and K.S.Kim [11]. The addition of crosslinking agent loading lead to foam was more flexible may be due to the mobility of chain by three dimensional networks.

As there was higher crosslinking agent loading in the lighter density foams, foams with more soft and flexibility which affect by increasing of degree of crosslinking or decreasing of crytallinity led to decreasing of mechanical properties.

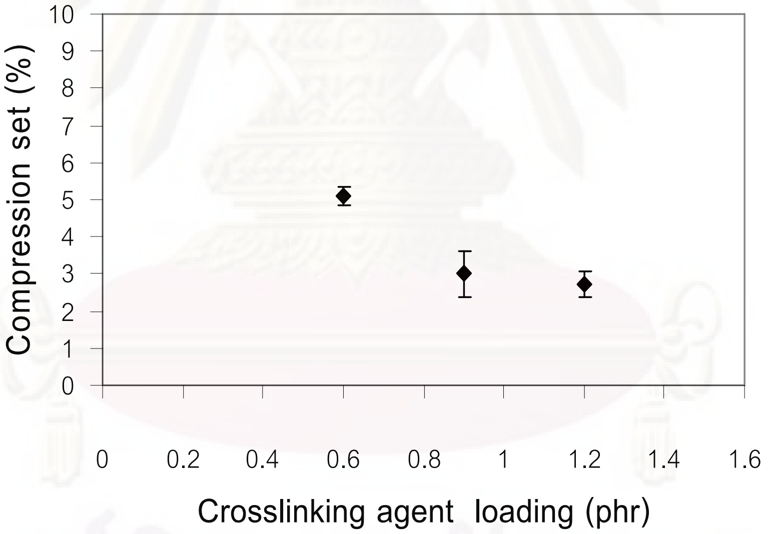


Figure 5.15 Compression set of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 18wt%VA, ADC 17 phr with different crosslinking agent loading

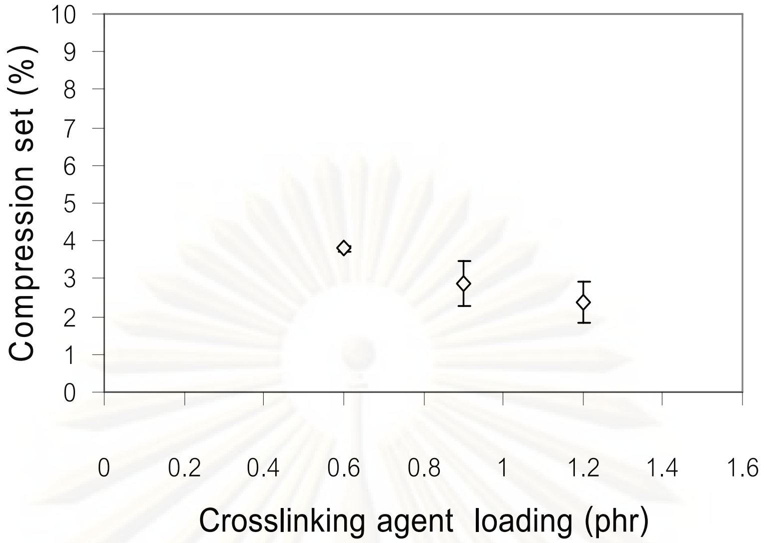


Figure 5.16 Compression set of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 28wt%VA, ADC 17 phr with different crosslinking agent loading

5.3 Effect of Blend Compositions on Properties of LDPE/EVA Blend Foam

Effect of blend compositions on properties of LDPE/EVA blend foam divide 2 factor include ratio of LDPE/EVA and %vinyl acetate in ethylene vinyl acetate copolymer (%VA).

5.3.1 Effect of Ratio of LDPE/EVA on Properties of LDPE/EVA Blend Foam

The effect of ratio of LDPE/EVA on foam densities of LDPE/EVA blend foam with EVA 18 and 28wt%VA, ADC loading of 17 phr at different crosslinking agent loadings are shown in Figure 5.17 and 5.18.

The result showed that the decreasing of EVA content in ratio of LDPE/EVA was 80/20 wt/wt slightly decreased foam densities of LDPE/EVA blend foam may be due to increasing of degree of crosslinking lead to reduce the foam densities which it can be seen the degree of crosslinking form gel content of LDPE/EVA blend foams.

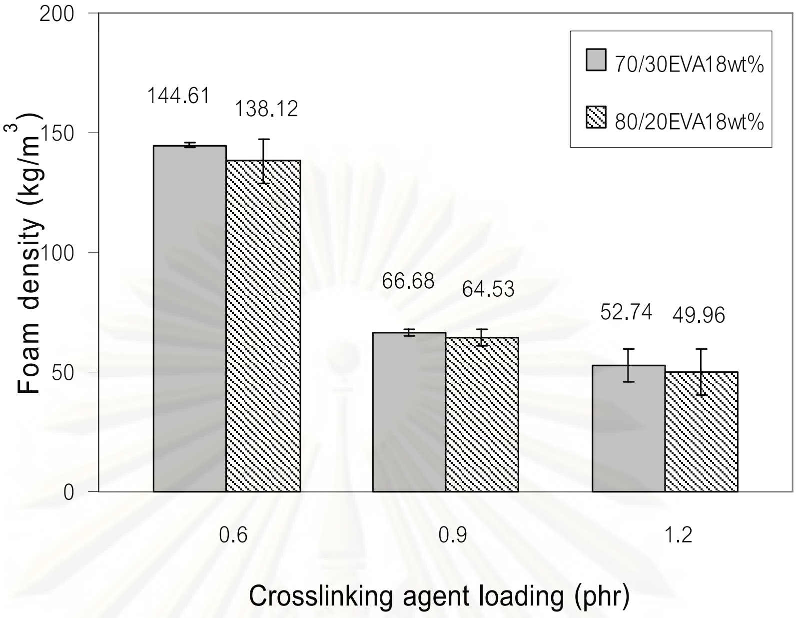


Figure 5.17 Densities of LDPE/EVA blend foams at LDPE/EVA 70/30 and 80/20 wt/wt, EVA with 18 wt%VA, ADC 17 phr at different crosslinking agent loadings

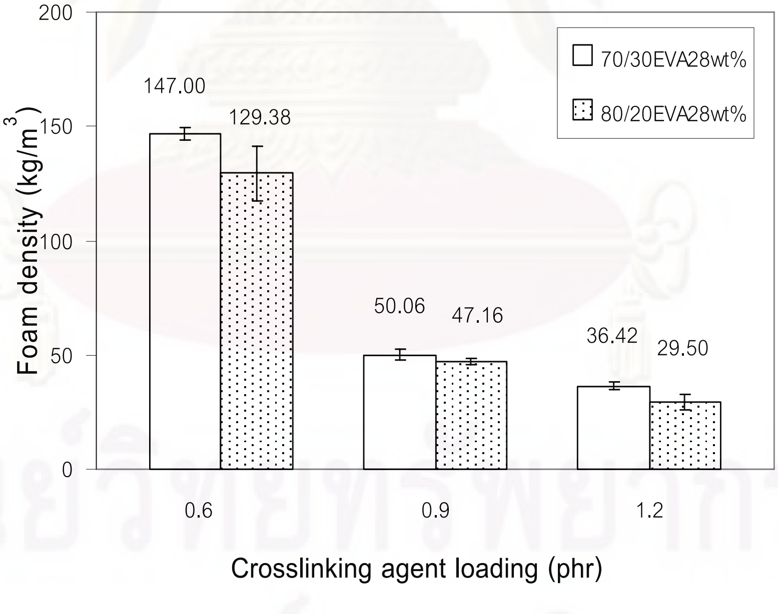


Figure 5.18 Densities of LDPE/EVA blend foams at LDPE/EVA 70/30 and 80/20 wt/wt, EVA with 28 wt%VA, ADC 17 phr at different crosslinking agent loadings

From Figure 5.19 and 5.20 showed that the ratio of LDPE/EVA on gel content of LDPE/EVA blend foam with EVA 18 and 28wt%VA, ADC loading of 17 phr at different crosslinking agent loadings.

It found that decreasing of EVA content slightly increased the gel content. These results indicate decreasing of EVA content probably increased the degree of crosslinking.

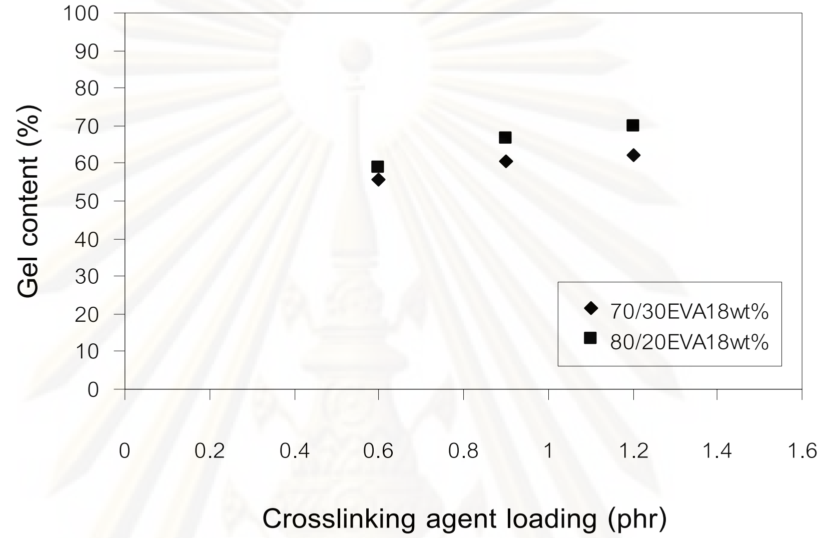
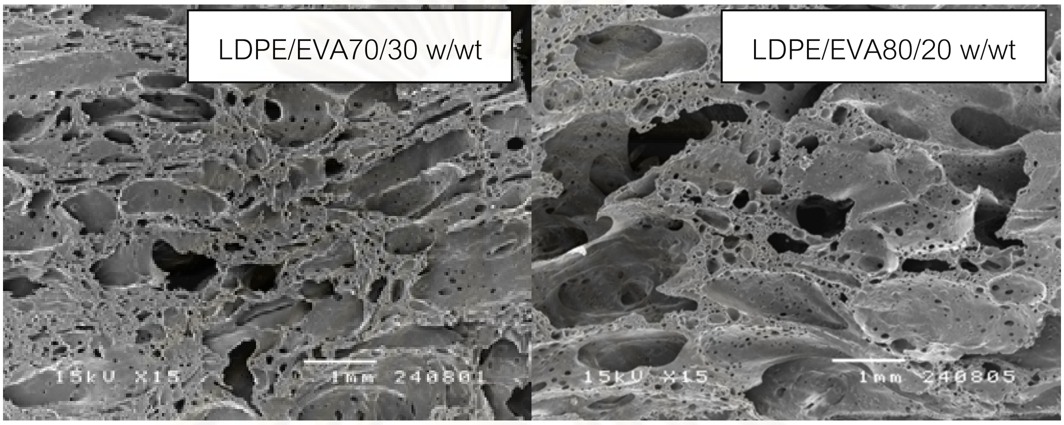


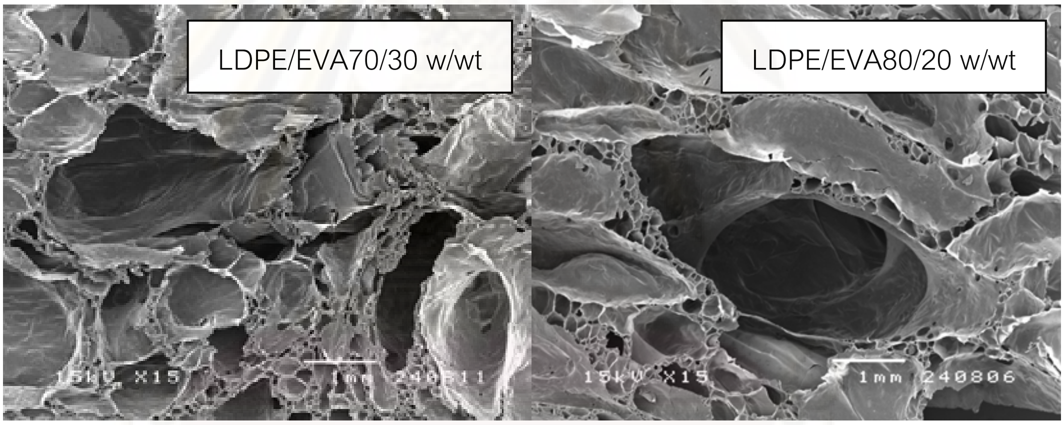
Figure 5.19 Gel contents of LDPE/EVA blend foams at LDPE/EVA 70/30 and 80/20wt/wt, EVA with 18wt%VA, ADC 17 phr at different crosslinking agent loadings

Figure 5.20 Gel contents of LDPE/EVA blend foams at LDPE/EVA 70/30 and 80/20wt/wt, EVA with 28wt%VA, ADC 17 phr at different crosslinking agent loadings

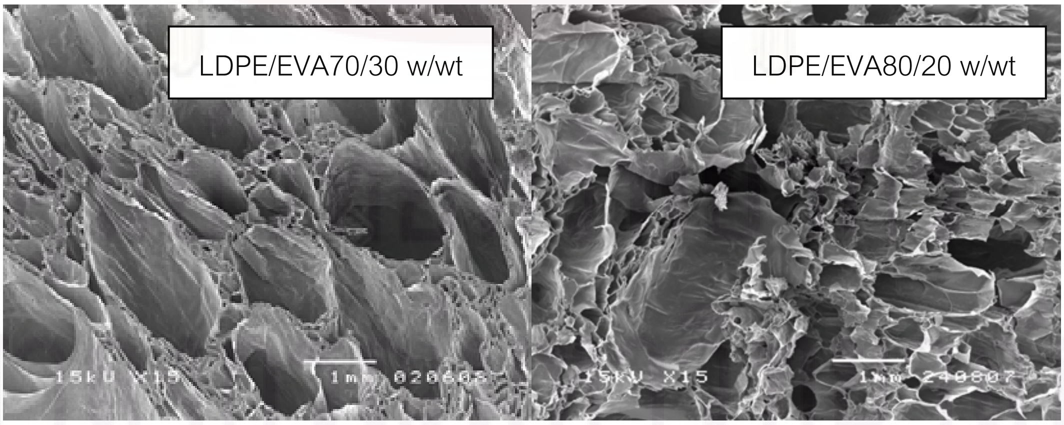
The cell structures of LDPE/EVA blend foam with EVA 18 and 28wt%VA, amount of ADC 17 phr at different of crosslinking agent loadings are shown in Figure 5.21 and 5.22. It found that the cell structures of LDPE/EVA 80/20 wt/wt were similar as LDPE/EVA 70/30 wt/wt may be due to the decreasing of EVA content not affect cell structures.



(a) 0.60 phr

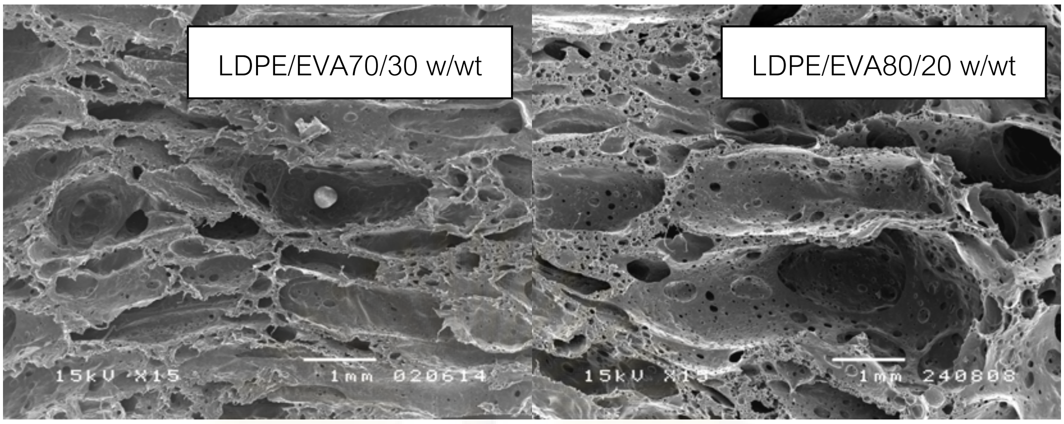


(b) 0.90 phr

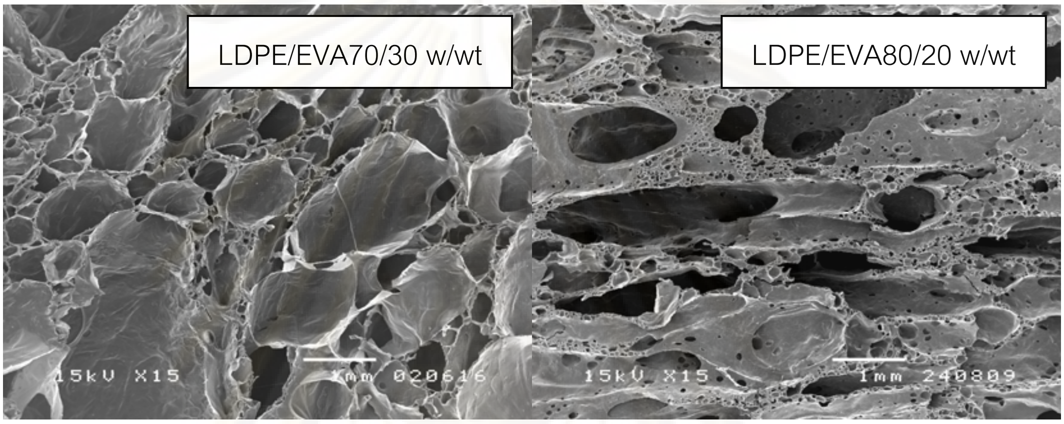


(c)1.20 phr

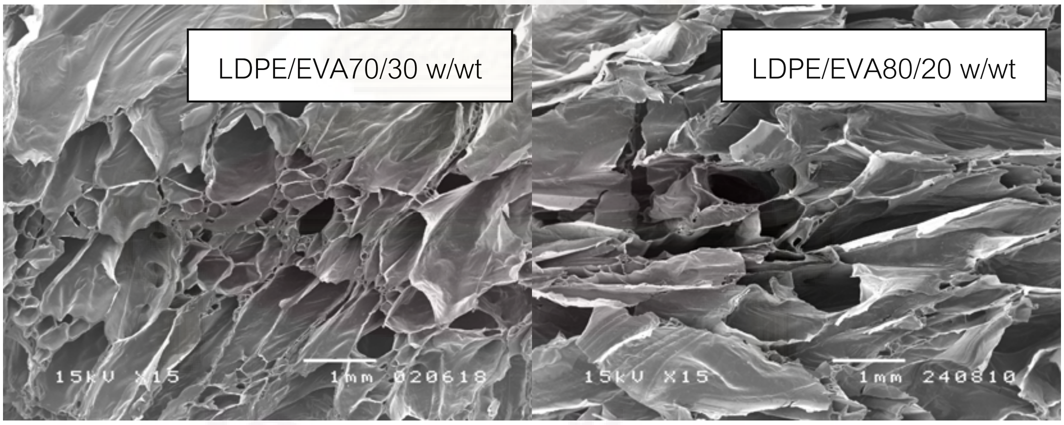
Figure 5.21 SEM images of LDPE/EVA blend foams which LDPE/EVA 80/20wt/wt, EVA with 18wt%VA and ADC 17 and 20 phr DCP 0.60, 0.90 and 1.20 phr



(a) 0.6 phr



(b) 0.9 phr



(c) 1.2 phr

Figure 5.22 SEM images of LDPE/EVA blend foams which LDPE/EVA 80/20wt/wt, EVA with 28wt%VA and ADC 17 and 20 phr DCP 0.60, 0.90 and 1.20 phr

The stress at break of LDPE/EVA blend foams with ratio of LDPE/EVA 70/30 and 80/20wt/wt, EVA with 18 and 28wt%VA are shown in Figure 5.23 and 5.24.

From Figure 5.23, it can be seen that the stress at break of LDPE/EVA blend foams in case EVA with 18wt%VA at LDPE/EVA 80/20wt/wt were lower than LDPE/EVA 70/30wt/wt may be due to degree of crosslinking too high with decreasing of ethylene vinyl acetate content related to the formation of network structure began to break down into small network structure led to stress at break fall [11].

But in case LDPE/EVA blend foams at EVA with 28wt%VA in Figure 5.24, both the stress at break of LDPE/EVA blend foams at ratio of LDPE/EVA 70/30 and 80/20wt/wt were very close may be due to gel content of at ratio of LDPE/EVA 70/30 and 80/20 wt/wt were similar.

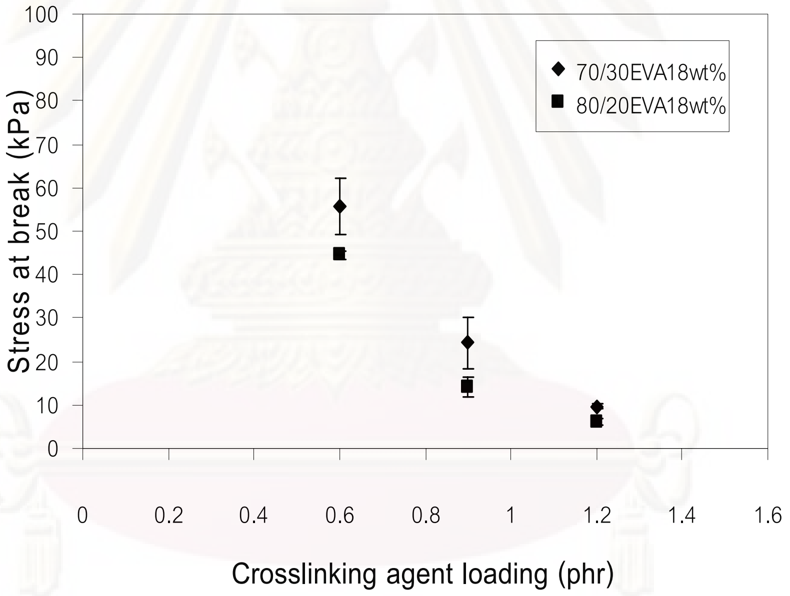


Figure 5.23 Stress at break of LDPE/EVA blend foams at LDPE/EVA 70/30 and 80/20wt/wt, EVA with 18wt%VA, ADC 17 phr at different crosslinking agent loadings

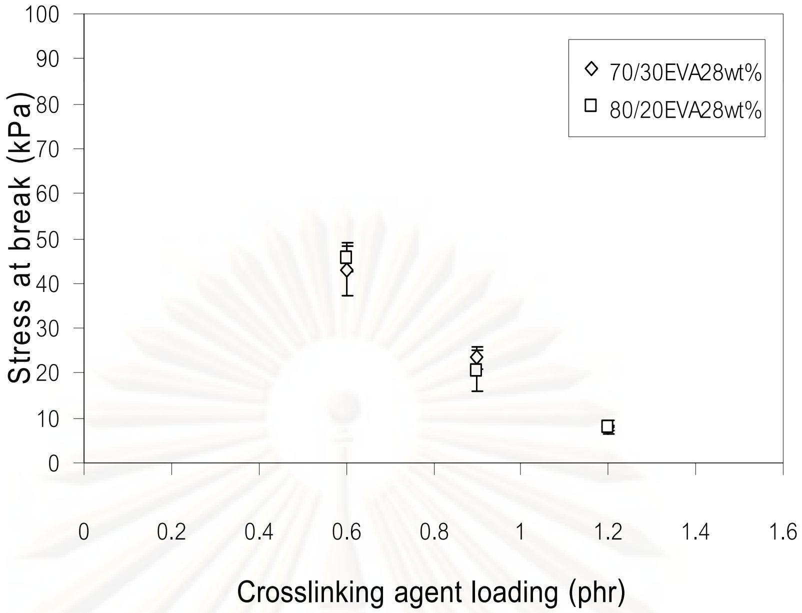


Figure 5.24 Stress at break of LDPE/EVA blend foams at LDPE/EVA 70/30 and 80/20wt/wt, EVA with 28wt%VA, ADC 17 phr at different crosslinking agent loadings

The Young's modulus of LDPE/EVA blend foams with LDPE/EVA 70/30 and 80/20wt/wt, EVA with 18 and 28wt%VA are shown in Figure 5.25 and 5.26.

It found that the Young's modulus of LDPE/EVA blend foams with EVA 18wt%VA were similar to in both case ratio of LDPE/EVA were 70/30 and 80/20wt/wt may be due to decreasing of ethylene vinyl acetate copolymer not affect Young's modulus.

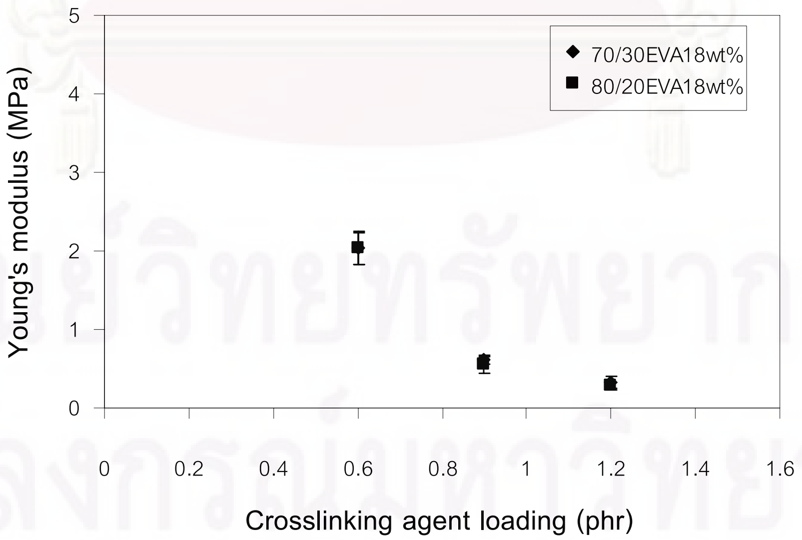


Figure 5.25 Young's modulus of LDPE/EVA blend foams at LDPE/EVA 70/30 and 80/20wt/wt, EVA with 18wt%VA, ADC 17 phr at different crosslinking agent loadings

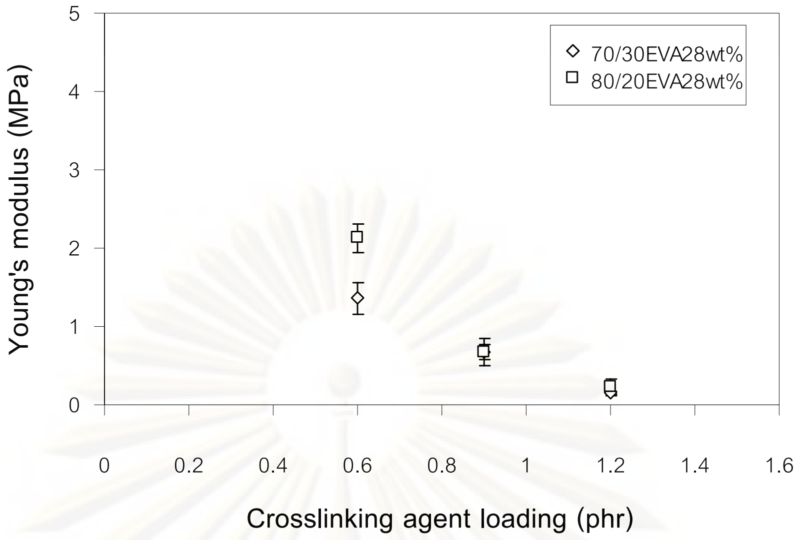


Figure 5.26 Young's modulus of LDPE/EVA blend foams at LDPE/EVA 70/30 and 80/20wt/wt, EVA with 28wt%VA, ADC 17 phr at different crosslinking agent loadings

Figure 5.27 and 5.28 showed that the compressive strength of LDPE/EVA blend foams with ratio of LDPE/EVA 70/30 and 80/20 wt/wt, EVA with 18 and 28wt%VA.

It found that the compressive strength of LDPE/EVA blend foams with ratio of LDPE/EVA were 80/20wt/wt, EVA with 18 and 28wt%VA were preferably similar to in case ratio of LDPE/EVA were 70/30wt/wt, EVA with 18 and 28wt%VA due to decreasing of ethylene vinyl acetate copolymer content not affect cell structure except in case LDPE/EVA blend foam with ratio of LDPE/EVA was 80/20 wt/wt, EVA 28wt%VA and DCP 0.9 phr was higher than value of ratio of LDPE/EVA was 70/30wt/wt due to cell wall had the holes occurred from slightly decreasing of gel content led to bending of cell wall was hindered.

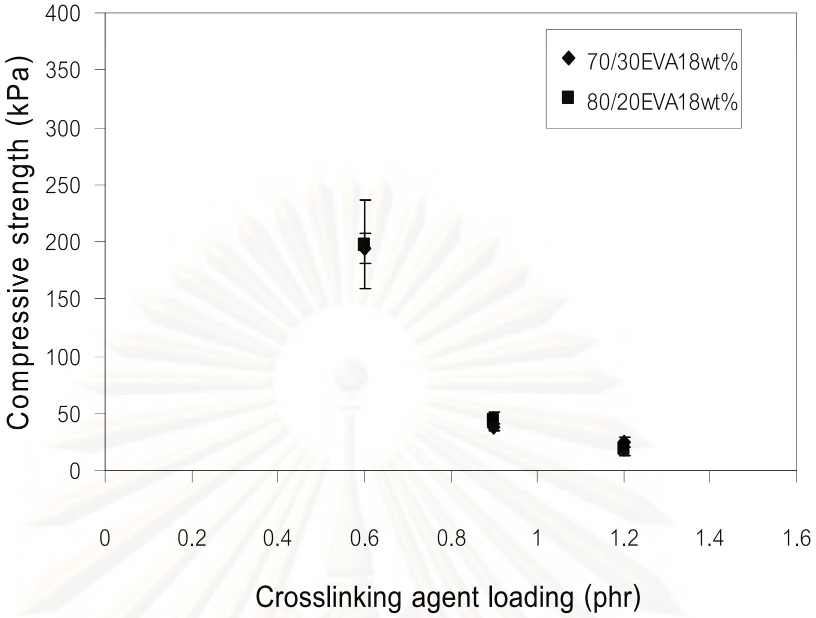


Figure 5.27 Compressive strength of LDPE/EVA blend foams at LDPE/EVA 70/30 and 80/20wt/wt, EVA with 18wt%VA, ADC 17 phr at different crosslinking agent loadings

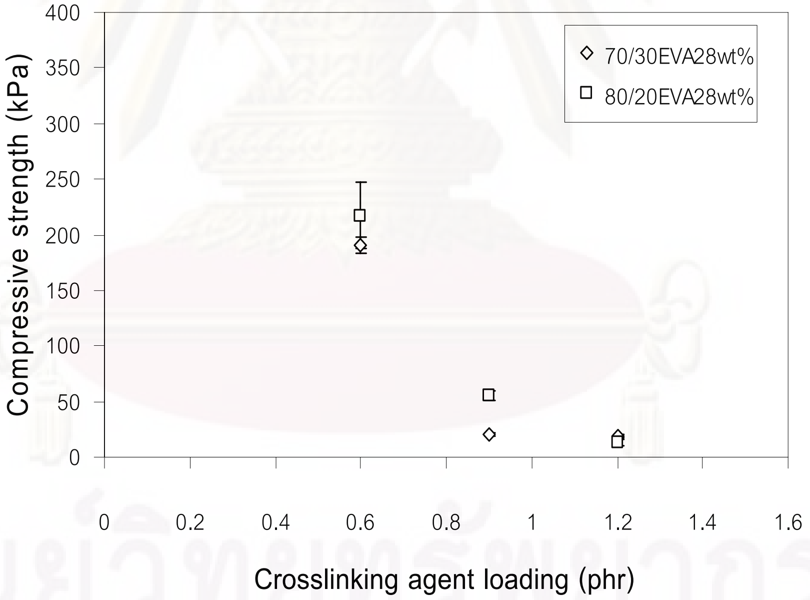


Figure 5.28 Compressive strength of LDPE/EVA blend foams at LDPE/EVA 70/30 and 80/20wt/wt, EVA with 28wt%VA, ADC 17 phr at different crosslinking agent loadings

The compression set of LDPE/EVA blend foams with ratio of LDPE/EVA 70/30 and 80/20wt/wt, EVA with 18 and 28wt%VA are shown in Figure 5.29-5.30.

The result showed that the compression set of the LDPE/EVA blend foams with slightly lower ethylene vinyl acetate copolymer content were more than the sample with higher ethylene vinyl acetate copolymer content may be due to decreasing of ethylene vinyl acetate content decreased flexibility, it reduce the recovery of LDPE/EVA blend foams.

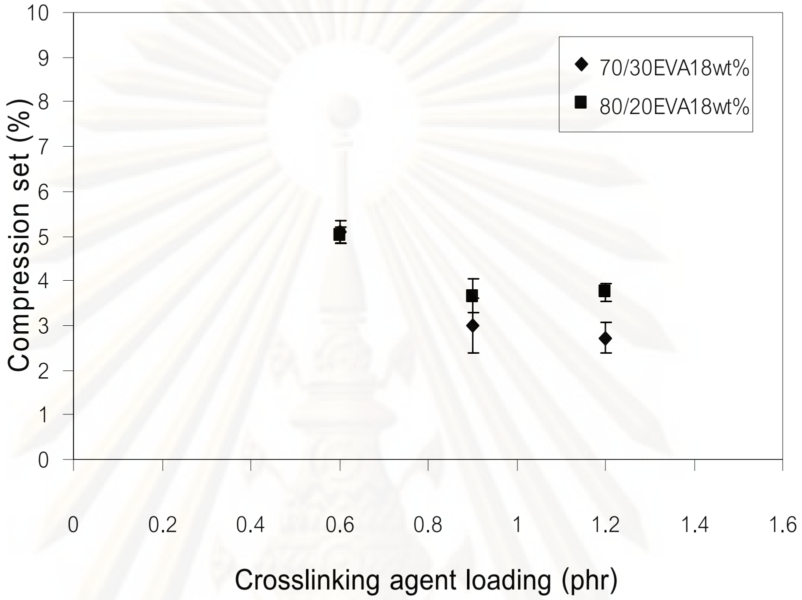


Figure 5.29 Compression set of LDPE/EVA blend foams at LDPE/EVA 70/30 and 80/20wt/wt, EVA with 18wt%VA, ADC 17 phr at different crosslinking agent loadings

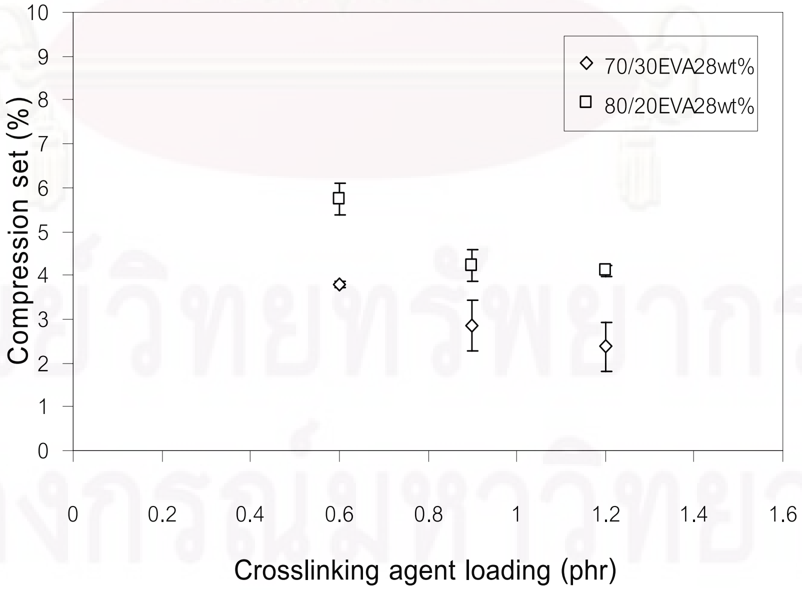


Figure 5.30 Compression set of LDPE/EVA blend foams at LDPE/EVA 70/30 and 80/20wt/wt, EVA with 28wt%VA, ADC 17 phr at different crosslinking agent loadings

5.3.2 Effect of %Vinyl acetate in Ethylene Vinyl Acetate Copolymer on Properties of LDPE/EVA Blend Foam

The comparison of properties of LDPE/EVA blend foam at different %vinyl acetate was determined at the same foam density and closed-cell structure. Figure 5.31, the result showed that foam densities of LDPE/EVA blend foam at different concentration of crosslinking agent loadings. It found that the foam densities divided 2 class included light weight (144.61-147.00 kg/m^3) and very light weight (50.06-52.74 kg/m^3 and 47.16-49.96 kg/m^3).

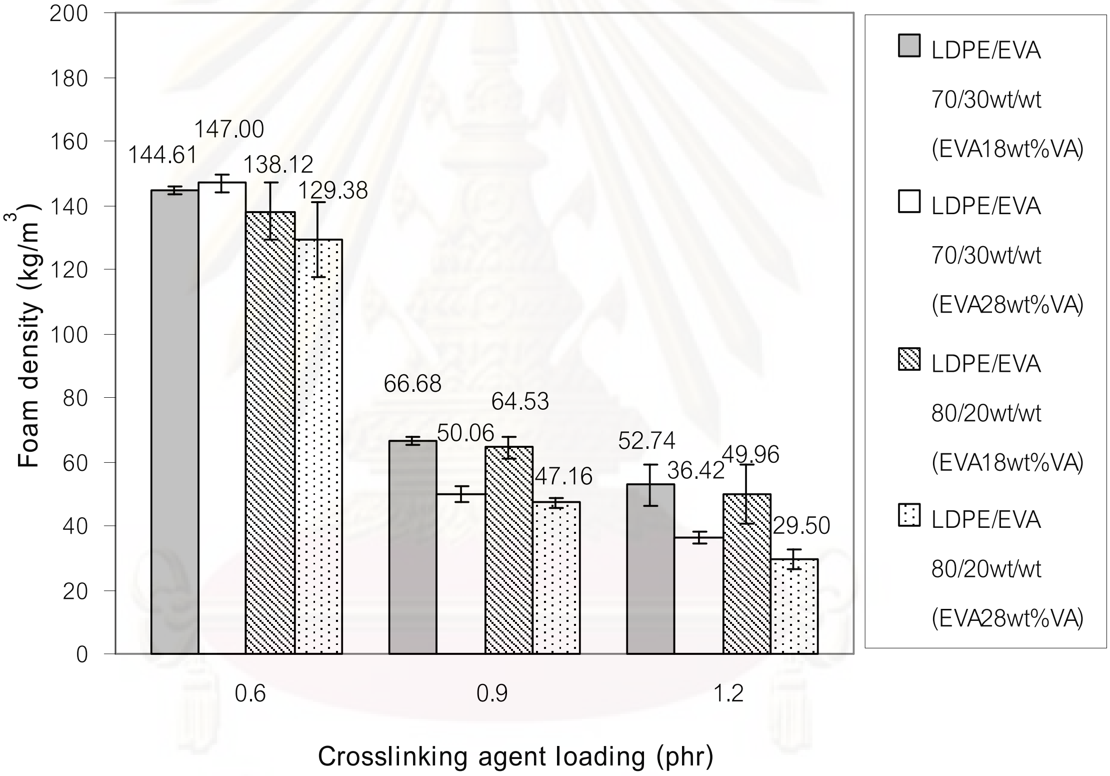


Figure 5.31 Foam densities of all formulations of LDPE/EVA blend foams

Table 5.1 The values of foam density of LDPE/EVA blend foam with different of %vinyl acetate and crosslinking agent loading

Foam density class	Ratio of LDPE/EVA (wt/wt)	%VA in EVA (wt%)	DCP loading (phr)	Foam density (kg/m^3)
Light	70/30	18	0.6	144.61
	70/30	28	0.6	147.00
Very light	70/30	18	1.2	52.74
	70/30	28	0.9	50.06
	80/20	18	1.2	49.96
	80/20	28	0.9	47.16

Form Table 5.1 , for very light weight and the same of foam density, it was found that in case LDPE/EVA with EVA 28wt%VA used the concentration of crosslinking agent loading (DCP) about 0.9 phr while in case LDPE/EVA with EVA 18wt%VA used the concentration of crosslinking agent loading (DCP) about 1.2 phr. These suggested the increasing vinyl acetate content in ethylene vinyl acetate copolymer helps to reduce crosslinking agent loading due to it enhance crosslinking of chains.

However, the effect of %VA in EVA copolymer on gel content of LDPE/EVA blend foams was not determined by gel content test due to the difference in solubility parameter of xylene and polymers [5].

The comparison of mechanical properties of LDPE/EVA blend foams with difference of %VA in EVA copolymer are shown in Figure 5.32-5.35.

The stress at break and Young's modulus as a function of foam density for LDPE/EVA with 18 and 28wt%VA are shown in Figure 5.32 and 5.33.

In light weight class, it was obvious that the stress at break and Young's modulus of LDPE/EVA with EVA 28wt%VA were lower than the values of LDPE/EVA with EVA 18wt%VA due to this should be relate to lower crystallinity of EVA with 28wt%VA than EVA with 18wt%VA used in the blend foam formulations.

At the foam density in very light weight class, the stress at break and Young's modulus of LDPE/EVA blend foam with EVA 28wt%VA showed the values were higher than LDPE/EVA blend foam with EVA 18wt%VA may be due to the degree of crosslinking of foam with 28%VA in EVA copolymer were higher than foam with 18%VA in EVA copolymer led to foam with EVA 28wt%VA were more strength.

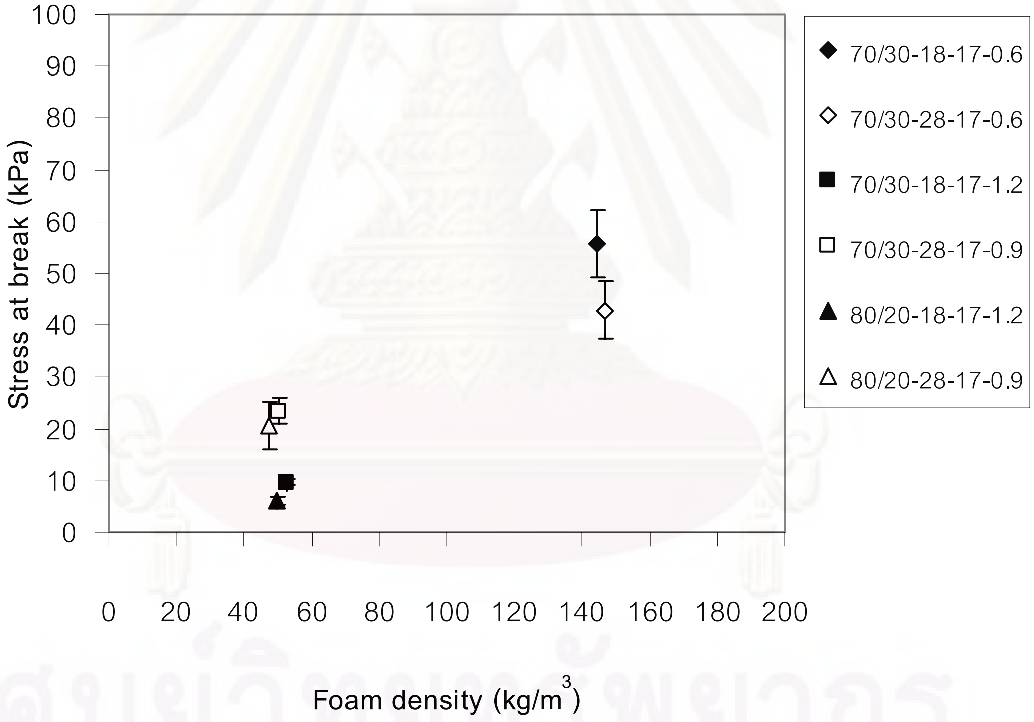


Figure 5.32 The relation between stress at break for LDPE/EVA18wt%VA and LDPE/EVA28wt%VA blend foams as function of foam density

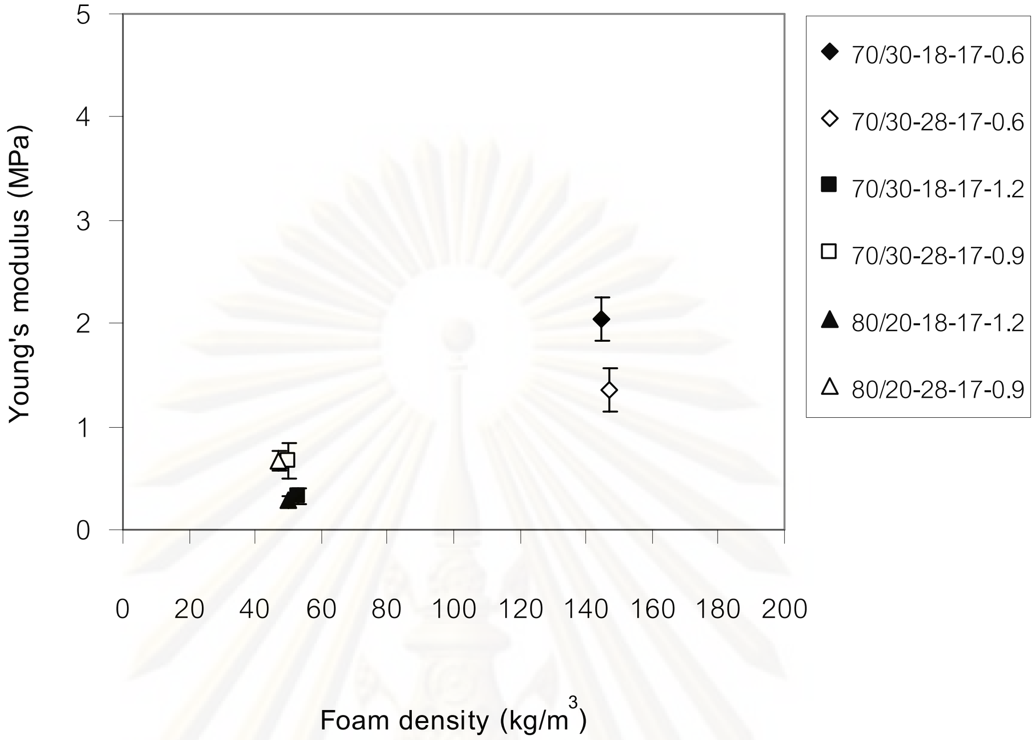


Figure 5.33 The relation between Young's modulus for LDPE/EVA18wt%VA and LDPE/EVA28wt%VA blend foams as function of foam density

The compressive strength as a function of foam density for LDPE/EVA with 18 and 28wt%VA is shown in Figure 5.34.

It found that the both compressive strength of LDPE/EVA with EVA 18wt%VA and EVA 28wt%VA were very close due to the similar of the cell structure which the compressive strength in linear elasticity controlled by cell wall bending and cell face stretching [8].

But the foam density in range 47.16-49.96 kg/m^3, it was obvious that the compressive strength of LDPE/EVA with EVA 28wt%VA was higher than the value of LDPE/EVA with EVA 18wt%VA due to cell wall of LDPE/EVA with EVA 28wt%VA had holes. The holes happened may be due to use crosslinking agent loading too low.

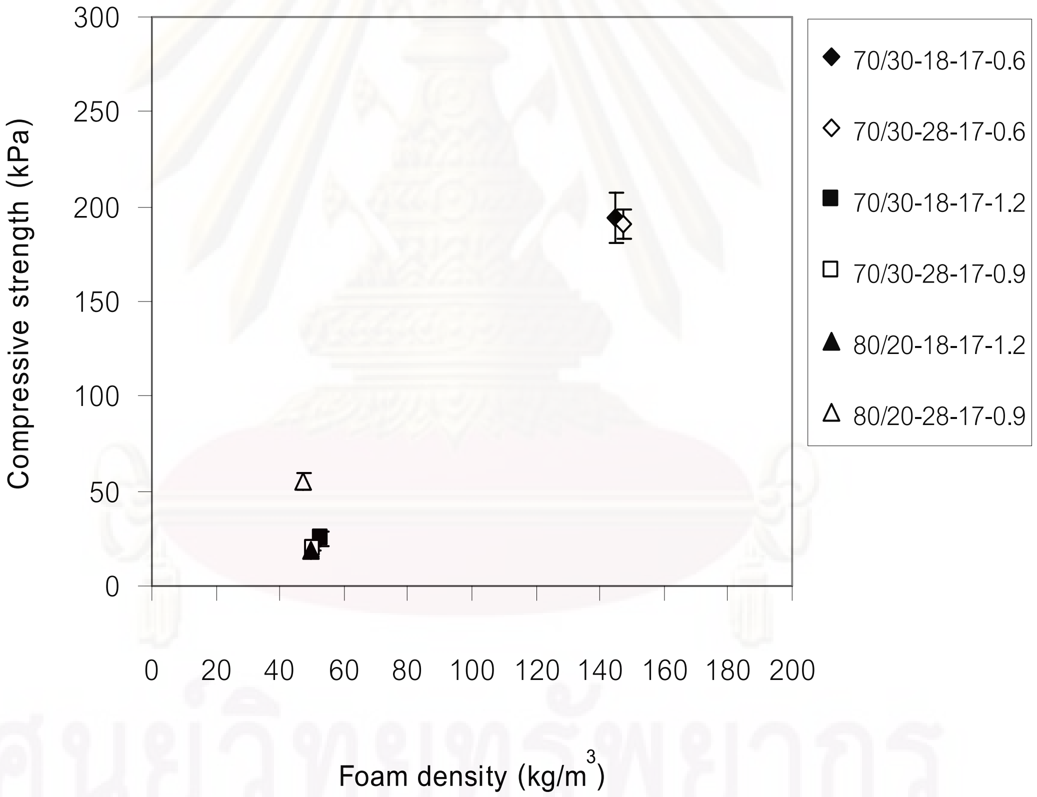


Figure 5.34 The relation between compressive strength for LDPE/EVA18wt%VA and LDPE/EVA28wt%VA blend foams at same of foam density

The influence of %VA in EVA copolymer on compression set of LDPE/EVA blend foam are shown in Figure 5.35.

The result showed that in light weight, the compression set of LDPE/EVA with EVA 28wt%VA was lower than the values of LDPE/EVA with EVA 18wt%VA due to the crystallinity of EVA with 28wt%VA was lower than EVA with 18wt%VA led to higher recover of foam with 28wt%VA.

For very light weight, it was found that the compression set of LDPE/EVA with EVA 28wt%VA were slightly higher than LDPE/EVA with EVA 18wt%VA may be due to higher degree of crosslinking of EVA with 28wt%VA affect to reduce flexibility of foam.

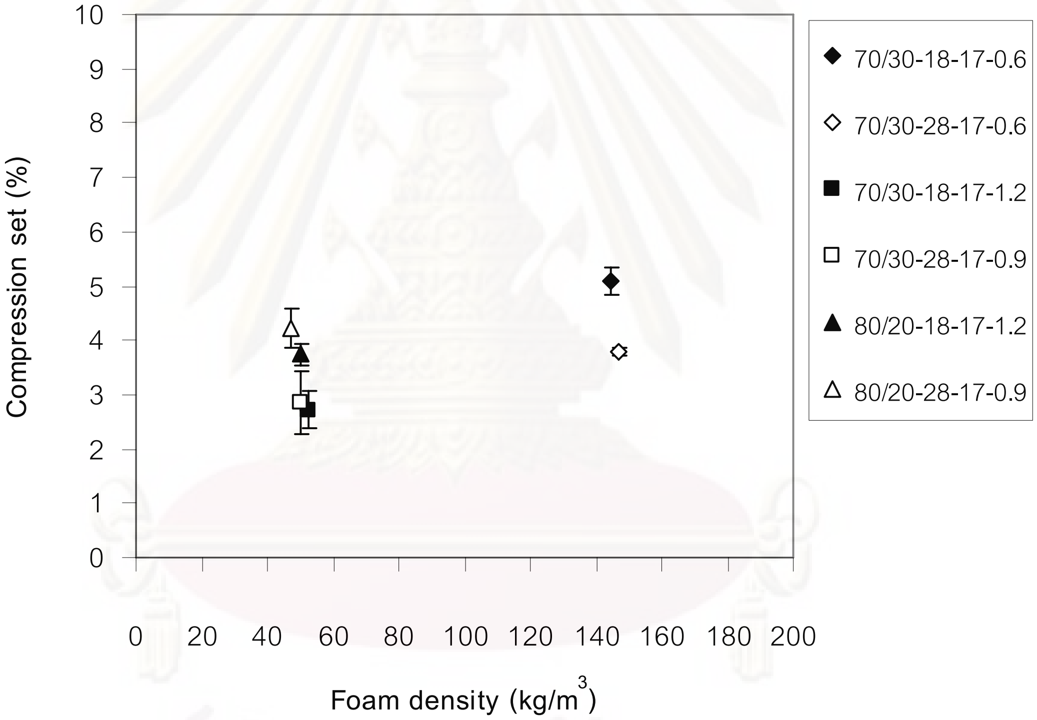


Figure 5.35 The relation between compression set for LDPE/EVA18wt%VA and LDPE/EVA28wt%VA blend foams at same of foam density

5.4 Effect of Chemical Blowing Agent Loading on Properties of LDPE/EVA Blend Foam

5.4.1 Effect of Chemical Blowing Loading on Foam Density of LDPE/EVA Blend Foam

The effect of chemical blowing loadings on foam density of LDPE/EVA at 70/30 wt/wt blend foam, EVA with 18wt%VA is shown in Figure 5.36.

The result showed that foam densities of LDPE/EVA blend foams increased with increasing of chemical blowing loadings may be due to increasing of chemical blowing loadings increase degree of crosslinking. Higher degree of crosslinking affects to enhance bubble resistance the blowing pressure in during bubble growth. Therefore, extension of cell wall reduced with increasing of chemical blowing loadings.

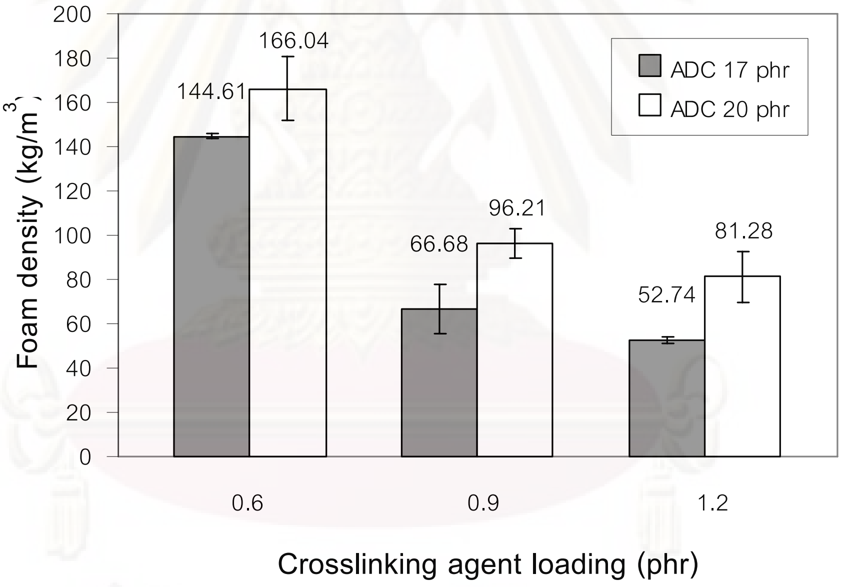


Figure 5.36 Densities of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 18wt%VA, ADC 17 and 20 phr at different crosslinking agent loadings

5.4.2 Effect of Chemical Blowing Agent Loading on Gel Content of LDPE/EVA Blend Foam

The change in gel content as a chemical blowing agent concentration for LDPE/EVA blend foam is shown in Figure 5.37.

It found that increasing of chemical blowing agent loading enhance the gel content due to the ammonia which is one of the decomposition products of the chemical blowing agent lead to crosslinking of polymer chains and also due to the increase in residue decomposition product of chemical blowing agent [5].

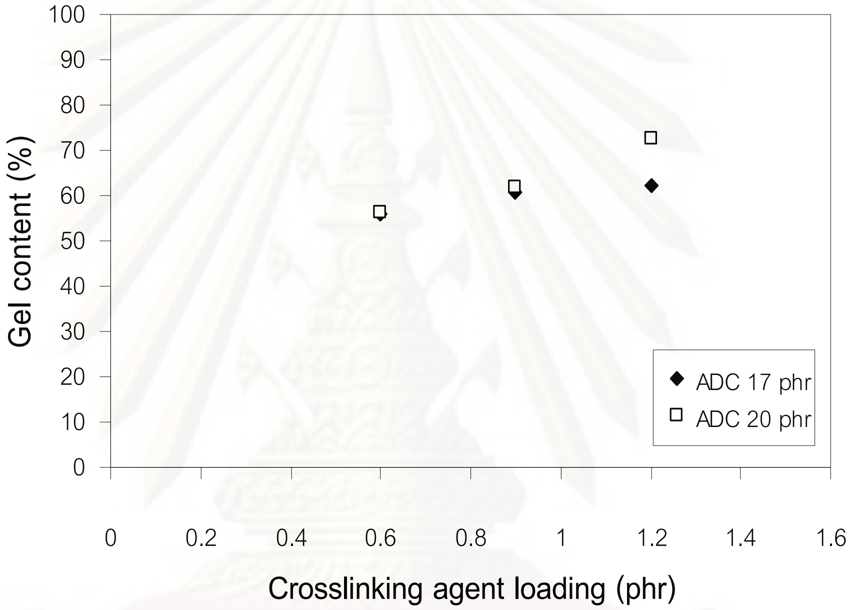


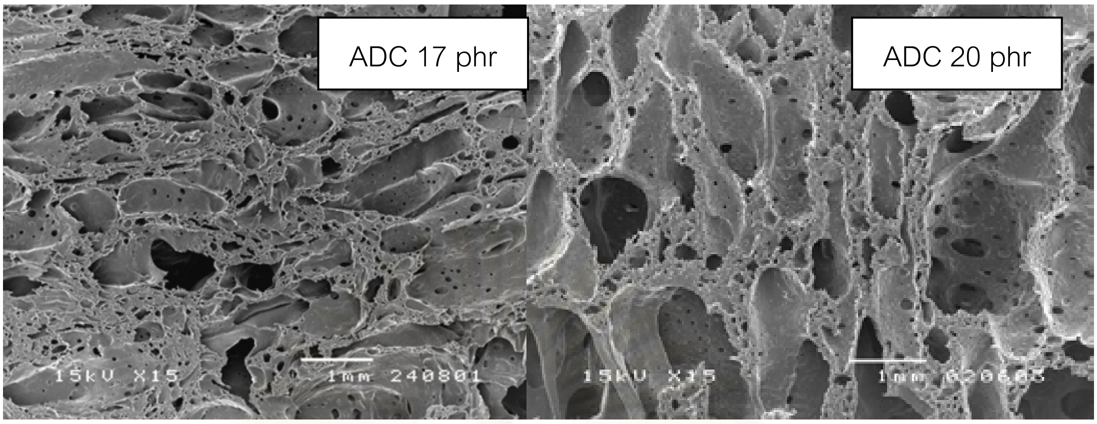
Figure 5.37 Gel contents of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 18wt%VA, Azo 17 and 20 phr at different crosslinking agent loadings

5.4.3 Effect of Chemical Blowing Agent Loading on Cell Structure of LDPE/EVA Blend Foam

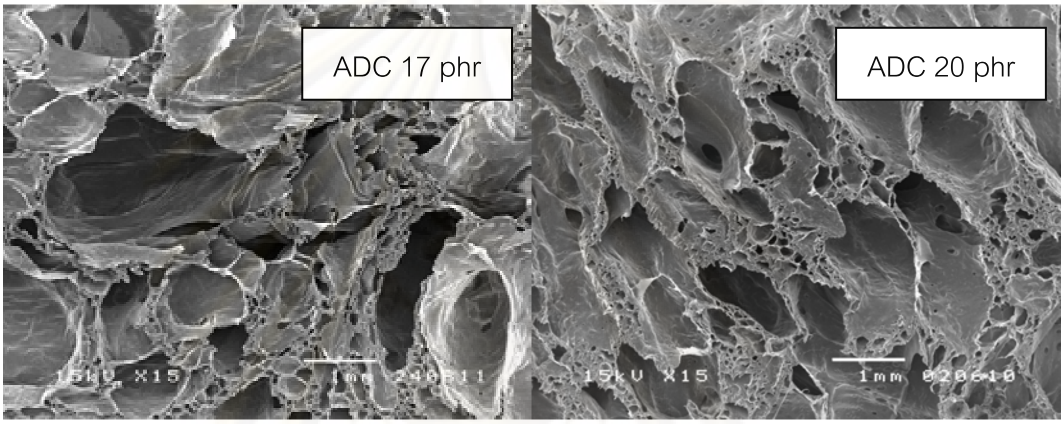
Furthermore, the addition of chemical blowing agent loadings affect cell structure of LDPE/EVA blend foams. It can be seen in Figure 5.38.

At amount of ADC 20 phr, it found that the holes occurred with as chemical blowing agent loading. The significant increase was only observed at in 0.9 phr.

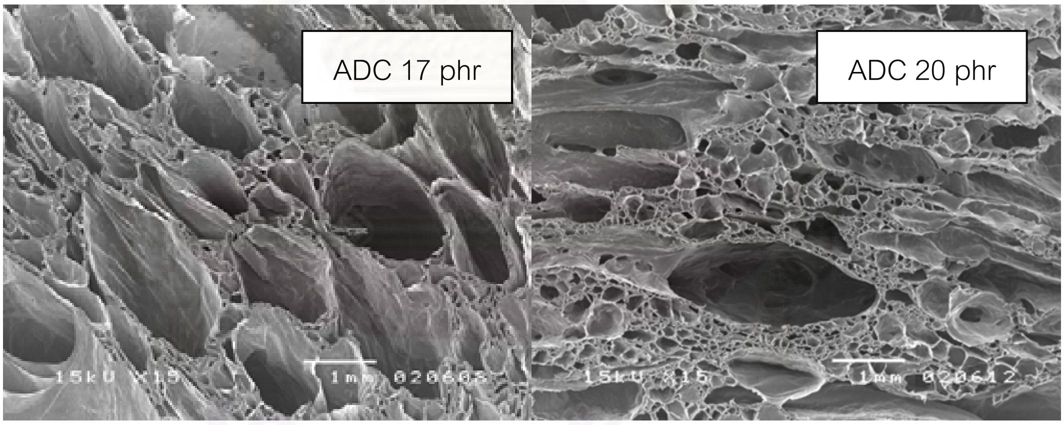
The cell wall of 20 phr was few holes may be due to the increasing of blowing pressure reduced bubble stability.



(a) 0.6 phr



(b) 0.9 phr



(c)1.2 phr

Figure 5.38 SEM images of LDPE/EVA blend at LDPE/EVA 70/30wt/wt, EVA with 18wt%VA and ADC 17 and 20 phr DCP 0.6, 0.9 and 1.2 phr

5.4.4 Effect of Chemical Blowing Agent Loading on Mechanical Properties of LDPE/EVA Blend Foam

The effect of concentration of chemical blowing agent loading on mechanical properties of LDPE/EVA blend foams, LDPE/EVA 70/30wt/wt, EVA with 18wt%VA are shown in Figure 5.39-5.41.

The effect of concentration of crosslinking agent loading on stress at break and Young's modulus of LDPE/EVA blend foams are illustrated Figure 5.39 and 5.40.

The result showed that the stress at break and Young's modulus increased with increasing of chemical blowing agent loading due to addition of chemical blowing agent loading increase degree of crosslinking and residue decomposition from chemical blowing agent. Increasing of degree of crosslinking also limit the mobility of macromolecular chain affect extension of chains is hindered [26].

Therefore, increasing of chemical blowing agent loading lead to LDPE/EVA blend foams were more strength.

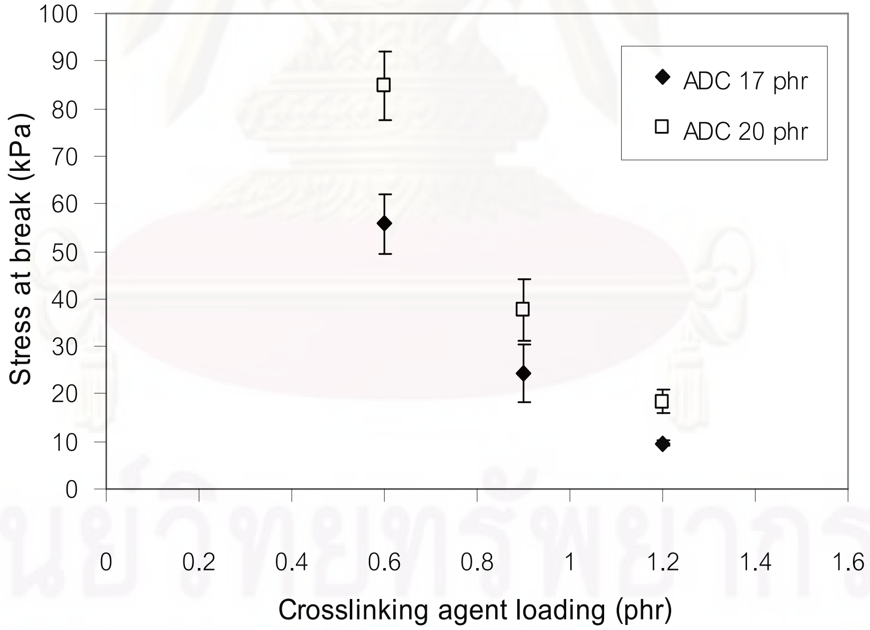


Figure 5.39 Stress at break of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 18wt%VA, ADC 17 and 20 phr at different crosslinking agent loadings

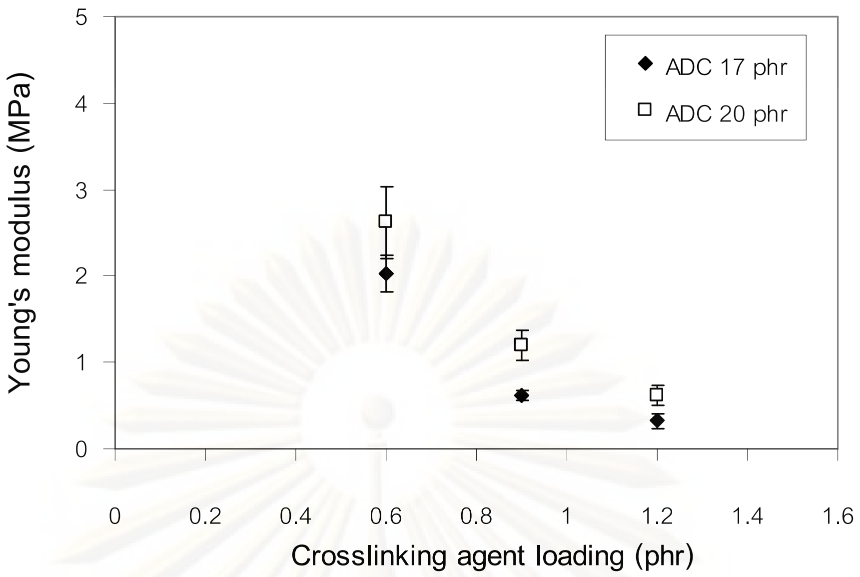


Figure 5.40 Young's modulus of LDPE/EVA blend foams, LDPE/EVA 70/30wt/wt, EVA with 18wt%VA, ADC 17 and 20 phr at different crosslinking agent loadings

The influence of chemical blowing agent loading on the compressive strength of LDPE/EVA blend foams is shown in Figure 5.41.

It can be seen that increasing of chemical blowing agent loading increased compressive strength may be due to increasing of chemical blowing agent loading enhance degree of crosslinking and residue decomposition from chemical blowing agent lead to cell wall bending is hindered.

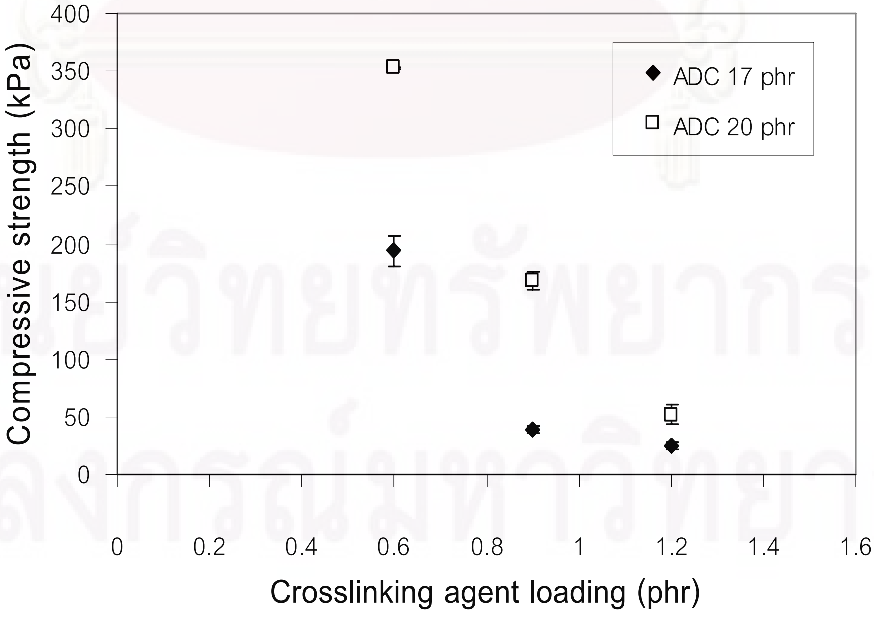


Figure 5.41 Compressive strength of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 18wt%VA, ADC 17 and 20 phr at crosslinking agent loadings

From Figure 5.42, show the flexibility of LDPE/EVA blend foams, LDPE/EVA 70/30wt/wt, EVA with 18wt%VA at different concentration of crosslinking agent loadings.

It was obvious that the value of compression set for higher chemical blowing agent loading increased due to the formation of structure network or higher residue from chemical blowing agent affect to cell wall stretching was difficult. Thus, the recovery of LDPE/EVA blend foams was reduced by increasing of chemical blowing agent loading.

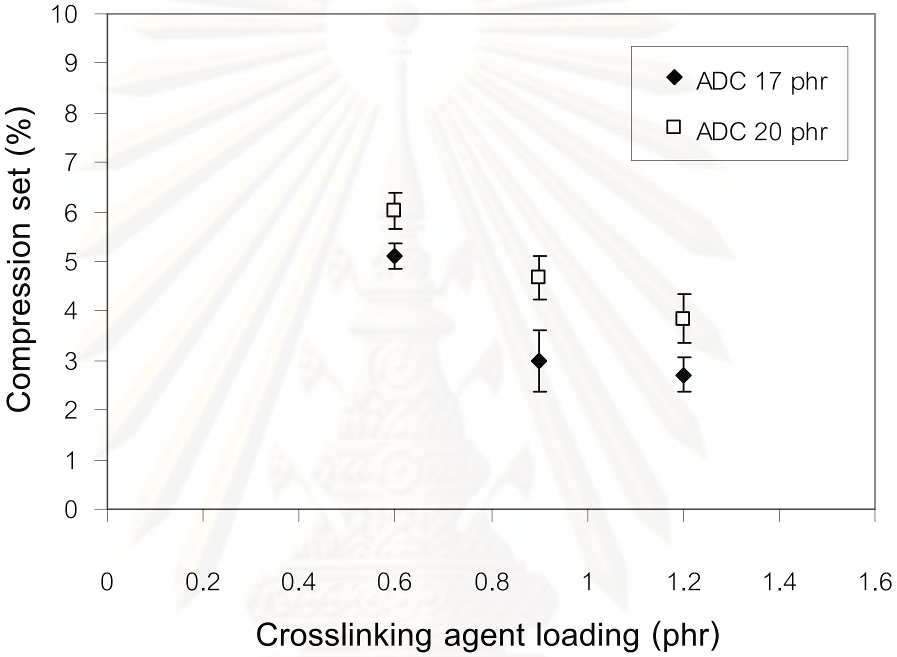


Figure 5.42 Compression set of LDPE/EVA blend foams at LDPE/EVA 70/30wt/wt, EVA with 18wt%VA, ADC 17 and 20 phr at different crosslinking agent loadings

5.5 Discussion of Effects of Blend Composition and Additives on Properties of LDPE/EVA Blend Foam

5.5.1 Effect of Crosslinking Agent Loading on Properties of LDPE/EVA Blend Foam

The addition of crosslinking agent loadings reduces foam density of LDPE/EVA blend foam due to degree of crosslinking increase with increasing of crosslinking agent loading. Polymer melt strength increases with increasing of degree of crosslinking lead to enhance extension of cell wall and thin cell wall.

From the gel content it could be seen that degree of crosslinking, the gel content increases with increasing of degree of crosslinking. This reflects the high degree of crosslinking reduce the mechanical properties.

Increasing of concentration of crosslinking agent loading in range 0.6-1.2 phr lead to cell walls were smooth, decreased tension properties, compressive strength and compression set. This could be due to the higher crosslinking of polymer chains affect the mobility macromolecular chain and is better extension of chain.

5.5.2 Effect of Blend Compositions on Properties of LDPE/EVA Blend Foam

5.5.2.1 Effect of Ratio of LDPE/EVA on Properties of LDPE/EVA Blend Foam

The effect of ratio of LDPE/EVA on foam density both LDPE/EVA blend foams with EVA 18 and 28wt%VA, the foam densities slightly decreased with decreasing of ethylene vinyl acetate copolymer content which it obvious that the increasing of gel content in case LDPE/EVA blend foams with EVA with 18wt%VA. Higher degree of crosslinking with the gel content increased lead to decrease stress at break due to the formation of network structure begin to break down into small network structure.

Furthermore, ratio of LDPE/EVA not affected to Young’s modulus and compressive strength in ratio of LDPE/EVA 70/30 and 80/20wt/wt but decreasing of ethylene vinyl acetate copolymer content affect to slightly reduce flexibility of LDPE/EVA blend foams. Therefore, there were no significant changes in the mechanical properties of the obtained foams.

5.5.2.2 Effect of %Vinyl Acetate in Ethylene Vinyl Acetate Copolymer on Properties of LDPE/EVA Blend Foam

In light weight class, mechanical properties of LDPE/EVA blend foams with EVA 28wt%VA were less than LDPE/EVA blend foams with EVA 18wt%VA may be due to decreasing of crystallinity lead to foams with EVA 28wt%VA more flexible than foams with EVA 18wt%VA.

In very light weight class, at the same foam density, the using of crosslinking agent loading of LDPE/EVA blend foams with EVA 28wt%VA were lower than LDPE/EVA blend foams with EVA 18wt%VA may be due to higher vinyl acetate content lead to increase chain transfer affect to enhance degree of crosslinking.

Moreover, the stress at break, Young’s modulus and compression set of LDPE/EVA blend foams with EVA 28wt%VA were higher than foams with EVA 18wt%VA due to lower degree of crosslinking. For the compressive strength of LDPE/EVA blend foams with EVA 28wt%VA were very closed to foams with EVA 18wt%VA due to cell structure were similar except in case 80/20-28-17-0.9, compressive strength higher than 70/30-28-17-0.9, 70/30-18-17-1.2 and 80/20-18-17-1.2 because cell wall had hole.

5.5.3 Effect of Chemical Blowing Agent Loading Agent on Properties of LDPE/EVA Blend Foam

The increasing of chemical blowing agent loadings increase foam density of LDPE/EVA blend foam due to higher degree of crosslinking and residue composition from chemical blowing agent affect enhance degree of resistance to the extension of cell wall in during bubble growth. Thus, extension of cell wall reduced and thick cell wall with increasing of chemical blowing loadings.

Increasing of concentration of chemical blowing agent loading also lead to increase tensile properties, compressive strength and compression set because degree of crosslinking too high and higher residue composition from chemical blowing agent affect cell wall bending and cell face stretching are hindered. The increasing of degree of crosslinking was obvious by increasing of gel content. These mechanical properties are inversely the case of increasing of crosslinking agent loadings due to degree of crosslinking too high; it can be seen from the increasing of gel content.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

In this chapter, section 6.1 provided the conclusions obtained from the experimental results of the effects of crosslinking agent loading, LDPE/EVA ratio and vinyl acetate content in EVA copolymer and chemical blowing agent loading on physical and mechanical properties of LDPE/EVA blend foam. Additionally, recommendations for future study were given in section 6.2.

6.1 Conclusions

From the results obtained in this work led to the following conclusion:

1. Increasing of crosslinking agent loading in range 0.6-1.2 phr led to lower foam density, cell walls were smooth, tensile and compression properties reduced and decreasing of compression set. This could be due to the increase in gel content or degree of crosslinking.

These suggest the increasing of crosslinking agent loading in range 0.6-1.2 phr lead to LDPE/EVA blend foam is more soft and flexibility.

While increasing of chemical blowing agent loading also led to higher foam density, tensile properties, compressive strength and compression set because crosslinking of polymer chain too high or higher residue composition from chemical blowing agent.

It is proposed the increasing of chemical blowing agent loading lead to LDPE/EVA blend foam is more strength.

2. The effect of ratio of LDPE/EVA on foam density both LDPE/EVA blend foams with EVA 18 and 28wt%VA, the foam densities and flexibility slightly decreased with decreasing of ethylene vinyl acetate copolymer content due to higher degree of crosslinking lead to stress at break decreased but ratio of LDPE/EVA not affected to elastic modulus and compressive strength.

3. In light weight class,the mechanical properties of LDPE/EVA blend foams with EVA 28wt%VA less than LDPE/EVA blend foams with EVA 18wt%VA due to decreasing of crystallinity of EVA 28wt%VA.

In very light weight class, the mechanical properties of LDPE/EVA blend foams with EVA 28wt%VA were higher than LDPE/EVA blend foams with EVA 18wt% because lower degree of crosslinking lead to cell wall bending is difficult.

6.2 Recommendations for future studies

From the previous conclusions, the following recommendations for future studies are proposed.

Improving process of foaming LDPE/EVA foam in order to improve cell structure includes cell size, cell size distribution and open-cell foam.

REFERENCES

[1] Klempher, D., and Frisch, K.C. Handbook of Polymeric Foams and Foam.Technology. NewYork: Hanser publisher, 1991.

[2] David Eaves. Handbook of polymer foam. United Kingdom: Shrewsbury, 2004.

[3] Patrick, C.L., Jin Wang, and Chul, B. P. Extruded open-cell foams using two semicrystalline polymers with different crystallization temperatures. Ind. Eng. Chem. Res. 45 (2006): 175-181.

[4] Zhe Xing, Guozhong Wu, Shirong Huang, Shimou Chen, and Hongyan Zeng. Preparation of microcellular cross-linked polyethylene foams by a radiation and supercritical carbon dioxide approach. Journal of Supercritical Fluids. 47 (2008): 281-289.

[5] Magdy, M. S., Hussien, A. Y., and Hannan, M. E. Effect of electron beam irradiation, EPDM and azodicarbonamide on the foam properties of LDPE sheet. Polymer-Plastic Technology and Engineering. 46 (2007): 1093-1101.

[6] Horng-Jer Tai. Bubble size distribution and elastic retraction in crosslinked metallocene polyolefin elastomer foams. Journal of Polymer Research. 12 (2005): 457-464.

[7] Zurina, M., Ismail, H., and Ratnam, C.T. Characterization of irradiation-induced crosslink of epoxidised natural rubber/ethylene vinyl acetate (ENR-50/EVA) blend. Polymer Degradation and Stability. 91 (2006): 2723-2730.

[8] Saudi Basic Industries Corporation. The world of polyethylene foam [online]. 2009. Available from: http://plastics.sabic.eu/technical/_en/theworldofpo.htm [2009, September 9]

[9] Rodriguez-Perez, M.A. Crosslinked Polyolefin Foams: Production, Structure, Properties and Applications. Adv Polm Sci 184 (2005): 97-126.

[10] Available from: http://composite.about.com/library/glossary/m/bldef-m3295.html. [2009, September 22]

[11] Kim, D.W., and Kim, K.S. Electron Beam Irradiation of Noncrosslinked LDPE-EVA Foam. Cellular Plastics. 38 (2002): 471-495.

[12] Nauta Warner Jan. Stabilisation of low density, closed cell polyethylene foam. Netherland: PrintPartners Ipskamp B.V., 2000.

[13] Fred, W. B., JR. Textbook of polymer science. 3rd ed. New York: A Wiley Interscience Publication, 1984.

[14] Ito et al. Method of producing open-cell foamed articles of cross-linked polyolefins. United states patent. (1984): No. 4,435,346.

[15] Takimoto et al. Crosslinked ethylene-olefin copolymer foams. United states patent. (2001): No. 6,197,841 B1.

[16] Plastic Additives and Compounding. 2001.

[17] Rodriguez-perez, M.A., Duijsens, A., and De Saja, J.A. Effect of addition of EVA on the technical properties of extruded foam profiles of Low-Density Polyethylene/EVA Blends. Applied Polymer Science. 68 (1998): 1237-1244.

[18] Reyes-Labarta, J.A., Olaya, M.M., and Marcilla, A. DSC and TGA study of the transitions involved in the thermal treatment of binary mixtures of PE and EVA copolymer with a crosslinking agent. Polymer 47 (2006): 8194-8202.

[19] Andrew, J.P., and Allison Calhoun. Polymer chemistry : properties and applications. 1st ed. USA: Hanser garder publications, 2006.

[20] Available from: http:// www. commons.wikimedia.org [2009, September 9]

[21] Available from: http:// www.specialchem4adhesives.com [2009, September 9]

[22] Alex, M. H. Ethylene-Vinyl Acetate (EVA) Copolymers: A General Review. AT Plastics Inc. 9 (1993): 30-38.

[23] Marcelo, G.A., Renan Demori, Ademir, J.Z., and Mara Zeni. Morphological analysis of polyethylene foams with post-use material incorporated. Polymer Bulletin 83 (2007): 83-90.

[24] Marcelo G. A., Renan Demori, Ademir, J. Z., and Mara Zeni. Mechanical properties of foams comprising virgin and waste polyethylene. Polymer Bulletin 59 (2007): 677-683.

[25] Siqin Dalai, and Chen Wenxin. Investigation of radiation-crosslinked foam of LDPE/EVA blends. Applied Polymer Science. 62 (1996): 75-80.

[26] Hussien, A. Y., Magdy, M.S., and Hanan, M.E. Characterization of LDPE and LDPE/EVA blends crosslinked by electron beam irradiation and foamed with chemical foaming agent. Polymer Reshearch 14 (2007): 351-357.

[27] I-Chun Liu, Ckih-Kuang Chuang, and Raymond Chien-Chao Tsiang. Foaming of Electron-Beam Irradiated LDPE Blends Containing Recycled Polyethylene Foam. Polymer Research 11 (2004): 149-159.

[28] Danaei, M., Sheikh, N., and Afshar Taromi, F. Radiation cross-linked polyethylene foam: Preparation and properties. Journal of cellular plastics.41 (2005): 551-562.

[29] Mahapatro, A., Mills, N.J., and Sims, G.L.A. Experiments and Modelling of the expansion of crosslinked polyethylene foams. Cellular Polymers 17 (1998): 252-270.

[30] Annual book of ASTM standards 2006. section 8 plastics (II). ASTM D 3575–00 Standard Test Methods for Flexible Cellular Materials Made From Olefin Polymer Volume 08.02, 2006.

[31] Annual book of ASTM standards 2006. section 8 plastics (II). ASTM D 3574–05 Standard Test Methods for Flexible Cellular Materials Slab, Bonded, and Molded Urethane Foam. Volume 08.02, 2006.

[32] Annual book of ASTM standards 2006. section 8 plastics (I). ASTM D D2765-01 Standard Test Methods for Determination of Gel Content and Swell Ratio of Crosslinked Ethylene Plastics. Volume 08.01, 2006.

APPENDICES

APPENDIX A

QUANTITY OF POLYMERS AND ADDITIVES FOR LDPE/EVA BLEND FOAM

Table A.1 Quantity of polymers and additives for LDPE/EVA blend foams

Run	LDPE/EVA Ratio (%wt)	%VA in EVA	Quantity Of AZO (phr)	Quantity of DCP (phr)	Quantity of polymers and additives (g)					
					LDPE	EVA	AZO	ZnO	DCP	Stearic acid
1	70/30	18	17	0.6	504	216	122.4	30.6	4.32	7.2
2	70/30	18	17	0.9	504	216	122.4	30.6	6.48	7.2
3	70/30	18	17	1.2	504	216	122.4	30.6	8.64	7.2
4	70/30	28	17	0.6	504	216	122.4	30.6	4.32	7.2
5	70/30	28	17	0.9	504	216	122.4	30.6	6.48	7.2
6	70/30	28	17	1.2	504	216	122.4	30.6	8.64	7.2
7	80/20	18	17	0.6	576	144	122.4	30.6	4.32	7.2
8	80/20	18	17	0.9	576	144	122.4	30.6	6.48	7.2
9	80/20	18	17	1.2	576	144	122.4	30.6	8.64	7.2

Table A.2 Quantity of polymers and additives for LDPE/EVA blend foams (cont.)

Run	LDPE/EVA Ratio (%wt)	%VA in EVA	Quantity Of AZO (phr)	Quantity of DCP (phr)	Quantity of polymers and additives(g)					
					LDPE	EVA	AZO	ZnO	DCP	Stearic acid
10	80/20	28	17	0.6	576	144	122.4	30.6	4.32	7.2
11	80/20	28	17	0.9	576	144	122.4	30.6	6.48	7.2
12	80/20	28	17	1.2	576	144	122.4	30.6	8.64	7.2
13	70/30	18	20	0.6	504	216	144	36	4.32	7.2
14	70/30	18	20	0.9	504	216	144	36	6.48	7.2
15	70/30	18	20	1.2	504	216	144	36	8.64	7.2

APPENDIX B

CALCULATION OF THE FOAM DENSITY

Calculation of the foam density by ASTM 3575 (method A)

$$D = \frac{m}{V} \tag{B.1}$$

D = Density (kg/m^3)

m = Mass (kg)

V = Volume (m^3)

Example: calculation of the Foam density of LDPE/EVA blend foam with ratio of LDPE/EVA 70/30 wt/wt, EVA 18wt%, ADC 17 phr and DCP 0.6 phr (70/30-18-17-0.6)

Weight of LDPE/EVA blend foam (70/30-18-17-0.6) = 2.9733 grams

Volume of LDPE/EVA blend foam (70/30-18-17-0.6) = 20.64 cm^3

$$D = 2.9733/20.64 = 0.14405 \text{ g/ cm}^3$$

$$= 144.05 \text{ kg/m}^3$$

APPENDIX C

CALCULATION OF GEL CONTENT

Calculation of the gel content by ASTM 2675-01 (method A)

$$\text{Extraction (\%)} = \left(\frac{\text{(weight lost during extraction)}}{\text{(weight of original specimen)}}\right) \quad \text{(C.1)}$$

$$\text{Extraction (\%)} = \left[\frac{(W_3 - W_4)}{(W_2 - W_1)}\right] \text{x100} \quad \text{(C.2)}$$

$$\text{Gel content (\%)} = 100 - \left(\left[\frac{(W_3 - W_4)}{(W_2 - W_1)}\right] \text{x100}\right) \quad \text{(C.3)}$$

W_1 = Weight of wire pouch

W_2 = Weight of wire pouch and sample

W_3 = Weight of wire pouch and sample and wire seal before extraction

W_4 = Weight of wire pouch and sample and wire seal after extraction

Example: calculation of the density of LDPE/EVA blend foam with ratio of LDPE/EVA 70/30 wt/wt, EVA 18wt%, ADC 17 phr and DCP 0.6 phr

W_1 = 1.3946

W_2 = 1.7244

W_3 = 1.7549

W_4 = 1.6090

Extraction (%) = [(1.7549-1.6090)/(1.7244-1.3946)] x100

= (0.1459/0.3298)x100

= 44.24%

Gel content (%) = 100 –44.24

= 55.76%

APPENDIX D

CALCULATION OF YOUNG MODULUS

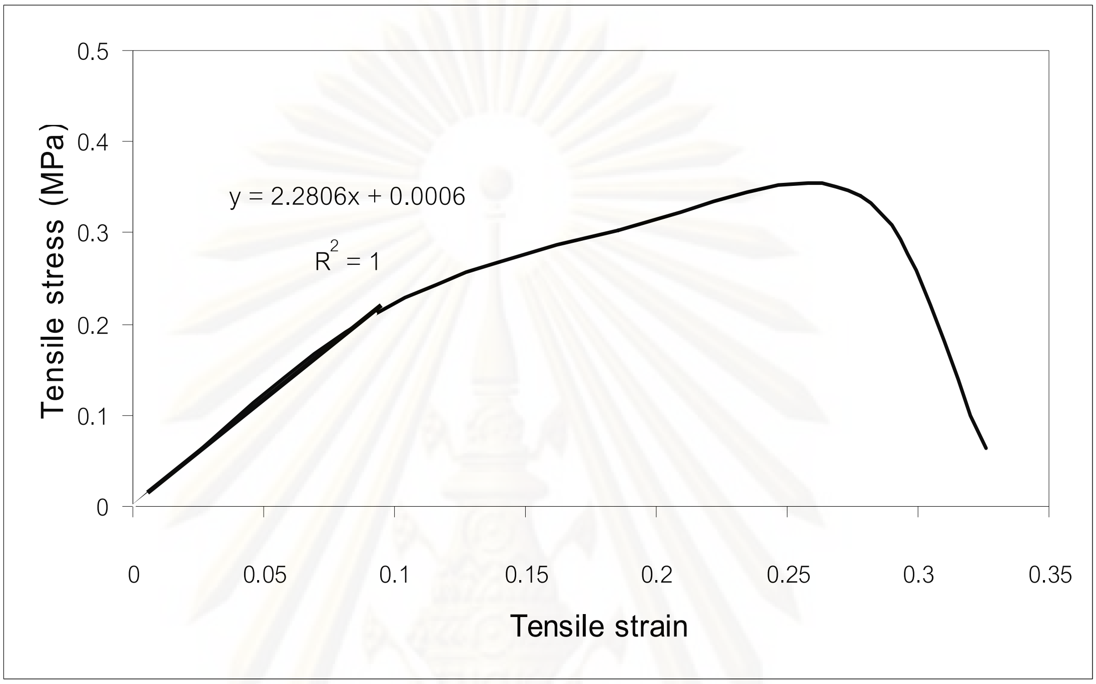


Figure D.1 The Tensile stress-strain curve of LDPE/EVA blend foam with ratio of LDPE/EVA 70/30 wt/wt, EVA 18wt%, ADC 17 phr and DCP 0.6 phr

Young’s modulus = slope of initially linear stress-strain curve

= 2.28 MPa

APPENDIX E

CALCULATION OF COMPRESSION SET

Calculation of Compression set by ASTM 3575

$$C_d = \frac{(t_o - t_f)}{t_o} \text{x100} \qquad \text{(F.1)}$$

C_d = Compression set expressed as a percent of the original thickness

t_o = Original thickness (mm)

t_f = Thickness of the specimen after the specified recovery period (mm)

Example: calculation of the compression set of. of LDPE/EVA blend foam with ratio of LDPE/EVA 70/30 wt/wt, EVA 18wt%, ADC 17 phr and DCP 0.6 phr

t_o = 28.52 mm

t_f = 27.13 mm

C_d = [(28.52-27.14)/28.52]x100

= 4.84 %

APPENDIX F

THE DATA OF FOAM DENSITY

Table F.1 Raw data for determining foam density of LDPE/EVA blend foam with ratio of LDPE/EVA 70/30wt/wt, EVA 18wt%VA, ADC 17 phr and DCP 0.6-1.2 phr

Formulation	Width(mm)	Length(mm)	Height(mm)	Volume(mm^3)	Volume(cm^3)	Weight(g)	Density(g/cm^3)	Density(kg/m^3)
70/30-18-17-0.6	25.91	28.40	28.05	20640.4242	20.6404	2.9733	0.14405	144.05
	27.99	28.32	28.83	22852.8721	22.8529	3.3331	0.14585	145.85
	27.54	29.26	28.79	23199.5693	23.1996	3.3392	0.14393	143.93
Average								144.61±1.07
70/30-18-17-0.9	27.68	28.28	27.50	21526.7360	21.5267	1.4274	0.06631	66.31
	26.62	28.04	27.09	20220.6478	20.2206	1.3768	0.06809	68.09
	27.00	28.04	26.41	19994.4828	19.9945	1.3124	0.06564	65.64
Average								66.68±1.27

* a-b-c-d denoted the LDPE/EVA ratio, %VA in EVA, ADC, DCP, respectively.

Table F.2 Raw data for determining foam density of LDPE/EVA blend foam with ratio of LDPE/EVA 70/30wt/wt, EVA 18wt%VA, ADC 17 phr and DCP 0.6-1.2 phr (cont.)

Formulation	Width(mm)	Length(mm)	Height(mm)	Volume(mm^3)	Volume(cm^3)	Weight(g)	Density(g/cm^3)	Density(kg/m^3)
70/30-18-17-1.2	31.53	30.86	27.17	26436.8393	26.4368	1.2958	0.04902	49.02
	27.90	28.86	28.48	22931.9251	22.9319	1.1212	0.04889	48.89
	27.27	28.50	28.12	21854.7234	21.8547	1.3180	0.06031	60.31
Average								52.74±6.56

* a-b-c-d denoted the LDPE/EVA ratio, %VA in EVA, ADC, DCP, respectively.

Table F.3 Raw data for determining foam density of LDPE/EVA blend foam with ratio of LDPE/EVA 70/30 wt/wt, EVA 28wt%VA, ADC 17 phr and DCP 0.6-1.2 phr

Formulation	Width(mm)	Length(mm)	Height(mm)	Volume(mm^3)	Volume(cm^3)	Weight(g)	Density(g/cm^3)	Density(kg/m^3)
70/30-28-17-0.6	27.30	25.11	26.58	18220.6697	18.2207	2.6022	0.14282	142.82
	27.84	26.83	26.96	20137.6965	20.1377	2.9556	0.14677	146.77
	27.43	28.90	28.27	22410.3923	22.4104	3.3935	0.15143	151.43
Average								147.00±2.79
70/30-28-17-0.9	25.00	25.00	25.40	15875.0000	15.8750	0.7802	0.04915	49.15
	25.48	24.40	23.86	14834.0483	14.8340	0.7151	0.04821	48.21
	29.31	24.69	23.74	17179.7810	17.1798	0.9075	0.05282	52.82
Average								50.06±2.44
70/30-28-17-1.2	25.75	30.39	27.92	21848.5866	21.8486	0.7595	0.03476	34.76
	29.28	27.23	27.44	21877.7583	21.8778	0.8366	0.03824	38.24
	28.37	24.20	26.12	17932.7905	17.9328	0.6504	0.03627	36.27
Average								36.42±1.74

* a-b-c-d denoted the LDPE/EVA ratio, %VA in EVA, ADC, DCP, respectively.

Table F.4 Raw data for determining foam density of LDPE/EVA blend foam with ratio of LDPE/EVA 80/20 wt/wt, EVA 18wt%VA, ADC 17 phr and DCP 0.6-1.2 phr

Formulation	Width(mm)	Length(mm)	Height(mm)	Volume(mm^3)	Volume(cm^3)	Weight(g)	Density(g/cm^3)	Density(kg/m^3)
80/20-18-17-0.6	31.93	27.47	32.23	28269.4841	28.2695	3.6862	0.13039	130.39
	29.91	30.78	27.71	25510.6518	25.5107	3.4614	0.13568	135.68
	30.11	31.09	27.02	25293.9597	25.2940	3.7505	0.14828	148.28
Average								138.12±9.19
80/20-18-17-0.9	30.26	32.81	33.04	32803.1230	32.8031	2.0722	0.06317	63.17
	30.88	27.11	24.93	20870.3190	20.8703	1.2932	0.06196	61.96
	29.99	26.28	27.70	21831.4004	21.8314	1.4944	0.06845	68.45
Average								64.53±3.45
80/20-18-17-1.2	28.76	28.75	25.17	20811.8145	20.8118	0.8163	0.03922	39.22
	29.82	27.49	29.44	24133.4930	24.1335	1.3690	0.05673	56.73
	31.48	27.67	32.25	28091.4141	28.0914	1.5151	0.05394	53.94
Average								49.96±9.40

* a-b-c-d denoted the LDPE/EVA ratio, %VA in EVA, ADC, DCP, respectively.

Table F.5 Raw data for determining foam density of LDPE/EVA blend foam with ratio of LDPE/EVA 80/20 wt/wt, EVA 28wt%VA, ADC 17 phr and DCP 0.6-1.2 phr

Formulation	Width(mm)	Length(mm)	Height(mm)	Volume(mm^3)	Volume(cm^3)	Weight(g)	Density(g/cm^3)	Density(kg/m^3)
80/20-28-17-0.6	30.21	28.27	30.34	25911.4735	25.9115	3.0677	0.11839	118.39
	28.20	24.93	26.51	18637.2193	18.6372	2.5159	0.13500	135.00
	26.63	30.05	25.53	20429.9102	20.4299	2.7529	0.13475	134.75
Average								129.38±11.74
80/20-28-17-0.9	26.30	28.84	29.17	22125.2116	22.1252	1.0043	0.04539	45.39
	31.93	26.29	31.67	26585.0553	26.5851	1.2793	0.04812	48.12
	30.05	26.98	29.20	23673.8708	23.6739	1.1359	0.04798	47.98
Average								47.16±1.54
80/20-28-17-1.2	32.30	30.23	29.77	29068.2913	29.0683	0.8487	0.02920	29.20
	30.66	26.59	30.44	24816.1917	24.8162	0.6552	0.02640	26.40
	31.46	29.18	31.64	29045.6086	29.0456	0.9553	0.03289	32.89
Average								29.50±3.25

* a-b-c-d denoted the LDPE/EVA ratio, %VA in EVA, ADC, DCP, respectively.

Table F.6 Raw data for determining foam density of LDPE/EVA blend foam with ratio of LDPE/EVA 70/30 wt/wt, EVA 18wt%VA, ADC 20 phr and DCP 0.6-1.2 phr

Formulation	Width(mm)	Length(mm)	Height(mm)	Volume(mm^3)	Volume(cm^3)	Weight(g)	density(g/cm^3)	Density(kg/m^3)
70/30-18-20-0.6	25.95	27.93	26.04	18873.3623	18.8734	3.1126	0.16492	164.92
	30.45	29.06	28.85	25528.7015	25.5287	3.8854	0.15220	152.20
	30.70	26.15	25.85	20752.5093	20.7525	3.7559	0.18099	180.99
Average								166.04±14.43
70/30-18-20-0.9	29.55	29.75	30.28	26619.5265	26.6195	2.8361	0.10654	106.54
	24.50	26.07	25.99	16600.2029	16.6002	1.3889	0.08367	83.67
	32.11	28.22	26.81	24293.7260	24.2937	2.3914	0.09844	98.44
Average								96.21±11.60
70/30-18-20-1.2	30.42	30.98	33.60	31665.0298	31.6650	2.7101	0.08559	85.59
	30.18	26.09	25.11	19771.5186	19.7715	1.6434	0.08312	83.12
	26.30	29.84	28.61	22452.8991	22.4529	1.6868	0.07512	75.12
Average								81.28±5.47

* a-b-c-d denoted the LDPE/EVA ratio, %VA in EVA, ADC, DCP, respectively.

APPENDIX G

THE DATA OF GEL CONTENT

Table G.1 Raw data for determining gel content of LDPE/EVA blend foam

Formulation	Weight of wire pounch (W_1) (g)	Weight of wire pounch and sample (W_2) (g)	Weight of wire pounch and sample and wire seal before extraction (W_3) (g)	Weight of wire pounch and sample and wire seal after extraction (W_4) (g)	**Extraction (%)**	**Gel content (%)**
70/30-18-17-0.6	1.3946	1.7244	1.7549	1.6090	44.24	55.76
70/30-18-17-0.9	1.4185	1.6954	1.7278	1.6189	39.33	60.67
70/30-18-17-1.2	1.4384	1.6766	1.7162	1.6259	37.91	62.09
70/30-28-17-0.6	1.4229	1.7473	1.7856	1.6493	42.02	57.98
70/30-28-17-0.9	1.4411	1.7566	1.7943	1.6903	32.96	67.04
70/30-28-17-1.2	1.4865	1.7875	1.8254	1.7378	29.10	70.90

*a-b-c-d denoted the LDPE/EVA ratio, %VA in EVA, ADC, DCP, respectively.

Table G.2 Raw data for determining gel content of LDPE/EVA blend foam (cont.)

Formulation	Weight of wire pouch (W_1) (g)	Weight of wire pouch and sample (W_2) (g)	Weight of wire pouch and sample and wire seal before extraction (W_3) (g)	Weight of wire pouch and sample and wire seal after extraction (W_4) (g)	**Extraction** **(%)**	**Gel content** **(%)**
80/20-18-17-0.6	1.4111	1.7321	1.7704	1.6384	41.12	58.88
80/20-18-17-0.9	1.4339	1.7446	1.8017	1.6985	33.22	66.78
80/20-18-17-1.2	1.5187	1.8106	1.8490	1.7613	30.04	69.96
80/20-28-17-0.6	1.4331	1.7531	1.8100	1.6912	37.13	62.88
80/20-28-17-0.9	1.5446	1.8614	1.9015	1.7937	34.03	65.97
80/20-28-17-1.2	1.5460	1.8437	1.9018	1.8090	31.17	68.83
70/30-18-20-0.6	1.5328	1.8327	1.8709	1.7403	43.55	56.45
70/30-18-20-0.9	1.4752	1.7797	1.8177	1.7011	38.29	61.71
70/30-18-20-1.2	1.4834	1.7517	1.7907	1.7172	27.39	72.61

* a-b-c-d denoted the LDPE/EVA ratio, %VA in EVA, ADC, DCP, respectively.

APPENDIX H

THE DATA OF MECHANICAL PROPERTIES

Table H.1 Mechanical properties data of LDPE/EVA blend foam with ratio of LDPE/EVA 70/30 wt/wt, EVA 18wt%VA, ADC 17 phr and DCP 0.6-1.2 phr

Formulation	Stress at break (kPa)	Young's modulus (MPa)	Compressive strength (kPa)	Compression set (%)
70/30-18-17-0.6	63.00	2.28	179.30	4.84
	51.20	1.91	204.66	5.12
	53.00	1.91	199.18	5.34
Average	55.73±6.36	2.03±0.21	194.38±13.34	5.10±0.25
70/30-18-17-0.9	30.9	0.63	30.55	2.32
	22.9	0.67	38.81	3.17
	19	0.56	34.91	3.53
Average	24.27±6.07	0.62±0.06	38.26±3.11	3.01±0.62
70/30-18-17-1.2	10.20	0.31	22.42	2.31
	9.50	0.40	29.17	2.93
	9.30	0.25	23.06	2.91
Average	9.67±0.47	0.32±0.08	24.88±3.72	2.72±0.35

* a-b-c-d denoted the LDPE/EVA ratio, %VA in EVA, ADC, DCP, respectively.

Table H.2 Mechanical properties data of LDPE/EVA blend foam with ratio of LDPE/EVA 70/30 wt/wt, EVA 28wt%VA, ADC 17 phr and DCP 0.6-1.2 phr

Formulation	Stress at break (kPa)	Young's modulus (MPa)	Compressive strength (kPa)	Compression set (%)
70/30-28-17-0.6	43.30	1.24	189.98	3.85
	37.20	1.23	183.39	3.73
	48.10	1.60	198.79	3.80
Average	42.87±5.46	1.3.6±0.21	190.72±7.73	3.79±0.06
70/30-28-17-0.9	23.20	0.63	20.64	2.59
	21.10	0.52	21.82	3.53
	26.00	0.85	18.58	2.47
Average	23.43±2.46	0.67±0.17	20.35±1.64	2.86±0.58
70/30-28-17-1.2	8.00	0.18	16.88	2.21
	8.70	0.14	18.48	2.99
	7.40	0.12	19.70	1.92
Average	8.03±1.40	0.15±0.03	18.35±1.41	2.38±0.56

* a-b-c-d denoted the LDPE/EVA ratio, %VA in EVA, ADC, DCP, respectively.

Table H.3 Mechanical properties data of LDPE/EVA blend foam with ratio of LDPE/EVA 80/20 wt/wt, EVA 18wt%VA, ADC 17 phr and DCP 0.6-1.2 phr

Formulation	Stress at break (kPa)	Young's modulus (MPa)	Compressive strength (kPa)	Compression set (%)
80/20-18-17-0.6	43.40 45.20 44.90	1.81 2.06 2.22	240.66 189.13 163.53	5.17 5.07 4.82
Average	44.50±0.96	2.03±0.2.1	197.77±39.29	5.02±0.18
80/20-18-17-0.9	16.70 12.60 13.00	0.67 0.47 0.51	34.38 49.15 47.27	3.96 3.23 3.77
Average	14.10±2.26	0.55±0.11	43.60±8.04	3.66±0.38
80/20-18-17-1.2	7.00 5.40 6.20	0.32 0.31 0.24	16.99 23.27 17.20	3.79 3.90 3.54
Average	6.20±0.80	0.29±0.04	19.15±3.57	3.74±0.19

* a-b-c-d denoted the LDPE/EVA ratio, %VA in EVA, ADC, DCP, respectively.

Table H.4 Mechanical properties data of LDPE/EVA blend foam with ratio of LDPE/EVA 80/20 wt/wt, EVA 28wt%VA, ADC 17 phr and DCP 0.6-1.2 phr

Formulation	Stress at break (kPa)	Young's modulus (MPa)	Compressive strength (kPa)	Compression set (%)
80/20-28-17-0.6	42.60	2.26	185.57	5.89
	48.90	1.92	222.72	6.01
	45.70	2.20	243.54	5.34
Average	45.73±3.15	2.13±0.18	217.28±29.36	5.75±0.36
80/20-28-17-0.9	17.30	0.63	99.51	4.46
	25.80	0.77	82.07	4.42
	18.80	0.61	80.94	3.80
Average	20.63±4.54	0.67±0.09	87.50±10.41	4.23±0.37
80/20-28-17-1.2	7.90	0.34	12.41	4.21
	7.40	0.20	11.24	3.97
	8.50	0.16	15.75	4.14
Average	7.93±0.55	0.23±0.09	13.13±2.34	4.11±0.12

* a-b-c-d denoted the LDPE/EVA ratio, %VA in EVA, ADC, DCP, respectively.

Table H.5 Mechanical properties data of LDPE/EVA blend foam with ratio of LDPE/EVA 70/30 wt/wt, EVA 18wt%VA, ADC 20 phr and DCP 0.6-1.2 phr

Formulation	Stress at break (kPa)	Young's modulus (MPa)	Compressive strength (kPa)	Compression set (%)
70/30-18-20-0.6	78.60	2.72	351.87	5.88
	92.80	2.16	353.48	5.77
	83.00	2.98	353.49	6.42
Average	84.80±7.27	2.62±0.42	352.94±0.93	6.02±0.35
70/30-18-20-0.9	39.60	1.15	173.70	5.17
	42.80	1.38	159.31	4.48
	30.40	1.06	172.37	4.38
Average	37.60±6.44	1.20±0.17	168.46±7.95	4.67±0.43
70/30-18-20-1.2	17.20	0.73	45.23	3.35
	16.80	0.51	50.54	3.84
	21.20	0.62	60.65	4.35
Average	18.40±2.43	0.62±0.11	52.14±7.83	3.85±0.50

* a-b-c-d denoted the LDPE/EVA ratio, %VA in EVA, ADC, DCP, respectively.

APPENDIX I

LIST OF PUBLICATIONS

Phansiri Suktha and Varun Taepaisitphongse. “Effects of Blend Composition and Crosslinking Agent on Physical and Mechanical Properties of LDPE/EVA Blend Foams”, 2nd Polymer Graduate Conference of Thailand, The Faculty of Science, Chulalongkorn University, Bangkok, Thailand, May 21-22, 2009.

VITA

Miss Phansiri Suktha was born on February 21, 1985 in Phranakhon Si Ayutthaya province, Thailand. She graduated at high school level in 2002 from Phachi Suntorn Witthayanukul School, Phranakhon Si Ayutthaya, Thailand. She received the Bachelor Degree of Chemistry from Faculty of Science, King Mongkut's University of Technology North Bangkok, Thailand in 2006. After graduation, she entered study for a Master's Degree of Chemical Engineering at Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand.