การพัฒนาฟิล์มบรรจุภัณฑ์คอมโพสิตพอลิเอททิลีนชนิดความหนาแน่นต่ำ-ซิโอไลต์ เพื่อยืดอายุการเก็บรักษาพืชผลสด

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DEVELOPMENT OF PACKAGING FILM FROM LDPE/ZEOLITE COMPOSITES FOR EXTENDING SHELF LIFE OF FRESH PRODUCES

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
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In this study, LDPE/zeolite composite films were prepared via twin screw extruder attached with blown film set. LDPE and maleic anhydride grafted low density polyethylene (PE-g-MA) was melt blended with zeolite. The effect of PE-g-MA to zeolite ratio, type and content of zeolite on the dispersion of zeolite in composite films was determined. In addition, thermal, mechanical, and gas permeability properties of these composite films were also studied. The chosen composite film was investigated the efficiency on prolonging shelf life and maintaining quality of lime and mango fruits. From SEM results, LDPE/zeolite composite films with PE-g-MA/zeolite ratios of 3.0 and 4.0 showed better dispersion and distribution than those with other ratios. The addition of PE-g-MA into LDPE matrix decreased melting temperature (T_m) and the formation of crystalline phase of LDPE which was confirmed by DSC results. However, the addition of zeolite into LDPE matrix did not affect the formation of crystalline phase. In addition, it was found that LDPE/zeolite composite film at zeolite 5A of 3 phr and PE-g-MA/zeolite ratio of 3.0 exhibited the optimal mechanical and gas permeability properties. The composite film used as packaging prolonged shelf life of mango fruit for 4 weeks while mango fruits inside LDPE packaging film found CO_2 injury symptom due to excess CO_2 at the third week of storage. For six weeks after storage the chosen composite film delayed green color variation, peduncle drop, and CO_2 injury symptom of lime fruits more than neat LDPE film for lime fruits packing for six weeks.

Department : Chemical Engineering	Student's Signature ....
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เนตรนภา ลามอ : การพัฒนาฟิล์มบรรจุภัณฑ์คอมโพสิตพอลิเอททิลีนชนิดความหนาแน่นต่ำ-ซิโอไลต์เพื่อยืดอายุการเก็บรักษาพืชผลสด. (DEVELOPMENT OF PACKAGING FILM FROM LDPE/ZEOLITE COMPOSITES FOR EXTENDING SHELF LIFE OF FRESH) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : ผศ.ดร.อนงค์นาฏ สมหวังธนโรจน์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม : อ.ดร.อภิตา บุญศิริ, 111 หน้า.

ในงานวิจัยนี้ฟิล์มคอมโพสิตพอลิเอททิลีนชนิดความแน่นต่ำ/ซิโอไลต์ถูกเตรียมขึ้นด้วยวิธีการขึ้นรูปแบบเป่ากลวงโดยใช้เครื่องอัดรีดชนิดสกรูคู่ในการหลอมเหลวผสมพอลิเอททิลีนชนิดความแน่นต่ำ มาเลอิกแอนด์ไฮไดร์ต่อกิ่งด้วยพอลิเอททิลีนชนิดความแน่นต่ำและซิโอไลต์ อิทธิพลของอัตราส่วนระหว่างมาเลอิกแอนด์ไฮไดร์ต่อกิ่งด้วยพอลิเอททิลีนชนิดความแน่นต่ำต่อซิโอไลต์ ชนิดและปริมาณของซิโอไลต์ต่อการกระจายตัวของซิโอไลต์ในฟิล์มคอมโพสิต รวมถึงสมบัติทางความร้อน สมบัติทางกลและสมบัติความสามารถในการซึมผ่านก๊าซได้ถูกนำมาศึกษา ประสิทธิภาพของฟิล์มคอมโพสิตที่ถูกเลือกเป็นบรรจุภัณฑ์ในการยืดอายุและรักษาคุณภาพของมะนาวและมะม่วงถูกศึกษา จากผล SEM พบว่าฟิล์มคอมโพสิตพอลิเอททิลีนชนิดความแน่นต่ำ/ซิโอไลต์ที่มีอัตราส่วนระหว่างมาเลอิกแอนด์ไฮไดร์ต่อกิ่งด้วยพอลิเอททิลีนชนิดความแน่นต่ำต่อซิโอไลต์เป็น 3 และ 4 มีการกระจายตัวของซิโอไลต์ในฟิล์มคอมโพสิตดีกว่าฟิล์มคอมโพสิตที่อัตราส่วนอื่นๆ การเติมมาเลอิกแอนด์ไฮไดร์ต่อกิ่งด้วยพอลิเอททิลีนชนิดความแน่นต่ำช่วยทำให้อุณหภูมิการหลอมเหลวและเปอร์เซ็นต์ผลึกลดลงซึ่งยืนยันได้จากผลของ DSC อย่างไรก็ตามการเติมซิโอไลต์ลงในเมทริกซ์พอลิเอททิลีนชนิดความหนาแน่นต่ำไม่ส่งผลต่อเปอร์เซ็นต์ผลึก นอกจากนี้ฟิล์มคอมโพสิตพอลิเอททิลีนชนิดความแน่นต่ำ/ซิโอไลต์ที่มีซิโอไลต์ 3 ส่วนในพอลิเมอร์ 100 ส่วนและมีอัตราส่วนระหว่างมาเลอิกแอนด์ไฮไดร์ต่อกิ่งด้วยพอลิเอททิลีนชนิดความแน่นต่ำต่อซิโอไลต์เป็น 3 พบว่ามีสมบัติทางกลและสมบัติความสามารถในการซึมผ่านก๊าซดี และเมื่อนำฟิล์มคอมพอสิตมาบรรจุผลมะม่วงพบว่าสามารถยืดอายุและเก็บรักษาได้นาน 4 สัปดาห์ ขณะที่ฟิล์มพอลิเอททิลีนชนิดความหนาแน่นต่ำพบความเสียหายของผลมะม่วงโดยที่เปลือกมีอาการสีเทาดำจากการสะสมของก๊าซคาร์บอนไดออกไซด์ภายในภาชนะบรรจุที่สูงเกินกว่าผลมะม่วงจะทนทานได้ตั้งแต่สัปดาห์ที่ 3 หลังจากนำฟิล์มคอมพอสิตมาบรรจุผลมะนาวเป็นเวลา 6 สัปดาห์ พบว่าสามารถชะลอการเปลี่ยนแปลงสีเขียวของเปลือกผล การหลุดร่วงของขั้วผล และลดความเสียหายจากก๊าซคาร์บอนไดออกไซด์ที่สะสมมากเกินไปได้ดีกว่าผลมะนาวที่บรรจุในฟิล์มชนิดพอลิเอททิลีนความหนาแน่นต่ำ

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CONTENTS

page

ABSTRACT (THAI)…………………………………………………………… iv
ABSTRACT (ENGLIGH).. v
ACKNOWLEDGEMENTS.. vi
CONTENTS.. vii
LIST OF TABLES………………………………………………………….. x
LIST OF FIGURES………………………………………………………… xii

CHAPTER

- I INTRODUCTION………………………………………………………... 1
  - 1.1 General introduction………………………………………………… 1
  - 1.2 Objectives…………………………………………………………… 3
  - 1.3 Scopes of the research………………………………………………. 3
  - 1.4 Benefits of the research……………………………………………... 3
- II THEORY……………………………………………………………….. 4
  - 2.1 Low density polyethylene (LDPE)…………………………………. 4
  - 2.2 Zeolites……………………………………………………………… 5
  - 2.3 Compatibilizers……………………………………………………... 7
  - 2.4 Extrusion process…………………………………………………… 7
    - 2.4.1 Blown film extrusion……………………………………….. 8
  - 2.5 Postharvest biology…………………………………………………. 8
  - 2.6 Lime fruits…………………………………………………………... 9
  - 2.7 Mango fruits………………………………………………………… 10
  - 2.8 Modified Atmosphere Packaging (MAP)…………………………... 11
- III LITERATURE REVIEWS……………………………………………….. 13
- IV EXPERIMENTS………………………………………………………….. 18
  - 4.1 Materials……………………………………………………………….. 18
  - 4.2 Preparation of LDPE/zeolite composite film via melt processing method……………………………………………………………. 18

CHAPTER page

4.3 Specimen characterizations………………………………………… 20
    4.3.1 Scanning Electron Microscope (SEM)……………………… 20
    4.3.2 Differential Scanning Calorimetry (DSC)............................ 20
    4.3.3 Tensile measurement... 20
    4.3.4 Oxygen permeability analysis……………………………….. 21
    4.4.5 Carbon dioxide permeability analysis……………………….. 21
    4.4.6 Water vapour permeability analysis………………………… 22
    4.4.7 Ethylene adsorption………………………………………….. 22
    4.4.8 Determination of inorganic content…………………………. 23
4.4 Packing of fresh postharvest produces……………………………... 23
    4.4.1 Plant material and sample preparation……………………… 24
        4.4.1.1 Lime fruits………………………………………….. 24
        4.4.1.2 Mango fruits………………………………………... 24
    4.4.2 Packaging procedure………………………………………… 24
    4.4.3 Visual observation…………………………………………… 25
    4.4.4 Weight loss (%)……………………………………………… 25
    4.4.5 The concentration of gases in the packages………………… 25
    4.4.6 Colormetric measurement…………………………………… 26
    4.4.7 Fruit firmness………………………………………………... 26
    4.4.8 Total soluble solids (TSS) content and Titratable Acidity (TA)………………………………………………………… 27
    4.4.9 Vitamin C contents………………………………………….. 28
    4.4.10 Ripen – mango fruits……………………………………… 28
    4.4.11 Sensory evaluation………………………………………... 28
V RESULTS AND DISCUSSION………………………………………… 29
5.1 Zeolite characterization…………………………………………….. 29
5.2 Zeolite dispersion in LDPE/zeolite composite films……………….. 30
5.3 Thermal properties of LDPE/zeolite composite films……………… 34
5.4 Effect of PE-g-MA/zeolite ratio on the mechanical and gas permeability properties of LDPE/zeolite composite films……... 37

CHAPTER page

5.5 Effect of zeolite loading on the mechanical and gas permeability properties of LDPE/zeolite composite films……………………….. 42
5.6 Effect of zeolite types on the mechanical and gas permeability properties of LDPE/zeolite composite films……………………….. 46
5.7 Packing of fresh postharvest produces……………………………… 51
  5.7.1 The packing of lime fruits…………………………………… 51
  5.7.2 The packing of mango fruits………………………………... 58
    5.7.2.1 The quality of green mature mango fruits……….... 58
    5.7.2.2 The quality of ripen – mango fruits……………….. 66
VI CONCLUSIONS………………………………………………………. 75
REFFERENCES……………………………………………………………….. 77
APPENDICES…………………………………………………………………. 83
Appendix A Polymer properties……………………………………… 84
Appendix B Inorganic contents of pristine zeolite…………………… 85
Appendix C Average inorganic contents of LDPE/zeolite composite films………………………………………………….. 86
Appendix D Sensory table record…………………………………….. 87
Appendix E Melting (T_m) and crystallization (T_c) temperature of neat LDPE, PE-g-MA, and LDPE/zeolite composite films…….. 88
Appendix F Determination of degree of crystallinity (DSC experiments)……………………………………… 89
Appendix G Average data of mechanical and gas permeability properties of films………………………………………. 91
Appendix H Statistic analysis…………………………………………. 94
Appendix I Statistic data……………………………………………... 97
VITA………………………………………………………………………… 111

LIST OF TABLES

TABLE page

4.1 Sample code of LDPE/zeolite composite films……………………. 19

A.1 LDPE properties……………………………………………….... 84

A.2 PE-g-MA properties…………………………………………..… 84

B.1 Inorganic contents of pristine zeolite……………………………… 85

C.1 Average inorganic contents of LDPE/zeolite composite films……. 86

D.1 Sensory table record…………………………………………….. 87

E.1 Melting (T_m) and crystallization (T_c) temperature of neat LDPE, PE-g-MA, and LDPE/zeolite composite films…………………….. 88

F.1 Area under DSC heating peak, degree of crystallinity of neat LDPE, PE-g-Ma, and LDPE/zeolite composite films……………... 90

G.1 Mechanical properties of films (part I) in MD…………………….. 91

G.2 Mechanical properties of films (part I) in TD……………………... 91

G.3 Mechanical properties of films (part II) in MD……………………. 91

G.4 Mechanical properties of films (part II) in TD…………………….. 92

G.5 Mechanical properties of films (part III) in MD…………………… 92

G.6 Mechanical properties of films (part III) in TD……………………. 92

G.7 Gas permeability properties of films (part I)………………………. 93

G.8 Gas permeability properties of films (part II)………………………. 93

G.9 Gas permeability properties of films (part III)…………………….. 93

H.1 Weight loss of lime fruits after 1 week of storage…………………. 94

I.1 Lightness (L*) of lime fruits……………………………………….. 97

I.2 Greenness (-a*) of lime fruits……………………………………… 97

I.3 Yellowness (b*) of lime fruits …………………………………….. 98

I.4 Weight loss of lime fruits………………………………………….. 98

I.5 Firmness of lime fruits…………………………………………….. 98

I.6 Total soluble solids content of lime fruits…………………………. 99

I.7 Titratable acidity of lime fruits…………………………………….. 99

I.8 TSS/TA ratio of lime fruits………………………………………… 99

I.9 Vitamin C contents of lime fruits………………………………….. 100

TABLE page

I.10 Oxygen accumulation in the package of lime fruits……………….. 100
I.11 Carbon Dioxide accumulation in the package of lime fruits………. 100
I.12 Ethylene accumulation in the package of lime fruits……………… 101
I.13 Lightness (L*) of mango peel……………………………………… 101
I.14 Lightness (L*) of mango pulp……………………………………... 101
I.15 Greenness (-a*) of mango peel…………………………………….. 102
I.16 Greenness (-a*) of mango pulp…………………………………… 102
I.17 Yellowness (b*) of mango peel……………………………………. 102
I.18 Yellowness (b*) of mango pulp……………………………………. 103
I.19 Weight loss of mango fruits……………………………………….... 103
I.20 Firmness of mango fruits…………………………………………... 103
I.21 Total soluble solids content of mango fruits……………………… 104
I.22 Titratable acidity of mango fruits………………………………….. 104
I.23 TSS/TA ratio of mango fruits……………………………………… 104
I.24 Vitamin C contents of mango fruits……………………………….. 105
I.25 Oxygen accumulation in the package of mango fruits…………….. 105
I.26 Carbon Dioxide accumulation in the package of mango fruits……. 105
I.27 Ethylene accumulation in the package of mango fruits……………. 106
I.28 Lightness (L*) of ripen - mango peel……………………………… 106
I.29 Lightness (L*) of ripen - mango pulp……………………………… 106
I.30 Greenness (-a*) of ripen - mango peel…………………………….. 107
I.31 Greenness (-a*) of ripen - mango pulp…………………………….. 107
I.32 Yellowness (b*) of ripen - mango peel…………………………… 107
I.33 Yellowness (b*) of ripen - mango pulp……………………………. 108
I.34 Firmness of ripen - mango fruits…………………………………... 108
I.35 Total soluble solids content of ripen - mango fruits……………….. 108
I.36 Titratable acidity of ripen - mango fruits………………………….... 109
I.37 TSS/TA ratio of ripen - mango fruits……………………………… 109
I.38 Vitamin C contents of ripen - mango fruits……………………….... 109

LIST OF FIGURES

FIGURE page

2.1 Both short and long chains branching of LDPE…………………… 4

2.2 The structure of a partially crystalline polymer…………………… 4

2.3 Framework of zeolite A……………………………………………. 6

2.4 Framework of zeolite X…………………………………………… 6

2.5 Illustration of a single-screw extruder…………………………….. 7

2.6 Schematic of a basic blown film line……………………………… 8

2.7 The appearance of lime fruits……………………………………… 10

2.8 The appearance of mango fruits…………………………………… 11

4.1 Oxygen permeation analyzer; OX-TRAN 2/21, Mocon, USA…… 21

4.2 Carbon dioxide permeation analyzer; PERMATAN-C 4/41, Mocon, USA……………………………………………………. 22

4.3 The equipment of ethylene adsorption test………………………… 23

4.4 Gas chromatograph for C_2H_4 (a) and O_2/CO_2 (b) test; GC-8A, Shimadzu, Japan…………………………………………………… 26

4.5 Color meter; Minolta CR 400, Konica Minolta Sensing, Japan…... 26

4.6 Fruit firmness tester; Black&Decker, and prove with various sizes. 27

5.1 SEM micrographs of 4A zeolite (a), T zeolite (b), 5A zeolite (c), and 13X zeolite (d)………………………………………………… 29

5.2 SEM micrographs of both sides of LDPE/zeolite composite films at the PE-g-MA/zeolite ratio of 0 (a), 1.0 (b), 2.0 (c), 3.0 (d), and 4.0 (e) at fixed zeolite content of 3 phr…………………………….. 31

5.3 SEM micrographs of both sides of LDPE/zeolite composite films with various zeolite contents; 1 phr (a), 3 phr (b), 5 phr (c), and 7 phr (d) at fixed PE-g-MA/zeolite ratio of 3.0……………………… 32

5.4 SEM micrographs of both sides of LDPE/zeolite composite films with various zeolite types; T zeolite (a), 4A zeolite (b), 5A zeolite (c), and 13X zeolite at fixed PE-g-MA/zeolite ratio of 3.0 and zeolite content of 3 phr……………………………………………. 33

FIGURE page

5.5 SEM micrographs of interfacial area of the composite films……… 33

5.6 DSC heating curves (a) and DSC cooling curves (b) of neat LDPE and LDPE/zeolite composite films with various PE-g-MA/zeolite ratios at fixed zeolite loading of 3 phr…………………………….. 34

5.7 DSC heating curves (a) and DSC cooling curves (b) of neat LDPE and LDPE/zeolite composite films with various zeolite loading at fixed PE-g-MA/zeolite ratio of 3.0………………………………… 35

5.8 DSC heating curves (a) and DSC cooling curves (b) of neat LDPE and LDPE/zeolite composite films with various zeolite types at fixed PE-g-MA/zeolite ratio of 3.0 and zeolite loading of 3 phr….. 36

5.9 Effect of the PE-g-MA/zeolite ratio on tensile strength at yield (a), Young's modulus (b), and elongation at break (c) of LDPE/zeolite composite films at fixed zeolite content of 3 phr………………….. 38

5.10 Effect of the PE-g-MA/zeolite ratio on gas permeability of LDPE/zeolite composite films at fixed zeolite content of 3 phr…… 40

5.11 Effect of the PE-g-MA/zeolite ratio on ethylene adsorption of LDPE/zeolite composite films at fixed zeolite content of 3 phr…… 41

5.12 Effect of zeolite contents on tensile strength at yield (a), Young's modulus (b), and elongation at break (c) of LDPE/zeolite composite films at fixed PE-g-MA/zeolite ratio of 3.0…………..… 43

5.13 Effect of zeolite contents on gas permeability of LDPE/zeolite composite films at fixed PE-g-MA/zeolite ratio of 3.0……………. 45

5.14 Effect of zeolite contents on ethylene adsorption of LDPE/zeolite composite films at fixed PE-g-MA/zeolite ratio of 3.0……………. 46

5.15 Effect of zeolite type on tensile strength at yield (a), Young's modulus (b), and elongation at break (c) of LDPE/zeolite composite films at fixed PE-g-MA/zeolite ratio of 3.0 and zeolite loading of 3 phr…………………………………………………….. 48

FIGURE page

5.16 Effect of zeolite type on gas permeability of LDPE/zeolite composite films at fixed PE-g-MA/zeolite ratio of 3.0 and zeolite loading of 3 phr 50

5.17 Effect of zeolite type on ethylene adsorption of LDPE/zeolite composite films at fixed PE-g-MA/zeolite ratio of 3.0 and zeolite loading of 3 phr 50

5.18 Lightness (a), greenness (b), and yellowness (c) of limes without packaging film (control,┈■┈) and inside neat LDPE (--▲--) and composite packaging film (—●—) stored at 10°C for 8 weeks 52

5.19 The percentage of weight loss (a) and firmness (b) of limes without packaging film (control,┈■┈) and inside neat LDPE (--▲--) and composite packaging film (—●—) stored at 10°C for 8 weeks 53

5.20 Total soluble solids content (a) and titratable acidity (b) of limes without packaging film (control, ┈■┈) and inside neat LDPE (--▲--) and composite packaging film (—●—) stored at 10°C for 8 weeks 53

5.21 TSS/TA ratio of limes without packaging film (control, ┈■┈) and inside neat LDPE (--▲--) and composite packaging film (—●—) stored at 10°C for 8 weeks 54

5.22 Vitamin C (V_c) contents of limes without packaging film (control, ┈■┈) and inside neat LDPE (--▲--) and composite packaging film (—●—) stored at 10°C for 8 weeks 54

5.23 Ethylene (a), carbon dioxide (b), and oxygen (c) accumulation of limes inside neat LDPE (--▲--) and composite packaging film (—●—) stored at 10°C for 8 weeks 55

5.24 The appearance of all tested limes without packaging film and with LDPE and composite packaging film stored at 10°C for 8 weeks 57

FIGURE page

5.25 Lightness, greenness, and yellowness of peel and pulp of mangoes without packaging film (a, ···■··· and d, ···□···) and inside neat LDPE (b, --▲-- and e, --△--) and composite packaging film (c, —●— and f, —○—), respectively, stored at 12°C for 5 weeks…... 59

5.26 The percentage of weight loss (a) and firmness (b) of mangoes without packaging film (control, ···■···) and inside neat LDPE (--▲--) and composite packaging film (—●—) stored at 12°C for 5 weeks…………………………………………………………. 60

5.27 Total soluble solids content (a) and titratable acidity (b) of mangoes without packaging film (control, ···■···) and inside neat LDPE (--▲--) and composite packaging film (—●—) stored at 12°C for 5 weeks……………………………………………………… 61

5.28 TSS/TA ratio of mangoes without packaging film (control, ···■···) and inside neat LDPE (--▲--) and composite packaging film (—●—) stored at 12°C for 5 weeks……………………………….. 61

5.29 Vitamin C (V_c) contents of mangoes without packaging film (control, ···■···) and inside neat LDPE (--▲--) and composite packaging film (—●—) stored at 12°C for 5 weeks………………... 62

5.30 The peel appearance of all tested mangoes without packaging film and with LDPE and composite packaging film stored at 12°C for 5 weeks…………………………………………………………….. 64

5.31 The pulp appearance of all tested mangoes without packaging film and with LDPE and composite packaging film stored at 12°C for 5 weeks…………………………………………………………….. 65

5.32 Ethylene (a), carbon dioxide (b), and oxygen (c) contents of mangoes inside neat LDPE (--▲--) and composite packaging film (—●—) stored at 12°C for 5 weeks………………………………… 66

FIGURE page

5.33 Lightness, greenness, and yellowness of peel and pulp of ripen - mangoes without packaging film (a, ····■···· and d, ····□····) and inside neat LDPE (b, --▲-- and e, --△--) and composite packaging film (c, —●— and f, —○—), respectively, stored at 12°C for 5 weeks.. 67

5.34 Firmness (a), total soluble solids contents (b), titratable acidity (c), TSS/TA ratio (d) and Vitamin C (V_c) contents (e) of ripen - mangoes without packaging film (control, ····■····) and inside neat LDPE (--▲--) and composite packaging film (—●—) stored at 12°C 68

5.35 The peel appearance of all tested ripen - mangoes without packaging film and with LDPE and composite packaging film stored at 12°C.. 71

5.36 The pulp appearance of all tested ripen - mangoes without packaging film and with LDPE and composite packaging film stored at 12°C.. 72

5.37 The core appearance of all tested ripen - mangoes without packaging film and with LDPE and composite packaging film stored at 12°C.. 73

5.38 Sensory evaluation of all tested ripen - mangoes without packaging film and with LDPE and composite packaging film stored at 12°C, 0 to 5 weeks (a – f).. 74

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CHAPTER I

INTRODUCTION

1.1 General Introduction

Nowadays, Thailand has more exportation of agricultural produces than the past and the damage of these produces both before or during exporting has still been more than 35% [1] compared to all produces in which the value of damaged produces is around 10,000 million Baht. This damage is a result of the lack of knowledge about post harvest biology; that is, most entrepreneur and agriculturist do not clearly know that fruits and vegetables are still living organisms after harvesting, taking in oxygen and giving out carbon dioxide. This process was known as respiration which works by burning the plant sugars in oxygen to release carbon dioxide, water and energy. Slowing down respiration by refrigeration reduces the amount of energy produced, and if there is not enough energy then the physiological functions depending on its kind slow down or cease. Such functions include aging or senescence in leafy vegetables and ripening of fruits. Although refrigeration does slow down respiration it is not always a suitable way, for a variety of reasons, i.e. the lack of proper management of post harvest produces such as prolonging life and qualitative storage technique, the damaging produces during transportation and also unsuitable packages [2].

Therefore, the control of various factors that affects on the damage of agricultural produces is very important. The factors affecting on this problem such as temperature; it should be low temperature, humidity; it should be high humidity, gas composition of atmosphere; it should be proper especially O_2 and CO_2, not over or not enough, etc. These factors are external factors that can be controlled but internal factors such as gas from plant respiration and photosynthesis, i.e. O_2, CO_2 and water vapour including ethylene gas from plant production, can accumulate within agricultural produce packages. These gases are difficult to control because they can occur naturally. The packages used to contain the produces are one of the important factors. If they have proper water vapour and gas permeability, they can reduce those problems.

The packages, which are used for agricultural produces, are made of various materials depending on applications such as woods, papers and also plastics. Plastic packaging is mostly used in the present due to easy production, light weight and recycle-ability. Plastic packaging has several types such as plastic sack, plastic bottle, and film plastic. Only film plastic is interested in this study. Polyethylene, especially low density polyethylene (LDPE) [3], is widely used to produce film packaging for fruits and vegetables [4-6]. It is sometimes not good enough for gas permeability, so it must be perforated to have good ventilation. The hole size should be 0.5 – 2.0 cm in diameter which is large enough to prevent the occurrence of water drops within package and anaerobic respiration that leads to perishableness. But the perforation of packaging are poorly beauty and easy to tear. In addition, microorganism may also enter to agricultural produces within packages. Moreover, all ethylene gas should be removed out of the packages. It is due to ethylene gas which is the ripening agent and causes fruits to ripen and decay.

Therefore, this research was aimed to improve gas permeability of LDPE blown film, which is used as fresh produce package, to extend shelf life of fresh vegetables and fruits without the perforation of film packaging. Several types of zeolite were used as fillers; zeolite 4A, zeolite 5A and zeolite 13X. In addition, this work also studied mechanical and thermal properties of films. The best formula, which had the proper properties, would be chosen as fresh produce package and would be tested with lime and mango, which were climacteric and non-climacteric fruit, respectively, and then compared to pure LDPE blown film under the same condition.

1.2 Objectives

1. To study the effect of PE-g-MA to zeolite ratio, zeolite loading, and zeolite type on mechanical, thermal and gas permeability properties of LDPE/zeolite composite films.
2. To determine the efficiency of chosen film on prolonging shelf life and maintaining quality of fresh produces.

1.3 Scopes of the research

1. Vary PE-g-MA to zeolite ratio in LDPE/zeolite composite films.
2. Vary the type and content of zeolite of LDPE/zeolite composite films.
3. Characterize LDPE/zeolite composite films in which mechanical, thermal and gas permeability properties of these materials were studied.
4. Package fresh produces and test all appropriate qualities.

1.4 Benefits of the research

1. Understand an influence of PE-g-MA to zeolite ratio, zeolite loading, zeolite type, and particle dispersion on mechanical and thermal properties, and gas permeability of LDPE/zeolite composite films.
2. Use these materials as packaging films to maintain quality and extend shelf life of fresh produces.

CHAPTER II

THEORY

2.1 Low density polyethylene (LDPE)

Low-density polyethylene (LDPE) is a thermoplastic material composed of polymers of ethylene. Molecular structure of LDPE is shown in figure 2.1. The density varies between about 0.916 g/cm^3 and 0.935 g/cm^3. It has a melting temperature range from 107 to 120^{o}C and it is partially amorphous and partially crystalline, as known as semi-crystalline. The structure of a partially crystalline polymer is shown in figure 2.2.

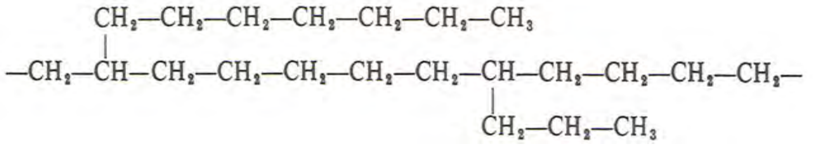

Figure 2.1: Both short and long chains branching of LDPE [7]

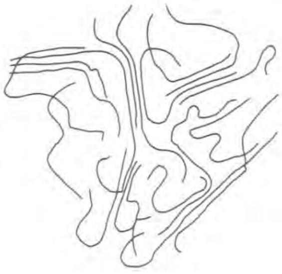

Figure 2.2: The structure of a partially crystalline polymer [8]

Linear polymer chains afford packing of molecules and hence a higher degree of crystallinity is obtained, on the other hand, side chain branching reduces the degree of crystallinity. The great length of polymer chains makes it has more entanglement of polymer chains and this prevents complete crystallization on cooling. The crystallinity increases physical, mechanical and barrier properties such as density, tensile strength and impact strength. That is, the structure of the low density polyethylene molecule also affects properties. LDPE has good chemical resistance, good toughness and flexibility but low heat resistances.

The other characteristics of LDPE which have led it to widespread use are low cost, easy processibility, freedom from odor and toxicity, clarity in thin films, and low permeability to water vapour but good for gases [9]. Major uses for LDPE are in packaging, building, and agricultural applications such as plastic bags, food storage containers, extrusion coating on paperboard and aluminum laminated for beverage cartons, and etc.

2.2 Zeolites

A zeolite has been defined by Smith as a ‘crystalline aluminosilicate with a tetrahedral framework structure enclosing cavities occupied by cations and water molecules, both of which have enough freedom of movement to permit cation exchange and reversible dehydration’. The unit cell formula is usually written as

$$\mathbf{M_n^+\left[(AlO_2^-)_x(SiO_2)_y\right].zH_2O}$$

where M_n^+ is the cation which balances the negative charge associated with the framework aluminum ions [10].

There are two kinds of zeolite, natural and synthetic zeolite. Natural zeolites are widely used in the agricultural industry and also found applications in paper, cements and concrete industries. The synthetic zeolites are made commercially for specific uses or produced to study about their chemistry by scientists [11]. The examples of synthetic zeolites are zeolite A, X, and Y.

Zeolite A is the simplest synthetic zeolite with a Si/Al ratio of 1. It has a cubic structure as shown in figure 2.3. The sodium form of zeolite A has a pore opening of approximately 4 angstrom, called zeolite 4A. If the soidium ion is exchanged with the larger potassium ion, the pore opening is reduced to approximately 3 angstrom. And the pore opening increases to approximately 5 angstrom if the sodium ion is exchanged with calcium because one calcium ion replaces two sodium ions. Ion exchange with other cations is sometimes used for particular separation purposes. Zeolite X is another synthetic zeolite with a Si/Al ratio of 2 to 3. It has a pore opening of the sodium form of zeolite X (13X) which is approximately 8 angstrom and the framework is shown in figure 2.4. [12]

Figure 2.3: Framework of zeolite A [12]

Figure 2.4: Framework of zeolite X [12]

Because of their unique porous properties, zeolites are used in a variety of applications with a global market of several million tons per annum. In the western world, major uses are in petrochemical cracking, ion-exchange (water softening and purification), and the separation and removal of gases and solvents. Other applications are in agriculture, animal husbandry and construction. Moreover, they are also referred to as molecular sieves. [13]

2.3 Compatibilizers

A compatibilizer, a block copolymer of the two components of the immiscible blend, is used to tighten bond between two phases and allow energy to be transferred from one phase to the other. This means that the minor component can improve the mechanical properties of the major component rather than worsen them. Graft copolymers are also used as compatibilizer [14] such as maleic anhydride grafted polyethylene (PE-g-MA) and maleic anhydride grafted polypropylene (PP-g-MA).

2.4 Extrusion process

In the extrusion process, polymer is propelled continuously along a screw through regions of high temperature and pressure where it is melted and compacted, and finally forced through a die shaped to give the final object. [15]

The screw of an extruder is divided into three sections as shown in figure 2.5, each section with a specific purpose. The first section is called the feed section that picks up the plastic solid, usually in the form of particulate solids such as pellet and powder, from the hopper and conveys them forward by the action of the screw to the next section, known as the compression section, where the material begins to melt. The resin should be fully melted in the final section of the screw, known as the metering section. A pressure in the polymer melt is built up in the metering section to force the plastic pass through the die.

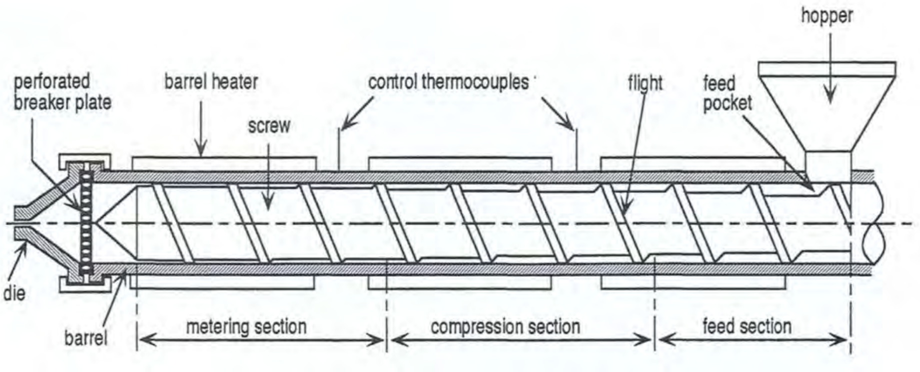

Figure 2.5: Illustration of a single-screw extruder [16]

2.4.1 Blown film extrusion

One of the most common methods of film manufacture is blown film extrusion. The process consists of the extrusion of a plastic through a circular die and bubble expanded. Blown film extrusion is shown in figure 2.6. In this figure, the molten polymer from the extruder is fed through the die from the side and emerges through a die ring. The tube is expanded into a bubble of the required diameter by internal air. The bubble pressure is maintained by pinch rolls at one end and by the die at the other. It is important that the pressure of the air is kept constant in order to ensure uniform thickness and width of film. The external air passed outside of the expanding bubble to stabilize the blown film and to cool the bubble. The blown film product is then collected by winding onto rolls. Biaxial orientation can be achieved in this technique; that is, machine direction (MD) and transverse direction (TD).

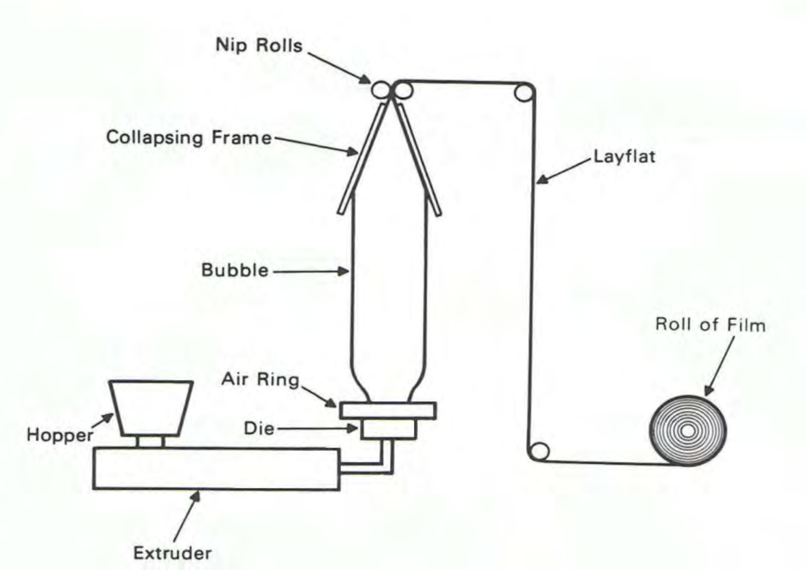

Figure 2.6: Schematic of a basic blown film line [17]

2.5 Postharvest biology

Plants after harvest are still active biological system. They breathe, release heat and carbon dioxide (CO_2) from respiration, and lose moisture from transpiration. Therefore, freshness of postharvest produces depends on their food and water collected in their cell and respiration rate of each kind of plants. Respiration can be determined by measuring oxygen (O_2) and carbon dioxide (CO_2) contents while their cells are alive. It is found that plants have short-term storage if they have high respiration; that is, they deteriorate and ripen quickly.

Fruits can be divided into two categories according to respiration rate while ripening; that is, climacteric and non-climacteric fruits. Climacteric fruits have high respiration rate while ripening because increased ethylene concentration inside the fruit activates their respiration rate such as banana, tomato, and mango. For non-climacteric fruits, respiration rate depends on ethylene concentration and ethylene synthesis rate which are still low until deterioration such as cucumber, orange, and pineapple.

Respiration, transpiration, and ethylene production of postharvest produces are internal factors affecting on their shelf life and quality. Respiration is the process of oxidizing food molecules, like sugar/starch turned into carbon dioxide, water and energy in the form of ATP for use by all the energy-consuming activities of the cell. Not only fresh produces lose water by respiration, but also by transpiration that water in liquid form in plants is converted into vapor and released to the atmosphere. These processes enhance quality deterioration and weight loss of fresh produces. In addition, ethylene gas which occurs in nature acts as a plant hormone that accelerates respiration, leading to senescence, and also ripening of many kinds of fruit. It causes rapid deterioration, microbial infection and shelf-life reduction. To maintain quality and freshness of the fresh produces and reduce the effects from microorganisms, it is possible to act on processing or, more usually, on Modified Atmosphere Packaging (MAP) together with proper low storage temperature to develop low oxygen and elevate carbon dioxide inside packaging. Therefore, a proper combination of product characteristics and film permeability results in the evolution of an appropriate atmosphere within packages. [18]

2.6 Lime fruit

Limes are native to Southeast Asia and are cultivated in tropical regions. The lime is a small tree, crooked and prickly, only reaching as a rule a height of 8 feet.

The leaves are ovate oblong, and the stalk is not winged like that of the orange and lemon tree. The flowers are small and white and the fruit about half the size of a lemon, with a smoother, thinner rind, having a greenish tinge in its yellow. The size of lime fruit generally is about 4 – 4.5 centimeters. The juice is principally used in the manufacture of citric acid, and for medicinal purposes is often used indiscriminately with that of the lemon, although its flavor is not so popular. Oil of limes is used for flavorings purposes, especially in mineral waters and artificial lime-juice cordials, consisting of sweetened solutions of tartaric acid [19]. The lime fruit is non-climacteric fruit that respiration rate does not accelerate after harvest and this fruit produce very small quantities of ethylene.

Figure 2.7: The appearance of lime fruits [20]

2.7 Mango fruit

The mango is native to southern Asia, especially Burma and eastern India. It was widespread on to Malaya, eastern Asia and eastern Africa [21]. It was known for its unique flavor and attractive appearance.

Mango trees (*Mangifera indica*) reach 35-40 m in height, with a crown radius of 10 m. The leaves are evergreen, alternate, simple, 15-35 cm long and 6-16 cm wide. The flowers are produced in terminal panicles 10-40 cm long; each flower is small and white with five petals with 5-10 mm long, with a mild sweet odor suggestive of lily of the valley. The fruit takes three to six months to ripen. The ripe fruit is variable in size and color, and may be yellow, orange, red or green when ripe, depending on the cultivar [22].

Mangos basically require a frost-free climate. Flowers and small fruit can be killed if temperatures drop below 40°F, even for a short period. Young trees may be seriously damaged if the temperature drops below 30°F, but mature trees may withstand very short periods of temperatures as low as 25°F. The mango must have warm, dry weather to set fruit. Mangos luxuriate in summer heat and resent cool summer fog. Wet, humid weather favors anthracnose and poor fruit set.

Mango fruit will have the best flavor if allowed to ripen on the tree. Ripening fruit turns the characteristic color of the variety and begins to soften to the touch, much like a peach. Ripe mango fruits are considered an excellent source of vitamin A, C, B1 and B2. The darker orange flesh has the most vitamin A, but without a doubt all mangoes have a lot of vitamins and minerals [23]. Mango fruits are climacteric fruits that respiration rate of fruits increases to a maximum just prior to full ripening and exhibit this increase in respiratory rate along with ethylene evolution just prior to senescence.

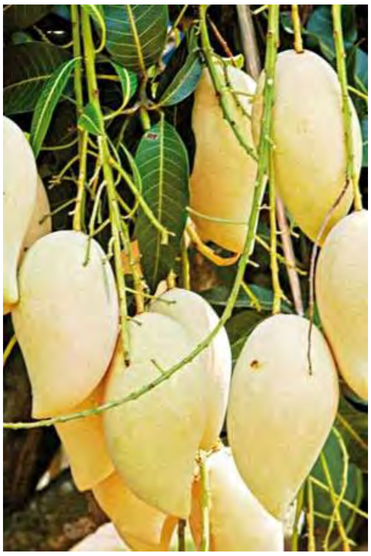

Figure 2.8: The appearance of mango fruits [24]

2.8 Modified Atmosphere Packaging (MAP)

Modified Atmosphere Packaging (MAP) is a technique used for prolonging the shelf life period of fresh or minimally processed foods due to it slows the nature deterioration of the product. In this preservation technique the air surrounding the product in the package is changed to another composition due to respiration (evolution of CO_2, utilization of O_2) and transpiration (water vapor caused saturated atmosphere). If the permeability of the packaging film is adapted to the products respiration, an equilibrium modified atmosphere will establish in the package and the shelf life of the product will increase [25]. However, the thickness and type of film, the type of fruit, the fruit's weight, the fruit's maturity, the surrounding temperature, and microbial infection affect the modified atmosphere.

CHAPTER III

LITERATURE REVIEWS

The reviews studied the previous researches regarding the effects of surface coating on filler in polymer composites, processing method, mechanical properties and gas permeability, i.e. oxygen (O_2), carbon dioxide (CO_2), water vapour and ethylene gas (C_2H_4), of polymer composites and also the determination of gas composition inside agricultural produce packaging, i.e. O_2, CO_2, water vapour and C_2H_4.

Nowadays, plastic film packaging, which is mostly produced by the blown film process, is consumed in vast quantities. Polyethylene, especially low density polyethylene (LDPE), is widely used for food packaging because it offers the advantages of being inert, permeable to O_2, CO_2, C_2H_4 (g) and comparatively less permeable to water vapour. However, neat polymer does not respond to gas permeability enough. Thus, more porosity of film packaging is demanded. Zeolite, used as filler, has microstructure that is mostly used for adsorption, permeability and separation applications [26, 27]. Therefore, adding zeolite into polymer film interests us.

Zeolites are aluminosilicate crystalline and highly porous materials. The composition of Al/Si in their structure is one of the important factors in determining the hydrophobicity and hydrophilicity. The higher the relative composition ratio of the Si component in zeolite, the higher the hydrophobicity of the zeolites obtained [28]. Zeolites have been used in the field of adsorption, ion exchange, and catalysis [29]. Peiser, G. and Suslow, T. V. [30] studied factors affecting ethylene adsorption by zeolite. The results showed that heated zeolite and ethylene control (potassium permanganate) exhibited the ability to remove ethylene. It meant that heat treatment removed other volatiles or water vapour from some or all of the ethylene adsorption sites. Ethylene separation from methane on 4A, 5A, CaX and 13X zeolites and H-mordenite were determined [31]. The results showed that CaX and 5A zeolites have a higher ethylene/methane separation than others because of the interactions between the ethylene double bond (π-bond) and the cationic sites in the zeolite micropores. Moreover, zeolites can improve the mechanical properties and gas permeability of their composites [26, 27, 32].

It is well known that adding filler into polymer matrix affects on properties of composites. The increased filler content in the composite leads to higher values of modulus because of a stiffening of the composite structure. However, poor compatibility between polymer matrix and filler still exists due to the difference of their polarity; i.e. polymer is hydrophobic but most filler is hydrophilic. Therefore, filler surface treatment is very important for improving both particle/particle and matrix/filler interaction or wettability [33]; that is, the compatibility of composites is enhanced. The filler is often coated by a variety of surface modifiers such as fatty acids, phosphates, silanes, titanates or zirconates [34]. Stearic acid (STAC) was the most widely used to coat fillers such as calcium carbonate ($CaCO_3$) surface modifications and zeolite surface modification. Not only stearic acid, but also silanes have been used as zeolite surface modifier such as methyltriethoxysilane (MTES), 3-aminopropyltriethoxysilane (AMPTES) and 3-mercaptopropyltrimethoxysilane (MPTES), γ–aminopropyltriethoxysilane (γ-APS), (3-aminopropyl)-diethoxymethyl silane (APDEMS), 3-(trimethoxysilyl)-1-propanethiol (MS) and (3-aminopropyl)-triethoxysilane (AS). In addition, silane coupling agents are used for $CaCO_3$ surface coating such as triethoxy-silyl derivatives of saturated carboxylic acids, organofunctional glycidyl silane coupling agents, methacrylic functional silane coupling agents and aminofunctional silane coupling agents. The amount of coupling agent added is around 1 %wt that will give the better mechanical properties of composites. The excess coupling agent has an influence on the tensile properties of composites; that is, all tensile properties of the composites decreased but the reinforcement of the stiffness increased. The filler surface treatment was performed by two major methods; i.e. treatment on dry powder of filler [35] and treatment in coupling agent solution such as silane agent [36, 37] and stearic acid.

The effects of surface coating on properties of composites can be found in many literatures[28, 32, 33, 38-42]. The value of tensile yield stress, tensile strength, Young's modulus and elongation at break of coated filler filled polymer composites was higher than uncoated filler filled polymer composites [32, 33]. In some cases, $CaCO_3$ treated by silanes had slightly effect on Young's modulus of PP/$CaCO_3$ composites but had much more effect on tensile strength of PP/$CaCO_3$ composites [31]. However, Kim, H., et al found that surface treatment hardly modifies the tensile strength of composites compared to untreated composites but enhanced elongation and Young's modulus [28]. It may be concluded that chemical structure of coupling agents had an effect on properties of composites.

Not only filler surface treatment, but many researchers also used compatibilizer [39-42] to increase interfacial adhesion between polymer and filler. Maleic anhydride grafted polyethylene (PE-g-MA) has been widely used for LDPE composite system [39, 41, 42]. In addition, maleic anhydride grafted polypropylene (PP-g-MA) was also used as a compatibilizer for LDPE composite system [42]. The tensile strength is significant improved in the compatibilized system, which is close to that of pure LDPE, compared to the uncompatibilized system [39]. It could be due to the reaction between the hydroxyl groups of filler and the maleic anhydride groups permitting a finer dispersion of filler in polymer matrix [39].

The condition of compounding process is very important because it affects properties of the composites. Twin-screw extruder is generally used for compounding filler and polymer matrix in which temperature gradient of the barrel of the extruder is maintained differently upon type of polymer matrix. The compound is re-extruded to formed blown films using film blowing process. Blow-up ratio (BUR), which is the ratio of the diameter of the final bubble film to the diameter of the die, and draw-down ratio (DDR), which is the ratio of the final film velocity to the initial polymer velocity, affect on properties of blown films such as thickness, orientation characteristics and tear strength [43]. However, Shah, R. K., et al showed that BUR and DDR did not affect on properties of blown film [43].

One of properties of blown film that must be studied is gas permeability. The gas permeability and diffusivity are decreased and increased, respectively, by increasing film thickness and this is related to the amount of degree of crystallinity of polymer. However, some literature [44] indicated that the permeability was independent on the film thickness. This could be due to different film production method. In addition, temperature also affects on permeability and diffusivity; that is, permeability and diffusivity increased as temperature increased.

As we have known, postharvest produce still respires, so O_2, CO_2, C_2H_4 and water vapour from plant production can accelerate the ripening and the deterioration of fruits, vegetables and floral products. Ethylene gas not only produces from engine combustion, but also from industrial waste. In order to extend shelf life of fresh produce, O_2, CO_2, C_2H_4 must be controlled properly. Therefore, we expect that adding zeolites into polymer matrix and keeping the packages at low temperature could improve gas permeation of this film and extend shelf life of fresh produces.

Postharvest technologies developed for fresh fruit have tended to concentrate on quarantine, disease control, packaging, and long-term storage so that business expansion can occur in the marketing of the fresh fruit. Hot water treatment is an effective postharvest treatment for mango. Hot water treatment has been used to prevent rot development, stem-end-rot infestations, and has been shown in numerous emperate, sub-tropical and tropical fruit, vegetables and flowers [45]. Furthermore, dipping harvested fruits in hot water minimizes fruit fly damage and anthracnose. For mango fruit, immersion in hot water at 42 - 49^{o}C for 25-120 min had been reported to induce a range of external and internal heat injuries [46]. In addition, hot water immersion treatment at 52^{o}C for 5 minutes and 53^{o}C for 3 minutes was also used in many literatures [47-51]. In addition, cooling water was also used to cool the skin and core temperature down to room temperature after dipping in hot water such as 25^{o}C for 60 min and 10^{o}C for 3 min [51, 52]. Postharvest fungicide treatment is very important and also used for postharvest produce such as sodium hypochlorite, imidazole, and prochloraz. Furthermore, hot water containing fungicide treatment can also be effective in the control of stem-end-rot caused by the fungus *Dothiorella dominicana* [53] and *Lasiodiplodia theobromae* [51].

Modified atmospheres (MA) can be used to supplement the maintenance of optimum temperature and relative humidity for preserving quality and reducing postharvest losses of tropical fruits during transport and storage. In MA, the O_2 level is reduced and the CO_2 level is increased at a rate determined by the respiration rate of the commodity, the storage temperature, and the permeability of the package. There is a wide range of plastic films used for Modified atmosphere Packaging (MAP). These include polyethylene (LDPE, HDPE, LLDPE), polypropylene (PP), and polyvinyl chloride (PVC). Mango and lime were used in this study because these fruits are very important economic fruits in Thailand. Moreover, the value of lime is high in low season. Many literatures were reported the package for prolonging shelf life of lime and mango fruits [54-58]. Polypropylene bag with an eight pinholes was used to prolong shelf life of mango cv. Nam Dok Mai for three weeks stored at 10°C but peel, pulp and seed of fruits still shown chilling injury symptom due to over CO_2 accumulation [58]. The mango fruits cvs. Tommy Atkins and Keitt kept in microperforated polyethylene stored at 12°C still showed chilling injury symptom [57]. High gas permeable package was interested in packaging field because it delayed ripening and extended shelf life of mango cv. Nam Dok Mai See Thong for 3 weeks without chilling injury symptom [55]. Additionally, polyethylene bags extended shelf life of lime fruits for seven weeks stored at 10°C. Moreover, wax coating [54, 57, 59] has been also practiced to extend shelf life of fruits. Fruit flavor is the critical parameter to be monitored after coating application. However, the advantage of the package is the fungi or disease cannot spread to another fruit.

CHAPTER IV

EXPERIMENTS

4.1 Materials

LDPE was supplied from Siam Cement Group (SCG), Thailand. It had melt flow rate of 5.00 g/10 min and melting point of 110°C. Four types of zeolites which were 4A powder, T powder, 5A and 13X Molecular sieve powder were supplied by Huiying Chemistry Industry (Xiamen) Co., Ltd. Compatibilizer used in this study was maleic anhydride grafted polyethylene (PE-g-MA) which was acquired from Creative Polymers Ltd. The properties of polymer materials were shown in Appendix A.

4.2 Preparation of LDPE/zeolite composite films via melt processing method

Zeolite powder was dried at 130°C for 3 hours in the oven to remove the absorbed water. Zeolite powder, PE-g-MA and LDPE were mixed together and then placed into a hopper of screw feeder at different PE-g-MA to zeolite ratio (1:1, 2:1, 3:1 and 4:1) in experimental part I, at different zeolite loading (1, 3, 5 and 7 phr) in experimental part II and at different types of zeolites (4A, T, 5A and 13X) in experimental part III. The pellets of LDPE/zeolite composites were compounded by using a twin screw extruder, Thermo Hakke Rheomex, Germany, with a barrel temperature of 150°C in a feeding zone and 155°C in the other zones and a screw speed of 150 rpm and then dried at 70°C for 4 hours in the oven to remove moisture. The films were formed by using a twin screw extruder which was attached to annular die (blown film die) with a barrel temperature of 150°C in a feeding zone and 180°C for the other zones and a screw speed of 190 rpm except in experimental part II. It was due to higher viscosity at the higher zeolite contents. Therefore, the films were formed with a barrel temperature of 150°C in a feeding zone and 200°C for the other zones and a screw speed of 190 rpm. The sample code of each composite film was shown in table 4.1.

Table 4.1: Sample code of LDPE/zeolite composite films

Sample code	**Detail**
LDPE-1	Neat LDPE for part I
LP3Z3	Composite film with zeolite 4A at the PE-g-MA/zeolite ratio of 1.0 and zeolite loading of 3 phr
LP6Z3	Composite film with zeolite 4A at the PE-g-MA/zeolite ratio of 2.0 and zeolite loading of 3 phr
LP9Z3-1	Composite film with zeolite 4A at the PE-g-MA/zeolite ratio of 3.0 and zeolite loading of 3 phr for experimental part I
LP12Z3	Composite film with zeolite 4A at the PE-g-MA/zeolite ratio of 4.0 and zeolite loading of 3 phr
LDPE-2	Neat LDPE for part II
LP3Z1	Composite film with zeolite 4A at the PE-g-MA/zeolite ratio of 3.0 and zeolite loading of 1 phr
LP9Z3-2	Composite film with zeolite 4A at the PE-g-MA/zeolite ratio of 3.0 and zeolite loading of 3 phr for experimental part II
LP15Z5	Composite film with zeolite 4A at the PE-g-MA/zeolite ratio of 3.0 and zeolite loading of 5 phr
LP21Z7	Composite film with zeolite 4A at the PE-g-MA/zeolite ratio of 3.0 and zeolite loading of 7 phr
LP9T3	Composite film with zeolite T at the PE-g-MA/zeolite ratio of 3.0 and zeolite loading of 3 phr
LP9A3	Composite film with zeolite 5A at the PE-g-MA/zeolite ratio of 3.0 and zeolite loading of 3 phr
LP9X3	Composite film with zeolite 13X at the PE-g-MA/zeolite ratio of 3.0 and zeolite loading of 3 phr

4.3 Specimen characterizations

4.3.1 Scanning Electron Microscope (SEM)

Dispersion of zeolite in the LDPE/zeolite composite films was observed by means of scanning electron microscopy (SEM), JEOL/JSM-54TOLV (Japan). Before observing the dispersion of zeolite in LDPE/zeolite composite films, the surface of LDPE/zeolite composite films were coated with gold to obtain conductivity. Both sides of all neat LDPE and LDPE/zeolite composite films were determined.

4.3.2 Differential Scanning Calorimetry (DSC)

Thermal transitions of neat LDPE and LDPE/zeolite composite films were determined by means of differential scanning calorimetry (DSC). All of the composite films were heated from 50 to 180^{o}C at heating rate 10^{o}C/min and then were isothermal treated at 180^{o}C for at least one minute to remove the thermal history of LDPE matrix. After that the composite films were cooled at the same cooling rate of 10^{o}C/min until their temperature approached 50^{o}C. In this process, all composite films were analyzed under nitrogen atmosphere. The values of melting temperature (T_m), crystallization temperature (T_c), and the degree of crystallinity were determined.

4.3.3 Tensile measurement

Tensile tests were performed by using Universal Testing Machine (Instron 5567, NY, USA), which was used to determine Young's modulus, percentage of elongation at break and tensile strength at yield of neat LDPE and LDPE/zeolite composite films according to ASTM D 882. All tested specimens were required in rectangular shape with the width of 10 mm, the length of 130 mm and the thickness of 50±5 μm. In this standard, initial grip separation of 50 mm and rate of grip separation of 500 mm/min were used for LDPE/zeolite composite films whose percentage of elongation at break was greater than 100. On the other hand, initial grip separation of 100 mm and rate of grip separation of 50 mm/min were set for LDPE/zeolite composite films whose percentage of elongation at break was between 20 and 100. Moreover, twenty five tests were repeated for each sample set in order to reduce the deviation and approach the accurate value.

4.3.4 Oxygen permeability analysis

Oxygen permeability analysis of neat LDPE films and LDPE/zeolite composite films had been investigated by using oxygen permeation analyzer; OX-TRAN 2/21, Mocon, USA as shown in figure 4.1. All of composite films were required in circular shape with thickness of 50±5 μm and approximate tested area of 100 cm^2. Four films were repeated for each batch in order to obtain the accurate value. The test film was attached to a diffusion chamber. Oxygen (99.9%), test gas, was introduced into the tested cell at the rate of 40 sccm, chamber temperature of 23^{o}C and atmospheric pressure. Oxygen molecule passed through composite films together with nitrogen, carrier gas, and transported to sensor to detect the amount of oxygen which passed through composite films and displayed in the unit of cc/m^2.day according to ASTM D1434 - 82.

Figure 4.1: Oxygen permeation analyzer; OX-TRAN 2/21, Mocon, USA

4.3.5 Carbon dioxide permeability analysis

Carbon dioxide permeability analysis of neat LDPE films and LDPE/zeolite composite films had been investigated by using carbon dioxide permeation analyzer; PERMATAN-C 4/41, Mocon, USA as shown in figure 4.2. All of composite films were required in circular shape with thickness of 50±5 μm and approximate tested area of 50 cm^2. Four films were repeated for each batch in order to obtain the accurate value. The test film was attached to a diffusion chamber. Carbon dioxide (99.9%), test gas, was introduced into the tested cell at rate of 100 sccm, chamber temperature of 23°C and atmospheric pressure. Carbon dioxide molecule passed through composite films together with nitrogen, carrier gas, and transported to sensor to detect amounts of carbon dioxide which passed through composite films and displayed in the unit of cc/m^2.day according to ASTM D1434 - 82.

Figure 4.2: Carbon dioxide permeation analyzer; PERMATAN-C 4/41, Mocon, USA

4.3.6 Water vapour permeability analysis

Water vapour permeability analysis of neat LDPE films and LDPE/zeolite composite films had been investigated by using water vapor permeation analyzer; Illinois Instruments, Inc., USA. All of composite films were required to be at least 4 inches in diameter with thickness of 50±5 μm. Four films were repeated for each batch in order to obtain the accurate value. The test film was attached to a diffusion chamber. Nitrogen was then introduced into the upper half of the chamber while a moisture-free (99.99% zero grade N_2) carrier gas flow through the lower half. Molecules of water vapor diffusing through the film into the lower chamber were conveyed to the sensor by the carrier gas. The water vapor transmission rate of the test film was displayed as g/m^2/day according to ASTM F1249-01.

4.3.7 Ethylene adsorption

Ethylene adsorption of neat LDPE films and LDPE/zeolite composite films had been investigated. All of composite films were required in rectangular shape with thickness of 50±5 μm and approximate tested area of 50 cm^2. The test film was attached to a large stopper with the approximate tested volume of 700 ml as shown in figure 4.3. Pure ethylene was then introduced into the bottle. Ethylene concentration was investigated immediately after introducing ethylene and every week for 5 weeks by gas chromatography. Ethylene adsorption was recorded from the different between the first and final concentration.

Figure 4.3: The equipment of ethylene adsorption test

4.3.8 Determination of inorganic content

Inorganic content or zeolite in all composite films were determined by placing around 1 gram of sample in crucibles and taking into a furnace at 600°C for 2 hours. The remained ash in each crucible was weighed to determine inorganic content.

4.4 Packing of fresh postharvest produces

Lime and mango fruits that were non-climacteric and climacteric produces, respectively, were chosen to determine the efficiency of composite film to maintain quality and prolong their shelf life. In this study, the physiological and chemical qualities of lime and mango fruits in each type of packaging were investigated compared with unpackaged fruit to determine senescence variation such as color, hardness, and ascorbic acid. The data were recorded every week until they senesced depending on the produce.

4.4.1 Plant material and sample preparation

4.4.1.1 Lime fruits

Limes (cv. Pan) were harvested at Kamphaeng Saen, Nakhon Phatom province. They were transported to the postharvest laboratory, Kasetsart University, Kamphaeng Saen Campus by refrigerated truck for packing and quality test. The lime fruits were sorted to exclude those with obvious defects. They were washed in 200 ppm of chlorinated water before dipped in 250 ppm of prochloraz for 3 minutes and dried at room temperature by a fan, respectively.

4.4.1.2 Mango fruits

Mangoes (cv. Nam Dok Mai See Thong) were harvested at Pongtalong, Nakhon Ratchasima province. They were transported to the postharvest laboratory, Kasetsart University, Kamphaeng Saen Campus by refrigerated truck for packing and quality test. The mango fruits were sorted to exclude those with obvious defects. The fruit peduncles were cut into 0.5 centimeters in length and the latex was dried by placing the cut peduncle on a sacket covered with a piece of cleaned paper for 30 minutes. After that, the appropriate maturity fruits were sorted by submersed in 2%NaCl and 200 ppm of chlorinated water, respectively. The salt-floated fruits which also sink in the chlorinated water were treated 52^{o}C warm water for 5 minutes following with hydrocooled at 3^{o}C for 5 minutes and dipped in 250 ppm of prochloraz for 3 minutes, respectively. The fruits were then dried at room temperature by a fan.

4.4.2 Packaging procedure

The lime and mango fruits were packaged using two different packaging films, neat LDPE and LDPE/zeolite composite films compared with unpackaged fruits. The bags were hermetically sealed and stored at 10±1^{o}C and 88±1% relative humidity for lime fruits and 12±1^{o}C and 88±1% relative humidity for mango fruits. Samples were analyzed every week during storage with four replications until fruit senescence.

4.4.3 Visual observations

The lime and mango fruits were investigated every week for apparent physiological breakdown such as softening, blown spot, and carbon dioxide injury symptom by photograph. The shelf life of each package was determined as the number of days until first signs of deterioration.

4.4.4 Weight loss (%)

Fruit weight was measured at the beginning of storage (day 0) and every week of storage with electric balance (Ohaus Corp., USA) having least count of 0.01 g. Weight loss was determined by dividing the weight change during storage by the original weight.

$$\%\text{Weight loss} = \frac{(W_o - W_f)}{W_o} \times 100 \qquad \text{(a)}$$

where W_o is the weight on the first day and W_f is the weight on the investigated storage day.

4.4.5 The concentration of gases in the packages

The O_2, CO_2, and C_2H_4 concentration in the packages were monitored every week by gas chromatography. The gas chromatograph (model GC-8A, Shimadzu corporation, Japan), as shown in figure 4.4. Gas chromatograph (GC) equipped with a 6 ft × 1/8 inch stainless steel molecular sieve 5A column (80/100) at 70^oC with thermal conductivity detector (TCD) at 150^oC and helium (He) as carrier gas was used to determine O_2 and CO_2 concentration. But GC equipped with a 6 ft × 2 mm glass Porapak Q column (80/100) at 80^oC with TCD at 150^oC and nitrogen (N_2) as carrier gas was used to determine C_2H_4 concentration. 3 ml sample of the package headspace was removed by a syringe. The 1 ml gas sample was injected in the GC system and the data were reported in the unit of percentage for O_2 and CO_2 and ppm for C_2H_4.

Figure 4.4: Gas chromatograph for C_2H_4 (a) and O_2/CO_2 (b) test; GC-8A, Shimadzu, Japan

4.4.6 Colormetric measurement

Fruits color measurement was performed through a color meter (Color meter: CR-400, Konica Minolta Sensing, Inc., Japan), as shown in figure 4.5, in order to evaluate the visual color changes. Colormetric measurement was made on the peel and pulp of mango fruit and on the peel of lime fruit. Two measurements were taken at random locations on the site of each fruit. Color was expressed in the L* (lightness), a* (redness and greenness), b* (yellowness and blueness) mode as recommended by the Commission International de l'Eclairage (CIE). The color meter was calibrated on a standard white tile before each series of measurements.

Figure 4.5: Color meter; Minolta CR-400, Konica Minolta Sensing, Japan

4.4.7 Fruit firmness

Fruit firmness is the best measurement of ripeness. It is defined as the force necessary to break the flesh tissues and it is related to different stages during the ripening process. Lime was determined by the fruit deformation while mango was determined by flesh fruit to evaluate the fruit firmness. The fruit firmness tester (Black&Decker) was shown in figure 4.6, with a 2-mm-diameter, 5-mm-diameter and 11-mm-diameter cylindrical probe which was used depend on fruit ripeness. The probe was pressed vertically against the surface of fruit samples. Two measurements were taken at random locations on the site of each fruit sample. The point of measurement should be flat without defects on the pulp. The firmness was expressed as kilogram so it should be multiply with 9.81 into the unit of newton (N).

Figure 4.6: Fruit firmness tester; Black&Decker, and prove with various sizes

4.4.8 Total Soluble Solids (TSS) content and Titratable Acidity (TA) [60]

Total soluble solids (TSS) content also contributes to fruit quality imparting sensory attributes. It was determined by squeezing a few drops of juice on a refractometer (ATAGO, Japan) and the quantity of TSS was expressed in ^{o}Brix. Titratable acidity was determined by titrating of 5 mL of fruit juice with 0.1 M NaOH and the volume of NaOH would be calculated to obtain the percentage of titratable acidity as shown below

$$\%\mathrm{TA} = \frac{\mathrm{mL\,of\,NaOH} \times \mathrm{N\,of\,NaOH} \times \mathrm{meq.wt.of\,citric\,acid}}{\mathrm{mL\,of\,sample}} \times 100 \qquad \text{(a)}$$

where meq. wt. of citric acid of lime and mango fruit is 0.06404. Since the sweetness and sourness of fruits are important criteria for flavor, the ratio of TSS to TA should be also considered.

4.4.9 Vitamin C contents [60]

Vitamin C contents were determined by titration fruit juice with indophenol solution. The 2 mL of fruit juice was added into Erlenmeyer flask containing 5 mL of oxalic acid - acetic acid and then immediately titrated with indophenol solution until the color of solution changed to pink for at least 5 seconds. Ascorbic acid saturated solution was used as a standard solution. Ascorbic acid content would be calculated as shown below

$$\frac{\text{mg ascorbic acid}}{\text{mL}} = \text{mL of indophemol solution} \times \text{mg eq. ascorbic acid} \times \text{mL of sample} \tag{b}$$

where mg eq. ascorbic acid is was calculated from indophenol solution used for ascorbic acid saturated solution.

4.4.10 Ripen - mango fruits

To confirm the quality of the mango fruit, all mangoes after being kept for each week were ripen with aqueous solution containing 0.1% of Tween and 500 ppm of ethephon. The fruits were immersed in this aqueous solution and were then allowed to dry and stored at room temperature until ripening. After that the ripen-fruits were tested fruit firmness, color change, TSS, TA, and Vitamin C contents accompanied with sensory evaluation.

4.4.11 Sensory evaluation

Sensory quality of ripen-mangoes was evaluated by four assessors. Off-odor was evaluated immediately after opening the packages. Packaged and unpackaged fruits were evaluated visual quality, aroma, flavor, taste, texture, and discoloration. They were scored on a six point scale (0 – 5) as shown in appendix D and each sample was assessed two times.

CHAPTER V

RESULTS AND DISCUSSION

Experimental results were divided into four sections. First of all, the zeolite characterization was presented, followed by the discussion of the zeolite dispersion and thermal properties of the LDPE/zeolite composite films. Then, the effect of the PE-g-MA/zeolite ratio, zeolite loading, and zeolite type on mechanical properties and gas permeability of LDPE/zeolite composite films was described. The results obtained from the composite films were compared to data measured on neat LDPE films. Finally, the LDPE/zeolite composite film which had the optimal properties was used as packaging for lime and mango and their quality were discussed.

5.1 Zeolite characterization

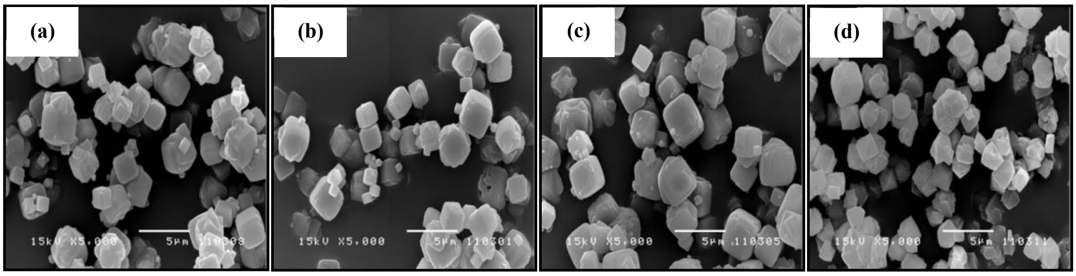

Figure 5.1: SEM micrographs of 4A zeolite (a), T zeolite (b), 5A zeolite (c), and 13X zeolite (d)

Generally, zeolites used in this study had cubic shape except 13X powder as can be seen in figure 5.1. All of them had various sizes and were agglomerated with approximately 5 micrometers because of interaction between polar particles. The specific surface area of the zeolites was determined by nitrogen adsorption (BET method), that was, 3.95, 6.64, 481.03, and 602.51 m^2/g for 4A, T, 5A, and 13X zeolite, respectively.

5.2 Zeolite dispersion in LDPE/zeolite composite films

As mentioned earlier, maleic anhydride grafted polyethylene (PE-g-MA) was used to aid the dispersion of zeolite particles in the LDPE matrix. Figure 5.2 showed representative SEM images for LDPE/zeolite composite films with various ratios of PE-g-MA/zeolite at fixed zeolite content of 3 phr. The agglomeration of zeolite particles was clearly shown for low PE-g-MA/zeolite ratio on both sides of composite films. Better dispersion and distribution of zeolite was obtained as the ratio of PE-g-MA/zeolite increased, especially at PE-g-MA/zeolite ratios of 3.0 and 4.0, although some agglomerates still existed. The SEM micrographs of all LDPE/zeolite composite films with various zeolite contents at fixed PE-g-MA/zeolite ratio of 3.0 were shown in figure 5.3. All SEM micrographs showed good dispersion and distribution of particle in LDPE matrix. As the zeolite contents increased, the denser of filler population was observed. When types of zeolite were varied at the fixed PE-g-MA/zeolite ratio of 3.0 and zeolite contents of 3 phr, all composite films had similar dispersion and distribution as shown in figure 5.4. These results demonstrated that adding PE-g-MA provided good particle dispersion if the proper amounts were used. In addition, good interfacial adhesion of the composites could be obtained as shown in figure 5.5. The cavities between zeolite particle and LDPE matrix were almost absence.

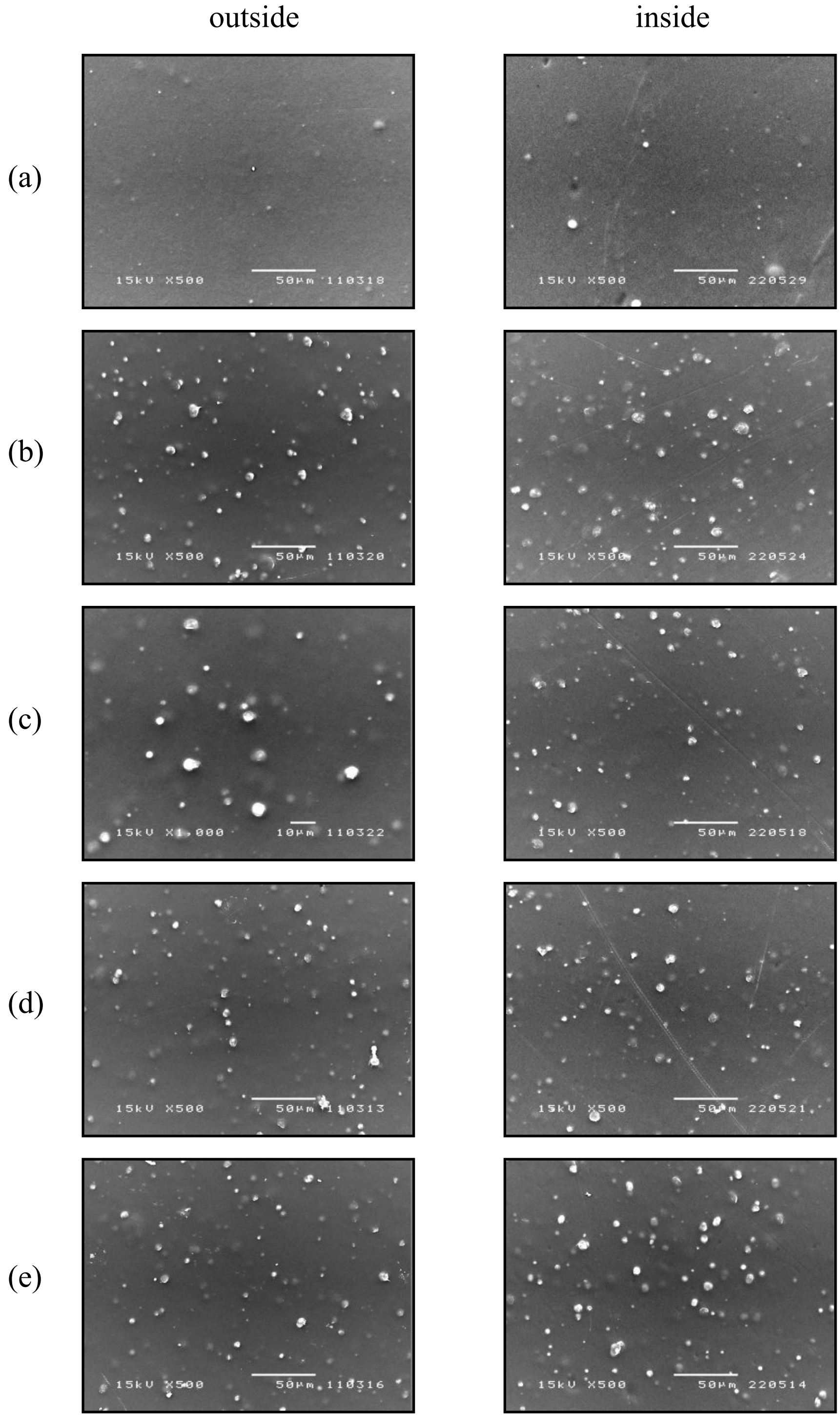

Figure 5.2: SEM micrographs of both sides of LDPE/zeolite composite films at the PE-g-MA/zeolite ratio of 0 (a), 1.0 (b), 2.0 (c), 3.0 (d), and 4.0 (e) at fixed zeolite content of 3 phr

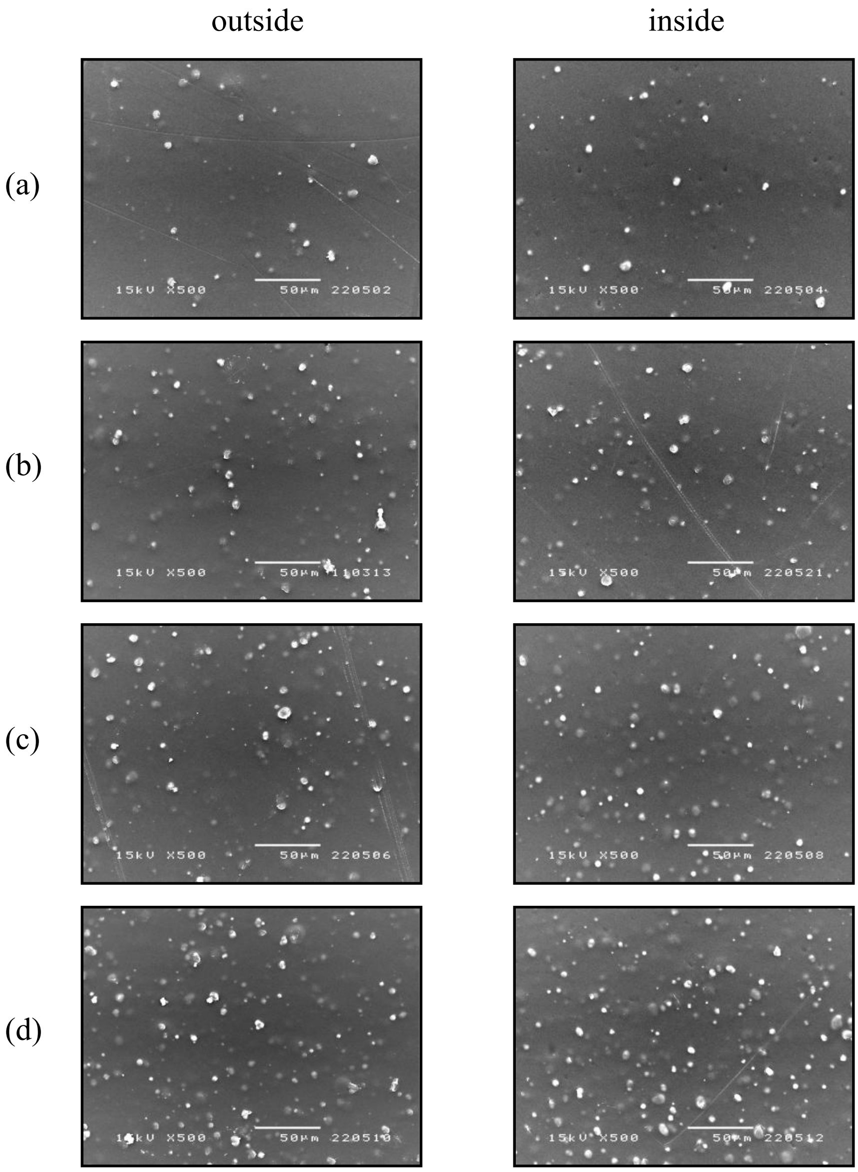

Figure 5.3: SEM micrographs of both sides of LDPE/zeolite composite films with various zeolite contents; 1 phr (a), 3 phr (b), 5 phr (c), and 7 phr (d) at fixed PE-g-MA/zeolite ratio of 3.0

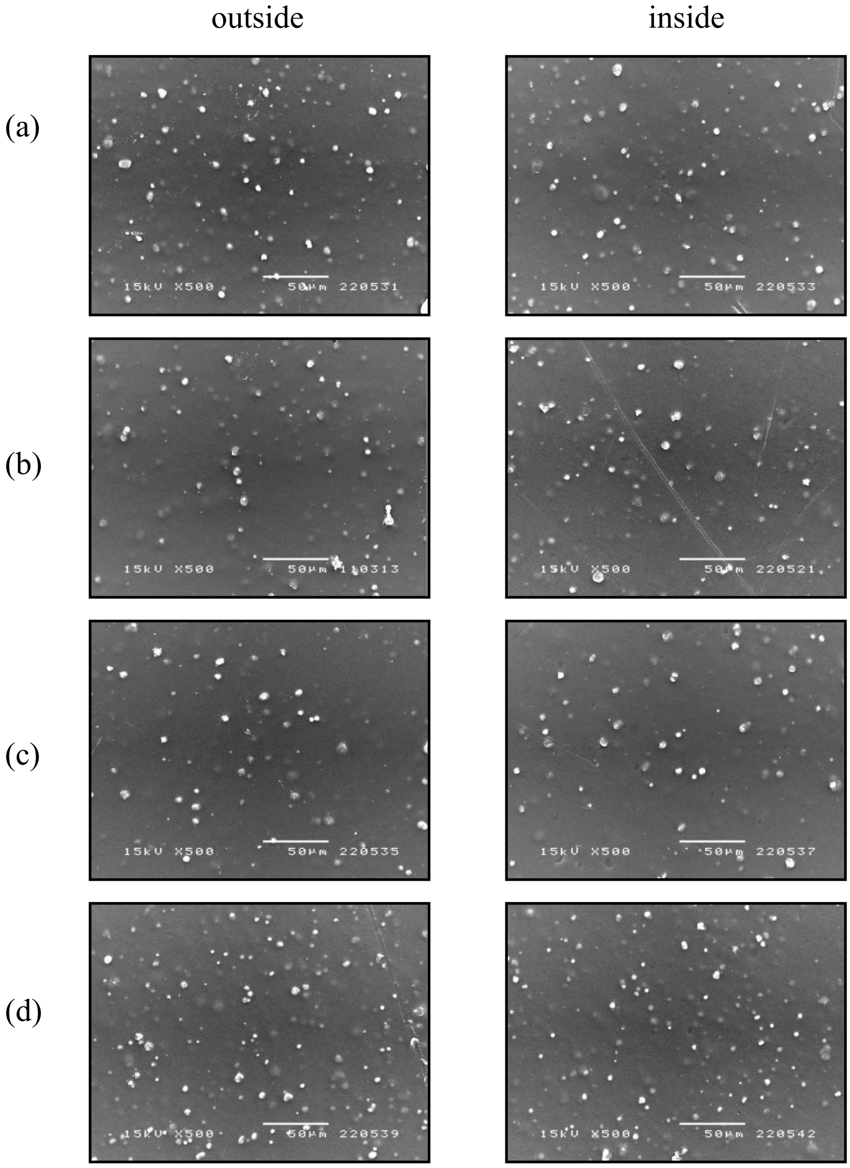

Figure 5.4: SEM micrographs of both sides of LDPE/zeolite composite films with various zeolite types; T zeolite (a), 4A zeolite (b), 5A zeolite (c), and 13X zeolite at fixed PE-g-MA/zeolite ratio of 3.0 and zeolite content of 3 phr

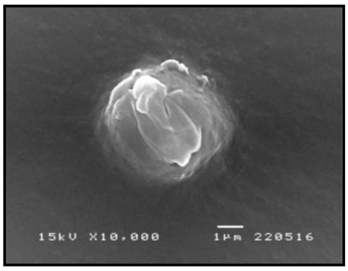

Figure 5.5: SEM micrographs of interfacial area of the composite films

5.3 Thermal properties of LDPE/zeolite composite films

To investigate the effect of PE-g-MA/zeolite ratio, zeolite contents and zeolite types on crystalline form in the polymer matrix, the specimens were heated at 10°C/min in the temperature range of 50 – 180°C and then were cooled at 10°C/min until their temperature approached 50°C by using a differential scanning calorimeter. Differential scanning calorimetry (DSC) was principally used to obtain quantitative evaluation of the thermal behavior of specimens and to estimate the degree of crystallinity in the samples as shown in Table F.1 (appendix F).

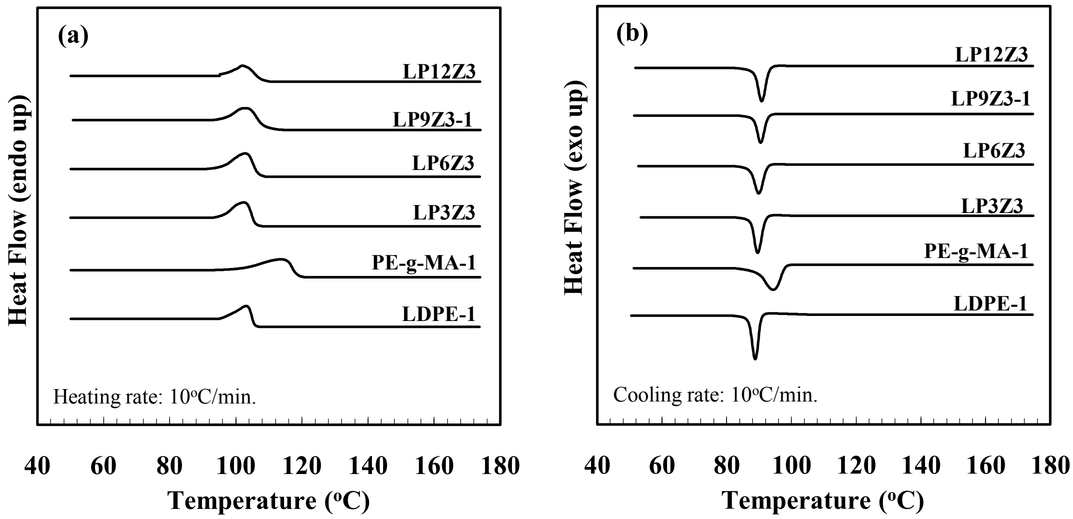

Figure 5.6: DSC heating curves (a) and DSC cooling curves (b) of neat LDPE and LDPE/zeolite composite films with various PE-g-MA/zeolite ratios at fixed zeolite loading of 3 phr

Figure 5.6 showed the effect of PE-g-MA/zeolite ratio on the thermal properties of composite film. Neat LDPE film (LDPE-1) and PE-g-MA showed melting peak at 103.19°C and 113.97°C, respectively, as can be seen in figure 5.6. After mixing LDPE with various PE-g-MA/zeolite ratios at fixed zeolite content, all composite films still exhibited one melting peak and the melting temperature (T_m) of composite films slightly decreased compared with that of neat LDPE. In addition, the area under DSC heating peak decreased with increasing the PE-g-MA/zeolite ratio indicated that the use of enthalpy to melt crystalline phase of polymer decreased. The degree of crystallinity of composite films can be identified by determining area under

DSC heating peak of sample. Therefore, the samples with higher PE-g-MA/zeolite ratio showed lower crystallinity. After heating to 180°C, all composite films were then cooled at 10°C/min. An exothermic crystallization peak of neat LDPE (LDPE-1) exhibited one crystallization temperature (T_c) at 88.91°C. Interestingly, the use of higher PE-g-MA/zeolite ratio would shift T_c to the higher values, which was consistent with the work of Mirzadeh, A., et al [29]. However, the PE-g-MA/zeolite ratio in this range seemed to be relatively intensive to T_m and T_c values.

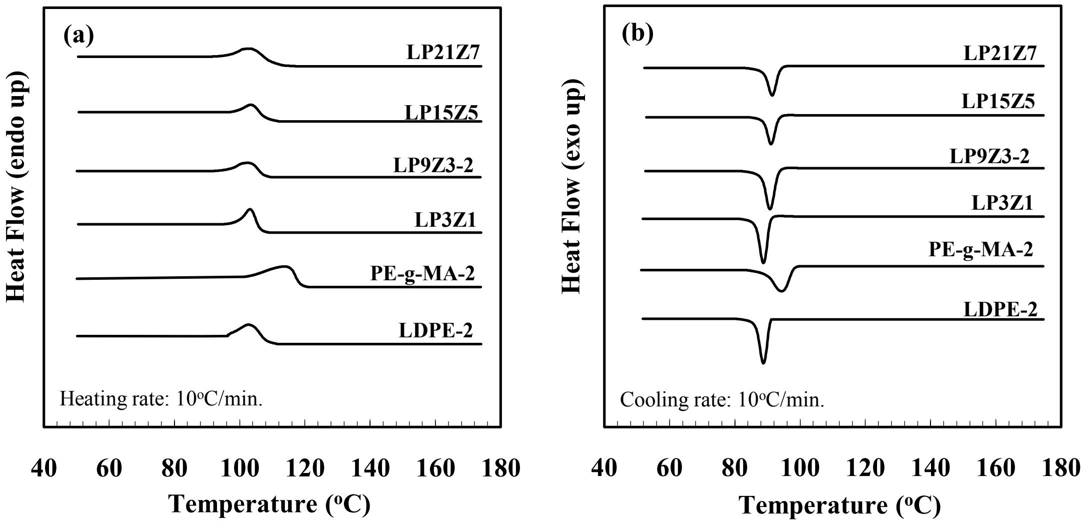

Figure 5.7: DSC heating curves (a) and DSC cooling curves (b) of neat LDPE and LDPE/zeolite composite films with various zeolite loading at fixed PE-g-MA/zeolite ratio of 3.0

The effect of zeolite loading on thermal properties of LDPE/zeolite composite films at fixed PE-g-MA/zeolite ratio of 3.0 was shown in figure 5.7. The composite films including neat LDPE film (LDPE-2) were extruded at higher temperature than those in previous part because of higher viscosity of composite film with high zeolite loading. All films exhibited one melting peak in which T_m value of composite films was less than that of neat LDPE film (LDPE-2). T_m of all LDPE/zeolite composite films was almost the same. Moreover, the addition of zeolite into LDPE matrix did not hinder or enhance the formation of crystalline phase of LDPE [43]. This idea was supported by the observed degree of crystallinity of composite films. Although LP9Z3-1 and LP9Z3-2 had the same formula with different condition of blown film extrusion made them had exhibited different thermal properties. LP9Z3-2 showed lower degree of crystallinity than LP9Z3-1. It could be explained by the effect of draw-down ratio (DDR) and process temperature. The higher DDR, used in the film production of LP9Z3-1, made more limitation in the mobility of polymeric chains. Moreover, the faster cooling process made it also showed higher degree of crystallinity.

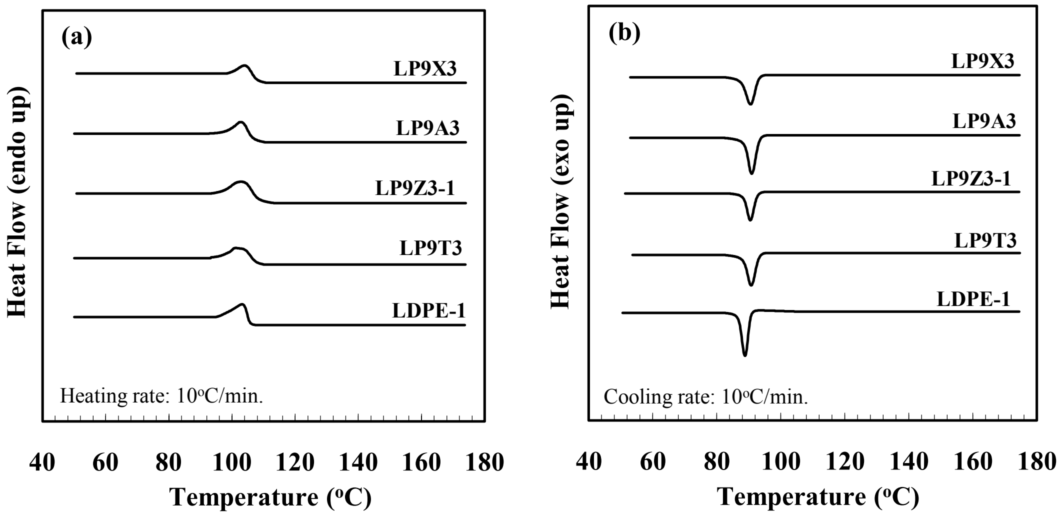

Figure 5.8: DSC heating curves (a) and DSC cooling curves (b) of neat LDPE and LDPE/zeolite composite films with various zeolite types at fixed PE-g-MA/zeolite ratio of 3.0 and zeolite loading of 3 phr

In the final part of thermal experiment, various types of zeolite were used. Zeolite T and 4A are structurally identical and contain the monovalent Na^+ ion while zeolite 5A contains the divalent Ca^{2+} ions. In addition, surface treatment was achieved in zeolite T. Actually, zeolite T, 4A, and 5A are the same type, that is zeolite A but they are different in pore size. Zeolite 13X contain monovalent Na^+ ion and has larger pore size than other. All films were formed at the same temperature as in part I and the effect of zeolite types on thermal properties of the composite film were shown in figure 5.8. T_m and T_c of composite film with zeolite T, 4A, and 5A were almost the same but were different from those with zeolite 13X especially T_m value. T_m of composite film with zeolite 13X was higher than that of neat LDPE. It demonstrated that the composite film with the same type of zeolite had the same thermal properties.

5.4 Effect of PE-g-MA/zeolite ratio on the mechanical and gas permeability properties of LDPE/zeolite composite films

Mechanical properties of composite films

In this study, tensile strength at yield, Young's modulus or E-modulus, and elongation at break of composite films in both directions, i.e. machine (MD) and transverse (TD) direction, were determined. Tensile strength at yield was used to identify maximum stress which materials began to deform. Young's modulus was used to indicate the stiffness of materials which was determined from the first linear slope of stress – strain curve. In addition, elongation at break was also defined as strain at the specimen began to deform permanently.

The mechanical properties of films were shown in figures 5.9. Figure 5.9 (a) exhibited how the tensile strength at yield varied with the ratio of PE-g-MA/zeolite at fixed zeolite content of 3 phr. Tensile strength at yield increased as the ratio increased in both MD and TD. Generally, the tensile strength reflects the nature of the interface between polymer and filler [61, 62]. As more PE-g-MA was added in the composite, better zeolite dispersion was achieved as mentioned above. This increases the interfacial adhesion between polymer and filler, resulting in an increase of the tensile strength at yield. However, when the PE-g-MA/zeolite ratio reached the optimal value at 3 phr, further adding PE-g-MA in the composite resulted in the decrease in tensile strength at yield. This could be due to the excess of PE-g-MA where mechanical properties are lower than the LDPE matrix. The chain scission would also occur due to the presence of PE-g-MA which could also reduce the mechanical properties of composite films [63].

Not only tensile strength at yield, but Young's modulus also increased as the PE-g-MA/zeolite ratio increased as can be seen in figure 5.9 (b). As known, PE-g-MA was needed to achieve better dispersion of zeolite in LDPE matrix and, as a consequence, improved stiffness of composite films [61]. It was a result from the presence of maleic anhydride in material. PE-g-MA had the lower mechanical properties than LDPE because of its lower molecular weight material [62, 64].

Moreover, the presence of zeolite also increased the stiffness of all composite films. As mentioned above, the dispersion of zeolite particles in composite films containing PE-g-MA/zeolite ratios of 3.0 and 4.0 were much enhanced compared to compositions based on other ratios. Generally, the Young's modulus enhancement of composite films in both directions, MD and TD, were in the same trend. In addition, Young's modulus in MD was generally almost the same value as that in TD. It was due to similar polymer chain orientation and zeolite dispersion in both directions that polymer chain orientation in MD and TD was obtained from the velocity of film winding and an expansion of the bubble, respectively. However, Young's modulus seemed relatively insensitive to the PE-g-MA/zeolite ratio in this range.

The elongation at break of LDPE/zeolite composite films at various ratios of PE-g-MA to zeolite was shown in figure 5.9 (c). The elongation at break slightly decreased as the PE-g-MA/zeolite ratio increased. It was clear that the presence of PE-g-MA accelerated the decrease in the elongation at break compared with neat LDPE. As results, mechanical properties could be reduced when composites had excess low molecular weight chains. In addition to the previous results, the decrease in degree of crystallinity of polymer, as mentioned above, dropped in mechanical properties in blending LDPE and PE-g-MA but the presence of filler in composites developed mechanical properties.

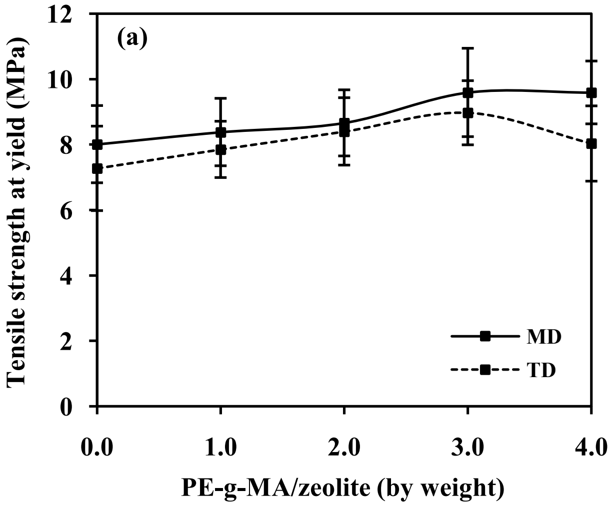

Figure 5.9: Effect of the PE-g-MA/zeolite ratio on tensile strength at yield (a), Young's modulus (b), and elongation at break (c) of LDPE/zeolite composite films at fixed zeolite content of 3 phr

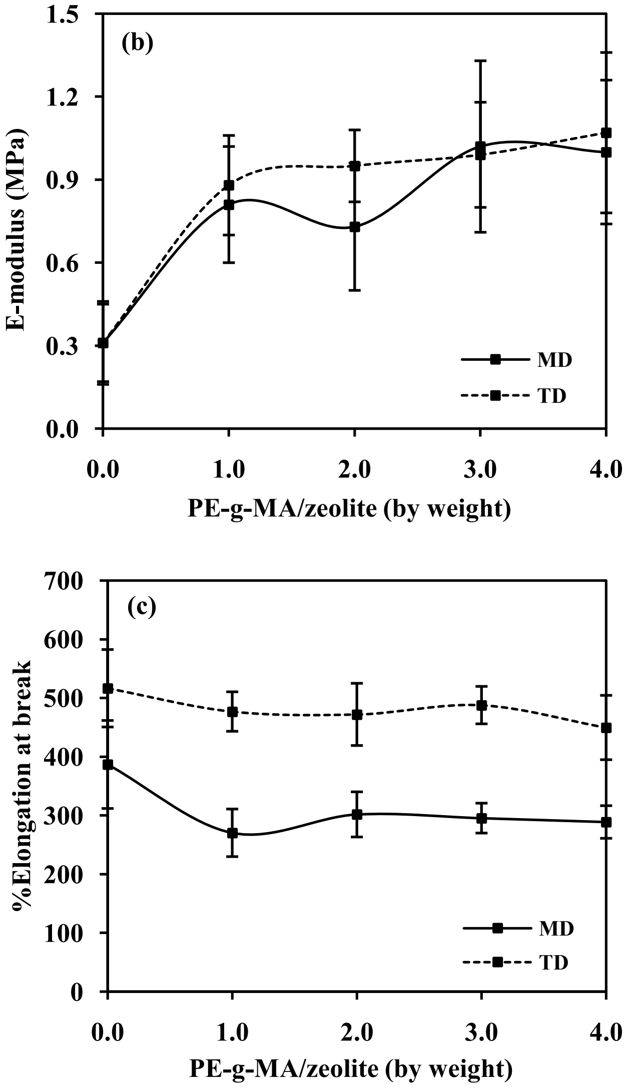

Figure 5.9 (cont'): Effect of the PE-g-MA/zeolite ratio on tensile strength at yield (a), Young's modulus (b), and elongation at break (c) of LDPE/zeolite composite films at fixed zeolite content of 3 phr

Gas permeability of composite films

There are four possible ways for gas permeation through composite films. That was, gas could be permeated through amorphous part of polymer, the interfacial voids between polymer and filler, porous filler, and other voids [65]. As mentioned above, the degree of crystallinity decreased as the PE-g-MA/zeolite ratio increased. This result indicated that the composite film with higher PE-g-MA/zeolite ratio had more amorphous phase and then gas should be more permeated through this composite film.

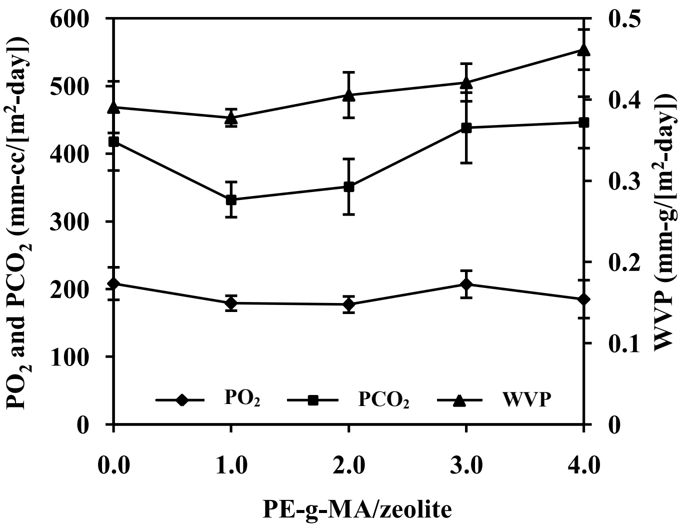

Figure 5.10: Effect of the PE-g-MA/zeolite ratio on gas permeability of LDPE/zeolite composite films at fixed zeolite content of 3 phr

Figure 5.10 showed gas permeability, i.e. oxygen, carbon dioxide, and water vapour, of LDPE/zeolite composite films with various PE-g-MA/zeolite ratios at fixed zeolite content of 3 phr. Similar trends were found for permeability of all gases. Interestingly, permeability of all gases slightly decreased at the ratio of 1.0 and slightly increased at the ratio of 2.0 until 4.0 except oxygen permeability at the ratio of 4.0 slightly decreased. Moreover, the permeability of all gases of composite films at the ratio of 1.0 and 2.0 were less than those of neat LDPE. It was due to the effect of the partial pore blockage of zeolites induced by polymer affected gas permeability; therefore, gas permeability would decrease. In addition, agglomeration of zeolites or poor zeolite dispersion, which was also the cause of this problem, made them less efficiency. It was supported by SEM results as mentioned above. Furthermore, the presence of PE-g-MA helped reduce the interface voids between polymer and filler and resulted in a decrease in gas permeability.

Ethylene adsorption of composite film

Figure 5.11 showed ethylene adsorption of LDPE/zeolite composite films with various PE-g-MA/zeolite ratios at fixed zeolite content of 3 phr. The results revealed the value of ethylene adsorption of LDPE/zeolite composite films were around four times more than that of neat LDPE film. It indicated that the addition of zeolite resulted in an increase of ethylene adsorption in composite films. In addition, ethylene adsorption of composite films increased as PE-g-MA increased. PE-g-MA had low molecular weight and caused chain scission of LDPE. If the use of PE-g-MA increased, short LDPE chains would be increased which caused less partial pore blockage of zeolite [26] resulted in an increase in efficiency of permeability and adsorption of zeolite. As a result, ethylene adsorption of composite films increased.

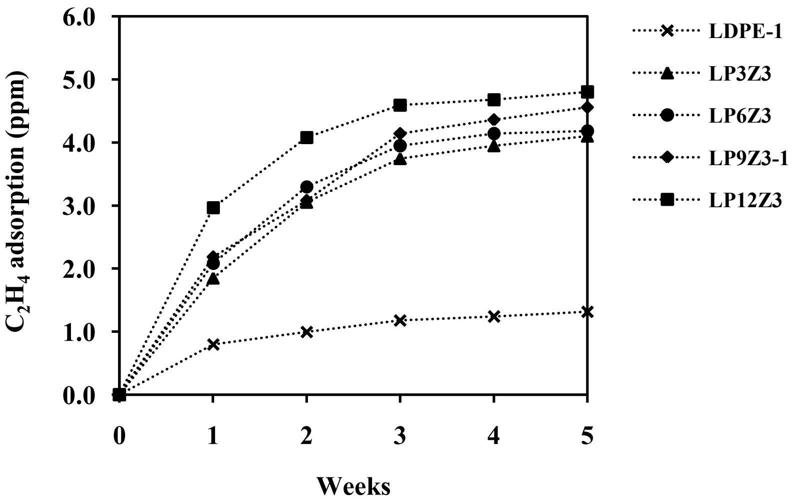

Figure 5.11: Effect of the PE-g-MA/zeolite ratio on ethylene adsorption of LDPE/zeolite composite films at fixed zeolite content of 3 phr

From the overall results in this section, the composite films with PE-g-MA/zeolite ratio of 3.0 showed the optimal mechanical properties and gas permeability. Therefore, in the next part the effect of zeolite loading with this fixed PE-g-MA/zeolite ratio was presented. Although the composite films with a PE-g-MA/zeolite ratio of 4.0 showed generally the same properties, it exhibited lower elongation at break in TD than those with a PE-g-MA/zeolite ratio of 3.0 and lower oxygen permeability than that of neat LDPE films.

5.5 Effect of zeolite loading on the mechanical and gas permeability properties of LDPE/zeolite composite films

Mechanical properties of composite films

The mechanical properties of LDPE composite film at fixed PE-g-MA/zeolite ratio of 3.0 were shown in figures 5.12. The tensile strength at yield of LDPE/zeolite composite films was shown in figure 5.12 (a) as a function of the filler loading. The tensile strength at yield of the composite films was slightly increased with increasing zeolite contents until 3 phr. Tensile strength at yield of 3 phr of zeolite in composite was 19.29% and 17.67% higher than that of neat LDPE in MD and TD, respectively. When zeolite content was over 3 phr, the tensile strength at yield of the composite films decreased in both MD and TD.

Interestingly, Young's modulus of LDPE/zeolite composite films showed obviously the peak at zeolite content of 3 phr as seen in figure 5.12 (b). This was caused by the presence of compatibilizer. The PE-g-MA amount was higher as the zeolite content increased, a softening of the film could be thus observed with an increasing the amount of PE-g-MA. Young's modulus of composite films was thus the result of a competition between the stiffening effect of a better dispersion of zeolite particle in LDPE matrix and the softening effect of the compatibilizer [35]. Young's modulus of composite with zeolite contents less than 3 phr increased with increasing zeolite contents and that represented the balance between stiffening and softening effects. On the other hand, for those composite films filled with over 3 phr of zeolite, the PE-g-MA amounts in the matrix was greater thus the softening effect would seem to be prevalent, leading to weaker modulus.

However, elongation at break of composite films decreased in both MD and TD when increasing zeolite content as shown in figure 5.12 (c). For elongation at break in MD, it fell from 408.06% for neat LDPE to 312.30% elongation in the case of 1 phr of zeolite content, decreasing by 23.47%. There was slightly drop until 7 phr of zeolite contents. In addition, there was a slight decrease by 0.82% in TD between neat LDPE and the case of 1 phr of zeolite content. There was a continuous decrement by 45.29% between neat LDPE and in the case of 7 phr of zeolite contents. In general, elongation of composite decreased due to increasing the amount of zeolite contents.

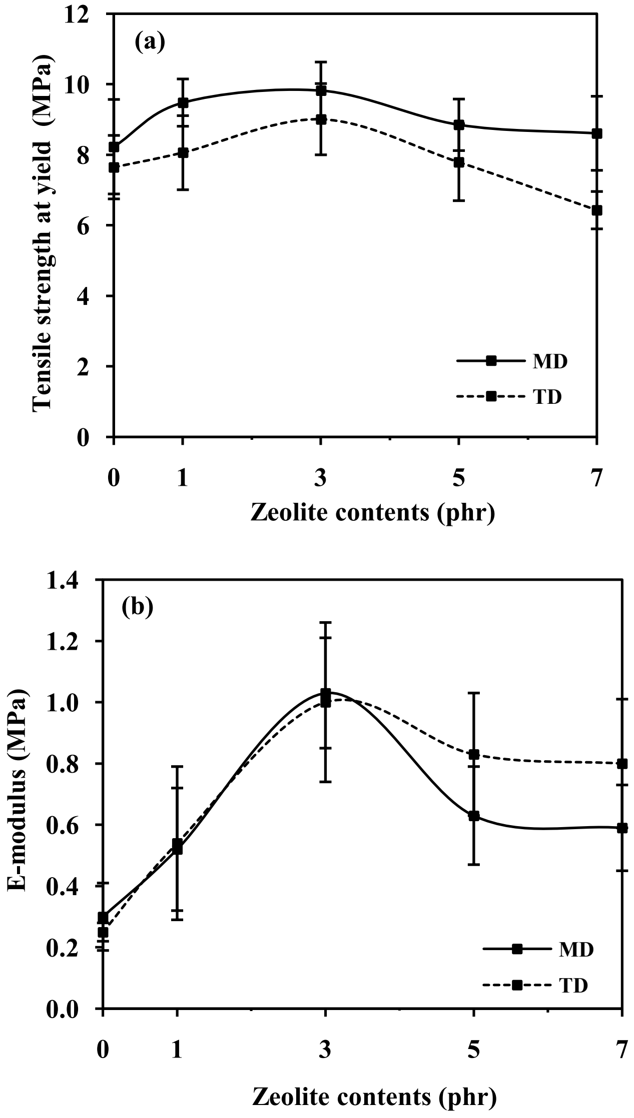

Figure 5.12: Effect of zeolite contents on tensile strength at yield (a), Young's modulus (b), and elongation at break (c) of LDPE/zeolite composite films at fixed PE-g-MA/zeolite ratio of 3.0

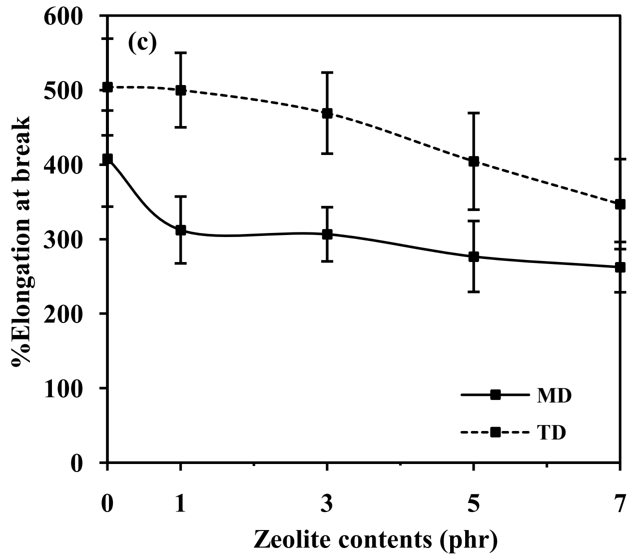

Figure 5.12 (cont'): Effect of zeolite contents on tensile strength at yield (a), Young's modulus (b), and elongation at break (c) of LDPE/zeolite composite films at fixed PE-g-MA/zeolite ratio of 3.0

Gas permeability of composite films

Figure 5.13 showed gas permeability, i.e. oxygen, carbon dioxide, and water vapour, of LDPE/zeolite composite films with various zeolite contents at fixed PE-g-MA/zeolite ratio of 3.0. Water vapor permeability of composite film increased, from 0.42 to 0.52 mm-g/[m^2-day], between 0 phr zeolite (neat LDPE) and 7 phr zeolite composite film, which is an increase by 24.45% when compared with that of neat LDPE. However, their carbon dioxide and oxygen permeability remained steady in the case of 1 phr of zeolite content in LDPE/zeolite composite films. There was then a gradual drop for composite with 3 phr of zeolite contents, decreasing by 7.07%, and then it increased until 7 phr of zeolite contents for carbon dioxide permeability, increasing by 4.46%. For oxygen permeability, there was slightly decreased by 10.70%; from 231.25 mm-cc/[m^2-day] for neat LDPE to 206.50 mm-cc/[m^2-day] for 5 phr of zeolite in LDPE/zeolite composite films and then it increased to 241.25 mm-cc/[m^2-day] in 7 phr of zeolite contents. These results showed a decrease then an increase with increasing zeolite contents because of the effect of the inhibition of polymer chain mobility near the polymer-zeolite interface and the partial pore blockage of zeolites induced by polymer [26]. A part of zeolite pores may be narrowed, thus leading to a permeability decrease in LDPE/zeolite composite film. When zeolite content reached 7 phr, the positive effect of using high zeolite contents lead to a permeability increase in LDPE/zeolite composite film. It was demonstrated that zeolite contents used in this research was too small amount, thus gas permeability of zeolite in composite films was not so obvious. It was due to those two mentioned effects. Furthermore, the molecular polarity, size, and shape of tested gases may still play an important role to the adsorption on zeolite. Water vapour had more molecular polarity and smaller molecular size than other gases, thus the result of water vapour permeability of LDPE/zeolite composite films could be seen obviously. However, oxygen and carbon dioxide permeability showed insignificant differences.

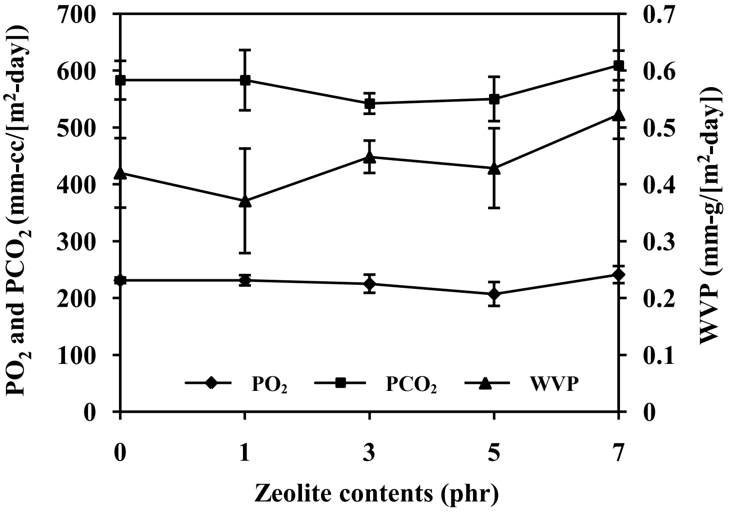

Figure 5.13: Effect of zeolite contents on gas permeability of LDPE/zeolite composite films at fixed PE-g-MA/zeolite ratio of 3.0

Ethylene adsorption of composite film

Effect of zeolite contents on ethylene adsorption of LDPE/zeolite composite films at fixed PE-g-MA/zeolite ratio of 3 was shown in figure 5.14. Ethylene adsorption increased as zeolite contents increased. However, ethylene adsorption of composite films with zeolite contents of 7 phr was less than those with zeolite contents of 3 and 5 phr. It may be due to excess zeolite in the polymer matrix which caused agglomeration of particles. The adsorption of zeolites was thus decreased.

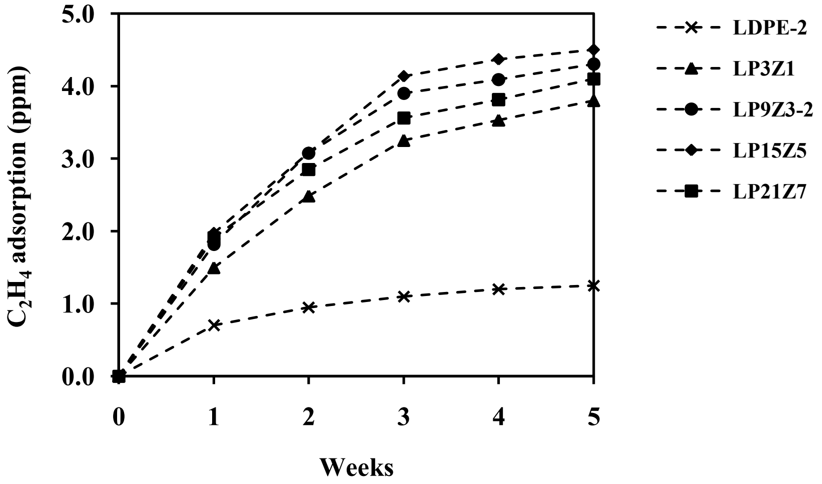

Figure 5.14: Effect of zeolite contents on ethylene adsorption of LDPE/zeolite composite films at fixed PE-g-MA/zeolite ratio of 3.0

From the overall results in this section, the composite films with zeolite content of 3 phr and the PE-g-MA/zeolite ratio of 3.0 was chosen to determine the effect of zeolite type on the properties of composite film in the next part. It was due to the composite films with zeolite content of 3 phr showed the best tensile strength and E-modulus values. Although oxygen and water vapour permeability of this film was not the best results, its result was still satisfied. In addition, gas permeability of the composite film with zeolite content of 3 phr was better than those with zeolite content of 5 phr and mechanical properties of the composite film with zeolite content of 3 phr was better than those with zeolite content of 7 phr.

5.6 Effect of zeolite type on the mechanical properties and gas permeability of LDPE/zeolite composite films

Mechanical properties of composite films

The mechanical properties of LDPE/zeolite composite films with various zeolite types at fixed PE-g-MA/zeolite ratio of 3.0 and zeolite loading of 3 phr were shown in figures 5.15. The tensile strength at yield was shown in figure 5.15 (a). The tensile strength of all composite films was higher than that of neat LDPE film and was almost the same value except that of the film with zeolite 4A in MD. The tensile strength in MD of film with zeolite 4A was 18.55% lower than that of other composite films. For the tensile strength at yield in TD, neat LDPE film, composite film with zeolite 5A and 13X exhibited approximately the same value. In addition, composite film with zeolite 4A showed the highest value of tensile strength in TD which was 23.40% higher than neat LDPE film.

Young's modulus of LDPE/zeolite composite films showed better value than that of neat LDPE film in both MD and TD as shown in figure 5.15 (b). Young's modulus of LDPE/zeolite composite film with zeolite 4A showed the best value in TD which was 223.71% higher than that of neat LDPE film. However, the value of Young's modulus of all LDPE/zeolite composite films was around the same in MD which was around 3 times higher than that of neat LDPE film.

The effect of zeolite type on the elongation at break of LDPE/zeolite composite films at fixed PE-g-MA/zeolite ratio of 3.0 and zeolite loading of 3 phr was showed in figure 5.15 (c). The elongation at break in TD of all composite films showed slightly lower than that of neat LDPE film, decreasing around 5.55% to 17.91%. For MD, the elongation at break of all composite films was the same value and lower than that of neat LDPE film around one fourth. As mentioned above, adding particle lead to lower elongation of film. In addition, zeolite 13X showed different shape from zeolite 4A, T and 5A, which was cubic shape, resulting in a decrease in elongation. From the mechanical properties results, various zeolites used in this study gave the same value of mechanical properties of composite film due to the same size and shape for zeolite 4A, T, and 5A except zeolite 13X.

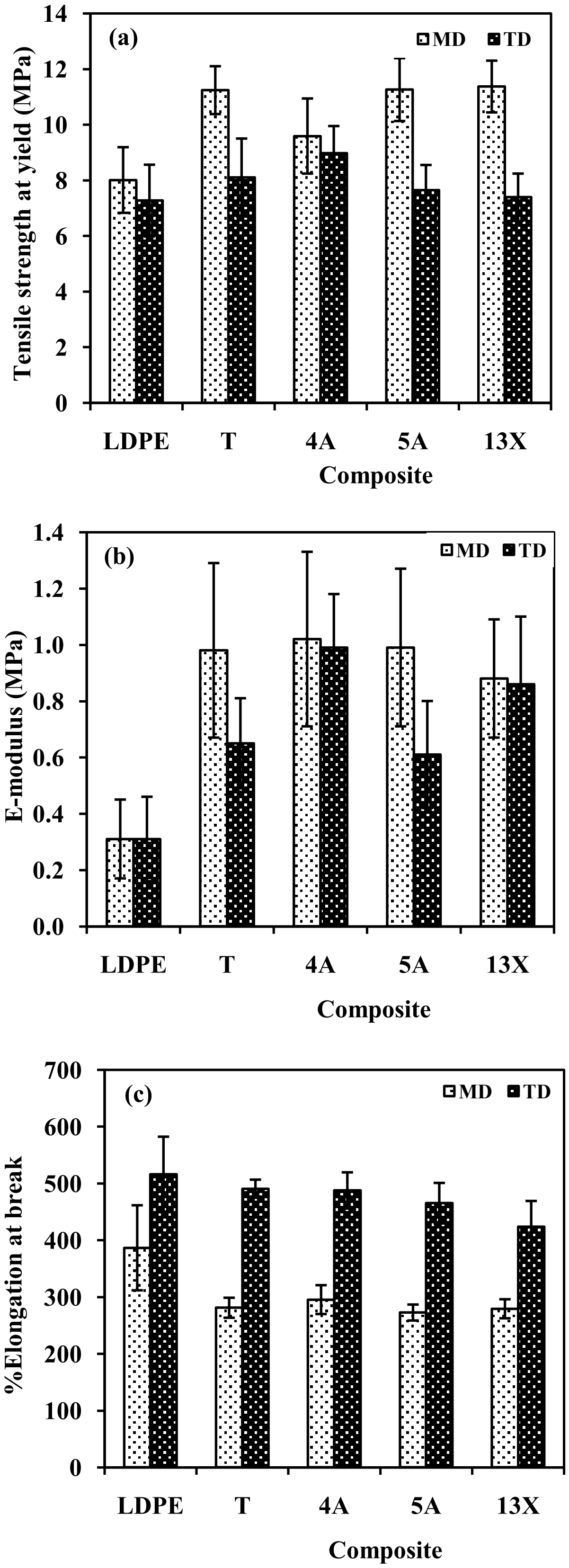

Figure 5.15: Effect of zeolite type on tensile strength at yield (a), Young's modulus (b), and elongation at break (c) of LDPE/zeolite composite films at fixed PE-g-MA/zeolite ratio of 3.0 and zeolite loading of 3 phr

Gas permeability of composite films

Figure 5.16 showed gas permeability, i.e. oxygen, carbon dioxide, and water vapour, of LDPE/zeolite composite films with various zeolite types at fixed PE-g-MA/zeolite ratio of 3.0 and zeolite loading of 3 phr. All gas permeability of the composite film was higher than those of neat LDPE film because the crystalline phase of the composite film was lower than that of neat LDPE film and the porous structure of zeolite in the films. Oxygen permeability of composite film with zeolite T showed the highest value at 258.50 mm-cc/[m^2-day], then that with zeolite 5A, 13X, and 4A were with 237.00, 227.50, and 207.75 mm-cc/[m^2-day], respectively. In addition, carbon dioxide permeability of composite film with zeolite 5A showed the highest value at 622.25 mm-cc/[m^2-day], then that with zeolite T, 13X, and 4A were lower, respectively. However, water vapour of the composite film was the same. From the results, it was demonstrated that the composite with zeolite T and 5A showed the better permeability than other films. It was due to the pore size of zeolite 5A was larger than tested gases and larger than those of zeolite T and 4A. In addition, zeolite T, which was low polarity from surface treatment, had good interaction with low polarity substance such as O_2. Although the pore size of zeolite 13X was the largest, gas permeability of this composite film did not show the best value. It may be due to more polarity of zeolite 13X. Highly polar zeolites had strong interaction with polar substances. In addtion, the effect of the partial pore blockage of zeolites affected the efficiency of gas permeability. However, the strong interaction also inhibited the diffusive movement of permeating molecules. Thus, there was a trade-off between strong adsorption and fast diffusion [66]. Interestingly, the composite film with zeolite T and 4A showed the different gas permeability although it was the same zeolite type. It was demonstrated that the surface treatment of zeolite T affected gas permeability.

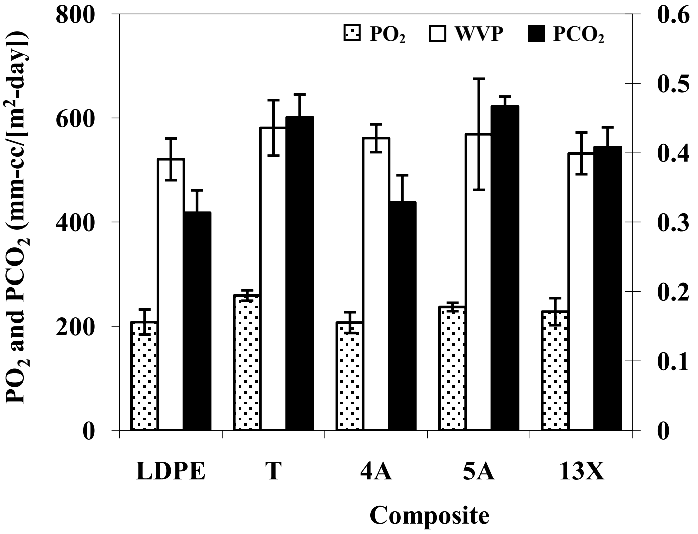

Figure 5.16: Effect of zeolite type on gas permeability of LDPE/zeolite composite films at fixed PE-g-MA/zeolite ratio of 3.0 and zeolite loading of 3 phr

Ethylene adsorption of composite films

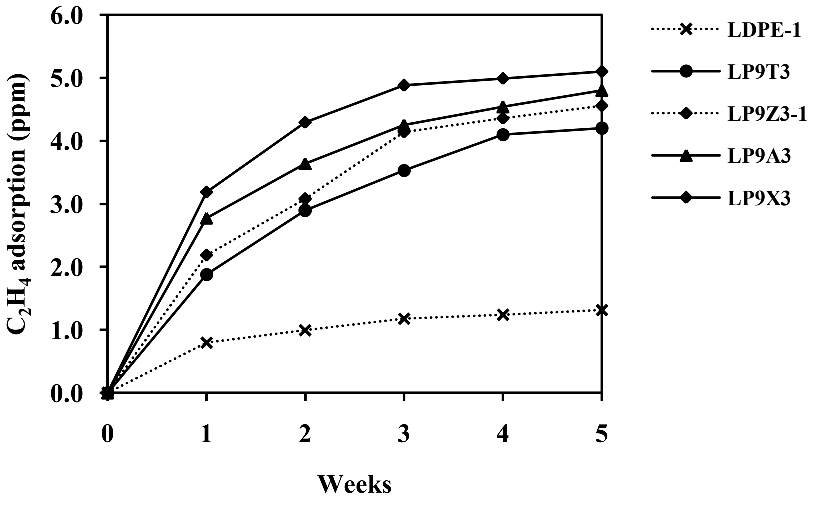

Figure 5.17: Effect of zeolite type on ethylene adsorption of LDPE/zeolite composite films at fixed PE-g-MA/zeolite ratio of 3.0 and zeolite loading of 3 phr

Figure 5.17 showed ethylene adsorption of LDPE/zeolite composite films with various zeolite types at fixed PE-g-MA/zeolite ratio of 3.0 and zeolite loading of 3 phr. The results revealed ethylene adsorption of composite film with zeolite type X was more than other composite films due to its large pore size and more polarity of zeolite 13X. The composite film with zeolite T showed ethylene adsorption less than composite film with zeolite 4A although zeolite T and 4A were the same zeolite type. It was due to the polarity of zeolite T was less than that of zeolite 4A. Moreover, different pore size of zeolite also showed the different results. Zeolite 4A and 5A was the same type but different pore size. As the result, ethylene adsorption of composite film with zeolite 5A was more than those with zeolite 4A.

From all results in this section, the composite film with zeolite 5A was chosen to determine the efficiency of composite film to maintain quality and prolong shelf life of fresh produce. Although the composite film with zeolite T showed the same properties, the cost of zeolite T was around two times higher than that of zeolite 5A. Moreover, ethylene adsorption of composite with zeolite T was less than those with zeolite 5A.

5.7 Packing of fresh postharvest produces

Lime and mango fruits were used in this study. The results of the LDPE/zeolite 5A composite packaging film containing with lime fruit were reported firstly, followed by those with mango fruit. Maturity indices are the most important factor to determine storage-life and quality. Examples of these indices are total soluble solids (TSS) content, titratable acidity (TA), ratio of TSS/TA and flesh firmness. Most maturity indices are also involved in the factors of quality; such as color and firmness.

5.7.1 The packing of lime fruits

The comparison of color change of lime fruits without packaging and inside neat LDPE and composite packaging film was shown in figure 5.18. Lightness (L*), greenness (-a*), and yellowness (b*) of limes with and without packaging were not significant different after two, four, and one weeks of storage, respectively. After that only limes without packaging showed obviously an increase of a* and b* values as shown in figure 5.18 (b) and (c). It indicated that the peel color of unpackaged limes began to turn yellow while the peel color of limes inside packaging was still green. As the peel color changed from dark green to yellow, brightness of color or L* value also increased as seen in figure 5.18 (a).

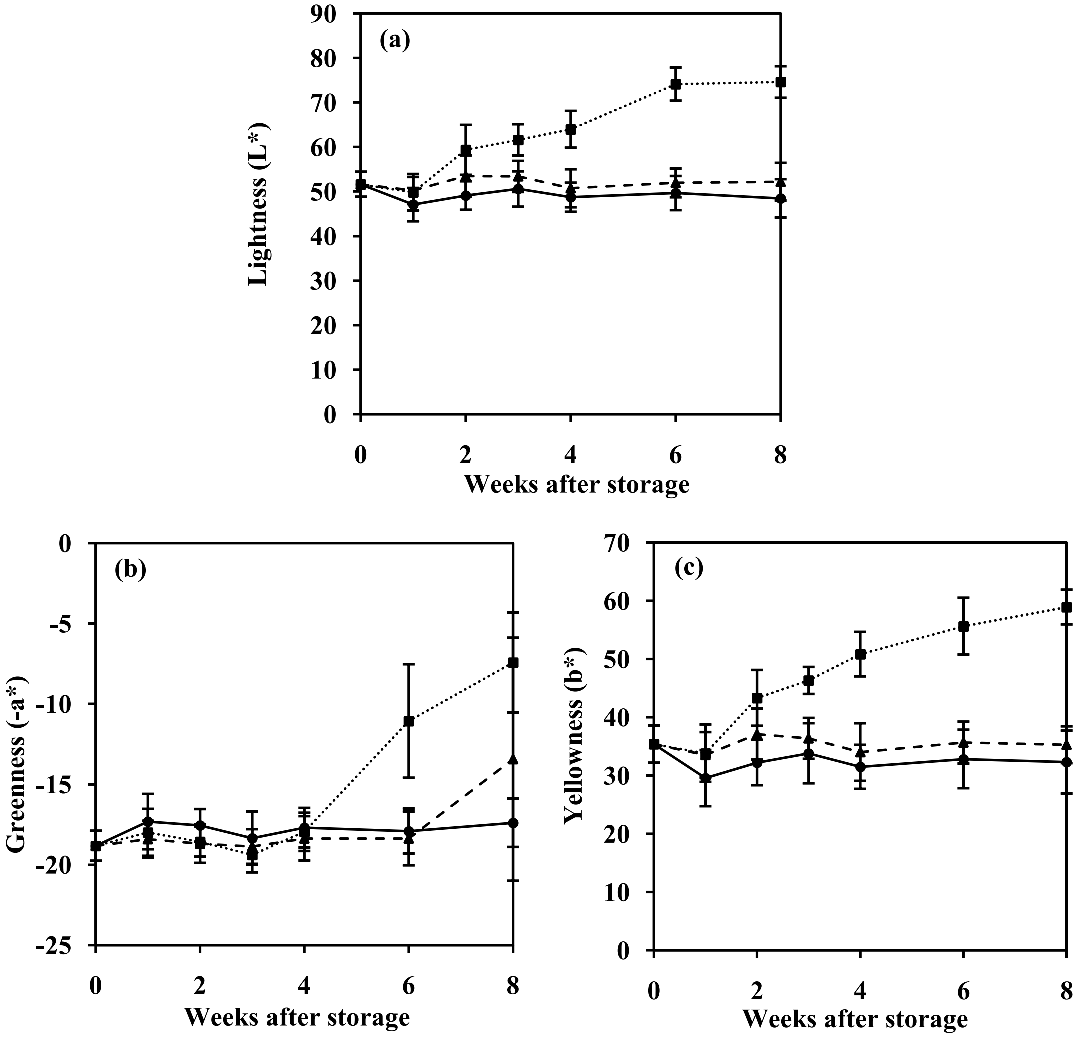

Figure 5.18: Lightness (a), greenness (b), and yellowness (c) of limes without packaging film (control, ···■···) and inside neat LDPE (--▲--) and composite packaging film (—●—) stored at 10°C for 8 weeks

Figure 5.19 showed the percentage of weight loss and firmness of lime without packaging film and inside neat LDPE and composite packaging film stored at 10°C for 8 weeks. The results showed clearly that the percentage of weight loss of the control fruits increased with increasing storage weeks as shown in figure 5.19 (a). It was indicated that both LDPE and composite packaging film reduced the weight loss of lime by 9.97 and 10.51%, respectively after 8 weeks of storage. This result was consistent with Khuttiyawech, C., et al [54]. The water loss of lime affected fruit deformation, especially the control fruits. If the water loss was high, the hardness would be also high resulted in low deformation. The firmness result of lime was shown in figure 5.19 (b). However, the percentage of weight loss and firmness of lime inside both packaging film showed insignificant differences.

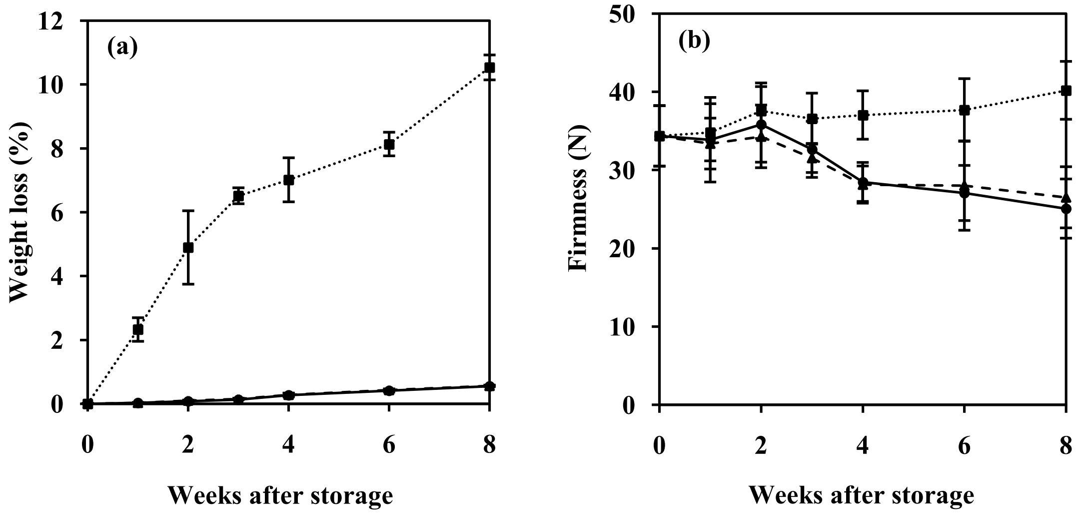

Figure 5.19: The percentage of weight loss (a) and firmness (b) of limes without packaging film (control, ···■···) and inside neat LDPE (--▲--) and composite packaging film (—●—) stored at 10°C for 8 weeks

Generally, TSS, TA, TSS/TA ratio, and V_c contents in 100 milligrams of juice showed generally insignificant differences that indicated were the same stage of maturity after storage. The results were shown in figure 5.20 to 5.22.

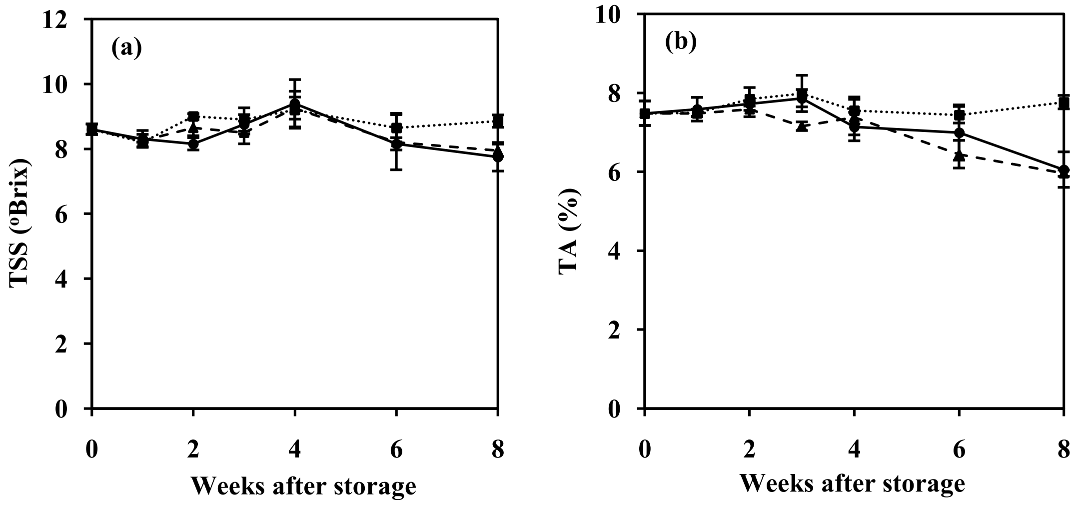

Figure 5.20: Total soluble solids content (a) and titratable acidity (b) of limes without packaging film (control, ···■···) and inside neat LDPE (--▲--) and composite packaging film (—●—) stored at 10°C for 8 weeks

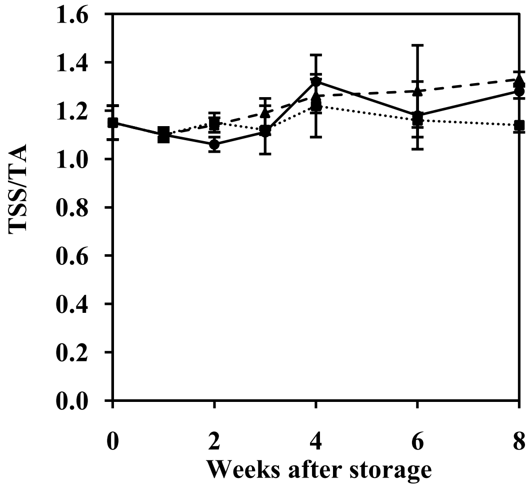

Figure 5.21: TSS/TA ratio of limes without packaging film (control, ···■···) and inside neat LDPE (--▲--) and composite packaging film (—●—) stored at 10°C for 8 weeks

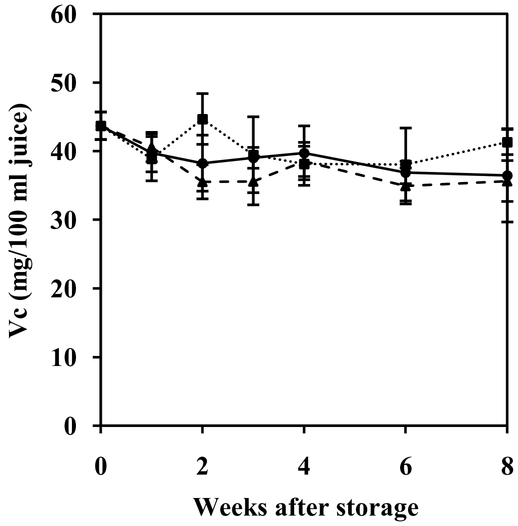

Figure 5.22: Vitamin C (V_c) contents of limes without packaging film (control, ···■···) and inside neat LDPE (--▲--) and composite packaging film (—●—) stored at 10°C for 8 weeks

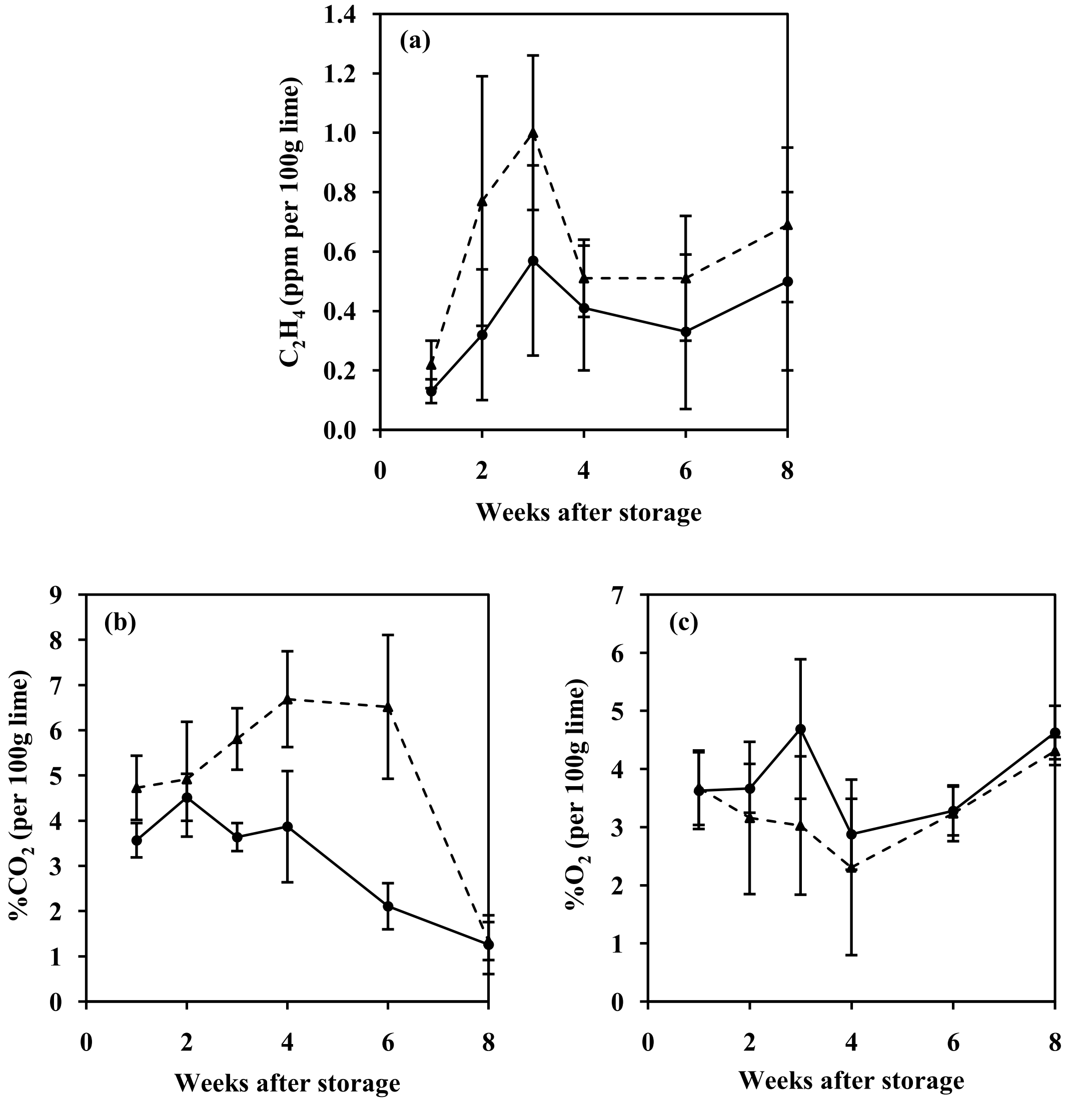

Figure 5.23: Ethylene (a), carbon dioxide (b), and oxygen (c) accumulation of limes inside neat LDPE (--▲--) and composite packaging film (—●—) stored at 10°C for 8 weeks

The accumulation of gases inside both packaging film was shown in figure 5.23. Ethylene accumulation inside the packaging film was shown in figure 5.23 (a). Ethylene accumulation inside LDPE packaging film showed higher value than those inside composite packaging film. The higher C_2H_4 accumulation caused limes lost their green color and dropped their peduncle which reduced marketability of green limes. Although ethylene accumulation inside LDPE packaging film was higher than that inside composite packaging film, limes inside LDPE packaging film were not apparently yellow. However, peduncle drop of limes inside LDPE packaging film was found at the third week of storage while those inside composite packaging film were found after six weeks of storage. Moreover, CO_2 and O_2 inside LDPE packaging film were higher and lower than those inside composite packaging film that were shown in figure 5.23 (b) and (c), respectively, which resulted in anaerobic respiration of limes in LDPE packaging film. Furthermore, the fruits inside LDPE packaging film were found CO_2 injury symptom that inhibited normal aroma development more than those inside composite packaging film after six weeks of storage. Half of limes inside LDPE packaging film were found brown skin due to CO_2 injury while three-sixteenths fruits or 18.75% inside composite packaging film were found. The appearance of all tested fruits was shown in figure 5.24.

From all results, it was found that fruits inside packaging film had longer shelf life than those without packaging film. It indicated that the package had more efficiency to extend shelf life of lime. Although the fruits inside composite packaging film were the same shelf life as those inside LDPE packaging film, the brown skin due to CO_2 injury symptom of fruits inside composite packaging film was approximately 31.75% less than those inside LDPE packaging film. However, the efficiency of composite packaging film was not good enough when compared with the previous research [54] because of the different factors such as film thickness and the quantity of lime fruits inside packaging film.

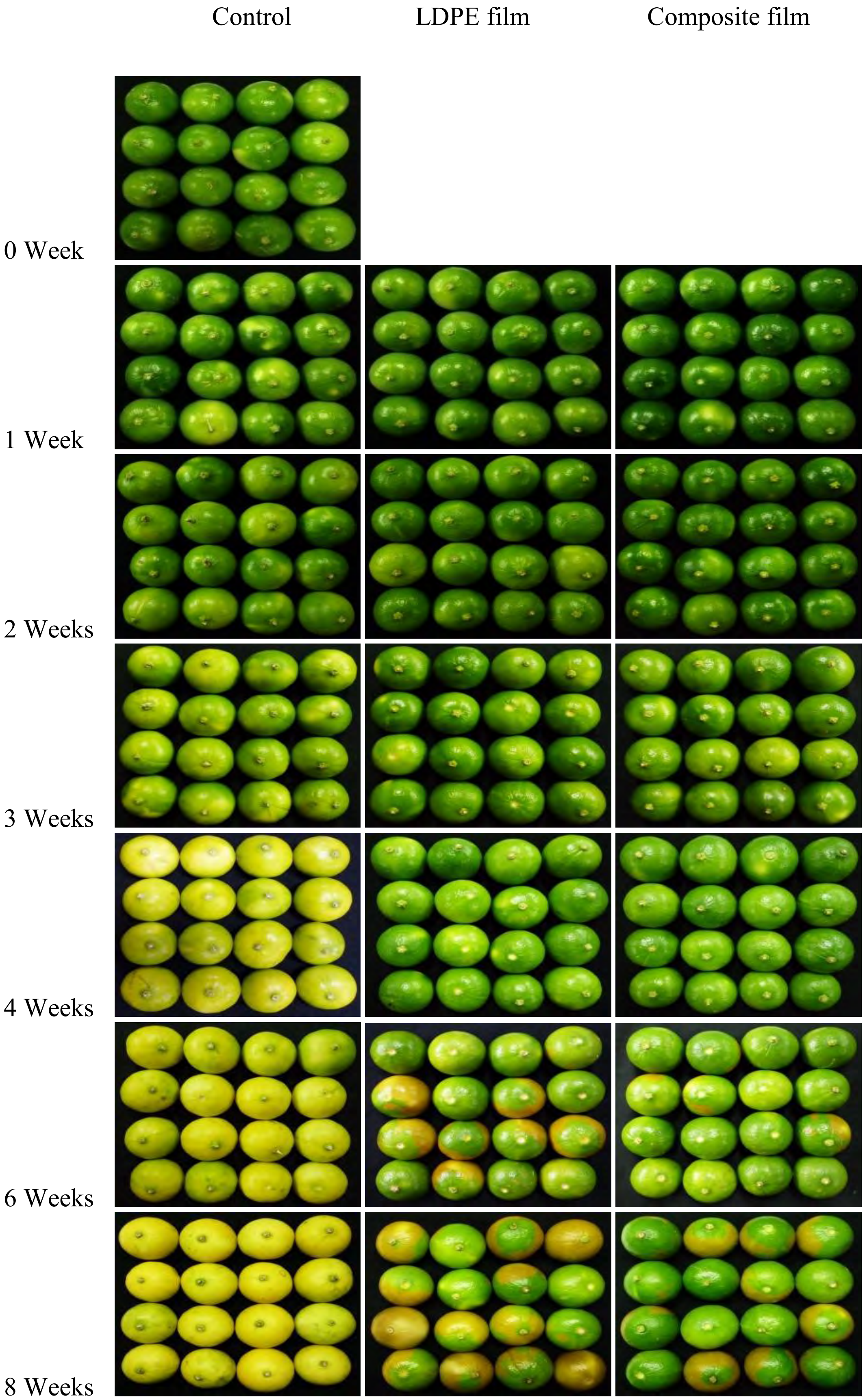

Figure 5.24: The appearance of all tested limes without packaging film and with LDPE and composite packaging film stored at 10°C for 8 weeks

5.7.2 The packing of mango fruits

The green mature mangoes were tested on their quality every week after storage at 12°C. The fruits after being kept for each week were treated with aqueous solution containing 0.1% of Tween and 500 ppm of ethephon to ripen the fruits. Physical and chemical of ripen-fruits were investigated to confirm their quality. In addition, sensory quality of ripen-mangoes was also tested.

5.7.2.1 The quality of green mature mango fruits

Color change was determined for both peel and pulp of mangoes and the results were shown in figure 5.25. The peel color of the fruits without packaging or control began to turn more yellow and brighter than those inside both LDPE and composite packaging after keeping for one week and be apparently yellowness after keeping for two weeks, suggesting that packing the fruit in package reduced peel color development. After peeled off, L* and a* value were insignificantly different but b* value were significantly different. It was indicated that the pulp of all mangoes showed the same brightness and greenness but different in yellowness. The pulp of control fruits showed obviously yellowness color after three weeks of storage that indicated the control fruits begun ripening.

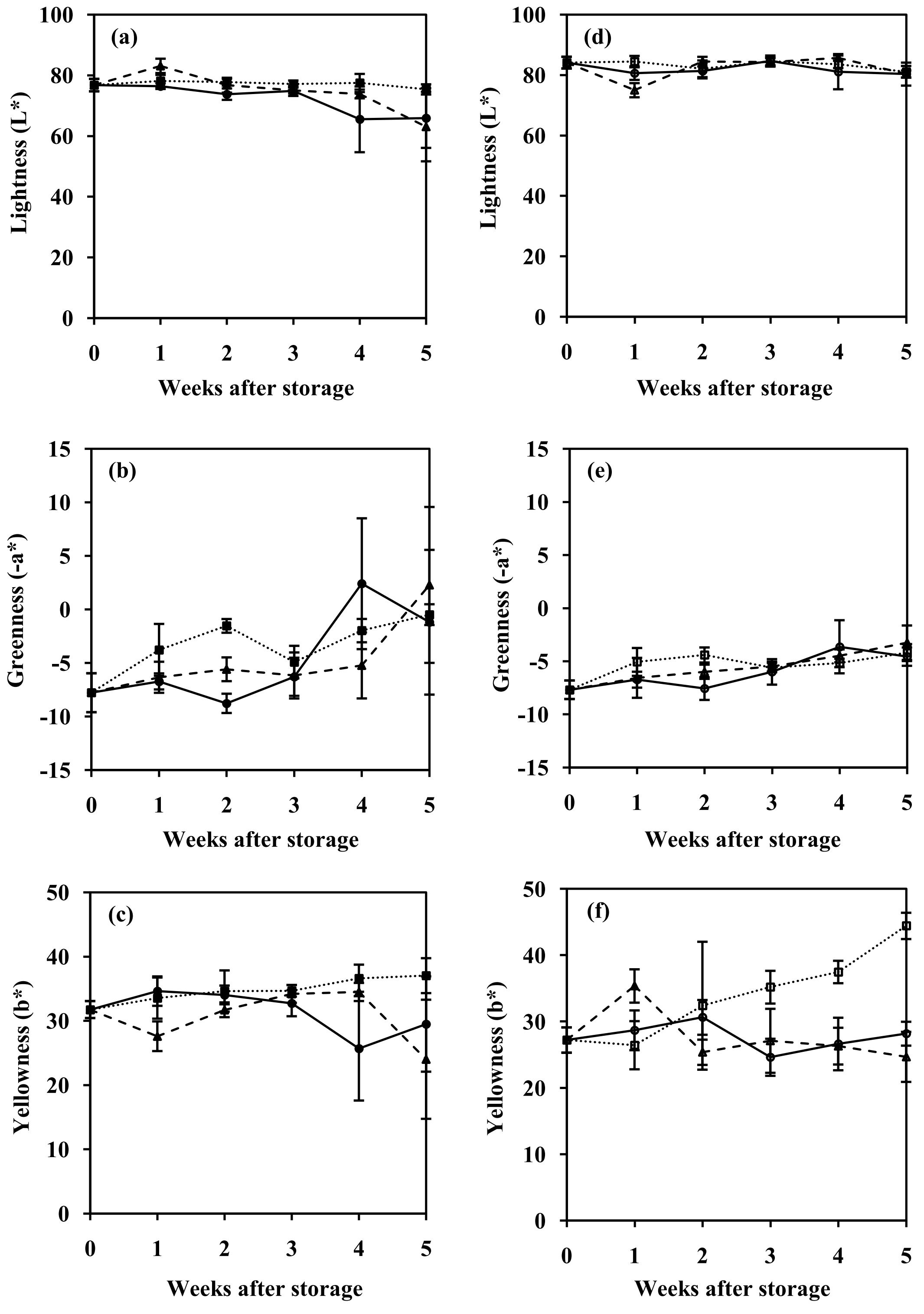

Figure 5.25: Lightness, greenness, and yellowness of peel and pulp of mangoes without packaging film (a, ····■···· and d, ····□····) and inside neat LDPE (b, --▲-- and e, --△--) and composite packaging film (c, —●— and f, —○—), respectively, stored at 12°C for 5 weeks

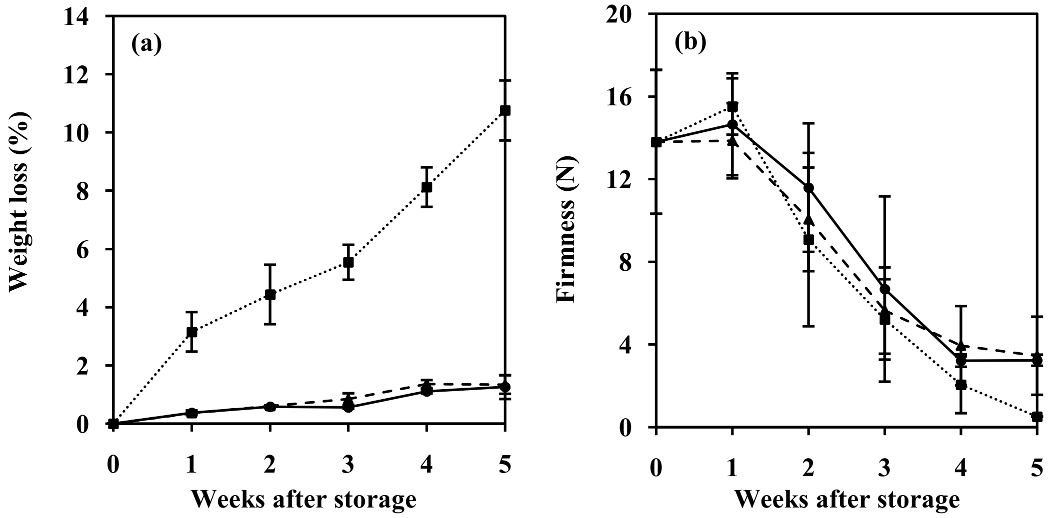

Figure 5.26: The percentage of weight loss (a) and firmness (b) of mangoes without packaging film (control, ····■····) and inside neat LDPE (--▲--) and composite packaging film (—●—) stored at 12°C for 5 weeks

Figure 5.26 showed the percentage of weight loss and firmness of mangoes without packaging film and inside neat LDPE and composite packaging film stored at 12°C for five weeks. The results clearly showed that the longer storage time increased the percentage of weight loss of mangoes without packaging film or control as shown in figure 5.26 (a). The control fruits lost water content during storage, reaching 10.76±1.03% after 5 weeks of storage. Flesh firmness of all samples has decreased in the same trend for four weeks after storage. However, the control fruits significantly lost flesh firmness more than the fruits in the packaging film at the fifth week of storage, indicating the induction of ripening process. The result of fruit firmness was shown in figure 5.26 (b). Moreover, the percentage of weight loss and firmness of mango fruits inside both packaging film were insignificantly different. TSS and TSS/TA of unpackaged fruits were greatly increased concomitantly with the decreasing of TA and faster than those inside both packaging film, which was in agreement with the research of Tefera, A., et al [47]. The results were shown in figure 5.27 and 5.28. This indicated that the development of fruit ripening of control fruits were more than those inside both packaging because the package retarded the respiration rate of fruits due to evolution of CO_2, utilization of O_2 which affected TA content, delaying TA content.

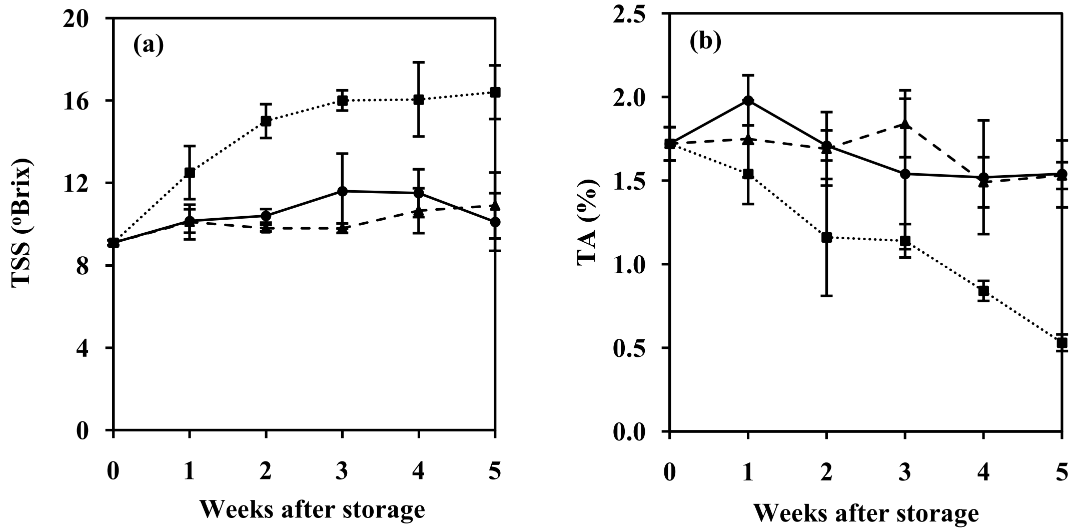

Figure 5.27: Total soluble solids content (a) and titratable acidity (b) of mangoes without packaging film (control, ┈■┈) and inside neat LDPE (--▲--) and composite packaging film (—●—) stored at 12°C for 5 weeks

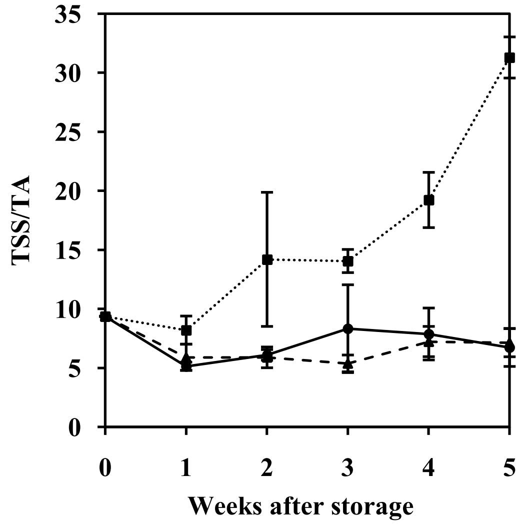

Figure 5.28: TSS/TA ratio of mangoes without packaging film (control, ┈■┈) and inside neat LDPE (--▲--) and composite packaging film (—●—) stored at 12°C for 5 weeks

In addition, V_c contents of mangoes were also varied during storage and showed insignificant differences. Although, there were no significant differences in weight loss, TSS, and TA between mangoes inside LDPE and composite packaging film, CO_2 injury symptom was found on the fruits inside neat LDPE packaging film which the peel turned brown, as seen in figure 5.30, inhibited normal aroma development, and appeared off flavors at the third week of storage and the symptom were more severe at the fourth week of storage. Furthermore, some of mango pulp inside LDPE packaging film also showed apparently brown at the fourth week of storage as seen in figure 5.31. It could be due to the CO_2 and O_2 accumulation inside neat LDPE packaging film which was much higher and lower than those in composite packaging film, respectively. Gas accumulations inside both packaging film were shown in figure 5.32. It suggested that the composite packaging film delayed the respiration of mangoes due to low CO_2 release and high O_2 remain. It was noticeable that O_2 inside both packages increased sharply at the second week of storage and decreased rapidly at the third week of storage. The decrease in O_2 may be resulted in an increase of C_2H_4 because O_2 was used to synthesize C_2H_4 (Methionine cycle) [67]. An increase of ethylene also related to a decrease of fruit firmness.

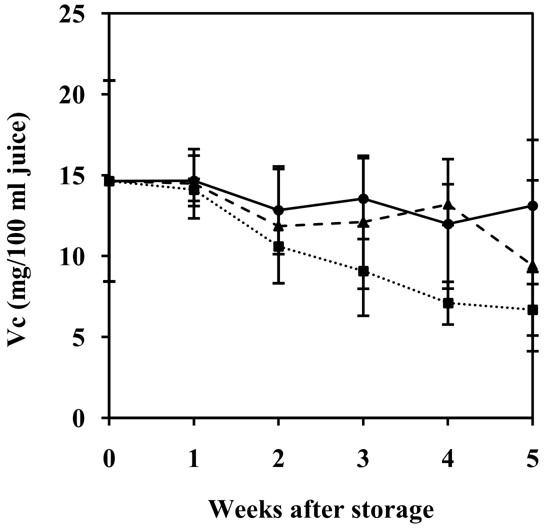

Figure 5.29: Vitamin C (V_c) contents of mangoes without packaging film (control, ···■···) and inside neat LDPE (--▲--) and composite packaging film (—●—) stored at 12°C for 5 weeks

From all results, it was found that the shelf life of fresh mangoes inside composite packaging film was 2 and 1 weeks longer than those without packaging film and inside neat LDPE packaging film, respectively. It indicated that composite packaging film had more efficiency to extend shelf life of mangoes than LDPE packaging film and delayed ripening of mango fruits compared with control fruits. Although the unpackaged fruits were not found brownish skin, the fruits were too ripened. Interestingly, high gas permeable package [55] which oxygen transmission rate (OTR) was four times more than the chosen composite film but the shelf life of mango was two weeks less than those inside the chosen composite film. At three weeks of storage, weight loss of fruits inside the chosen composite film was 50% less than those inside high gas permeable package. It may be due to higher humidity inside the package resulted in the lower water loss. In addition, O_2 and CO_2 accumulation inside the chosen composite film was less than those inside high gas permeable package by decreasing 69% and 34%, respectively. It demonstrated that CO_2 which was released from fruit could permeate through the chosen composite film more than through high gas permeable package. CO_2 accumulation inside high gas permeable package was thus higher and affected the shelf life of mangoes.

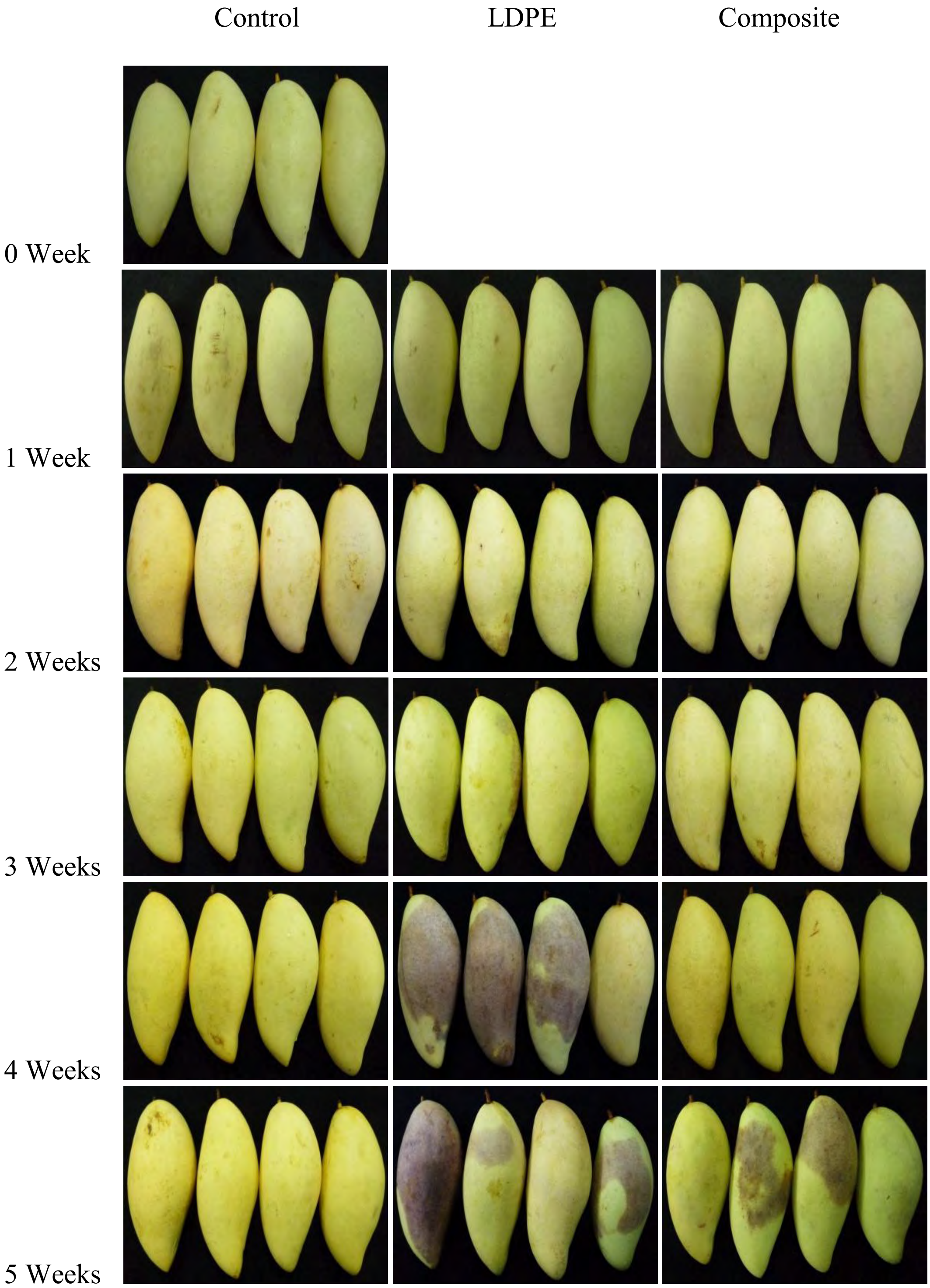

Figure 5.30: The peel appearance of all tested mangoes without packaging film and with LDPE and composite packaging film stored at 12°C for 5 weeks

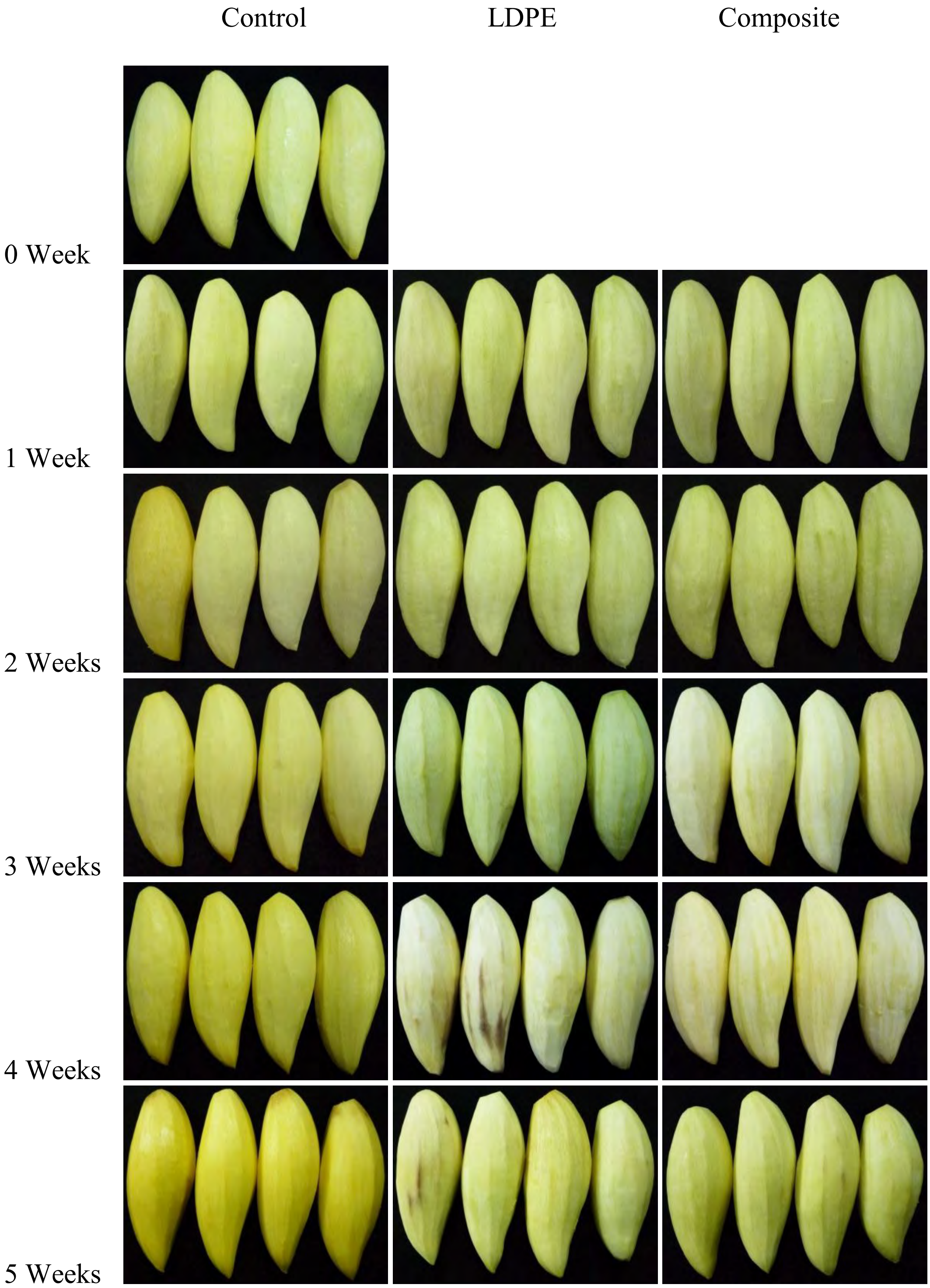

Figure 5.31: The pulp appearance of all tested mangoes without packaging film and with LDPE and composite packaging film stored at 12°C for 5 weeks

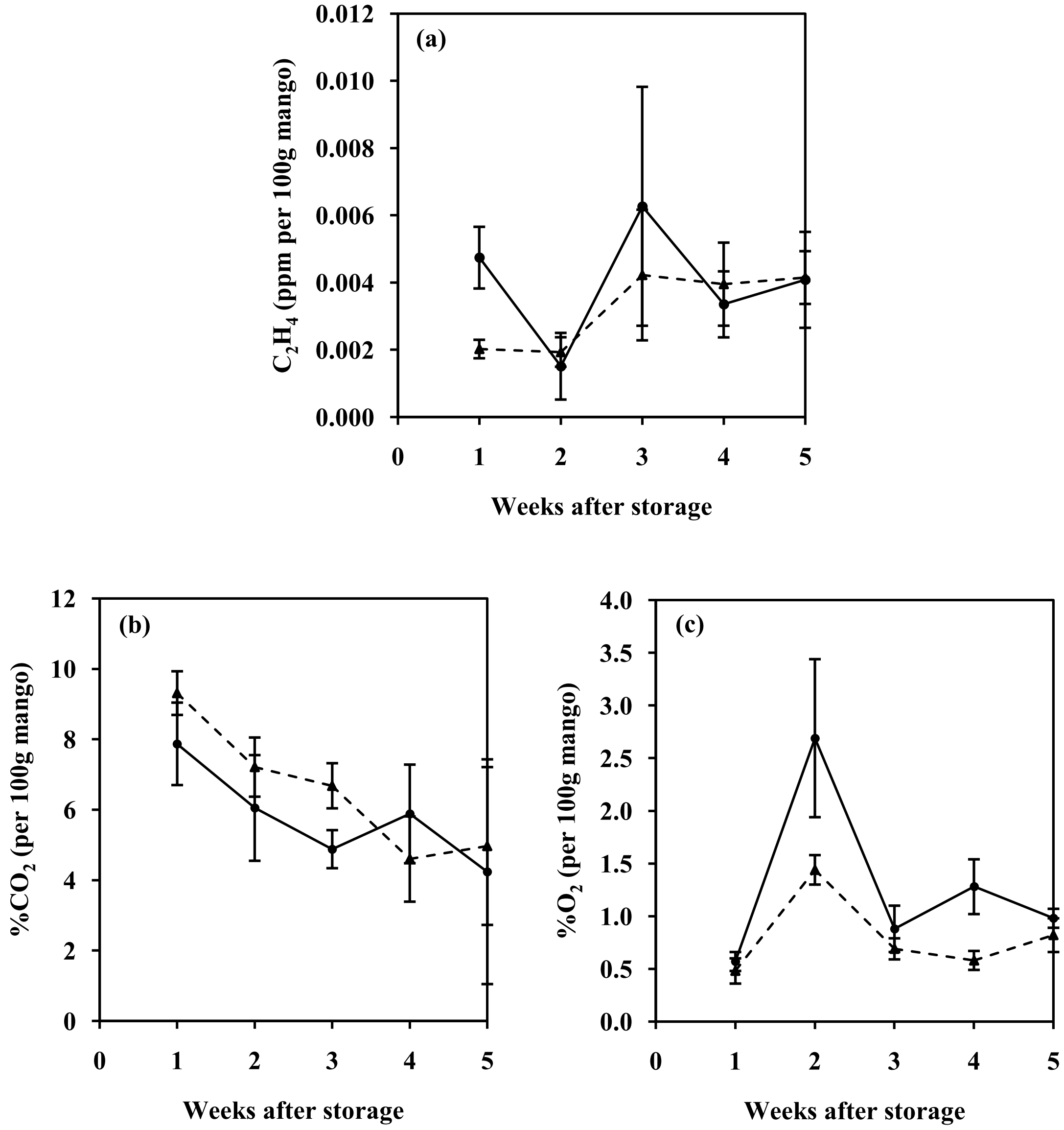

Figure 5.32: Ethylene (a), carbon dioxide (b), and oxygen (c) contents of mangoes inside neat LDPE (--▲--) and composite packaging film (—●—) stored at 12°C for 5 weeks

5.7.2.2 The quality of ripen - mango fruits

Figure 5.33 showed color development of ripen - mangoes. Lightness, greenness, and yellowness values of all ripen - mangoes for each week showed generally insignificant differences. It indicated the same peel and pulp color. In addition, the yellow skin of mangoes was increased as longer storage duration.

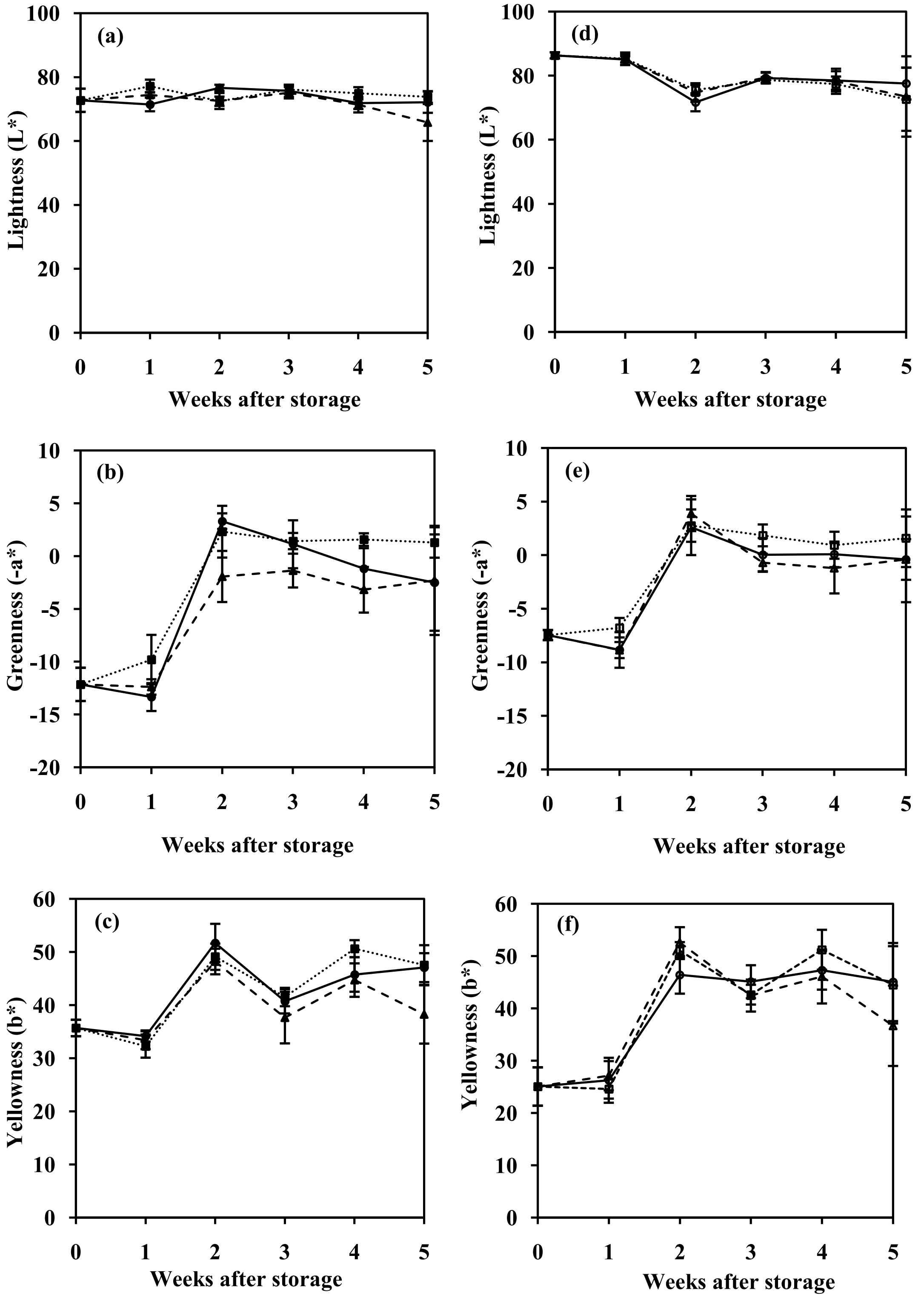

Figure 5.33: Lightness, greenness, and yellowness of peel and pulp of ripen - mangoes without packaging film (a, ⋯■⋯ and d, ⋯□⋯) and inside neat LDPE (b, --▲-- and e, --△--) and composite packaging film (c, —●— and f, —○—), respectively, after storage at 12°C

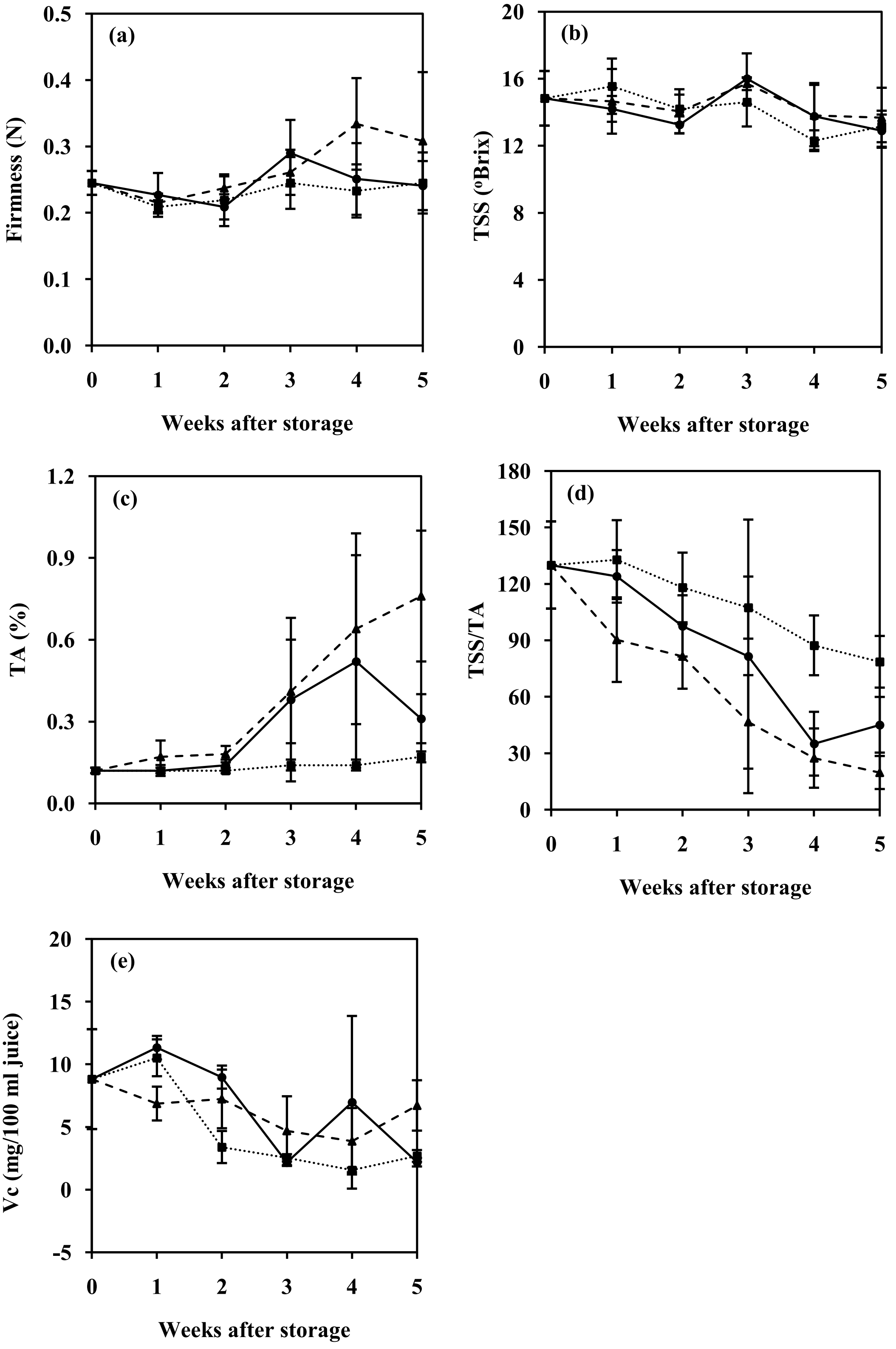

Figure 5.34: Firmness (a), total soluble solids contents (b), titratable acidity (c), TSS/TA ratio (d) and Vitamin C (V_c) contents (e) of ripen - mangoes without packaging film (control, ···■···) and inside neat LDPE (--▲--) and composite packaging film (—●—) after storage at 12°C

Flesh firmness, TSS, and V_c contents of all ripen - mangoes for each week showed also generally insignificant differences as can be seen in figure 5.34. Interestingly, the acid contents of fruits inside both LDPE and composite packaging film showed apparently an increase of TA after three weeks of storage and increased until the fifth week of storage. General, the acid was used in the respiration cycle (Kreps cycle) [2]. It indicated that the respiration of fruits was reduced due to the retardation of respiration by packaging film. TSS/TA ratio of mangoes inside packaging was lower than those without packaging owing to a decrease of TA. The unpackaged fruits were thus sweeter than those inside packaging film.

The peel, pulp, and core of all tested ripen-mangoes were shown in figure 5.35, 5.36, and 5.37, respectively. Peel of all ripen-mangoes showed the same appearance for the first three weeks after storage. The peel and pulp of mango fruits inside LDPE packaging film showed bad appearance (brown skin) at the third week of storage and the symptom was more severe at the fourth week of storage. This brown skin caused by CO_2 injury symptom resulted in unusual ripen - fruit. Although both peel and pulp of the controlled ripen - fruits did not show brown skin, the chilling injury was found after three weeks of storage and was severe at the fourth week of storage. Moreover, disease was also found in some of control fruit at the fourth week of storage.

To quantitatively determine the influence of film permeability on the ripen-mango sensory quality loss, the ripen-mango should be tasted and scented compared with the control ripen-fruits. Results of assessment of quality and acceptance of ripen-mangoes were shown in figure 5.38. Ripen - mangoes after being kept inside LDPE packaging film showed generally less quality than the control fruits and those inside composite packaging film such as aroma, taste, visual quality, and satisfaction. However, the quality’s difference between the control ripen-fruits and ripen-mangoes after being kept inside composite packaging film were not statistically significant, suggesting that composite packaging films preserved the sensory quality of packed mango fruit for 4 weeks. It was important evidence that the composite packaging film could maintain quality and prolong shelf life of fresh mango fruits.

As known, the role of packaging film was primarily to reduce the respiration rate of fruit and vegetables by retarding their metabolic activities. Reduced respiration also retards softening, and slows down various composition changes such as TSS, which are associated with ripening. However, both mango and lime fruits inside the chosen composite film showed better quality than those inside LDPE film and longer shelf life than control fruits.

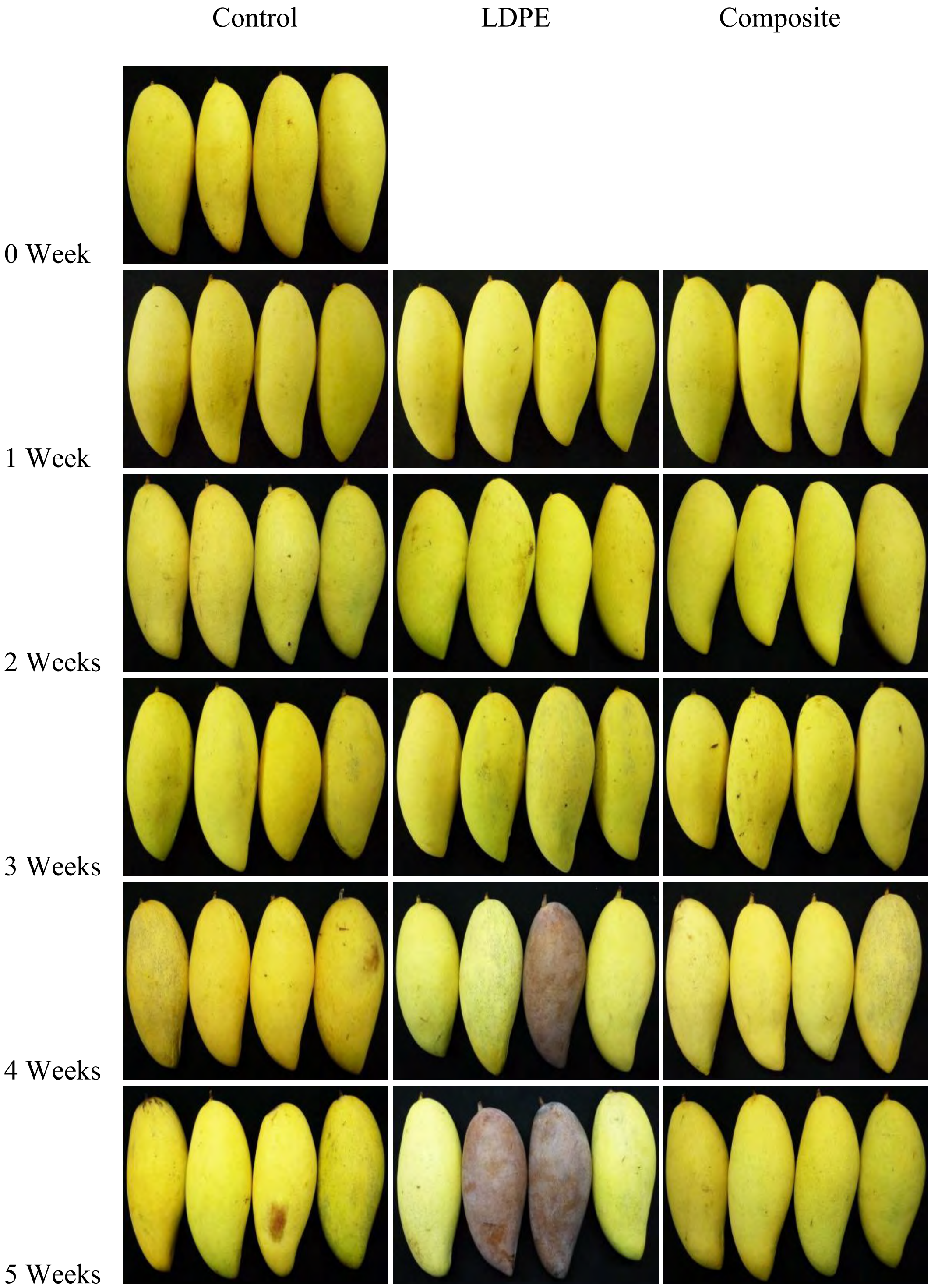

Figure 5.35: The peel appearance of all tested ripen - mangoes without packaging film and with LDPE and composite packaging film after storage at 12°C

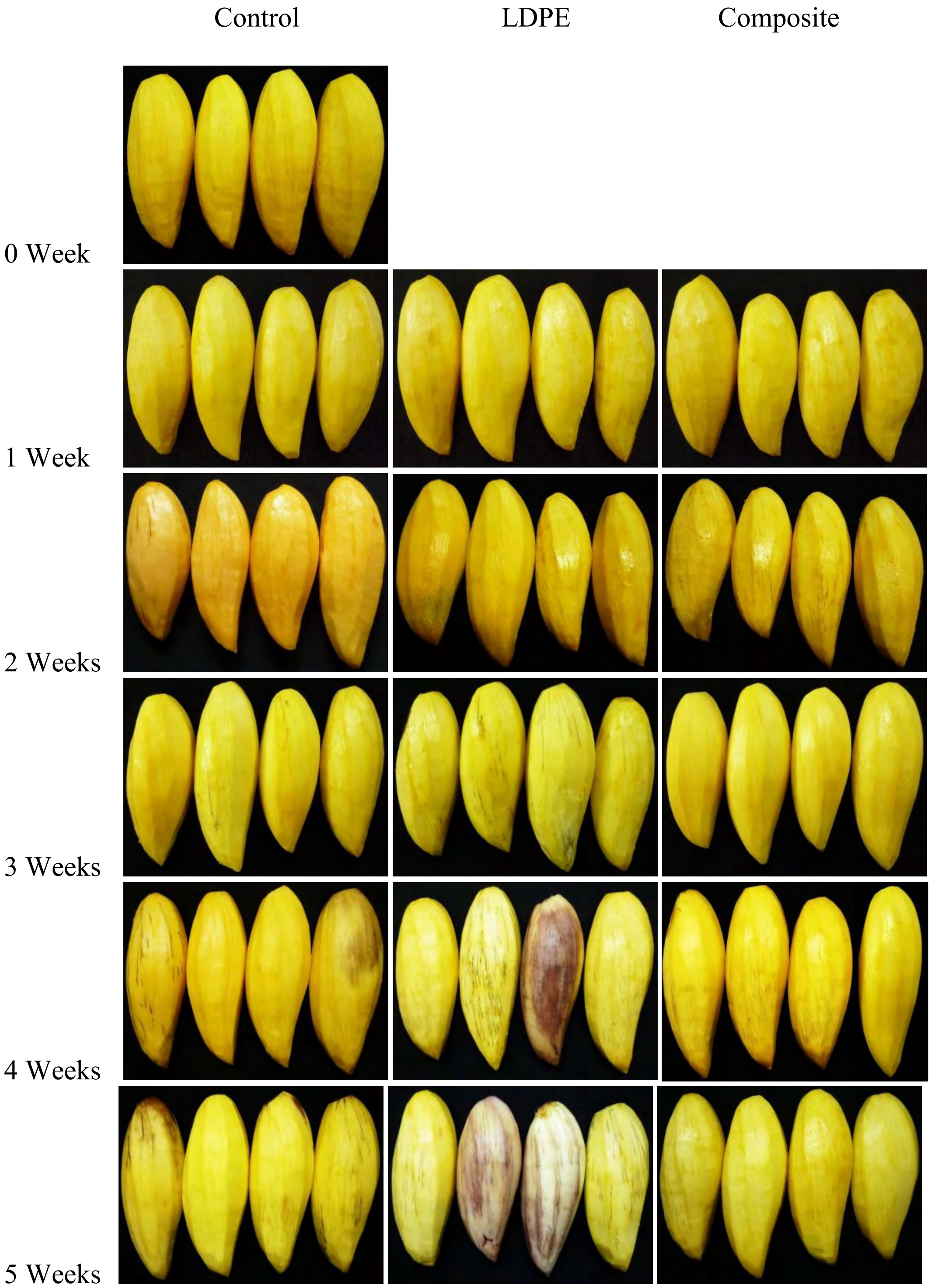

Figure 5.36: The pulp appearance of all tested ripen - mangoes without packaging film and with LDPE and composite packaging film after storage at 12°C

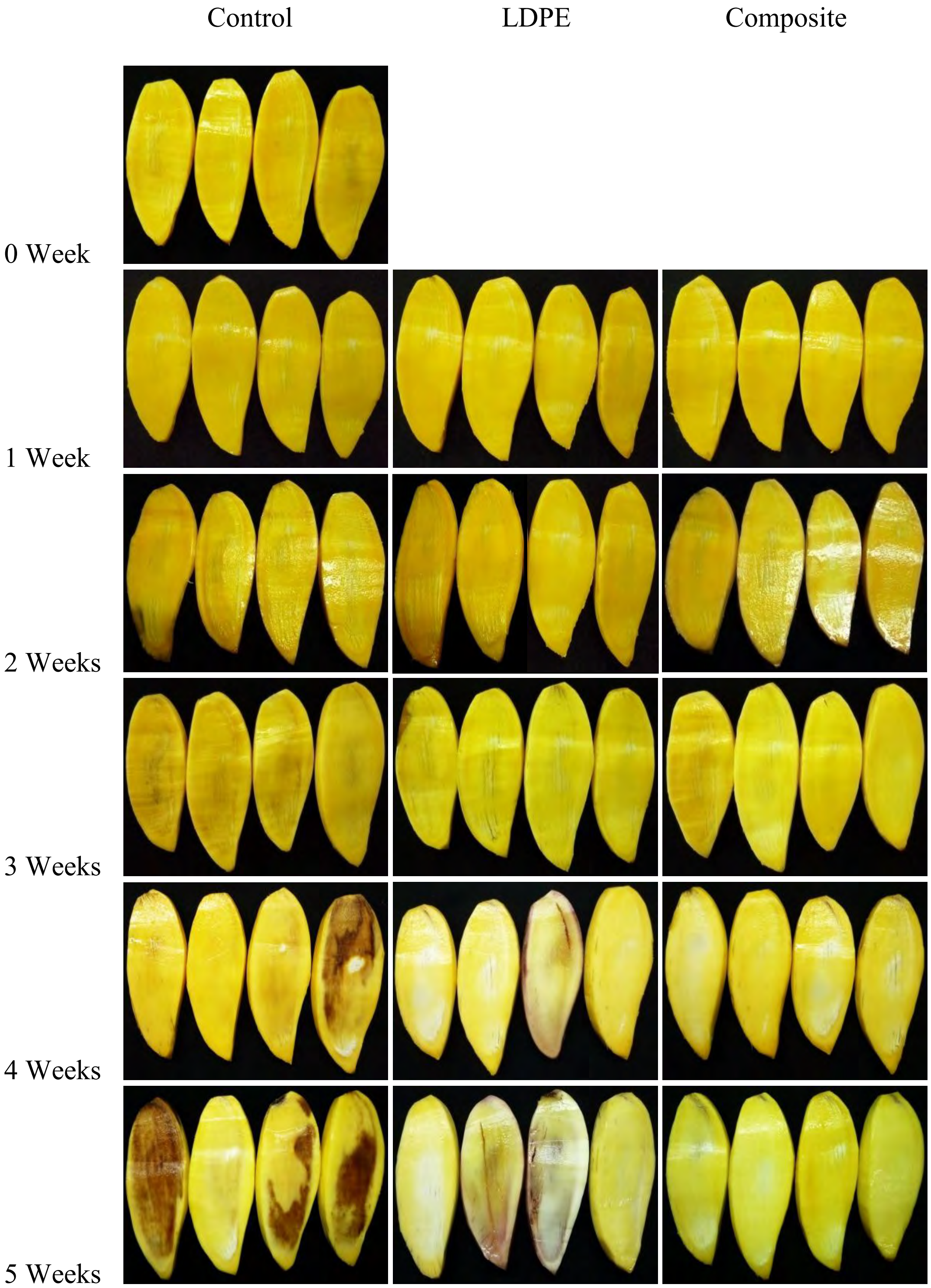

Figure 5.37: The core appearance of all tested ripen - mangoes without packaging film and with LDPE and composite packaging film after storage at 12°C

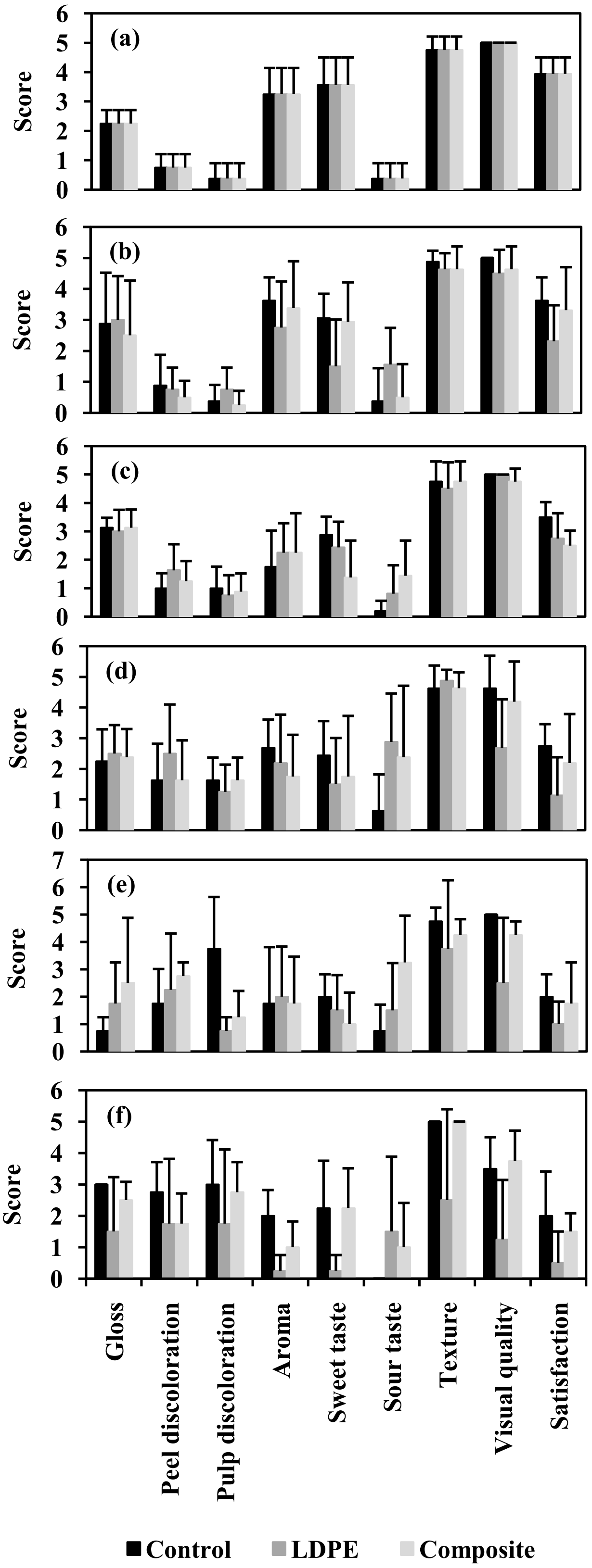

Figure 5.38: Sensory evaluation of all tested ripen - mangoes without packaging film and with LDPE and composite packaging film after storage at 12°C, 0 to 5 weeks (a - f)

CHAPTER VI

CONCLUSIONS

LDPE matrix melted mixing with zeolite powder and PE-g-MA was extruded by twin screw extruder attached to blown film die at different PE-g-MA/zeolite ratio, zeolite loading, and zeolite type. The effect of PE-g-MA to zeolite ratio, zeolite loading, and zeolite type on particle dispersion, mechanical, thermal and gas permeability properties of LDPE/zeolite composite films was studied. Furthermore, the composite film with appropriate properties was used as packaging for fresh produces. Lime and mango fruit was chosen to determine the efficiency of composite film to maintain quality and prolong their shelf life compared with neat LDPE film while being kept at low temperature. The measurement of physiological and chemical change of both produces, such as visual quality, fruit firmness, gas accumulation inside packaging, total soluble solids (TSS) content, and titratable acidity (TA), was also studied.

SEM results indicated that PE-g-MA provide good particle dispersion and distribution in LDPE/zeolite composite film, especially at the PE-g-MA/zeolite of 3.0. Good zeolite dispersion leaded to good mechanical property. The composite film with the higher PE-g-MA/zeolite ratio also leaded to good gas permeability because of high amorphous phase and low degree of crystallinity of LDPE. In this study, addition of zeolite in composite film was limited at 3 phr because higher loading than 3 phr decreased the mechanical properties of composite film. In addition, the use of various types of zeolites in composite films provided generally insignificantly different results of mechanical properties but the gas permeability results showed significant difference. From overall results, the LDPE/zeolite 5A composite film at fixed PE-g-MA/zeolite ratio of 3.0 and zeolite loading of 3 phr had the optimal properties and was chosen to use as packaging.

Although limes inside composite packaging film was the same shelf life as those inside LDPE packaging film, CO_2 injury symptom of limes inside composite packaging film was approximately 31.75% less than those inside LDPE packaging film. In addition, the composite packaging film also delayed peduncle drop and green color development. Mango fruits packing test showed the efficiency of composite packaging film on quality and shelf life of fruits by retardation of fruit ripening. The shelf life of fresh mangoes inside composite packaging film was 2 and 1 weeks longer than those without packaging film and inside neat LDPE film, respectively. All tested mangoes were ripen to investigate sensory quality. The mango fruits inside LDPE packaging film showed generally less acceptance than those inside composite packaging film at the fourth week of storage. In addition, there were no significant difference between the quality of control fruits and mango fruits inside composite packaging film. It confirmed that the chosen composite packaging films preserved the sensory quality of packed mango fruit for 4 weeks and was more efficient than LDPE packaging film.

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APPENDICES

Appendix A

Polymer properties

Table A.1: LDPE properties

Property	**Test method**	**Value**
Melt flow rate (g/10 min)	ASTM D 1238 @ 190°C, 2.16 kg	5.00
Density (g/cm^3)	ASTM D 1505	0.919
Melting point (°C)	ASTM D 2117	110

Table A.2: PE-g-MA properties

Property	**Value**
Melt flow rate (g/10 min)	1.58
Volatiles (%)	0.02
Maleic anhydride (residual)	< 0.1

Appendix B

Table B.1: Inorganic contents of pristine zeolite

Sample	**Inorganic contents (wt%)**
4A powder	85.94 ± 0.52
T powder	87.60 ± 0.18
5A powder	86.70 ± 0.34
13X powder	86.33 ± 0.39

Appendix C

Table C.1: Average inorganic contents of LDPE/zeolite composite films

Sample code	Zeolite type	Fixed PE-g-MA contents (phr)	Fixed zeolite contents (phr)	Inorganic contents (phr)
LP3Z3	4A	3	3	2.99 ± 0.04
LP6Z3	4A	6	3	3.00 ± 0.08
LP9Z3-1	4A	9	3	2.98 ± 0.04
LP12Z3	4A	12	3	2.98 ± 0.02
LP3Z1	4A	3	1	0.92 ± 0.01
LP9Z3-2	4A	9	3	2.98 ± 0.04
LP15Z5	4A	15	5	4.41 ± 0.03
LP21Z7	4A	21	7	6.57 ± 0.07
LP9T3	T	9	3	2.99 ± 0.09
LP9A3	5A	9	3	2.79 ± 0.07
LP9X3	13X	9	3	3.00 ± 0.01

Remark: LP9Z3-1 and LP9Z3-2 were the same formula but proceeded with different temperature.

Appendix D

Table D.1: Sensory table record

Sample code:					**Date:**			
Gloss	None	0	1	2	3	4	5	Excellent
Peel discoloration	None	0	1	2	3	4	5	Severe
Pulp discoloration	None	0	1	2	3	4	5	Severe
Aroma	Complete lack of characteristic aroma	0	1	2	3	4	5	Full characteristic aroma
Sweet taste	None	0	1	2	3	4	5	Severe
Sour taste	None	0	1	2	3	4	5	Severe
Texture	Poor	0	1	2	3	4	5	Excellent
Visual quality	Poor	0	1	2	3	4	5	Excellent
Satisfaction	Poor	0	1	2	3	4	5	Excellent

Appendix E

Table E.1: Melting (T_m) and crystallization (T_c) temperature of neat LDPE, PE-g-MA, and LDPE/zeolite composite films

Sample code	**Melting temperature,T_m (^oC)**	**Crystallization temperature,T_c (^oC)**
LDPE-1	103.19	88.91
PE-g-MA-1	113.97	94.47
LP3Z3	103.04	89.53
LP6Z3	102.95	89.92
LP9Z3-1	102.91	90.44
LP12Z3	102.08	90.94
LDPE-2	102.80	90.19
PE-g-MA-2	112.47	94.87
LP3Z1	103.18	89.61
LP9Z3-2	103.27	90.74
LP15Z5	103.54	91.06
LP21Z7	103.34	91.51
LP9T3	102.49	90.84
LP9A3	102.97	91.00
LP9X3	104.01	90.60

Appendix F

Determination of degree of crystallinity (DSC experiment)

The degree of crystallinity of composite films can be identified by determining the area under DSC heating peak of the sample according to the following equation

$$\text{The degree of crystallinity} = \frac{C}{(A \times D) + (B \times E)}$$

$$D = \frac{F}{F+G}$$

$$E = \frac{G}{F+G}$$

where A = area under DSC peak of pure LDPE
B = area under DSC peak of pure PE-g-MA
C = area under DSC peak of composite film
D = fraction of LDPE in composite film
E = fraction of PE-g-MA in composite film
F = weight portion of LDPE in composite film
G = weight portion of PE-g-MA in composite film

The area under DSC heating peak and degree of crystallinity of neat LDPE, PE-g-MA, and composite films were summarized in table F.1. For example, the degree of crystallinity of a PE-g-MA/zeolite ratio of 1.0 composite film at fixed zeolite content of 3 phr (LP3Z3) was determined by using above equation.

$$D = \frac{100}{100+3} = 0.97 \quad \text{and} \quad E = \frac{3}{100+3} = 0.03$$

then $$\text{Degree of crystallinity} = \frac{305.780}{(363.037 \times 0.97) + (403.202 \times 0.03)} = 0.84$$

Table F.1: Area under DSC heating peak, and degree of crystallinity of neat LDPE, PE-g-MA and LDPE/zeolite composite films

Sample code	Area	Degree of crystallinity
LDPE-1	363.037	1.00
PE-g-MA-1	403.202	1.00
LP3Z3	305.780	0.84
LP6Z3	265.662	0.73
LP9Z3-1	253.609	0.69
LP12Z3	226.217	0.62
LDPE-2	295.517	1.00
PE-g-MA-2	313.202	1.00
LP3Z1	205.517	0.69
LP9Z3-2	200.248	0.67
LP15Z5	180.248	0.61
LP21Z7	172.358	0.58
LP9T3	259.059	0.71
LP9A3	245.168	0.67
LP9X3	263.215	0.71

Appendix G

Average data of mechanical and gas permeability properties of films

Table G.1: Mechanical properties of films (part I) in MD

Sample	Tensile strength at yiled (MPa)	Elongation at break (%)	E - modulus (MPa)
LDPE-1	8.01 ± 1.18	386.58 ± 74.89	0.31 ± 0.14
LP3Z3	8.38 ± 1.03	270.27 ± 40.50	0.81 ± 0.21
LP6Z3	8.66 ± 1.01	301.59 ± 38.41	0.73 ± 0.23
LP9Z3-1	9.59 ± 1.35	295.29 ± 25.44	1.02 ± 0.31
LP12Z3	9.59 ± 0.96	288.69 ± 27.75	1.00 ± 0.26

Table G.2: Mechanical properties of films (part I) in TD

Sample	Tensile strength at yiled (MPa)	Elongation at break (%)	E - modulus (MPa)
LDPE-1	7.27 ± 1.29	516.30 ± 65.92	0.31 ± 0.15
LP3Z3	7.85 ± 0.86	476.70 ± 33.59	0.88 ± 0.18
LP6Z3	8.04 ± 1.03	471.81 ± 52.95	0.95 ± 0.13
LP9Z3-1	8.97 ± 0.98	487.62 ± 31.87	0.99 ± 0.19
LP12Z3	8.03 ± 1.15	449.50 ± 54.76	1.07 ± 0.29

Table G.3: Mechanical properties of films (part II) in MD

Sample	Tensile strength at yiled (MPa)	Elongation at break (%)	E - modulus (MPa)
LDPE-2	8.23 ± 1.34	408.06 ± 64.46	0.30 ± 0.11
LP3Z1	9.48 ± 0.67	312.30 ± 44.83	0.52 ± 0.20
LP9Z3-2	9.82 ± 0.81	306.45 ± 36.34	1.03 ± 0.18
LP15Z5	8.85 ± 0.73	276.76 ± 47.55	0.63 ± 0.16
LP21Z7	8.61 ± 1.05	262.42 ± 33.74	0.59 ± 0.14

Table G.4: Mechanical properties of films (part II) in TD

Sample	Tensile strength at yiled (MPa)	Elongation at break (%)	E - modulus (MPa)
LDPE-2	7.65 ± 0.90	504.11 ± 64.89	0.25 ± 0.03
LP3Z1	8.06 ± 1.05	499.96 ± 50.00	0.54 ± 0.25
LP9Z3-2	9.01 ± 1.01	469.08 ± 54.41	1.00 ± 0.26
LP15Z5	7.79 ± 1.09	404.36 ± 64.82	0.83 ± 0.20
LP21Z7	6.43 ± 0.53	346.97 ± 60.35	0.80 ± 0.21

Table G.5: Mechanical properties of films (part III) in MD

Sample	Tensile strength at yiled (MPa)	Elongation at break (%)	E - modulus (MPa)
LDPE-1	8.01 ± 1.18	386.58 ± 74.89	0.31 ± 0.14
LP9T3	11.24 ± 0.86	280.95 ± 17.63	0.98 ± 0.31
LP9Z3-1	9.59 ± 1.35	295.29 ± 25.44	1.02 ± 0.31
LP9A3	11.26 ± 1.13	272.53 ± 14.07	0.99 ± 0.28
LP9X3	11.37 ± 0.93	279.11 ± 16.78	0.88 ± 0.21

Table G.6: Mechanical properties of films (part III) in TD

Sample	Tensile strength at yiled (MPa)	Elongation at break (%)	E - modulus (MPa)
LDPE-1	7.27 ± 1.29	516.30 ± 65.92	0.31 ± 0.15
LP9T3	8.10 ± 1.40	490.63 ± 15.92	0.65 ± 0.16
LP9Z3-1	8.97 ± 0.98	487.62 ± 31.87	0.99 ± 0.19
LP9A3	7.65 ± 0.90	465.18 ± 35.65	0.61 ± 0.19
LP9X3	7.39 ± 0.85	423.83 ± 45.19	0.86 ± 0.24

Table G.7: Gas permeability properties of films (part I)

Sample	**PO_2 (mm-cc/[m^2-day])**	**PCO_2 (mm-cc/[m^2-day])**	**WVP (mm-g/[m^2-day])**
LDPE-1	208 ± 24	418 ± 43	0.39 ± 0.03
LP3Z3	179 ± 11	332 ± 26	0.37 ± 0.01
LP6Z3	177 ± 12	351 ± 41	0.41 ± 0.03
LP9Z3-1	207 ± 20	438 ± 52	0.42 ± 0.02
LP12Z3	185 ± 28	446 ± 38	0.46 ± 0.02

Table G.8: Gas permeability properties of films (part II)

Sample	**PO_2 (mm-cc/[m^2-day])**	**PCO_2 (mm-cc/[m^2-day])**	**WVP (mm-g/[m^2-day])**
LDPE-2	231 ± 5	583 ± 34	0.42 ± 0.06
LP3Z1	231 ± 9	583 ± 53	0.37 ± 0.09
LP9Z3-2	225 ± 16	542 ± 18	0.45 ± 0.03
LP15Z5	207 ± 21	550 ± 39	0.43 ± 0.07
LP21Z7	241 ± 15	609 ± 26	0.52 ± 0.04

Table G.9: Gas permeability properties of films (part III)

Sample	**PO_2 (mm-cc/[m^2-day])**	**PCO_2 (mm-cc/[m^2-day])**	**WVP (mm-g/[m^2-day])**
LDPE-1	208 ± 24	418 ± 43	0.39 ± 0.03
LP9T3	259 ± 10	601 ± 44	0.44 ± 0.04
LP9Z3-1	207 ± 20	438 ± 52	0.42 ± 0.02
LP9A3	237 ± 8	622 ± 19	0.43 ± 0.08
LP9X3	228 ± 26	544 ± 38	0.34 ± 0.03

Appendix H

Statistical analysis

In this study, analysis of variance (ANOVA) was used to test for differences among at least three groups. The F-test was used for comparisons of the components of the total deviation. For example, statistical calculation of weight loss of lime fruits after 1 week of storage is shown below:

Table H.1: Weight loss of lime fruits after 1 week of storage

Sample no.	**Weight loss of lime fruits (%)**		
	Without packaging	**Inside LDPE packaging**	**Inside composite packaging**
1	1.98	0.03	0.03
2	2.06	0.03	0.02
3	2.78	0.03	0.03
4	2.44	0.03	0.02
Sum	**9.26**	**0.12**	**0.10**
AVG	**2.315a**	**0.030b**	**0.025b**

From table H.1, the differences can be calculated as following:

Degree of freedom among groups = k – 1 = 3 - 1 = 2

Degree of freedom within groups = k(n – 1) = 3(4 - 1) = 9

$$T^2 = (9.26 + 0.12 + 0.10)^2 = 89.87$$

$$\frac{T^2}{N} = 89.87/(4\times3) = 7.49$$

$$\sum_{j=1}^{k} T_j^2 = 9.26^2 + 0.12^2 + 0.10^2 = 85.77$$

$$\frac{\sum_{j=1}^{k} T_j^2}{n} = 85.77/4 = 21.44$$

Sum square between group (SS_B) $= \dfrac{\sum_{j=1}^{k} T_j^2}{n} - \dfrac{T^2}{N}$

$= 21.44 - 7.49 = 13.95$

Total sum of square $= \sum_{j=1}^{k}\sum_{i=1}^{n_i} X_{ij}^2$

$= (1.98)^2 + (2.06)^2 + (2.78)^2 + (2.44)^2 + (0.03)^2 + (0.03)^2 + (0.03)^2 + (0.03)^2 + (0.03)^2 + (0.02)^2 + (0.03)^2 + (0.02)^2$

$= 21.85$

Sum square total (SS_T) $= \sum_{j=1}^{k}\sum_{i=1}^{n_i} X_{ij}^2 - \dfrac{T^2}{N}$

$= 21.85 - 7.49 = 14.36$

Sum square within group (SS_W) $= SS_T - SS_B$

$= 14.36 - 13.95 = 0.41$

Mean square between groups (MS_B) $= \dfrac{SS_B}{k - 1}$

$= \dfrac{13.95}{3 - 1} = 6.975$

Mean square within group (MS_W) $= \dfrac{SS_w}{k(n - 1)}$

$= \dfrac{0.41}{3(4 - 1)} = 0.045$

$$F_{obs} = \frac{MS_B}{MS_W} = \frac{6.975}{0.045} = 155$$

The F-ratio can be thought of as a measure of how different the means are relative to the variability within each sample. In an ANOVA, the F-ratio is the statistic used to test the hypothesis that the effects are real, in the other words, that the means are significantly different from one another. The F-ratio which cuts off various proportions of the distributions may be computed for different values of df_1 and df_2. These F-ratios are called F_{crit} values and be found in the F-table. Hence, F_{crit} values is 4.26 at $df_1 = 2$, $df_2 = 9$, and alpha is 0.05.

From the result, F_{obs} values is higher than F_{crit} values that means there are statistically significant differences at least one pair. Duncan's multiple range test will be used after an ANOVA to find which pair is significant differences. Firstly, the average of each treatment is ranked from smallest to largest value and then look up in the r-table for the r value. It depends on the degrees of freedom within the treatment (f) and the alphas (α). The statistic R is calculated and compared with the subtraction of each of the treatment. If the calculated subtraction is greater than the table value, then there is a significant difference between the means pairs. From this sample, we can calculate as follows.

Ranking the average values,	0.025	0.030	2.315
	(1)	(2)	(3)

Statistical R $= r_{\alpha}(p,f)\sqrt{\frac{MS_W}{n}}$ which the p values will be calculated by subtracting the mean ranks and add one.

Hence $\sqrt{\frac{MS_W}{n}} = \sqrt{\frac{0.045}{4}} = 0.11$

From r-table, the statistical R at different p values is shown below.

p	2	3
$r_{0.05}(p,9)$	3.199	3.339
R	0.34	0.36

Comparison between the statistic R and the subtraction of each of the treatment is shown as below.

		R
(3) - (2) = 2.315 – 0.030 = 2.285	>	0.34
(3) - (1) = 2.315 – 0.025 = 2.290	>	0.36
(2) - (1) = 0.030 – 0.025 = 0.005	<	0.34

From the results, there are two pairs of significant differences or there are two groups. It means the mango fruits without packaging were different from those inside packaging and an alphabetic character is used to show the group as seen in table H.1.

Appendix I

Statistical data

Table I.1: Lightness (L*) of lime fruits

Lightness (L*)	Control fruits	Lime fruits inside LDPE packaging	Lime fruits inside composite packaging	F-test
0 day	51.61 ± 2.81	51.61 ± 2.81	51.61 ± 2.81	ns
1 week	49.83 ± 4.09 a	50.22 ± 3.04 a	47.05 ± 3.74 b	*
2 weeks	59.35 ± 5.61 a	53.49 ± 4.62 b	49.10 ± 3.20 c	*
3 weeks	61.60 ± 3.52 a	53.38 ± 3.49 b	50.56 ± 3.97 c	*
4 weeks	63.98 ± 4.12 a	50.73 ± 4.27 b	48.71 ± 3.27 b	*
6 weeks	74.13 ± 3.72 a	51.94 ± 3.23 b	49.65 ± 3.83 b	*
8 weeks	74.60 ± 3.55 a	52.20 ± 4.23 b	48.46 ± 4.32 c	*

Table I.2: Greenness (-a*) of lime fruits

Greenness (-a*)	Control fruits	Lime fruits inside LDPE packaging	Lime fruits inside composite packaging	F-test
0 day	-18.84 ± 0.93	-18.84 ± 0.93	-18.84 ± 0.93	ns
1 week	-18.00 ± 1.46	-18.42 ± 1.14	-17.33 ± 1.72	ns
2 weeks	-18.57 ± 0.94 b	-18.70 ± 1.20 b	-17.57 ± 1.02 a	*
3 weeks	-19.39 ± 1.10	-18.88 ± 1.08	-18.35 ± 1.65	ns
4 weeks	-17.97 ± 1.19	-18.37 ± 1.38	-17.71 ± 1.23	ns
6 weeks	-11.07 ± 3.53 a	-18.38 ± 1.67 b	-17.92 ± 1.40 b	*
8 weeks	-7.43 ± 3.11 a	-13.45 ± 7.56 b	-17.40 ± 1.51 c	*

Table I.3: Yellowness (b*) of lime fruits

Yellowness (b*)	**Control fruits**	**Lime fruits inside LDPE packaging**	**Lime fruits inside composite packaging**	**F-test**
0 day	35.37 ± 3.21	35.37 ± 3.21	35.37 ± 3.21	ns
1 week	33.82 ± 4.94 a	33.54 ± 3.90 a	29.54 ± 4.82 b	*
2 weeks	43.31 ± 4.79 a	37.09 ± 4.38 b	32.22 ± 3.90 c	*
3 weeks	46.30 ± 2.32 a	36.36 ± 3.51 b	33.81 ± 5.16 b	*
4 weeks	50.82 ± 3.82 a	34.01 ± 4.95 b	31.47 ± 3.78 b	*
6 weeks	55.62 ± 4.88 a	35.64 ± 3.59 b	32.83 ± 5.02 b	*
8 weeks	58.91 ± 2.98 a	35.27 ± 3.16 b	32.29 ± 5.40 c	*

Table I.4: Weight loss of lime fruits

Weight loss (%)	**Control fruits**	**Lime fruits inside LDPE packaging**	**Lime fruits inside composite packaging**	**F-test**
1 week	2.32 ± 0.37 a	0.03 ± 0.00 b	0.03 ± 0.00 b	*
2 weeks	4.89 ± 1.15 a	0.10 ± 0.01 b	0.08 ± 0.01 b	*
3 weeks	6.51 ± 0.25 a	0.15 ± 0.02 b	0.13 ± 0.01 b	*
4 weeks	7.01 ± 0.69 a	0.28 ± 0.04 b	0.27 ± 0.06 b	*
6 weeks	8.13 ± 0.37 a	0.43 ± 0.02 b	0.41 ± 0.05 b	*
8 weeks	10.53 ± 0.39 a	0.56 ± 0.02 b	0.55 ± 0.02 b	*

Table I.5: Firmness of lime fruits

Firmness (N)	**Control fruits**	**Lime fruits inside LDPE packaging**	**Lime fruits inside composite packaging**	**F-test**
0 day	34.36 ± 3.86	34.36 ± 3.86	34.36 ± 3.86	ns
1 week	34.82 ± 3.65	33.37 ± 3.25	33.87 ± 5.40	ns
2 weeks	37.57 ± 3.55	34.29 ± 4.00	35.83 ± 4.83	ns
3 weeks	36.56 ± 3.26 a	31.54 ± 1.86 b	32.64 ± 3.59 b	*
4 weeks	37.02 ± 3.09 a	28.13 ± 2.38 b	28.47 ± 2.49 b	*
6 weeks	37.67 ± 4.01 a	28.01 ± 5.71 b	27.06 ± 3.52 b	*
8 weeks	40.18 ± 3.70 a	26.51 ± 3.91 b	25.07 ± 3.78 b	*

Table I.6: Total soluble solids content of lime fruits

TSS (^{o}Brix)	Control fruits	Lime fruits inside LDPE packaging	Lime fruits inside composite packaging	F-test
0 day	8.60 ± 0.16	8.60 ± 0.16	8.60 ± 0.16	ns
1 week	8.20 ± 0.00	8.25 ± 0.19	8.30 ± 0.26	ns
2 weeks	9.00 ± 0.08 a	8.65 ± 0.25 b	8.15 ± 0.19 c	*
3 weeks	8.90 ± 0.36	8.50 ± 0.35	8.75 ± 0.30	ns
4 weeks	9.20 ± 0.57	9.25 ± 0.34	9.40 ± 0.73	ns
6 weeks	8.65 ± 0.44	8.20 ± 0.85	8.15 ± 0.19	ns
8 weeks	8.85 ± 0.19 a	7.95 ± 0.19 b	7.15 ± 0.44 b	*

Table I.7: Titratable acidity of lime fruits

TA (%)	Control fruits	Lime fruits inside LDPE packaging	Lime fruits inside composite packaging	F-test
0 day	7.48 ± 0.31	7.48 ± 0.31	7.48 ± 0.31	ns
1 week	7.49 ± 0.09	7.48 ± 0.09	7.58 ± 0.30	ns
2 weeks	7.84 ± 0.29	7.58 ± 0.19	7.72 ± 0.06	ns
3 weeks	7.98 ± 0.46 a	7.15 ± 0.11 b	7.86 ± 0.22 a	*
4 weeks	7.55 ± 0.34	7.38 ± 0.45	7.14 ± 0.36	ns
6 weeks	7.44 ± 0.21 a	6.44 ± 0.35 b	6.99 ± 0.70 ab	*
8 weeks	7.76 ± 0.17 a	5.96 ± 0.08 b	6.05 ± 0.45 b	*

Table I.8: TSS/TA ratio of lime fruits

TSS/TA	Control fruits	Lime fruits inside LDPE packaging	Lime fruits inside composite packaging	F-test
0 day	1.15 ± 0.07	1.15 ± 0.07	1.15 ± 0.07	ns
1 week	1.10 ± 0.01	1.10 ± 0.03	1.10 ± 0.02	ns
2 weeks	1.15 ± 0.04 a	1.14 ± 0.03 a	1.06 ± 0.03 b	*
3 weeks	1.12 ± 0.10	1.19 ± 0.06	1.11 ± 0.01	ns
4 weeks	1.22 ± 0.13	1.26 ± 0.07	1.32 ± 0.11	ns
6 weeks	1.16 ± 0.03	1.28 ± 0.19	1.18 ± 0.14	ns
8 weeks	1.14 ± 0.03 c	1.33 ± 0.03 a	1.28 ± 0.03 b	*

Table I.9: Vitamin C contents of lime fruits

Vitamin C (mg/ 100 ml juice)	Control fruits	Lime fruits inside LDPE packaging	Lime fruits inside composite packaging	F-test
0 day	43.66 ± 2.00	43.66 ± 2.00	43.66 ± 2.00	ns
1 week	38.87 ± 3.22	40.57 ± 2.14	39.72 ± 2.76	ns
2 weeks	44.66 ± 3.70 b	35.51 ± 2.49 a	38.22 ± 4.08 b	*
3 weeks	39.45 ± 5.53	35.55 ± 3.40	39.00 ± 1.52	ns
4 weeks	38.12 ± 3.13	38.48 ± 2.20	39.73 ± 3.92	ns
6 weeks	38.03 ± 5.31	34.90 ± 2.62	36.86 ± 1.63	ns
8 weeks	41.30 ± 1.83	35.62 ± 2.98	36.45 ± 6.80	ns

Table I.10: Oxygen accumulation in the package of lime fruits

O_2 accumulation (%)	Inside LDPE packaging	Inside composite packaging	F-test
1 week	3.68 ± 0.64	3.63 ± 0.66	ns
2 weeks	3.16 ± 1.31	3.67 ± 0.42	ns
3 weeks	3.03 ± 1.19	4.69 ± 1.20	ns
4 weeks	2.31 ± 1.51	2.88 ± 0.61	ns
6 weeks	3.24 ± 0.48	3.28 ± 0.42	ns
8 weeks	4.31 ± 0.24	4.63 ± 0.46	ns

Table I.11: Carbon dioxide accumulation in the package of lime fruits

CO_2 accumulation (%)	Inside LDPE packaging	Inside composite packaging	F-test
1 week	4.73 ± 0.71 a	3.57 ± 0.38 b	*
2 weeks	4.92 ± 1.27	4.52 ± 0.52	ns
3 weeks	5.81 ± 0.68 a	3.64 ± 0.31 b	*
4 weeks	6.69 ± 1.06 a	3.87 ± 1.23 b	*
6 weeks	6.52 ± 1.59 a	2.11 ± 0.51 b	*
8 weeks	1.34 ± 0.42	1.26 ± 0.65	ns

Table I.12: Ethylene accumulation in the package of lime fruits

C_2H_4 accumulation (ppm)	Inside LDPE packaging	Inside composite packaging	F-test
1 week	0.22 ± 0.08	0.13 ± 0.04	ns
2 weeks	0.77 ± 0.42	0.32 ± 0.22	ns
3 weeks	1.00 ± 0.26	0.57 ± 0.32	ns
4 weeks	0.51 ± 0.13	0.41 ± 0.21	ns
6 weeks	0.51 ± 0.21	0.33 ± 0.26	ns
8 weeks	0.69 ± 0.26	0.50 ± 0.30	ns

Table I.13: Lightness (L*) of mango peel

Lightness (L*)	Control fruits	Mango fruits inside LDPE packaging	Mango fruits inside composite packaging	F-test
0 day	76.77 ± 2.04	76.77 ± 2.04	76.77 ± 2.04	ns
1 week	78.11 ± 2.01 b	83.11 ± 2.36 a	76.44 ± 0.94 b	*
2 weeks	77.74 ± 1.12 a	76.73 ± 2.46 a	73.79 ± 1.88 b	*
3 weeks	77.12 ± 1.15 a	75.04 ± 1.02 b	74.89 ± 1.69 b	*
4 weeks	77.46 ± 3.00 a	73.85 ± 1.44 a	65.48 ± 10.83 b	*
5 weeks	75.36 ± 1.68 a	63.10 ± 11.45 b	65.91 ± 9.83 b	*

Table I.14: Lightness (L*) of mango pulp

Lightness (L*)	Control fruits	Mango fruits inside LDPE packaging	Mango fruits inside composite packaging	F-test
0 day	84.12 ± 1.94	84.12 ± 1.94	84.12 ± 1.94	ns
1 week	84.45 ± 1.88 a	74.99 ± 2.34 c	80.64 ± 2.24 b	*
2 weeks	82.07 ± 2.76 ab	84.44 ± 1.59 a	81.37 ± 2.47 b	*
3 weeks	84.55 ± 1.31	84.30 ± 1.30	84.63 ± 1.83	ns
4 weeks	83.52 ± 1.21	85.64 ± 0.84	81.12 ± 5.82	ns
5 weeks	81.10 ± 1.91	80.34 ± 1.18	80.31 ± 3.80	ns

Table I.15: Greenness (-a*) of mango peel

Greenness (-a*)	Control fruits	Mango fruits inside LDPE packaging	Mango fruits inside composite packaging	F-test
0 day	-7.79 ± 1.82	-7.79 ± 1.82	-7.79 ± 1.82	ns
1 week	-3.78 ± 2.42 a	-6.34 ± 1.45 b	-6.73 ± 0.75 b	*
2 weeks	-1.54 ± 0.64 a	-5.60 ± 1.11 b	-8.78 ± 0.90 c	*
3 weeks	-4.93 ± 1.52	-6.17 ± 2.15	-6.30 ± 1.78	ns
4 weeks	-1.99 ± 1.09 b	-5.24 ± 3.08 b	2.39 ± 6.11 a	*
5 weeks	-0.49 ± 0.97	2.28 ± 7.28	-1.20 ± 6.76	ns

Table I.16: Greenness (-a*) of mango pulp

Greenness (-a*)	Control fruits	Mango fruits inside LDPE packaging	Mango fruits inside composite packaging	F-test
0 day	-7.69 ± 0.87	-7.69 ± 0.87	-7.69 ± 0.87	ns
1 week	-5.07 ± 1.31	-6.57 ± 1.88	-6.74 ± 0.75	ns
2 weeks	-4.42 ± 0.71 a	-5.99 ± 0.67 b	-7.58 ± 1.07 c	*
3 weeks	-5.60 ± 0.44	-5.51 ± 0.46	-6.01 ± 1.20	ns
4 weeks	-5.16 ± 0.40	-4.50 ± 0.61	-3.64 ± 2.50	ns
5 weeks	-4.19 ± 0.80	-3.26 ± 1.62	-4.57 ± 0.86	ns

Table I.17: Yellowness (b*) of mango peel

Yellowness (b*)	Control fruits	Mango fruits inside LDPE packaging	Mango fruits inside composite packaging	F-test
0 day	31.74 ± 1.33	31.74 ± 1.33	31.74 ± 1.33	ns
1 week	33.52 ± 3.20 a	27.58 ± 2.31 b	34.61 ± 2.29 a	*
2 weeks	34.62 ± 3.21 a	31.70 ± 1.15 b	34.01 ± 1.46 a	*
3 weeks	34.66 ± 0.91 a	34.17 ± 1.38 ab	32.73 ± 2.04 b	*
4 weeks	36.62 ± 2.11 a	34.47 ± 1.41 a	25.70 ± 8.12 b	*
5 weeks	37.02 ± 2.72 a	24.00 ± 9.27 b	29.49 ± 7.42 b	*

Table I.18: Yellowness (b*) of mango pulp

Yellowness (b*)	Control fruits	Mango fruits inside LDPE packaging	Mango fruits inside composite packaging	F-test
0 day	27.21 ± 1.91	27.21 ± 1.91	27.21 ± 1.91	ns
1 week	26.43 ± 3.63 b	33.36 ± 2.51 a	28.68 ± 3.00 b	*
2 weeks	32.39 ± 9.64	25.37 ± 1.90	30.63 ± 2.62	ns
3 weeks	35.18 ± 2.47 a	27.10 ± 4.82 b	24.61 ± 2.79 b	*
4 weeks	37.47 ± 1.69 a	26.30 ± 2.77 b	26.61 ± 3.96 b	*
5 weeks	44.42 ± 1.98 a	24.67 ± 3.77 c	28.17 ± 1.80 b	*

Table I.19: Weight loss of mango fruits

Weight loss (%)	Control fruits	Mango fruits inside LDPE packaging	Mango fruits inside composite packaging	F-test
1 week	3.16 ± 0.68 a	0.36 ± 0.03 b	0.38 ± 0.08 b	*
2 weeks	4.44 ± 1.02 a	0.60 ± 0.02 b	0.58 ± 0.05 b	*
3 weeks	5.54 ± 0.60 a	0.85 ± 0.20 b	0.56 ± 0.05 b	*
4 weeks	8.13 ± 0.68 a	1.36 ± 0.14 b	1.11 ± 0.07 b	*
5 weeks	10.76 ± 1.03 a	1.35 ± 0.32 b	1.26 ± 0.41 b	*

Table I.20: Firmness of mango fruits

Firmness (N)	Control fruits	Mango fruits inside LDPE packaging	Mango fruits inside composite packaging	F-test
0 day	13.80 ± 3.49	13.80 ± 3.49	13.80 ± 3.49	ns
1 week	15.51 ± 1.36	13.85 ± 1.82	14.65 ± 2.46	ns
2 weeks	9.07 ± 4.19	10.05 ± 2.51	11.59 ± 3.11	ns
3 weeks	5.21 ± 1.95	5.64± 2.09	6.68 ± 4.48	ns
4 weeks	2.05 ± 1.37 b	3.94 ± 1.92 a	3.22 ± 0.30 ab	*
5 weeks	0.51 ± 0.00 b	3.45 ± 1.89 a	3.24 ± 0.27 a	*

Table I.21: Total soluble solids content of mango fruits

(TSS) °Brix	Control fruits	Mango fruits inside LDPE packaging	Mango fruits inside composite packaging	F-test
0 day	9.10 ± 0.12	9.10 ± 0.12	9.10 ± 0.12	ns
1 week	12.50 ± 1.29 a	10.10 ± 0.84 b	10.15 ± 0.57 b	*
2 weeks	15.00 ± 0.82 a	9.80 ± 0.16 b	10.40 ± 0.33 b	*
3 weeks	16.00 ± 0.49 a	9.80 ± 0.23 b	11.60 ± 1.82 b	*
4 weeks	16.05 ± 1.80 a	10.65 ± 1.09 b	11.50 ± 1.16 b	*
5 weeks	16.40 ± 1.30 a	10.90 ± 1.60 b	10.10 ± 1.40 b	*

Table I.22: Titratable acidity of mango fruits

TA (%)	Control fruits	Mango fruits inside LDPE packaging	Mango fruits inside composite packaging	F-test
0 day	1.72 ± 0.10	1.72 ± 0.10	1.72 ± 0.10	ns
1 week	1.54 ± 0.18 b	1.75 ± 0.23 ab	1.98 ± 0.15 a	*
2 weeks	1.16 ± 0.35 b	1.69 ± 0.22 a	1.71 ± 0.09 a	*
3 weeks	1.14 ± 0.10 b	1.84 ± 0.20 a	1.54 ± 0.45 ab	*
4 weeks	0.84 ± 0.06 b	1.49 ± 0.15 a	1.52 ± 0.34 a	*
5 weeks	0.53 ± 0.05 b	1.53 ± 0.08 a	1.54 ± 0.20 a	*

Table I.23: TSS/TA ratio of mango fruits

TSS/TA	Control fruits	Mango fruits inside LDPE packaging	Mango fruits inside composite packaging	F-test
0 day	9.37 ± 0.00	9.37 ± 0.00	9.37 ± 0.00	ns
1 week	8.20 ± 1.19 a	5.89 ± 1.11 b	5.14 ± 0.34 b	*
2 weeks	14.19 ± 5.68 a	5.89 ± 0.88 b	6.10 ± 0.45 b	*
3 weeks	14.05 ± 0.98 a	5.38 ± 0.71 b	8.32 ± 3.72 b	*
4 weeks	19.22 ± 2.34 a	7.23 ± 1.28 b	7.87 ± 2.20 b	*
5 weeks	31.29 ± 1.74 a	7.14 ± 1.20 b	6.72 ± 1.60 b	*

Table I.24: Vitamin C contents of mango fruits

Vitamin C (mg/ 100 ml juice)	Control fruits	Mango fruits inside LDPE packaging	Mango fruits inside composite packaging	F-test
0 day	14.64 ± 6.21	14.64 ± 6.21	14.64 ± 6.21	ns
1 week	14.09 ± 0.68	14.47 ± 2.14	14.65 ± 1.56	ns
2 weeks	10.60 ± 2.28	11.85 ± 3.53	12.83 ± 2.71	ns
3 weeks	9.07 ± 2.76	12.09 ± 4.11	13.55 ± 2.50	ns
4 weeks	7.09 ± 1.32	13.18 ± 1.26	11.99 ± 4.00	ns
5 weeks	6.68 ± 1.59	9.40 ± 5.28	13.10 ± 4.08	ns

Table I.25: Oxygen accumulation in the package of mango fruits

O_2 accumulation (%)	Inside LDPE packaging	Inside composite packaging	F-test
1 week	0.48 ± 0.12	0.57 ± 0.09	ns
2 weeks	1.44 ± 0.14 b	2.69 ± 0.75 a	*
3 weeks	0.69 ± 0.10	0.88 ± 0.22	ns
4 weeks	0.58 ± 0.09 b	12.8 ± 0.26 a	*
5 weeks	0.82 ± 0.16	0.98 ± 0.09	ns

Table I.26: Carbon dioxide accumulation in the package of mango fruits

CO_2 accumulation (%)	Inside LDPE packaging	Inside composite packaging	F-test
1 week	9.31 ± 0.62	7.87 ± 1.17	ns
2 weeks	7.21 ± 0.84	6.05 ± 1.50	ns
3 weeks	6.68 ± 0.64 a	4.88 ± 0.54 b	*
4 weeks	4.60 ± 1.21	5.88 ± 1.40	ns
5 weeks	4.97 ± 2.24	4.24 ± 3.19	ns

Table I.27: Ethylene accumulation in the package of mango fruits

C_2H_4 accumulation (ppm)	Inside LDPE packaging	Inside composite packaging	F-test
1 week	0.0020 ± 0.0003 b	0.0047 ± 0.0009 a	*
2 weeks	0.0019 ± 0.0004	0.0015 ± 0.0010	ns
3 weeks	0.0042 ± 0.0019	0.0063 ± 0.0036	ns
4 weeks	0.0040 ± 0.0012	0.0034 ± 0.0010	ns
5 weeks	0.0042 ± 0.0008	0.0041 ± 0.0014	ns

Table I.28: Lightness (L*) of ripen - mango peel

Lightness (L*)	Control fruits	Mango fruits inside LDPE packaging	Mango fruits inside composite packaging	F-test
0 day	72.72 ± 3.62	72.72 ± 3.62	72.72 ± 3.62	ns
1 week	77.16 ± 2.02	74.41 ± 0.85	71.43 ± 2.15	ns
2 weeks	72.42 ± 1.46 b	72.49 ± 2.50 b	76.62 ± 0.96 a	*
3 weeks	76.06 ± 1.39	75.10 ± 1.80	75.68 ± 1.92	ns
4 weeks	74.90 ± 1.92 a	71.33 ± 2.41 b	71.80 ± 1.82 b	*
5 weeks	73.76 ± 1.82 a	65.78 ± 5.79 b	72.13 ± 3.33 a	*

Table I.29: Lightness (L*) of ripen - mango pulp

Lightness (L*)	Control fruits	Mango fruits inside LDPE packaging	Mango fruits inside composite packaging	F-test
0 day	86.36 ± 0.97	86.36 ± 0.97	86.36 ± 0.97	ns
1 week	85.32 ± 1.92	85.13 ± 0.97	85.03 ± 1.71	ns
2 weeks	75.57 ± 1.52 a	74.75 ± 2.91 a	71.70 ± 2.81 b	*
3 weeks	78.64 ± 0.89	79.48 ± 1.65	79.26 ± 1.67	ns
4 weeks	77.42 ± 2.32	78.26 ± 3.92	78.51 ± 2.88	ns
5 weeks	72.66 ± 9.86	73.52 ± 12.54	77.54 ± 4.97	ns

Table I.30: Greenness (-a*) of ripen - mango peel

Greenness (-a*)	Control fruits	Mango fruits inside LDPE packaging	Mango fruits inside composite packaging	F-test
0 day	-12.15 ± 1.58	-12.15 ± 1.58	-12.15 ± 1.58	ns
1 week	-9.80 ± 2.34	-12.39 ± 0.73	-13.35 ± 1.32	ns
2 weeks	2.31 ± 2.45 a	-1.93 ± 2.42 b	3.31 ± 0.74 a	*
3 weeks	1.42 ± 0.77 a	-1.37 ± 1.60 b	1.12 ± 2.27 a	*
4 weeks	1.56 ± 0.60 a	-1.19 ± 2.16 b	-3.19 ± 1.94 c	*
5 weeks	1.29 ± 1.44	-2.30 ± 5.17	-2.51 ± 4.56	ns

Table I.31: Greenness (-a*) of ripen - mango pulp

Greenness (-a*)	Control fruits	Mango fruits inside LDPE packaging	Mango fruits inside composite packaging	F-test
0 day	-7.47 ± 0.47	-7.47 ± 0.47	-7.47 ± 0.47	ns
1 week	-6.78 ± 0.91	-8.87 ± 0.75	-8.86 ± 1.66	ns
2 weeks	2.75 ± 1.51 ab	3.88 ± 1.64 a	2.60 ± 2.60 b	*
3 weeks	1.84 ± 1.02 a	-0.72 ± 0.84 b	0.04 ± 1.55 b	*
4 weeks	0.92 ± 1.26	0.07 ± 2.35	-1.23 ± 1.19	ns
5 weeks	1.57 ± 2.69	-0.40 ± 4.00	-0.41 ± 1.90	ns

Table I.32: Yellowness (b*) of ripen - mango peel

Yellowness (b*)	Control fruits	Mango fruits inside LDPE packaging	Mango fruits inside composite packaging	F-test
0 day	35.68 ± 1.54	35.68 ± 1.54	35.68 ± 1.54	ns
1 week	32.27 ± 2.18	33.38 ± 1.69	34.17 ± 1.05	ns
2 weeks	49.10 ± 2.47	48.20 ± 2.41	51.70 ± 3.60	ns
3 weeks	41.51 ± 1.73	37.64 ± 4.86	40.70 ± 228	ns
4 weeks	50.61 ± 1.61 a	45.76 ± 3.15 b	44.70 ± 3.25 b	*
5 weeks	47.54 ± 3.73 a	38.23 ± 5.49 b	47.05 ± 2.72 a	*

Table I.33: Yellowness (b*) of ripen - mango pulp

Yellowness (b*)	**Control fruits**	**Mango fruits inside LDPE packaging**	**Mango fruits inside composite packaging**	**F-test**
0 day	25.06 ± 3.67	25.06 ± 3.67	25.06 ± 3.67	ns
1 week	24.58 ± 1.84 b	27.12 ± 2.79 ab	26.25 ± 4.30 a	*
2 weeks	51.06 ± 1.62 a	52.63 ± 2.91 a	46.43 ± 3.61 b	*
3 weeks	42.63 ± 1.89	42.45 ± 3.06	5.10 ± 3.16	ns
4 weeks	51.22 ± 3.82	47.31 ± 5.17	46.11 ± 3.72	ns
5 weeks	44.51 ± 7.39	36.67 ± 7.68	45.04 ± 7.47	ns

Table I.34: Firmness of ripen - mango fruits

Firmness (N)	**Control fruits**	**Mango fruits inside LDPE packaging**	**Mango fruits inside composite packaging**	**F-test**
0 day	0.25 ± 0.02	0.25 ± 0.02	0.25 ± 0.02	ns
1 week	0.21 ± 0.01	0.22 ± 0.01	0.23 ± 0.03	ns
2 weeks	0.22 ± 0.04	0.24 ± 0.02	0.21 ± 0.02	ns
3 weeks	0.25 ± 0.04	0.26 ± 0.03	0.29 ± 0.05	ns
4 weeks	0.23 ± 004 b	0.33 ± 0.07 a	0.25 ± 0.05 b	*
5 weeks	0.25 ± 0.05	0.31 ± 0.10	0.24 ± 0.04	ns

Table I.35: Total soluble solids content of ripen - mango fruits

TSS (°**Brix)**	**Control fruits**	**Mango fruits inside LDPE packaging**	**Mango fruits inside composite packaging**	**F-test**
0 day	14.83 ± 1.63	14.83 ± 1.63	14.83 ± 1.63	ns
1 week	15.55 ± 1.65	14.65 ± 1.93	14.20 ± 0.77	ns
2 weeks	14.20 ± 0.85	14.05 ± 1.32	13.25 ± 0.50	ns
3 weeks	14.60 ± 1.45	15.70 ± 0.38	16.00 ± 1.51	ns
4 weeks	12.30 ± 0.62	13.80 ± 1.83	13.75 ± 1.99	ns
5 weeks	13.15 ± 0.94	13.67 ± 1.79	12.90 ± 0.96	ns

Table I.36: Titratable acidity of ripen - mango fruits

TA (%)	Control fruits	Mango fruits inside LDPE packaging	Mango fruits inside composite packaging	F-test
0 day	0.12 ± 0.01	0.12 ± 0.01	0.12 ± 0.01	ns
1 week	0.12 ± 0.02	0.17 ± 0.06	0.12 ± 0.01	ns
2 weeks	0.12 ± 0.01 b	0.18 ± 0.03 a	0.14 ± 0.02 b	*
3 weeks	0.14 ± 0.02	0.41 ± 0.19	0.38 ± 0.30	ns
4 weeks	0.14 ± 0.02	0.64 ± 0.35	0.52 ± 0.39	ns
5 weeks	0.17 ± 0.02	0.76 ± 0.24	0.31 ± 0.09	ns

Table I.37: TSS/TA ratio of ripen - mango fruits

TSS/TA	Control fruits	Mango fruits inside LDPE packaging	Mango fruits inside composite packaging	F-test
0 day	130.01 ± 23.17	130.01 ± 23.17	130.01 ± 23.17	ns
1 week	132.89 ± 20.96 a	90.35 ± 22.48 b	123.99 ± 13.97 a	*
2 weeks	118.09 ± 18.51 a	81.44 ± 17.18 b	97.64 ± 16.28 ab	*
3 weeks	107.38 ± 16.51	46.63 ± 24.85	81.46 ± 72.70	ns
4 weeks	87.33 ± 15.90 a	27.39 ± 15.75 b	35.04 ± 16.95 b	*
5 weeks	78.58 ± 13.73 a	19.73 ± 8.78 b	45.10 ± 14.80 b	*

Table I.38: Vitamin C contents of ripen - mango fruits

Vitamin C (mg/ 100 ml juice)	Control fruits	Mango fruits inside LDPE packaging	Mango fruits inside composite packaging	F-test
0 day	8.81 ± 3.98	8.81 ± 3.98	8.81 ± 3.98	ns
1 week	10.51 ± 1.47 a	6.86 ± 1.35 b	11.32 ± 0.94 a	*
2 weeks	3.39 ± 1.28 b	7.23 ± 2.34 a	8.97 ± 0.92 a	*
3 weeks	2.53 ± 0.29	4.69 ± 2.75	2.17 ± 0.29	ns
4 weeks	1.56 ± 0.18	3.85 ± 2.65	6.96 ± 6.89	ns
5 weeks	2.68 ± 0.47	6.71 ± 2.01	2.18 ± 0.34	ns

Remark:

1. The data shown in each table were average data and standard deviation of each treatment including with statistical difference.
2. ns = the data were insignificant differences
3. * = the data were significant differences
4. An alphabetic character was used as the sign of statistical difference

VITA

Miss Netnapha Lamo was born in Nonthaburi, Thailand on May 21, 1983. She completed senior high school at Cholprathanwittaya School, Thailand in 2001 and received Bachelor degree with 2nd degree honors from the Department of Industrial Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Thailand in 2005. She worked at ICI PAINTS (THAILAND) LIMITED for one and half years after that she continued her study for Master degree at Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University Bangkok, Thailand.

She was invited for oral presentation in Seventh International Conference on Composite Science and Technology (ICCST/7) that was organized by Institute of Materials Systems, College of Engineering, American University of Sharjah. This conference was held during January 20-22, 2009 at American University of Sharjah, United Arab Emirates. In addition, she was also invited for oral presentation in KU conference 47th that was an annual event organized by Kasetsart University. This conference was held during March, 17-20, 2009 at Kasetsart University, Bangkhen Campus Bangkok, Thailand.