

การเตรียมไฟล์พอลิยูรีเทนชีวภาพจากพอลิออลชีวภาพ

นางสาวทศชา สนจ้อย



จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

บทคัดย่อและแฟ้มข้อมูลฉบับเต็มของวิทยานิพนธ์ตั้งแต่ปีการศึกษา 2554 ที่ให้บริการในคลังปัญญาจุฬาฯ (CUIR)

เป็นแฟ้มข้อมูลของนิสิตเจ้าของวิทยานิพนธ์ ที่ส่งผ่านทางบัณฑิตวิทยาลัย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาค้นคว้าตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต

The abstract and full text of theses from the academic year 2011 in Chulalongkorn University Intellectual Repository (CUIR) are the thesis authors' files submitted through the University Graduate School.

สาขาวิชาวัสดุศาสตร์ ภาควิชาวัสดุศาสตร์

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2558

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

PREPARATION OF BIO-BASED POLYURETHANE FOAMS FROM BIO-
BASED POLYOLS

Miss Tatcha Sonjui



A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy Program in Materials Science

Department of Materials Science

Faculty of Science

Chulalongkorn University

Academic Year 2015

Copyright of Chulalongkorn University

Thesis Title	PREPARATION OF BIO-BASED POLYURETHANE FOAMS FROM BIO- BASED POLYOLS
By	Miss Tatcha Sonjui
Field of Study	Materials Science
Thesis Advisor	Assistant Professor Nantana Jiratumnukul, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial
Fulfillment of the Requirements for the Doctoral Degree

..... Dean of the Faculty of Science
(Associate Professor Polkit Sangvanich, Ph.D.)

THESIS COMMITTEE

..... Chairman
(Associate Professor Nisanart Traiphol, Ph.D.)

..... Thesis Advisor
(Assistant Professor Nantana Jiratumnukul, Ph.D.)

..... Examiner
(Assistant Professor Sireerat Charuchinda, Ph.D.)

..... Examiner
(Assistant Professor Siriwan Kittinaovarat, Ph.D.)

..... External Examiner
(Associate Professor Cholticha Noomhorm, Ph.D.)

ทัชชา สนธิชัย : การเตรียมโฟมพอลิยูรีเทนชีวภาพจากพอลิออลชีวภาพ (PREPARATION OF BIO-BASED POLYURETHANE FOAMS FROM BIO-BASED POLYOLS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร. นันทนา จิรธรรมนุกูล, 144 หน้า.

งานวิจัยนี้เป็นการศึกษาการเตรียมพอลิออลชีวภาพจากกรดชีวภาพโดยพอลิออลชีวภาพเตรียมได้โดยการทำปฏิกิริยาการควบแน่นระหว่างกรดซัคซินิกและไกลคอล 7 ชนิด โดยศึกษาผลกระทบของความยาวสายโซ่ของไกลคอลและชนิดของไกลคอล ซึ่งแบ่งออกเป็น 2 ชนิดคือ ไกลคอลเดี่ยวและไกลคอลผสม ที่มีต่อสมบัติของพอลิออลที่เตรียมได้ จากนั้นนำพอลิออลชีวภาพที่เตรียมได้มาเตรียมโฟมพอลิยูรีเทน โดยเปรียบเทียบสมบัติของโฟมพอลิยูรีเทนชีวภาพที่เตรียมกับโฟมพอลิยูรีเทนที่เตรียมจากพอลิออลทางการค้า ผลพบว่าโฟมพอลิยูรีเทนที่เตรียมจากพอลิออลชีวภาพชนิดไกลคอลผสมจากไดเอทิลีนไกลคอลและกลีเซอรอลให้โฟมที่มีสมบัติที่ดีกว่าโฟมพอลิยูรีเทนที่เตรียมจากพอลิออลทางการค้า ในด้านของความสม่ำเสมอของเซลล์ โฟม เซลล์โฟมมีขนาดเล็กกว่าและโฟมมีค่าการทนต่อแรงกดอัดสูงกว่า จากนั้นศึกษาผลกระทบของค่าดัชนีไอโซไซยานเนตที่มีต่อสมบัติของโฟม โดยทำการเตรียมโฟมพอลิยูรีเทนจากพอลิออลชีวภาพซึ่งได้จากปฏิกิริยาการควบแน่นของกรดซัคซินิกและไกลคอลผสมจากไดเอทิลีนไกลคอลและกลีเซอรอล โดยนำพอลิออลนี้มาทำปฏิกิริยากับเมทิลีนไดฟีนิลไดไอโซไซยานเนตที่ค่าดัชนีไอโซไซยานเนตต่าง ๆ กัน เปรียบเทียบกับโฟมที่เตรียมจากพอลิออลทางการค้าที่ค่าดัชนีไอโซไซยานเนตต่าง ๆ กันด้วย พบว่าโฟมทั้งสองชนิดที่เตรียมจากพอลิออลชีวภาพและพอลิออลทางการค้าให้ขนาดของเซลล์โฟมที่ไม่แตกต่างกันเมื่อเตรียมจากค่าดัชนีไอโซไซยานเนตต่างกัน ในขณะที่ความหนาแน่นและค่าการทนต่อแรงกดอัดของโฟมมีค่าสูงขึ้นเมื่อค่าดัชนีไอโซไซยานเนตสูงขึ้น โฟมที่เตรียมจากพอลิออลชีวภาพที่ค่าดัชนีไอโซไซยานเนตเท่ากับ 200 ให้ค่าการทนต่อแรงกดอัดสูงที่สุดเมื่อเปรียบเทียบกับโฟมทุกสูตรที่เตรียม ดังนั้น โฟมสูตรนี้จึงถูกนำมาใช้เตรียมโฟมนาโนคอมพอสิตเพื่อศึกษาถึงผลกระทบของดินกระจายตัว 2 ชนิดที่ผสมลงในสูตรโฟม โดยดินกระจายตัวชนิดแรกได้ผ่านการปรับปรุงคุณสมบัติให้มีช่องว่างระหว่างชั้นดินเพิ่มขึ้น ส่วนดินกระจายตัวอีกชนิดนั้นไม่ได้ผ่านการปรับปรุงคุณสมบัติ อัตราส่วนของดินกระจายตัวที่ผสมในสูตรโฟมคือ 0.5, 1, 1.5, 2, 3, 5 และ 7 ส่วนในร้อยส่วนพอลิออล ผลพบว่าโฟมพอลิยูรีเทนที่ผสมด้วยดินที่ปรับปรุงคุณสมบัติที่อัตราส่วน 1 ส่วนในร้อยส่วนพอลิออลนั้นให้ค่าการทนต่อแรงกดอัดสูงที่สุด

ภาควิชา วัสดุศาสตร์

ลายมือชื่อนิติคุณ

สาขาวิชา วัสดุศาสตร์

ลายมือชื่อ อ.ที่ปรึกษาหลัก

ปีการศึกษา 2558

5472824423 : MAJOR MATERIALS SCIENCE

KEYWORDS: BIO-BASED POLYESTER POLYOL, BIO-BASED POLYURETHANE FOAM, SUCCINIC ACID, NANOCCLAY, NANOCOMPOSITE

TATCHA SONJUI: PREPARATION OF BIO-BASED POLYURETHANE FOAMS FROM BIO-BASED POLYOLS. ADVISOR: ASST. PROF. NANTANA JIRATUMNUKUL, Ph.D., 144 pp.

Bio-based polyester polyols from bio-based acid were synthesized by condensation reaction using succinic acid (SA) and seven different glycols. The effects of chain length of glycol and glycol types (neat or mixed glycols) used to prepare polyols toward physical and mechanical properties of the prepared polyurethane (PU) foams were investigated relatively to PU foam prepared from a commercial polyester polyol. It was found that PU foam prepared from SA and mixture of diethylene glycol (DEG) and glycerol provided good cell size and smallest cell dimension resulting highest compressive strength relative to other types of polyols used in PU foams preparation. The effect of isocyanate (NCO) index on morphology and mechanical properties of foams were also studied. PU foams were prepared from mixed DEG-glycerol polyol and polymeric methylene diphenyl diisocyanate (PMDI) at different NCO indexes relative to PU foams prepared from commercial polyol. The results showed that cell size of PU foams prepared from bio-based polyol were virtually insensitive to NCO indexes, but density and compressive strength increased as the NCO indexes increased. This results was also found in PU foams prepared from commercial polyol. PU foam prepared from bio-based polyol at NCO index of 200 provided highest compressive strength. PU foam/clay nanocomposites were prepared by incorporating two types of clays into PU foam prepared from mixed DEG-glycerol polyol and PMDI at NCO index of 200. The clay contents, both modified (C30B) and unmodified (MMT), were varied at the levels of 0.5, 1, 1.5, 2, 3, 5, and 7 php. It was found that PU foam incorporated with nanoclay C30B at 1 php imparted highest compressive strength.

Department: Materials Science Student's Signature

Field of Study: Materials Science Advisor's Signature

Academic Year: 2015

ACKNOWLEDGEMENTS

It is a pleasure to appreciate the many people who made this dissertation possible.

I would like to express my sincere gratitude and deep appreciation to my advisor, Asst. Prof. Nantana Jiratumnukul, Ph.D., for her unfailing support and patience in my Ph.D. study. She offered guidance, encouragement, and many good ideas. All her help made it possible for me to complete this project.

I also appreciate my committee members Assoc. Prof. Cholticha Noomhorm, Ph.D., Asst. Prof. Sireerat Charuchinda, Ph.D., and Asst. Prof. Siriwan Kittinaovarat, Ph.D. for their valuable time, helpful suggestions and critical reviews on the dissertation.

I sincerely thank Department of Materials Science, Chulalongkorn University and all staffs in the department especially Mr.Sompong Chutikulswadi for his kindly help through my experimental set up and his teaching on every testing machines I need to use. I would also like to thank to my friends. This work would also not have been possible without the support and cheer from them.

Finally, I owe my love and respect to my parents and my brothers who have always been the source of my unconditional love, understanding and generous encouragement throughout my entire study.

CONTENTS

	Page
THAI ABSTRACT	iv
ENGLISH ABSTRACT.....	v
ACKNOWLEDGEMENTS	vi
CONTENTS.....	vii
CHAPTER I INTRODUCTION.....	19
1.1 General introduction	19
1.2 Objectives of the present study.....	22
1.3 Scopes of the research	23
CHAPTER II THEORY AND LITERATURE REVIEWS	25
2.1 Introduction to polymeric foams	25
2.1.1 Closed cell foams	25
2.1.2 Opened cell foams	26
2.1.3 Rigid foams	27
2.1.4 Flexible foams	27
2.2 Principles of foam formation	27
2.2.1 Bubble formation.....	28
2.2.2 Bubble growth	29
2.3 Application of cellular polymers	32
2.4 Polyurethane foams (PU foams).....	32
2.5 Raw materials used in PU foams	34
2.5.1 Isocyanates	34
2.5.1.1 Toluene diisocyanate (TDI).....	34
2.5.1.2 4,4' Diphenylmethane diisocyanate, or methylene diphenylene diisocyanate (MDI).....	35
2.5.1.3 Polymeric 4,4' diphenylmethane diisocyanate (PMDI).....	35
2.5.1.4 Isocyanate index	36
2.5.2 Polyols	37
2.5.2.1 Polyether polyols	37

	Page
2.5.2.2 Polyester polyols	38
2.5.2.3 Polyol characterizations.....	39
2.5.2.3.1 Hydroxyl number.....	39
2.5.2.3.2 Functionality	40
2.5.2.3.3 Molecular weight and molecular weight distribution	40
2.5.2.3.4 Equivalent weight	41
2.5.2.3.5 Viscosity	41
2.5.2.3.6 Acid number	42
2.5.3 Catalysts	42
2.5.4 Blowing agents	43
2.5.5 Surfactants	43
2.5.6 Additives	44
2.5.6.1 Flame retardants	44
2.5.6.2 Fillers.....	44
2.5.6.3 Coloring materials	44
2.5.6.4 Chain extenders/crosslinking agents	44
2.6 Chemical reactions of PU foams	45
2.6.1 Primary reactions of isocyanates.....	45
2.6.1.1 Reaction with hydroxyl compounds.....	45
2.6.1.2 Reaction with water.....	46
2.6.1.3 Reaction with amines	47
2.6.2 Secondary reactions of isocyanates.....	47
2.6.2.1 Reaction with urethanes	48
2.6.2.2 Reaction with urea.....	48
2.7 Manufacture of PU foams.....	48
2.7.1 Laboratory production of PU foams.....	49
2.8 Bio-based polyester polyols.....	49
2.8.1 Synthesis of polyester polyols.....	49

	Page
2.8.2 Succinic acid.....	51
2.8.3 Polyester polyols from succinic acid.....	52
2.9 Polyurethane foam nanocomposites	53
2.9.1 Clay and organoclay	54
2.9.1.1 Clay	54
2.9.1.2 Organoclay	57
2.9.1.3 Dispersion of clay in polymer matrix.....	58
2.10 Literature reviews	60
2.10.1 Bio-based polyols	61
2.10.2 PU foam/clay nanocomposites	62
CHAPTER III EXPERIMENT	66
3.1 Materials	66
3.2 Instruments	68
3.3 Methods	69
3.3.1 Synthesis of bio-based polyester polyols	69
3.3.2 Preparation of bio-based polyurethane foams	72
3.3.3 Preparation of bio-based polyurethane foams with different isocyanate indexes.....	74
3.3.4 Preparation of PU foam/clay nanocomposites	75
3.4 Characterizations	76
3.4.1 Viscosity	76
3.4.2 Hydroxyl number and Acid number.....	77
3.4.3 Chemical structure.....	77
3.4.3.1 Fourier transforms infrared (FTIR) analysis	77
3.4.3.2 Nuclear Magnetic Resonance (NMR) analysis	78
3.4.4 Molecular weights	79
3.4.5 Foam formation time	79
3.4.6 Morphology analysis	80
3.4.7 Foam density	81

	Page
3.4.8 Compressive strength	81
3.4.9 Dispersion of clays in PU matrix	82
3.4.10 Thermal stability.....	83
CHAPTER IV RESULTS AND DISCUSSION.....	84
4.1 Synthesis of bio-based polyester polyols.....	84
4.1.1 Chemical structure.....	86
4.1.1.1 NMR spectra.....	86
4.1.1.2 FTIR spectra	88
4.1.2 Physical properties	91
4.1.2.1 Acid number	91
4.1.2.2 Hydroxyl number (OH number).....	91
4.1.2.3 Viscosity	92
4.1.2.4 Molecular weights	95
4.1.3 Selection of polyols for PU foams preparation	97
4.2 Characteristics and properties of bio-based polyurethane foams	98
4.2.1 Chemical structure.....	98
4.2.2 Foam formation time	102
4.2.3 Morphology	103
4.2.4 Foam density	109
4.2.5 Compressive strength	110
4.2.6 Thermal stability.....	113
4.2.7 Selection of polyols to study the effect of isocyanate index on the properties of polyurethane foams	115
4.3 Effect of isocyanate index on properties of polyurethane foams.....	116
4.3.1 Chemical structure.....	116
4.3.2 Foam formation time	118
4.3.3 Morphology	119
4.3.4 Foam density	124
4.3.5 Compressive strength	125

	Page
4.3.6 Selection of foam formulation to use in PU foam/clay nanocomposites study	127
4.4 Characteristics and properties of bio-based polyurethane foams/clay nanocomposites	128
4.4.1 Chemical structure.....	129
4.4.2 Dispersion of clays in PU foams	130
4.4.3 Foam formation time	132
4.4.4 Morphology	134
4.4.5 Foam density	142
4.4.6 Compressive strength	143
4.4.7 Thermal stability.....	144
CHAPTER V CONCLUSION.....	1
5.1 Conclusion	1
5.2 Suggestion for future work	2
REFERENCES	3
Appendix A.....	8
VITA.....	13

LIST OF FIGURES

	Page
Figure 1.1 Characteristics of polyurethane materials	19
Figure 1.2 General reaction of polyurethane synthesis from diol and diisocyanate.....	20
Figure 2.1 Closed cell foam structures (a) discrete cell dispersed in foam (b) cells in contact with each other	25
Figure 2.2 Idealized representation of opened cell foam structure	26
Figure 2.3 (a) Opened cell structural element (b) Closed cell structural element	26
Figure 2.4 Schematic representations of cellular structures at different stages of foam	30
Figure 2.5 Schematic representation of closed cell deformation	32
Figure 2.6 Toluene diisocyanate isomers used for PU foams manufacture	34
Figure 2.7 Molecular structure of MDI	35
Figure 2.8 Molecular structure of PMDI	35
Figure 2.9 Example of aliphatic and aromatic dicarboxylic acids used in the production of polyester polyols	38
Figure 2.10 Reaction of hydroxyl end groups with phthalic anhydrides	40
Figure 2.11 Catalyst for the reaction between isocyanates with hydroxyl or water	47
Figure 2.12 Production of polyester polyols from (a) adipic acid and 1,4-butanediol, and (b) phthalic anhydride and diethylene glycol	50
Figure 2.13 Chemical structure of succinic acid.....	51
Figure 2.14 Various chemicals and products that can be synthesized from succinic acid.....	52

Figure 2.15 Production of succinate polyester polyols from succinic acid and glycol.....	53
Figure 2.16 Silicon-Oxygen Tetrahedron, (SiO ₄)	54
Figure 2.17 The tetrahedral sheet, [Si ₄ O ₁₀] ⁴⁻ (Top view)	55
Figure 2.18 Aluminum Octahedron, Al(OH) ₆ ³⁻	55
Figure 2.19 Structural scheme of the montmorillonite	57
Figure 2.20 Illustration of the three different types of polymer/clay nanocomposites: (a) phase separated microcomposite, (b) intercalated nanocomposite, (c) exfoliated nanocomposite	59
Figure 3.1 Chemical structure of glycols used in the experiment.....	71
Figure 3.2 The experiment set up for the synthesis of bio-based succinate polyols.....	72
Figure 3.3 The schematic diagram of lab scale PU foam formation.....	73
Figure 3.4 Brookfield viscometer model RVT	77
Figure 3.5 Thermo Scientific Nicolet 6700 FTIR spectrophotometer	78
Figure 3.6 Varian Mercury-VX 400 MHz BB NMR spectrometer	78
Figure 3.7 Class VP CTO-10ACvp Gel Permeation Chromatography	79
Figure 3.8 SZ-CTV Olympus Optical Microscope	80
Figure 3.9 Ametek UTM Hounsfield testing equipment model LLOYD 500.....	81
Figure 3.10 Bruker AXS model D8 X-ray diffractometer	82
Figure 3.11 Mettler Toledo TGA/STDA 851e Thermogravimetric Analyzer.....	83
Figure 4.1 Production of bio-based succinate polyol from succinic acid and excess glycol.....	85
Figure 4.2 ¹ H-NMR spectrum of bio-based succinate polyol prepared from SA and DEG at the molar ratio of 1:2.....	87
Figure 4.3 ¹ H-NMR spectrum of bio-based succinate polyol prepared from SA and mixed DEG-glycerol at the molar ratio of 1:1.5:0.33	88

- Figure 4.4** FTIR spectra of the synthesized bio-based succinate polyols from reaction of SA and neat glycol at the molar ratio of 1:2, (a) SA:DEG, (b) SA:TEG, (c) SA:TTEG, and (d) SA:PEG300 89
- Figure 4.5** FTIR spectra of the synthesized bio-based succinate polyols from reaction of SA and mixed glycol at the molar ratio of 1:1.5:0.33, (a) SA:DEG:Gly, (b) SA:TEG:Gly, (c) SA:TTEG:Gly, and (d) SA:PEG300:Gly 90
- Figure 4.6** Appearance of the synthesized bio-based succinate polyols 93
- Figure 4.7** A five-repeat unit computer model of succinate polyols with an even numbered carbon glycol (1,4-butanediol, (a)) and an odd numbered carbon glycol (1,3-propanediol, (b)) 95
- Figure 4.8** Polyurethane synthesis from synthesized bio-based polyester polyols with 4,4' PMDI 98
- Figure 4.9** FTIR spectra of bio-based PU foams prepared from SA and neat-glycol polyols at the molar ratio of 1:2, (a) SA:DEG, (b) SA:TEG, (c) SA:TTEG, and (d) SA:PEG300 100
- Figure 4.10** FTIR spectra of bio-based PU foams prepared from SA and mixed-glycol polyols at the molar ratio of 1:1.5:0.33, (a) SA:DEG:Gly, (b) SA:TEG:Gly, (c) SA:TTEG:Gly, and (d) SA:PEG300:Gly 101
- Figure 4.11** Cubic specimens of bio-based PU foams prepared from SA and neat-glycol polyols (top), PU foams prepared from SA and mixed-glycol polyols (bottom) 105
- Figure 4.12** OM images of the bio-based PU foams prepared from SA and neat-glycol polyols at the molar ratio of 1:2; (a) SA:DEG, (b) SA:TEG, (c) SA:TTEG and (d) SA:PEG300 106
- Figure 4.13** OM images of bio-based PU foams prepared from SA and mixed-glycol polyols at the molar ratio of 1:1.5:0.33; (a) SA:DEG:Gly, (b) SA:TEG:Gly, (c) SA:TTEG:Gly and (d) SA:PEG300:Gly 107
- Figure 4.14** Cubic specimen and OM image of the PU foam prepared from SA and commercial polyester polyol (A8360) 108

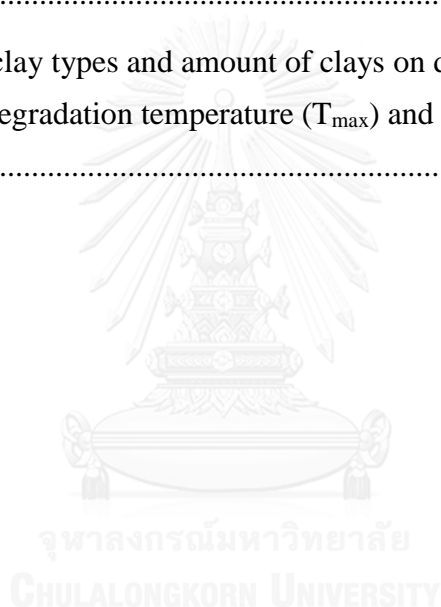
Figure 4.15 Bulk density of the PU foams prepared from neat or mixed-glycol polyols relative to one prepared from commercial polyol (A8360)	110
Figure 4.16 Compressive strength of the PU foams prepared from neat or mixed-glycol polyols relative to one prepared from commercial polyol (A8360)	112
Figure 4.17 TGA curves of PU foams prepared from neat or mixed-glycol polyols relative to one prepared from commercial polyol (A8360)	114
Figure 4.18 FTIR spectra of PU foams prepared from mixed DEG-glycerol polyol at different NCO indexes, (a) NCO100, (b) NCO150, (c) NCO200 and PU foams prepared from commercial polyol at different NCO indexes (d) NCO100, (e) NCO150, (f) NCO200.....	118
Figure 4.19 Cubic specimen of PU foams prepared from mixed DEG-glycerol polyol (top) and PU foams prepared from commercial polyol (bottom) at different NCO indexes	121
Figure 4.20 OM images of PU foams prepared from mixed DEG-glycerol polyol at different NCO indexes, (a) NCO100, (b) NCO125, (c) NCO150, (d) NCO 175 and (e) NCO200.....	122
Figure 4.21 OM images of PU foams prepared from commercial polyol at different NCO indexes, (a) NCO100, (b) NCO125, (c) NCO150, (d) NCO 175 and (e) NCO200.....	123
Figure 4.22 Bulk density of PU foams prepared from SA and mixed DEG-glycerol polyol and PU foam prepared from commercial polyester polyol at different NCO indexes	124
Figure 4.23 Compressive strength of PU foams prepared from mixed DEG-glycerol polyol and PU foam prepared from commercial polyester polyol at different NCO indexes	126
Figure 4.24 Reaction of trimerization of NCO groups to produce isocyanurate ring	126
Figure 4.25 FTIR spectra of Cloisite 30B (a), MMT (b), neat PU foam (c) and PU foam/clay nanocomposites incorporated with both clays at different clay contents, (d) 1 php C30B, (e) 1 php MMT, (f) 7 php C30B, and (g) 7 php MMT	130

- Figure 4.26** XRD pattern of the clays, neat PU foam and PU foam/clay nanocomposites..... 131
- Figure 4.27** Cubic specimen of bio-based PU foams incorporated with nanoclay Cloisite 30B (top) and MMT (bottom) at different clay contents..... 135
- Figure 4.28** Optical microscopy images of PU foams incorporated with nanoclay Cloisite 30B at different clay contents, (a) neat PU foam, (b) 0.5 php, (c) 1 php, (d) 1.5 php, (e) 2 php, (f) 3 php, (g) 5 php and (h) 7 php 137
- Figure 4.29** Optical microscopy images of PU foams incorporated with MMT at different clay contents, (a) neat PU foam, (b) 0.5 php, (c) 1 php, (d) 1.5 php, (e) 2 php, (f) 3 php, (g) 5 php and (h) 7 php 139
- Figure 4.30** Bulk density of PU foams incorporated with C30B and MMT at different clay contents..... 143
- Figure 4.31** Compressive strength of PU foams incorporated with C30B and MMT at different clay contents 144
- Figure 4.32** TGA curves of neat PU foam and PU foam/clay nanocomposites.. 146

LIST OF TABLES

	Page
Table 2.1 Industrial classification of foams by their bulk density	31
Table 2.2 General applications of PU foams	33
Table 2.3 Summary of foam polyol properties	39
Table 2.4 Classification scheme and ideal chemical composition of clay minerals in soils	56
Table 3.1 Information of all materials used in this research	66
Table 3.2 Information of the instruments.....	68
Table 3.3 Polyols formulation of bio-based succinate polyols	70
Table 3.4 Foam formulations of bio-based polyurethane foams.....	73
Table 3.5 Foam formulation of bio-based polyurethane foams with different isocyanate indexes	74
Table 3.6 Foam formulation of neat PU foam and PU foam/clay nanocomposites.....	76
Table 4.1 Acid number, OH number and viscosity of bio-based polyester polyols synthesized from SA and neat glycol or mixed glycol	94
Table 4.2 Molecular weights of the synthesized bio-based polyester polyols	96
Table 4.3 Selected polyols formulation for bio based PU foams preparation.....	97
Table 4.4 Foam formation time of the bio-based PU foams prepared from synthesized bio-based succinate polyols.....	103
Table 4.5 Cell dimensions and height of PU foams after rising	108
Table 4.6 Density and compressive strength of PU foams prepared from neat or mixed-glycol polyols relative to one prepared from commercial polyol (A8360).....	113
Table 4.7 Effect of glycol chain length and glycol types on the decomposition temperature (T_{onset}), degradation temperature (T_{max}) and char residue of the PU foams.....	115

Table 4.8 Effect of NCO indexes on the foam formation time of the PU foams	119
Table 4.9 Effect of NCO indexes on density, compressive strength and cell dimensions of PU foams prepared from mixed DEG-glycerol polyol and PU foam prepared from commercial polyol.....	127
Table 4.10 Properties of the typical industrial rigid PU foam	128
Table 4.11 Effect of clays on the foam formation times of the neat PU foam and PU foam/clay nanocomposites.....	133
Table 4.12 Effect of clays on density, compressive strength and cell dimensions of PU foams	141
Table 4.13 Effect of clay types and amount of clays on decomposition temperature (T_{onset}), degradation temperature (T_{max}) and char residue of the PU foams.....	147



CHAPTER I

INTRODUCTION

1.1 General introduction

Polyurethanes are versatile materials and have various applications in industry due to their wide range of hardness, stiffness and densities. Polyurethane (PU) materials consist of soft solid elastomers used for gel pads and print rollers, low density elastomers used in footwear, hard solid plastics used as electronic instrument bezels and structural parts, flexible foams used in upholstery and bedding, and rigid foams used for thermal insulation. Figure 1.1 outlines the characteristics of polyurethane materials. Globally, over three quarters of the PU are consumed in the form of either flexible or rigid foams [1].

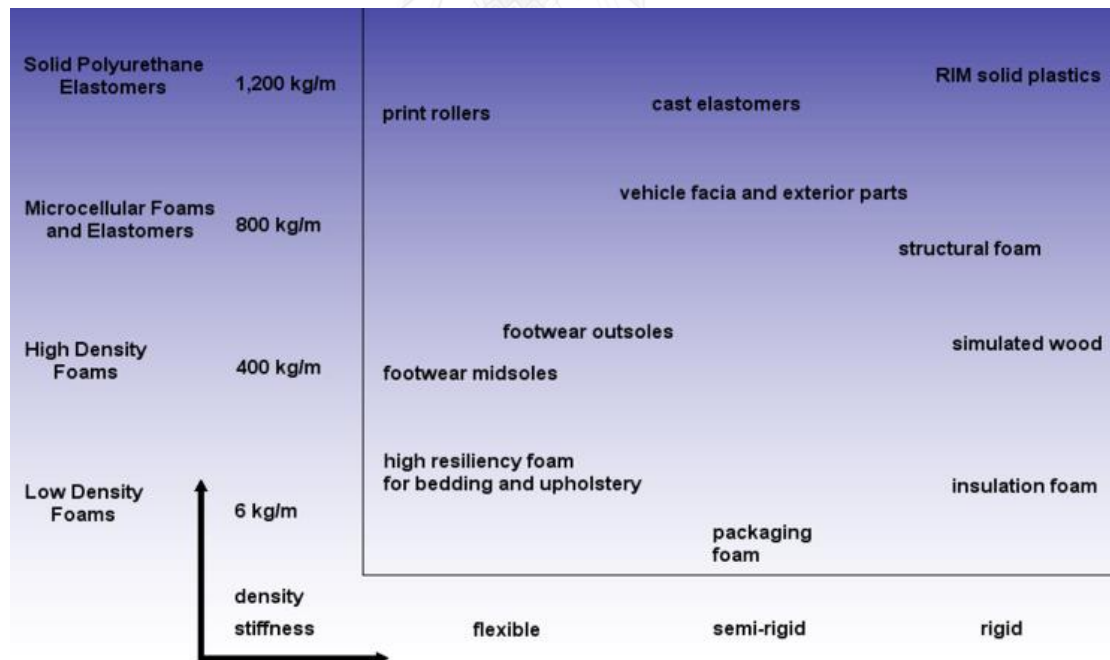


Figure 1.1 Characteristics of polyurethane materials [2]

The two essential components used to produce PU are the isocyanates with more than one reactive isocyanate group per molecule ($-N=C=O$) and polyols with two or more

reactive hydroxyl groups per molecule (-OH). The isocyanate group will react with hydroxyl group of polyol resulting urethane linkage. The general PU reaction is shown in Figure 1.2:

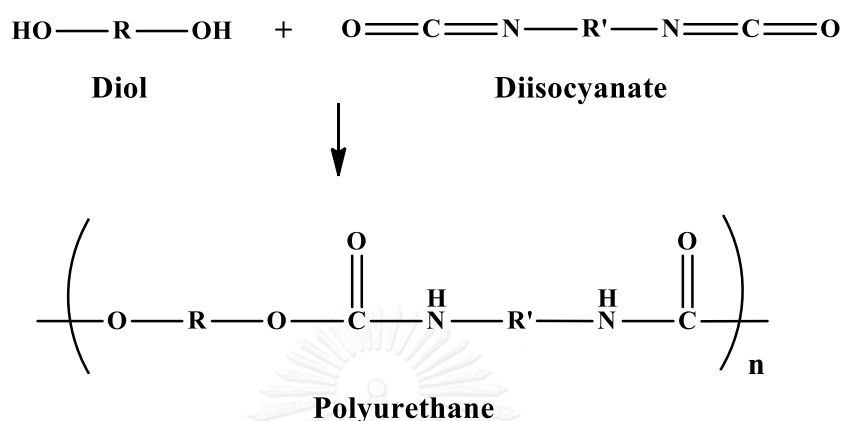


Figure 1.2 General reaction of polyurethane synthesis from diol and diisocyanate

Rigid PU foams have been used in many applications such as cushioning, freezers, insulation, refrigerators, packaging and structural materials. As structural materials, they have excellent mechanical properties and energy absorption capabilities. Rigid PU foam is usually synthesized by the reaction of diisocyanate and polyol. In general, catalyst, blowing agent and surfactant are also employed to regulate the properties and morphology of the foam cell structures. The properties of rigid PU foam depend on the geometry and structure of the foam and their density [3, 4].

In polyurethane industry, both isocyanates and polyols are usually made from feedstocks derived from petroleum. Most of the polyols (75%) used for general PU synthesis are polyether polyols, obtained from the reaction between a “starter” polyol and an alkylene oxide, both are petroleum based. The 25% remaining are polyester polyols synthesized by the polycondensation reaction from a dicarboxylic acid and a glycols [5]. However, they have some disadvantages as they are non-renewable resources and cause environmental pollutions. These problems could be partially addressed by producing polyols from renewable resources. In recent decades, various

factors spurred researchers to explore alternative resources as a feedstock for polyol production [6].

A renewable resource that commonly use to synthesize polyol for PU is natural acid or bio-based acid. Succinic acid (SA) can be derived from fermentation of agricultural carbohydrates such as corn starch and cassava starch. It has a wide range of applications in many industries including specialty chemicals market for various products such as polymers, pharmaceuticals, food, fibers, metals, coatings, solvents, diesel fuel oxygenates, lubricating oils, and cosmetics. In addition, SA can be used to produce new chemicals for various applications such as 1,4-butanediol (BDO), polybutylene succinate (PBS), plasticizers and polyesters polyols. The global bio based succinic acid market is expected to reach market volume of 710.0 kilotons by 2020, growing at a compound annual growth rate of 45.6% during 2013-2020 [7].

Thailand has abundant agricultural products to produce SA such as cassava and sugar cane. Thus, it could have advantage to use SA as a precursor for polyester polyol synthesis. The obtained bio-based polyester polyol will be used in PU foam production.

Nanocomposites are materials that incorporate nanosized particles into a matrix of standard materials resulting drastically improved in materials properties such as toughness, mechanical strength and electrical or thermal conductivity. The effectiveness amount of the nanoparticles addition is between 0.5 and 5% by weight [8].

Nanoclay is defined as nanoparticles since one dimension of nanoclay is in nanometer range. The single layer thickness of a nanoclay platelet is about 1 nm and the lateral dimensions of the layer may vary from 200 to 2000 nm. Nanoclay is potentially well suited for making hybrid composites because their lamellar elements have high in-plane strength and stiffness and a high aspect ratio. The rich intercalation chemistry of nanoclay allows them to be chemically modified to be more compatible with polymers.

To add more value to SA is to use it to synthesized bio-based polyester polyols and use the synthesized polyols to prepare bio-based rigid polyurethane foams. Rigid PU foam is one of the most important materials used in the construction industry and the global appliances (freezers, refrigerator, etc.) industry with excellent characteristics as , heat-insulation, sound-absorption, as well as being lightweight and shock-proof. As a structural material, it is important to improve the mechanical properties of the foams. Such improvement can be done by reinforcement of the polymer matrix with nanoparticles. The nanosized particles most commonly used in rigid PU foams are silicate-layered nanoclays.

In this study, bio-based succinate polyols were synthesized by condensation reaction using succinic acid with different types of glycols. The physical properties of synthesized bio-based succinate polyols were characterized. Bio-based PU foams were prepared using the synthesized bio-based succinate polyols with PMDI. Thermal stability, mechanical and physical properties of the prepared PU foams were studied relatively to PU foams prepared from commercial polyol derived from petrochemical. The PU foam with optimum isocyanate index giving highest compressive strength was selected to prepare PU foam/clay nanocomposites. The effects of the amounts of montmorillonite clays (both unmodified and organically modified) on mechanical properties, thermal stability and morphology of PU foams were investigated relatively to neat PU foam.

1.2 Objectives of the present study

1. To synthesize and characterize the bio-based polyester polyols from succinic acid using different types of glycols.
2. To prepare the bio-based rigid polyurethane foams using the synthesized bio-based succinate polyols.

3. To study the effects of different chain length and types of glycols used to prepare bio-based succinate polyols on mechanical and physical properties and thermal stability of the prepared bio-based polyurethane foams compare to commercial polyol derived from petrochemical.
4. To study the effects of different isocyanate indexes used in bio-based polyurethane foams preparation toward the properties of PU foams relative to those PU foams prepared from commercial polyol.
5. To study the effects of the amounts of montmorillonite clays (both unmodified and organically modified) on mechanical properties, thermal stability and morphology of PU foams relatively to the neat PU foam.

1.3 Scopes of the research

This research work can be divided into two parts as follow.

Part I: Bio-based polyester polyols from bio-based acid were synthesized by condensation reaction using succinic acid (SA) and seven different glycols that are ethylene glycol (EG), 1,4-butanediol (1,4-BTD), diethylene glycol (DEG), triethylene glycol (TEG), tetraethylene glycol (TTEG), polyethylene glycol average molecular weight 300 (PEG300), and glycerol (Gly). The effects of chain length of glycol and glycol types (neat or mixed glycols) used to prepare polyols toward physical and mechanical properties of the prepared PU foams were taken relatively to PU foam prepared from a commercial polyester polyol. The PU foam formulation, that provided good morphology and mechanical properties, was selected to study the effect of isocyanate index from 100 to 200. PU foam with optimum isocyanate index, that gave highest compressive strength, was then chosen to prepare the PU foam/clay nanocomposites.

Part II: PU foam/clay nanocomposites were prepared by incorporating two types of clays into PU foam with optimum isocyanate index that gave highest compressive strength from part I. The nanoclays used in this study were the organically modified nanoclay Cloisite 30B (C30B) and the unmodified clay (MMT). The clay contents of PU foam/clay nanocomposites were varied at the levels of 0.5, 1, 1.5, 2, 3, 5, and 7 php. The composition of each clay was analyzed by X-ray diffraction (XRD). Moreover, the mechanical properties, thermal stability and morphology of PU foam/clay nanocomposites were investigated.



CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Introduction to polymeric foams

Polymeric foams are complex three phase materials. An initial mixture of liquid monomer or polymer phase and gas bubbles from a blowing agent is progressively grown into a solid gas structured material, where the gas phase forms a multitude of randomly packed cells inside the solidified polymer matrix.

According to their complex nature, polymeric foams have been classified in a variety of ways, usually in term of either the cellular morphology mechanical behavior or composition. With respect to the cell structure, polymeric foams can be divided into two classes as:

2.1.1 Closed cell foams

The gas is dispersed in the foam of discrete gas bubble (Figure 2.1) and the polymer matrix exists as only continuous phase. Gas transport takes place by diffusion through the cell wall. Closed cell foams are generally formed by high pressure condition.

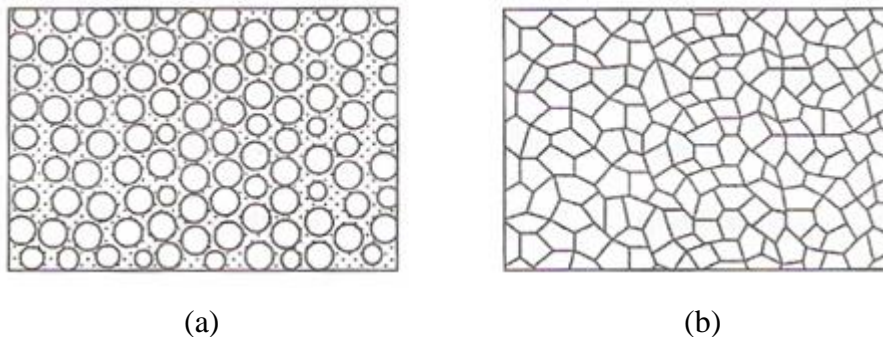


Figure 2.1 Closed cell foam structures (a) discrete cell dispersed in foam (b) cells in contact with each other [9]

2.1.2 Opened cell foams

The void (gas cell) coalesces so that the combined solid and gaseous phases are continuous (Figure 2.2). Therefore, the gas is able to flow through the polymer matrix under the action of some driving force. Open cell foams are generally formed during processing under ambient, i.e. low pressure, atmospheric conditions.

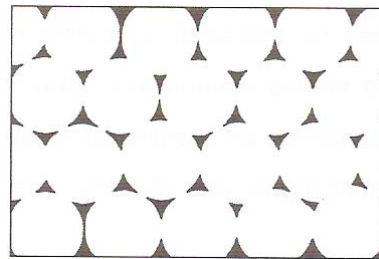


Figure 2.2 Idealized representation of opened cell foam structure [9]

In general, the cellular morphological form opened and closed cells so that a polymer foam does not always completely opened or completely closed cells. The main physical difference between the two types of foam cell, i.e. opened and closed cell, is depicted in Figure 2.3.

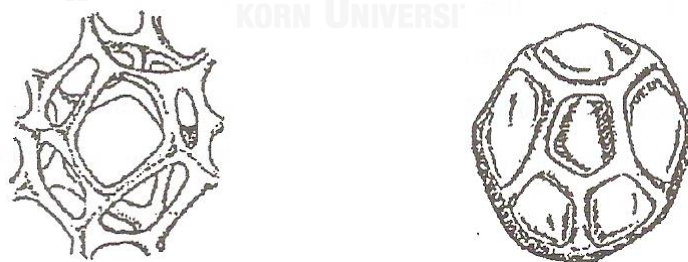


Figure 2.3 (a) Opened cell structural element (b) Closed cell structural element [9]

The opened cell structure, Figure 2.3 (a), consists of a lattice of struts, whereas for the closed cell structure, Figure 2.3 (b), in addition to the struts there are windows or membranes of base polymer between the strut faces. These membranes are usually

significantly thinner than the dimensions of the struts themselves but provide additional support and therefore stiffness and strength to the cell.

Cellular polymers can also be classified, according to their stiffness, into two types such as rigid and flexible foams depending upon the chemical composition, the rigidity of the polymer backbone, the degree of crystallization and the degree of crosslink (if any).

2.1.3 Rigid foams

The polymers exist as hard materials. Typical examples include most polyolefins, polystyrene, phenolics, polycarbonates, and some polyurethane foams.

2.1.4 Flexible foams

The polymers exist as soft materials. Typical examples include rubber foams, flexible PU foams, and plasticized poly (vinyl chloride) foams.

Intermediate between these two types is a class of cellular polymer known as semi-rigid foams. Although these materials have an elastic modulus higher than that of flexible foams, the stress-strain behavior is nevertheless closer to that of flexible foams than that exhibited by rigid foams.

2.2 Principles of foam formation

The mechanism of polymeric foam formation involves (i) the nucleation of gas bubble in the liquid polymer, (ii) the growth and stabilization of these bubbles, and (iii) the solidification of the polymeric phase by crosslinking or cooling to give a structurally stable cellular system.

2.2.1 Bubble formation

The first step of foam production is the initiation of gas bubble in the liquid polymer. This process is known as nucleation. In many cases, it is necessary to add nucleating agents such as silica to control cell size and cell distribution. Several techniques used to entrain the gas in the liquid polymer before expansion which can be described as follows

(a) Blowing by vapor from a volatile liquid

The liquid blowing agent is incorporated into the polymer at atmospheric pressure and is converted into vapor by heat from a crosslink reaction. PU foams blown with chlorofluorocarbons are examples of this method.

(b) Thermal decomposition of a chemical blowing agent

The solid blowing agent (BA) is intimately mixed with the polymer, preferably in the liquid state, and the mixture heated to a temperature at which the BA decomposes to give off an inert gas such as carbon dioxide (CO₂) or nitrogen (N₂). The polymer is then hardened either by gelation at this temperature (thermosetting plastics) or by cooling to room temperature (thermoplastics).

(c) Blowing due to an *'in situ'* chemical reaction

Gas is formed by reaction of two chemicals and evolution occurs simultaneously with polymerization and crosslinking. This is an important process for the manufacture of PU foams.

(d) Mechanical entrapment of gas

Air is beaten into the liquid polymer to give a stable liquid foam, which is then cured either chemically or by heating. An open cell structure is formed. However, this method gives a poor coarse cell structure.

2.2.2 Bubble growth

Lowering of the melt pressure relieves the super saturation of the material, after which no new bubbles are formed. The solubilized gas then diffuses into the existing bubbles, causing them to expand. The initial bubble is spherical in shape and grows as a result of the differential pressure (ΔP) between the inside and outside of the cell. At equilibrium, ΔP , the interfacial surface tension (γ), and radius (r) of the bubble are related as follows,

$$\Delta P = (2\gamma) / (r)$$

Saunders [10] reported that a better bubble stability, a small average cell size, and more even bubble size distribution is produced at low interfacial surface tension. Schematic representations of idealized cellular structures at different stages of bubble expansion are shown in Figure 2.4. The foam depicted in Figure 2.4 (a) shows the bubbles uniformly dispersed throughout the liquid medium and if stabilized in this condition the foam would clearly have a high density. As the gas volume fraction increases, Figure 2.4 (b), the foam density decreases. For spherical bubbles of uniform size, the lowest density is achieved when the bubbles are closed packed.

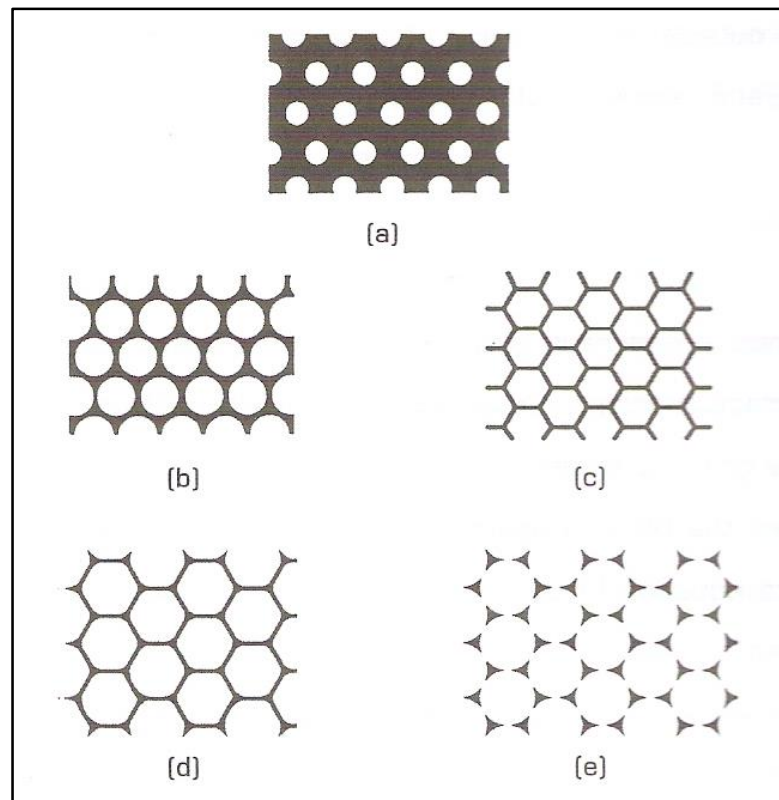


Figure 2.4 Schematic representations of cellular structures at different stages of foam [9]

On further expansion, the bubbles eventually touch each other and the internal gas pressure presses the cells together causing the polymer to fill the interstices. Thus, the cells become bounded by polyhedral, often represented in an idealized form as a pentagonal dodecahedron with planes surfaces of uniform thickness, but simplistically shown in two dimensions as a hexagonal honeycomb (Figure 2.4 (c)). Depending on the physical state of the liquid system, i.e. its viscosity and surface energy, gravitational and other force may cause the liquid material to concentrate at intersection of the elements of the associated cells as depicted in Figure 2.4 (d). At this stage the foam is of low density and is closed cell. However, the membranes between the cell structures, which represent the interface between the gas bubbles, may become ruptured and give

varying degrees of connectivity between the cells. This give rise to an open cell structure as represented in Figure 2.4 (e).

Polymeric foams are typically classified according to their density (Table 2.1), which ranges from 16 kg/m³ (very light foam) to 960 kg/m³ (super-heavy foam) according to the needs of a wide range of applications [11, 12].

Table 2.1 Industrial classification of foams by their bulk density

Foam type	Density range (kg/m ³)
Very light	3< ρ <50
Light	50< ρ <200
Medium	200< ρ <500
Heavy	500< ρ <700
Super heavy	700< ρ <900

Most of the physical properties of polymeric foams are directly related to their apparent density, ρ :

$$\rho = m / V$$

where: m is the total mass of foam and V is the total volume of foam.

The mechanical properties of rigid foams differ markedly from those of flexible foams. Compressive properties are perhaps the most important mechanical properties of cellular polymers. Compressive energy absorption characteristics and deformation characteristics of foam depend mainly on density, type of the base polymer, and the predominance of either opened or closed cells.

In simple terms, closed cell foam deformation involves cell wall bending/buckling (reversible), gas compression, cell wall stretching/yielding (non-reversible). Figure 2.5 showed the structure of closed cell foam deformation.

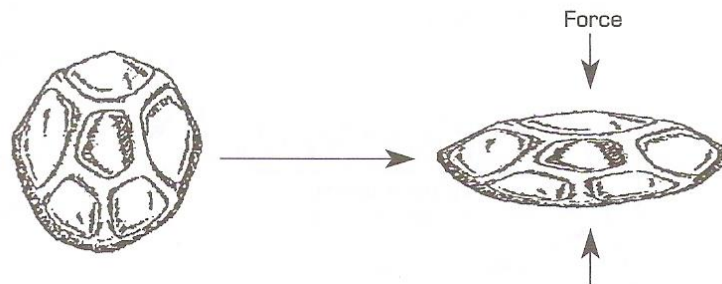


Figure 2.5 Schematic representation of closed cell deformation [3]

Closed cell rigid foams (e.g. PS and PU foams) exhibit from very limited to no yielding behavior. Consequently, gas compression and matrix strength play important roles during the mechanical deformation of rigid foams. In addition, cell rupture often occurs during the energy absorption process.

2.3 Application of cellular polymers

Approximately 90% of total foam usage derives from their excellent thermal insulation and energy absorbing characteristic. Rigid closed cell foams are particularly suitable for thermal insulation because in addition to their low thermal conductivity they are easy to dispense and have low moisture absorption. PS and PU foams are extensively used for these applications.

2.4 Polyurethane foams (PU foams)

Polyurethane foams are the most widely used polymeric foams in the world, finding applications in almost all modern industries. Over three quarters of the global consumption of polyurethane products is in the form of foams [4]. PU foams are divided into three groups: flexible foam, semi-rigid foam, and rigid foam. They are

made from different formulations and with different compositions. In general, flexible foams are used for packaging and cushioning, while rigid foams are for building insulation. Table 2.2 lists common application of different types of PU foams.

Table 2.2 General applications of PU foams [13]

Foams	Markets	Applications
Flexible PU	Transportation	Seating, pads, liners, dampening, carpet backing, filters, flooring, armrests, trim
	Furniture	Bedding, padding, flooring
	Recreation	Sport mats, toys, helmet liner, chest protection
	Packaging	Electronic, computer, equipment
Semi-rigid PU	Automotive	Dash panel, liner, visor
	Footwear	Soles
Rigid PU	Construction	Insulation, flooring, siding
	Appliance	Refrigerator frame, door, dishwasher door

PU has been developed for versatile applications, such as paints, coatings, adhesives, elastomers, and foams. The high degree of vapor permeability and water resistance of PU film enables it to be used for flexible surface coating. PU adhesives have been extensively used for bonding between core material and sheathing in structural panels as well as between interiors in automotive vehicles [14, 15]. For implanting medical devices, PU elastomer outperforms silicon elastomer with regards to its high abrasion and fatigue resistance under dynamic loading [16]. Insulation is one of them. PU foams have advantages of lightweight, low cost, and especially good

adherence toward the surface of sheathing layer. More importantly, they are popular insulating materials with excellent insulating properties for their lowest thermal conductivity over other cellular materials. Hence, PU foams take up a considerable fraction of PU production [17].

2.5 Raw materials used in PU foams

PU foams are manufactured on the basis of polyether- or polyester urethanes and the main reactions involved in the production of all types of PU foams are based on the reactivity of isocyanates. A typical reaction mixture for the production of PU foams consists of isocyanate, polyol, catalyst, blowing agent, and additives.

2.5.1 Isocyanates

The most common isocyanates are toluene diisocyanate (TDI) and 4,4'-diphenylmethane diisocyanate (MDI). Other isocyanates that are used are generally blends with TDI and MDI.

2.5.1.1 Toluene diisocyanate (TDI) (liquid, boiling point 120°C)

TDI is the most commonly available mixture of 80:20 and 65:35 of the 2,4 and 2,6 isomers as can be seen in Figure 2.6.

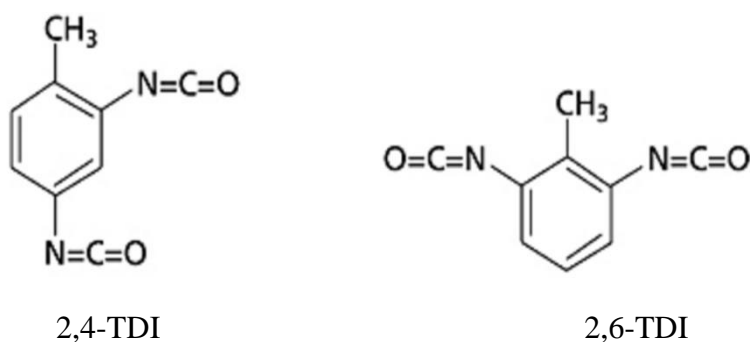


Figure 2.6 Toluene diisocyanate isomers used for PU foams manufacture [18]

TDI has a relatively high vapor pressure. It gives rise to the risk of airborne exposure to workers. As a consequence, it is quite difficult material to handle on site, in transport and in the laboratory; therefore, usage has been limited in favor of MDI which shows lower volatility.

2.5.1.2 4,4' Diphenylmethane diisocyanate, or methylene diphenylene diisocyanate (MDI) (solid, melting point 38°C, boiling point 195°C)

Pure MDI is a crystalline solid at room temperature so it must be heated slightly in order to convert into a more manageable form, i.e., a fairly high viscosity liquid.

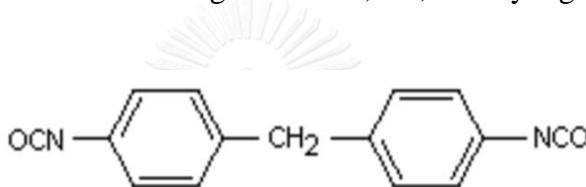


Figure 2.7 Molecular structure of MDI [9]

2.5.1.3 Polymeric 4,4' diphenylmethane diisocyanate (PMDI) (liquid, b.p. 330°C, flash point $\geq 204^\circ\text{C}$).

Polymeric MDI is a polymethylene polyphenyl isocyanate that contains MDI. PMDI is high reactivity, low viscosity and applicable to many foam processes, coatings, adhesives and elastomers.

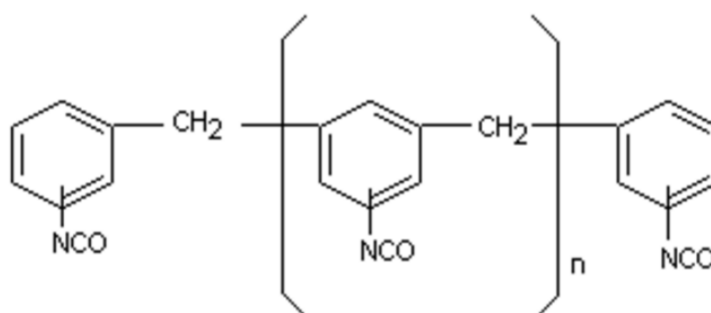


Figure 2.8 Molecular structure of PMDI [9]

Alternatively, handling of PMDI can be facilitated by producing an oligomeric mixture containing approximately 55% MDI, 25% MDI trimer (functionality = 2 to 3) and 20% of polymeric MDI. This is known as polymeric MDI and is a liquid at ambient temperatures.

Cavender and Hawker [19] reported that the main reasons why TDI has been used for a long time (and still is) is because the cost of TDI production is considerably lower than for MDI and, more importantly, the final properties of the foam are relatively better for TDI systems than for MDI based systems. However, polymeric MDI and mixtures of MDI and TDI are becoming competitive in some areas such as self-skinning foams, high quality cushioning foams and high resilience foams. It should be noted that isocyanates are toxic materials necessitating great care in their use. The main health effects of isocyanates are on the respiratory system, i.e. they could induce bronchial spasms, sore throats, and tightness of the chest. MDI has the lowest toxicity rating of the isocyanates.

2.5.1.4 Isocyanate index

The amount of isocyanate used relative to the theoretical equivalent amount is known as the Isocyanate Index:

$$\text{Isocyanate Index} = \frac{\text{Actual amount of isocyanate used} \times 100}{\text{Theoretical amount of isocyanate required}}$$

The isocyanate index has a pronounced effect on the stiffness or hardness of the final foam. In principle, a higher isocyanate index raises the actual amount of reacting isocyanate, increasing the cross-links in the polymer network which in turn increases the hardness or stiffness of molded foams. However, increasing the hardness of the foams by increasing the isocyanate index has its limit. There is a point beyond which the hardness does not increase anymore and other physical properties begin to

deteriorate. In the PU industry, isocyanate index commonly range from 80 to 100 for flexible PU foams [11]. Many of the rigid PU foams produced in the 1990s are urethane-modified isocyanurate foams. In the formulation of poly(urethane isocyanurate) foams an excess of PMDI is used. The isocyanate index can range from 105 to 300 and higher [3].

2.5.2 Polyols

The polyol used for the manufacture of PU foams is usually either polyether or polyester type polyols. They are ‘prepolymer’ whose structure determines the final PU foams properties with a large dependence being on their molecular weight and functionality. Generally, flexible foam polyols have molecular weights of 1,000-6,500 g/mol, functionality 2.0-3.0 and hydroxyl value 28-160 mg KOH/g, whereas rigid foam polyols have molecular weights of 150-1,000 g/mol, functionality 2.5-8.0 and hydroxyl value 250-1,000 mg KOH/g. The rigidity of the foam can be increased by reducing the chain segment length between junction points-this effectively produces more tightly crosslinked networks. In the foam industry, three types of polyol are prevalent; i.e., polyether polyol, polyester polyol and copolymer polyol [4].

2.5.2.1 Polyether polyols

Approximately 90% of polyols used in PU foams production are hydroxyl terminated polyethers due to their low cost and ease of handling (low viscosity). Polyether-based foams show better resilience and resistance to hydrolysis than polyester-based foams. They are produced by the ring opening of alkylene oxides using a polyfunctional initiator. Ethylene or propylene oxides are the most commonly used polyols. The polyols used for making flexible foams have molecular weight ranging from 3,000 to 6,000 g/mol whereas the molecular weight of rigid foam is approximately

500 g/mol in order to reduce the distance between crosslinks. The reactions are base-catalysed.

2.5.2.2 Polyester polyols

Compared with polyether polyols, polyester polyols tend to be more reactive, produce foams with better mechanical properties, are less susceptible to yellowing in sunlight and are less soluble in organic solvents. However, they are more expensive, more viscous; therefore, they are more difficult to handle. Consequently, they are only used in applications that require their superior properties [9]. Polyester polyols are made by condensation reactions between diols (and triols) and dicarboxylic acids such as: adipic acid, sebacic acid and phthalic acid as their formulas are shown in Figure 2.9.

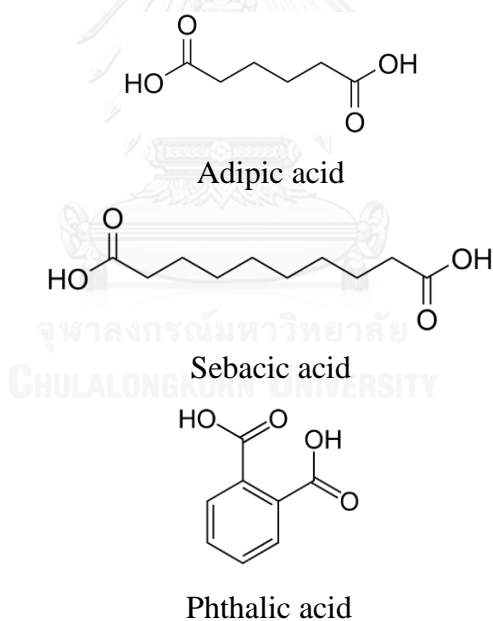


Figure 2.9 Example of aliphatic and aromatic dicarboxylic acids used in the production of polyester polyols [9]

Table 2.3 Summary of foam polyol properties

Properties	Polyether polyol	Polyester polyol	Copolymer polyol
Viscosity	Low	High	Medium
Hydrolytic stability	Excellent	Fair	Excellent
Oil/Solvent stability	Fair	Excellent	Good
Strength	Fair	Excellent	Very good
Resilience	good	fair	excellent

2.5.2.3 Polyol characterizations

The basic major criteria for characterizing a polyol are shown as follow:

2.5.2.3.1 Hydroxyl number

The first common characteristic of polyols for polyurethanes is the presence of terminal hydroxyl groups. The hydroxyl number is defined as the numerical value of quantities of terminal hydroxyl groups available for reaction with isocyanates. The number of hydroxyl (or hydroxyl index) is expressed in milligrams of potassium hydroxide equivalent per gram of sample (mg KOH / g) according to ASTM E222. The most important analytical method to determine the number of hydroxyl (OH) is the reaction of hydroxyl end groups with organic anhydrides (acetic anhydride or phthalic anhydride). Acid carboxyl groups as a result of this reaction are neutralized with equimolecular amount of potassium hydroxide [20]. Reaction of polyol with phthalic anhydride is shown in Figure 2.10.

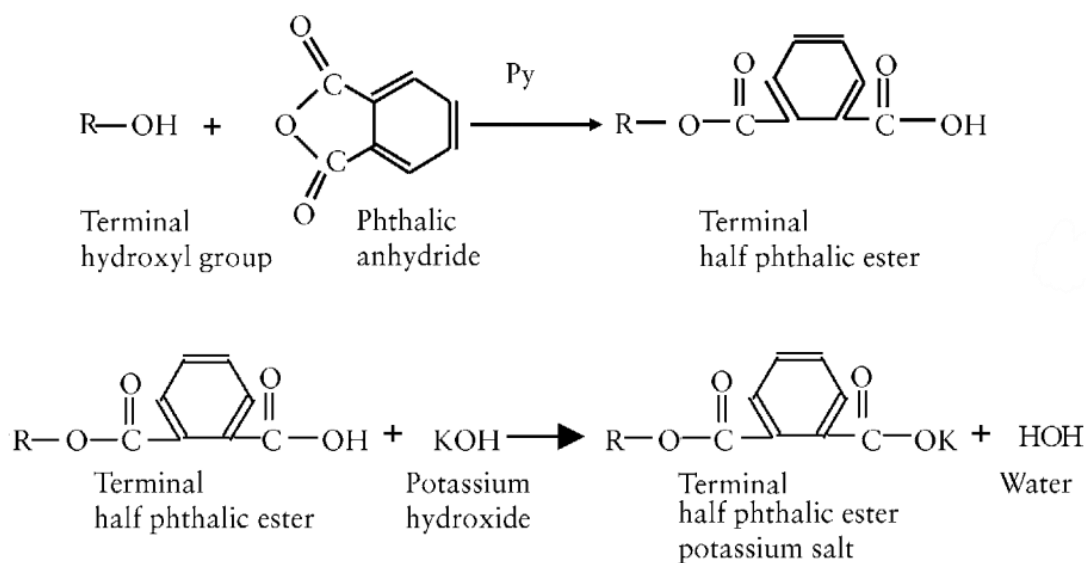


Figure 2.10 Reaction of hydroxyl end groups with phthalic anhydrides

2.5.2.3.2 Functionality

Functionality is the second important characteristic of a polyol and is defined as the number of hydroxyl groups/molecule of polyol. A mixture of two polyols with different functionalities (f_1 and f_2), the equivalent functionality, f_e , of the polyol mixture is calculated using the general formula:

$$f_e = x_1 \cdot f_1 + x_2 \cdot f_2$$

where: x_1 and x_2 are the molar ratios of each polyol in the mixture and f_1 and f_2 are the functionalities of the corresponding polyols.

2.5.2.3.3 Molecular weight and molecular weight distribution

The properties of a polyurethane are greatly influenced by the types of isocyanates and polyols used to make it. Long chain of polyols contributed soft and elastic polymer while short chains with lots of crosslinks produce a hard and rigid polymer. Therefore, molecular weights of polyols used to synthesize PU foams are important to be considered. Polyols used to make rigid PU foams have molecular

weights in the hundreds, while those used to make flexible PU foams have molecular weights up to ten thousand or more.

The polydispersity index or molecular weight distribution (MWD) is an important characteristic of polyols, differentiating the polyols from the unitary low molecular weight polyols of organic chemistry. As in all polymers, the MWD of polyols is given by the ratio between weight average molecular weight (M_w) and the number average molecular weight (M_n) both being determined by GPC.

$$\text{MWD} = \frac{M_w}{M_n}$$

2.5.2.3.4 Equivalent weight

It is defined as the molecular weight of a polyol divided by its functionality. In practice, the equivalent weight is calculated from the analyzed hydroxyl (OH) number from the following expression. The equivalent weight is necessary for the isocyanate requirement calculations.

$$\text{Equivalent Weight} = \frac{56.1 \times 1000}{\text{OH number}}$$

2.5.2.3.5 Viscosity

The viscosity is an important characteristic of polyols. A special characteristic of all polyols is the fact that practically all of them are liquid at room temperature or at low temperatures (40-60 °C). This fact is a really important technological advantage, because the high MW polyurethane polymer is obtained using only low viscosity or medium viscosity liquid intermediates, which are very easy to process. The viscosity gives an indication of the processability of a polyol.

2.5.2.3.6 Acid number

The acid number is expressed as the number of milligrams of potassium hydroxide required to neutralize the acidity of one gram sample. Acid number is important to correct the value of hydroxyl number, in order to obtain the real value for OH (for a good correction of the OH value, the acid number is added to the determined value of OH). It is a measure of polyesterification from acid groups, which together with the hydroxyl groups will not react with KOH. For some polyols, such as polyester polyols or reactive flame retardants, the maximum acidity accepted is around 2 mg KOH/g. Acid number in polyols is determined according to ASTM D4662.

2.5.3 Catalysts

Catalysts exert an influence upon the rate of competing reactions and have a major effect on the ultimate properties of the final foam. The formation of urea and urethane linkages establishes the physical properties of the polymer and these are dependent on the type and concentration of catalysts used. A typical catalyst system would consist of a mixture of a tertiary amine and organo-metallic compounds. Each catalyst type is specific for a particular chemical reaction. Catalyst mixtures are generally necessary to control the balance of the polymerization and the gas generation reactions, where both of them are exothermic reactions. Getting the correct balance of polymerization and foaming is of major importance in the production of closed cell foam. If too much gas is evolved before a sufficient amount of polymerization has taken place, the gas will burst through the weak cell walls. The open cell structure is formed. On the other hand, if polymerization is completed before sufficient gas has been generated, high density foam will be obtained. Thus, blends of catalysts are required to balance the relative chemical reaction rates [9].

2.5.4 Blowing agents

The most commonly used blowing agent is water. It produces carbon dioxide (CO₂) gas by the reaction with diisocyanate. Typical water concentrations are 3-5 parts of water per 100 parts of polyester polyol and 1.8-5 parts of polyether polyol. The reaction of water with an isocyanate is exothermic and results in the formation of active urea sites which form crosslinks via hydrogen bonding. To reduce the high crosslink density of the foam, auxiliary blowing agents are used to produce low density foams with a softer feel than water-blown foams, and to produce closed cell flexible foams. The auxiliary blowing agents used for this purpose are the chlorofluorocarbon and methylene dichloride. These materials volatilize due to the exothermic heat of reaction of isocyanates and increase the gas volume without increasing the degree of crosslinking. Due to the problems related to the earth's atmosphere, other types of auxiliary blowing agents such as hydro fluorocarbon which they do not contain chlorine were considered [11].

2.5.5 Surfactants

Surfactants are essential additives used in PU foams formulations. They assist in mixing incompatible components of the formulation, controlling cell size, open cell content, and uniformity through reduce surface tension. The most important surfactants are based on water-soluble polyether siloxanes. It has been found that increasing the level of surfactant in the PU foams formulation causes a reduction in the rate of foam rise. This can be explained by the fact that increasing the surfactant level will effectively reduce functional group concentration. Consequently, the rate of foam rise, temperature rise, and overall reaction rate are reduced. There is a critical level of surfactant which the foam produced will suffer from coarse cell structure and collapse. Just above this critical level, good open cell foams are produced. At higher levels of surfactant, silicone foams with closed cell are produced. At much higher levels of

surfactant, the foams produced show a high level of shrinkage, poor compression set and poor load-bearing capacity [9].

2.5.6 Additives

2.5.6.1 Flame retardants

These are normally based on halogen or phosphorous containing compounds. The addition of small amounts of fire retardant has little or no effect on foam physical properties, but adverse effects are noticeable when higher amounts are used [9, 11].

2.5.6.2 Fillers

Particulate fillers tend to reduce flammability, increase compression resistance, compressive strength, and weight of seat cushion. Reinforcing fibrous fillers increase stiffness, heat resistance, and tensile strength. Typical fillers include carbon black, clay, calcium carbonate, glass fibers, and microspheres. Carbon fibers are used in high performance composites [9, 11].

2.5.6.3 Coloring materials

Pigments must be inert to isocyanates, stable at reaction temperatures, and free of contaminants that can affect foaming [9].

2.5.6.4 Chain extenders/crosslinking agents

These are low molecular weight polyols or amines. They are generally used for producing foams of high flexibility by chain extension. Load-bearing capacity of foam is improved by augmenting the degree of crosslinking of the polymer by using polyfunctional reagents [9].

Physical properties of the final PU foams are influenced by hydrogen bonding between the NH-groups in the urethane/urea linkage and either ether oxygen atoms in

polyether or carbonyl oxygen atoms in polyester. Hydrogen atoms which are bonded to ether oxygen atoms are much weaker than those bonded to carbonyl oxygen atoms in polyester. This is the reason why polyether PU foams feel softer than those based on polyester polyols. Flexibility causes by the degree of crosslinking and is then determined largely by the functionality of the hydroxyl ended species (polyol). The use of highly branched polyols produces rigid foams with high crosslink density.

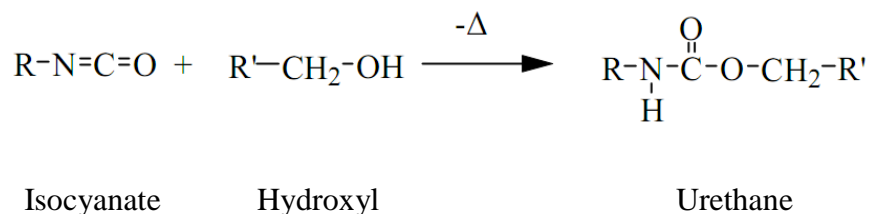
2.6 Chemical reactions of PU foams

Polyurethane chemistry is based on the high reactivity of the isocyanate group with any compound containing active hydrogen. Most polyurethanes are formed by exothermic reaction between di-or polyfunctional isocyanate and di-or polyfunctional hydroxyl species.

2.6.1 Primary reactions of isocyanates

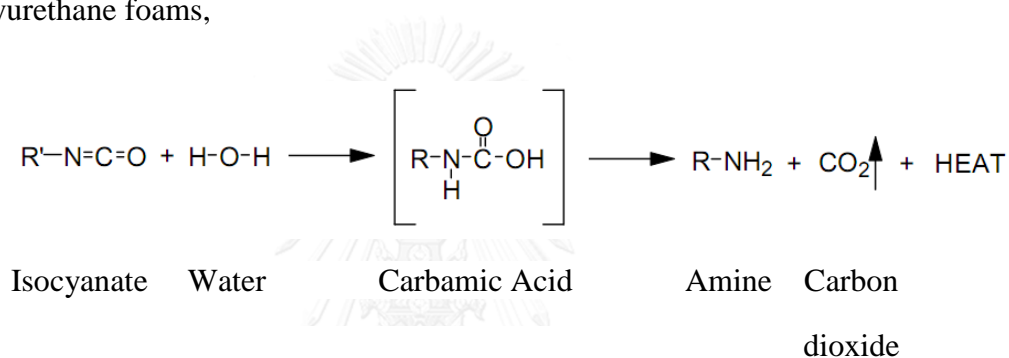
Primary isocyanate reactions are very fast reactions. They produce urethane, amine and substituted ureas, all of which still contain active hydrogen atoms. In the presence of suitable catalysts at elevated temperatures, controlled secondary reactions occur which strongly influence the physical properties of the foam by introducing chain branching and crosslinking [21].

2.6.1.1 Reaction with hydroxyl compounds - the reaction between an isocyanate and a polyol produces a urethane,



This reaction is known as the '*gelling reaction*'. Since it is an exothermic reaction it must be temperature controlled. The rate of polymerization is affected by the chemical structure the isocyanate and polyol. A catalyst is used to accelerate the reaction rate.

2.6.1.2 Reaction with water - the reaction between an isocyanate and water released carbon dioxide and an amine via a transient unstable carbamic acid. This reaction is a very convenient source of a gas necessary to generate the cellular structure of polyurethane foams,



This reaction is known as the '*blowing reaction*' because the CO₂ gas produced is used for blowing the foam. The reaction of isocyanate with water is more exothermic than the reaction with hydroxyl.

Generally, one mole of water can be reacted with two -NCO groups. This reaction is very important in order to calculate the correct quantity of isocyanate needed for polyurethane formulations.

Water is considered, in polyurethane foam manufacture, as a chemical blowing agent, because the gas generation is a consequence of a chemical reaction.

The reaction between isocyanates and alcohols or water is catalyzed by tertiary amines with low steric hindrance, and some tin, lead or mercury compounds as shown in Figure 2.11:

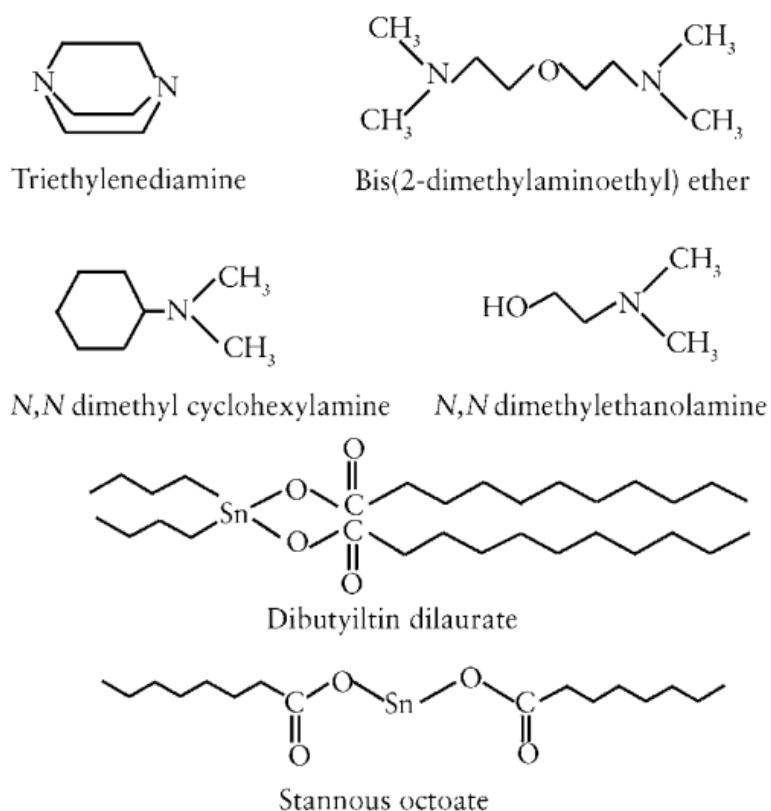
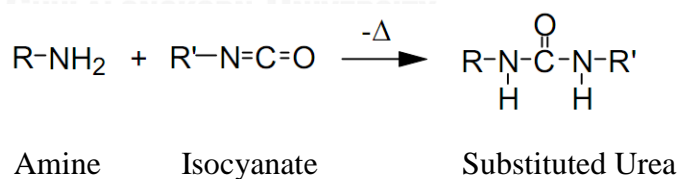


Figure 2.11 Catalyst for the reaction between isocyanates with hydroxyl or water [20]

2.6.1.3 Reaction with amines - the reaction of an isocyanate with an amine forms a urea linkage,

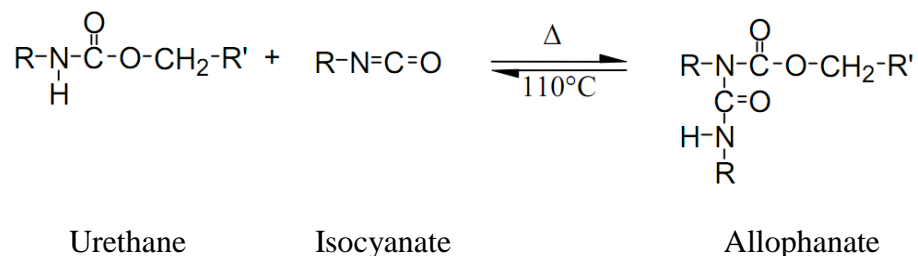


Reaction of unhindered isocyanates with primary amine occur approximately 100-1000 times faster than with primary alcohols.

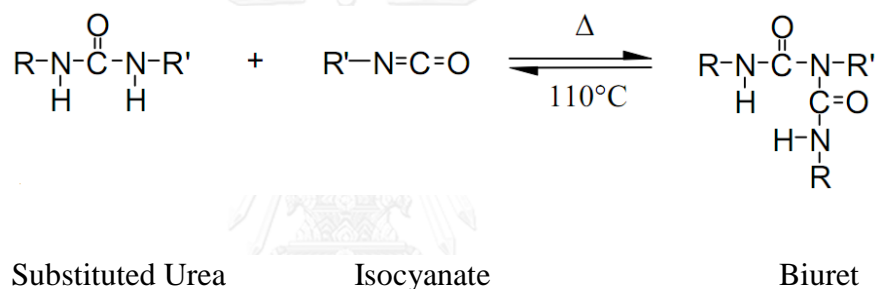
2.6.2 Secondary reactions of isocyanates

Isocyanate may react, under suitable conditions, with the active hydrogen atoms of urethane and urea linkage from the primary reaction as shown follows:

2.6.2.1 Reaction with urethanes - isocyanate can react with the active hydrogen atoms of urethane linkages to form branched allophanates,



2.6.2.2 Reaction with urea - isocyanate can also react with the active hydrogen atoms of substituted ureas to form branched (biuret) structure,

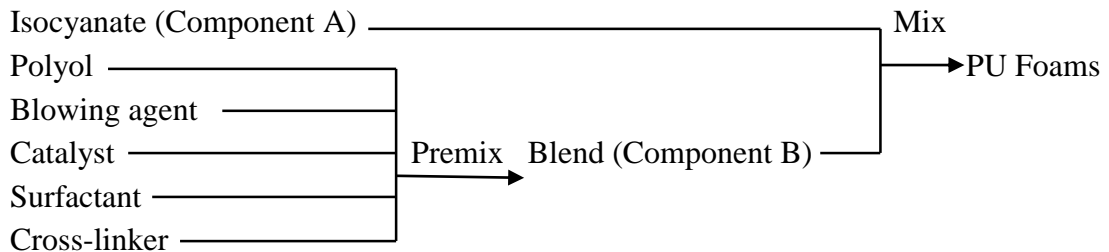


Reactions of isocyanate with both urethanes and ureas produce crosslinking. At temperature below 100°C these reactions are 100 times slower than the primary reactions. Generally, reaction of isocyanates with urea groups is significantly faster and occurs at low temperature than with urethane groups.

2.7 Manufacture of PU foams

There are three kinds of foaming systems for PU foam production. They are the one-shot one-step system, the quasi-prepolymer system, and the full-prepolymer system [18]. Currently, the one-shot system is the major process for both flexible and rigid foam production in the foam industry. The schematic diagram of the one-shot system is shown below. In the one-shot process, polyol, water and other foam

formulation ingredients are rapidly and intensively mixed and then added to the isocyanate for mixing and pouring for foaming.



2.7.1 Laboratory production of PU foams

In the laboratory scale, the key to making foams is to find a method for rapid intensive mixing of the ingredients and then pouring the rapidly reacting mixture into a box, usually a disposable paper board container in which the expanding foam can rise. Usually, a standard laboratory mixing and pouring procedure includes the use of a commercial drill press fitted with a shaft. An impeller that can turn at 2,000 to 4,000 rpm is fixed at the end of shaft. The lower impeller speed is used to mix lower viscosity (lower molecular weight) polyols. In this procedure, polyol, catalyst, water, and surfactant are weighed and poured into the container and mixed for 10 to 30 s. Stop stirring for 15 s, allowing the mixture to de-gas. Then the isocyanate is rapidly added and stirring continues for another 10 s. During this process an electric timer can be used to record the mixing times. When the mixing is finished, the mixture is rapidly poured into an open-top container to form foams to a desired shape [11].

2.8 Bio-based polyester polyols

2.8.1 Synthesis of polyester polyols

Polyester polyols with linear structures are mainly produced by condensation polymerization of dicarboxylic acids or their esters or anhydrides with monomeric diols, such as diethylene glycol and 1,4-butanediol. With the addition of triols, such as

glycerol and 1,1,1-trimethylol propane, branched polyester polyols can be obtained. Based on the polyol structure, polyester polyols can be classified into aliphatic and aromatic polyester polyols. Adipic acid and phthalic anhydride is the most commonly used dicarboxylic acid/anhydride in the production of aliphatic and aromatic polyester polyols, respectively. Typical polyester polyols obtained with the reaction between adipic acid and 1,4-butanediol, or between phthalic anhydride and diethylene glycol, are shown in Figure 2.12. Polyester polyols are usually waxy solids or liquids with high viscosity. As ester groups are more susceptible to hydrolytic attack than ether groups, polyester polyols are less water-resistant than polyether polyols.

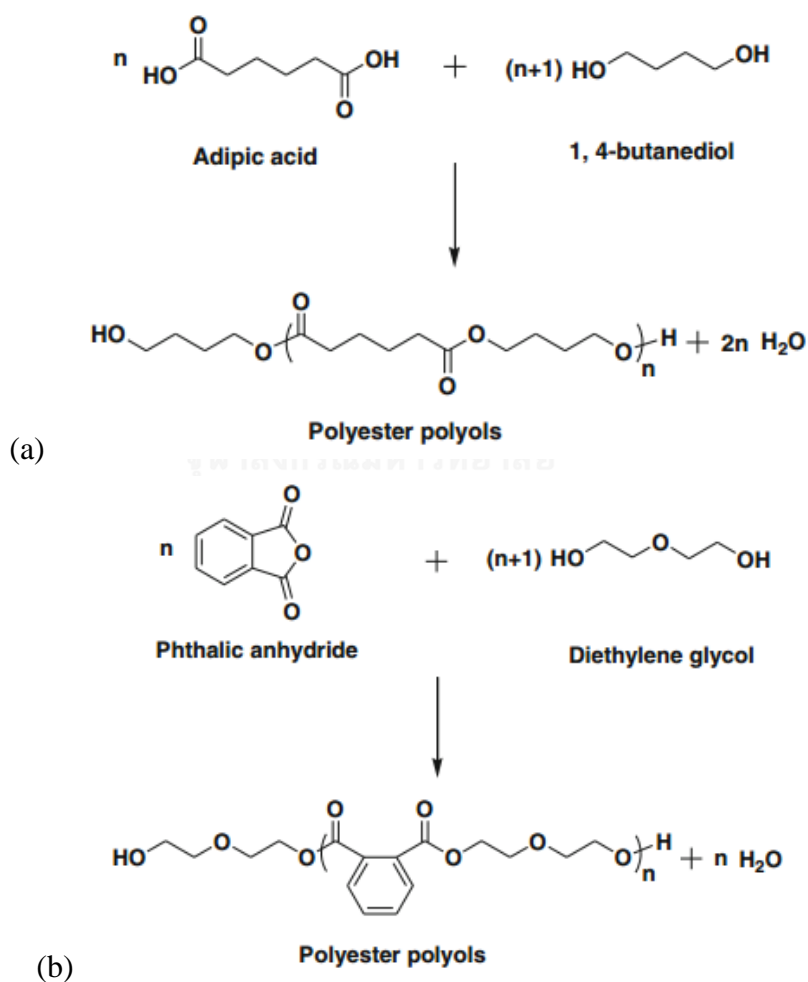


Figure 2.12 Production of polyester polyols from (a) adipic acid and 1,4-butanediol, and (b) phthalic anhydride and diethylene glycol [22]

Polyester polyol can be synthesized in a large variety of polyester polyol structures. For example to use one type of glycol and one type of dicarboxylic acid, but many other combinations are possible, such as using one dicarboxylic acid and two types of glycol or to use a glycol together with a small quantity of triol, to obtain a branched polyester polyol [20].

Recently, concerns about the sustainability of petroleum-based PUs have led to increased demand for bio-based polymeric materials from renewable resources like natural acid because of their important availability, sustainability, biodegradability, and added values.

2.8.2 Succinic acid

Succinic acid or SA is one of bio-based acid which interested in using to prepare polyester polyol for PU foam since its renewable resource and can reduce environmental impact causing the global warming problem. SA is an aliphatic dicarboxylic acid (as shown in Figure 2.13 that can be obtained from the fermentation of sugars and has been noted as one of the most important value added chemicals from biomass from which many other industrially important chemicals can be derived.

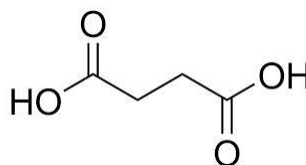


Figure 2.13 Chemical structure of succinic acid

Succinic acid, derived from fermentation of agricultural carbohydrates, has a wide range of applications in many industries and has a specialty chemical market in industries producing various chemicals and products such as food and pharmaceutical products, surfactants and detergents, green solvents and biodegradable plastics, and ingredients to stimulate animal and plant growth as shown in Figure 2.14.

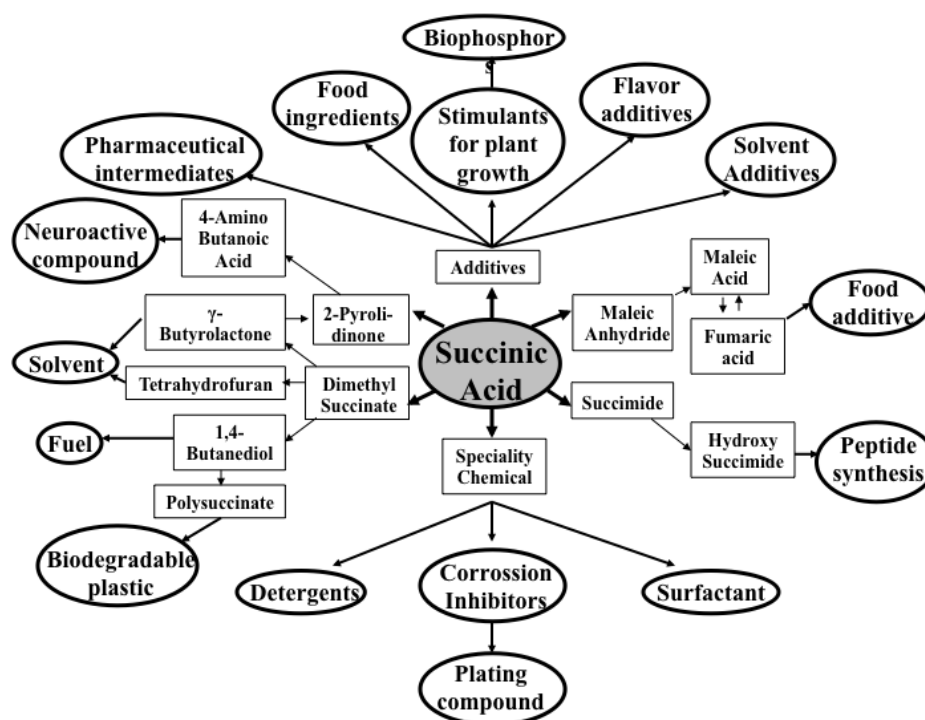


Figure 2.14 Various chemicals and products that can be synthesized from succinic acid

Succinic acid can be used to produce polyester polyols with renewable content up to 100%, that are comparable in performance to adipic acid polyols, and that, long term, have more price stability than polyols derived from petroleum.

Thailand has abundant agricultural products to produce SA such as cassava and sugar cane. Thus, it could have advantage to use SA as a precursor for polyester polyol synthesis. The obtained bio-based polyester polyol will be used in PU foam production.

2.8.3 Polyester polyols from succinic acid

The synthesis and molecular weight control of succinate polyols follows the principles of condensation polymerization established by Carothers. The modified Carother's equation shown in Figure 2.15 is for an off-stoichiometric ratio of acid to

glycol using excess glycol. Using this relationship, it is possible to control the degree of polymerization and hence the hydroxyl number for the polyols.

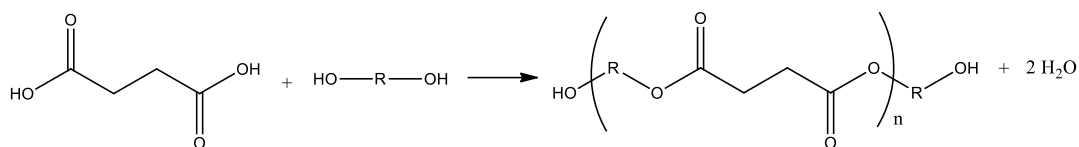


Figure 2.15 Production of succinate polyester polyols from succinic acid and glycol

The physical properties of the succinate polyols are controlled by the type of glycol or glycol mixture reacted with the succinic acid. As a result of the structural influence of the polyol, it is possible to make a range of polyester polyols with different hydroxyl number, functionality and viscosity values.

2.9 Polyurethane foam nanocomposites

Though polyurethanes present a wide range of physical and chemical properties derived from the specific control of their formulation, enabling their use in almost all types of applications, from coatings or adhesives to composites or even foams, they still present some limitations, such as relatively low thermal stability and mechanical strength. This fact is more marked in the case of PU foams, as foaming, while it improves some of PU's characteristics such as thermal insulation, further decreases its mechanical strength. The incorporation of nanosized reinforcements to PU and later foaming could overcome some of these limitations, as it has been shown that their addition to PU could counteract the loss in mechanical properties inherent to foaming by their mechanical reinforcement and direct effect on the development of a finer and more uniform cellular structure, the combination of which could promote the formation of stronger PU foams, further expanding their possible range of applications. The incorporation of nanosized particles into a polymer matrix and later foaming results in what is known as “polymer foam nanocomposites” [8].

The nanosized particles most commonly used in PU foams are silicate-layered nanoclays, and particularly unmodified or organically modified montmorillonite (MMT).

2.9.1 Clay and organoclay

2.9.1.1 Clay

Clay minerals are group of hydrous layered magnesium or alumino-silicates (phyllosilicates) containing several main elements as iron, alkaline, and alkaline earth metals. The crystalline lattices are classified as three-dimensional, two-dimensional (layered) or mono-dimensional (fibrous structures). Clay used in this research is two dimensional layered, which each magnesium or alumino phyllosilicate is essentially composed of two types of sheets, octahedral and tetrahedral sheet. A continuous linkage of SiO_4 tetrahedra through sharing of three oxygen atoms with three adjacent tetrahedral produces a sheet with a planar network as seen in Figure 2.16. In such a sheet the tetrahedral silica groups are arranged in the form of a hexagonal network, which is repeated indefinitely to form a phyllosilicate with the composition $[\text{Si}_4\text{O}_{10}]^{4-}$ as shown in Figure 2.17. A side view of the tetrahedral sheet shows that it is composed of three parallel atomic planes, which are composed of oxygen, silicon, and oxygen, respectively [23, 24].

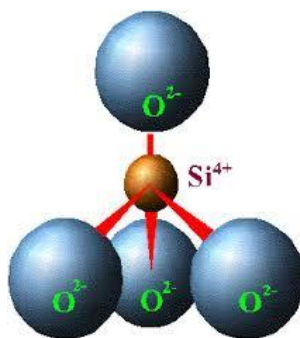


Figure 2.16 Silicon-Oxygen Tetrahedron, (SiO_4) [25]

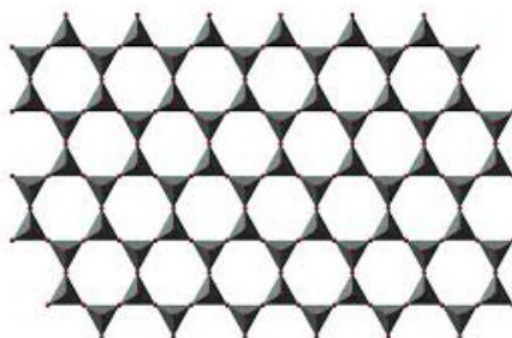


Figure 2.17 The tetrahedral sheet, $[\text{Si}_4\text{O}_{10}]^{4-}$ (Top view) [25]

An octahedral sheet is obtained through condensation of single $\text{Mg}(\text{OH})_6^{4-}$ or $\text{Al}(\text{OH})_6^{3-}$ octahedral as seen in Figure 2.18. Each O atom is shared by three octahedra, but two octahedra can share only two neighboring O atoms. In this sheet the octahedral groups are arranged to form a hexagonal network, which is repeated indefinitely to form an $[\text{Mg}_6\text{O}_{12}]^{12-}$ or $[\text{Al}_4\text{O}_{12}]^{12-}$ layer [23].

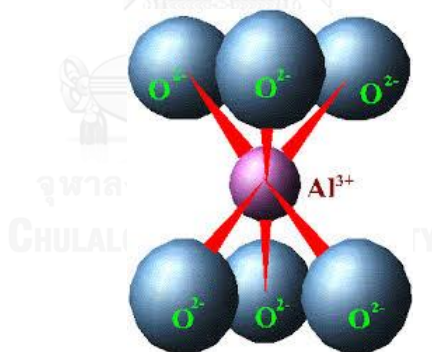


Figure 2.18 Aluminum Octahedron, $\text{Al}(\text{OH})_6^{3-}$ [25]

The hydrated aluminosilicates can be neutral or ionic exchangers and the groups treated in this work involve basically the phyllosilicates of the smectite group (sometimes known as the montmorillonite group), which consist of tetrahedral octahedral-tetrahedral (TOT) layer group. The common groups of the phyllosilicate minerals occurring in soils and sediments are listed in Table 2.4 [23].

Table 2.4 Classification scheme and ideal chemical composition of clay minerals in soils [23]

Group	Subgroup	Ideal chemical composition
Smectite	Beidellite	$[(Al_{4.00})(Si_{7.50-6.80}Al_{0.50-1.20})O_{20}(OH)_4]Na_{0.50-1.20}$
	Montmorillonite	$[(Al_{3.50-2.80}Mg_{0.50-1.20})(Si_8)O_{20}(OH)_4]Na_{0.50-1.20}$
	Nontronite	$[(Fe_{4.00})(Si_{7.50-6.80}Al_{0.50-1.20})O_{20}(OH)_4]Na_{0.50-1.20}$
	Hectorite	$[(Mg_{5.50-4.80}Li_{0.50-1.20})(Si_8)O_{20}(OH)_4]Na_{0.50-1.20}$
	Saponite	$[(Mg_{6.00})(Si_{7.50-6.80}Al_{0.50-1.20})O_{20}(OH)_4]Na_{0.50-1.20}$

Montmorillonite is one in the smectite group which has a low thermal expansion coefficient and high gas barrier properties. The composition of the montmorillonite is variable and depends on its own genesis, which is attributed to the characteristic of different cationic exchange capacity. A small fraction of the tetrahedral Si atom is isomorphically substituted by Al and/or a fraction of the octahedral atoms (Al or Mg) is substituted by atoms of lower oxidation number. The resulting charge deficiency is balanced by hydrated cations, mainly K, Na, Ca, and Mg, of which more than 80% is located between the parallel clay layers as shown in Figure 2.19. These ions are hydrated due to the fact that, in nature, smectite are formed in aqueous environments. Because they are hydrated, these cations are only loosely held by the negatively charged clay layers. Smectite saturated with other cations dissociate in aqueous suspensions into exchangeable cations and tactoids, which are composed of several parallel TOT layers, held together by electrostatic forces by some of the exchangeable cations that remain in the interlayer space. Water and polar organic molecules are attracted by the exchangeable cations and may intercalate between the layers, causing the structure to expand in the direction perpendicular to the layers. The interlayer space between the

TOT layers, obtained as a result of the expansion of the clay, has special chemical properties. The swelling of this space depends on several factors, such as the exchangeable cation, the humidity of the environment, the vapor pressure, and the temperature [23, 24].

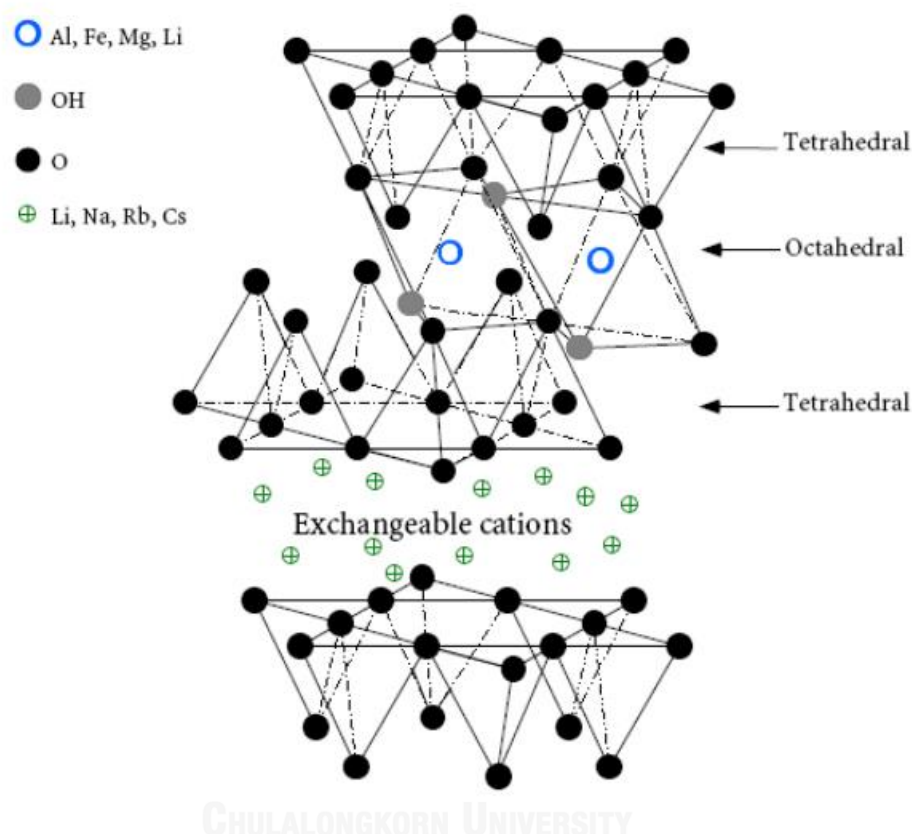


Figure 2.19 Structural scheme of the montmorillonite [26]

2.9.1.2 Organoclay

In the present clay minerals are used as fillers in different products. The interactions between organic matter and clay minerals are among the most widespread reactions in nature. The interactions include cation exchange and adsorption of polar and nonpolar molecules. Smectite and especially montmorillonite have been the most studied minerals of all clay. These minerals are able to swell and adsorb polar organic compounds into their interlayer space. The presence of small inorganic cations in the interlayer makes this space hydrophilic. However, inorganic exchangeable cation can

also be replaced by a quaternary ammonium cation in the interlayer. This treatment is used to enhance the hydrophobic properties of the clay. This modified clay is commonly referred to as “organoclay”. There are two types of organoclay: those saturated with large quaternary ammonium cations with one or two long alkyl chains and those saturated with small quaternary ammonium aliphatic and aromatic cations. Some investigators use the term “organophilic clay” for the first type and the “adsorptive clay” for the organoclay saturated with small quaternary ammonium cations. For example, the exchange reaction between an inorganic metallic cation, M^{m+} , initially saturating a smectite mineral, M^{m+} -Smec, and an aqueous solution of an aliphatic ammonium salt such as ethylammonium chloride, $C_2H_5NH_3Cl$, can be formulated by the following equation [23]:



2.9.1.3 Dispersion of clay in polymer matrix

Polymers have been successfully reinforced by glass fibers and other inorganic materials. In these reinforced composites, the polymer and additives are not homogeneously dispersed on a nanometer level. If nanometer range dispersion could be achieved, the mechanical and barrier properties might be further improved. Clay mineral is a potential nanoscale additive because it comprises silicate layers in which the fundamental unit is 1 nm thick planar structure. Also, it undergoes intercalation with various organic molecules. The intercalation causes an increase in the distance between silicate layers, which is dependent on the molecular size of the organic molecule. The dispersion of clay minerals in polymer matrix can be classified in three different types of nanocomposite such as phase separated microcomposite, intercalated nanocomposite and exfoliated nanocomposite as shown in Figure 2.20.

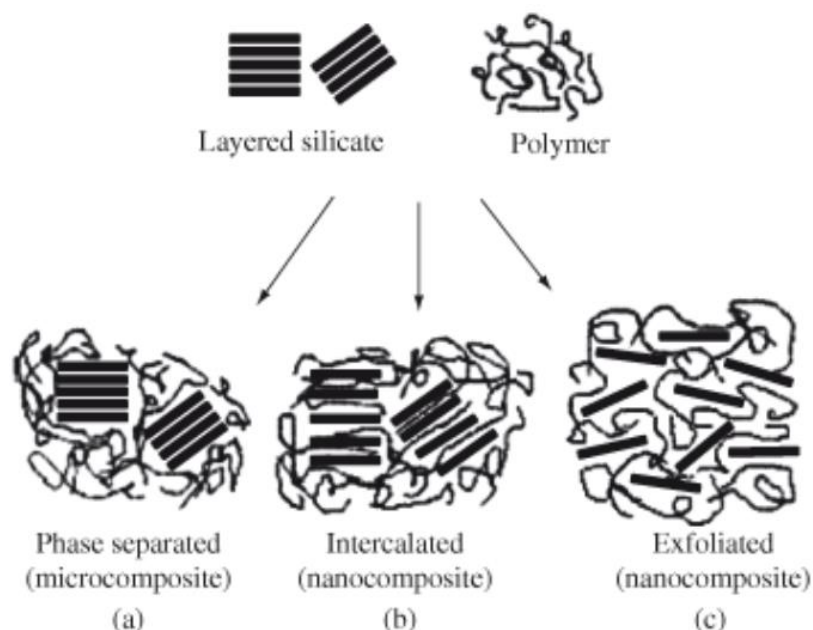


Figure 2.20 Illustration of the three different types of polymer/clay nanocomposites: (a) phase separated microcomposite, (b) intercalated nanocomposite, (c) exfoliated nanocomposite [27]

In a phase separated microcomposite the registry of the clay nanolayers is retained when mixed with the polymer. There is no intercalation of the polymer into the clay structure. Consequently, the clay fraction in phase separated clay composites plays little or no functional role and acts mainly as a filling agent for economic considerations. Intercalated nanocomposites are formed when polymer chains are inserted into the clay galleries with fixed interlayer spacing. Exfoliated nanocomposites are formed when the silicate nanolayers are individually dispersed in the polymer matrix. The average distance between the segregated layers is dependent on the clay loading. Exfoliated nanocomposites show greater phase homogeneity than intercalated nanocomposites. More importantly, each nanolayer in an exfoliated nanocomposite contributes fully to interfacial interactions with the matrix. This structural distinction is the primary reason why the exfoliated clay state is especially

effective in improving the reinforcement and other performance properties of clay composite materials.

In general, polymer/clay nanocomposites can be prepared via in situ intercalative polymerization of monomers, polymer intercalation by the solution method and melt intercalation. In situ polymerization involves the insertion of a suitable monomer into the clay galleries followed by polymerization. In the solution route, the organoclay and the polymer are dispersed in a polar organic solvent. Selection a proper solvent is the primary criterion to achieve the desired level of exfoliation of organoclay in the polymers. Solution intercalation method is not an effective way to prepare commercial nanocomposites because of high costs of solvent, which are also environmental unfriendly. Furthermore, a compatible polymer/clay solvent system is not always available. Melt intercalation is broadly applicable to many commodity and engineering polymers. Melt compounding is a flexible and commercial process capable of producing a variety of products on large volume scales. Moreover, the high shear environment of the melt extruder can assist the delamination or exfoliation of clay platelets. The disadvantage of melt intercalation is related to a low thermal stability of the onium modifiers [24].

2.10 Literature reviews

In recent decades, various factors spurred researchers to explore alternative resources as the feedstock of polyol [6]. A renewable resource that commonly use to synthesized polyol for polyurethane is natural acid. This section considers the most relevant works published in the last years about bio-based polyols synthesized from natural acid and the properties of PU materials prepared from the synthesized bio-based polyol.

2.10.1 Bio-based polyols

Many research have been reported about using lactic acid as a precursor to produce bio-based polyol such as Ahn et al. [28] produced poly(butylene succinate) (PBS) and poly(butylene succinate-*co*-butylene adipate) (PBSA) from succinic acid and adipic acid with 1,4-butanediol by a two-step reaction of esterification and deglycolization. They found that the obtained biodegradable aliphatic polyester had a higher molecular weight than 100,000 g/mol and increasing the amount of adipic acid in the polymer from 0% to 60% reduced the polyester melting point from 114 °C to 32 °C, and then from 60% to 100% increased it again to 60 °C for polybutylene adipate (PBSA).

Zeng et al. [29, 30] were successfully prepared an aliphatic polyester based poly(ester urethane) (PEU) consisting of poly(L-lactic acid) (PLLA) and poly(ethylene succinate) (PES) or poly(butylene succinate) (PBS) by condensation polymerization. They claimed that the PEUs synthesized with high molecular weight and excellent tensile properties could find some applications in biomaterials and environmental friendly materials.

Sonnenschein et al. [31] reported on succinic acid based polyester polyols prepared with butanediol and compares them to polybutylene adipate, a common polyester polyol derived from petrochemicals. The thermoplastic polyurethane was synthesized via standard condensation polymerization techniques. Thermoplastic polyurethanes made using polybutylene succinate exhibited higher glass transition temperatures and abrasion resistance than those with polybutylene adipate.

Coggio et al. [32] prepared two polyester polyols with an average molecular weight of 1,000 and 2,000 g/mol based on succinic acid and 1,6-hexanediol were synthesized and studied for use in making polyurethane dispersions and coatings. Similar polyols were prepared from 1,6-hexanediol and adipic acid, the most common aliphatic diacid used, to synthesize polyester polyols as control samples. All

synthesized polyester polyols are white solids at room temperature and transform into clear light-yellow liquids above $\sim 50^{\circ}\text{C}$. All polyester polyols exhibit melting endotherms at $44\text{-}54^{\circ}\text{C}$. Succinates and adipates polyols with the same molecular weight have similar melting points; however, increasing the molecular weight from 1,000 to 2,000 g/mol causes a slight increase in the T_m for both types of polyester polyols.

From the above research works, bio-based polyester polyols were prepared from bio-based acid, mostly lactic acid and succinic acid. Since bio succinic acid market is forecast to grow at a significant rate over the next seven years. Therefore, the aim of this work is to use succinic acid as a precursor to produce bio-based polyester polyols for PU foams.

2.10.2 PU foam/clay nanocomposites

This section refer the most related works that have been published about rigid and flexible PU nanocomposite foams, focusing on the influence of the incorporation of different types of clays on the structural and mechanical properties of the resulting foams.

Widya and Macosko [33] incorporated montmorillonite-based organoclay into rigid PU foams. They reported that the addition of 1wt% clay reduced cell size and increased cell number density on 300-isocyanate index foams. Both smaller cell size and dispersed nanoclay decreased the permeability of blowing agent. The compression strengths decreased with clay loading for the 250-isocyanate index foams, probably because the presence of clay interfered with the polymer formation. But there was no significant difference when compared with that of the 300-isocyanate index foams, because the reduction in compression strength caused by clay might have been offset by the decrease in cell size.

Xu, Tang et al. [34] have demonstrated that the addition of 2 php of an organically modified nanoclay significantly improved the tensile and compressive strengths of rigid PU foams prepared using water as a blowing agent (around 112% increment in terms of the tensile strength and about 155% in terms of the compressive strength measured at 10% deformation), even at comparatively lower relative densities, related to a combination of the finer cellular structure of PU nanocomposite foams promoted by an effective cell nucleation effect of the cell dispersed clay layers and a higher hydrogen bonding between the PU and clay's organomodifier.

Mondal and Khakhar [35] prepared medium-density rigid PU foams with improved compressive and storage moduli by incorporating variable concentrations of different types of unmodified and organically modified montmorillonites, showing promising applications as structural elements. The improvement in mechanical properties was related to the mechanical reinforcement effect of the well-dispersed clay layers and especially the finer foam cellular structure resulting from effective clay layer cell nucleation during foaming. In a similar way, Chen et al. [36] have recently prepared rigid PU foams with improved mechanical properties through the incorporation of both intercalated and previously calcined modified kaolin, another type of layered silicate. Once again, the better mechanical properties of rigid PU foams with the calcined kaolin were related to their better dispersion in PU when compared to the intercalated kaolin.

Related to the importance of proper clay dispersion in attaining an effective mechanical reinforcement of rigid PU foams, Valizadeh et al. [37] encountered an optimum nanoclay concentration of 1% for compressive strength and moduli improvement of rigid PU foams prepared using a blowing agent mixture of cyclo and normal pentanes. Further nanoclay addition resulted in foams with poorer mechanical properties, which the authors related to a tendency of clay layers to reaggregate at higher contents.

As dispersion and layer intercalation/partial exfoliation have been shown to be critical in terms of attaining the highest possible mechanical reinforcement possibilities of silicate-layered nanoclays, several works have focused on developing different strategies to promote clay layer intercalation/exfoliation and improve surface interaction with PU. The most used one has been the surface modification of nanoclays prior to mixing with PU's formulation or the combination of previous clay modification with the application of ultrasounds during mixing.

For instance, Seo et al. [38] have shown that the application of ultrasounds in combination with MDI surface modified nanoclay resulted in an improved rupture of clay aggregates and intercalation of the layers in the PU matrix, improving the efficiency of clay modification and ultimately resulting in PU foams with finer cellular structures and improved flexural and tensile strengths.

Xu et al. [39] have specifically studied how the surface modification of montmorillonite (MMT) using different organomodifiers (cetyltrimethyl ammonium bromide, methyl tallow bis(2-hydroxyethyl) quaternary ammonium chloride and tris(hydroxymethyl) aminomethane) and later incorporation into a PU foam formulation affected the final properties of the resulting rigid PU foams. Modification using organomodifiers that contained hydroxyl groups that could react with isocyanate led to partial exfoliation of the clay layers in the PU foams, ultimately resulting in foams with finer cellular structures and higher specific compressive strengths at relatively high fillers amounts, once again demonstrating the importance of dispersion and clay layer exfoliation. Sarier and Onder [40] have analyzed the possible use of MMT particles modified with different types of low molecular weight polyethylene glycols as mechanical reinforcements in rigid PU foams. Comparatively, PU foams with 2 wt% of modified MMT particles presented a higher storage elastic modulus than the unfilled PU foams, which was related to a good dispersion of the MMT layers throughout the PU and improved interaction of the modified layers with PU's molecules.

Liang and Shi [41] prepared rigid PU nanocomposite foams from MDI and soybean-based polyols by incorporating from 0.5 to 3 php of nanoclay. Both the compressive strength and modulus increased significantly for a 0.5 php concentration of clay (respectively 98 and 26% increments when compared to the unfilled soybean-oil based PU foam), progressively decreasing by further increasing the amount of nanoclay. Both tendencies were related in the case of the first to a proper clay dispersion and high cell density and small cell size of the resulting PU foams, and in the case of the higher clay amounts to insufficient nanoparticle dispersion and as a consequence nonuniform foam cellular structure.

Recently, Fan et al. [42] prepared and characterized rigid PU composite foams containing 15% of soybean-based polyol reinforced with variable concentrations (from 1 to 7 wt%) of hollow glass microspheres and unmodified montmorillonite nanoclays. Though from 1 to 3 wt% glass microsphere content, the compressive strength of PU foams decreased slightly, it increased up until 7 wt%, reaching at this microsphere content a compressive strength comparable to that of unfilled PU foams made from 100% petroleum-based polyol. On the contrary, PU composite foams reinforced with 7 wt% nanoclay presented lower compressive strengths, related to the lower density of these foams and partially opened cell walls promoted by the clay nanoparticles. However, an analysis of the specific compressive modulus showed that PU foams reinforced with 5 to 7 wt% microspheres and 3 to 7 wt% nanoclay presented similar compressive properties than those of unfilled PU foams, mainly explained by the finer cellular structure of the filled foams.

CHAPTER III

EXPERIMENT

3.1 Materials

Materials used in this research are summarized in Table 3.1. All materials were used as received without further purification.

Table 3.1 Information of all materials used in this research

Materials	Trade name	Grade	Manufacturer
1. Succinic acid (SA)	-	Analytical Reagent	UNIVAR
2. 1,4-butanediol (BDO)	-	Analytical Reagent	Sigma-Aldrich
3. Ethylene glycol (EG)	-	Analytical Reagent	Sigma-Aldrich
4. Diethylene glycol (DEG)	-	Analytical Reagent	Sigma-Aldrich
5. Triethylene glycol (TEG)	-	Analytical Reagent	Sigma-Aldrich
6. Tetraethylene glycol (TTEG)	-	Analytical Reagent	Sigma-Aldrich
7. Polyethylene glycol Mw 300 (PEG300)	-	Analytical Reagent	Sigma-Aldrich
8. Glycerol (Gly)	-	Analytical Reagent	Sigma-Aldrich
9. Stannous octoate	-	Analytical Reagent	Sigma-Aldrich

Table 3.1 Information of all materials used in this research (continued)

Materials	Trade name	Grade	Manufacturer
10. Polymeric Methylene diphenyl diisocyanate (PMDI)	B9001	A high functionality polymeric MDI obtained after the distillation of one part of pure 4,4' MDI isomer Functionality: 2.7 NCO content: 31.5 wt%	Supported by Yantai Wanhua PU Co., Ltd.
11. N, N-dimethyl cyclohexylamine (DMCHA)	-	Analytical Reagent	Supported by Huntsman International
12. Polyether dimethyl siloxane	TEGOSTAB B 8462	Analytical Reagent	Supported by Goldschmidt, Germany
13. Distilled water	-	-	Distilled in our lab
14. Commercial polyester polyol	POLIMAXX A8360	Poly (diethylene glycol phthalate)	Supported by IRPC polyol
15. Organically modified clay	Cloisite 30B	Natural montmorillonite modified with a quaternary ammonium salt	Supported by Southern Clay products, USA.
16. Unmodified clay	MMT	Natural montmorillonite	Sibelco Minerals Co., Ltd., Thailand

3.2 Instruments

The instruments used in this research are summarized in Table 3.2.

Table 3.2 Information of the instruments

Instrument	Model	Manufacturer
1. Brookfield viscometer	RVT	Brookfield Engineering Laboratories, Inc., USA
2. Fourier transform infrared spectroscopy (FT-IR)	Nicolet 6700	Thermo Scientific, USA
3. Optical microscope (OM)	SZ-CTV	Olympus; Tokyo, Japan
4. Online color video camera	SSC-E458P	Sony; Tokyo, Japan
5. Universal Testing Machine, LLOYD	LLOYD 500	Ametek
6. X-ray diffractometer (XRD)	D8	Bruker AXS, Germany
7. Thermogravimetric analysis (TGA)	TGA/STDA 851 ^e thermal analyzer	TA instruments, Switzerland
8. Proton Nuclear Magnetic Resonance Spectrometer (¹ H-NMR)	Mercury-VX 400 MHz BB	Varian
9. GPC	Class VP	Shimadzu Corporation, Japan

3.3 Methods

The methods of this research work can be divided into two parts as follow.

PART I: The first part is to synthesize bio-based polyester polyol by condensation reaction using succinic acid (SA) and seven different types of glycols. The effects of chain length of glycol and glycol types (neat or mixed glycols) used to prepare polyester polyols toward physical and mechanical properties of the prepared PU foams were investigated relatively to PU foam prepared from a commercial polyester polyol. The PU foam formulation, that provided good morphology and mechanical properties, was selected to study the effect of isocyanate index from 100 to 200. PU foam with optimum isocyanate index, that gave highest compressive strength, was then chosen to prepare the PU foam/clay nanocomposites.

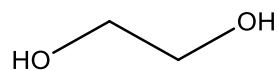
3.3.1 Synthesis of bio-based polyester polyols

The bio-based polyester polyols were synthesized from SA and seven different types of glycols that are 1,4-butanediol (BDO), ethylene Glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), tetraethylene glycol (TTEG), polyethylene glycol average molecular weight 300 (PEG300), and glycerol (Gly) as shown in Table 3.3. The chemical structures of glycols used in this research are also shown in Figure 3.1. The synthesized polyols were separated into two groups as a) SA with neat glycol (BDO, EG, DEG, TEG, TTEG and PEG300) and b) SA with mixed glycols (BDO, EG, DEG, TEG, TTEG and PEG300 were mixed with Gly separately). The functionality of the polyols for both groups was fixed at 2. To a 250 ml round bottomed flask, equipped with a magnetic stirrer, thermocouple and distillation condenser, the reactants were added and heated to 190 °C for 1 h under atmosphere. The pressure was then reduced to 160 mmHg for 1 h, the stannous octoate catalyst was added to the mixture and the reaction temperature was kept at 190°C under reduced pressure to remove water as a

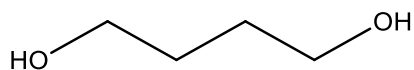
by-product from the reaction [28]. The extent of polycondensation reaction (esterification) was monitored by acid value determination. Reactions were completed when the acid values were less than 2.0 mg KOH/g. The hydroxyl number of polyol was determined by acetic anhydride-pyridine method. The experiment set up for the synthesis of bio-based succinate polyols is shown in Figure 3.2.

Table 3.3 Polyols formulation of bio-based succinate polyols

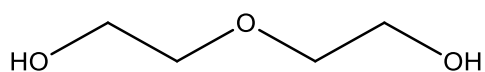
Group	Component	Molar ratio	Functionality
Neat-glycol polyols	SA:BDO	1:2	2
	SA:EG		
	SA:DEG		
	SA:TEG		
	SA:TTEG		
	SA:PEG300		
Mixed-glycol polyols	SA:BDO:Gly	1:1.5:0.33	2
	SA:EG:Gly		
	SA:DEG:Gly		
	SA:TEG:Gly		
	SA:TTEG:Gly		
	SA:PEG300:Gly		



Ethylene Glycol (EG)



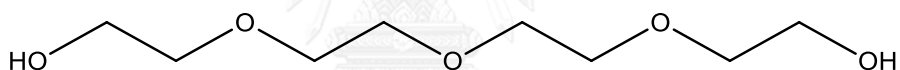
1,4-butanediol (BDO)



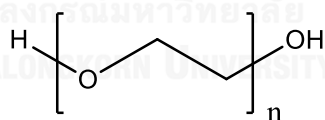
Diethylene glycol (DEG)



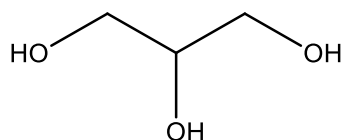
Triethylene glycol (TEG)



Tetraethylene glycol (TTEG)



Polyethylene glycol average molecular weight 300 (PEG300)



Glycerol (Gly)

Figure 3.1 Chemical structure of glycols used in the experiment



Figure 3.2 The experiment set up for the synthesis of bio-based succinate polyols

3.3.2 Preparation of bio-based polyurethane foams

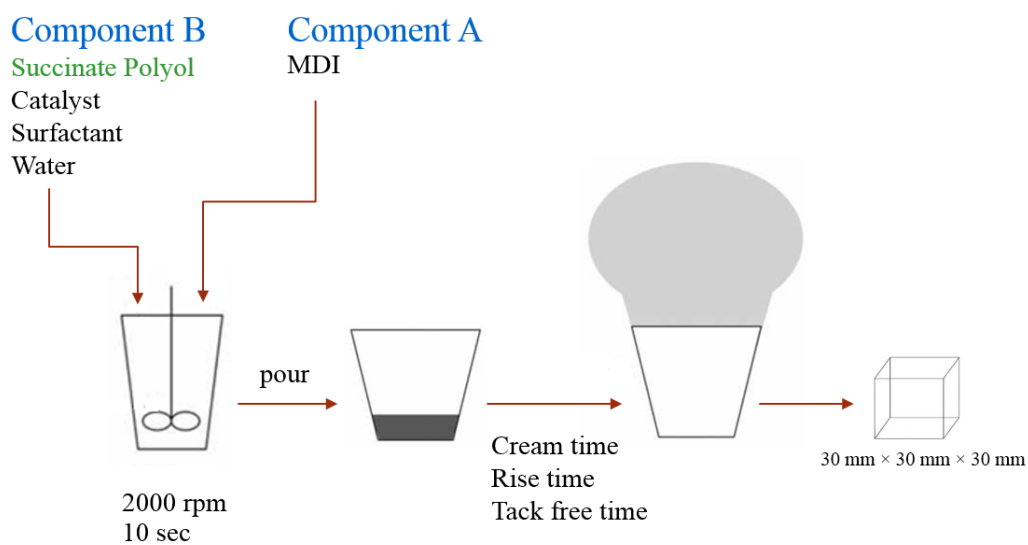
Bio-based PU foams were prepared by mixing various synthesized bio-based polyester polyols with PMDI. The isocyanate index (isocyanate equivalents/polyol equivalents) was fixed at 100. The basic formulations used to prepare foams in this research are given in Table 3.4. First, the ingredients in component B were all mixed simultaneously by stirring for 30 s at 2000 rpm in a disposable paper cup. The mixture was allowed to degas for 2 min. Then the component A (PMDI) was added and mixed for 10 s at the same speed. The reaction mixture was then quickly poured into an uncovered mold to create a foam substance at room temperature and was allowed to cure at room temperature for 7 days. After curing, the foam were cut and used as samples in various testing. The schematic diagram of lab scale PU foam formation is shown in Figure 3.3.

Table 3.4 Foam formulations of bio-based polyurethane foams

Ingredients	Concentration, php ^a
Component A	
Isocyanate index ^b of PMDI	100
Component B	
Bio-based succinate polyol	100
DMCHA (gelling catalyst)	1
TEGOSTAB [®] B 8462 (surfactant)	2.5
Distilled water (blowing agent)	3

^aThe concentration of all ingredients are expressed in parts per hundred parts of polyol, which conventionally dictates that the sum of all polyols adds up to 100 parts.

^bThe amount of isocyanate is based on the isocyanate index. The isocyanate index is the amount of isocyanate used relative to the theoretical equivalent amount.

**Figure 3.3** The schematic diagram of lab scale PU foam formation

3.3.3 Preparation of bio-based polyurethane foams with different isocyanate indexes

Bio-based PU foams were prepared using all synthesized bio-based polyester polyols at isocyanate index of 100. The polyester polyol, synthesized with optimum ratio of SA and glycols, was used to prepare PU foam. The PU foam formulation providing the best cellular morphology and mechanical properties, was selected to study the effect of isocyanate index on mechanical properties of foams. The isocyanate indexes were varied from 100 to 200 (component A). The rest of ingredients in component B were fixed at the same concentrations as the experimental in 3.3.2. The formulation used to prepare foams with different isocyanate indexes is shown in Table 3.5. The calculation of actual amount of isocyanate index used in the experiment is shown in Appendix A.

Table 3.5 Foam formulation of bio-based polyurethane foams with different isocyanate indexes

Ingredients	Concentration, php
Component A	
Isocyanate index of PMDI	100, 125, 150, 175, 200
Component B	
Selected bio-based succinate polyol	100
DMCHA (gelling catalyst)	1
TEGOSTAB [®] B 8462 (surfactant)	2.5
Distilled water (blowing agent)	3

PART II: The second part of this research is to improve the properties of bio-based PU foams by incorporating clays into PU foams. PU foam with optimum isocyanate index providing highest compressive strength from part I was chosen to prepare the PU foam/clay nanocomposites. Two types of clays with various clay levels were incorporated into PU foams. The morphology, mechanical properties and thermal stability of PU foam/clay nanocomposites were investigated relative to neat PU foam.

3.3.4 Preparation of PU foam/clay nanocomposites

PU foam/clay nanocomposite was prepared in the same fashion as neat PU foam. Nanoclay, cloisite 30B (C30B) and unmodified clay (MMT) were incorporated into PU foam formulation with various amount of 0.5, 1, 1.5, 2, 3, 5 and 7 php. The effect of clay types and clay contents on thermal stability, morphology and mechanical properties of the prepared PU foam/clay nanocomposites were investigated. The isocyanate index of all foam formulations was fixed at 200. All PU foams were prepared by one-shot and free-rising method, the chemical compositions used in foam formulations are shown in Table 3.6. First, the clay (C30B or MMT) was premixed with polyol in a disposable paper cup by stirring at 2000 rpm for 30 s. Water, catalyst, and surfactant were then added to the mixture and mixed thoroughly for an additional 15 s. This polyol mixture (component B) was allowed to degas for 120 s. Thereafter, PMDI (component A) was rapidly added into the cup and mixed at the same speed for another 10 s. The resulting mixture was immediately poured into an uncovered mold to create a foam substance at room temperature and was allowed to cure at room temperature for 7 days. After curing, the foam was cut and used as sample in various testings.

Table 3.6 Foam formulation of neat PU foam and PU foam/clay nanocomposites

Ingredients	Concentration, php
Component A	
Isocyanate index of PMDI	200
Component B	
Selected bio-based succinate polyol	100
DMCHA (gelling catalyst)	1
TEGOSTAB® B 8462 (surfactant)	2.5
Distilled water (blowing agent)	3
Clays (C30B or MMT)	0, 0.5, 1, 1.5, 2, 3, 5 and 7

3.4 Characterizations

3.4.1 Viscosity

The viscosity of the synthesized bio-based succinate polyols were measured using a Brookfield viscometer model RVT as shown in Figure 3.4. All synthesized polyols were taken at RV spindle 3 at 10 rpm at 25 °C. An average of three measurements was reported.



Figure 3.4 Brookfield viscometer model RVT

3.4.2 Hydroxyl number and Acid number

The hydroxyl number (OH numbers) is defined as the number of milligrams of potassium hydroxide needed, for each gram of sample, to neutralize the acetic acid generated during the reaction between the polyols and excess acetic anhydride. Hydroxyl numbers of the synthesized polyols were examined in accordance with ASTM D4274-05 test method D.

The acid number is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of chemical substance. The Acid number of the synthesized polyol was analyzed according to ASTM D7253.

3.4.3 Chemical structure

3.4.3.1 Fourier transforms infrared (FTIR) analysis

The functional groups of the synthesized polyols and the PU foam samples prepared from the synthesized polyols were investigated using Thermo Scientific Nicolet 6700 FTIR spectrophotometer as shown in Figure 3.5. Infrared spectra were

recorded in the wave number range of 4000-400 cm^{-1} . Spectra were obtained from 64 scans taken at a resolution of 4 cm^{-1} . The foam specimens were ground into powders and KBr sample pellet was made. The synthesized polyols were analyzed using the Attenuated Total Reflection (ATR) mode.



Figure 3.5 Thermo Scientific Nicolet 6700 FTIR spectrophotometer

3.4.3.2 Nuclear Magnetic Resonance (NMR) analysis

^1H -NMR spectra of the synthesized polyols were recorded using a Varian Mercury-VX 400 MHz BB NMR spectrometer (Figure 3.6) at room temperature by dissolving the samples in CDCl_3 . The observed ^1H chemical shifts were reported in parts per million (ppm).



Figure 3.6 Varian Mercury-VX 400 MHz BB NMR spectrometer

3.4.4 Molecular weights

Average molecular weight and polydispersity index (DI) values of the synthesized polyols were estimated by Gel Permeation Chromatography (GPC) model class VP CTO-10ACvp. Figure 3.7 showed the GPC machine used in this research. The samples were conducted in Tetrahydrofuran (THF) at 40°C with flow rate of 1 cm³/min using an isocratic pump, a solvent delivery system (LC-10AT) and a differential refractive index detector (RID-10A). A Shodex HPLC KF-805L C701094 packed column was used for the analyses. A volume of 100 µl of sample solution in THF (with a concentration of 1% w/v) was injected. Polystyrene standards with narrow molecular weight distributions were used to generate a calibration curve.



Figure 3.7 Class VP CTO-10ACvp Gel Permeation Chromatography

3.4.5 Foam formation time

Kinetics of the foam formation are followed by the physical change of some properties such as cream time, rise time, and tack free time [38]. The cream time corresponds to the start of bubble rise and hence the mixture becomes cream like due to the introduction of foam bubbles. Rise time is the time that foam reach to its largest volume or maximum height. At tack free time, the outer surface of the foam loses its

stickiness and the foam can be removed from the mold. These times were measured by a digital stop watch.

3.4.6 Morphology analysis

The morphology of the PU foam samples was studied with the SZ-CTV Olympus Optical Microscope as shown in Figure 3.8. Thin slice, less than 1 mm, was cut from each foam sample. Images were captured by an online color video camera model SSC-E458P Sony. Cell dimensions of the foam were measured from captured images by manually selecting the cell windows using an image analysis software (Image Pro Express version 6.0; Media Cybernetics, Silver Spring, MD). Only those cell windows for which the entire window came into focus were taken. Fifty cell measurements were made for each specimen [35].



Figure 3.8 SZ-CTV Olympus Optical Microscope

3.4.7 Foam density

The density of the PU Foam samples were measured according to ASTM D1622-03 with sample size of 30×30×30 mm (width × length × thickness) and the average value of three samples were reported.

3.4.8 Compressive strength

The compressive properties of the foams were measured under ambient conditions using Ametek UTM Hounsfield testing equipment model LLOYD 500 as shown in Figure 3.9. The compressive stress at 10% strain in the parallel to foam rise direction was performed according to ASTM D 1621-00. The size of the specimen was 30 × 30 × 30 mm (width × length × thickness), and the rate of crosshead movement was fixed at 2.5 mm/min for each sample and the load cell used was 1000 N. The strength of three specimens per sample was measured and the average of these values was reported.



Figure 3.9 Ametek UTM Hounsfield testing equipment model LLOYD 500

3.4.9 Dispersion of clays in PU matrix

The dispersion of clays in PU foams were determined by an X-ray diffraction spectroscopy (XRD) using Bruker AXS model D8 X-ray diffractometer as shown in Figure 3.10 with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) was used to generate X-ray at 40 kV and a current of 40 mA. Scans were taken over the 2θ range of $2\text{--}12^\circ$ with the scanning speed at $1^\circ/\text{min}$. The d-spacing was calculated according to Bragg's law:

$$n\lambda = 2d \sin\theta$$

where n is an integer representing the order of the diffraction peak, λ is the wavelength of the X-ray, d is the interplanar spacing generating the diffraction, and θ is the diffraction angle.



Figure 3.10 Bruker AXS model D8 X-ray diffractometer

3.4.10 Thermal stability

The degradation temperature of PU foams were determined by Thermogravimetric Analysis (TGA) using Mettler Toledo TGA/STDA 851^e Thermogravimetric Analyzer as shown in Figure 3.11. About 3-5 mg of each sample was heated under nitrogen atmosphere from 50 to 700°C at a heating rate of 10°C/min.

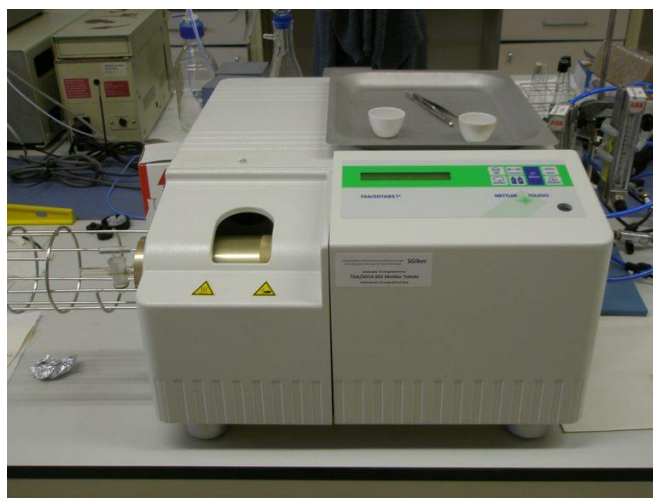


Figure 3.11 Mettler Toledo TGA/STDA 851e Thermogravimetric Analyzer

CHAPTER IV

RESULTS AND DISCUSSION

The results of this research can be divided into two parts. The first part involved the synthesis of bio-based polyester polyols from succinic acid (SA) and seven different glycols and characterization including physical properties testing. The obtained bio-based succinate polyols were used to make bio-based PU foams. The physical and mechanical properties and thermal stability of PU foams were tested relatively to one from commercial polyol. The effect of isocyanate index on mechanical property of PU foams was also reported.

The second part involved preparation of bio-based PU foam/clay nanocomposites using the synthesized polyester polyol from the first part. The properties of bio-based PU foam/clay nanocomposites were characterized and investigated.

4.1 Synthesis of bio-based polyester polyols

In this research, polyester polyols were synthesized from SA and seven types of glycols. The production of bio-based polyester polyol was conducted via condensation polymerization in a 1:2 molar ratio of SA and Glycol, respectively. The hydroxyl terminated polyol was obtained as shown in Figure 4.1. The synthesized polyols had hydroxyl groups terminated due to the excessive amounts of glycols used in the reaction. Free glycol remaining in polyol acted as a liquidifier and helped reducing the amount of free carboxylic acid left in the polyol [43].

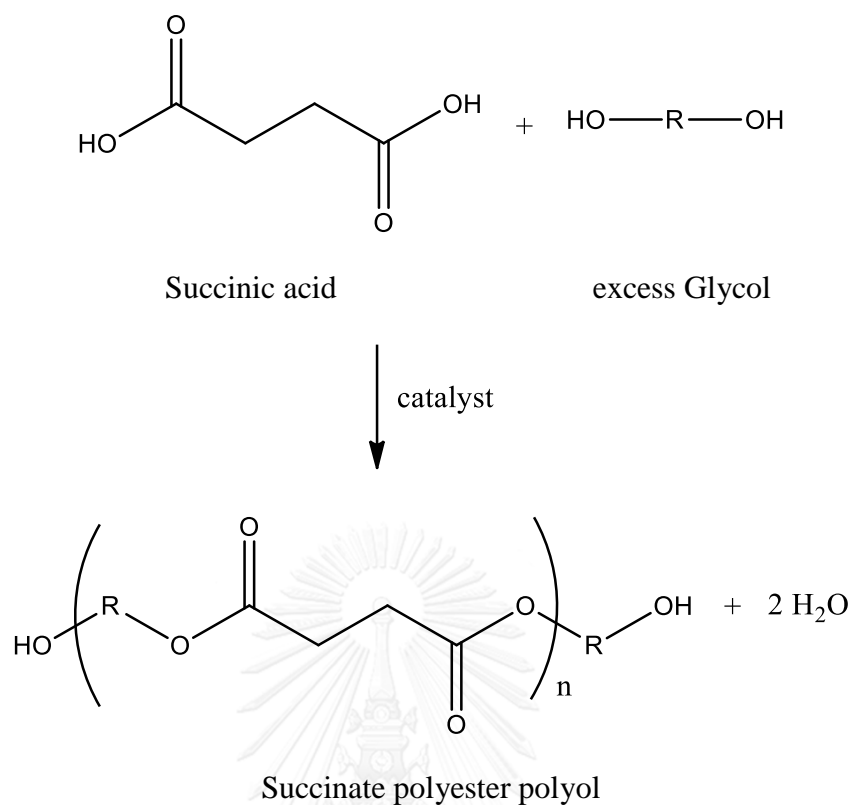


Figure 4.1 Production of bio-based succinate polyol from succinic acid and excess glycol

4.1.1 Chemical structure

Dihydroxyl terminated bio-based polyester polyol was synthesized by condensation polymerization of SA and neat or mixed glycols with the feed molar ratio of 1:2 and 1:1.5:0.3, respectively. With excessive amount of glycol, the polyol was terminated by hydroxyl groups. The average functionality of terminated hydroxyl functional group of both formula was equal to 2. The chemical structures of the synthesized bio based polyester polyols were investigated by $^1\text{H-NMR}$ spectroscopy and FTIR spectroscopy.

4.1.1.1 NMR spectra

The $^1\text{H-NMR}$ spectrum of bio-based polyester polyol prepared from SA and DEG in the feed molar ratio of 1:2 is shown in Figure 4.2. The peaks presented at chemical shift of 2.62 ($\delta\text{H}^{\text{a}}$), 3.58 ($\delta\text{H}^{\text{b}}$) and 3.69 ($\delta\text{H}^{\text{c}}$) ppm were assigned to the methylene protons in the repeating units of diethylene succinate polyols. The peaks at chemical shift of 4.23 ($\delta\text{H}^{\text{d}}$) and 2.85 ($\delta\text{H}^{\text{e}}$) ppm were defined as the methylene protons connecting with ester bonds and hydroxyl groups at the terminus of diethylene succinate polyol chain. $^1\text{H-NMR}$ spectrum of polyol prepared from SA and mixed DEG-glycerol at the molar ratio of 1:1.5:0.33 is also shown in Figure 4.3. It was found that the peaks of methylene proton of mixed DEG-glycerol polyol were similar to those of neat DEG-glycol polyol. This was due to the higher amount of DEG than glycerol used in the polyol synthesis, resulting $^1\text{H-NMR}$ spectrum was not different with polyol synthesized from SA and DEG. However, the existing peak at 4.18 ($\delta\text{H}^{\text{f}}$) ppm was observed. This indicated that there was some glycerol groups terminated in the polyol chains [44].

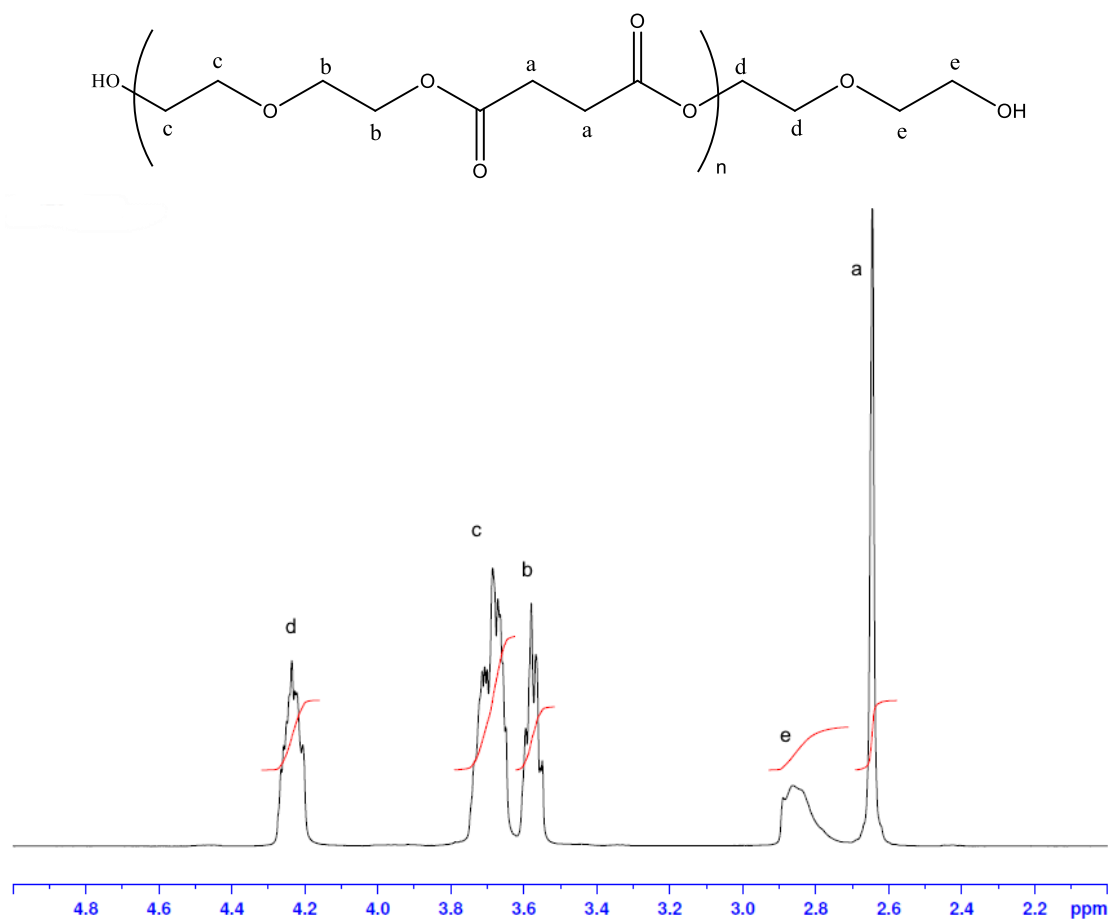


Figure 4.2 $^1\text{H-NMR}$ spectrum of bio-based succinate polyol prepared from SA and DEG at the molar ratio of 1:2

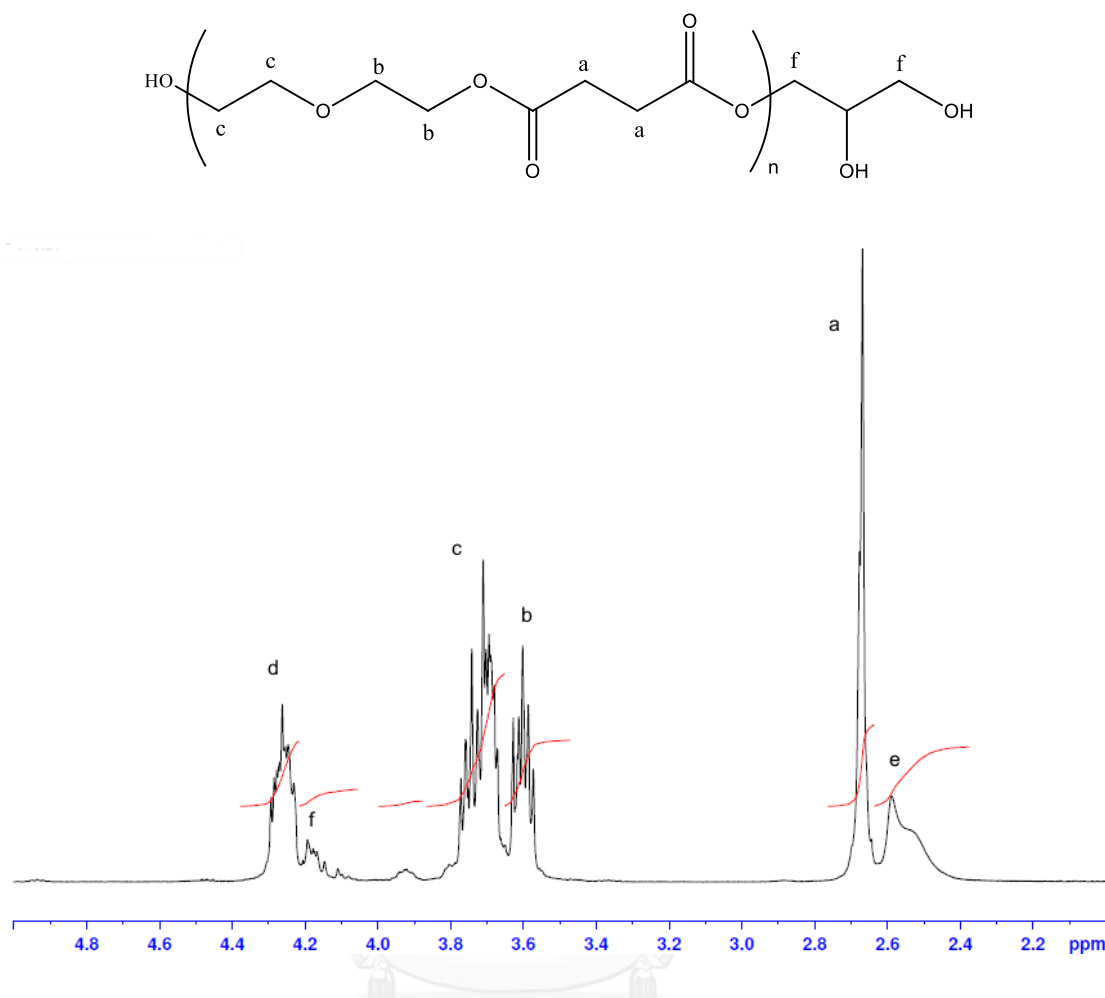


Figure 4.3 ¹H-NMR spectrum of bio-based succinate polyol prepared from SA and mixed DEG-glycerol at the molar ratio of 1:1.5:0.33

4.1.1.2 FTIR spectra

FTIR is used to characterize the functional groups presented in polymers. The FTIR spectra of synthesized bio-based succinate polyols are shown in Figure 4.4 and 4.5. The strong and broad peak of O-H stretching appeared at 3430 cm^{-1} indicated that all the synthesized polyols have terminated hydroxyl groups at the end of the polymer chains. The peaks of C-H stretching appeared between 2970 cm^{-1} and 2850 cm^{-1} . In the C=O stretching of aliphatic ester, the peak at 1730 cm^{-1} are observed. The existence of C-O stretching in O=C-O groups are confirmed by the presence of the peak around $1130\text{-}1080\text{ cm}^{-1}$ [45].

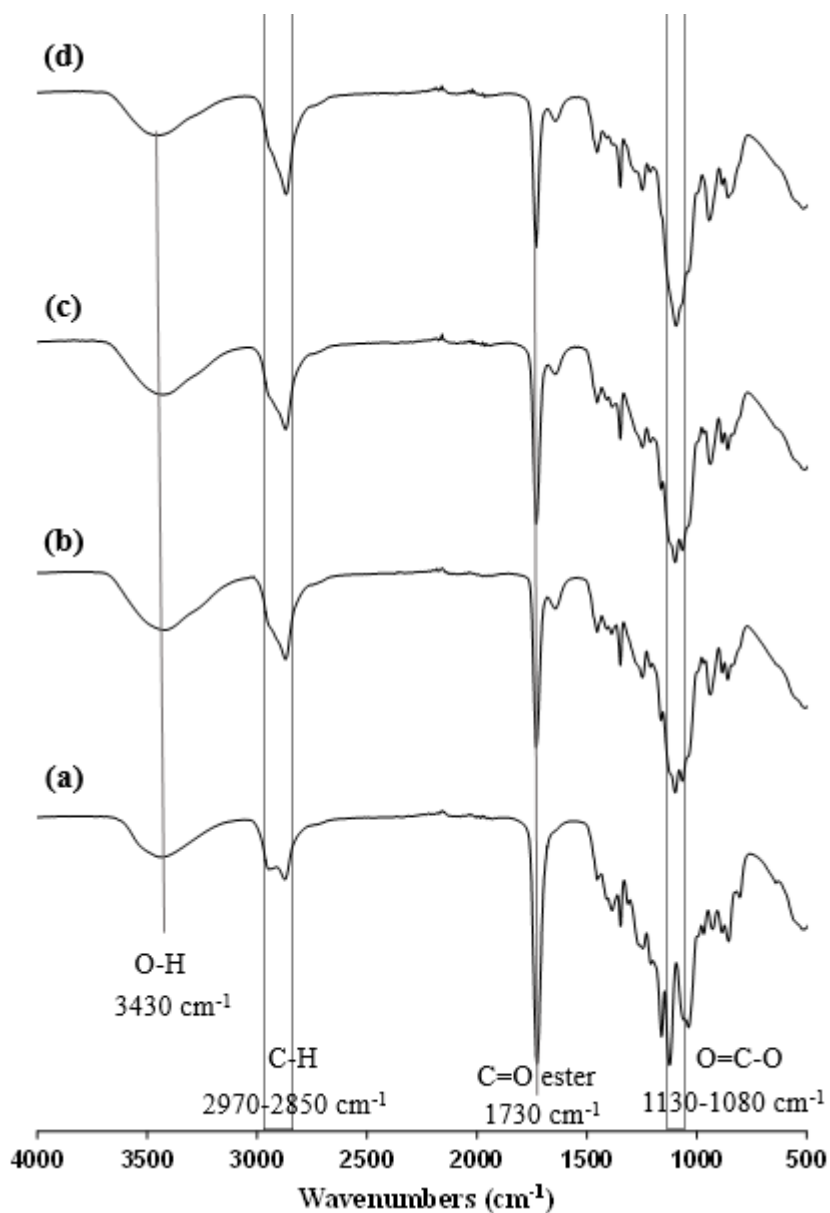


Figure 4.4 FTIR spectra of the synthesized bio-based succinate polyols from reaction of SA and neat glycol at the molar ratio of 1:2, (a) SA:DEG, (b) SA:TEG, (c) SA:TTEG, and (d) SA:PEG300

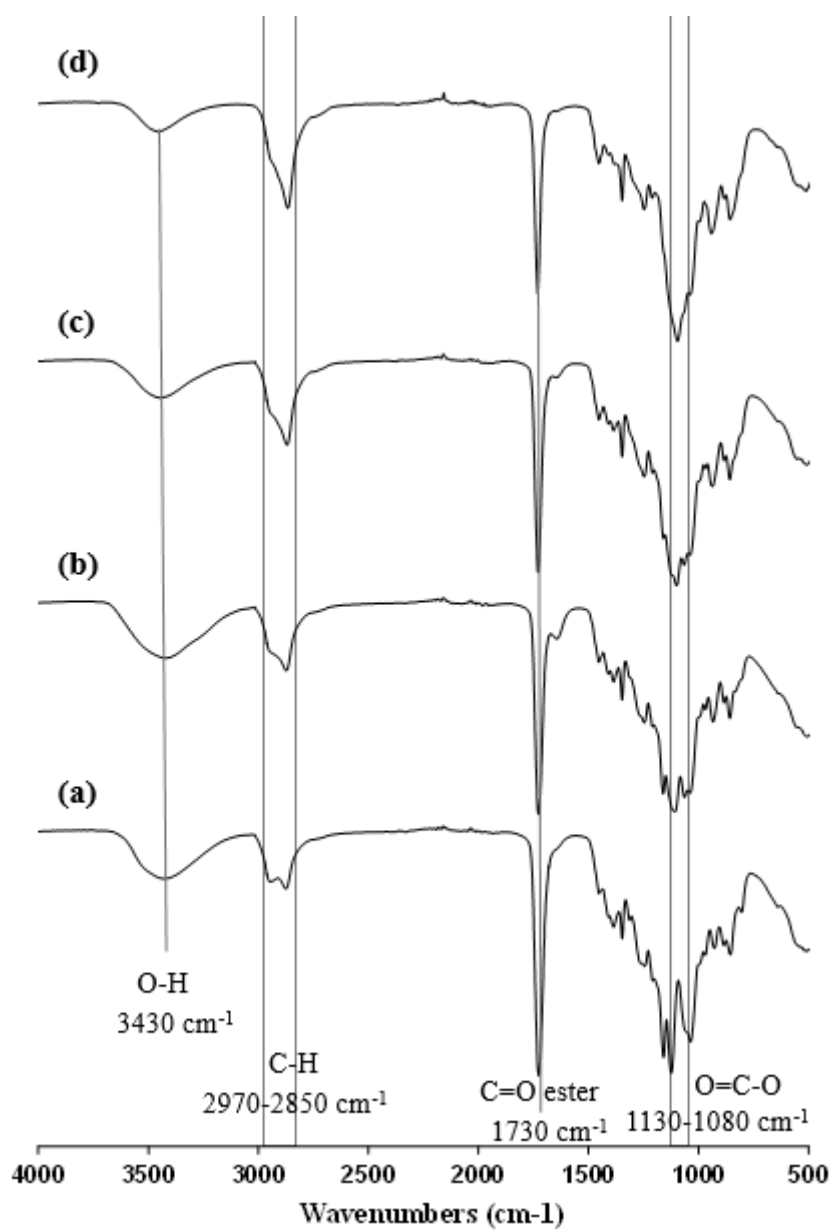


Figure 4.5 FTIR spectra of the synthesized bio-based succinate polyols from reaction of SA and mixed glycol at the molar ratio of 1:1.5:0.33, (a) SA:DEG:Gly, (b) SA:TEG:Gly, (c) SA:TTEG:Gly, and (d) SA:PEG300:Gly

4.1.2 Physical properties

The physical properties such as acid number, hydroxyl number and viscosity of the bio-based polyester polyols synthesized from SA and different types of glycols were reported.

4.1.2.1 Acid number

The acid number is expressed as the number of milligrams of potassium hydroxide required to neutralize the acidity of one gram sample. For polyester polyols used in PU foams production, the maximum acidity accepted is around 2 mg KOH/g [20]. The acid number of all synthesized bio based polyester polyols are reported in Table 4.1. The presence of stannous octoate catalyst, the reaction time of 8-10 hours was used to obtain the target acid number of < 2 mg KOH/g. This confirmed that carboxylic groups from SA were completely reacted. The calculation of acid number in Table 4.1 is shown in Appendix A.

4.1.2.2 Hydroxyl number (OH number)

The OH number is the amount of available reactive hydroxyl groups on polyol molecules. The OH number of synthesized polyols and commercial polyol are shown in Table 4.1. The polyol prepared from alkyl chain glycol such as EG and BDO had high OH number. Polyol prepared from BDO had OH number slightly lower than one prepared from EG due to the longer alkyl chain length of BDO providing lower hydroxyl end group relative to polyol prepared from EG at the same molar ratios. The polyols prepared from ether glycol showed similar trend in that the OH number decreased with increasing chain length of glycols (DEG < TEG < TTEG < PEG300). The longer ether chain length caused lower hydroxyl end group compared with polyol prepared from shorter chain length at the same molar ratios. However, OH numbers of

the polyols prepared from neat glycol and mixed glycols were not significantly different. The calculation of OH number in Table 4.1 is shown in Appendix A.

4.1.2.3 Viscosity

The viscosity of the polyester polyols is an important parameters for room temperature curable polyurethanes. The viscosity of a polymer is affected by many variables such as the molar mass, structure and conformation of the polymer molecules [46]. The results of viscosities of prepared polyols and commercial polyol are shown in Table 4.1. When the ether glycol (DEG, TEG, TTEG, PEG300) was used to prepare bio-based succinate polyols, it showed that the viscosity of the polyols decreased as the chain length of glycols increased (DEG < TEG < TTEG < PEG300). This can be found not only with the neat glycol but also with the mixed glycols. This might be because, the amount of hydrogen bonding of the polyols decreased as the chain length of the glycol increased. The slip resistance among the molecules decreased, resulting lower viscosity [20]. Moreover, the polyols prepared from mixed glycols had higher viscosity than those prepared from neat glycols. This was because the glycerol used in mixed-glycol polyols containing three hydroxyl groups in one molecule acted as cross-linking agent and provided more branches in polymer chain. As a result, the higher viscosity was obtained.

When the alkyl glycol was used in polyol synthesis (EG and BDO), it was found that the polyols provided a solid substance at room temperature as well as ones using mixture of EG or BDO and glycerol as shown in Figure 4.6. This was due to an even-carbon number glycols such as EG and BDO, used to react with succinic acid, the carbonyl ester groups arranged on the opposite side of the polyol chain to minimize energy and enhance polarity, which allowed for stronger inter-chain alignment and hence the tendency to crystallize. The proton, carbon and oxygen atoms are distributed spatially so that the largest substituents are in anti-conformation, with dihedral angles

between the largest substituents of 180° along the chain. The arrangement of the molecules of polyol prepared from SA and BDO in Figure 4.7 (a) showed the increasing of the linearity. This linearity can explain why polyols with SA and BDO combinations tend to form waxy solids even in the mixture glycol systems. However, odd-carbon number glycol (such as 1,3-propanediol) force the carbonyls to the same side of the polyester chain and introduce a kink along the axis of the polyester chain as shown in Figure 4.7 (b) [47].

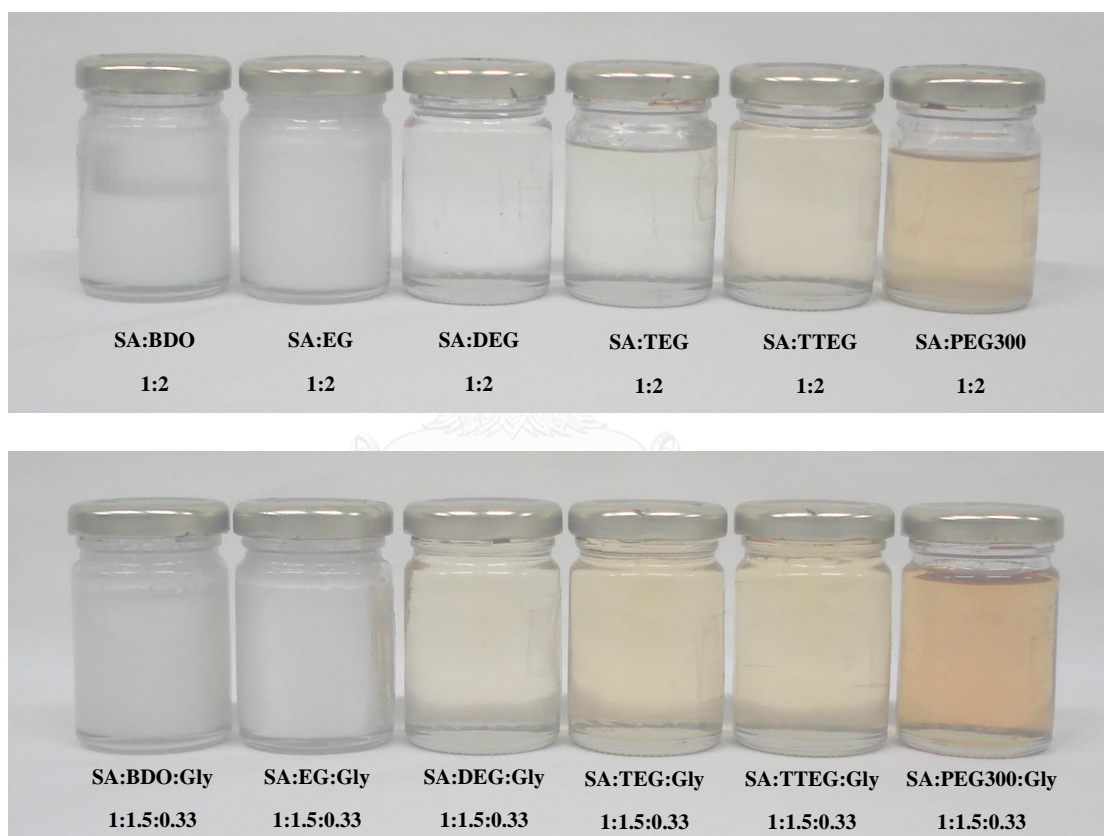


Figure 4.6 Appearance of the synthesized bio-based succinate polyols

Table 4.1 Acid number, OH number and viscosity of bio-based polyester polyols synthesized from SA and neat glycol or mixed glycol

Group	Component	Acid number (mg KOH/g)	OH number (mg KOH/g)	Viscosity @ 25 C (mPa s)
Neat-glycol polyols	SA:BDO	1.55	342.16	NA-solid
	SA:EG	1.51	353.77	NA-solid
	SA:DEG	0.44	293.94	450
	SA:TEG	1.14	281.98	400
	SA:TTEG	1.38	210.70	350
	SA:PEG300	1.65	145.76	325
Mixed-glycol polyols	SA:BDO:Gly	1.25	355.36	NA-solid
	SA:EG:Gly	1.09	369.38	NA-solid
	SA:DEG:Gly	1.23	308.55	1,362
	SA:TEG:Gly	1.09	261.42	1,175
	SA:TTEG:Gly	1.56	203.55	1,150
	SA:PEG300:Gly	1.50	181.41	825
	POLIMAXX A8360	2.0-3.0	352.16	1,100

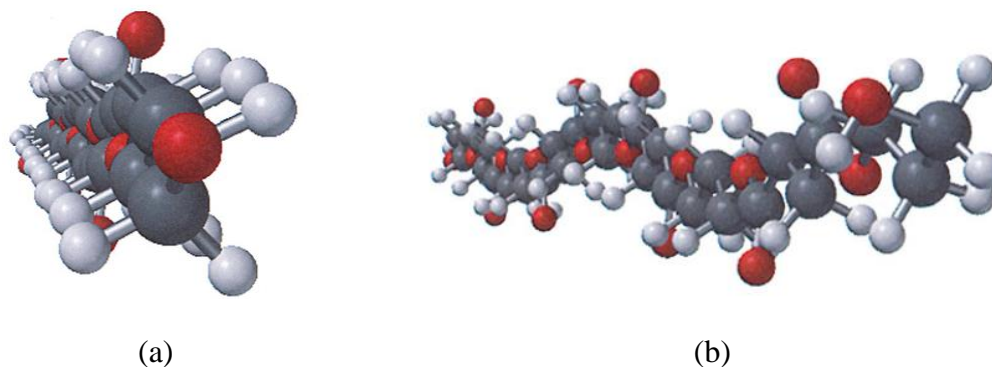


Figure 4.7 A five-repeat unit computer model of succinate polyols with an even numbered carbon glycol (1,4-butanediol, (a)) and an odd numbered carbon glycol (1,3-propanediol, (b)) [47]

4.1.2.4 Molecular weights

Bio-based polyester polyols were prepared by the reaction of succinic acid (SA) and glycols at temperature 190°C. This equilibrium process involves esterification reactions with evolving water, hydrolysis of ester links, and transesterification reactions, and results in a complex mixture of oligomers with a wide range of molecular weights [43]. The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (M_w/M_n) of the synthesized polyols are shown in Table 4.2. The results showed that M_n of the polyols slightly decreased but M_w slightly increased as the chain length of glycols used in the reaction increased. This is because of the effect of OH number of glycols. At the same functionality of polyols, the lower OH number of longer chain polyols, the higher M_w of polyols were obtained [48]. Polydispersity index values of all synthesized polyols are in the range of 1.86 to 3.99. Generally, the polyols used in rigid PU foam production have molecular weights around 150-1,000 g/mol [9]. All synthesized bio-based polyols had molecular weight in the range of 479 to 961 g/mol which is in the range of typical polyol for rigid PU foam preparation.

Table 4.2 Molecular weights of the synthesized bio-based polyester polyols

Polyols	M_n (g/mol)	M_w (g/mol)	M_w/M_n
SA:BDO	263	584	2.22
SA:EG	258	479	1.86
SA:DEG	265	709	2.95
SA:TEG	262	776	2.71
SA:TTEG	259	781	3.00
SA:PEG300	247	831	3.36
SA:BDO:Gly	248	632	2.55
SA:EG:Gly	259	555	2.14
SA:DEG:Gly	254	703	2.77
SA:TEG:Gly	252	828	3.28
SA:TTEG:Gly	253	854	3.38
SA:PEG300:Gly	241	961	3.99

4.1.3 Selection of polyols for PU foams preparation

In PU foam production, liquid polyol is required to react with isocyanate at room temperature [43]. Therefore the liquid polyols synthesized from SA and DEG, TEG, TTEG or PEG 300 were selected to prepare PU foams as well as the polyols using SA and mixture of DEG, TEG, TTEG or PEG 300 with glycerol. The solid form of polyols at room temperature were discarded. This included the polyols synthesized from SA with neat EG and BDO, and also SA with mixture of EG and BDO with glycerol. The selected polyols formulations are shown in Table 4.3.

Table 4.3 Selected polyols formulation for bio based PU foams preparation

Group	Component	Molar ratio	Functionality
Neat-glycol polyols	SA:DEG	1:2	2
	SA:TEG		
	SA:TTEG		
	SA:PEG300		
Mixed-glycol polyols	SA:DEG:Gly	1:1.5:0.33	2
	SA:TEG:Gly		
	SA:TTEG:Gly		
	SA:PEG300:Gly		

4.2 Characteristics and properties of bio-based polyurethane foams

A generalized polyurethane linkage from the synthesized bio-based polyester polyols with polyisocyanate in this research is shown in Figure 4.8. The PU foams were prepared from synthesized bio-based succinate polyols as shown in Table 4.3 with PMDI. All prepared PU foams were fixed at NCO index of 100.

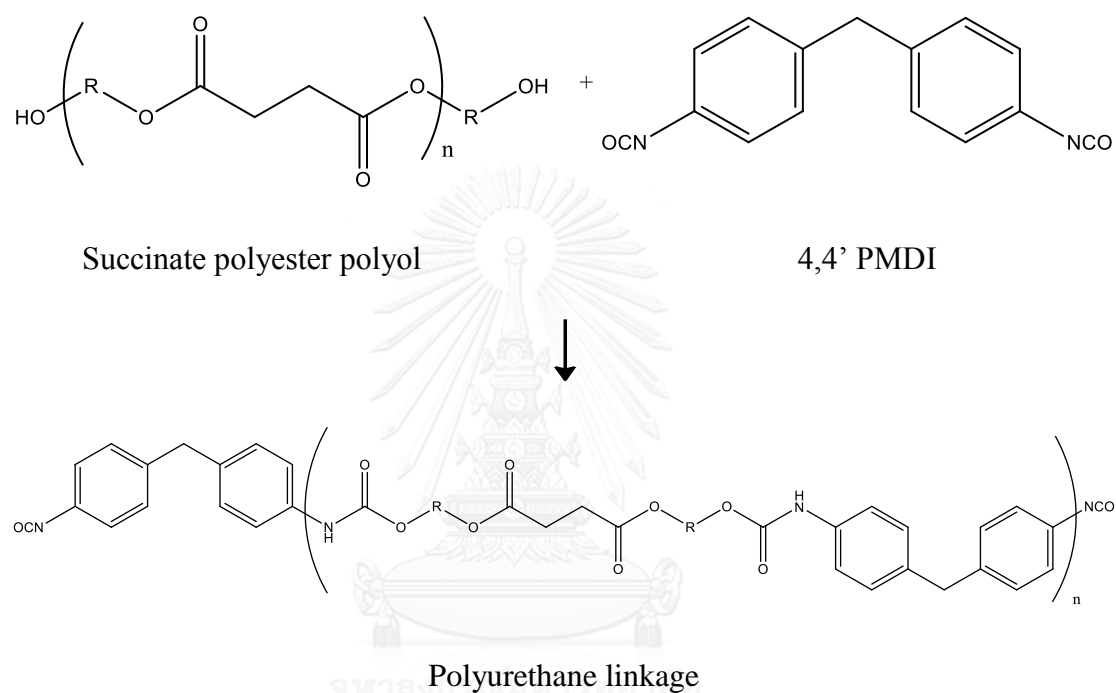


Figure 4.8 Polyurethane synthesis from synthesized bio-based polyester polyols with 4,4' PMDI

4.2.1 Chemical structure

The chemical structure of bio-based PU foams prepared from the synthesized bio-based succinate polyols were analyzed by FTIR spectroscopy. The FTIR spectra of PU foams prepared from neat-glycol polyols and mixed-glycol polyols are shown in Figure 4.9 and 4.10, respectively. The wide absorption band at 3350 cm^{-1} represented stretching vibration of N-H urethane hydrogen bonded. It can be seen that the peak for hydroxyl located at 3430 cm^{-1} almost disappears after succinate polyols reacted with

PMDI. The peak at 2200 cm^{-1} which is a characteristic peak of $\text{N}=\text{C}=\text{O}$ group are hardly observed, this indicated that isocyanate groups of PMDI were totally reacted [49]. The formation of urethane linkages was confirmed by the appearance of two absorption peaks. The first peak at 1600 cm^{-1} was due to $\text{C}=\text{O}$ stretching of urethane groups the other peak at 1535 cm^{-1} can be attributed to N-H stretching of urethane linkage. The carbonyl peak ($\text{C}=\text{O}$) were detected around 1735 cm^{-1} proved that the hydrogen bond was formed in PU foams [50]. The bands observed in between $2970\text{-}2850\text{ cm}^{-1}$ indicated the C-H stretching of $-\text{CH}_2$ group.



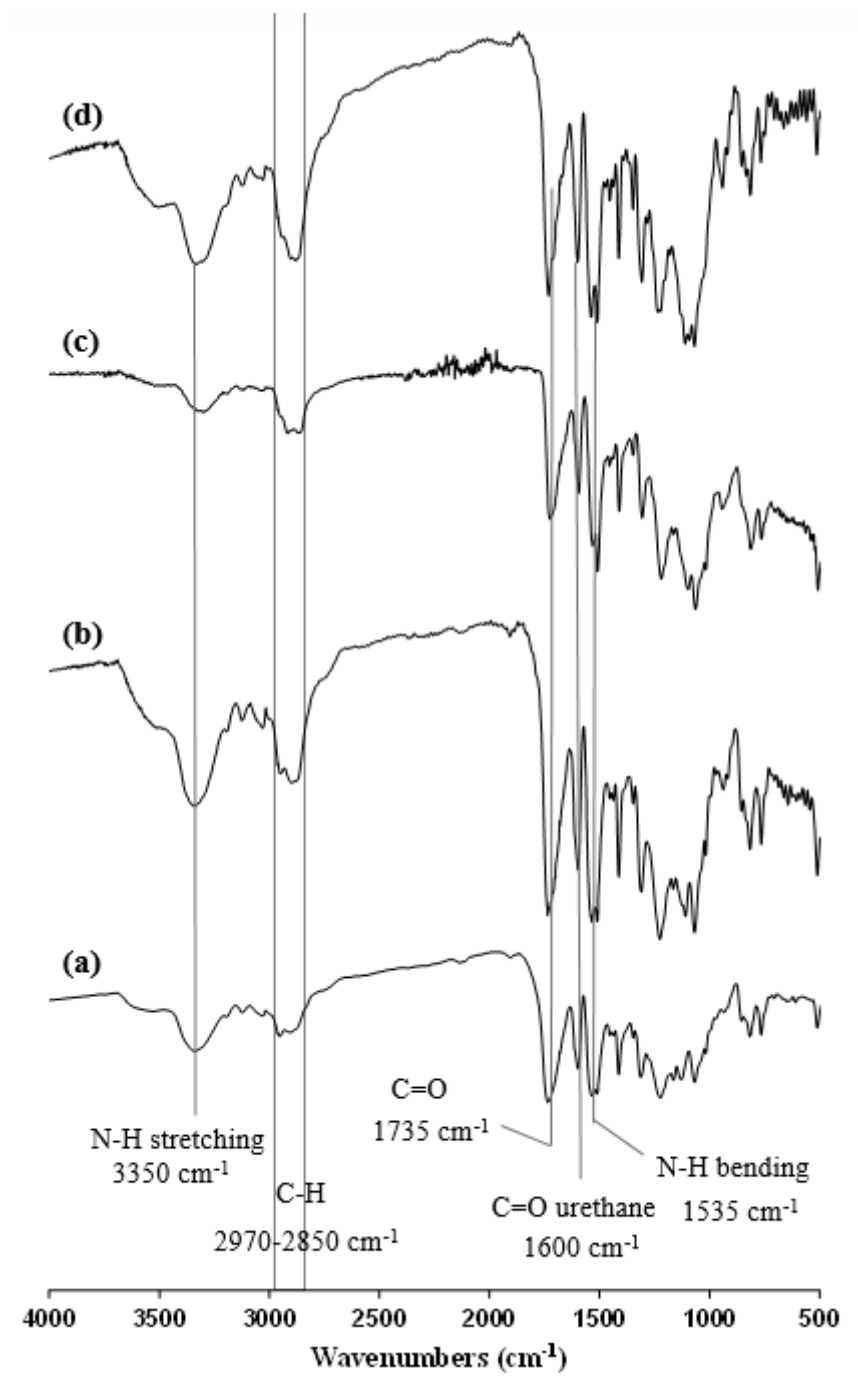


Figure 4.9 FTIR spectra of bio-based PU foams prepared from SA and neat-glycol polyols at the molar ratio of 1:2, (a) SA:DEG, (b) SA:TEG, (c) SA:TTEG, and (d) SA:PEG300

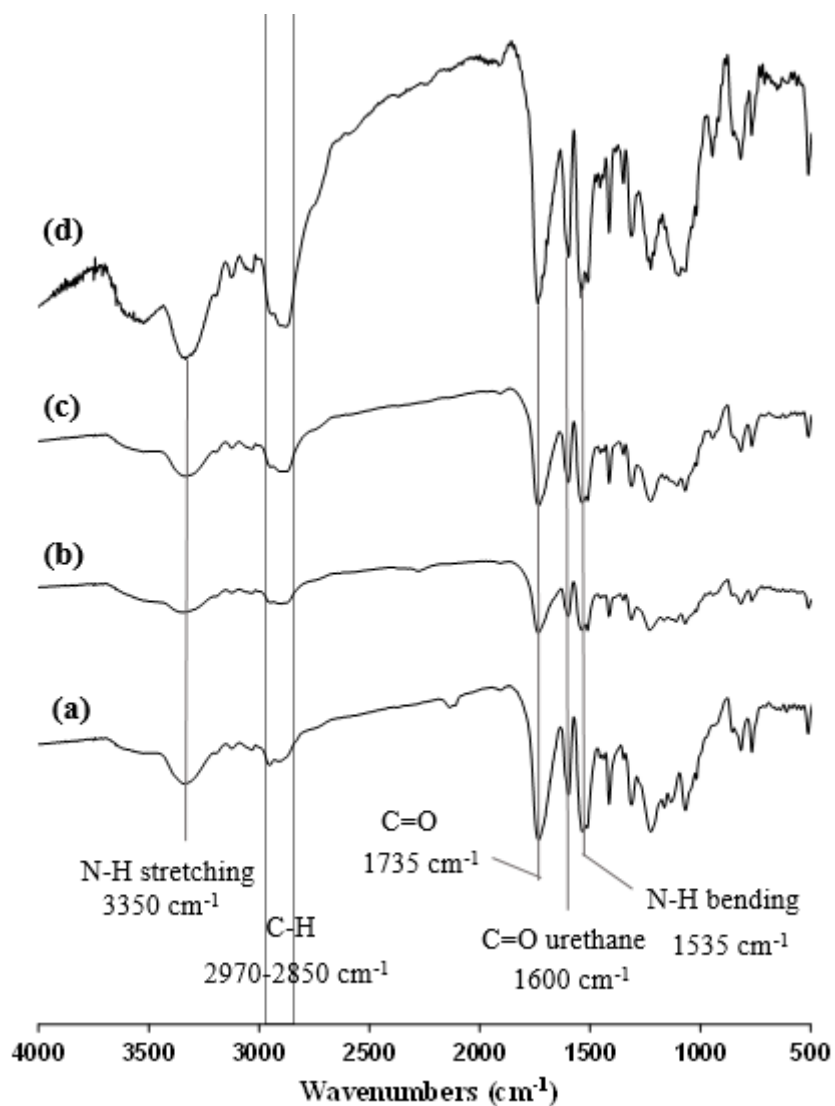


Figure 4.10 FTIR spectra of bio-based PU foams prepared from SA and mixed-glycol polyols at the molar ratio of 1:1.5:0.33, (a) SA:DEG:Gly, (b) SA:TEG:Gly, (c) SA:TTEG:Gly, and (d) SA:PEG300:Gly

4.2.2 Foam formation time

There are various types of times that involve during foam formation. Cream time is the time when the polyol and isocyanate mixture begins to change from the liquid state to a creamy and starts to expand subsequently. Rise time is the time that foam reach to its largest volume or maximum height. Tack free time is the time taken from the beginning as the formulation is poured till the point that the outer skin of the foam mass loses its stickiness or adhesive quality [51]. Foam formation times of the prepared PU foams are shown in Table 4.4. It was found that, the foam formation time of PU foams increased as the chain length of glycol in polyols increased (DEG < TEG < TTEG < PEG300). This phenomenon was found in all foams prepared from neat or mixed-glycol polyols. This indicated that the lower hydroxyl contents of the long chain polyols provided lower reactivity relative to the short chain polyols. Moreover, PU foam prepared from DEG-glycerol mixed glycol polyol showed shortest tack free time used in foam formation and the tack free time were similar to the foam prepared from commercial polyol (POLIMAXX A8360).

Table 4.4 Foam formation time of the bio-based PU foams prepared from synthesized bio-based succinate polyols

Sample	Cream time (± 1 s)	Rise time (± 1 s)	Tack free time (± 1 s)
SA:DEG	16	36	43
SA:TEG	17	41	61
SA:TTEG	19	46	83
SA:PEG300	25	52	92
SA:DEG:Gly	15	39	44
SA:TEG:Gly	17	42	53
SA:TTEG:Gly	22	45	70
SA:PEG300:Gly	23	48	81
POLIMAXX A8360	12	38	45

4.2.3 Morphology

In general, the physical properties of foam depend on the rigidity of the polymer matrix, as well as on the cellular structure of foam. The morphology and cellular structure of prepared PU foams were observed using an optical microscope (OM). Figure 4.11 showed the cubic specimens and OM images of PU foams prepared from bio-based succinate polyols. It was observed that the cubic specimens of foams prepared from neat-glycol polyols had larger pore size than ones prepared from mixed-glycol polyols. Moreover, the pore size of foams increased as the length of glycols chain (DEG < TEG < TTEG < PEG300) increased. The results of OM images showed

that the foams prepared from mixed-glycol polyols had regular cell size and there are more closed cells of spherical and polyhedral shape than those prepared from neat-glycol polyols. The average cell dimension, measure by image analysis of OM images by calculating the average of at least 50 cells [35], and volume of the foam samples are shown in Table 4.5. The cell dimension of PU foams increased as the chain length of the glycol in polyol used in the foam increased as shown in Figure 4.12 (a) to (d). This was also found in PU foams prepared from SA with mixed glycol polyols as shown in Figure 4.13 (a), (b), (c) and (d). In addition, PU foams prepared from neat or mixed PEG300 polyols showed large opened cell structure. The lower magnification of OM images was taken to show the overall foam sample having opened cell structure as shown in Figure 4.12 (d) and Figure 4.13 (d). However, foams prepared using mixed-glycol polyols had smaller cell dimensions than ones using neat-glycol polyols at the same glycol in polyols used in the foams.

Moreover, it was found that the volume of foam rising decreased as the chain length of the glycol in polyol increased. All foams prepared using neat-glycol polyols were found to have CO₂ gas released during the foam formation while the foams prepared using mixed-glycol polyols were not. This might be because the effect of glycerol used in mixed-glycol polyols could act as crosslinking agent causing PU foams had more polymer network, resulting PU foams had regular and smaller cell size. Moreover, PU foams prepared from neat-glycol polyols did not provide good morphology in that the foams had less volume than those prepared by mixed-glycol polyols. This might be because there were small amount of CO₂ gas released during the foam formation and caused the thick cell wall of PU foams. Due to the lower viscosity of neat-glycol polyols, the polymer could not maintain the CO₂ gas generated during foam formation resulting lower height of foams after rising. The higher viscosity of mixed-glycol polyols reduced cell drainage by gravity at the initial foaming stage, smaller cell size and higher closed cell contents occurred [17]. The cubic

specimen and OM image of PU foam prepared from commercial polyol are shown in Figure 4.14.



Figure 4.11 Cubic specimens of bio-based PU foams prepared from SA and neat-glycol polyols (top), PU foams prepared from SA and mixed-glycol polyols (bottom)

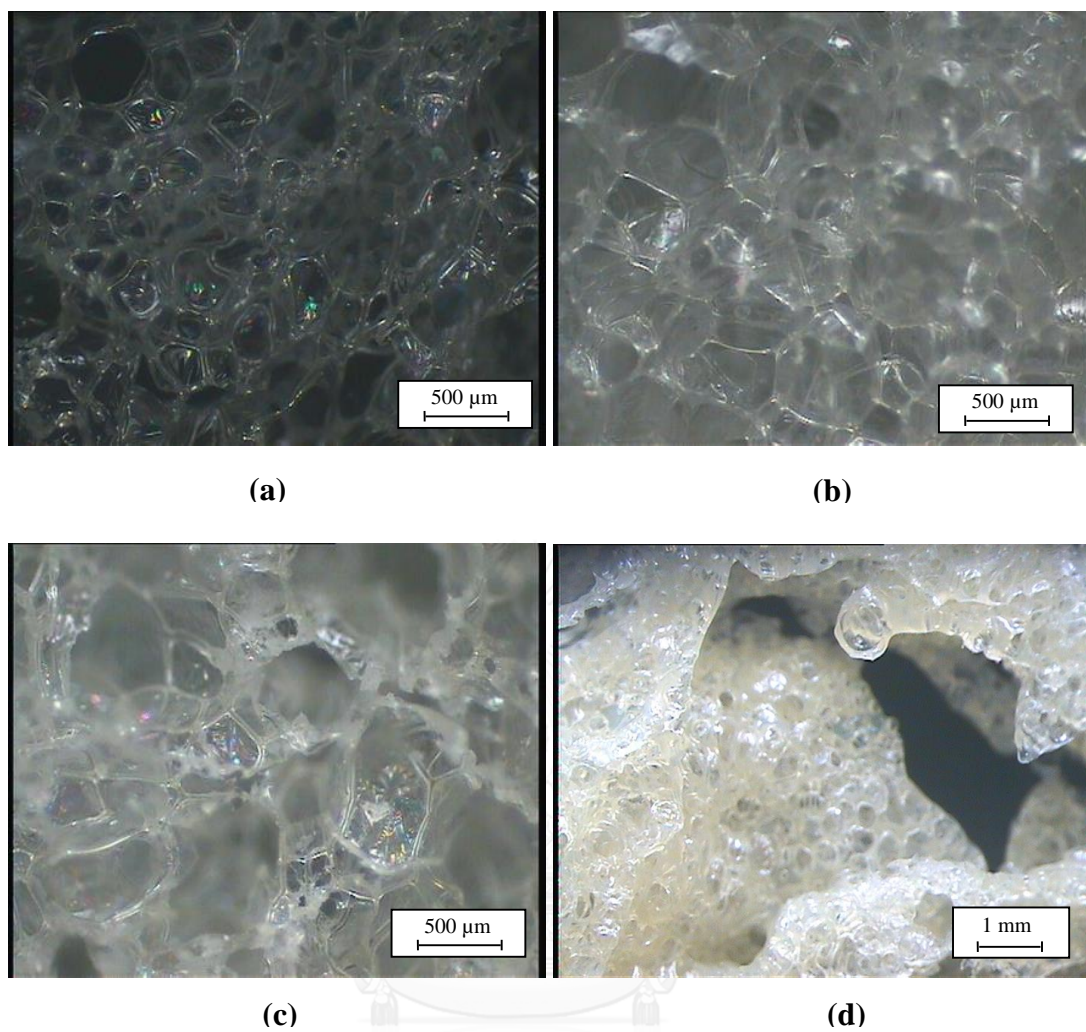


Figure 4.12 OM images of the bio-based PU foams prepared from SA and neat-glycol polyols at the molar ratio of 1:2; (a) SA:DEG, (b) SA:TEG, (c) SA:TTEG and (d) SA:PEG300

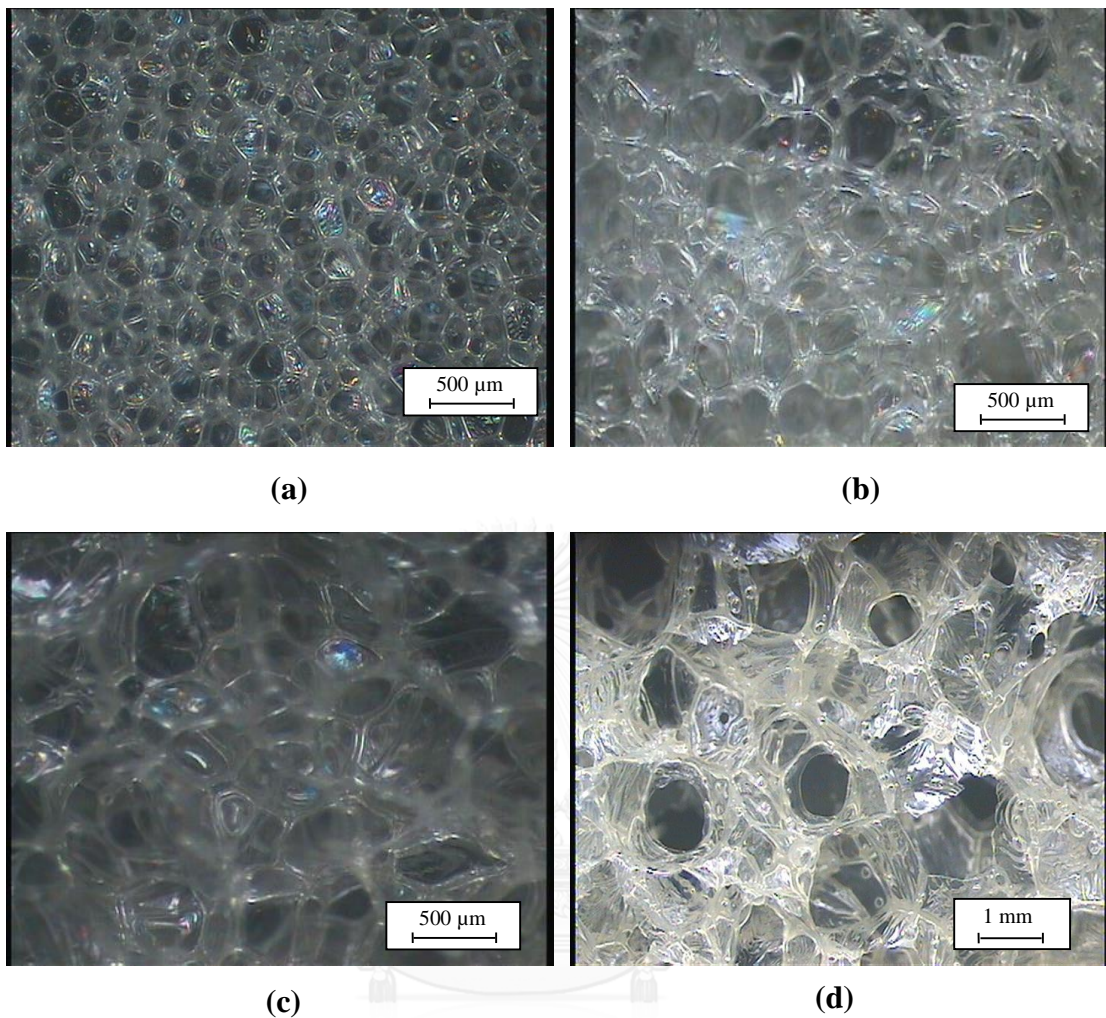


Figure 4.13 OM images of bio-based PU foams prepared from SA and mixed-glycol polyols at the molar ratio of 1:1.5:0.33; (a) SA:DEG:Gly, (b) SA:TEG:Gly, (c) SA:TTEG:Gly and (d) SA:PEG300:Gly



Figure 4.14 Cubic specimen and OM image of the PU foam prepared from SA and commercial polyester polyol (A8360)

Table 4.5 Cell dimensions and height of PU foams after rising

Foam sample	cell dimension (μm)	Foam height
SA:DEG	254.06 ± 36.38	8.82/10.00
SA:TEG	341.72 ± 48.60	7.88/10.00
SA:TTEG	385.71 ± 53.81	6.79/10.00
PA:PEG300	NA-large opened cell	5.12/10.00
SA:DEG:Gly	172.48 ± 39.19	10.00/10.00
SA:TEG:Gly	294.63 ± 24.06	8.15/10.00
SA:TTEG:Gly	322.16 ± 25.33	7.81/10.00
SA:PEG300:Gly	> 2000	5.87/10.00
POLIMAXX A8360	185.37 ± 45.69	9.83/10.00

4.2.4 Foam density

The specific properties of PU foams can be varied within limits by choice of raw materials, density, and method of applications. However, density is one of the main variables controlling most of the mechanical properties and has an effect much larger than that of other possible changes in polymer and foam structure. Hence, the study of the effect of density on the properties of rigid PU foams has acquired importance for the broad range of its applications [52]. The bulk densities of PU foams prepared from synthesized bio-based polyester polyols and commercial polyol (A8360) are shown in Figure 4.15 and Table 4.6. The blowing reaction of PU foams had effected to the foam density since the reaction released CO₂ gas causing the foam rise toward the top of a mold. The results showed that density of PU foams firstly decreased and then increased as the chain length of glycol used to synthesize polyol increased. This was because the low viscosity of longer chain length of glycol in polyol used in the foam, such as TTEG and PEG300, the reaction rate between polymerization of polyurethane and gas generation was imbalanced. The polymer could not maintain the CO₂ gas generated during foam formation resulting the small amount of CO₂ was released. Thus the density of PU foams prepared from longer chain-glycol polyols was increased. Moreover, foams prepared from neat-glycol polyols had higher density than those prepared from mixed-glycol polyols. Since the viscosity of polyols prepared from neat glycol-polyols was lower than ones with mixed-glycol polyols, this would cause the height of rising foam lower than the ones with mixed-glycol polyols. Therefore PU foams prepared from neat-glycol polyols had higher density than those prepared from mixed-glycol polyols.

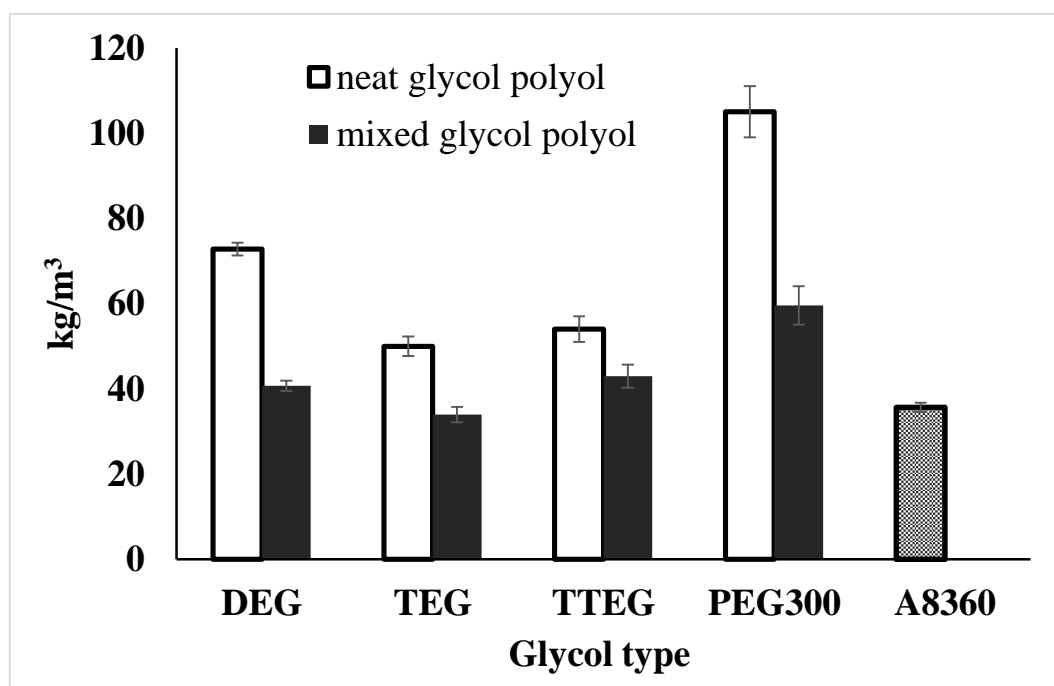


Figure 4.15 Bulk density of the PU foams prepared from neat or mixed-glycol polyols relative to one prepared from commercial polyol (A8360)

4.2.5 Compressive strength

Mechanical properties are important properties for foam application. The mechanical properties of polymer foams mainly depend on the intrinsic property of the polymer matrix such as density of foams and the geometric feature of the cells [53]. Compressive strength is the most important mechanical property used to evaluate the strength of PU foams. The compressive strength of PU foams prepared from synthesized bio-based polyester polyols relative to PU foams prepared from commercial polyol (A8360) are shown in Figure 4.16 and Table 4.6. It was observed that, the compressive strength of PU foams gradually decreased as the chain length of glycol used to synthesize polyol increased (DEG < TEG < TTEG). This might be because the longer chain polyols enhanced the flexibility of foams [46]. Moreover, polyols prepared from longer glycol chain length had lower hydroxyl number relative to short chain glycol polyols resulting provided less in urethane linkage and lower in

strength. The high cohesive interaction between these urethane linkages provided rigid structure, resulting PU foam to have better dimensional stability [54]. Moreover, the increasing in compressive strength was not only because of the effect of urethane linkage, but also because of the effect of small and closed cell foam structure. However, foams prepared from TTEG had slightly increased in compressive strength. This was because of higher polymer content per volume of the foam. From the morphology result in 4.2.3, the structure of foams prepared from neat or mixed-PEG300 glycol polyols (Figure 4.12 (d) and Figure 4.13 (d)) showed large opened cell size and had thicker cell wall compared with foams prepared from other types of glycols. Therefore, the foams provided high compressive strength because the effect of high polymer contents, rather than the effect of cell structure of PU matrix.

Foams prepared from mixed-glycol polyols had higher compressive strength than those prepared from neat-glycol polyols. Even though the density of foams prepared from neat-glycol polyols was higher than those prepared from mixed-glycol polyols, the compressive strength results did not show the same trend. This was due to the morphological aspects presented in Figure 4.12 and 4.13. Small and closed cell contributed to the increment in compressive strength of foams. The PU foam prepared from polyol obtained from the mixture of DEG and glycerol provided the highest compressive strength and was higher than one prepared from commercial polyol.

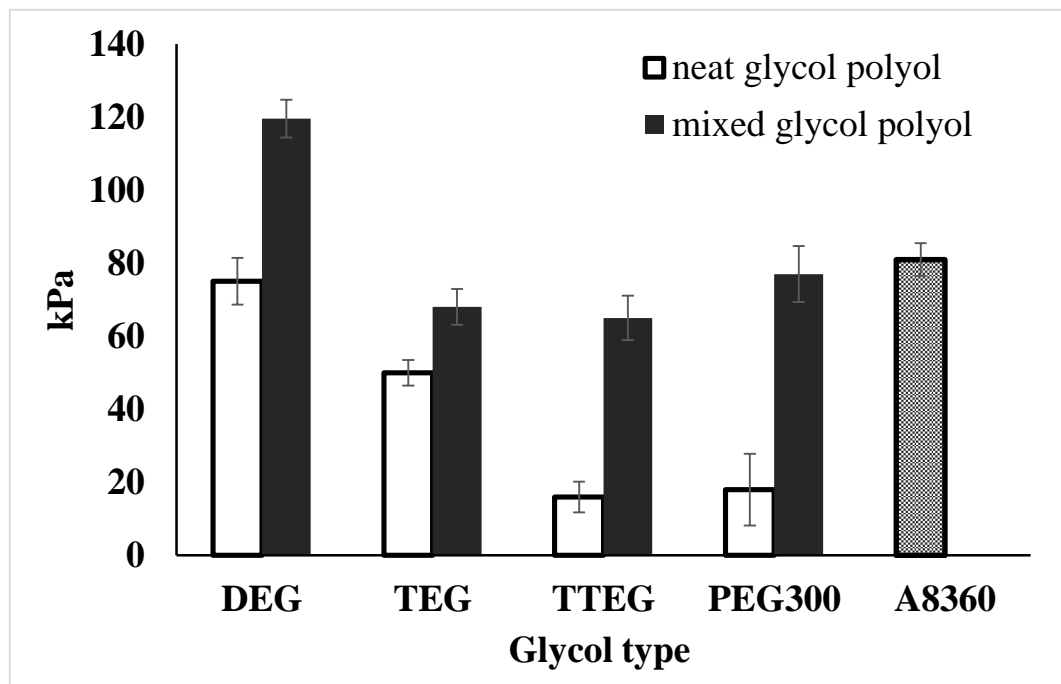


Figure 4.16 Compressive strength of the PU foams prepared from neat or mixed-glycol polyols relative to one prepared from commercial polyol (A8360)

Table 4.6 Density and compressive strength of PU foams prepared from neat or mixed-glycol polyols relative to one prepared from commercial polyol (A8360)

Foam sample	Density (kg/m ³)	Compressive strength at 10% strain (kPa)
SA:DEG	73.16	75.44
SA:TEG	50.38	50.73
SA:TTEG	54.23	16.95
PA:PEG300	105.10	18.24
SA:DEG:Gly	41.66	119.56
SA:TEG:Gly	34.23	68.47
SA:TTEG:Gly	43.97	65.15
SA:PEG300:Gly	59.58	77.62
POLIMAXX A8360	35.68	80.92

4.2.6 Thermal stability

Thermogravimetry analysis was used to investigate the degradation of the PU foams. The decomposition onset temperature (T_{onset}), designed as the temperature at which the sample loss 5 wt% weight [55], and the temperature at which the sample has the maximum degradation rate (T_{max}) for PU foams. Figure 4.17 and Table 4.7 presented the TGA analysis curves and data for PU foams prepared from neat or mixed-glycol polyols. It was found that PU foams prepared from mixed-glycol polyols had lower T_{onset} relative to those prepared from neat-glycol polyols. This was due to higher density of foams prepared from neat glycol polyols, the content of polymer in one unit

was higher than those prepared from mixed glycol polyols. As a result, char residue of the foams made from neat-glycol polyols was higher than ones prepared from mixed-glycol polyols. Moreover, PU foams prepared from mixed-glycol polyols provided slightly higher in T_{max} compared with ones prepared from neat-glycol polyols. This could be explained by the effect of network structure of foams. Using the mixture of DEG-glycerol polyol, the glycerol with three functionality per unit molecules can act as crosslinking agent when it reacted with PMDI. Thus, the obtained PU foam contained network structure which could delay the decomposition of the foam. Furthermore, thermal decomposition properties of PU foam prepared from commercial polyester polyol (A8360) was similar to those foams prepared from mixed-glycol polyols.

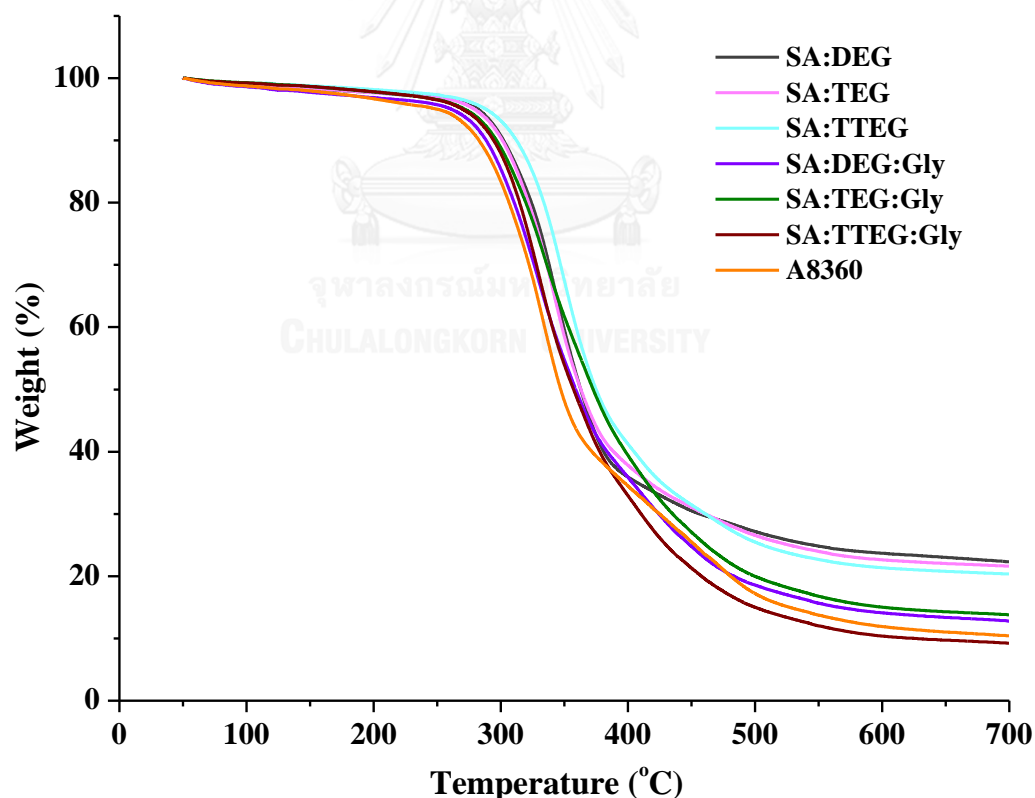


Figure 4.17 TGA curves of PU foams prepared from neat or mixed-glycol polyols relative to one prepared from commercial polyol (A8360)

Table 4.7 Effect of glycol chain length and glycol types on the decomposition temperature (T_{onset}), degradation temperature (T_{max}) and char residue of the PU foams

sample	$T_{\text{onset}}(^{\circ}\text{C})$	$T_{\text{max}} (^{\circ}\text{C})$	Char residue (wt%)
SA:DEG	308.34	376.74	28.76
SA:TEG	305.63	377.33	26.11
SA:TTEG	315.93	403.13	20.96
SA:DEG:Gly	290.36	401.78	12.79
SA:TEG:Gly	291.66	417.71	13.80
SA:TTEG:Gly	296.36	397.81	9.24
POLIMAXX A8360	292.90	388.93	10.40

4.2.7 Selection of polyols to study the effect of isocyanate index on the properties of polyurethane foams

The polyester polyol obtained from SA reacted with DEG-glycerol mixture was chosen to prepared PU foams with different isocyanate indexes (NCO index). Due to PU foams prepared from this type of polyol provided shortest foam formation time, closed cell with regular cell size and smallest cell dimension caused highest compressive strength relative to other types of polyols used in PU foams preparation. Moreover, a minimum compressive strength for closed cell rigid PU foam is generally around 150 kPa [3]. Therefore, PU foam prepared from the mixture of DEG-glycerol polyol, having the compressive strength value greater than 100 kPa, was selected to study the effect of NCO indexes on morphological and mechanical properties of PU foams. The mechanical properties of the prepared PU foams were investigated relative to those prepared from commercial polyol.

4.3 Effect of isocyanate index on properties of polyurethane foams

Isocyanate index (NCO index) is mole ratio of isocyanate groups to hydroxyl groups in the reactants mixture, namely $n(\text{NCO})/n(\text{OH})$. In order to make the polymerization reaction completely, mole ratio of isocyanate groups and hydroxyl groups should be equal theoretically, meaning $n(\text{NCO})/n(\text{OH}) = 1$. Water in PU formulation acted as blowing agent as well as chain extender. In addition, the formation of polyurethane foams has many side reactions of forming urea and biuret. These will consume some isocyanate groups. Consequently, NCO index used in foam preparation should be greater than 1 in practice [53].

In the early stage of the urethane-foam industry, incorporation of isocyanurate linkages into rigid urethane foam was attempted because polyester polyols have relatively high viscosities and low functionalities which make it difficult to produce dimensionally stable, highly cross-linked rigid urethane foams. For this reason isocyanurate linkages were used to increase the crosslink density, and low-functionality and low-viscosity polyesters were used. Accordingly, the NCO index employed was relatively high, typically 150 to 200 to incorporate isocyanurate linkages in rigid urethane foams [12].

In this study, the effect of NCO index of PMDI from 100 to 200 used in PU foams preparation was investigated toward the properties of PU foams, relative to those PU foams prepared from commercial polyol (A8360). The bio-based succinate polyol from reaction of SA and mixture of DEG-glycerol polyol, was used in PU foams preparation in this part.

4.3.1 Chemical structure

The FTIR spectra of PU foams prepared from DEG-glycerol polyol or commercial polyol and PMDI at different NCO indexes are shown in Figure 4.18 (a), (b), (c), (d), (e) and (f). All prepared PU foams showed the wide absorption bands at

3350 cm^{-1} represented stretching vibration of N-H urethane hydrogen bonded. It can be seen that the peaks for hydroxyl located at 3430 cm^{-1} almost disappears after succinate polyols reacted with PMDI. The 1410 cm^{-1} peaks were specified to the 6-membered ring of isocyanurate groups generated by NCO trimer [56]. The formation of urethane linkages was confirmed by the appearance of two absorption peaks. The first peak at 1600 cm^{-1} was due to C=O stretching of urethane groups the other peak at 1535 cm^{-1} can be attributed to N-H bending of urethane linkage. The carbonyl peak (C=O) were detected around 1735 cm^{-1} proved that the hydrogen bond was formed in PU foams [50].

The small peaks at 2275 cm^{-1} corresponded to free, unreacted isocyanate groups due to excess NCO index using in PU foam composites preparation. It was found that PU foams prepared from DEG-glycerol polyol or commercial polyol at NCO index 100 (Figure 4.18 (a) and (d)) did not showed the peaks at 2275 cm^{-1} . This was because the mole ratio of isocyanate groups and hydroxyl groups were equal ($n(\text{NCO})/n(\text{OH}) = 1$), which indicated that all NCO groups were reacted, resulting no peaks of NCO groups appeared. While PU foams prepared from DEG-glycerol polyol or commercial polyol at NCO indexes higher than 100 (Figure 4.18 (b), (c), (e) and (f)) showed small peaks at 2275 cm^{-1} corresponded to free NCO groups residual in the reaction. Poly(urethane-isocyanurate) are formed by the reaction of -NCO groups of isocyanates with hydroxyl groups of polyols, and isocyanurate rings are formed by the trimerisation of an excess of -NCO groups remaining in the reaction. This urethane-isocyanurate polymer has a relatively strong molecular structure because of the combination of strong chemical bonds. The ring structure of isocyanurate and high cross link density contributed to the greater stiffness than other PU foams [20].

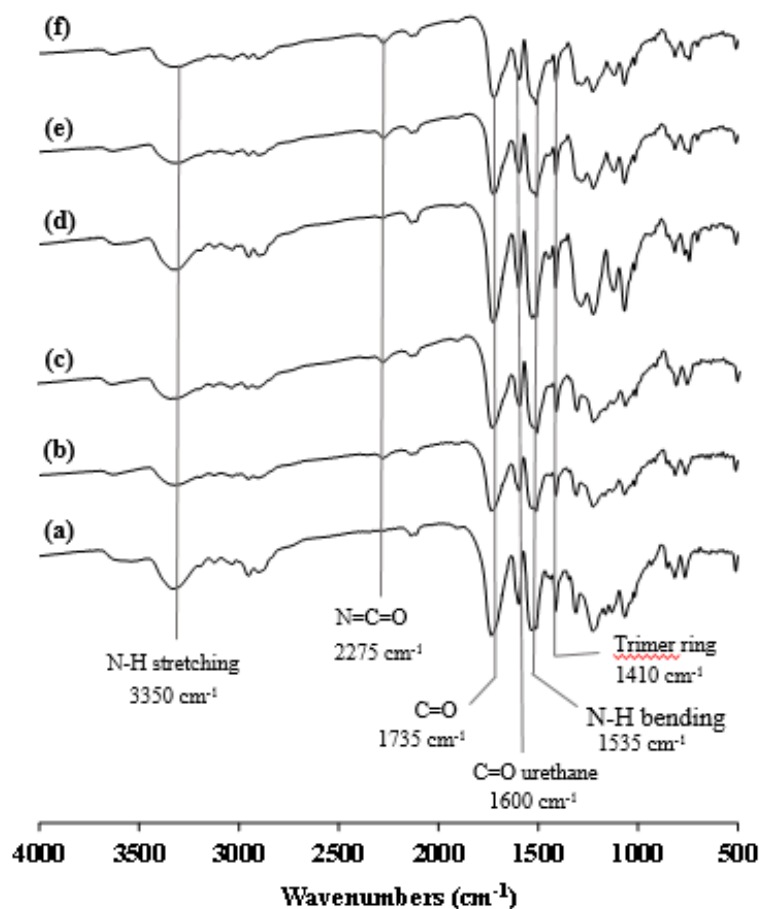


Figure 4.18 FTIR spectra of PU foams prepared from mixed DEG-glycerol polyol at different NCO indexes, (a) NCO100, (b) NCO150, (c) NCO200 and PU foams prepared from commercial polyol at different NCO indexes (d) NCO100, (e) NCO150, (f) NCO200

4.3.2 Foam formation time

The rates of foam formation reactions have been investigated by monitoring the foam formation time. The reaction parameters of foaming such as cream time, rise time and tack free time have been measured at constant mixing time by using high speed mechanical stirrer with different NCO indexes. Foam formation times of bio-based PU foams prepared from different NCO indexes are shown in Table 4.8. The results showed that cream time was insensitive to the NCO indexes. On the other hand, rise

time and tack free time increased with increasing NCO indexes. This might be because the excess molar ratio of PMDI provided more free NCO groups in the reaction resulting longer reaction time was taken. In addition, foam formation time of PU foams prepared from bio-based succinate polyol provided lower rise time and tack free time relative to one prepared from commercial polyol at the same NCO indexes.

Table 4.8 Effect of NCO indexes on the foam formation time of the PU foams

Polyol	NCO index	Cream time (± 1 s)	Rise time (± 1 s)	Tack free time (± 1 s)
SA:DEG:Gly 1:1.5:0.33	100	15	39	44
	125	16	41	49
	150	18	47	58
	175	17	52	87
	200	18	55	116
A8360	100	12	38	45
	125	13	48	56
	150	14	52	67
	175	13	57	93
	200	14	60	128

4.3.3 Morphology

The cell structure including cell size, cell distribution and cell orientation is typically examined by optical microscope (OM). The cubic specimens and OM images

of the PU foams as a function of NCO indexes are shown in Figure 4.19. It was found that the foams consisted of closed cell spherical and polyhedral shape. Cell dimensions of PU foams were obtained by the average of 50 cells diameter and the results are shown in Table 4.9. The OM images showed that cell structures and cell dimensions of PU foams prepared from succinate polyols and commercial polyol were virtually insensitive to the NCO indexes as shown in Figure 4.19 and 4.20.

Regarding to the cellular formation during foam preparation, exothermic heat of reaction caused the super saturation of the reactive mixture, leading to phase separation into vapor and diffused into the nuclei resulting small air bubbles entrapped during the mixing of raw materials. Then the nuclei grew into bubbles and spherical cells by coalescence with neighboring ones. When the spherical bubbles are separated by the cell membrane, they become polyhedral [57]. As the NCO index increased, elasticity of the cell wall increased by the allophanate crosslinks. The growth and coalescence of the bubbles became difficult afterward, caused the bubbles to be small. On the other hand, CO₂ blew and expanded new bubbles. The two conflicting forces were more or less balanced to give similar size of bubbles regardless of the NCO index [57]. In addition, PU foams prepared from succinate polyol had smaller cell sizes and cell dimensions relative to ones prepared from commercial polyol at the same NCO indexes.

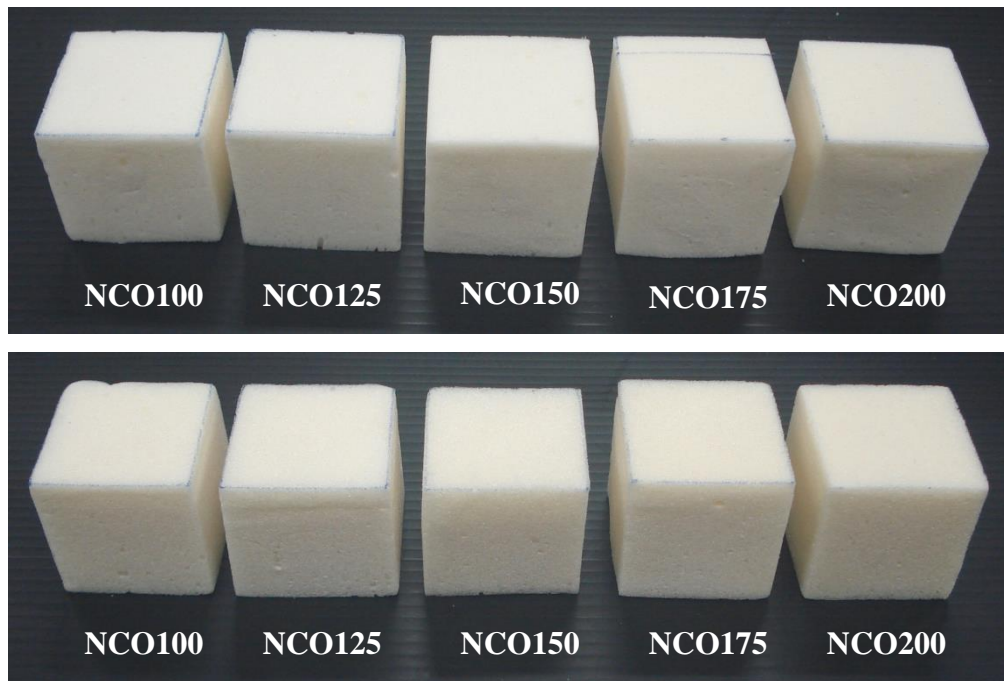


Figure 4.19 Cubic specimen of PU foams prepared from mixed DEG-glycerol polyol (top) and PU foams prepared from commercial polyol (bottom) at different NCO indexes

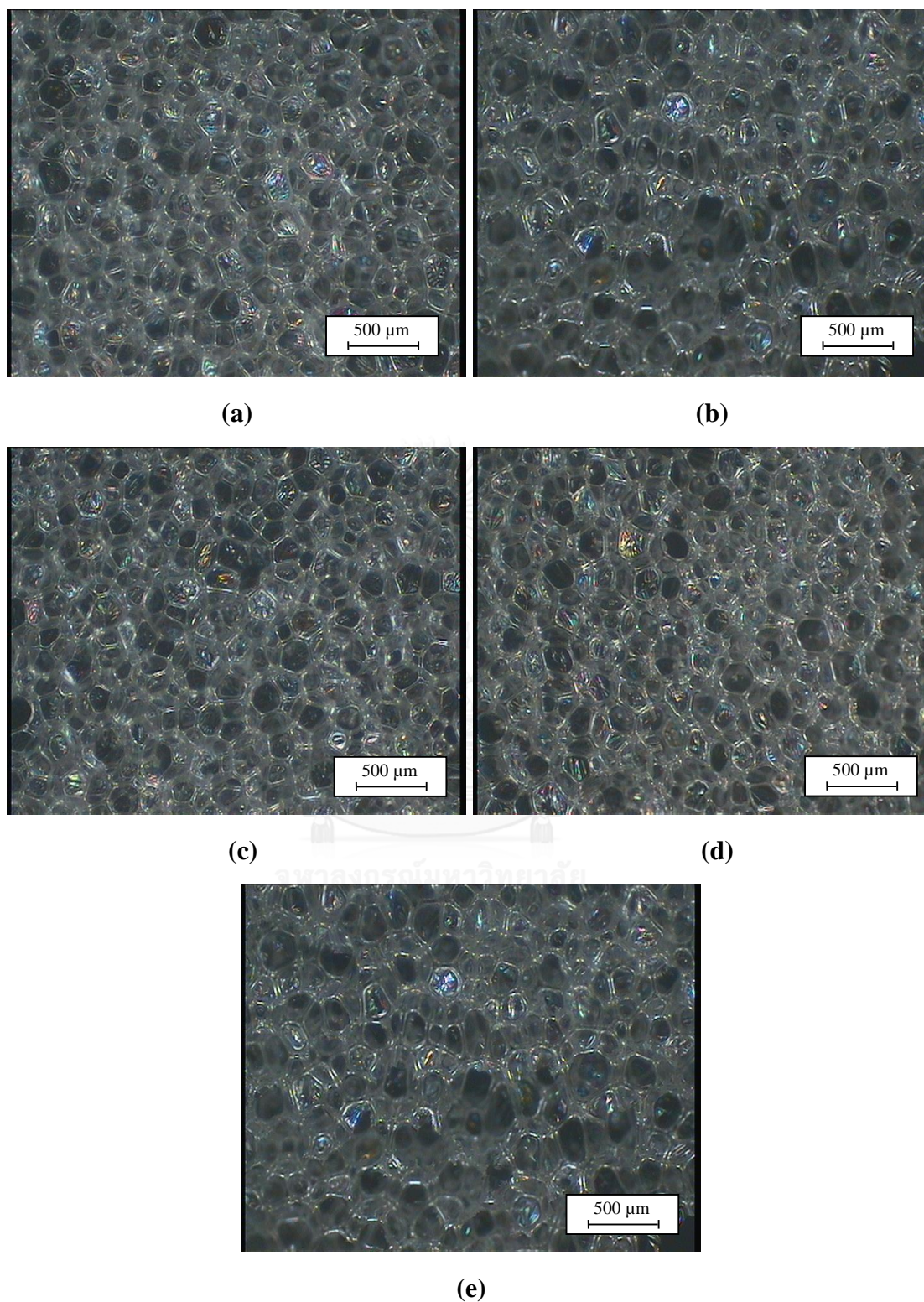


Figure 4.20 OM images of PU foams prepared from mixed DEG-glycerol polyol at different NCO indexes, (a) NCO100, (b) NCO125, (c) NCO150, (d) NCO 175 and (e) NCO200

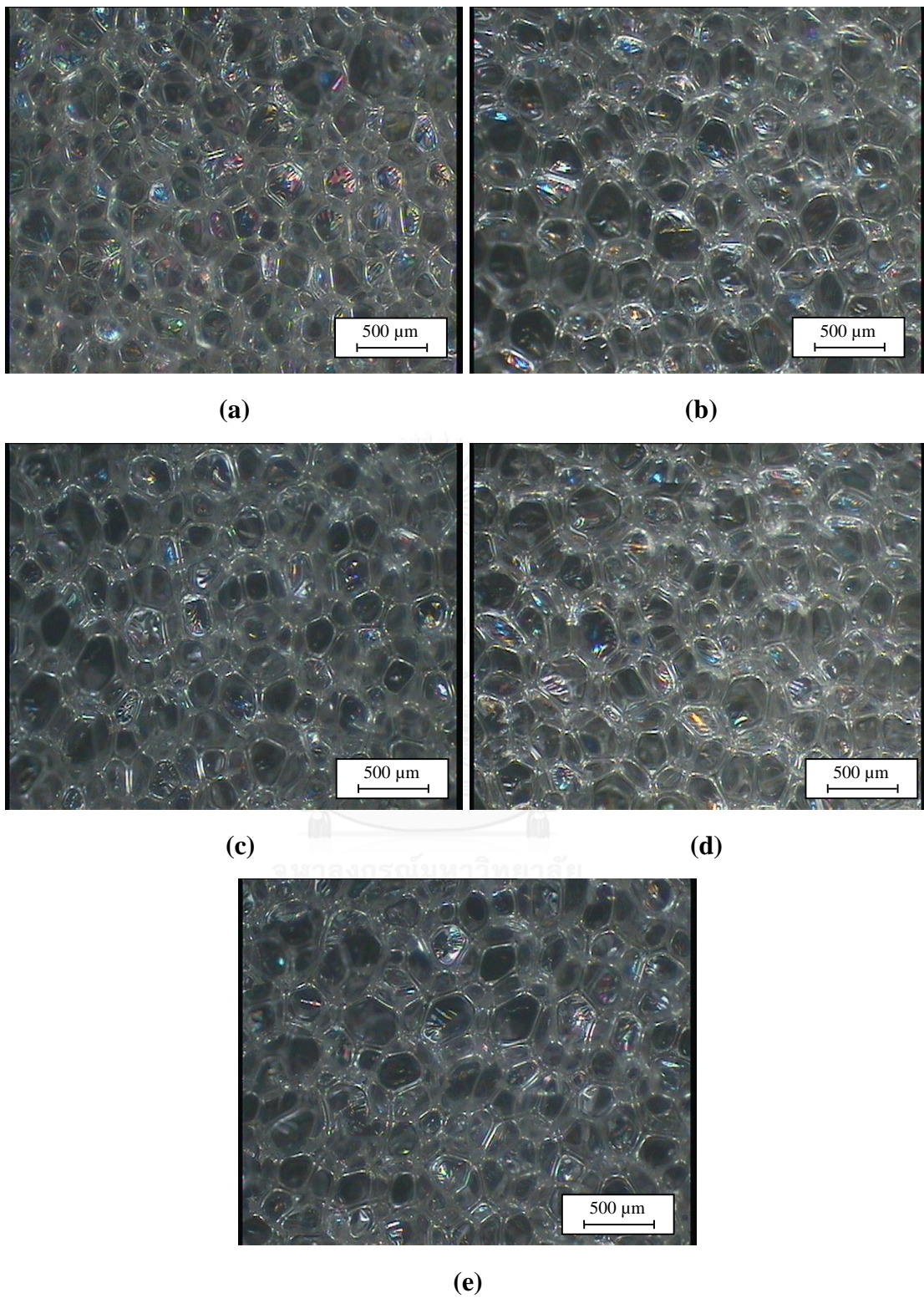


Figure 4.21 OM images of PU foams prepared from commercial polyol at different NCO indexes, (a) NCO100, (b) NCO125, (c) NCO150, (d) NCO 175 and (e) NCO200

4.3.4 Foam density

Density is another significant parameter which indicates the quality of PU foams regarding to comfort, support and durability. PU foams were prepared from SA reacted with mixed DEG-glycerol polyol and PMDI at different NCO indexes. The density measurement of the prepared foams was taken relatively to PU foams prepared from commercial polyol. The result of density measurement was shown in Figure 4.22 and Table 4.9. It was found that density increased continually as the NCO indexes increased in both PU foams prepared from bio-based polyols and commercial polyol. This might be because the viscosity of the bio-based polyol (1,362 mPa s @ 25°C) was higher than that of commercial polyol (1,100 mPa s @ 25°C). The height of foams after rising of bio-based PU foams was slightly lower than that of petrochemical foams at the same NCO indexes, thus higher in foam density.

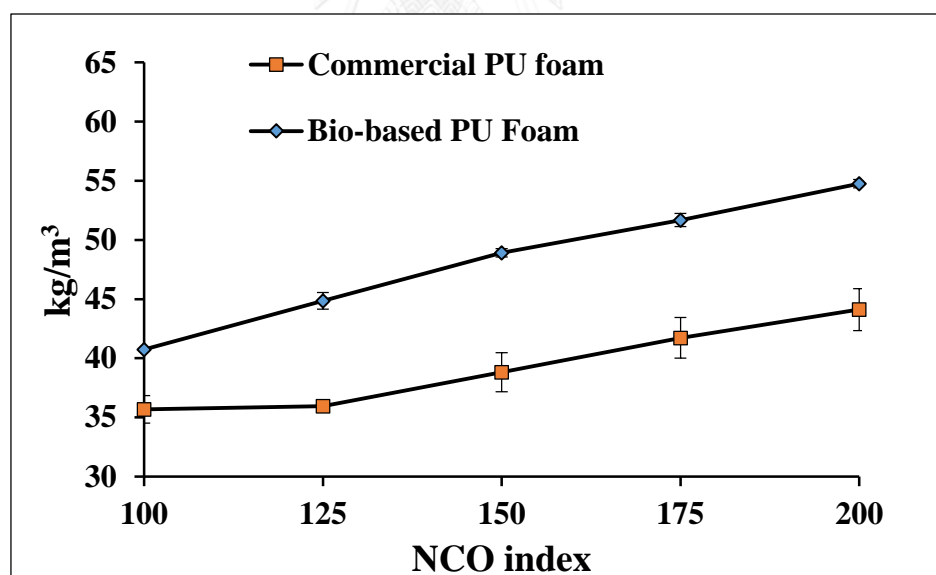


Figure 4.22 Bulk density of PU foams prepared from SA and mixed DEG-glycerol polyol and PU foam prepared from commercial polyester polyol at different NCO indexes

4.3.5 Compressive strength

In closed cell PU foam, the compressive strength is related to the morphology and density of the PU foam. Smaller cell size and higher density of foam can provide more support under loading. Figure 4.23 and Table 4.9 showed the results of compressive strength of PU foams prepared from mixed DEG-glycerol polyol and foams prepared from a commercial polyester polyol at different NCO indexes. The compressive strength of PU foams prepared from mixed DEG-glycerol polyol increased as the NCO index increased, as well as the PU foams prepared from the commercial polyol. This was because the isocyanurate groups generated from the excess NCO in PU reaction. The high cross-linked structures were obtained not only from polyester polyol with NCO, but also from the isocyanurate rings generated by the trimerisation of the excess of NCO groups. The reaction of trimerization of NCO groups to produce isocyanurate ring is shown in Figure 4.24. PU foam prepared from mixed DEG-glycerol polyol at NCO index of 200 provided highest compressive strength. However, high NCO index will lead to excessive crosslink, resulting in the increase of brittleness of the foams [33]. In addition, PU foams prepared from mixed DEG-glycerol polyol had higher compressive strength than those prepared from commercial polyol at the same NCO indexes. This was because PU foams prepared from mixed DEG-glycerol polyol had higher density and smaller cell size relative to those prepared from commercial polyol resulting in enhanced mechanical properties of PU foams.

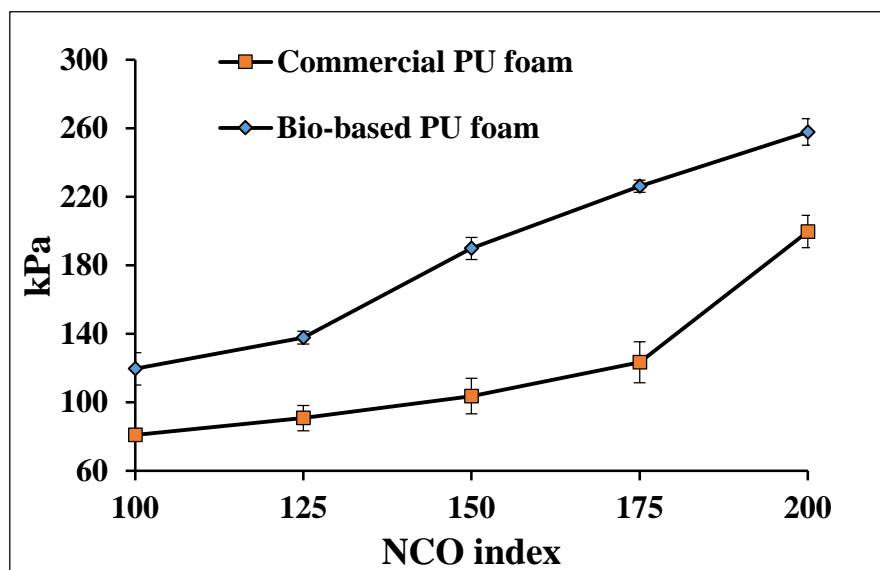


Figure 4.23 Compressive strength of PU foams prepared from mixed DEG-glycerol polyol and PU foam prepared from commercial polyester polyol at different NCO indexes

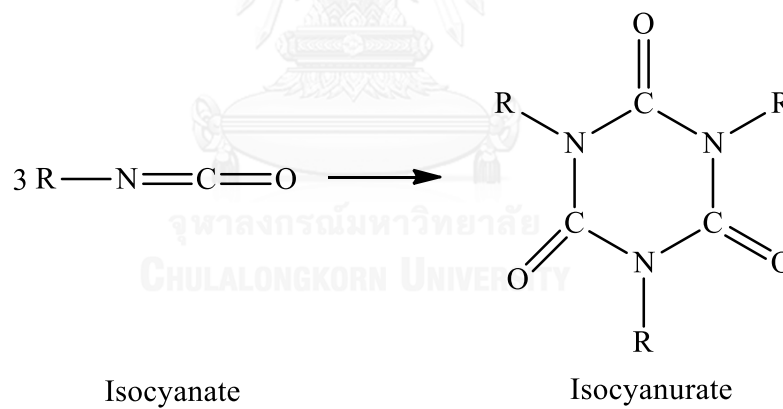


Figure 4.24 Reaction of trimerization of NCO groups to produce isocyanurate ring

Table 4.9 Effect of NCO indexes on density, compressive strength and cell dimensions of PU foams prepared from mixed DEG-glycerol polyol and PU foam prepared from commercial polyol

Polyol	NCO index	Density (kg/m ³)	Compressive strength at 10% strain (kPa)	Cell dimensions (μm)
SA:DEG:Gly 1:1.5:0.33	100	40.73	119.56	172.48 ± 27.34
	125	44.86	137.75	170.11 ± 28.09
	150	48.91	189.84	174.75 ± 30.18
	175	51.63	226.21	168.57 ± 28.22
	200	54.76	257.76	170.36 ± 23.46
A8360	100	35.68	80.92	185.37 ± 31.73
	125	35.95	90.82	189.09 ± 28.22
	150	38.82	103.60	183.79 ± 29.19
	175	41.72	123.40	187.95 ± 31.71
	200	44.12	199.64	191.62 ± 32.25

4.3.6 Selection of foam formulation to use in PU foam/clay nanocomposites study

PU foam with optimum isocyanate index, that gave highest compressive strength, was chosen to prepare the PU foam/clay nanocomposites. It was showed that PU foam prepared from mixed DEG-glycerol polyol at NCO index of 200 had highest compressive strength at 257.76 kPa and was in the range of the typical compressive

strength of rigid PU foam (> 150 kPa). In fact, the compressive strength of PU foams prepared from mixed DEG-glycerol polyol at NCO indexes of 150 and 175 were also higher than that of typical PU foam. However, some rigid PU foam applications are still require higher mechanical properties of foam. Therefore, the bio-based PU foam prepared with NCO index of 200 was chosen for PU foam composite study. Moreover, the chosen PU foam had density of 54.76 kg/m^3 which is slightly higher than the of typical density range of PU foam ($25\text{--}50 \text{ kg/m}^3$). While, the average cell dimensions of $170 \text{ }\mu\text{m}$ of the chosen foam, was lower than that of typical PU foam ($250\text{--}500 \text{ }\mu\text{m}$). The properties of typical rigid PU foam used in industry are summarized in Table 4.10.

Table 4.10 Properties of the typical industrial rigid PU foam [33]

Property	Typical rigid PU foam
Foam density (kg/m^3)	20-50
Cell dimension (μm)	250-500
Compressive strength (kPa)	> 150

4.4 Characteristics and properties of bio-based polyurethane foams/clay nanocomposites

The PU foam/clay nanocomposites were prepared using DEG mixed-glycerol polyol and PMDI at NCO index of 200. Two types of clays at various amounts were incorporated into the PU foam formulations. The clay contents, both modified (C30B) and unmodified (MMT), were varied at the levels of 0.5, 1, 1.5, 2, 3, 5, and 7 php. The properties of nanocomposite foams were characterized.

4.4.1 Chemical structure

The chemical structure of clays and bio-based PU foam/clay nanocomposites were analyzed by FTIR spectroscopy. FTIR spectra of natural montmorillonite and organically modified clay (C30B) are shown in Figure 4.25 (a) and (b). Both spectra showed the absorption band at 3630 cm^{-1} and 1639 cm^{-1} attributed to O–H stretching and O-H bending of the silicate layers, respectively. The peaks at 1040 cm^{-1} indicated the Si-O stretching, as well as peaks at 917 and 623 cm^{-1} corresponded to Al-O of the silicate layers of C30B and MMT [58]. However, there are some peaks in nanoclay C30B spectrum (Figure 4.25 (a)) which were not exhibited by the unmodified MMT clay. These peaks were located at 2926 , 2853 and 1469 cm^{-1} and were assigned to C–H stretching of methylene from chemical structure of the quaternary ammonium surfactant [59].

The FTIR spectra of neat PU foam and PU foam/clay nanocomposites are shown in Figure 4.25 (c), (d), (e), (f) and (g). The wide absorption bands at 3350 cm^{-1} represented stretching vibration of N-H urethane hydrogen bonded. The small peaks at 2275 cm^{-1} corresponded to free, unreacted isocyanate groups due to excess NCO index using in PU foam composites preparation. The 1410 cm^{-1} peaks were specified to the 6-membered ring of isocyanurate groups generated by NCO trimer [56]. The formation of urethane linkages was confirmed by the appearance of two absorption peaks. The first peak at 1600 cm^{-1} was due to C=O stretching of urethane groups the other peak at 1535 cm^{-1} can be attributed to N-H bending of urethane linkage. The carbonyl peak (C=O) were detected around 1735 cm^{-1} proved that the hydrogen bond was formed in PU foams [50]. Moreover, it was found that the positions of peaks for distinctive functional groups of neat PU foam and PU foam/clay nanocomposites were similar, meaning that the segmented structure of PU had not been affected by the presence of both clays. This might be due to small amount of clays did not react with the PU molecules, thus the PU samples did not cause any detectable change by FTIR [56].

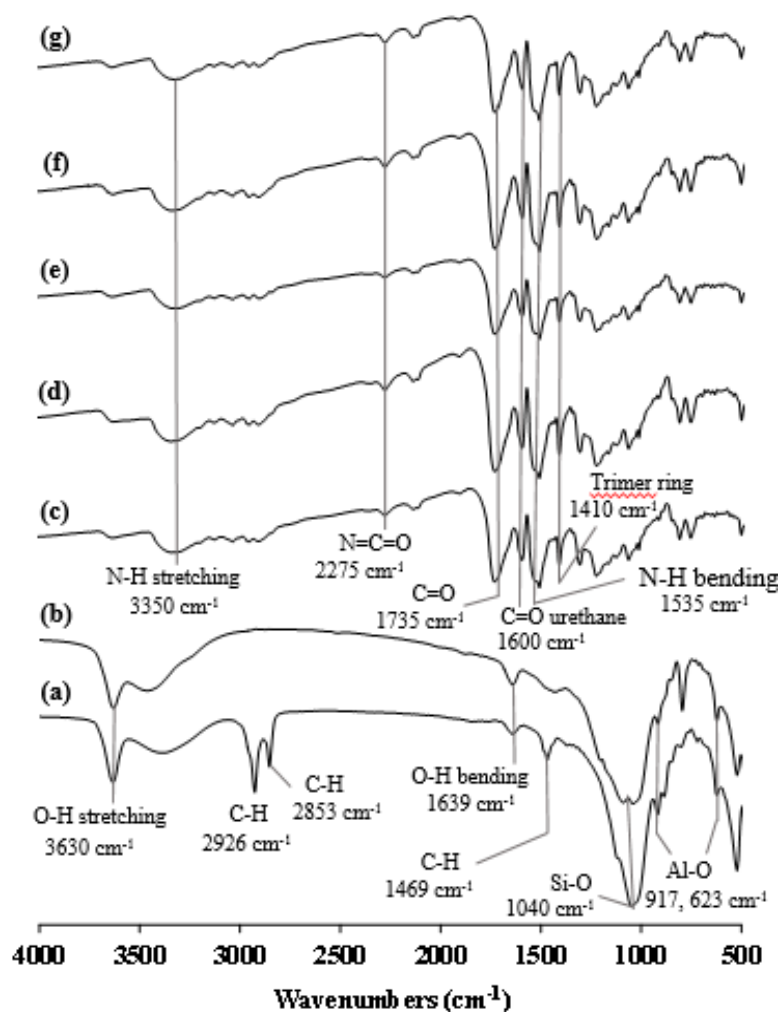


Figure 4.25 FTIR spectra of Cloisite 30B (a), MMT (b), neat PU foam (c) and PU foam/clay nanocomposites incorporated with both clays at different clay contents, (d) 1 php C30B, (e) 1 php MMT, (f) 7 php C30B, and (g) 7 php MMT

4.4.2 Dispersion of clays in PU foams

The distributions of clays in the PU foams prepared from bio-based succinate polyol were analyzed by X-ray diffraction (XRD) technique. XRD pattern of the clays, neat PU foam and PU foams composites with different amounts of the clays are shown in Figure 4.26. The XRD patterns of two different types of clays showed that the modified clay (C30B) had higher gallery spacing than the unmodified one (MMT). The peak at 2θ of C30B was less than 7 degree compared with MMT which appeared at 2θ

equal to 7.1 degree. The gallery spacing of MMT is equal to 1.23 nm while the gallery spacing of C30B is equal to 1.81. The nanocomposite foams, incorporated with 1 php of MMT and C30B, showed no peaks on the XRD profile. This indicated that the clay layers were exfoliated or delaminated in succinate polyol-based PU foams. However, when both clays with the amount of 7 php was incorporated into PU foams, the XRD pattern showed that 2θ peak had shifted to lower angle, resulting the d-spacing increased. PU foam incorporated with 7 php C30B showed the broadening peak at low angle around 2θ of 2-3.5 degree indicated that the clay was partially exfoliated. Meanwhile, PU foam incorporated with 7 php MMT showed 2θ peak at 6.56 degree corresponding to the gallery spacing of 1.37 nm compared with the gallery spacing of 1.23 nm of MMT clay. This indicated that PU foam incorporated with 7 php MMT showed intercalation structure. In addition, the XRD pattern of neat PU foam showed no peak of crystalline materials as any clay incorporated in foam preparation.

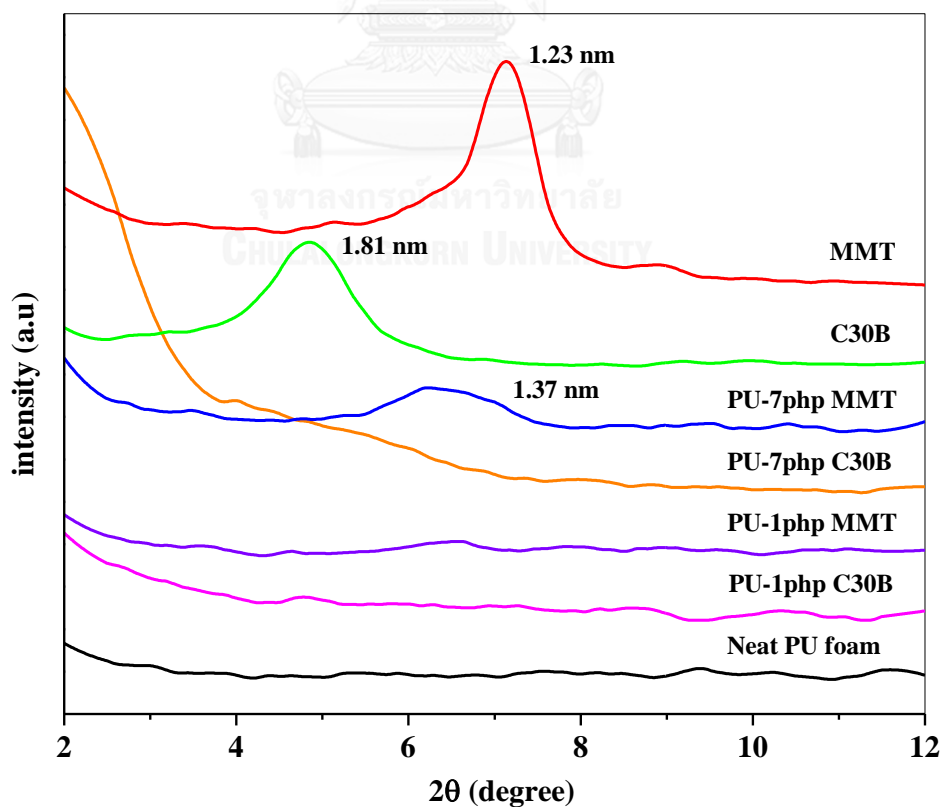


Figure 4.26 XRD pattern of the clays, neat PU foam and PU foam/clay nanocomposites

4.4.3 Foam formation time

Mechanisms of PU foam/clay nanocomposites formation were studied by monitoring the foam formation times. Foam formation times of the prepared PU foams are shown in Table 4.11. In PU foams incorporated with both unmodified (MMT) and modified clays (C30B), cream time was slightly lower than that of neat PU foam. Besides, cream time was not significantly different for all nanocomposite foams. Rise time of the foams increased while tack free time decreased as the clays content increased. The foams incorporated with nanoclay C30B had slightly lower in rise time and tack free time than ones incorporated with MMT at the same clay contents. Rise time of PU foam incorporated with 7 phr C30B increased from 55 s to 59 s, while tack free time decreased from 116 s to 98 s, respectively, relative to the neat PU foam. This might be because the nucleation site for bubble formation during foaming process increased when the clay contents increased, caused higher rise time of PU foams. While the tack free time decreased as the clay contents increased. This might be because of the excessive coalescence of the nucleating sites of gas bubbles resulting cell wall became thinner and broke afterward.

Table 4.11 Effect of clays on the foam formation times of the neat PU foam and PU foam/clay nanocomposites

Sample	Cream time (± 1 s)	Rise time (± 1 s)	Tack free time (± 1 s)
Neat PU foam	18	55	116
PU-0.5php C30B	19	54	115
PU-0.5php MMT	18	53	115
PU-1php C30B	18	52	114
PU-1php MMT	19	54	115
PU-1.5php C30B	19	55	114
PU-1.5php MMT	18	54	113
PU-2php C30B	18	53	113
PU-2php MMT	18	55	114
PU-3php C30B	19	55	111
PU-3php MMT	19	56	113
PU-5php C30B	18	58	107
PU-5php MMT	19	60	109
PU-7php C30B	19	59	98
PU-7php MMT	18	62	102

4.4.4 Morphology

Foam properties depend on at least one of the following parameters such as the foam density and the cellular structure. The structural character of foam such as the gas volume fraction, the number of cells, their shape, size and size-distribution, the thickness of the walls, and the relative number of closed and opened cells affected the physical properties of foams [60]. Optical microscopy was used to view the cell structure and its size of the prepared PU foam/clay nanocomposites as functions of clay types and amount of clay incorporated. PU foam after curing was cut into cubic specimens as shown in Figure 4.27. The optical microscopy images of succinate polyol-based PU foams incorporated with clays (C30B and MMT) were also shown in Figure 4.28 and 4.29 showed. It can be seen that the prepared foams consisted of spherical and polyhedral shape of voids which so called "cell". The OM images of PU foams incorporated with nanoclay C30B showed that cell size of PU foams decreased as the clay contents increased as shown in Figure 4.28 (a), (b), (c), (d), (e), (f) and (g). This result was also found in PU foams incorporated with MMT as shown in Figure 4.29 (a), (b), (c), (d), (e), (f) and (g). If the lower amount of clays was used to incorporate into PU foams, the smaller cell size and finer cell structure was obtained relative to PU foams incorporated with higher amount of clays. The reduction of cell size in PU foams composites might come from: (1) the viscosity of the polyol and clay mixture increased as the loading of clay increased. The increase in viscosity would cause the PU mixture difficult to rise during foaming process and resulted in smaller cell size (2) Clay could act as nucleation site during foaming process resulting in smaller cell size [61]. According to the increment of the nucleation site when the clay contents increased, the height of PU foams after rising was also increased. In foams with high clay content (7php), their cell walls became thinner and weaker, and these cells burst more easily in foam rising phase cause the non-uniform and broken cell

structure occurred. Thus, the closed cell contents of PU foams slightly decreased when the clay contents increased as shown in Figure 4.28 (h) and Figure 4.29 (h) [42].

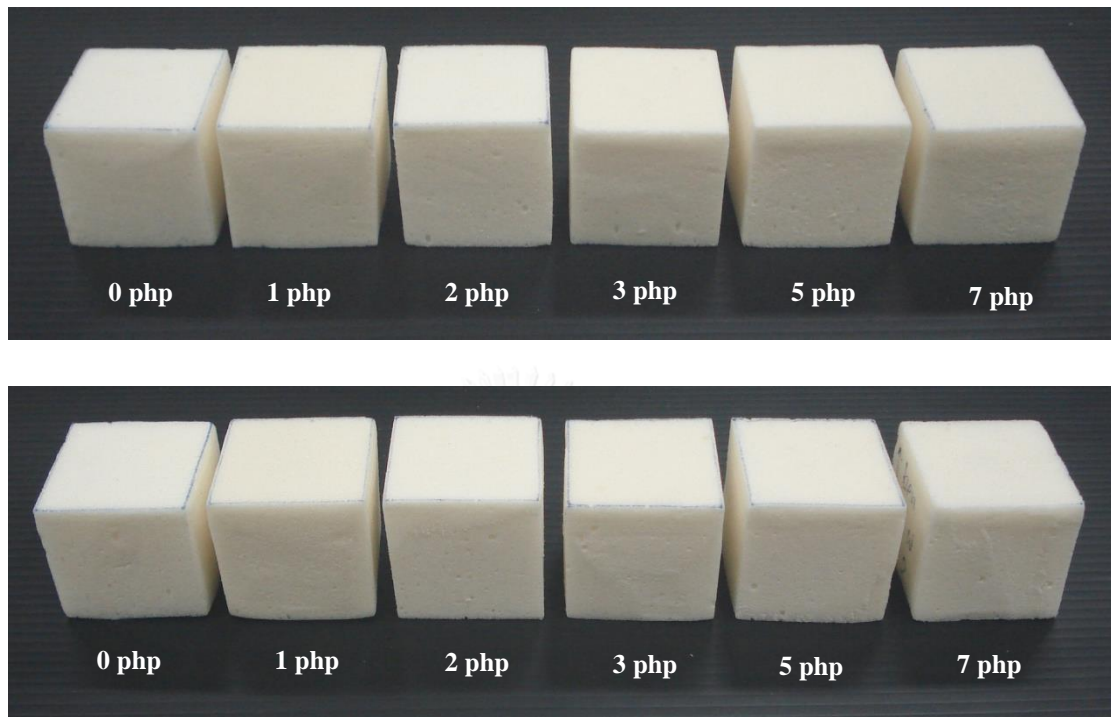
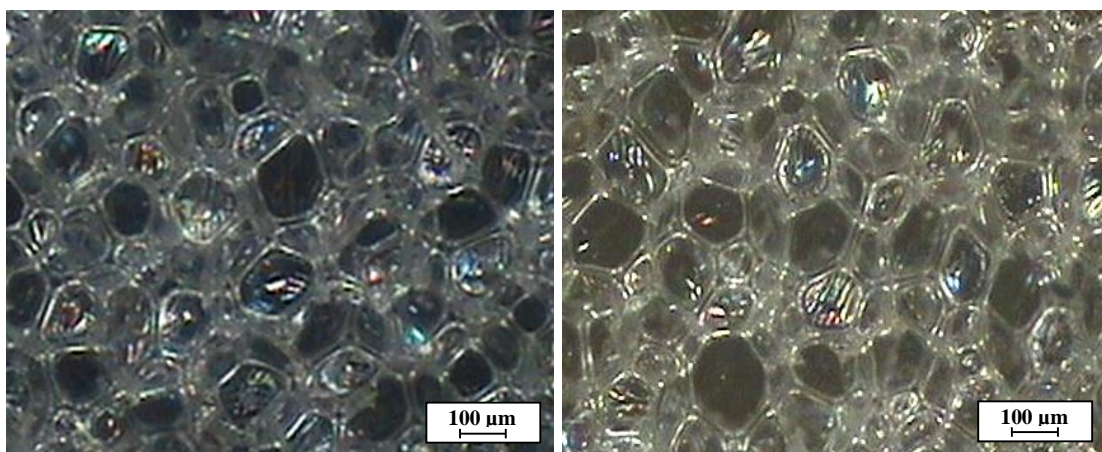
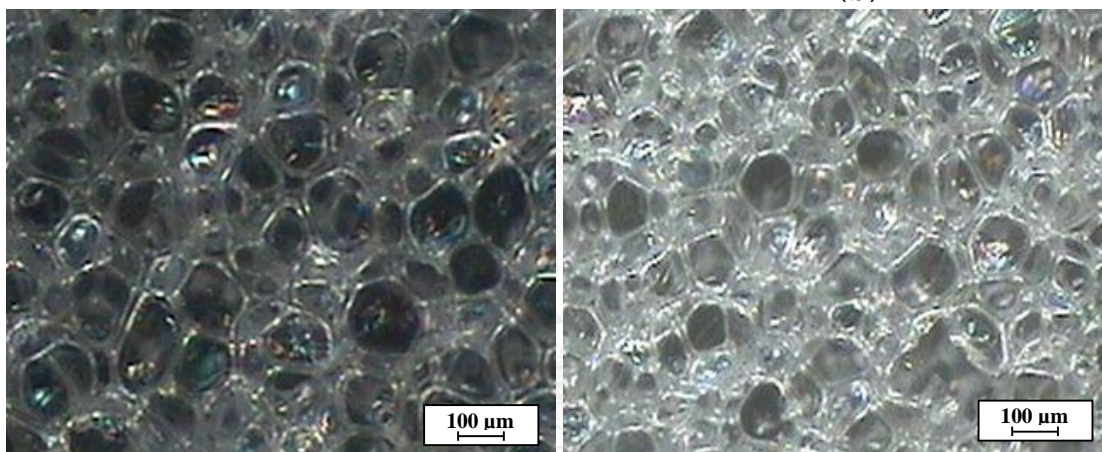


Figure 4.27 Cubic specimen of bio-based PU foams incorporated with nanoclay Cloisite 30B (top) and MMT (bottom) at different clay contents



(a)

(b)



(c)

(d)

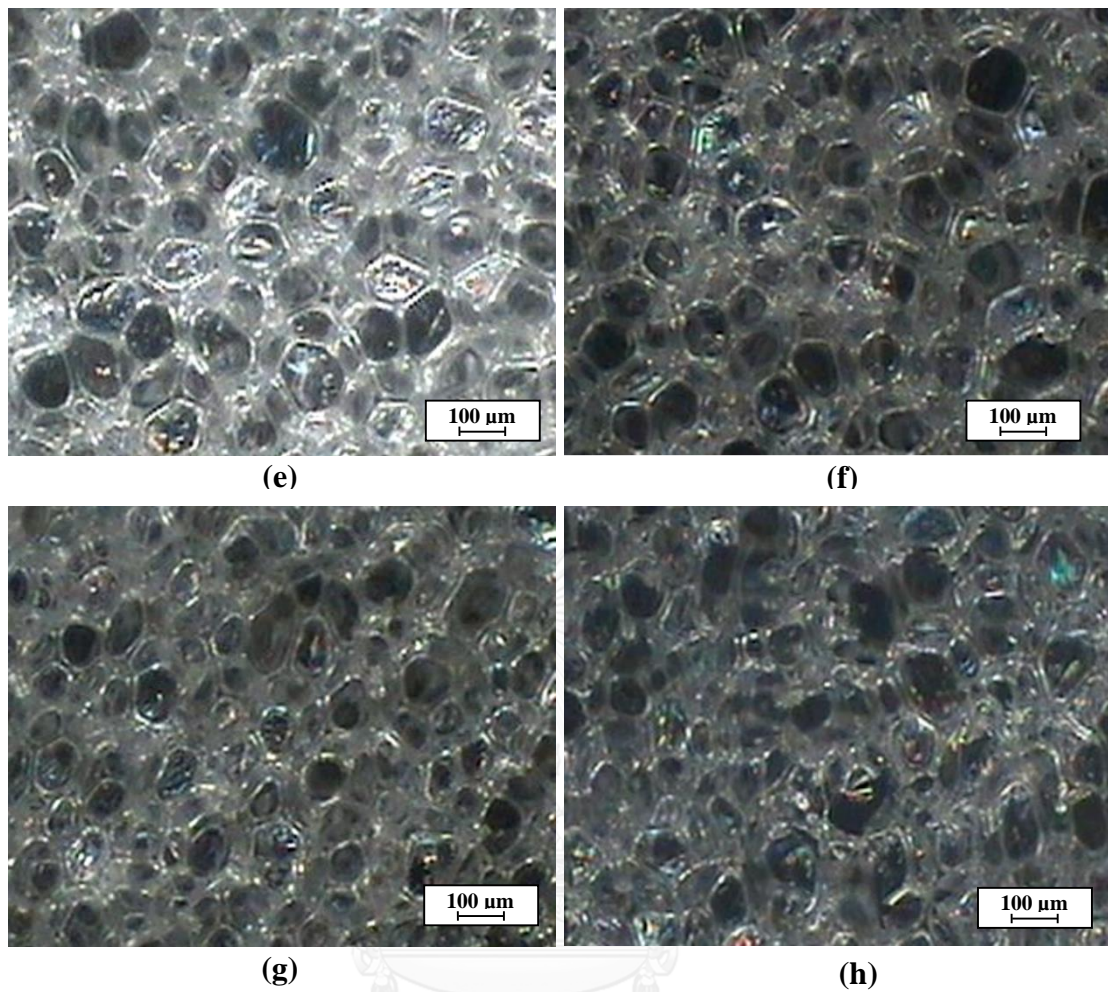
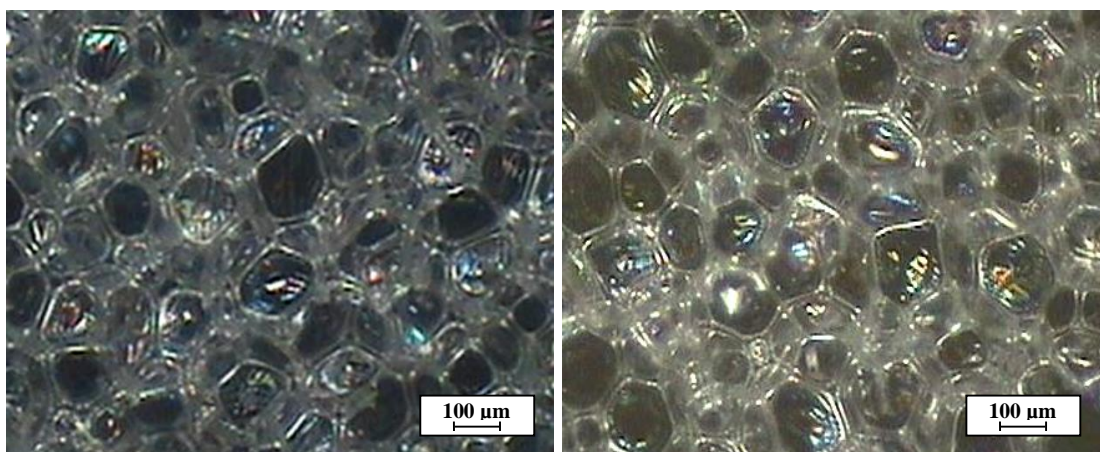
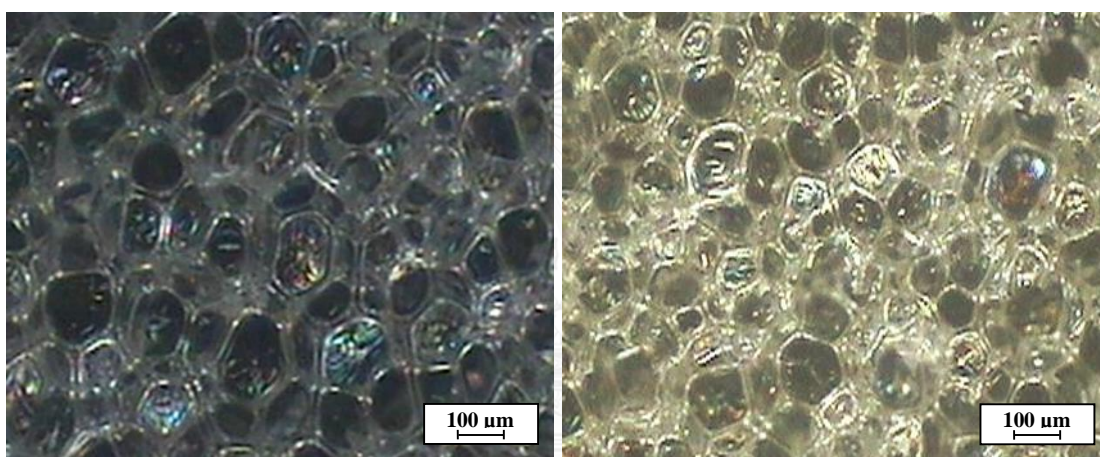


Figure 4.28 Optical microscopy images of PU foams incorporated with nanoclay Cloisite 30B at different clay contents, (a) neat PU foam, (b) 0.5 php, (c) 1 php, (d) 1.5 php, (e) 2 php, (f) 3 php, (g) 5 php and (h) 7 php



(a)

(b)



(c)

(d)

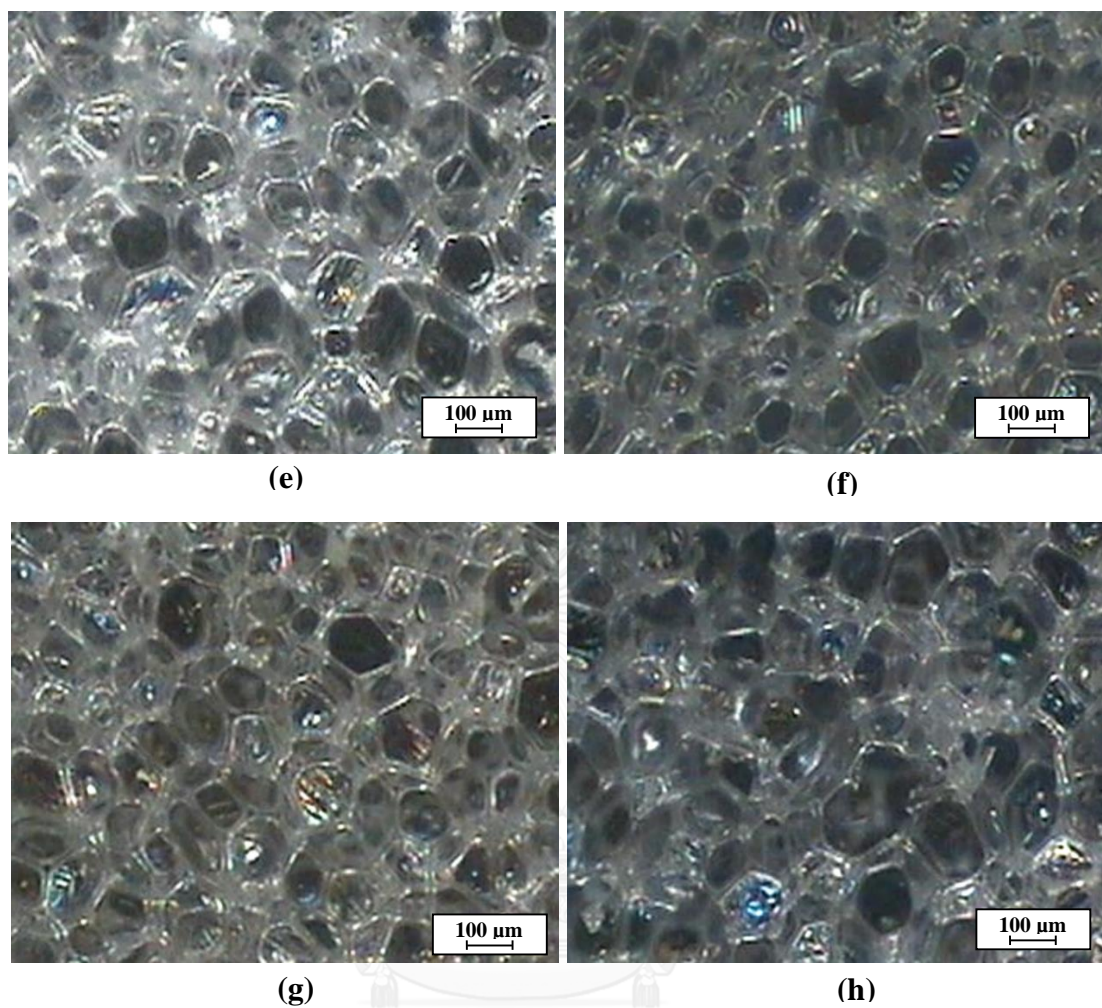


Figure 4.29 Optical microscopy images of PU foams incorporated with MMT at different clay contents, (a) neat PU foam, (b) 0.5 php, (c) 1 php, (d) 1.5 php, (e) 2 php, (f) 3 php, (g) 5 php and (h) 7 php

The cell size is important in controlling the mechanical and thermal properties of PU foam. The cell dimensions of PU foams were calculated for the average value of at least 50 cells [35]. The results are shown in Table 4.12. It was indicated that the cell dimension continuously decreased up to 5 php of both clays incorporated into PU foams, and then increased as the clay contents increased. The reduction in cell dimensions of PU foams incorporated with C30B and MMT were attributed to the fact that the clays acted as nucleation sites for gas bubbles and could increase the viscosity of the mixture, thus reducing the coalescence [35]. The increment of the cell size of PU foams incorporated with higher amount of clays (7 php C30B and 7 php MMT) caused the excessive coalescence of the nucleating sites. The cell dimensions of foams incorporated with nanoclay C30B had slightly smaller dimension relative to one incorporated with MMT at the same amount of clays.

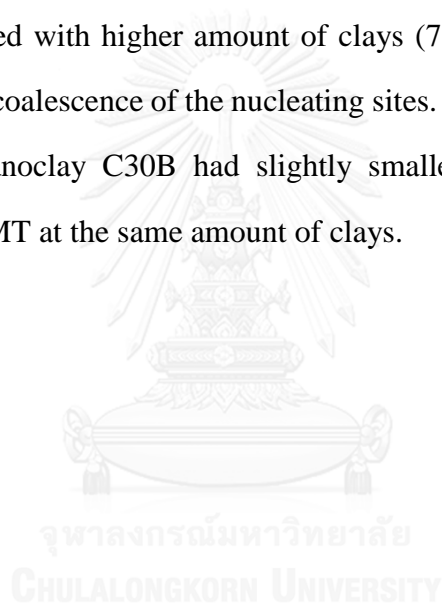


Table 4.12 Effect of clays on density, compressive strength and cell dimensions of PU foams

Sample	Density (kg/m ³)	Compressive strength at 10% strain (kPa)	Cell dimension (μm)
Neat PU foam	54.76	257.76	170.36 ± 33.73
PU-0.5php C30B	56.63	269.02	155.36 ± 31.27
PU-0.5php MMT	50.84	246.74	162.38 ± 29.89
PU-1php C30B	60.09	287.32	145.57 ± 27.44
PU-1php MMT	48.70	235.03	151.00 ± 27.22
PU-1.5php C30B	58.82	269.55	143.26 ± 28.53
PU-1.5php MMT	45.96	228.37	148.23 ± 26.64
PU-2php C30B	57.33	265.48	140.02 ± 31.08
PU-2php MMT	44.82	215.31	144.12 ± 27.14
PU-3php C30B	55.60	249.08	136.08 ± 28.43
PU-3php MMT	43.06	191.97	140.14 ± 29.35
PU-5php C30B	53.03	223.37	127.29 ± 25.22
PU-5php MMT	41.94	166.87	137.85 ± 24.80
PU-7php C30B	50.22	201.41	150.49 ± 35.69
PU-7php MMT	33.09	120.17	168.46 ± 32.78

4.4.5 Foam density

Foam density is an important parameter to control the mechanical properties of the foams [52]. The density of the PU foam may be varied by varying the amount of the blowing agent and proportion of filler materials. In the present study, the amount of blowing agent (distilled water) was fixed, the clay contents were varied from 1 to 7 php. The effect of organically modified clay (C30B) and the unmodified clay (MMT) on density of succinate polyol-based PU foams was shown in Figure 4.30 and Table 4.12. It was observed that the density of PU foams increased slightly with incorporation of lower amount of nanoclay C30B and then decreased as the clay contents further increased. PU foam incorporated with 1 php C30B provided maximum density. The density of foam incorporated with MMT decreased as the clay contents increased. Rapid mixing of the polyol mixture and isocyanate provided lots of microbubbles in the liquid system. This microbubbles served as sites for bubble growth. It was found that not only the microbubbles provide bubble growth, but the clays incorporated into the liquid system also provide more nucleation sites for bubble growth [42].

When the dispersibility of clay in liquid system was taken into consideration, it was found that the viscosity of polyol with nanoclay C30B mixture was higher than the viscosity of polyol with MMT. This revealed that nanoclay C30B was easier dispersed than MMT, resulting better dispersibility. Since the viscosity of polyol with C30B mixture was higher than the viscosity of one with MMT, this would cause the height of rising foam lower than the one with MMT at the same amount of clays. Therefore PU foams with nanoclay C30B had a higher density than ones with MMT. Moreover, the densities of PU foams decreased as the clay contents increased due to the formation of highly porous cell structure resulting broken cell wall and larger voids [62].

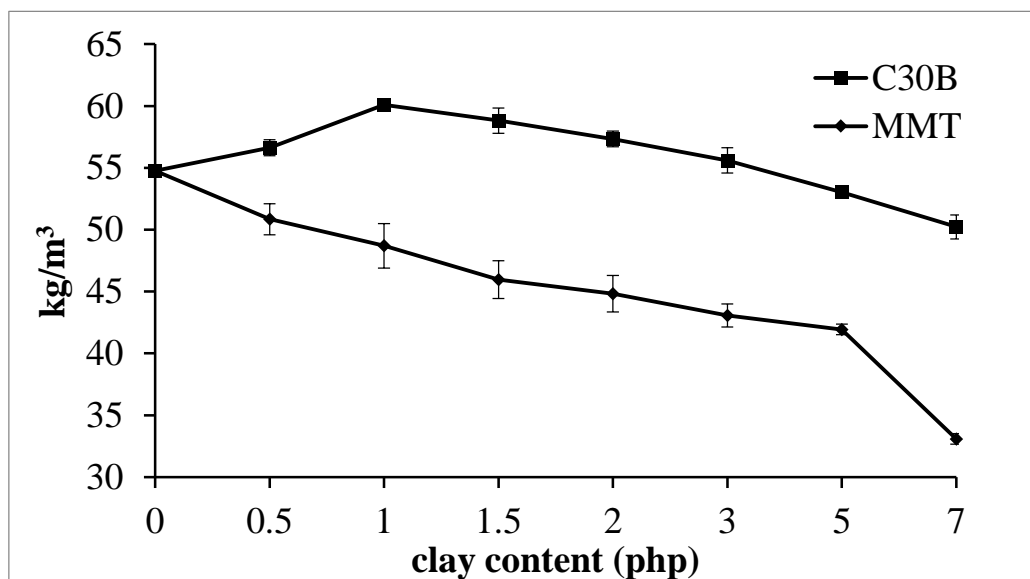


Figure 4.30 Bulk density of PU foams incorporated with C30B and MMT at different clay contents

4.4.6 Compressive strength

One of the important mechanical properties for rigid PU foam is compressive property. In general, foams with higher density and/or cross-linking density are more rigid as well as higher in compressive strength. PU foams incorporated with two types of clays at different amount were prepared and they were subjected to compressive stress at 10% strain. The compressive strength results of PU foams incorporated with nanoclay C30B and MMT at different clay contents are shown in Figure 4.31 and Table 4.12. It was found that incorporating of nanoclay C30B into PU foams can improved the compressive strength of the foams. The compressive strength was first increased at 1 php C30B, then decreased as the clay contents increased. While, the compressive strength of PU foams incorporated with MMT was drastically decreased as the clay contents increased. PU foam incorporated with 1 php C30B provided highest compressive strength. The compressive strength increased from 257.76 kPa to 287.32 kPa because of the higher density and smaller cell size relative to the neat PU foam.

The increment of compressive strength was because of the reduction of cell size, resulting more cell walls and struts per unit area of PU foams could support the foam structure under loading. The compressive strength of PU foams incorporated with MMT gradually decreased as the clay contents increased. This was because the decreasing in foam density of foams.

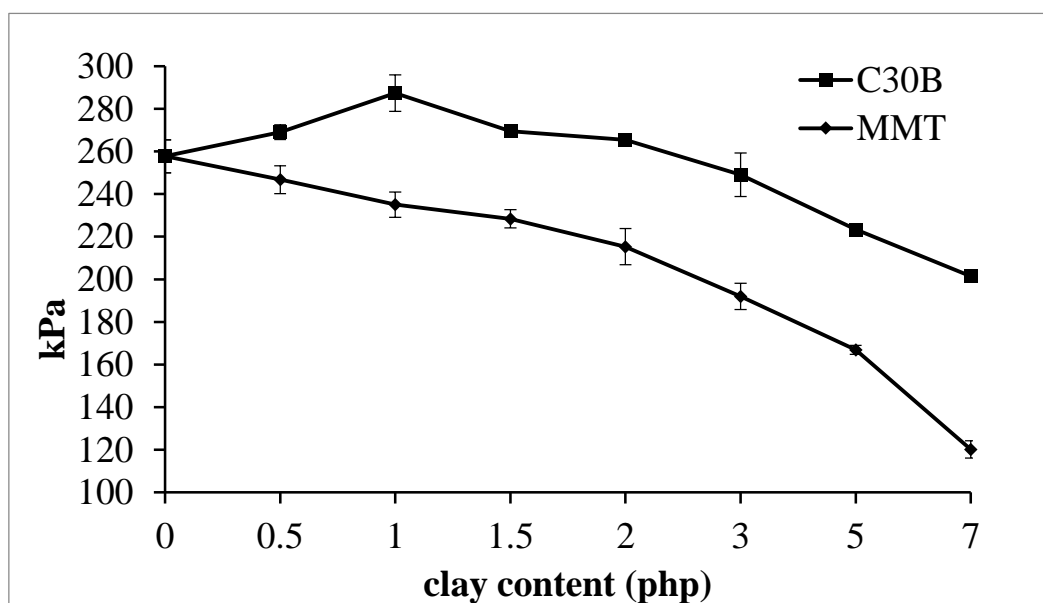


Figure 4.31 Compressive strength of PU foams incorporated with C30B and MMT at different clay contents

4.4.7 Thermal stability

PU foam/clay nanocomposites were prepared by incorporating two types of clays at the levels of 0.5, 1, 1.5, 2, 3, 5 and 7 php into PU foams prepared from SA and mixed DEG-glycerol at NCO index of 200. The thermal stability of neat PU foam and PU foam/clay nanocomposites were characterized using thermogravimetric analysis (TGA) technique. TGA analysis curves of neat PU foam and PU foams/clay nanocomposites are shown in Figure 4.32. The decomposition onset temperature (T_{onset}), designed as the temperature at which the sample loss 5wt% [55], and the temperature at which the sample has the maximum degradation rate (T_{max}) for PU

foams. The results showed that T_{onset} of PU foams was not affected by incorporation of both clays. However, T_{max} increased as the clay contents increased. This was found in PU foams incorporated with both clays. It could be explained by the presented of clay layers incorporated into PU foams. The clay layers could extend the pathway of the oxygen gas diffusion and volatile products throughout the foams [63], resulting higher in T_{max} . PU foams incorporated with higher amount of clays provided higher T_{max} relative to those incorporated with lower amount of clays.

Moreover, it was observed that incorporation of clays improved the char residue at high temperatures ($>390^{\circ}\text{C}$). Char residue increased linearly as the clay contents increased. The results are shown in Table 4.13. The char residue of PU foams incorporated with 7 php C30B and MMT provided highest values of 30.59 wt% and 31.89 wt%, respectively. The values were almost 100% higher than that of neat PU foam (15.76 wt%). The clay enhanced carbonaceous char formation by catalytic effect of clay. At higher temperature, clay degraded to form acidic protons on the clay layer [64]. These acidic protons had further favored the depolymerization, crosslinking and charring process and finally increased the char residue.

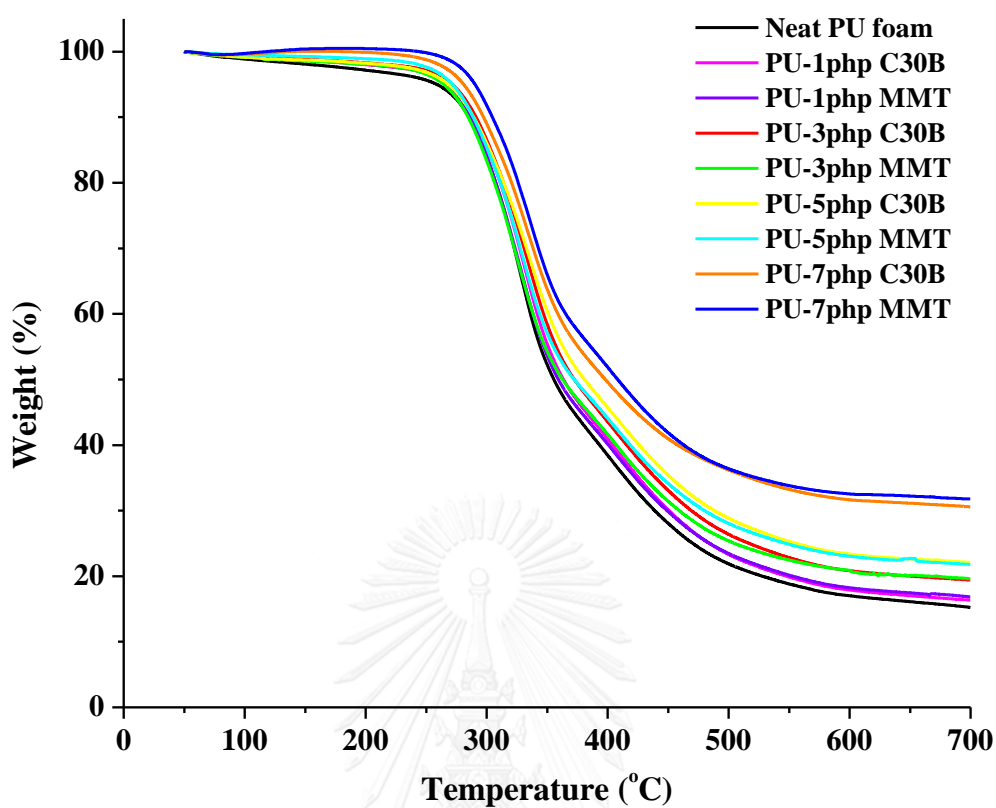


Figure 4.32 TGA curves of neat PU foam and PU foam/clay nanocomposites

Table 4.13 Effect of clay types and amount of clays on decomposition temperature (T_{onset}), degradation temperature (T_{max}) and char residue of the PU foams

sample	$T_{\text{onset}}(^{\circ}\text{C})$	$T_{\text{max}}(^{\circ}\text{C})$	Char residue (wt%)
Neat PU foam	288.53	387.79	15.76
PU-1php C30B	289.89	394.97	16.52
PU-1php MMT	283.69	393.51	17.10
PU-3php C30B	287.87	401.55	19.54
PU-3php MMT	272.76	400.70	19.72
PU-5php C30B	287.47	403.04	22.12
PU-5php MMT	287.57	397.21	21.91
PU-7php C30B	288.42	410.41	30.59
PU-7php MMT	292.74	403.84	31.89

CHAPTER V

CONCLUSION

5.1 Conclusion

Various bio-based polyester polyols were successfully synthesized by condensation reaction using succinic acid and seven types of glycols. When the ether glycol was used to prepare bio-based succinate polyols, the viscosity and OH number of the polyols decreased as the chain length of glycols used in polyols increased. Moreover, polyols prepared from mixed glycols had higher viscosity than those prepared from neat glycol. Polyols prepared from alkyl glycols provided solid substances at room temperature.

Bio-based PU foams were prepared from the synthesized bio-based succinate polyols and PMDI. Foams prepared from mixed-glycol polyols provided smaller cell size and there are more closed cells contents than those prepared from neat-glycol polyols. The density and compressive strength of PU foams prepared from neat or mixed-glycol polyols decreased as the chain length of glycol used in polyols increased. Foams prepared from neat-glycol polyols had higher density but lower compressive strength relative to those prepared from mixed-glycol polyols.

For thermal stability of prepared PU foams, it can be concluded that PU foams prepared from mixed-glycol polyol had lower T_{onset} but slightly higher in T_{max} relative to those prepared from neat-glycol polyols.

The effect of different NCO indexes of prepared PU foams were studied relative to PU foams prepared from commercial polyol. The morphology results by OM demonstrated that foam cell structures and cell dimensions of PU foams prepared from succinate polyol and commercial polyol were not affected by NCO indexes. The density and compressive strength of PU foams prepared from succinate polyol increased as the NCO index increased, as well as the PU foams prepared from commercial polyol. In addition, PU foams prepared from succinate polyol had higher density and compressive strength than those prepared from commercial polyol at the same NCO indexes.

The prepared PU foam/clay nanocomposites showed exfoliated dispersion of both clays (C30B and MMT) in PU matrix at 1 php. While at 7 php, the PU foam incorporated with MMT showed intercalation structure and PU foam incorporated with nanoclay C30B showed partially exfoliated structure in PU matrix. PU foam prepared from succinate polyol at 1 php C30B provided highest density and compressive strength. The T_{onset} of PU foams was not affected by incorporation of both clays, while T_{max} increased as the clay contents increased. Moreover, the char residue increased linearly with increasing the clay contents.

5.2 Suggestion for future work

This research work focused on improving mechanical properties of bio-based rigid PU foams prepared from bio-based succinate polyols for structural application. However, another useful application of closed cell rigid PU foams is using it as thermal insulation. Therefore, thermal properties of foams such as thermal conductivity should be investigated. In addition, high functionality of the synthesized polyols should be considered for PU foams preparation in order to compare the properties with PU foams prepared from high functionality commercial polyols.

REFERENCES

- [1] G., A. in Polyurethanes (PU), pp. 123-127. Munich: Kunststoffe International, 2008.
- [2] wikipedia. List of polyurethane applications 2015. Available from: https://en.wikipedia.org/wiki/List_of_polyurethane_applications [10 Dec 2015]
- [3] Szycher, M. Szycher's handbook of polyurethanes. CRC press, 1999.
- [4] Eaves, D. Handbook of polymer foams. polimeri 25 (2004): 1-2.
- [5] Nohra, B., Candy, L., Blanco, J.-F.o., Guerin, C., Raoul, Y., and Mouloungui, Z. From petrochemical polyurethanes to biobased polyhydroxyurethanes. Macromolecules 46(10) (2013): 3771-3792.
- [6] Niemeyer, T., Patel, M., and Geiger, E. A further examination of soy-based polyols in polyurethane systems. in Salt Lake City, UT: Alliance for the Polyurethane Industry Technical Conference, pp. 2-4, 2006.
- [7] World Bio Succinic Acid Market - Opportunities and Forecasts, 2013 - 2020 2014. Available from: <https://www.alliedmarketresearch.com/bio-succinic-acid-market> [26 Oct 2015]
- [8] Mittal, V. Polymer nanocomposite foams. CRC Press, 2013.
- [9] Pentrakoon, D. and Ellis, J.W. An introduction to plastic foams. Bangkok: Chulalongkorn University Press, 2005.
- [10] Saunder, J.H. The Formation Of Urethane Foams. Rubber Chem and Technology 33 (1960): 1293-1322.
- [11] Klempner, D. and Frisch, K.C. Handbook of polymeric foams and foam technology. Vol. 404: Hanser Munich etc., 1991.
- [12] Landrock, A.H. Handbook of plastic foams: types, properties, manufacture and applications. Elsevier, 1995.
- [13] Lee, S.-T., Park, C.B., and Ramesh, N.S. Polymeric foams: science and technology. CRC Press, 2006.
- [14] Schmelzer, H. Polyurethanes for flexible surface coatings and adhesives. Journal of Industrial Textiles 17(3) (1988): 167-182.
- [15] Engels, H.W., et al. Polyurethanes: Versatile materials and sustainable problem solvers for today's challenges. Angewandte Chemie International Edition 52(36) (2013): 9422-9441.
- [16] Kanyanta, V. and Ivankovic, A. Mechanical characterisation of polyurethane elastomer for biomedical applications. Journal of the Mechanical Behavior of Biomedical Materials 3(1) (2010): 51-62.
- [17] Tan, S., Abraham, T., Ference, D., and Macosko, C.W. Rigid polyurethane foams from a soybean oil-based polyol. Polymer 52(13) (2011): 2840-2846.
- [18] Ashida, K. Polyurethane and related foams: chemistry and technology. CRC press, 2006.
- [19] Cavender, K.D. and Hawker, L.E. Proc. 32nd SPI Annual Technical & Marketing Conference. in Lancaster, PA: Technomic Publishing Co., 1989.
- [20] Ionescu, M. Chemistry and technology of polyols for polyurethanes. iSmithers Rapra Publishing, 2005.
- [21] Fan, H. Polyurethane foams made from bio-based polyols. University of Missouri--Columbia, 2011.

- [22] Li, Y., Luo, X., and Hu, S. Bio-based Polyols and Polyurethanes. 2015, Springer.
- [23] Yariv, S. and Cross, H. Organo-clay complexes and interactions. CRC Press, 2001.
- [24] Tjong, S. Structural and mechanical properties of polymer nanocomposites. Materials Science and Engineering: R: Reports 53(3) (2006): 73-197.
- [25] Crain, E. Crain's petrophysical handbook. Spectrum (2000).
- [26] Giannelis, E., Krishnamoorti, R., and Manias, E. Polymer-silicate nanocomposites: model systems for confined polymers and polymer brushes. in Polymers in confined environments, pp. 107-147: Springer, 1999.
- [27] Hetzer, M. and De Kee, D. Wood/polymer/nanoclay composites, environmentally friendly sustainable technology: A review. Chemical engineering research and design 86(10) (2008): 1083-1093.
- [28] Ahn, B.D., Kim, S.H., Kim, Y.H., and Yang, J.S. Synthesis and characterization of the biodegradable copolymers from succinic acid and adipic acid with 1, 4-butanediol. Journal of applied polymer science 82(11) (2001): 2808-2826.
- [29] Zeng, J.-B., Li, Y.-D., Zhu, Q.-Y., Yang, K.-K., Wang, X.-L., and Wang, Y.-Z. A novel biodegradable multiblock poly (ester urethane) containing poly (L-lactic acid) and poly (butylene succinate) blocks. Polymer 50(5) (2009): 1178-1186.
- [30] Zeng, J.-B., Li, Y.-D., Li, W.-D., Yang, K.-K., Wang, X.-L., and Wang, Y.-Z. Synthesis and properties of poly (ester urethane) s consisting of poly (L-lactic acid) and poly (ethylene succinate) segments. Industrial & Engineering Chemistry Research 48(4) (2009): 1706-1711.
- [31] Sonnenschein, M.F., Guillaudeu, S.J., Landes, B.G., and Wendt, B.L. Comparison of adipate and succinate polyesters in thermoplastic polyurethanes. Polymer 51(16) (2010): 3685-3692.
- [32] Coggio, W.D., et al. Bio-Based Succinic Acid: A Versatile Building Block for Performance Driven PUD and Coatings. in American Coatings Conference, Biobased Coatings. Atlanta, 2014.
- [33] Widya, T. and Macosko, C.W. Nanoclay-modified rigid polyurethane foam. Journal of Macromolecular Science, Part B: Physics 44(6) (2005): 897-908.
- [34] Xu, Z., Tang, X., Gu, A., and Fang, Z. Novel preparation and mechanical properties of rigid polyurethane foam/organoclay nanocomposites. Journal of applied polymer science 106(1) (2007): 439-447.
- [35] Mondal, P. and Khakhar, D. Rigid polyurethane-clay nanocomposite foams: Preparation and properties. Journal of applied polymer science 103(5) (2007): 2802-2809.
- [36] Chen, X.G., Sang, X.M., Hou, G.X., and Yu, S.W. Preparation and Mechanical Properties of Polyurethane/Modified Kaolin Foam Composites. in Advanced Materials Research, pp. 1171-1175: Trans Tech Publ, 2011.
- [37] Valizadeh, M., Rezaei, M., and Eyvazzadeh, A. Effect of nanoclay on the mechanical and thermal properties of rigid polyurethane/organoclay nanocomposite foams blown with cyclo and normal pentane mixture. in Key Engineering Materials, pp. 584-589: Trans Tech Publ, 2011.

- [38] Seo, W., Park, J., Sung, Y., Hwang, D., Kim, W., and Lee, H. Properties of water-blown rigid polyurethane foams with reactivity of raw materials. Journal of applied polymer science 93(5) (2004): 2334-2342.
- [39] Xu, Z., Tang, X., Gu, A., Fang, Z., and Tong, L. Surface-modifiers of clay on mechanical properties of rigid polyurethane foams/organoclay nanocomposites. Journal of applied polymer science 105(5) (2007): 2988-2995.
- [40] Sarier, N. and Onder, E. Organic modification of montmorillonite with low molecular weight polyethylene glycols and its use in polyurethane nanocomposite foams. Thermochimica Acta 510(1) (2010): 113-121.
- [41] Liang, K. and Shi, S.Q. Nanoclay filled soy-based polyurethane foam. Journal of applied polymer science 119(3) (2011): 1857-1863.
- [42] Fan, H., Tekeei, A., Suppes, G.J., and Hsieh, F.-H. Properties of biobased rigid polyurethane foams reinforced with fillers: microspheres and nanoclay. International Journal of Polymer Science 2012 (2012).
- [43] Kadkin, O., Osajda, K., Kaszynski, P., and Barber, T.A. Polyester polyols: synthesis and characterization of diethylene glycol terephthalate oligomers. Journal of Polymer Science Part A: Polymer Chemistry 41(8) (2003): 1114-1123.
- [44] Shi, H., et al. Poly (glycerol sebacate)-modified polylactic acid scaffolds with improved hydrophilicity, mechanical strength and bioactivity for bone tissue regeneration. RSC Advances 5(97) (2015): 79703-79714.
- [45] Zeng, C., Zhang, N.W., and Ren, J. Synthesis and properties of bio-based thermoplastic polyurethane based on poly (L-lactic acid) copolymer polydiol. Journal of applied polymer science 125(4) (2012): 2564-2576.
- [46] Zhang, C. and Feng, S. Effect of glycols on the properties of polyester polyols and of room-temperature-curable casting polyurethanes. Polymer international 53(12) (2004): 1936-1940.
- [47] Coggio, W.D., et al. Advancing Adhesives: Bio-Based Succinic Acid Polyester Polyols. in *Center for Polyurethanes Industry's 2014 Technical Conference*. 2014: Texas, USA.
- [48] Chajęcka, J.M. Synthesis of Biodegradable and Biocompostable Polyesters. Dissertation, Instituto Superior Técnico, Universidade Técnica de Lisboa, Lisboa, 2011.
- [49] Narine, S.S., Kong, X., Bouzidi, L., and Sporns, P. Physical properties of polyurethanes produced from polyols from seed oils: II. Foams. Journal of the American Oil Chemists' Society 84(1) (2007): 65-72.
- [50] Badri, K.B.H., Sien, W.C., Shahrom, M.S.B.R., Hao, L.C., Baderuliksan, N.Y., and Norzali, N.R.a.A. FTIR spectroscopy analysis of the prepolymerization of palm-based polyurethane. Solid State Sci. Technol 18 (2010): 1-8.
- [51] Seo, W., et al. Mechanical, morphological, and thermal properties of rigid polyurethane foams blown by distilled water. Journal of applied polymer science 90(1) (2003): 12-21.
- [52] Thirumal, M., Khastgir, D., Singha, N.K., Manjunath, B., and Naik, Y. Effect of foam density on the properties of water blown rigid polyurethane foam. Journal of applied polymer science 108(3) (2008): 1810-1817.

- [53] Zhang, L., Ding, X., and Ou, Y. Properties of Rigid Polyurethane Foams Prepared with Synthesized PIPA Polyol. American Journal of Chemistry and Application 1(1) (2014): 7-14.
- [54] Fan, H., Tekeei, A., Suppes, G.J., and Hsieh, F.H. Rigid polyurethane foams made from high viscosity soy-polyols. Journal of applied polymer science 127(3) (2013): 1623-1629.
- [55] Camino, G., Tartaglione, G., Frache, A., Manferti, C., and Costa, G. Thermal and combustion behaviour of layered silicate–epoxy nanocomposites. Polymer Degradation and Stability 90(2) (2005): 354-362.
- [56] Chen, T.-K., Tien, Y.-I., and Wei, K.-H. Synthesis and characterization of novel segmented polyurethane/clay nanocomposites. Polymer 41(4) (2000): 1345-1353.
- [57] Kim, S.H., Kim, B.K., and Lim, H. Effect of isocyanate index on the properties of rigid polyurethane foams blown by HFC 365mfc. Macromolecular Research 16(5) (2008): 467-472.
- [58] Bora, M., Ganguli, J.N., and Dutta, D.K. Thermal and spectroscopic studies on the decomposition of [Ni {di (2-aminoethyl) amine} 2]-and [Ni (2, 2': 6', 2''-terpyridine) 2]-Montmorillonite intercalated composites. Thermochemica Acta 346(1) (2000): 169-175.
- [59] Cervantes-Uc, J.M., Cauich-Rodríguez, J.V., Vázquez-Torres, H., Garfias-Mesías, L.F., and Paul, D.R. Thermal degradation of commercially available organoclays studied by TGA–FTIR. Thermochemica Acta 457(1) (2007): 92-102.
- [60] Bonnaillie, L.M. Bio-based polymeric foam from soybean oil and carbon dioxide. ProQuest, 2007.
- [61] Shi, L., et al. Expandable graphite for halogen-free flame-retardant of high-density rigid polyurethane foams. Polymer-Plastics Technology and Engineering 44(7) (2005): 1323-1337.
- [62] Harikrishnan, G., Patro, T.U., and Khakhar, D. Polyurethane foam-clay nanocomposites: nanoclays as cell openers. Industrial & Engineering Chemistry Research 45(21) (2006): 7126-7134.
- [63] Berta, M., Lindsay, C., Pans, G., and Camino, G. Effect of chemical structure on combustion and thermal behaviour of polyurethane elastomer layered silicate nanocomposites. Polymer Degradation and Stability 91(5) (2006): 1179-1191.
- [64] Xie, W., Gao, Z., Pan, W.-P., Hunter, D., Singh, A., and Vaia, R. Thermal degradation chemistry of alkyl quaternary ammonium montmorillonite. Chemistry of Materials 13(9) (2001): 2979-2990.

APPENDIX



จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

Appendix A

Acid number, OH number and NCO index calculations

Acid number calculation

The acid number can be calculated, in milligrams of KOH per gram of sample, as follow equation:

$$\text{Acid Number} = \frac{A \times N \times 56.1}{W}$$

Where:

A = volume of KOH solution used in titration of the sample, ml

N = normality of the KOH solution, eq/L

W = weight of the sample used, g

56.1 = MW of KOH, g/mol

#Example Calculate the acid number of polyol prepared from SA and mixture of DEG and glycerol in the molar ratio of 1:1.5:0.33, respectively

$$\begin{aligned} \text{Acid Number} &= \frac{1.1 \times 0.02 \times 56.1}{1.0} \\ &= 1.23 \text{ mg KOH/g sample} \end{aligned}$$

OH number calculation

The hydroxyl number can be calculated, in milligrams of KOH per gram of sample, as follow equation:

$$\text{Hydroxyl number} = \frac{(A - B)N \times 56.1}{\text{g sample}}$$

Where:

A = volume of KOH solution used in titration of the blank, ml

B = volume of KOH solution used in titration of the sample, ml

N = normality of the KOH solution, eq/L

56.1 = MW of KOH, g/mol

#Example Calculate the hydroxyl number of polyol prepared from SA and mixture of DEG and glycerol in the molar ratio of 1:1.5:0.33, respectively

$$\begin{aligned} \text{Hydroxyl number} &= \frac{(24.2 - 18.7)1.0 \times 56.1}{1.0} \\ &= 308.55 \text{ mg KOH/g sample} \end{aligned}$$

NCO index calculation

#Example Calculate the parts by weight (pbw) of PMDI (B9001), molar mass = 365.8, functionality = 2.7 at an isocyanate indexes of 100, 125, 150, 175 and 200 required to react with the following formulation:

Formulation	Parts per hundred parts of polyol (g)
Component A	
PMDI (B9001), NCO indexes of 100, 125, 150, 175 and 200	?
Component B	
Bio-based polyester polyol (SA:DEG:Gly at the molar ratio of 1:1.5:0.33, OH number = 307.75 mg KOH/ g, functionality = 2)	100
catalyst	1
Syrfactant	2.5
Blowing agent (water, Mw = 18 g/mole, functionality = 2)	3

$$\text{Hydroxyl number} = \frac{56.1 \times \text{functionality} \times 1000}{\text{Molar mass}} = \frac{56.1 \times 1000}{\text{Equivalent weight}}$$

Where;

$$\text{Equivalent weight} = \frac{\text{Molar mass}}{\text{functionality}}$$

Therefore;

$$\text{Equivalent weight} = \frac{56.1 \times 1000}{\text{Hydroxyl number}}$$

$$\text{Equivalent weight of bio-based polyester polyol} = \frac{56.1}{308.55} \times 1000 = 181.8$$

$$\text{Equivalent weight of water} = \frac{18}{2} = 9.0$$

Note: Surfactants and catalysts are neglected in stoichiometric calculations because they do not react with NCO groups.

$$\text{Number of equivalent in formulation} = \frac{\text{parts per hundred parts of polyol (g)}}{\text{equivalent weight}}$$

Equivalent in the above formulation:

$$\text{Bio-based polyester polyol} = \frac{100}{181.8} = 0.55$$

$$\text{Water (blowing agent)} = \frac{3.0}{9.0} = 0.33$$

$$\text{Total equivalent weight} = 0.55 + 0.33 = 0.88$$

For stoichiometric equivalence, PMDI php is total equivalent \times equivalent weight because PMDI reacts with polyol and water.

Thus:

$$\text{PMDI (php)} = 0.881 \times \frac{\text{PMDI molar mass}}{\text{functionality}} = 0.88 \times \frac{365.8}{2.7} = 119.2$$

Note: 119.2 defines the isocyanate quantity at 100 index

Where;

$$\text{Isocyanate index} = \frac{\text{actual amount of isocyanate}}{\text{theoretical amount of isocyanate}} \times 100$$

Thus:

Isocyanate index = 100;

$$\text{Isocyanate actual} = \frac{119.2}{100} \times 100 = 119.2 \text{ php}$$

Isocyanate index = 125;

$$\text{Isocyanate actual} = \frac{119.2}{100} \times 125 = 149.0 \text{ php}$$

Isocyanate index = 150,

$$\text{Isocyanate actual} = \frac{119.2}{100} \times 150 = 178.8 \text{ php}$$

Isocyanate index = 175

$$\text{Isocyanate actual} = \frac{119.2}{100} \times 175 = 208.6 \text{ php}$$

Isocyanate index = 200;

$$\text{Isocyanate actual} = \frac{119.2}{100} \times 200 = 238.4 \text{ php}$$

Table A1 Isocyanate quantity at different NCO indexes in the above formulations

Formulation	NCO indexes				
	100	125	150	175	200
Bio-based polyester polyol	100	100	100	100	100
Catalyst	1	1	1	1	1
Surfactant	2.5	2.5	2.5	2.5	2.5
Blowing agent	3	3	3	3	3
PMDI (B9001)	119.2	149.0	178.8	208.6	238.4

VITA

The author who is responsible for this dissertation is Miss. Tatcha Sonjui. She was born on September 21st, 1984 in Nakhonsawan, Thailand. She received the bachelor's degree from the Department of Chemistry, Faculty of Science, Naresuan University. She continued her Master study in the field of Industrial Chemistry, Faculty of Science, Kasetsart University in 2006 and completed the program in 2009. After graduated, she started working as a Research and Development Scientist at Johnson and Johnson (Thailand) Limited. Then in 2011, she left to join the Department of Materials Science, Faculty of Science, Chulalongkorn University as a doctoral student, and earned Ph.D. in Materials Science in 2015.

Publication in this dissertation:

1. Sonjui, T. and Jiratumnukul, N. Physical Properties of Bio-Based Polyurethane Foams From Bio-Based Succinate Polyols. *Cellular Polymers* 34(6) (2015): 353-365.

Conference Presentation:

1. Sonjui, T. and Jiratumnukul, N. (2014) "Preparation and Characterization of Polyurethane Foams from Bio-Based Succinate Polyols" poster presentation conference on the 8th International Conference on Materials Science and Technology, December 15-16, 2014, Bangkok, Thailand.

2. Sonjui, T. and Jiratumnukul, N. (2015) "Effect of Glycols on the Properties of Bio-Based Succinate Polyols and Polyurethane Foams" poster presentation on The Global Human Resource Program Bridging across Physics and Chemistry, January 30th, 2015, Tokyo Metropolitan University (TMU), Japan

3. Sonjui, T. and Jiratumnukul, N. (2015) "Physical Properties of Bio-Based Polyurethane Foams from Bio-Based Succinate Polyols" oral presentation on 5th International Conference on Key Engineering Materials, March 21-23, 2015, Singapore