# การเตรียมโฟมพอลิยูรีเทนจากน้ำมันพืช

นางสาวปวีณา เอกพรรณ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
สาขาวิชาปิโตรเคมี
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2554

# PREPARATION OF POLYURETHANE FOAMS FROM VEGETABLE OILS

Miss Paweena Ekkaphan

A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy Program in Petrochemistry
Faculty of Science
Chulalongkorn University
Academic Year 2011

| | |
|---|---|
| Thesis Title | PREPARATION OF POLYURETHANE FOAMS FROM VEGETABLE OILS |
| By | Miss Paweena Ekkaphan |
| Field of Study | Petrochemistry |
| Thesis Advisor | Associate Professor Amorn Petsom, Ph.D. |
| Thesis Co-advisor | Associate Professor Nuanphun Chantarasiri, Ph.D. |

---

Accepted by the Graduate School, Chulalongkorn University in Partial Fulfillment of the Requirements for the Doctoral Degree

…………………………………… Dean of the Faculty of Science
(Professor Supot Hannongbua, Dr.rer.nat.)

THESIS COMMITTEE

……………………………………………….. Chairman
(Associate Professor Supawan Tantayanon, Ph.D.)

………………………………………………. Thesis Advisor
(Associate Professor Amorn Petsom, Ph.D.)

……………………………………………….. Thesis Co-advisor
(Associate Professor Nuanphun Chantarasiri, Ph.D.)

……………………………………………….. Examiner
(Associate Professor Wimonrat Trakarnpruk, Ph.D.)

……………………………………………….. External Examiner
(Damrong Sommit, Ph.D.)

ปวีณา เอกพรรณ: การเตรียมโฟมพอลิยูรีเทนจากน้ำมันพืช (PREPARATION OF POLYURETHANE FOAMS FROM VEGETABLE OILS) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. อมร เพชรสม, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: รศ. ดร. นวลพรรณ จันทรศิริ), 174 หน้า.

วัตถุประสงค์หลักของงานวิจัยนี้คือ การเตรียมพอลิออลชีวฐานสำหรับโฟมพอลิยูรีเทนแบบแข็ง โดยใช้น้ำมันพืช 3 ชนิด ได้แก่ น้ำมันเมล็ดแมงลัก น้ำมันเมล็ดงา และน้ำมันเมล็ดฟักทอง การสังเคราะห์พอลิออลฐานน้ำมันพืชมี 2 ขั้นตอน ประกอบด้วยปฏิกิริยาไฮดรอกซีเลชันและปฏิกิริยาแอลกอฮอไลซิส ซึ่งพอลิออลที่สังเคราะห์ได้มีค่าไฮดรอกซิลอยู่ในช่วง 340–383 มิลลิกรัมโพแทสเซียมต่อกรัม โฟมพอลิยูรีเทนแบบแข็งที่มีน้ำเป็นสารฟูถูกเตรียมขึ้นจากปฏิกิริยาของพอลิออลชีวฐานเหล่านี้กับพอลิเมอริกเมทิลีนไดเฟนิลไดไอโซไซยาเนต แล้วศึกษาผลของดัชนีไอโซไซยาเนต ปริมาณตัวเร่งปฏิกิริยา ปริมาณสารฟูและปริมาณสารลดแรงตึงผิวที่มีต่อเวลาในการทำปฏิกิริยาและความหนาแน่นของโฟม ผลการทดลองแสดงว่า ปัจจัยเหล่านี้ยกเว้นปริมาณสารลดแรงตึงผิวส่งผลอย่างมีนัยสำคัญขึ้นอยู่กับชนิดของพอลิออลที่สังเคราะห์ได้ เมื่อเพิ่มดัชนีไอโซไซยาเนตและปริมาณสารฟูส่งผลให้เวลาในการทำปฏิกิริยานานขึ้น โดยความหนาแน่นของโฟมจะค่อยๆ สูงขึ้นเมื่อดัชนีไอโซไซยาเนตสูงขึ้น แต่จะส่งผลในทางตรงข้ามกับผลของปริมาณสารฟู ในขณะที่เมื่อปริมาณตัวเร่งปฏิกิริยาเพิ่มขึ้นทำให้เวลาในการทำปฏิกิริยากับความหนาแน่นของโฟมลดลง ซึ่งโฟมพอลิยูรีเทนแบบแข็งฐานน้ำมันพืชเหล่านี้ แสดงค่าทนทานต่อแรงกดอัดค่อนข้างสูง (237.7–303.1 กิโลปาสกาล) ที่ความหนาแน่นในช่วง 40–45 กิโลกรัมต่อลูกบาศก์เมตร นอกจากนี้สัณฐานวิทยาของเซลล์โฟมซึ่งถูกตรวจสอบด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด ชี้ให้เห็นว่าโครงสร้างของเซลล์โฟมโดยส่วนมากเป็นเซลล์ปิดที่มีรูปร่างแบบพอลิโกนอล จากการวิเคราะห์ทางการทดลองเหล่านี้สนับสนุนว่าโฟมพอลิยูรีเทนแบบแข็งที่เตรียมขึ้นจากพอลิออลชีวฐานดังกล่าวแสดงสมบัติทางกายภาพ สมบัติเชิงกล และสมบัติทางความร้อนใกล้เคียงกับโฟมพอลิยูรีเทนแบบแข็งที่เตรียมจากพอลิออลทางการค้า

สาขาวิชา ปิโตรเคมี ลายมือชื่อนิสิต

ปีการศึกษา 2554 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก

ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม

# # 5073844823 : MAJOR PETROCHEMISTRY

KEYWORDS : VEGETABLE OIL / BIO-BASED POLYOLS / RIGID POLYURETHANE FOAM

PAWEENA EKKAPHAN: PREPARATION OF POLYURETHANE FOAMS FROM VEGETABLE OILS. ADVISOR: ASSOC. PROF. AMORN PETSOM, Ph.D., CO-ADVISOR: ASSOC. PROF. NUANPHUN CHANTARASIRI, Ph.D., 174 pp.

The preparation of bio-based polyols for rigid polyurethane (RPUR) foams is the main objective of this research. Three vegetable oils including hairy basil seed oil, sesame seed oil, and pumpkin seed oil have been used to synthesize bio-based polyols. The synthesis of vegetable oil-based polyols involved two steps, namely the hydroxylation and the alcoholysis reaction. The resulting polyols had the OH number in the range of 340–383 mg KOH/g. The water-blown RPUR foams were produced by the reaction of these bio-based polyols with polymeric methylene diphenyl diisocyanate (PMDI). The effects of isocyanate index, catalyst, blowing agent, and surfactant contents on the reaction time and their density were evaluated. The results showed that these parameters except the surfactant content significantly affected on the foaming time and foam density depending upon the synthesized polyol type. An increase in NCO index and blowing agent contents resulted in the longer reaction time, the foam density at higher NCO index was raised gradually that contrast to the effect of blowing agent content. As the catalyst contents increased, the reaction time was reduced with a decrease in density of foams. These vegetable oil-based RPUR foams exhibited relatively high compressive strength (237.7–303.1 kPa) with the density in the range of 40–45 kg/m$^3$. Additionally, the cell foam morphology investigated by scanning electron microscope indicated that their cellular structure presented mostly polygonal closed-cells. These detailed experimental analyses supported that the water-blown RPUR foams prepared from these bio-based polyols possessed comparable the physical, mechanical, and thermal properties to those obtained from the commercial polyols.

Field of Study: Petrochemistry　Student's Signature ..............................

Academic Year: 2011　Advisor's Signature ..............................

Co-advisor's Signature ..............................

# ACKNOWLEDGEMENTS

The author wishes to express her deep and sincere gratitude to her advisor Associate Professor Dr. Amorn Petsom and co-advisor Associate Professor Dr. Nuanphun Chantarasiri for very kind assistance, generous guidance, and encouragement throughout the course of this research.

The author also wishes to express gratitude to Associate Professor Dr. Supawan Tantayanon, Associate Professor Dr. Wimonrat Trakarnpruk, and Dr. Damrong Sommit serving as the chairman and members of this thesis committee, respectively, for all their valuable discussion and suggestion.

The author gratefully acknowledges financial support from 90th Year Chulalongkorn Scholarship, Chulalongkorn University and National Center of Excellence for Petroleum, Petrochemicals and Advanced Materials (NCE-PPAM). Definitely, the author sincerely thanks Huntsman (Thailand) Co., Ltd. and IRPC Public Co., Ltd. for their chemical support.

Absolutely, the author is grateful to Program in Petrochemistry, Faculty of Science, Chulalongkorn University and the Institute of Biotechnology and Genetic Engineering (IBGE), Chulalongkorn University for the support of chemicals and laboratory facility.

The author would like to thank all members of IBGE for their helpfulness and suggestions. Furthermore, many thanks are going to generous help of friends and whose suggestion and support are throughout this research. Finally, the author would like to express her special gratitude to her mother, family members for their inspiration, understanding, great support and encouragement throughout the entire course of her study.

# CONTENTS

PAGE

ABSTRACT (THAI)…………………………………………………………… iv
ABSTRACT (ENGLISH)……………………………………………............ v
ACKNOWLEDGEMENTS………………………………………………….. vi
CONTENTS……………………………………………………………….. vii
LIST OF TABLES………………………………………………………… xii
LIST OF FIGURES………………………………………………………... xiv
LIST OF ABBREVIATIONS AND SYMBOLS…………………………….. xviii

**CHAPTER I INTRODUCTION**………………………………………….. 1
- 1.1 The state of problem…………………………………………… 1
- 1.2 The objective and scope of the research……………………….. 3

**CHAPTER II THEORY AND LITERATURE REVIEWS**…………….. 5
- 2.1 An introduction to polyurethane technology …………………... 5
- 2.2 Chemistry of polyurethanes…………………………………….. 7
  - 2.2.1 Polymerization reaction……………………………… 9
  - 2.2.2 The gas producing reaction (blowing reaction)……… 9
  - 2.2.3 Additional crosslinking network formation………….. 10
- 2.3 Raw materials for rigid polyurethane foam formulation ………. 11
  - 2.3.1 Isocyanates…………………………………………… 11
  - 2.3.2 Polyols………………………………………………... 14
    - 2.3.2.1 Conventional polyether polyols…………… 15
    - 2.3.2.2 Conventional polyester polyols……………. 17
  - 2.3.3 Blowing agents……………………………………….. 20
  - 2.3.4 Catalysts……………………………………………… 21
  - 2.3.5 Surfactants…………………………………………… 23
- 2.4 Specification tests of reactive raw materials …………………... 24

PAGE

2.4.1 Analysis of isocyanates…………………………….. 24

2.4.1.1 Isocyanate content………………………….. 24

2.4.2 Analysis of polyols………………………………….. 25

2.4.2.1 Hydroxyl number…………………………... 25

2.4.2.2 Acid number……………………………….... 26

2.5 Formulation calculations……………………………………... 27

2.5.1 Functionality……………………………………….. 27

2.5.2 Equivalent ratio……………………………………. 27

2.5.3 Isocyanate index (NCO index)……………………….. 28

2.6 Rigid polyurethane foam preparation technology………………. 29

2.6.1 Process for producing rigid polyurethane foams……... 29

2.7 Characterization of rigid polyurethane foam properties………… 31

2.7.1 Density…………………………………………….. 31

2.7.2 Morphology………………………………………... 32

2.7.3 Compressive property……………………………... 32

2.7.4 Thermal conductivity…………………………….... 34

2.7.5 Thermal degradation profile………………………….. 36

2.8 Literature reviews on bio-based polyurethanes………………… 37

2.8.1 Polyols from vegetable oils…………………............... 38

2.8.1.1 Epoxidation/hydroxylation reaction………... 40

2.8.1.2 Hydroformylation/hydrogenation reaction…. 41

2.8.1.3 Ozonolysis reaction………………………… 42

2.8.1.4 Alcoholysis reaction………………………... 43

2.8.2 Polyols for cashew nut shell liquid…………………... 44

2.8.3 Polyurethane foams from bio-based polyols…………. 46

**CHAPTER III EXPERIMENTAL**……………………………………….. 51

3.1 Chemicals and raw materials …….…………………………….. 51

3.1.1 Polyols preparation from vegetable oil ……………… 51

3.1.2 Hydroxyl number and acid number of polyols……….. 52

**PAGE**

3.1.3 Rigid polyurethane foam preparation………………… 54

3.2 Synthesis of cashew nut shell liquid and vegetable oil-based polyols……………………………………………………….. 54

3.2.1 Hydroxylation of vegetable oils and CNSL………….. 54

3.2.2 Alcoholysis of hydroxylated vegetable oils………….. 55

3.3 Polyols characterization………………………………....... 56

3.3.1 Hydroxyl number……………………………………... 56

3.3.2 Acid number………………………………………….. 57

3.3.3 Water content……………………………………..…. 58

3.3.4 Viscosity measurement……………………………...... 59

3.3.5 Fourier transform infrared spectroscopy……………... 59

3.3.6 Nuclear magnetic resonance spectroscopy...………… 59

3.3.7 Electrospray ionization-mass spectrometry…………... 60

3.4 Rigid polyurethane foam preparation …….……………… 60

3.5 Foam properties measurement ………………………… 62

3.5.1 Density……………………………………………….... 62

3.5.2 Compressive testing…………………………………... 62

3.5.3 Scanning electron microscope………………………... 63

3.5.4 Thermal properties……………………………………. 63

3.5.4.1 Thermogravimetric analysis (TGA)………... 63

3.5.4.2 Thermal constant analyzer………………… 63

**CHAPTER IV RESULTS AND DISCUSSION**………………………….. 64

4.1 Synthesis and characterization of biopolyols............................ 64

4.1.1 Fourier transform infrared spectroscopy of biopolyols…………………………….................. 67

4.1.2 Nuclear magnetic resonance spectroscopy of biopolyols…………………………….................. 69

4.1.3 Electrospray ionization-mass spectrometry of biopolyols…………………………………………….. 73

**PAGE**

4.1.3.1 Qualitative analysis of synthesized biopolyols………………………………….. 73
4.1.3.2 Quantitative analysis of free triethanolamine presenting in biopolyols…………………… 81
4.2 External appearance of rigid polyurethane (RPUR) foams from vegetable oil-based polyols…………………………………….. 83
4.3 External appearance of rigid polyurethane (RPUR) foams from vegetable oil-based polyols …………….................................. 84
4.4 Study on the effects of reactive starting materials contents on foaming behavior and foam density……................................... 88
4.4.1 Effects of NCO index on reaction time and foam density……………………………....................... 88
4.4.2 Effects of blowing agent contents on reaction time and foam density……............................................... 92
4.4.3 Effects of catalyst contents on reaction time and foam density…………………............................... 95
4.4.4 Effects of surfactant contents on foaming behavior and foam density……………................................... 98
4.4.5 The optimal formulation of vegetable oil based-RPUR foams……………………………………… 101
4.5 Characterizations of rigid polyurethane foams from vegetable oil-based polyols……………………………………………….. 102
4.5.1 Isocyanate conversion of RPUR foams……………... 103
4.5.2 Physical and mechanical properties of rigid polyurethane foams from vegetable oil-based polyols 108
4.5.3 Morphology of RPUR foams………………………... 111
4.5.4 Thermal properties of rigid polyurethane foams……. 113
4.5.4.1 Thermal stability …………......................... 113
4.5.4.2 Thermal conductivity……………………..... 115

**PAGE**

**CHAPTER V CONCLUSION**………………………………………...….. 116

5.1 Vegetable oil-based polyols for rigid polyurethane foam preparation…………………………………………………… 116

5.2 Rigid polyurethane foam prepared from vegetable oil-based polyols………………………………………………….…...... 117

5.3 Suggestion for further study…………………………………….. 120

**REFERENCES**……………………………………………………… 121

**APPENDICES**……………………………………………………........ 128

**APPENDIX A**........................................................................... 129

**APPENDIX B**............................................................................ 132

**APPENDIX C**........................................................................... 136

**APPENDIX D**........................................................................... 138

**APPENDIX E**............................................................................ 155

**APPENDIX F**............................................................................ 165

**APPENDIX G**........................................................................... 171

**VITAE**……………………………………………………………...... 174

# LIST OF TABLES

**TABLES** **PAGE**

2.1 Characteristics of the production of PUR foam grades……………. 6
2.2 Applications of rigid polyurethane foam manufacturing………….. 7
2.3 The relative reactivity of isocyanates…………………………..... 8
2.4 The characteristics of TDI……………………………………........ 13
2.5 The characteristics of MDI……………………………………....... 14
2.6 Characteristics of some common used initiators for polyether polyols production………………………………………………… 16
2.7 Characteristics of some common used dicarboxylic acids for polyester polyols production……………………………………........ 17
2.8 The most used catalysts in rigid polyurethane foam production…... 22
2.9 Typical fatty acid compositions of selecting plant oils……............ 39
3.1 Characteristics and fatty acid composition of hairy basil seed oil, sesame seed oil and pumpkin seed oil…………...………………… 51
3.2 Commercial specifications of raw materials for rigid polyurethane foam preparation in this work…………………………………….... 53
3.3 Water-blown RPUR foams formulation…………………………... 61
4.1 Commercial specifications of raw materials for rigid polyurethane foam preparation in this work…………………………….……….... 66
4.2 The main structural components in synthesized vegetable oil-based polyols identified by ESI-MS in positive ionization mode……….. 75
4.3 The amount of unreacted triethanolamine in vegetable oil-based poyols detected by ESI-MS……………………………………….. 82
4.4 The reaction time and density of RPUR foams prepared from hairy basil seed oil biopolyol (HBOB)…………………………………... 85
4.5 The reaction time and density of RPUR foams prepared from sesame seed oil biopolyol (SSOB)………………………………… 86

**TABLES** **PAGE**

4.6 The reaction time and density of RPUR foams prepared from pumpkin seed oil biopolyol (POB)………………………………… 87

4.7 Effects of isocyanate index on reaction time and density of RPUR foams prepared at NCO indexes of 100–250, 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant ……………………... 90

4.8 Effects of blowing agent contents on reaction time and density of RPUR foams prepared at varying water content of 1.0–5.0 pbw, NCO index of 175, 1.0 pbw of catalyst, and 2.5 pbw of surfactant.. 93

4.9 Effects of catalyst (DMCHA) contents on reaction time and density of RPUR foams prepared at varying catalyst content at 0.25–2.0 pbw, NCO index of 175, 3.0 pbw of water, and 2.5 pbw of surfactant……………………….…………………………….. 96

4.10 Effects of surfactant contents on reaction time and density of RPUR foams prepared at varying surfactant (TEGOSTAB® B8460) content at 1.5–3.5 pbw, NCO index of 175, 3.0 pbw of water, and 1.0 pbw of catalyst……………………………………... 99

4.11 The optimal formulation of water-blown RPUR foams prepared from vegetable oil-based polyols…………………………………... 101

4.12 The main IR bands of rigid polyurethane foam system……………. 104

4.13 NCO conversion of RPUR foams prepared at the NCO indexes of 100–250 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant……………………………………………………….... 105

4.14 Mechanical properties of rigid polyurethane foams prepared from optimized formulations…………………………………………….. 108

4.15 Thermal conductivity of RPUR foams with density 40–45 kg/m$^3$… 115

5.1 Comparison of vegetable oil-based polyols properties…………….. 116

5.2 Comparison of rigid polyurethane foams prepared from plant oil-based polyols and commercial polyols…………………………….. 118

## LIST OF FIGURES

**FIGURES** **PAGE**

2.1 Chemical structures of toluene diisocyanate (TDI) isomers ……… 12
2.2 Chemical structures of diphenylmethane diisocyanate (MDI) isomers and polymeric diphenylmethane diisocyanate……………. 13
2.3 Structures of (a) sorbitol based and (b) sucrose based polyether used in rigid polyurethane foam production ………………………. 15
2.4 Structure of the aromatic polyester polyols used in RPUR foams… 18
2.5 Typical chemical structure of castor oil …………………………... 19
2.6 Commercial soy polyols used for polyurethane foam preparation… 19
2.7 The molecular structure of typical silicone surfactants used in PUR foams preparation ………………………………........................ 24
2.8 One-shot method for making rigid polyurethane foams ……......... 30
2.9 Lab scale preparation of RPUR foams……................................... 31
2.10 SEM images of opened- and closed-cell PUR foams……….…….. 32
2.11 Compression load defection test rig..……………………………... 33
2.12 Typical compressive stress-strain curve of rigid foams …………... 34
2.13 Structures of triglycerides and five dominating fatty acids ……….. 38
2.14 Epoxidation and hydroxylation reactions of vegetable oils, where X = –$OCH_3$ for (a), –OH for (b), –Cl or Br for (c), and –H for (d)... 40
2.15 Hydroformylation and hydrogenation reactions of vegetable oils… 42
2.16 Ozonolysis reaction of vegetable oils……………………………... 43
2.17 Typical transesterification of vegetable oils…………………..…… 44
2.18 Structures of four major components of cashew nut shell liquid (CNSL)…………………………………………………………….. 45
3.1 The appearance of hairy basil, sesame, and pumpkin seed oils…… 52
3.2 The appearance of epoxidized oils (left) and alcoholized oils (right)………………………………………………………………. 55
3.3 The appearance of CNSL (left) and hydroxylated CNSL (right)….. 55
3.4 Polyurethane foams from hydroxylated CNSL……………………. 56

**FIGURES** **PAGE**

3.5 The pictures of polyol samples in titration step for OH number measurement………………………………………………………. 57

3.6 VR 3000 Myr viscometer used for viscosity measurement of polyols……………………....................................................... 59

3.7 Laboratory RPUR foaming process……………………………... 61

3.8 Sample preparation for foam density measurement……………….. 62

4.1 The idealized synthesis route for preparation of vegetable oil-based polyols………………………………........................... 65

4.2 ATR-IR spectra of unmodified and modified vegetable oils (a) hairy basil seed oil (HBO), (b) hydroxylated HBO and (c) alcoholyzed hydroxylated HBO (HBOB)……………………….. 67

4.3 $^{1}$H NMR and $^{13}$C NMR spectra in $CDCl_3$ of hairy basil seed oil-based polyol (HBOB)…………………………………………….. 70

4.4 $^{1}$H NMR and $^{13}$C NMR spectra in $CDCl_3$ of sesame seed oil-based polyol (SSOB)…………………………………………………... 71

4.5 $^{1}$H NMR and $^{13}$C NMR spectra in $CDCl_3$ of pumpkin seed oil-based polyol (POB)……………………………………………….. 72

4.6 The positive ion ESI-MS spectra of synthesized vegetable oil-based polyols scanned at 70–1000 m/z, (a) hairy basil seed oil-based polyol, (b) sesame seed oil-based polyol, and (c) pumpkin seed oil-based polyol, respectively…….………………………….. 74

4.7 The structures of esters with triethanolamine and triglyceride mostly presenting in synthesized vegetable oil-based polyols ……. 80

4.8 The positive ion ESI-MS spectrum of triethanolamine …………… 81

4.9 The calibration curve of triethanolamine from ESI-MS data in a concentration range of 0.5–5.0 mg/L……………………………… 82

4.10 External appearance of RPUR foams prepared from (a) neat vegetable oil, (b) hydroxylated oils, and (c) alcololized oils……... 83

**FIGURES** **PAGE**

4.11 The external appearance of HBOB-based foams prepared at NCO indexes of 100–250, 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant……………………………………………….. 89

4.12 The external appearance of HBOB-based foams prepared at varying water content of 1.0–5.0 pbw, NCO index of 175, 1.0 pbw of catalyst, and 2.5 pbw of surfactant..…………………………….. 92

4.13 The external appearance of HBOB-based foams prepared at varying catalyst content at 0.25–2.0 pbw, NCO index of 175, 3.0 pbw of water, and 2.5 pbw of surfactant…………………………... 95

4.14 The external appearance of vegetable oil-based RPUR (a) HBOB foam, (b) SSOB foam, and (c) POB foam prepared at NCO index of 150–160, 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant……………………………………………………... 101

4.15 ATR-IR spectra of starting materials and RPUR foam (a) PMDI, (b) HBOB polyol, and (c) HBOB-RPUR foam…………………..… 102

4.16 ATR-IR spectra of HBOB-based RPUR foams prepared at NCO indexes of 100–250, 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant…………………………………………………... 103

4.17 The external appearance of RPUR foams prepared at NCO index of 100, 1.0 pbw of water, 2.5 pbw of surfactant, and without adding water: (a) Raypol® 4218 foams and (b) HBOB foams…….. 107

4.18 Compression strain versus stress curves of rigid polyurethane foams with foam density ranging from 40–45 kg/m$^3$, (a) in parallel to the foam rise direction and (b) in perpendicular to the foam rise direction.……………………………………………………… 110

4.19 SEM micrographs of resulting RPUR foams in top view (left) and side view (right) of foam rising direction (50×); (a) HBOB-RPUR, (b) SSOB-RPUR, (c) POB-RPUR, (d) Raypol® 4218-RPUR and (e) Raypol® 8360-RPUR foams……………………………………. 112

**FIGURES** **PAGE**

4.20 TGA thermograms and their derivative (DTG) curves of rigid polyurethane foams at the heating rate of 10°C/min under $N_2$ atmosphere..…………………………………………………….... 114

# LIST OF ABBREVIATIONS AND SYMBOLS

| | |
|---|---|
| $\lambda$ | thermal conductivity |
| $\mu$m | micrometer |
| °C | degree of Celsius |
| cm | centimeter |
| $cm^{-1}$ | unit of wavenumber |
| $cm^3$ | cubic centimeter |
| cP | centipoises |
| g/mL | gram per milliliter |
| g/mol | gram per mole |
| kcal/mol | kilocalorie per mole |
| $kg/m^3$ | kilogram per cubic meter |
| kPa | kilopascal |
| kV | kilovolt |
| mg KOH/g | milligram potassium hydroxide per gram |
| mm/min | millimeter per minute |
| mPa.s | milliPascal.second |
| N | normality |
| pbw | part by weight |
| s | second |
| W/mK | watt per milliKelvin |
| wt% | weight percentage |
| ASTM | American Society for Testing Materials |
| ATR-IR | Attenuated Total Reflectance-Infrared |
| CFC 11 | chlorofluorocarbon 11 |
| CNSL | cashew nut shell liquid |
| DBTDL | dibutyltin dilaurate |
| DEG | diethylene glycol |
| DMCHA | *N,N*-dimethylcyclohexylamine |
| DMT | dimethylterephthalate |
| DTG | derivative thermogravimetry |

| | |
|---|---|
| FTIR | Fourier Transform Infrared Spectroscopy |
| HBO | hairy basil seed oil |
| HCFCs | hydrogenchlorofluorocarbons |
| HFCs | hydrogenfluorocarbons |
| HDI | hexamethylene diisocyanate |
| HMDI | 4,4-dicyclohexyl diisocyante |
| IPDI | isoprene diisocyanate |
| MDI | methylene diphenyl diisocyanate |
| $\overline{M}_n$ | the number average molecular weight |
| NCO | isocyanate |
| OH | hydroxyl |
| PEG | polylene glycol |
| PET | polyethyleneterphthalate |
| PIR | polyisocyanurate |
| PMDETA | pentamethyldiethylene triamine |
| PMDI | polymeric methylene diphenyl diisocyanate |
| PO | pumpkin seed oil |
| PUR | polyurethane |
| RPUR | rigid polyurethane |
| SEM | scanning electron microscope |
| Sn Oct | stannous octoate |
| SSO | sesame seed oil |
| TCA | thermal constant analyzer |
| TDI | toluene diisocyanate |
| TEDA | triethylene diamine |
| TGA | thermogravimetric analysis |

# CHAPTER I

# INTRODUCTION

## 1.1 The state of problem

Polyurethane (PUR) foams are produced based on the basis of exothermic addition polymerization between two or more isocyanate groups and polyhydroxy compounds, namely polyols to form urethane linkage. This reaction will occur under room temperature by adding a small amount of suitable catalysts such as tertiary amine and tin compounds. The cell structure of foam is formed by stabilizing gas bubble generation in polymer matrix. Hence, the blowing agent and silicone surfactant are essentially required for this point. Nowadays, the choice of blowing agents is concerned not only on the foam property but also the environmental impact is acceptable [1]. Within this requirement, a green chemical blowing agent which distilled water is applied for many researches and industrial processes. Carbon dioxide gas evolves out via the highly exothermic reaction between them and isocyanates [2]. Based on the simple basic chemistry and processing of PUR foams, the world PUR foams production is recently increasing with the versatile applications especially automotive, footwear, furnishing, packaging, insulation, and constructions, etc. The wide variety of PUR foam grades can be manufactured by modify and control the nature of the main starting components (isocyanates and polyols) and the properties of end used products. Among others, closed-cell rigid polyurethane (RPUR) foams have various unique characteristics. They are easy to prepare at ambient condition without heating that make them on-site production. Their density can be varied in a wide range from 20 to 3000 kg/m$^3$ as well as they tolerate to non-polar organic solvents. In addition, low-density RPUR foams (20–50 kg/m$^3$) are extremely useful for an insulation material in the construction industry because of their high mechanical strength and low thermal conductivity when blown with proper blowing agents [1].

Commercially, both starting materials for PUR production are mainly derived from petrochemical precursors which are being exhausted rapidly and realizing to the environmental friendly requirements. To seeking for an alternative renewable resource, vegetable oils are available abundance with the cost effectiveness and have potential to replace the petroleum based PUR. Vegetable oils are reactive triglyceride molecules containing a variation of fatty acids proportion which can be modified by chemical reaction to gain polyalcohol compounds. On the other hand, the production of isocyanates to make PUR from an environmental friendly resource is difficult and challenge fields that have been achieved for near future [3]. Recently, the ongoing use of vegetable oils for polyol synthesis has been intensively investigated by many researchers. Although vegetable oils from agricultural harvests including castor oil, soybean oil, linseed oil, canola oil, and palm oil are widely used as the raw materials for polyol production but new alternative feedstock has been progressively discovered and developed [3–5].

In this study, the utilization of locally available vegetable oils in Thailand to produce polyols is our goal. Hairy basil seed oil, sesame seed oil, and pumpkin seed oil as a renewable resource for polyol preparation were used for recent work. Hairy basil seed oil is the byproduct from dried mucilage production from hairy basil seeds which used in health care products and pharmaceutical industries. The oil is extracted from dried hairy basil seeds in order to improve swelling property of mucilage in water, which gives about 18% oil by dried weight [6]. Hairy basil seed oil contains the high contents of unsaturated fatty acid composition including α-linolenic acid (54%), linoleic acid (22%), and oleic acid (18%). Because of its unique rank odor, pure hairy basil seed oil never been used for edible oils. However, pumpkin and sesame seed oils are edible oils with highly unsaturated fatty acid contents (oleic acid 34–37% and linoleic acid 47%). Therefore, we aimed use these oils to produce value-added products.

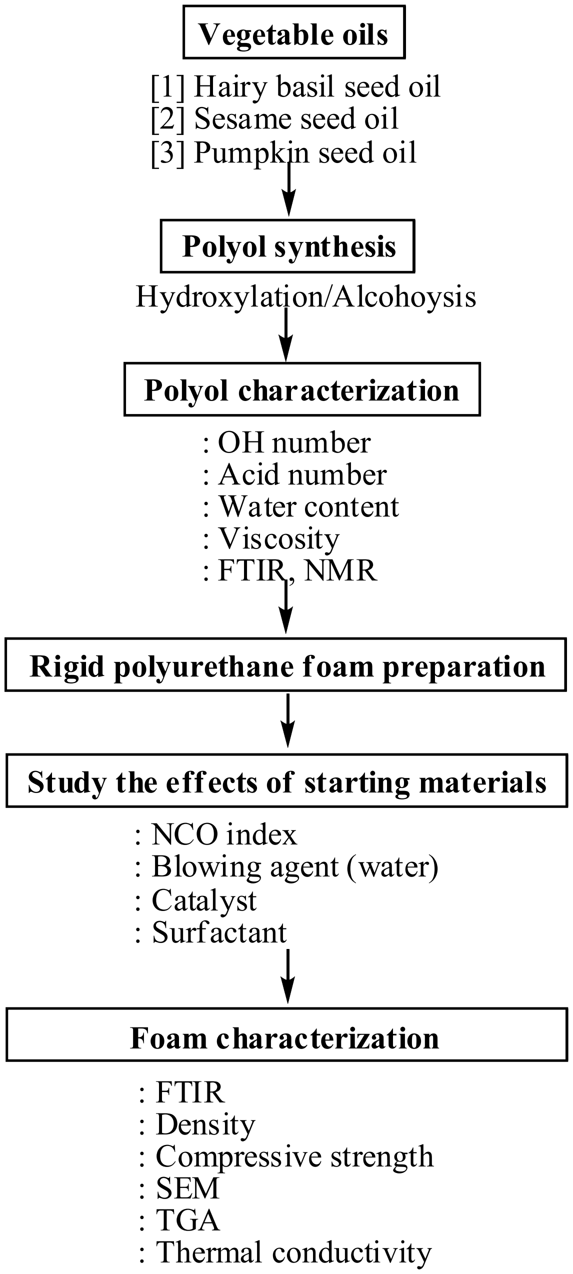
From the literature reviews, there are several methods to synthesize biobased polyols from vegetable oils. The conventional chemical methodology for functionality of unsaturated moieties to produce OH groups is the most operation such as an *in situ* epoxidization-hydroxylation at the double bonds with percarboxilic acids to obtain mostly secondary OH groups with low hydroxyl number [7–10], the hydroformylation with syngas ($H_2$/CO) in the presence of transition metal (rhodium or cobalt) catalysts following the hydrogenation of resulting aldehydes to form primary OH groups [11] and the ozonolysis of triglycerides forming aldehydes and subsequent reduction to primary OH groups [12–14]. In addition to the well-known alcoholysis of vegetable oils with polyfunctional alcohols in the presence of acidic or basic catalysts has been reported, the resulting products are the mixture of fatty acid alkyl esters [15–20]. Among the variety of chemical modification of vegetable oils, the *in situ* expoxidation-hydroxylation and alcoholysis reaction are used for preparation of biobased polyols in this work due to it is easy to operate and low cost.

## 1.2 The objective and scope of the research

The objectives of this work is to synthesize biobased polyols from three seed oils such as hairy basil seed oil, sesame seed oil, and pumpkin seed oil by two steps reaction. Firstly, hydroxylation reaction of seed oil occurred under excess performic acid condition and then the alcoholysis of hydroxylated seed oils with triethanolamine in the presence of lithium hydroxide as a catalyst was carried out.

The second purpose is the preparation of water-blown RPUR foams using these biobased polyols reacting with the polymeric methylene diphenyl diisocyanate (PMDI) in the presence of *N,N*-dicyclohexylamine (DMCHA) as catalyst and silicone surfactant. The relative effects of the amount of the foaming components on the reaction time and foam density were evaluated comparing with the commercial foams. Furthermore, the mechanical and thermal properties of optimized biobased foams were determined.

The scope of this research can be described by the following flow chart:

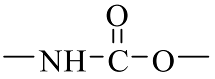

Vegetable oils
[1] Hairy basil seed oil
[2] Sesame seed oil
[3] Pumpkin seed oil
Polyol synthesis
Hydroxylation/Alcohoysis
Polyol characterization
: OH number
: Acid number
: Water content
: Viscosity
: FTIR, NMR
Rigid polyurethane foam preparation
Study the effects of starting materials
: NCO index
: Blowing agent (water)
: Catalyst
: Surfactant
Foam characterization
: FTIR
: Density
: Compressive strength
: SEM
: TGA
: Thermal conductivity

# CHAPTER II

# THEORY AND LITERATURE REVIEWS

## 2.1 An introduction to polyurethane technology

Polyurethane (PUR) was discovered by Otto Bayer and coworker in 1937 based on the addition polymerization of isocyanates and polyols to form urethane linkage as presented below:



$$-\mathrm{NH}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-$$

Urethane Group

The commercial PUR production firstly based on hexamethylene diisocyanate and butanediol that has similar properties to polyamides and is still used to make fibers for brushes [24]. In the 1950s, the PUR applications were expanded with the fast rate by the production of rigid and flexible foams from toluene diisocyanate (TDI) and polyether and polyester polyol manufacturers [25]. With this historical discovery and further development, PUR is not actually the most used plastic recently, but it is certainly the most versatile and diverse end-use products depending on a variety of starting components. Commercially, PUR are mainly available in two forms; PUR foams and non-foam applications. Non-foam products are coating, adhesives, elastomers, and sealants [1]. PUR foams are thermosetting materials comprising mainly flexible and rigid PUR foams that exhibit a numerous applications. Nowadays, the global PUR foam market accounts for more than 50% of overall polymeric foam production [1]. In 2010, the global PUR market, by product types is dominated by the flexible and rigid foams, which total accounted for 65.02% of the overall PUR market [26]. The other product types comprise of coatings, elastomers, adhesives, and sealants.

For PUR foam processing, they can be divided into three main forms by their stiffness and applications as flexible, semi-rigid, and rigid foams. The desired foam grades are produced by formulating the nature and amount of the starting materials including isocyanates, polyols, catalyst, blowing agent, surfactant, and other additives. Based on the basic chemistry and processing of PUR foams, the world PUR foams production is recently increasing with the versatile applications especially automotives, footwear, furnishing, packaging, insulations, and constructions, etc. A summary of foam grades is illustrated in Table 2.1.

**Table 2.1** Characteristics of the production of PUR foam grades [1–2, 25]

| Characteristics | Flexible PUR foam | Rigid PUR foam |
|---|---|---|
| Polyols | | |
| : Molecular weight | 1,000 to 6,500 | 150 to 1,600 |
| : Functionality | 2.0 to 3.0 | 3.0 to 8.0 |
| : OH value range (mg KOH/g) | 28 to 160 | 250 to 1,000 |
| Isocyanates | TDI based | MDI based |
| Density range (kg/m$^3$) | 5 to 200 | 20 to 800 |
| Key property | Absorption | Insulation |
| Markets | Furniture<br>Automotive part | Construction<br>Appliance |

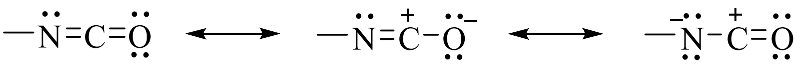
Within a variety of foam grades, rigid polyurethane (RPUR) foams have various unique characteristics. They are easy to prepare at ambient condition without heating that make them on-site production. Their density can be varied in a wide range from 20 to 800 kg/m$^3$ as well as they tolerate to non-polar organic solvents. In addition, low-density RPUR foams (20–50 kg/m$^3$) are extremely used for an insulation material in the construction industry because of their low thermal conductivity and high mechanical strength with light weight [1, 27–28]. From these several advantages make RPUR foams an attractive product feature for many industries that shown in the Table 2.2. [29].

**Table 2.2** Applications of rigid polyurethane foam manufacturing

| Rigid polyurethane foam applications | | |
|---|---|---|
| Appliance foams | Construction foams | Transportation foams |
| Domestic refrigerators | Lining boards | Sandwich panels for trucks |
| Domestic freezers | Roof boards | Reefer boxes |
| Commercial refrigerators | Pipe section | Flotation |
| Commercial freezers | Pipe-in-pipe | |
| Air-conditioning units | Cold store panels | |
| Water heaters | Doors | |
| Cool boxes | Food processing enclosures | |
| Flasks | Spray systems | |

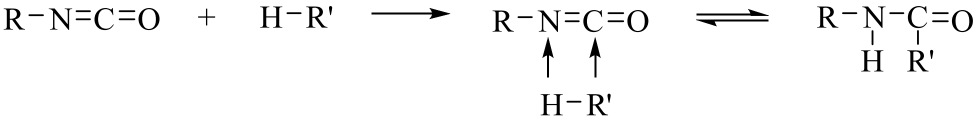
## 2.2 Chemistry of polyurethanes

Polyurethane chemistry is primary based on the reaction of isocyanates and polyols. The highly reactive isocyanate (–N=C=O) group which originates from its electronic structure can react vigorously with any active hydrogen compounds including amines, alcohols, and carboxylic acids. The resonance structure of NCO group can be represented following [24, 30]:



$$-\ddot{N}=C=\ddot{O} \longleftrightarrow -\ddot{N}=\overset{+}{C}-\ddot{O}^{-} \longleftrightarrow -\ddot{N}^{-}-\overset{+}{C}=\ddot{O}$$

It can explain that as an intermediate consequence, an oxygen atom has the highest electron density (electronegative), while the lowest one is a carbon atom (electropositive) and a nitrogen atom is rather less electronegative than oxygen atom. The susceptible isocyanates readily react with a hydrogen atom that is attached to atoms more electronegative than carbon atom. Therefore, the general reactions of NCO groups are an addition to the C=N [24, 30]:



$$R-N=C=O \;+\; H-R' \longrightarrow \underset{H-R'}{\underset{\uparrow\quad\uparrow}{R-N=C=O}} \rightleftharpoons R-\underset{H}{N}-\underset{R'}{C}=O$$

The nucleophillic center of the active hydrogen containing compounds attacks the electrophillic carbon, and then the hydrogen adds to the nitrogen atom. An increase in reactivity of the NCO groups is contributed by the electron withdrawing groups which attached to the isocyanate molecules. Conversely, the reactivity of NCO groups is reduced by the electron donating groups. Thus, aromatic isocyanates are more reactive than aliphatic isocyanates. The presence of electron withdrawing substituents on isocyanates increases the partial positive charge on the carbon atom and moves the negative charge further away from the reaction site. As a result of this character, the reaction between the electron donors and the carbon atom of isocyanates is fast. In addition, steric hindrance on the isocyanates or the active hydrogen compounds particularly affects the reaction. The reactivity of isocyanates against various active hydrogen compounds occurring in PUR formation is presented in Table 2.3

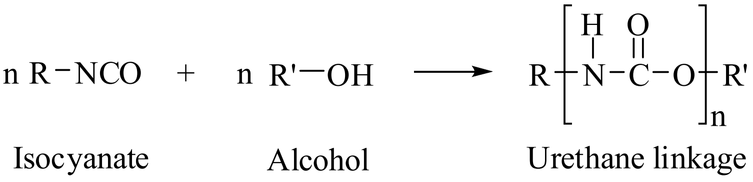
**Table 2.3** The relative reactivity of isocyanates [24, 31]

| Active hydrogen compound | Typical structure | Reaction rate (uncatalyzed at 25°C) |
|---|---|---|
| Primary aliphatic amine | $R–NH_2$ | 100,000 |
| Secondary aliphatic amine | $R_2–NH$ | 20,000–50,000 |
| Primary aromatic amine | $Ar–NH_2$ | 200–300 |
| Primary hydroxyl | $R–CH_2–OH$ | 100 |
| Water | HOH | 100 |
| Carboxylic acid | R–COOH | 40 |
| Secondary hydroxyl | $R_2–CH–OH$ | 30 |
| Urea | R–NH–CO–NH–R | 15 |
| Tertiary hydroxyl | $R_3–C–OH$ | 0.5 |
| Urethane | R–NH–COOR | 0.3 |

Water-blown PUR foam formation occurs via the reaction of isocyanates, which mainly comprises of the polymerization reaction to form polymer matrix and the gas releasing reaction by the reaction of isocyanates and water. The choices of starting materials provide the additional crosslinking formation to enhance rigidity of PUR foams. The main reactions of isocyanates in PUR foam systems are available following:

### 2.2.1 Polymerization reaction

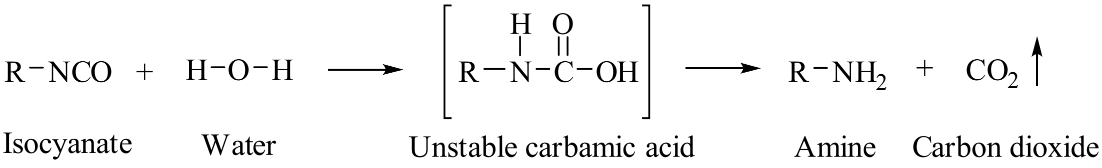
The addition polymerization between isocyanates and polyols, sometimes called gelling reaction, is the most important reaction in PUR synthesis leading to form urethane (carbamate) linkage. It is an exothermic reaction (24 kcal/mol of urethane):



$$n\,R{-}NCO + n\,R'{-}OH \longrightarrow R\left[\overset{H}{\underset{|}{N}}{-}\overset{O}{\underset{\|}{C}}{-}O\right]_n R'$$

### 2.2.2 The gas producing reaction (blowing reaction)

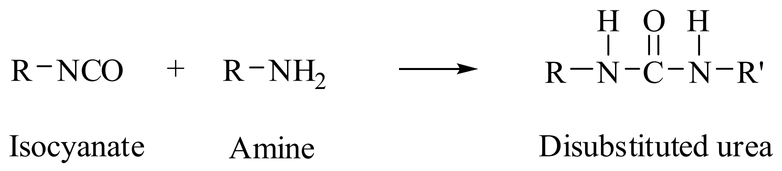
To be foam, polymeric matrix must be expanded or blown due to the gas evolution and heat release by the reaction of isocyanates and polyols that mentioned above. For PUR foam technology, the reaction between isocyanates and water is the conventional source of carbon dioxide gas to generate the cellular structure of PUR foams as shown following [1, 27]:



$$R{-}NCO + H{-}O{-}H \longrightarrow \left[R{-}\overset{H}{\underset{|}{N}}{-}\overset{O}{\underset{\|}{C}}{-}OH\right] \longrightarrow R{-}NH_2 + CO_2\uparrow$$

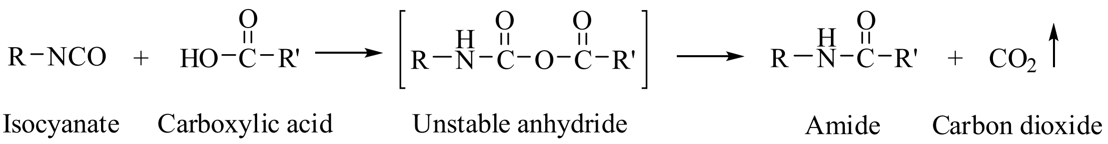
This blowing reaction is highly exothermic reaction with total heat release per mole of water being approximately 47 kcal/mol. Carbamic acid is a thermally unstable intermediate product which spontaneously decomposes to form an amine and carbon dioxide. Therefore, the actual amount of isocyanates needed for PUR foam formulation is calculated not only based on polyols equivalent but also related to water contents used for gas production. Two moles of isocyanates react with one mole of water.

Additionally, the amine further reacts rapidly with other isocyanate groups and generates a disubstituted urea (carbamide) resulting in a crosslinking network as presented below [1, 27]:



$$R{-}NCO + R{-}NH_2 \longrightarrow R{-}\overset{H}{\underset{|}{N}}{-}\overset{O}{\underset{\|}{C}}{-}\overset{H}{\underset{|}{N}}{-}R'$$

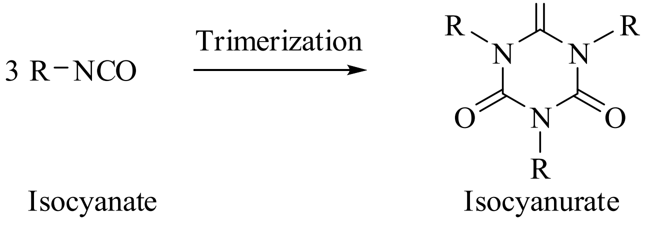
Moreover, the reaction between isocyanates and carboxylic acids can occur in polyol system having free acids to produce $CO_2$ and amides. The reactivity of isocyanates toward carboxylic acids is lower than the one with amine, primary alcohols, and water but is higher slightly than secondary alcohols that shown in Figure 2.3. The reaction can be expressed following [30]:



$$R{-}NCO + HO{-}\overset{O}{\underset{\|}{C}}{-}R' \longrightarrow \left[R{-}\overset{H}{N}{-}\overset{O}{\underset{\|}{C}}{-}O{-}\overset{O}{\underset{\|}{C}}{-}R'\right] \longrightarrow R{-}\overset{H}{N}{-}\overset{O}{\underset{\|}{C}}{-}R' + CO_2\uparrow$$

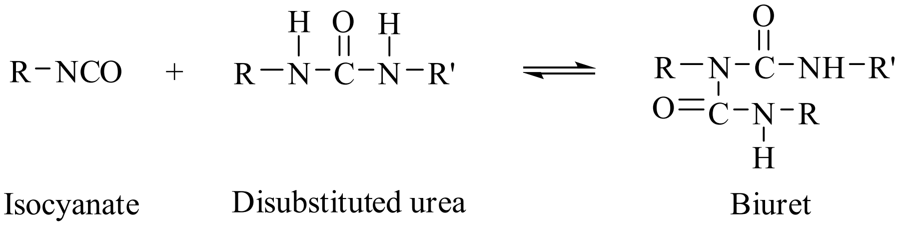
### 2.2.3 Additional crosslinking network formation

Depending on the variety of polyfunctional reactants, the crosslinked polymer is generated during PUR foam production which makes PUR foam more rigidity. For rigid PUR foam preparation, the trimerization of isocyanates forming isocyanurate rings is an important reaction which occurs in the presence of excess isocyanates content with a proper catalyst. The high crosslinking structures, isocyanurate rings are resulted from this reaction as follow:

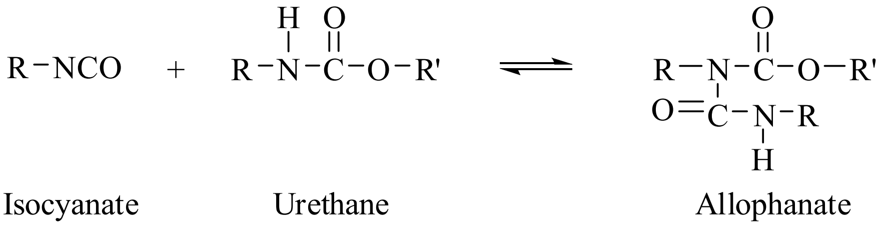


The isocyanuric rings are not reversible like other additional crosslinked polymers found in PUR system such as allophanates, biurets, and isocyanate dimers. They are thermally stable than urethane groups. PIR foams based MDI initially decompose above 270°C, while PUR foams start at lower temperature about 200–220°C [32]. With this reason, PUR/PIR foams are usually used for building insulation applications.

The other additional crosslinked polymers can be found in PUR system. The active hydrogen on disubstituted urea formed by the reaction of isocyanates and amine can react with excess isocyanates to produce a biuret. This reaction is exothermic reaction and occurs at lower temperature around 100°C. The biuret formation is presented following:



Similarly to the biuret formation, urethane groups containing active hydrogen itself can react with an isocyanate to form an allophanate group:



This reaction is reversible reaction and occurs at higher temperature greater than 110°C without adding catalyst but it can proceed also at lower temperature when the high excess amount of isocyanates is used. The other additional crosslinking reactions during PUR polymerization reaction are found elsewhere as the formation of uretidinedione or carbodiimide by dimerization of isocyanates [1–2, 30].

## 2.3 Raw materials for rigid polyurethane foam formulation

### 2.3.1 Isocyanates

Isocyanate compounds can be categorized into aliphatic, cyclo-aliphatic, and aromatic isocyanates. Among others, aromatic isocyanates including toluene diisocyanate (TDI), methylene diphenyl diisocyanate (MDI), and their polymeric products (PMDI) display the highest consumption approximately 95% for PUR foam manufacturer because of their higher reactivity than aliphatic isocyanates as well as lower cost production [1–2 , 28]. While aliphatic isocyanates including isoprene diisocyanate (IPDI), hexamethylene diisocyanate (HDI), or 4,4-dicyclohexyl diisocyanate (HMDI) are used for special applications including light, weather, and heat resistant coatings [33].

Toluene diisocyanate (TDI) is originally produced based on the phosgenation of toluene diamine [27, 33]. These were firstly used for PUR commercial production in early developments. After the 1960s, the global use of TDI was changed when methylene diphenyl diisocyanate (MDI) and polymeric methylene diphenyl diisocyanate (PMDI) became available in commercial scale and took place in 1984 [1]. Although the price of TDI is lower than MDI, the volatility of TDI is relatively high and difficult to handle. Therefore the uses of TDI have been limited and that of MDI is favor due to its lower volatility. However TDI has been predominantly used to make flexible polyurethane foams which is commercially supplied as the isomeric mixture of 2,4-TDI and 2,6-TDI with the weight ratio of 80:20 (TDI 80) or 65:35 (TDI 65) [24, 27]. The chemical structures of TDI are presented in Figure 2.1 below:

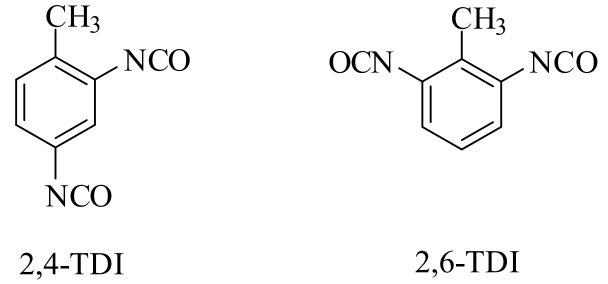
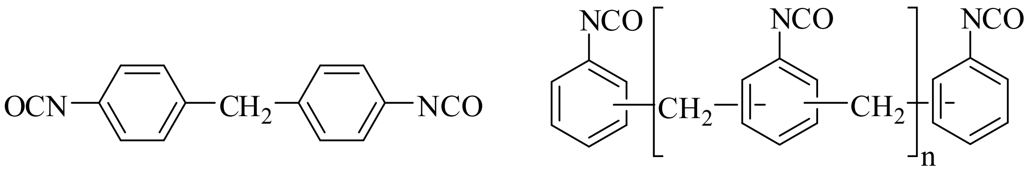


**Figure 2.1** Chemical structures of toluene diisocyanate (TDI) isomers.

The second most important aromatic isocyanates in PUR foam technology, MDI is manufactured by the phosgenation of products from the acid-catalyzed condensation reaction of aniline and formaldehyde [1, 27]. The commercial products are available as pure MDI and crude MDI or polymeric MDI [30]. Pure MDI, commercially known as monomeric MDI having two NCO groups per mol predominantly contains about 98% of 4,4-MDI with remaining 2,4- and 2,2-isomers. Pure MDI mostly used for PUR elastomers and some flexible foam applications. On the other hand, crude MDI also called polymeric MDI (PMDI or PAPI) comprises monomeric 4,4-MDI around 48–50% and higher functionality oligomeric MDI having

3, 4, and 5 aromatic rings. The main applications for PMDI are rigid and semi-rigid PUR foams, as well as polyisocyanurate (PIR) foams. The chemical structures of MDI are exhibited in Figure 2.2 following:



4,4-MDI    Polymeric MDI (PMDI)

2,4-MDI    2,2-MDI

**Figure 2.2** Chemical structures of diphenylmethane diisocyanate (MDI) isomers and polymeric diphenylmethane diisocyanate.

Table 2.4 and Table 2.5 illustrate the characteristics of TDI and MDI, respectively.

**Table 2.4** The characteristics of TDI [27, 30]

| Property | Isomeric TDI ratio (2,4-TDI : 2,6-TDI) | | |
|---|---|---|---|
| | 80:20 | 65:35 | Pure 2,4-TDI |
| Physical state at 25°C | Liquid | Liquid | Liquid |
| Color | Colorless | Colorless | Colorless |
| Molecular weight, g/mol | 174.16 | 174.16 | 174.16 |
| Equivalent weight, g/OH group | 87.08 | 87.08 | 87.08 |
| Functionality, NCO groups/mol | 2 | 2 | 2 |
| Viscosity, mPa.s at 25°C | 3–6 | 3–6 | 3–6 |
| Specific gravity, g/mL at 25°C | 1.21 | 1.21 | 1.21 |
| Vapor density (air = 1) | 6.0 | 6.0 | 6.0 |
| Freezing point, °C | 14.0 | 8.5 | 21.4 |

**Table 2.5** The characteristics of MDI [27, 30]

| Property | Monomeric MDI | Polymeric MDI |
|---|---|---|
| Physical state at 25°C | Solid | Liquid |
| Color | White to light yellow | Dark blown (opaque) |
| Molecular weight, g/mol | 250.26 | Approximately 340 |
| Functionality, NCO groups/mol | 2 | 2.2–3.0 |
| NCO content, %weight | 33.5 | Approximately 31 |
| Viscosity, mPa.s at 25°C | – | 100–800 |
| Density, g/mL | 1.20 at 40°C | 1.23 at 25°C |
| Vapor density (air=1) | 8.5 | 8.5 |
| Freezing point, °C | 38 | <10 |

### 2.3.2 Polyols

Any molecules that possessing proton donor or active hydrogen such as hydroxyls, carboxyls, and amines can react with isocyanates. The reaction of isocyanates and polyhydroxyl compounds which commonly called polyols is the primary reaction in PUR technology. Therefore, polyols are the second most ingredients to the isocyanates. Polyols used for PUR preparation are liquid oligomeric compounds containing two or more OH groups per mole such as polyethers, polyesters, hydroxyl terminated polyolefins, and hydroxyl containing vegetable oils [27, 30].

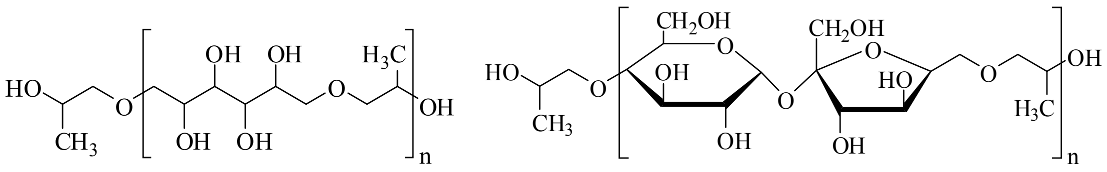
The selection of polyols in PUR foam production is concerned with a requirement of foam stiffness and end-used product properties. Therefore, their functionality, molecular weight and hydroxyl (OH) number are the key properties of polyols that above represented in Table 2.1. The rigidity of foams can be enhanced by diminishing the polyols chain length. For rigid PUR foam preparation, the important characteristics of polyols are high functionality about 3–8 OH groups/mol with short chain structure. Due to these characteristics making high crosslinked polymer contributes to an increase in the rigidity of PUR foams. Typically, the OH number of polyols used for RPUR foam manufacturing is in the range of 300–600 mg KOH/g.

Therefore, the viscosity of these polyols is generally high being in the range of 2,000–50,000 mPa.s at 25 °C, which results from the high content of hydrogen bonds formed between the OH groups.

The most important petroleum based polyols used for RPUR manufacturing is polyether polyols containing primary and/or secondary OH groups followed by polyester polyols. Compared with polyesters, polyether polyols provide higher hydrolysis resistant of resulting foams. They have various functionality, wide range equivalent weight, and lower viscosity. They are easy to handle as well as a favorable cost. Conversely, polyester polyols are less susceptible to photo-oxidation at elevated temperatures and are less soluble in organic solvents [1, 27].

### 2.3.2.1 Conventional polyether polyols

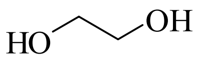
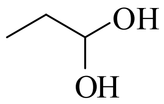
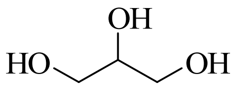
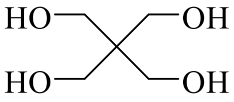
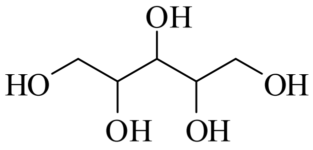
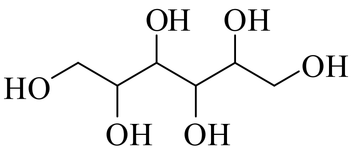
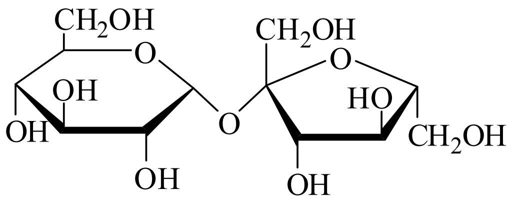
Conventional polyether polyols are produced by the anionic polymerization of alkylene oxides usually propylene glycol, onto a polyfunctional starter or initiator in the presence of catalyst. The performances of obtained polyols including functionality and equivalent weight as well as the production cost are controlled by the choice of original initiators. The most important initiator for polyether polyols is an active hydrogen containing compounds either polyalcohols or polyamines that having low molecular weight and functionality be in the range 2–8, as presented in Table 2.6 and the examples of commercial polyether polyols used in RPUR foam production are shown in Figure 2.3.



(a) Poly (propyleneoxy) sorbitol (b) Poly (propyleneoxy) sucrose

**Figure 2.3** Structures of (a) sorbitol based and (b) sucrose based polyether used in rigid polyurethane foam production.

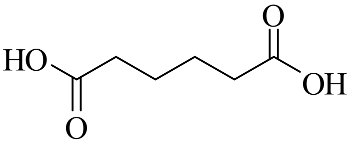
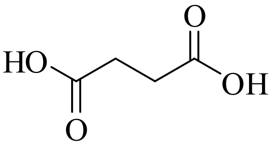
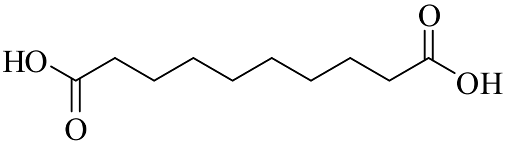
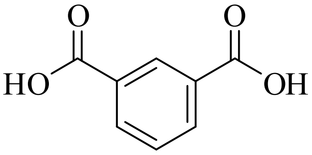
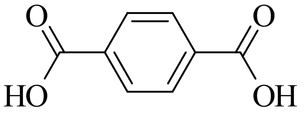
**Table 2.6** Characteristics of some common used initiators for polyether polyols production [27, 30]

| Initiator | | Molecular weight (g/mol) | OH number (mg KOH/g) |
|---|---|---|---|
| <u>Functionality = 2</u> | | | |
| Ethylene glycol |  | 62.07 | 1801.0 |
| Propylene glycol |  | 76.09 | 1474.6 |
| <u>Functionality = 3</u> | | | |
| Glycerol |  | 92.09 | 1827.3 |
| <u>Functionality = 4</u> | | | |
| Pentaerythritol |  | 136.15 | 1650.0 |
| <u>Functionality = 5</u> | | | |
| Xylitol |  | 152.15 | 1845.4 |
| <u>Functionality = 6</u> | | | |
| Sorbitol |  | 182.17 | 1847.7 |
| <u>Functionality = 8</u> | | | |
| Sucrose |  | 342.30 | 1311.1 |

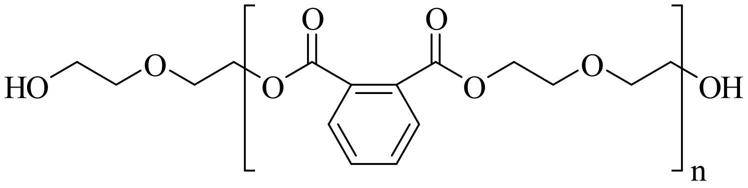
### 2.3.2.2 Conventional polyester polyols

Polyester polyols are firstly manufactured by the polycondensation reaction of dicarboxylic acids (i.e., adipic acid, phthalic acid or sebasic acids) and glycols (i.e., ethylene glycol, propylene glycol, or trimethylolpropane) in the presence of specific catalysts such as *p*-toluene sulfonic acid, stannous octoate, or zinc acetate [30]. The most of dicarboxylic acids used for industrial polyester polyols manufacturing are shown in Table 2.7.

**Table 2.7** Characteristics of some common used dicarboxylic acids for polyester polyols production [30]

| Structure and name | Molecular weight (g/mol) | Acid number (mg KOH/g) |
|---|---|---|
| <br>Adipic acid | 146.14 | 767.8 |
| <br>Succinic acid | 118.09 | 950.1 |
| <br>Sebacic acid | 202.25 | 555.4 |
| <br>Isophthalic acid | 166.14 | 675.3 |
| <br>Terephthalic acid | 166.14 | 757.4 |

Typically, petroleum based polyester polyols used for RPUR foams are almost containing aromatic rings in order to increase stiffness of foams and the examples of industrial polyester polyols used in RPUR foam production are shown in Figure 2.4.



Poly (diethylene glycol) phthalate

**Figure 2.4** Structure of the aromatic polyester polyols used in RPUR foams.

Although, the resulting RPUR foams of polyester polyols have superior physico-mechanical properties but the high price of polyols production is necessary considered. Therefore, the polyester polyols consumption in early RPUR foam production was replaced by the lower cost, higher functionality, and lower viscosity of polyether polyols. The further development of aromatic polyester polyols technology is achieved by using the cheap raw materials from recycled waste products included dimethylterephthalate (DMT) from bottom residue of DMT fabrication and polyethyleneterphthalate (PET) from recovery PET packing wastes by glycolysis route [1, 33].

The aromatic polyester poyols generally have OH number in the range of 250–350 mg KOH/g, functionality of 2–3 OH groups/mol, and viscosity of 8,000–22,000 mPa.s at 25°C. With these characteristics make them suitable used for rigid PUR/PIR foams for building insulation because the polyols used in rigid PUR/PIR foams system do not require very high functionality and OH number. High crosslink rigid PIR foam is developed based on trimerization of excess NCO groups. Therefore, the presence of isocyanuric rings and aromatic polyesters in rigid PUR/PIR foams provide the excellent physico-mechanical properties such as intrinsic thermal and fire resistance and low level of smoke production [1, 30].

Recently, polyester polyols derived from vegetable oils are a new class for RPUR foam technology with environmental friendly requirements. For instance, castor oil based polyols has been mostly reported due to their molecule having hydroxyl groups in nature (OH number = 160 mg KOH/g and functionality = 2.7). The structure of castor oil is shown in Figure 2.5 below [24, 34]:

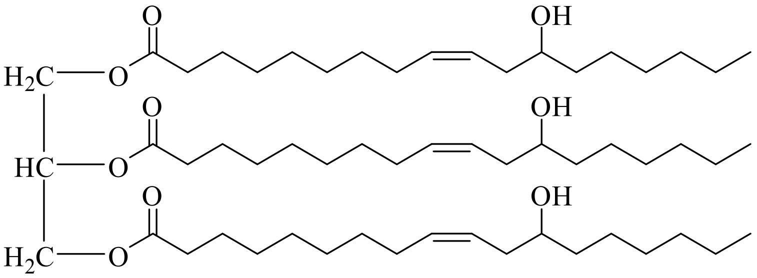


**Figure 2.5** Typical chemical structure of castor oil.

In addition, formiated soy bean based polyols also were revealed with formula structure (Figure 2.6) following [5, 24]:

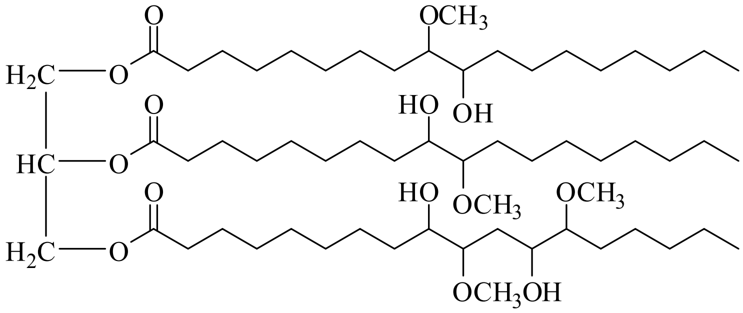


**Figure 2.6** Commercial soy polyols used for polyurethane foam preparation.

The attractive features of these oil based polyols over with petroleum based polyols are more hydrolytic stability, compatible with hydrocarbon blowing agents, and higher hydrophobicity as well as comparable price with petrochemical products. However, the oil based polyols have molecular weight about 1000, functionality varied from 2–8, and high OH number resulting the relative higher viscosity (2000–12,000 cP) than propylene oxide based polyols and make them a limit of use [24]. The reviews of biobased polyols will describe in the next part.

### 2.3.3 Blowing agents

To make foam, a blowing agent plays an important role to generate gas bubbles in polymer matrix. Besides this function, it predominantly governs the cell structure or morphology of resulting foams which can further define their physical and mechanical properties [1, 27]. For PUR foam preparation, there two types of blowing agents comprising chemical and physical blowing agents as well as the combination of them.

The chemical blowing agents can generate gas bubbles by the chemical reaction. The conventional blowing agent used in PUR foam synthesis is water. It reacts with isocyanates to produce carbon dioxide gas and urea linkage. Within the very high exothermic reaction, the cellular structure of foams will be formed by $CO_2$ gas expansion through PUR phase. In the practice, water contents used in PUR formulations are 3–5 parts of water per 100 parts of polyester polyols and 2–5 parts per 100 parts of polyether polyols [28]. The role of water is important not only for the foam expansion with produced $CO_2$, but the polyurea is also formed that resulting in an effect of the mechanical properties of PUR foams. Although, the use of water as the chemical blowing agent enhances the rigidity of PUR foams as well as gives an environmental friendly respect but the insulation performance of resulting foams is the lowest compared with other blowing agents [1–2, 27]. Due to the insulation property of low density RPUR foams depends on the type of trapped gas in foam cells. $CO_2$ is soluble in PUR matrix and can diffuse out of the foam cells faster than air diffuse into the cells, therefore this phenomenon makes the foam shrinkage. Most flexible PUR foams recently use water as the blowing agent. For rigid PUR foam systems, the development of water-blown foams has been studied and reported in many publications [27].

On the other hand, physical blowing agents are mostly low boiling point inert liquid that should dissolve well in the reaction mixture and do not react with other reactive starting materials. They can be vaporized by the heat of foaming reaction and should be as gas in the foam cells that possesses low gaseous thermal conductivity. They should be low price and readily available as well as also be non-toxic and environmentally acceptable [1]. The choices of physical blowing agents are now including hydrocarbons (pentane), hydrogenchlorofluorocarbons (HCFCs), and hydrogenfluorocarbons (HFCs) are used for replacement of chlorofluorocarbon 11 (CFC 11).

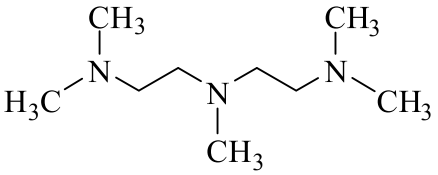
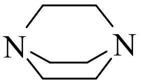
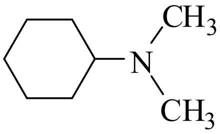
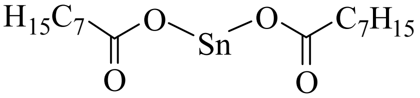
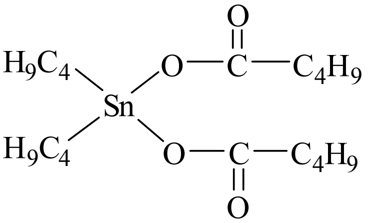
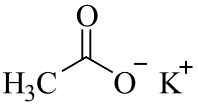
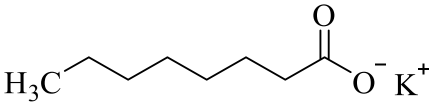
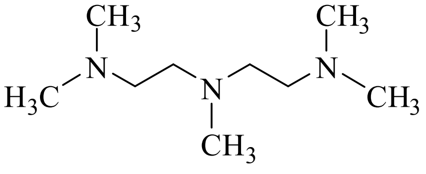
### 2.3.4 Catalysts

Polyurethane foams are highly complex systems which require the balance of various simultaneous chemical reactions including both of polymerization and gas producing reaction. Several types of catalysts for RPUR foams synthesis are reported and used to control these processes. They can be classified to three types upon the main reaction purposes including [1]:

a) the gelling catalysts for the polymerization reaction of isocyanates and polyols to form urethane linkages,
b) the blowing catalysts for the gas generation reaction of isocyanates and water to produce $CO_2$ and polyurea,
c) the trimerization catalysts for the cyclotrimerization reaction between isocyanates itself.

To obtain the desired foam products, the specific formulation needs to optimize in order to balance these reactions. Typically, catalysts used for RPUR foams manufacturing include tin compounds, tertiary amines, and potassium salts. Their catalytic activity depends on the basicity with steric hindrance on the active site playing a second role. For example, the activity of tertiary amines is reduced in the presence of residual acidic compounds in polyols formulation [1]. Table 2.8 summarizes the most important catalysts now used in RPUR foam preparation.

**Table 2.8** The most used catalysts in rigid polyurethane foam production [1]

| Catalysts type | Structure | Action |
|---|---|---|
| Tertiary amines | | |
| Pentamethyldiethylene triamine (PMDETA) |  | Blowing |
| Triethylene diamine (TEDA, DABCO) |  | Gelling |
| Dimethylcyclohexylamine (DMCHA) |  | Blowing/gelling |
| Tin compounds | | |
| Stannous octoate (Sn Oct) |  | Gelling |
| Dibutyltin dilaurate (DBTDL) |  | Gelling |
| Alkali metal salts | | |
| Potassium acetate (K Ac) |  | Gelling/trimer |
| Potassium octoate (K Oct) |  | Gelling/trimer |
| Quaternary ammonium salts | | |
| 2-hydroxylpropyltrimethyl ammonium fomiate (TMR-2) |  | Gelling/trimer |

### 2.3.5 Surfactants

The cellular structure of PUR foams is formed as the results of the development of unstable gas bubbles evaporation in PUR phase and then the foam cells lead to collapse if the continuing reaction without the foam stabilizers. Therefore, a surfactant is an essential additive in PUR foam formulations and plays two purposes in the foam processing [1, 28]. Firstly, it assists the incompatible foaming ingredients such as hydrophobic polyols, hydrophilic blowing agent and catalyst as well as isocyanates in the mixing step. It reduces their surface tension and acts as an emulsifier. The second important function of surfactant is predominantly to stabilize foam cells during gas bubble nucleation in the polymer matrix. This phenomenon can be explained by the Marangoni effect that is the dynamic mechanism. It stabilizes the polymerizing liquid-gas interface during an increase in foam volume about 30–50 times of initial volume. The fast migration of surfactant stabilizes toward the interface between new surface area that generated by the continuously expanding foam with high tension. Surfactants regulate the cellular structure including opened-, closed cell content, and the cell size and then have a significant effect on the foam properties [1, 28].

Polydimethylsiloxane polyether copolymer, so-called silicone surfactants are mostly used in PUR foam preparation with typically adding about 0.4–2.0 parts of 100 parts of polyol used in formulation [1]. Moreover, they become as plasticizers in PUR systems at the high level used. The choice of polysiloxane structures used in each PUR foam formulation is different based on the desired foam properties. The molecular structure of polysiloxane can be adjusted by varying the chain length and the composition of polysiloxane backbone or the pendent polyether chains. The molecular structure of typical silicone surfactants is represented in Figure 2.7.

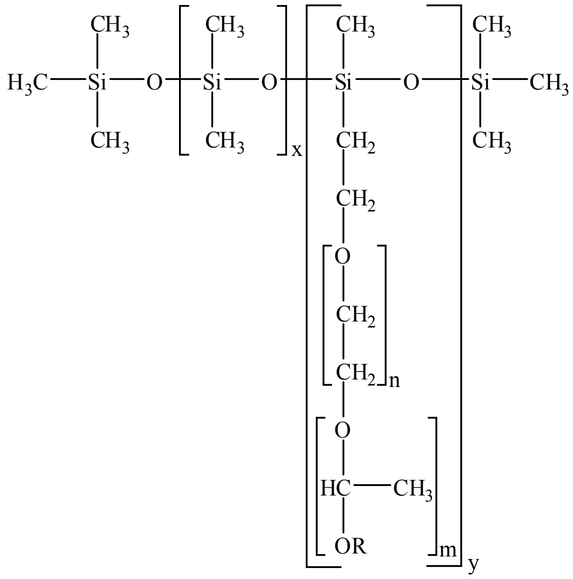


Figure 2.7 The molecular structure of typical silicone surfactants used in PUR foams preparation [1].

## 2.4 Specification tests of reactive raw materials

The analytical characteristics of reactive components are essential quality control for formulating PUR foam production. Therefore, the foaming process and further defining the products properties are regulated by the calculation of raw material proportion. The main characteristics of both isocyanates and polyols are described following:

### 2.4.1 Analysis of isocyanates

### 2.4.1.1 Isocyanate content

The most important characteristic of polyisocyanates is isocyanate (NCO) content. NCO content is the weight percent of NCO groups present in the sample, expressed as %NCO. It is measured following ASTM D 5155–07 [35]. The weighed aromatic isocyanate sample is firstly dissolved in the solution mixture of dry toluene and excess dibutylamine. Isocyanates reacts equivalent with dibutylamine. The residual dibutylamine is then back-titrated with 0.1 N hydrochloric standard solution up to the endpoint. The isocyanate content is calculated from the following equation:

$$\%\text{NCO} \quad = \quad \frac{(V_b - V_s) \times N_{\text{HCl}} \times 4.202}{W_s}$$

where $V_b$ is the volume in mL of HCl required for the blank titration (toluene/ dibutylamine solution), $V_s$ is the volume in mL of HCl used for the sample back-titration, $N_{\text{HCl}}$ is the concentration in normal of HCl standard solution, $W_s$ is the sample weight (g), and 4.202 is the constant combining the equivalent weight of a NCO group (42.02) mg/meq, conversion of gram to 1000 mg, and conversion to 100%.

### 2.4.2 Analysis of polyols

#### 2.4.2.1 Hydroxyl number

The first general characteristic of polyols for PUR technology is the presence of terminal hydroxyl groups which referred as hydroxyl group content or OH number. It is necessary to know the OH content of polyols in order to formulate PUR systems.

The OH number is defined as the quantitative value of the amount of OH groups per gram of polyols, which is determined according to ASTM D 4274–05 [36]. Firstly, the suitable amount of sample was esterified with phthalic anhydride/pyridine solution. The sample solution was then back-titrated with 0.5 N sodium hydroxide (NaOH) standard solution. The OH number were calculated and expressed in milligram of potassium hydroxide (KOH) per gram of sample as the equation below:

$$\text{OH number} \quad = \quad \frac{(V_b - V_s) \times N_{\text{KOH}} \times 56.1}{W_s}$$

where $V_b$ is the volume in mL of NaOH required for the blank titration (phthalic anhydride/pyridine solution), $V_s$ is the volume in mL of NaOH used for the sample back-titration, $N_{\mathrm{NaOH}}$ is the concentration in normal of NaOH standard solution, 56.1 is the molecular weight of KOH (g/mol), and $W_s$ is the sample weight (g).

In the case of polyols containing free acids, the accurate OH numbers must be calculated as:

$$\text{The correct OH number} = \text{OH number} + \text{Acid number}$$

Hydroxyl content in percent (%OH) is another form of expressing the concentration of OH groups in any polyols. The sum of the atomic weights in the OH groups is 17 g/OH group. It can be calculated from the proportion which takes into account that OH number of 56.1 corresponds to 1.7% OH groups. Thus, the content of OH groups (%OH) is equal to [24, 27]:

$$\text{OH content (\%OH)} = \frac{1.7 \times \text{OH number}}{56.1}$$

#### 2.4.2.2 Acid number

Acid number is the quantity of residual acidic groups in polyols and used as the correction factor in the OH number calculation. The acid number of polyols was evaluated following ASTM D 4662–03 [37]. The proper sample weight was dissolved in a toluene/ethanol solution and then titrated instantly with 0.1 N KOH standard solution. The acid number was calculated using the following equation:

$$\text{Acid number (mg KOH/g)} = \frac{(V_s - V_b) \times N_{\mathrm{KOH}} \times 56.1}{W_s}$$

where $V_s$ is the volume in mL of KOH standard solution consumed for the sample titration, $V_b$ is the volume in mL of KOH solution used for the titration of toluene/ethanol blank solution. $N_{\mathrm{KOH}}$ is the normality of KOH solution, 56.1 is the molecular weight of KOH (g/mol), and $W_s$ is the weight of sample used (g).

## 2.5 Formulation calculations

### 2.5.1 Functionality

Functionality is the second important characteristic of polyols and is defined as the number of hydroxyl groups per molecule of polyols that is practically very difficult to measure. The most usual and practical method for functionality determination is related on the estimation of the number average molecular weight ($\overline{M}_n$) of polyols together with OH number determination. The functionality is calculated by using the fundamental equation [24, 27]:

$$\overline{M}_n = \frac{56.1 \times \text{functionality}}{\text{OH number (mg KOH/g)}} \times 1000$$

### 2.5.2 Equivalent ratio

If the OH number or OH content of polyols and the NCO content (%NCO) of isocyanates are known, the stoichiometric amount of two components is calculated easily. Typically, the PUR formulation needs to find how much isocyanates contents (gram) that reacts at the stoichiometric molar ratio (1:1) with amount (gram) of polyols, or vice versa. It can calculate from equation below [24, 27]:

$$\text{Amount of polyols (g)} = \frac{\text{amount of isocyanate (g)} \times \%\text{NCO} \times 17.01}{\%\text{OH} \times 42.02}$$

Alternatively, it can calculate the stoichiometric ratio in the term of the equivalent weight. Based on chemical reaction, the equivalent weight ratio of isocyanates to polyols is 1:1. Weight equivalent means the weight of components that have 1 mol of reactive functional groups, and is calculated by dividing number average molecular weight ($\overline{M}_n$), by the functionality of materials [24, 27]:

$$\text{Equivalent weight} = \frac{\overline{M}_n}{\text{functionality}}$$

Additionally, equivalent weight of polyols can calculate if we know their OH number [24, 27]:

$$\text{Equivalent weight (polyols)} = \frac{56.1 \times 1000}{\text{OH number}}$$

Moreover, we can calculate the number average molecular weight of both isocynates and polys if we know their functionality and contents of reactive groups [24, 27]:

$$\overline{M}_n \text{ (isocyanates)} = \frac{\text{functionality} \times 42.02 \times 100}{\text{\%NCO}}$$

$$\overline{M}_n \text{ (polyols)} = \frac{\text{functionality} \times 17.01 \times 100}{\text{\%OH}}$$

### 2.5.3 Isocyanate index (NCO index)

On the urethane formation chemistry, one NCO group of polyisocyanate reacts with one OH group of polyols. The stoichiometric NCO/OH molar ratio equals 1:1, commonly referred as an isocyanate index = 100. For rigid PUR foam systems, the NCO groups can react with any active hydrogen compounds. When using water as the blowing agent, the NCO groups react with water to release carbon dioxide that is the major purpose to making gas bubbles in PUR matrix and the rigidity of PUR foams is also occurred owing to the addition crosslink networks by reacting NCO groups itself or the other species in PUR system. Practically, the actual amount of isocyanates using in RPUR foam formulation that expressing in NCO index is therefore required over 100 about 5–20% [1]:

$$\text{NCO index} = \frac{\text{actual amount of NCO used}}{\text{theoretical amount of NCO required}} \times 100$$

where theoretical amount of NCO required could be calculated from the total equivalent weight of active hydrogen compounds that react with NCO groups such as polyols, water, and residual acids.

The conventional way to calculate the amount of isocyanates required to react with a given polyols, you must know the desired NCO index, the isocyanate equivalent weight, the weight fractions of isocyanate reacting with 100 parts by weight of polyols (pbw), the equivalent weights of the polyols and any water presented in the system. The analytical data required for the calculating formulations are the functionality, molecular weight and content of isocyanate (%NCO), the OH number of polyols, the acid number, water content, and other reactive additives.

## 2.6 Rigid polyurethane foam preparation technology

The preparation of PUR foams is simultaneously occurred by PUR formation and gas generation. The basic components for PUR foam formulations are described in the details above, including isocyanates, polyols, catalyst, blowing agent, and surfactant. RPUR foam compositions differ from those of flexible foams due to the presence of their cellular structure, higher density, and crosslink polymer matrix. The specific characteristics of raw materials typically used in RPUR foams are presented below [1, 27]:

**Isocynates:** polymeric isocyanate (PMDI), crude MDI or crude TDI
**Polyols:** (a) polyether polyols with OH number be in the range of 350–500, functionality 2–8, and typically molecular weight about 400 g/mol
(b) aromatic polyester polyols
**Catalyst:** tertiary amines or tin compounds
**Blowing agent:** water, HFCs, or pentane
**Surfactant:** silicone surfactant

### 2.6.1 Process for producing rigid polyurethane foams

The most used technique to obtain RPUR foams is the one-shot technique, which is the very efficient mixing of all the raw materials containing two components in the short time (seconds). RPUR foams are prepared by together mixing component A (isocyanates) and component B (a blend of polyols, catalyst, and surfactant) at ambient temperature without heating [1]. In order to facilitate the efficiently mixing of various components used within the very short time, a mixture of the compositions that do not react with other (polyols, catalyst, and surfactant) is made before foaming

[30]. Consequently, the calculated isocyantes (component B) is added in premix systems. Schematic diagrams of this system are shown in Figure 2.8 below:

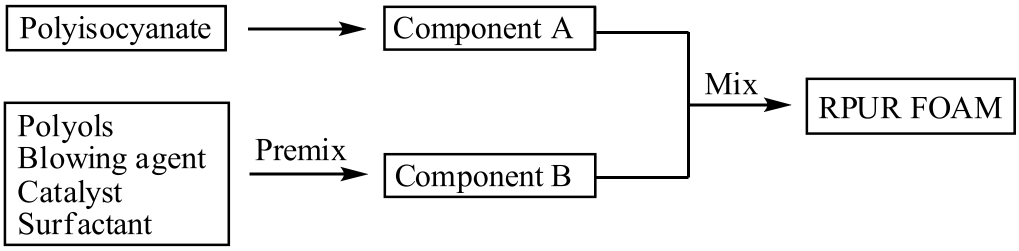


**Figure 2.8** One-shot method for making rigid polyurethane foams.

For a laboratory RPUR foam preparation, the hand mixing method sometimes called cup foaming is used mainly for developing and checking raw material systems in formulation, which produces smaller rigid foam buns. The process needs the high speed electrical stirrer, paper or plastic cups, stopwatch, and solvent for cleaning mixing blade (e.g., acetone). During the foaming in cup test, the foaming profile or reaction times should be recorded by stopwatch, which include following [2, 27]:

(a) cream time: (seconds) the time at which the foam mixture starts to expand due to the fine bubbles begin to appear and can be usually observed that a clear dark blown mixture turns creamy,

(b) gel time: (seconds to minutes) the time at which the foam mixture starts to gel because of the cross-linking network formation as the appearance of non-flowing or jelly like systems can be observed,

(c) tack free time: (minutes) the time at which the outer surface of foam can be touched with a wooden stick without sticking and this refers that the foaming reaction has been completed,

(d) rise time: (minutes) the time at which the foam stops rising as observed visually.

Foam cup test is produced to determine or adjust the reaction times of starting material system and the foam density. As the results have to be reproducible, the same condition must be making foams with constant foam density. The foaming cup test procedure is displayed in Figure 2.9.

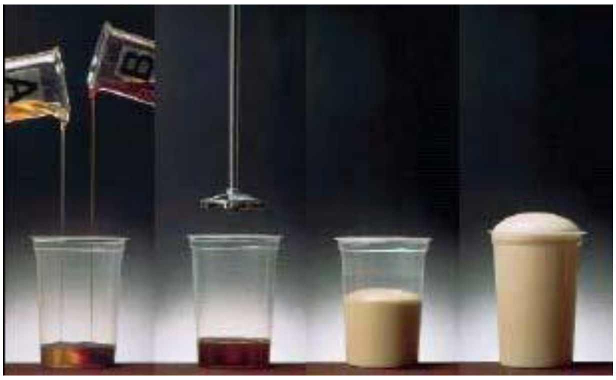


**Figure 2.9** Lab scale preparation of RPUR foams [38].

## 2.7 Characterization of rigid polyurethane foam properties

### 2.7.1 Density

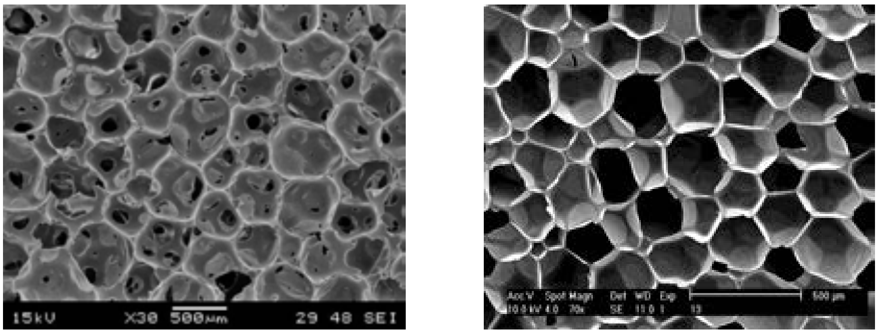
Density is an important key property of polyurethane foam due to it regulates the compressive strength and thermal conductivity of the foam as all other things being constant. It is interesting to note that it is governed by the cellular structure of foam, cell size, closed-, and opened cell contents.

Foam density can be evaluate as the apparent core density – the weight of cellular materials in air per unit volume of sample, after all foaming surface have been cut off, according to ASTM D 1622–08 [39]. The test specimens are generally cubic rectangular shape whose volume is not less than 16.4 $\mathrm{cm}^3$. The specimen is measured dimension using a vernier caliper and accurately weighed on a balance, which calculating its density as follows:

$$\text{Density (kg/m}^3\text{)} \quad = \quad \frac{\text{Sample weight}}{\text{Volume}}$$

### 2.7.2 Morphology

Polymeric foams contain porous structures perceived as gaseous voids surrounded by a dense polymer phase. Therefore, cellular microstructure– closed or opened cells, cell size and cell distribution is an important characteristic of foams that observed using scanning electron microscope (SEM). These characteristics strongly regulate mechanical performance of foam materials. Traditionally, the idealized rigid PUR foams present mostly closed-cell and highly uniform. Their cellular structure comprises of spherical cell shape with struts (cell edges) and thin cell window films. The closed-cell foams normally have lower moisture coefficient, higher density, and dimensional stability as well as higher stiffness compared to the opened-cell foams [25]. The opened- and closed cell structures of PUR foams are shown in Figure 2.10 [40].



Opened-cells Closed-Cells

**Figure 2.10** SEM images of opened- and closed-cell PUR foams.

Moreover, RPUR foams made in conditions allowing free rising in three dimensions, they can display substantial anisotropy in their structural and property. This phenomenon lead to the differences in physical properties measured in the parallel and the perpendicular of foam rising directions. Manufacturers will sometimes report properties measured in these two directions [33].

### 2.7.3 Compressive property

Foam behavior in compression is the most important mechanical property for any suitable end-use applications. The mechanical properties of rigid foams differ markedly from those of flexible foams depended on their cellular structure. Therefore, the compression test method provides the information about the behavior of cellular materials under an applied compressive load relating to the deformation of sample [28, 40]. Compressive properties mainly depend on foam density, type of base polymer, and the presence of any opened- or closed cells.

The compression load deflection is the method used to determine compressive stress-strain responses of foams. The test method is somewhat similar to that developed for non-cellular plastics. Test on rigid and flexible foams can be determined following ASTM D 1621–04. A universal testing machine fitted with a compression rig (cage) consisting of two parallel flat plates (Figure 2.11) is test. From this curve provides the compressive strength, Young's modulus, and other important values of foams.

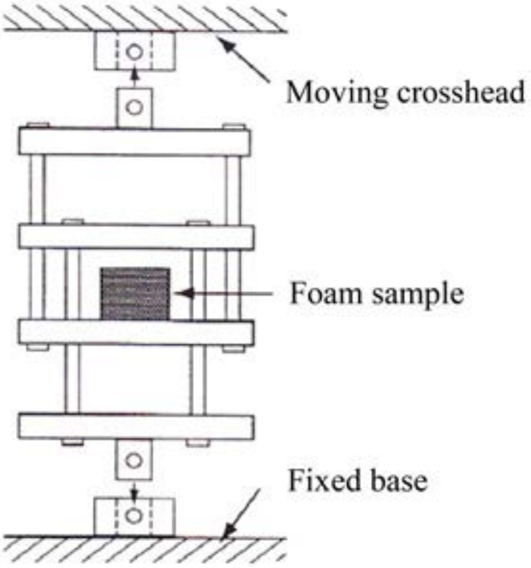


**Figure 2.11** Compression load defection test rig [28].

The typical compressive stress-strain curves of RPUR foam display three regions related to a deformation mechanism, as shown in Figure 2.12.

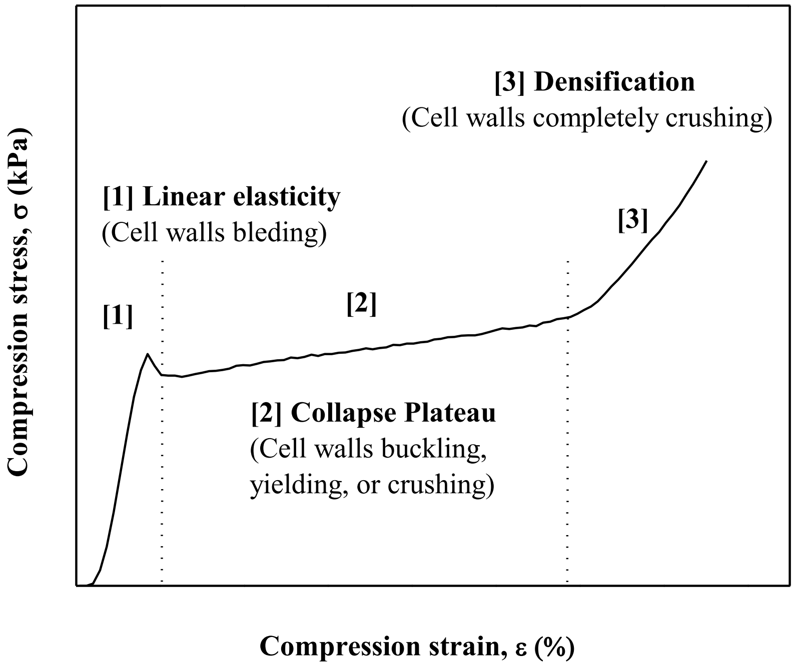


**Figure 2.12** Typical compressive stress-strain curve of rigid foams.

The initial linear domain at low stress associates to the elasticity of the materials resulting from cell window stretching because of trapped gas pressure and their slope is the Young’s modulus. Following the long linear plateau region is observed at the stress value which does not change much. This collapse plateau corresponds to cell collapse gradually by elastic buckling of cell walls or in brittle foams depending on the nature of solid polymer and cell morphology. The stress at the yield point if presents before 10% deformation or, in the absence of yield point, the stress at 10% deformation is compressive strength. When the cell walls have almost completely collapse and crushing, the stress level is increased rapidly through the solid polymer itself. This third domain can be referred as densification [33].

### 2.7.4 Thermal conductivity

A major application for rigid PUR foams is thermal insulation in areas such as building construction, transportation, and appliances. Although in construction applications mineral wool remains the insulating material most used, but rigid PUR foams are also used in very significant amounts with their superior properties including better insulation, light weight, easier handling, no water absorption (closed-cell foams), compensates for their generally higher cost [33].

Thermal conductivity (λ or K value) is a specific material property and this term refers as a measure of the capacity of a material to conduct heat through its mass. It represents the heat flow in watts (W) through a 1 $m^2$ surface area and 1 m sample thickness when the temperature difference between the two surfaces in the direction of heat flow amounts to 1 Kelvin (K). The unit of measurement for thermal conductivity (λ) is W/mK. The thermal conductivity of rigid PUR foams depends on the cell gas used, density, temperature, behavior in the presence of water and moisture, and time of measurement.

Rigid PUR and PIR foams have an excellent thermal conductivity between 20–30 mW/mK with their density being in the range 30–100 kg/$m^3$ at high compressive strength of 100–1000 kPa. For water-blown RPUR foams, $CO_2$ gas with its moderate gas thermal conductivity provides a very attractive option used for foaming expansion because of its low global warming potential compared with other commercial physical blowing agents and their simply producing reaction. But some advantages of those used are the diffusion of $CO_2$ out from foam cells to outer and replaced by air making shrinkage. As a result, the thermal conductivity is higher with air replacement after treated by time [1].

There are four parameters that mechanically regulate the thermal conductivity of foams including conduction of heat through the solid polymer, conduction of heat through the gas, convection of heat through the cells, and radiation through cell walls and across voids. For low density RPUR foams (30–50 kg/$m^3$) with cell size being in the range of 10–200 μm, the convection may be neglected and therefore their thermal conductivity is significantly governed by the gas conduction [1].

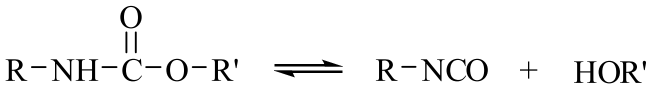
For closed-cell RPUR foams, as the foam density decreases, the thermal conductivity through the solid polymer reduces correspondingly and the overall thermal conductivity of the foam is decreased relatively to their density. The effect of cell size on thermal conductivity in PUR foams with cell diameters less than 200 μm is relatively small, but the tendency of conductivity is reduced as the cell size decreases [33].

### 2.7.5 Thermal degradation profile

Stability of polyurethane foams under evaluated heating environmental varies with the structure of base polymer. Therefore, thermal stability of PUR foams mainly corresponds to the urethane group and a few common chemical groups presented in urethane materials including ether or ester groups.

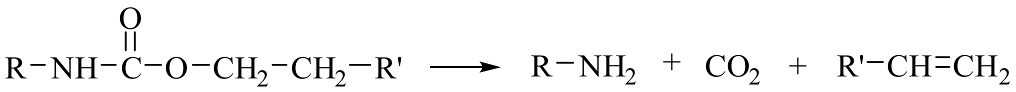
The urethane group displays relatively low thermally stable. Thermal degradation of urethane depends on the groups to which it is attached. The highest initial dissociation temperature about 250°C can be observed for aliphatic isocyante-aliphatic alcohol systems, then being aromatic isocyante-aliphatic alcohol (200°C), aliphatic isocycanate-aryl alcohol (180°C), and the lowest for aromatic isocyanate-aromatic alcohol (120°C) [24]. Thermal decomposition of urethanes proceeds in one of three basic reactions following:

(1) dissociation of urethane group to initial components:



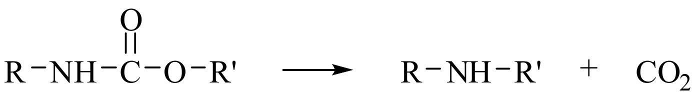
$$\mathrm{R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O{-}R'} \rightleftharpoons \mathrm{R{-}NCO} + \mathrm{HOR'}$$

(2) formation of primary amine and olefin:



$$\mathrm{R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_2{-}CH_2{-}R'} \longrightarrow \mathrm{R{-}NH_2} + \mathrm{CO_2} + \mathrm{R'{-}CH{=}CH_2}$$

(3) decomposition resulting in the formation of secondary amine and $CO_2$



$$\mathrm{R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O{-}R'} \longrightarrow \mathrm{R{-}NH{-}R'} + \mathrm{CO_2}$$

Degradation products can further react forming many products. These reactions occur both in oxidative (air) and inert (nitrogen) atmosphere at the same heating rate, except the further course of reaction varies. Therefore, burning of polyurethanes can generate toxic isocyanates, which should be taken into account when these products are used for building insulation. The thermal degradation profile of PUR foams can be observed by thermogravimetric analysis (TGA). The onset temperature of degradation of PUR both in air and $N_2$ atmosphere are the same. The urethane group is firstly degradation followed by the dissociation of the soft segments such as polyol backbones.

Degradation of polyols occurs faster in air than in nitrogen. Polyether based urethanes have lower thermally stable than the corresponding polyester based, particularly in the presence of oxygen, because of the increased sensitivity of the alpha C-atom in ethers towards oxidation. The sensitivity to oxidation increases in polyesters with decreasing number of $CH_2$ groups between two ester groups, or if tertiary carbon is present in the chain, as in the case of polypropylene glycols.

Thermal stability of PUR foams can be evaluated by weight loss or loss of properties and the results may not occur simultaneously. Thermal stability is governed not only by chemical composition, but also by the size of the product. In principle, thermal stability is higher if the ratio of surface to volume of the body is lower. Thus, fibers are very sensitive to oxidation because the degradation products can diffuse out easily and have no time to undergo recombination into a more stable product. The order of thermal stabilities of other crosslinked isocyanate products is given as follows: isocyanurate (>270°C), urea (≥180°C), urethane (≥150°C), biuret (≥120°C), and allophanate (≥120°C) [24].

## 2.8 Literature reviews on bio-based polyurethanes

Commercially, the two major starting materials for PUR production derived from petroleum based precursors which are being exhausted rapidly. As an increase in PUR consumption, the escalating price of petrochemicals and respect for the environmental friendly effects are recently contributing to the development of PUR from alternative renewable resources. It is noted that the terminology of bio-based polyurethanes refers as the polyurethanes which using polyols obtained from renewable resources, while the isocyanates based natural sources are the challenge fields. In this part, we would present some approaches of polyols from renewable resources.

### 2.8.1 Polyols from vegetable oils

To seeking for an alternative renewable resource, vegetable oils are available abundance with the cost effectiveness and have potential to replace the petroleum based polyols. Naturally presenting vegetable oils are mainly triglyceride molecule containing a variation of fatty acids proportion. The oil composition may also vary depending on the plant, the crop, the season, and the growing conditions [3]. The characteristics of individual vegetable oil are controlled by the fatty acids and their composition. Each fatty acid is indentified by the number of carbon atoms in its hydrocarbon chain ranging from C8 to C22 and some presence of double bonds in chain. The typical structure of triglyceride and five fatty acids mostly found in edible vegetable oils are shown in Figure 2.13.

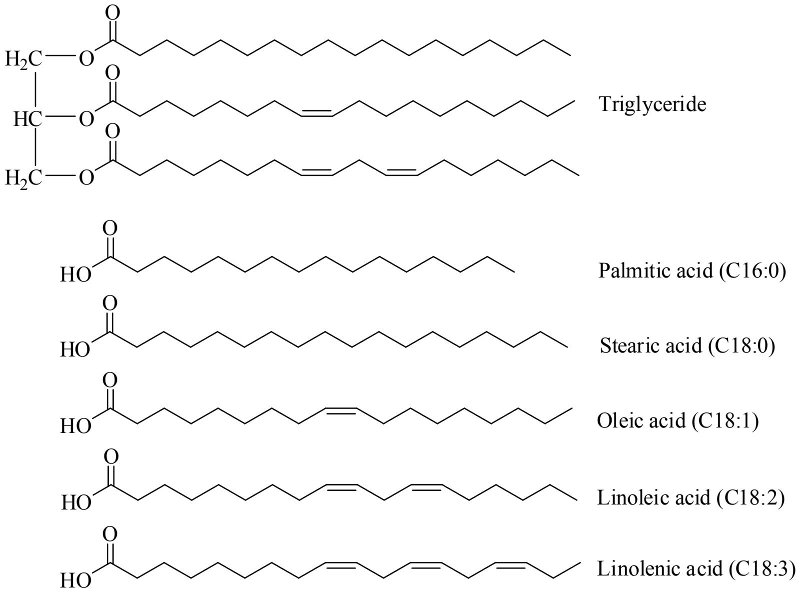


**Figure 2.13** Structures of triglycerides and five dominating fatty acids.

Based on the unsaturated fatty acid contribution, vegetable oils can be categorized into three groups with their iodine ($I_2$) number (mg $I_2$/g oil); drying ($I_2$ number ≥150), semidrying ($I_2$ number 110–150), and nondrying oils ($I_2$ number ≤110) [24]. Selecting vegetable oils and their fatty acid profiles such as soybean, castor, canola, palm, linseed, rapeseed, sunflower, and safflower are presents in Table 2.9 [41].

Vegetable oils are triglycerides containing reactive moiety including double bonds and ester groups that can be modified by the chemical reaction to produce polyhydroxy compounds which used as polyols comparable to petroleum based polyols for PUR foam preparation. Recently, the ongoing use of plant oils for polyols synthesis has been intensively investigated by many researchers. Although seed oils from agricultural harvests including castor oil, soybean oil, linseed oil, canola oil, and palm oil are widely used as the raw materials for polyols production but new alternative feedstock has been progressively discovered and developed.

**Table 2.9** Typical fatty acid compositions of selecting plant oils [3, 41]

| Plant oil | Fatty acid profile (wt%), (carbon atoms : number of double bonds) | | | | | |
|---|---|---|---|---|---|---|
| | Palmitic (16:0) | Stearic (18:0) | Oleic (18:1) | Linoleic (18:2) | α-Linolenic (18:3) | Erucic (22:1) |
| Soybean | 10.6 | 4.0 | 23.3 | 53.7 | 7.6 | - |
| Castor[a] | 2.0 | 1.0 | 7.0 | 3.0 | - | - |
| Canola | 4.0 | 1.8 | 60.9 | 21.0 | - | - |
| Palm | 44.4 | 4.1 | 39.3 | 10.0 | 0.4 | - |
| Linseed | 6.0 | 4.0 | 22.0 | 16.0 | 52.0 | - |
| Rapeseed | 3.8 | 1.2 | 18.5 | 14.5 | 11.0 | 41.1 |
| Sunflower | 7.0 | 4.5 | 18.7 | 67.5 | 0.8 | - |
| Safflower | 6.8 | 2.3 | 12.0 | 77.7 | 0.4 | - |

[a] Contains 85 – 95% of ricinoleic acid (C18:1, OH at C12)

Among others, castor oil has hydroxyl groups naturally in their molecular structure. Due to it consists of a high content of ricinoleic acid (83.6–90%), which is C18 fatty acid, and unique having both double bonds (C9–C10) and OH groups at C12. Therefore it is primary interest for biobased polyols in PUR technology. Soybean oil is now the alternative choice of biobased polyols because of their high double bond content and relative low price as well as market available.

There are four major chemical routes for the syntheses of vegetable oil based polyols which have been investigated currently follow:

### 2.8.1.1 Epoxidation/hydroxylation reaction

The first approach is the modification of double bonds to produce OH groups. Thus the selection of vegetable oils depending on their unsaturated fatty acid levels so the higher double bond levels provides the higher OH contents in resulting polyols. The most study with this fundamental is the epoxidation of double bond to produce epoxides followed by the ring-opening of resulting products to obtain polyols mostly containing secondary OH groups [7–10]. This process sometimes called hydroxylation reaction is presented in Figure 2.14.

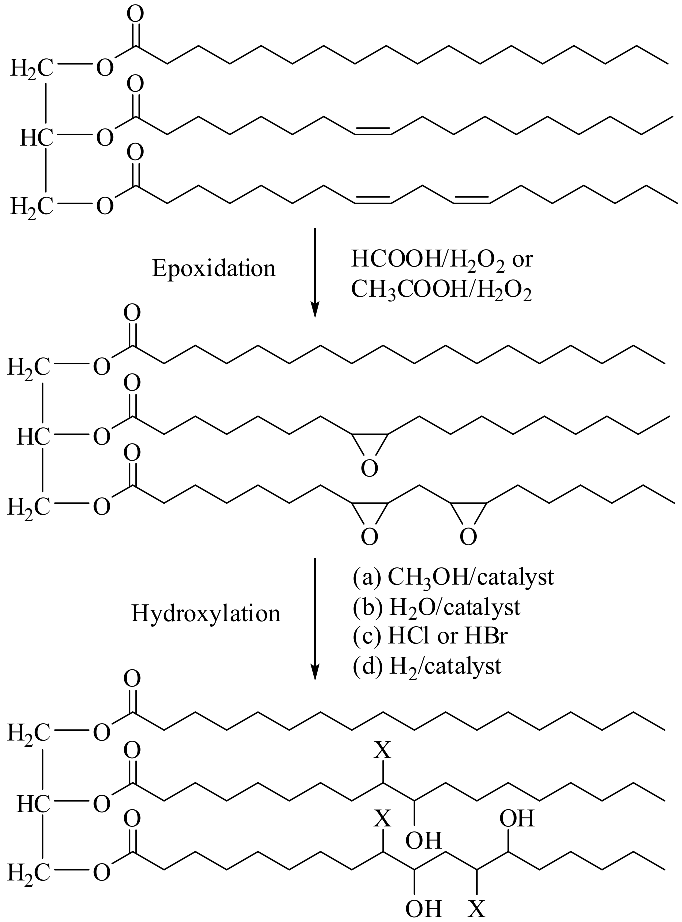


**Figure 2.14** Epoxidation and hydroxylation reactions of vegetable oils, where X = $-OCH_3$ for (a), –OH for (b), –Cl or Br for (c), and –H for (d).

The epoxidation step is occurred by the use of oxidizing agents such as peroxy acids. The reactions of formic acid or acetic acid with hydrogen peroxide generated performic or peracetic acids are currently used in the several industrial processes. However, the loss of epoxide contents is considered during the ongoing of reaction with the period of times. The side reaction of reactive epoxide involves the hydrolysis of oxiranes with water or acid presented in reaction systems to form OH groups which further react with any epoxides leading to polyether formation between fatty acid chains. As a result, the obtained products have a high viscosity. While the ring opening procedure to convert epoxidaized oils to hydroxylated oil including hydrolysis, alcoholysis, or hydrogenation have been studied and the obtained polyols have a different characteristics due to the condition used. All resulting polyols from this approach mostly have secondary OH groups at the middle of fatty acid chains and higher viscosity compared to the commercial polyols, which frequently have primary OH groups and lower viscosity. Therefore, this is a limit used for polyurethane preparation. Although the weak points of biopolyols from this approach have been achieved but can be compensated with their lower cost and easy to operation. Therefore the *in situ* expoxidation-hydroxylation and alcoholysis reaction are used for preparation of biobased polyols in this work.

#### 2.8.1.2 Hydroformylation/hydrogenation reaction

Due to the limited use of secondary OH groups containing polyols from vegetable oils, the several technologies have been studied and developed to overcome this point. The second technology is the hydroformylation with syngas ($H_2$/CO) in the presence of transition metal (rhodium or cobalt) catalysts following the hydrogenation of resulting aldehydes to form primary OH groups as shown in Figure 2.15 [11]. The OH content of resulting polyols depends on the variety of catalysts used.

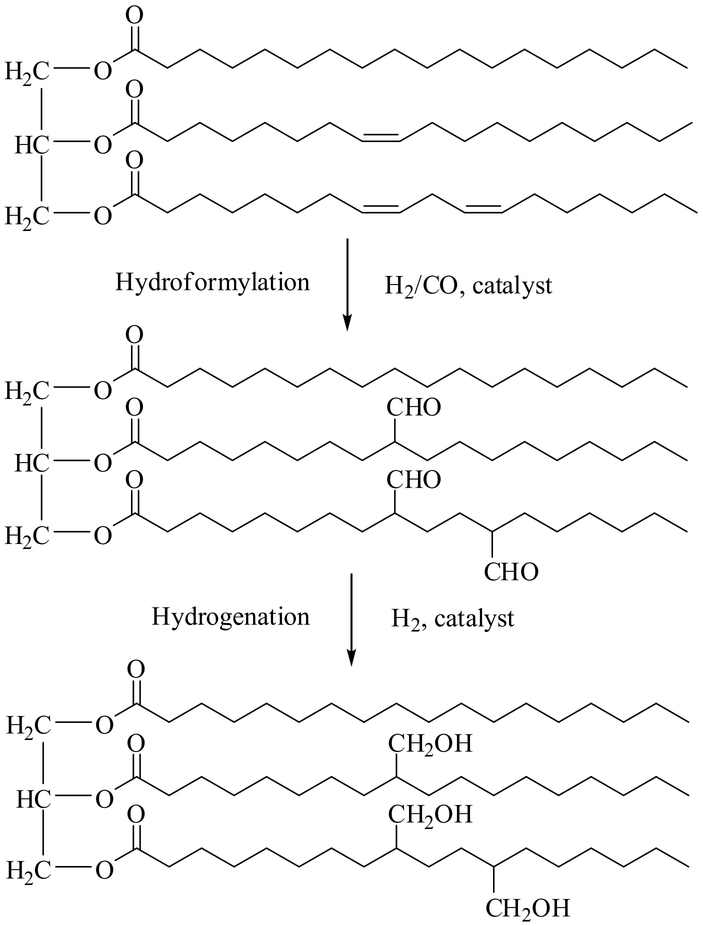


**Figure 2.15** Hydroformylation and hydrogenation reactions of vegetable oils.

### 2.8.1.3 Ozonolysis reaction

Moreover, the clean ozonolysis of triglycerides forming aldehydes and subsequent reduction to primary OH groups has been revealed as Figure 2.16 [12–14]. Ozone ($O_3$) is the ozonlysis agent which is firstly cut at the double bond position in fatty acid chain to form aldehydes which further reduction to obtain a primary OH moiety at the chain end using a reducing agent such as sodium borohydride.

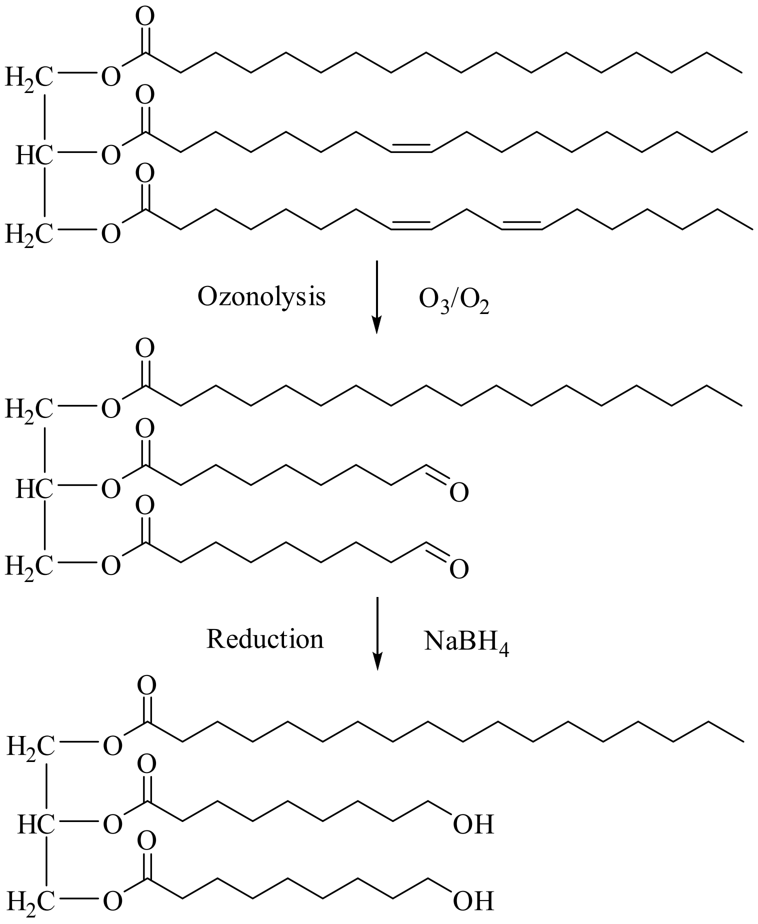


**Figure 2.16** Ozonolysis reaction of vegetable oils.

### 2.8.1.4 Alcoholysis reaction

In addition, the well-known alcoholysis or transesterification of vegetable oils with polyfunctional alcohols in the presence of acidic or basic catalysts has been reported and the resulting products are the mixture of fatty acid alkyl ester as monoesters and diesters. The polyfunctional alcohols are mostly used for this reaction such as glycerol, triethanolamine, pentaerythritol, and trimethylolpropane. The obtained polyols consist of primary OH groups and fatty acid dangling chains. These chains may act as a plasticizer in PUR system. The typical alcoholysis of vegetable oils with glycerol is shown in Figure 2.17. The obtained product is the mixture of mono- and diglycerides. The several vegetable oil-based poyols produced from this basic reaction are commercially available [15–20]. The most common used oils are soybean, castor, palm, linseed, and canola oils.

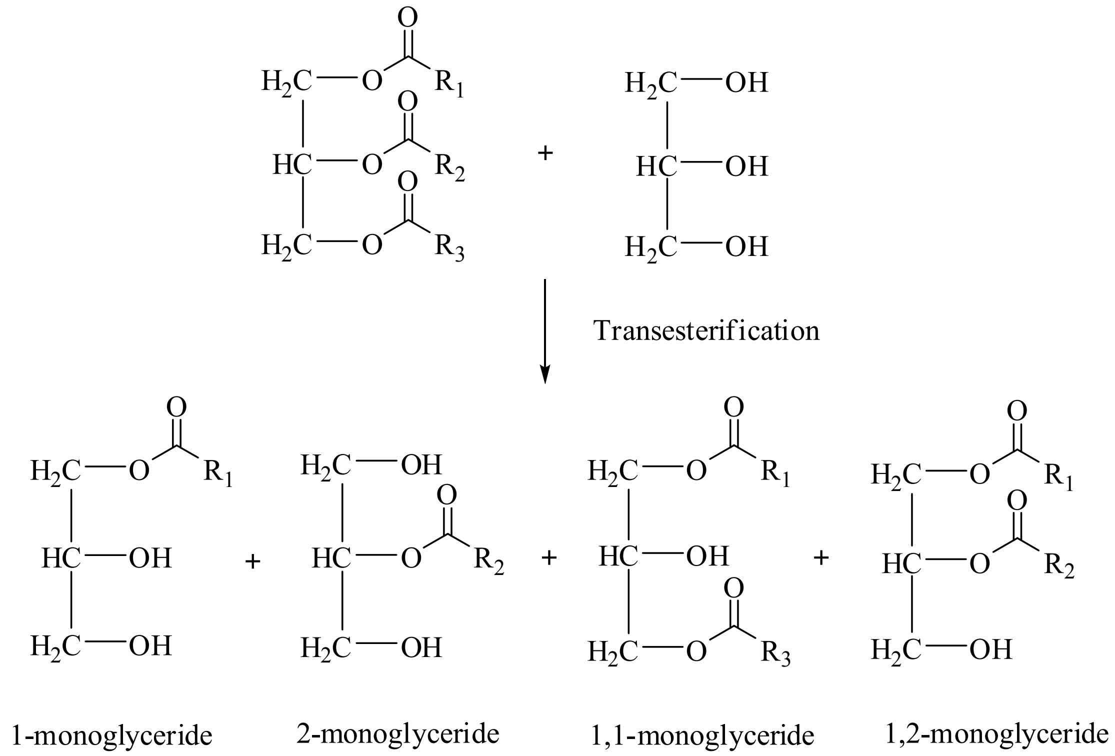


**Figure 2.17** Typical transesterification of vegetable oils [42].

### 2.8.2 Polyols for cashew nut shell liquid

Among the other renewable resources used to produce the biobased polyurethanes, cashew nut (*Anacardium occidentale* L.) shell liquid (CNSL) has been studied. CNSL is an agricultural byproduct obtained from typical roasting and technical extracting shell process, which is a viscous reddish brown liquid consisting of the variety of phenolic compounds containing a long alky chain at *meta* position. The four major components of natural CNSL include anacadic acid (60–65%), cardol (15–20%), cardanol (10%), and 2-methyl cardol (2–5%) that shown in Figure 2.19. After the heating process, anacadic acid is decarboxylated to form cardanol. The resulting CNSL finally comprises 83–84% of cardanol.

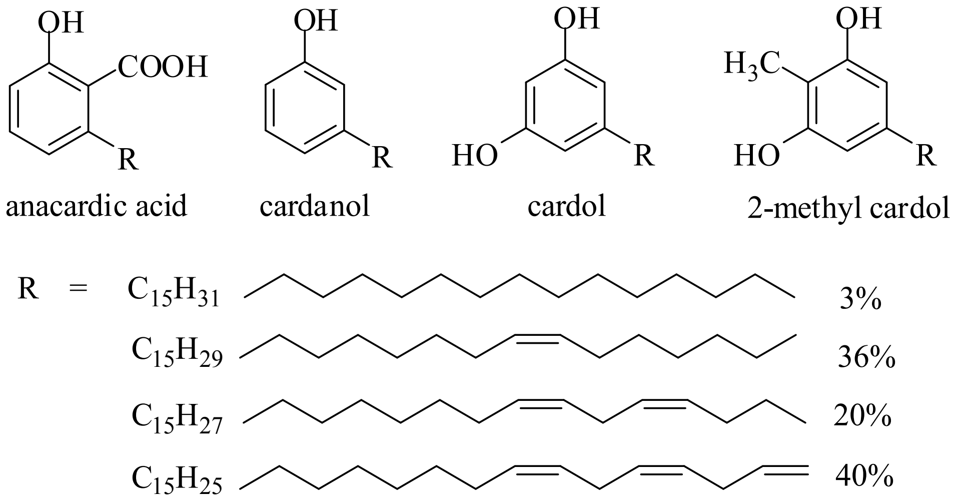


**Figure 2.18** Structures of four major components of cashew nut shell liquid (CNSL) [45].

Based on the interesting structure of CNSL constituents especially cardanol, makes it attractive properties in polymers derived phenol such as good processability, high solubility in organic solvents, good thermal stability, and good electrical insulation. Many polymer researches form CNSL have been synthesized and developed in the recent year, and their typical applications include epoxy resins, paints, vanishes, and coating [42]. Practically, polymers from CNSL can synthesized either by the condensation with active hydrogen compounds such as formaldehyde or by chain-reaction polymerization via the unsaturated position in the alkyl chain using acid catalysts or functionalization at the OH group subsequently oligomerization to obtain functionalized prepolymer [46].

In polyurethane applications, there are a few methodologies to synthesize a new class of polyols from CNSL or cardanol and its products provides better thermal, mechanical, and chemical properties for instance:

Suresh *et al.* [47] successfully synthesized a new class of cardanol-based polyols by two-step reaction. Cardonal was firstly reacted with epichlorohydrin to form monoglycidyl ether, followed by ring opening reaction under acid condition to produce a diol. The alternative triol was synthesized by the reaction with diethanolamine or the reaction of glycerol monochlorohydrin with cardanol. The OH number of these resulting polyols was in the range of 140–265 mg KOH/g.

Polyurethane films were prepared by the reaction of these cardanol-based polyols with diphenylmethane diisocyanate (MDI) at NCO/OH ratio = 1. The obtained PUR films given an excellent properties including hardness, thermal stability, and mechanical properties.

Cardanol-based polyols were produced by typical process based on epoxidation/hydroxylation reaction and used for rigid polyurethane foam preparation that was studied by Suresh *et al* [48]. The cardanol-based polyols were synthesized by the reaction of cardanol with performic aid, and further hydrolyzed by sodium acetate and had the OH value in the range of typically 350–400 mg KOH/g. To make rigid PUR foams, cardanol-based polyols reacted with the preferred polymeric MDI at 10% in excess of the stoichiometric NCO/OH ratio. The resulting foams were expected to provide higher thermal stability and lower water absorption compared to other vegetable oil-based foams.

Reese *et al.* [49] reported the CNSL-based polyether polyols containing primary OH groups from the alkoxylation of CNSL with alkylene oxides such as ethylene oxide or propylene oxide in the presence of alkali hydroxides such as sodium or potassium hydroxides as a catalyst. The synthesized CNSL-based polyols had the OH numbers be in the range of 180–300 g KOH/g which were suitable for flexible PUR foam applications.

### 2.8.3 Polyurethane foams from bio-based polyols

In recent years, there are many researches that revealed on the polyurethane from renewable resources. Several kinds of vegetable oil based polyols had been synthesized by the variety of chemical reactions and applied in PUR systems that described before. In this chapter we would review on the example of vegetable oil based- and starch based polyols for polyurethane foam preparation for instance:

Guo *et al.* [50] reported on the preparation of rigid PUR foams blown with HCFC and cyclopentane using soybean-based polyols. Soy polyols were synthesized by the ring-opening of epoxidized soybean oil with methanol. The resulting soy polyols had the OH number be in the range of 184–215 mg KOH/g with the relative high viscosity (6000–10400 mPa.s at 30°C). Rigid PUR foams were prepared using these soy polyols reacting with PMDI. Both types and amounts of constituents in foam formulation including blowing agent, catalyst, surfactant, water, crosslinker, and NCO index had the variable effects on density and mechanical properties of foams. Moreover, soy-based polyols blown with both HCFC and cyclopentane showed the satisfactory mechanical strength and insulation conductivity comparable to commercial foams but the higher thermal stability (in $N_2$ and air) than reference foams.

In early 2001, Hu *et al.* [15] successfully prepared rigid polyurethane foams using biobased polyols from rapeseed oil. The polyols was synthesized by two step reactions comprising firstly hydroxylation followed by alcoholysis reaction. The hydroxylation step was carried out using performic acid, and further alcoholyzed with triethanolamine in the presence of lithium hydroxide as catalyst. The OH number of rapeseed oil-based polyol increased to 367 mg KOH/g that comparable to commercial polyester polyol, while its viscosity was higher than one. Rigid PUR foams from this rapeseed oil-based polyols were produced and some physical and mechanical properties were characterized. It was found that the compressive strength of rapeseed oil-based foam was slightly lower than those of commercial foam, while its density was higher. However, the rapeseed oil-based polyols was an alternative raw material that could be used for rigid PUR foam production by optimized formulation.

Narine *et al.* [51] prepared water blown rigid polyurethane foams using three types of North American seed oil based polyols. For instance, polyols from canola oil containing primary OH groups were produced by the alternative and clean ozololysis and hydrogenation reaction, commercial soy polyols produced by epoxidation and hydroxylation based method, and unmodified crude castor oil. Their OH number were quite low (153–186 mg KOH/g), thus the foam formulation should add glycerol as a crosslinker and reacted with aromatic diphenylmethane diisocyanate (MDI) to obtain rigid PUR foams based seed oils. It was found that the canola oil-based polyol displayed the highest reactivity because of the presence of primary H groups. Moreover, the structure of polyols showed the effects on mechanical and thermal properties as well as the microstructure of foams. The fatty acid chain or dangling chain of seed oil-based polyols acted as plasticizer in PUR foam system. As a result, the rigidity of foams was reduced, while their flexibility was increased.

Chuayjuljit *et al.* [52] reported rigid polyurethane foams from palm oil-based polyols. A polyol preparation step, palm oil was transesterified with pentaerythritol using calcium oxide as a catalyst. The obtained polyol had a hydroxyl value of 385 mg KOH/g with a very high viscosity of 355 poises. After that water blown RPUR foams were prepared by the reaction of synthesized polyols with PMDI using *N,N*-dimethylcyclohexylamine (DMCHA) as a catalyst and silicone surfactant. The effect of catalyst and surfactant content on the foam properties had been studied. At the rising catalyst level, the density of palm oil-based foams was reduced and its compressive strength was increased, while the enhancement of surfactant content did not significant effect on both properties. In addition, SEM micrograph of their foam cells showed mostly closed-cells and uniform with the increasing surfactant content.

Rigid polyurethane foams from two types of seed oil-based polyols including soybean oil and castor oil were prepared and further characterized for their mechanical and thermal properties as well as morphology. This work was investigated by Veronese *et al* [20]. Soy oil-based polyols was synthesized by the epoxidation with performic acid following the transesterification with triethanolamine catalyzed by strong base. The soy-based poyols had the OH number about 477 mg KOH/g. On the other hand, cartor oil-based polyol was only prepared transesterification with triethanolamine or glycerol under the same condition as soy polyols and the resulting castor oil-polyols had the OH number as 441 and 393 mg KOH/g, respectively. RPUR foams prepared from these synthesized polyols and diphenylmethane diisocyanate (MDI) were achieved and compared to those of commercial polyether polyol at NCO/OH ratio 1.2:1. The apparent density of all vegetable oil-based foams was 50 ± 1 kg/m$^3$ and their compress strength was about 200 kPa that was relatively low compared with the commercial foams. The foams cells in vegetable oil-based foams contained mostly open-cells and were less uniform than commercial foams. However, they displayed excellent potential as a renewable resource for polyols used for RPUR foam preparation.

Four types of polyols from plant oils including rapeseed, sunflower, flaxseed, and castor oils were produced in the work of Stirna *et al.* [17]. The choice of polyols synthesis routes comprised transesterification with triethanolamine or amidization with diethanolamine and the resulting products mainly contained fatty acid monoester or their amides, respectively. Their OH number was in the range of 290–318 mg KOH/g which suitable for water blown rigid polyurethane/polyisocyanurate (PUR/PIR) foams at the optimal NCO index as 150–200 having the good physical and mechanical properties. The storage stability of these vegetable oil-based polyols premix systems was evaluated during the period of 12 months. Based on storage times, the acid value of these polyols increased resulting in the reducing reactivity of polyols.

Rigid polyurethane foams from plam oil-based polyols as a new type of natural based polyols were developed by Tanaka *et al* [16]. At polyols preparing step, palm oil was transesterified with glycerol using t-butylalcohol as a solvent and sodium hydroxide as catalyst. After that water blown PUR foams were prepared by the reaction of synthesized polyols with PMDI using dibutyltin dilaurate (DBTDL) as a catalyst, polylene glycol (PEG) or diethylene glycol (DEG) as chain extenders at molecular ratio of isocyanate to hydroxyl groups at 1.2. The apparent densities of the PEG-contained foams were in the wide range between 50 and 130 kg/m$^3$, whereas the DEG contained foams had almost the same values of 60 to 70 kg/m$^3$. The foams were characterized for their compressive strength and thermal conductivity. It was found that the resulted PUR foams became more flexible at the higher palm oil-based polyols content and indicated that the polyols chain acted as soft segment in PUR systems.

Yao *et al.* [53] studied polyurethane foams using liquefied corn starch as polyols. Firstly, corn starch (60% by weight) was liquefied using polyethylene glycol/glycerol as liquefaction reagent in the presence of sulfuric acid as a catalyst under reduced-pressure refluxing condition operated at 150°C for 2 hours. The liquefied starch polyols had the OH number ranging from 270 to 369 mg KOH/g, which suitable for PUR foam production. Rigid and flexible PUR foams blown with water were obtained from the reaction of liquefied starch and diphenylmethane diisocyanate (MDI). It was found that the surfactant types showed the effect on the closed- and opened-cell contents. At the higher opened-cell content with the continued cell structure displays the excellent water-absorbing property.

Biodegradable and highly resilient flexible polyurethane foams using liquefied bark and corn starch were discovered in the work of Ge *et al.* [54]. Liquefaction of bark and starch was prepared using the solvent mixture of polyethylene glycol/glycerol and sulfuric acid at the weight ratio of 94:5:1 under reflux condition under $N_2$ at 150°C. The flame resistant property of resulting foam was improved that was the result from the insoluble residual from bark liquefaction. On the other hand, PUR foams replacing with corn starch exhibited the decrease in density and compressive strength with increasing amount of corn starch and the maximum resilience value was obtained with the weight ratio of bark to starch as 1:1. Additionally, the biodegradable properties of foams were conducted by soil burial test for 6 months with 15.6% weight loss.

Kim *et al.* [55] reported the preparation of rigid polyurethane foams using polyols from corn starch. The mixture of polyols comprised corn starch content about 30–50% by weight, polyethylene glycol, glycerol, and water was premixed and heated at 95°C for 1 hour and further reacted with toluene 2,4-diisocyanate (2,4-TDI) in order to make foam. The mechanical and thermal properties of resulting foams were studied. It was found that rigid PUR foams were not produced at the low quantity of starch and low NCO/OH molar ratio. On the other hand, the higher starch contents and NCO/OH molar ratio was resulting in the higher compressive strength and thermal stability of foams.

# CHAPTER III

# EXPERIMENTAL

## 3.1 Chemicals and raw materials

### 3.1.1 Polyols preparation from vegetable oils

Hairy basil seed oil, sesame seed oil, pumpkin seed oil, and cashew nut shell liquid (CNSL) were kindly provided from the Institute of Biotechnology and Genetic Engineering, Chulalongkorn University (Bangkok, Thailand). Their characteristics and fatty acid profile were illustrated in Table 3.1. Hydrogen peroxide (30 wt%) from Merck, formic acid (98 wt%) from Fisher Scientific, triethanolamine (85 wt%) from Ajax Finechem and lithium hydroxide (99 wt%) from Fluka were used for vegetable oil-based polyols preparation. Their appearance was shown in Figure 3.1.

**Table 3.1** Characteristics and fatty acid composition of hairy basil seed oil, sesame seed oil and pumpkin seed oil

| | Hairy basil seed oil | Sesame seed oil | Pumpkin seed oil |
|---|---|---|---|
| Color (naked eyes) | Light yellow | Light blown | Dark green |
| Viscosity (at 25ºC, cP) | 123±6 | 136±3 | 160±6 |
| Acid value (mg KOH/g) | 8.23±0.05 | 7.23 ± 0.18 | 2.13±0.14 |
| Water content (wt%) | 0.10 | 0.08 | 0.09 |
| *Fatty acid profile (wt%)* | | | |
| Palmitic acid (C16:0) | 6.56 | 11.40 | 13.04 |
| Stearic acid (C18:0) | 2.84 | 4.30 | 4.60 |
| Oleic acid (C18:1) | 14.21 | 37.00 | 34.82 |
| Linoleic acid (C18:2) | 22.14 | 47.30 | 47.55 |
| α-Linolenic acid (C18:3) | 54.26 | – | – |
| Total unsaturated FFAs | 90.61 | 84.30 | 82.37 |

**Figure 3.1** The appearance of hairy basil, sesame, and pumpkin seed oils.

### 3.1.2 Hydroxyl number and acid number of polyols

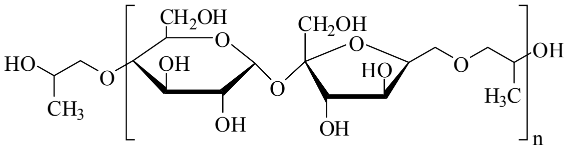
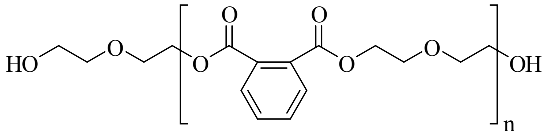
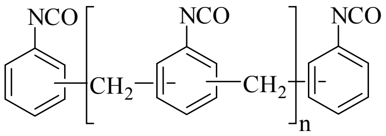
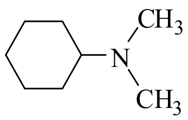
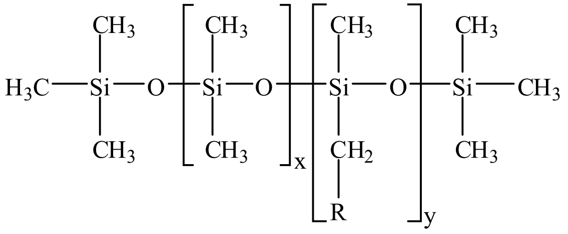
Phthalic anhydride from Sigma-Aldrich, pyridine, sodium hydroxide, and potassium hydrogen phthalate from Carlo Erba were used for determination of OH numbers of synthesized polyols according to ASTM D 4274–05.

Ethanol (95%) obtained from Merck, potassium hydroxide, and toluene from Carlo Erba were used for determination of acid numbers of polyols according to ASTM D 4662–03.

### 3.1.3 Rigid polyurethane foam preparation

For the preparation of water-blown RPUR foams, the isocyanate Suprasec® 5005, the commercial sucrose-based polyether polyols Raypol® 4218, phthalate-based polyester polyols Raypol® 8360, the surfactant TEGOSTAB® B8460, and the foaming catalyst DMCHA (*N,N*-dimethylcyclohexylamine) were supplied from Huntsman (Thailand) Co., Ltd. and IRPC Public Co., Ltd. The commercial specifications of RPUR foam raw materials used in this work are presented in Table 3.2.

**Table 3.2** Commercial specifications of raw materials for rigid polyurethane foam preparation in this work

| Material | Structure and name | Description |
|---|---|---|
| Polyols | <br>Poly (propyleneoxy) sucrose | Tradename: Raypol® 4218<br>Appearance: Clear yellow liquid<br>OH no.: 438.93 g KOH/g<br>Acid no.: 0.10 g KOH/g<br>Viscosity at 25°C: 5340 cP |
| | <br>Poly (diethylene glycol) phthalate | Tradename: Raypol® 8360<br>Appearance: Clear yellow liquid<br>OH no.: 360.12 g KOH/g<br>Acid no.: 1.62 g KOH/g<br>Viscosity at 60°C: 121 cP |
| Isocyanate | <br>Polymeric diphenylmethane diisocyante | Tradename: PMDI<br>Appearance: Dark blown liquid<br>NCO content: 30.9 %wt<br>Average functionality: 2.7<br>Viscosity at 25°C: 220 cP |
| Catalyst | <br>Dimethylcyclohexylamine | Tradename: DMCHA<br>Appearance: colorless liquid, intense amine-like odor |
| Surfactant | <br>Polydimethylsiloxane polyether | Tradename: TEGOSTAB® B8460<br>Appearance: viscous colorless liquid |

## 3.2 Synthesis of vegetable oil and cashew nut shell liquid based polyols

The vegetable oil-based polyols from hairy basil seed oil, sesame seed oil, and pumpkin seed oil could be synthesized by two steps reaction comprising hydroxylation followed by alcoholysis reaction. These typical methods have been reported in several works [15–20]. CNSL-based polyols was synthesized by single reaction as the hydroxylation reaction. The basic chemistry of both reactions was described in Chapter II. In this research, the practical method to synthesize these polyols is following:

### 3.2.1 Hydroxylation of vegetable oils and CNSL

A portion of 30 wt% of hydrogen peroxide (0.27 mol, 27.60 mL) and 98 wt% of formic acid (0.54 mol, 20.80 mL) were mixed in a three-neck round bottom flask equipped with a stirrer, reflux condenser, and a thermometer. The mixture was heated to 40ºC with constant stirring. Then the vegetable oil (0.18 mol, 50.00 g) was added dropwise and the temperature was kept at 40–50ºC for 3 hours. After that the reaction mixture was allowed to cool to room temperature. The liquid separated clearly in two layers. The acid phase in the bottom layer was removed, and the hydroxylated oil in the upper layer was recovered and distilled under vacuum to eliminate the remaining water and acid. The hydroxylated hairy basil seed oil and sesame seed oil were light pale yellow viscous liquid whereas the hydroxylated pumpkin seed oil was dark green liquid with the highest viscosity.

In the case of CNSL based polyol, the hydroxylated CNSL was synthesized using the ratio of CNSL/formic acid/hydrogen peroxide as 1:1:2 mol. Firstly, formic acid and CNSL were mixed together in a three-neck round flask and stirred well in cooling bath (0°C). Then a drop wise of 30 wt% hydrogen peroxide was added into the mixture under this condition. After the addition was completed, the reaction temperature was raised to 40°C and kept the reaction at this condition for 24 hours. The resulting product was neutralized with barium hydroxide and washed with water until neutral to litmus and dried over anhydrous sodium sulfate. The dark blown viscous CNSL-based polyol was obtained.

### 3.2.2 Alcoholysis of hydroxylated vegetable oils

The hydroxylated vegetable oil (1 mol, 50.00 g), 85 wt% of triethanolamine (3 mol, 30.17 g) and lithium hydroxide (0.2 wt% of total weight, 0.16 g) were added together in a flask with mechanical stirrer and thermometer well. The reaction mixture was constantly stirred as the temperature was raised to 150ºC in 0.5 hours. The reaction was continued at this temperature for 2.5 hours. The obtained polyols were dark pale yellow liquid and high viscosity. The resulting polyols did not require any further purification before used.

The pictures of epoxidized and alcoholized oils are shown in Figure 3.2.

**Figure 3.2** The appearance of epoxidized oils (left) and alcoholized oils (right).

**Figure 3.3** The appearance of CNSL (left) and hydroxylated CNSL (right).

Due to the polyols from CNSL being dark blown liquid (Figure 3.3), it was difficult to observe the endpoint in titration for OH number measurement. The OH number of hydroxylated CNSL was in the range of 96.47±16.95 mg KOH/g which was unsuitable for rigid PUR foam preparation. The error of its OH number made foam hard to reproduce production. At stoichiometric NCO/OH ratio as 1.0, 1.0 pbw of catalyst, 3.0 pbw of water, and 2.5 pbw of surfactant, CNSL-based polyols reacted with isocyanates rapidly leading to foam formation within a short time. In addition, PUR foam using CNSL-based polyols gave bad appearance such as brittle and fragile as well as the core foam being soft (Figure 3.4). It might be resulted from the variety of CNSL composition that shown in Figure 2.19 providing the uncontrollable polyols formation. Therefore, in this research part we would like to concentrate only of vegetable oil-based RPUR foams.

**Figure 3.4** Polyurethane foams from hydroxylated CNSL.

## 3.3 Polyols characterization

### 3.3.1 Hydroxyl number

The OH number of synthesized polyols was determined according to ASTM D 4274–05, test method D-reflux phthalation. Firstly, the suitable amount of sample was esterified with accurately 25.00 mL of phthalic anhydride/pyridine solution by refluxing at 115±2°C for 1 hour. After cool down to room temperature, the sample solution was then back-titrated with 0.5 N sodium hydroxide (NaOH) standard solution using phenolphthalein indicator and the endpoint color as pink for at least 15 seconds (Figure 3.5). A blank (phthalic anhydride/pyridine solution) was determined in the same procedure.

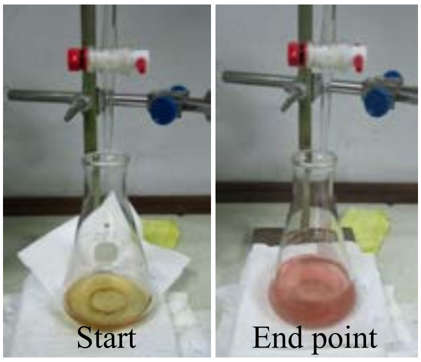


**Figure 3.5** The pictures of polyol samples in titration step for OH number measurement.

The OH number were calculated and expressed in mg of potassium hydroxide (KOH) per gram of sample as the equation below:

$$\text{OH number} \quad = \quad \frac{(V_b - V_s) \times N_{KOH} \times 56.1}{W_s}$$

where $V_b$ is the volume in mL of NaOH required for the blank titration, $V_s$ is the volume in mL of NaOH used for the sample back-titration, $N_{NaOH}$ is the concentration in normal of NaOH standard solution, 56.1 is the molecular weight of KOH (g/mol), and $W_s$ is the sample weight (g). The sample size used in this determination should be adjusted to give the $V_b - V_s$ be ranging 18 to 22 mL. In the case of polyols containing free acids, the accurate OH numbers must be calculated as:

$$\text{The correct OH number} \quad = \quad \text{OH number} \quad + \quad \text{Acid number}$$

### 3.3.2 Acid number

The acid number of polyols was evaluated following ASTM D 4662–03. The proper sample weight was completely dissolved in a 50 mL of toluene/ethanol (1:1) solvent and then titrated instantly with 0.1 N KOH standard solution at temperature below 30°C and the endpoint color as pink for at least 15 seconds. The acid number was calculated using the following equation:

$$\text{Acid number (mg KOH/g)} \quad = \quad \frac{(V_s - V_b) \times N_{KOH} \times 56.1}{W_s}$$

where $V_s$ is the volume in mL of KOH standard solution consumed for the sample titration, $V_b$ is the volume in mL of KOH solution used for the titration of toluene/ethanol blank solution. $N_{KOH}$ is the normality of KOH solution, 56.1 is the molecular weight of KOH (g/mol), and $W_s$ is the weight of sample used (g).

### 3.3.3 Water content

The water content of polyols is defined as the water concentration (mg/kg or percentage) containing in the synthesized polyols that could be determined using a Metrohm 831 KF coulometer with 703 Ti stand. The coulometric Karl Fischer titration procedure was performed according to ASTM D 6304–07, procedure C-water evaporator accessory. The conceptual coulometric Karl Fischer method is based on the iodometric titration, which is the quantitative reaction of water with the Karl Fischer reagent consisting iodine and sulfur dioxide in the presence of methanol and pyridine as an organic base.

Firstly, take a suitable volume of an anolyte for water determination in a titration vessel and then immerse a pair of platinum electrodes for potentiometric titration with constant current in this solution. Then, immerse the iodide production system filled with a catholyte for water determination in the anolyte solution. Switch on the electrolytic system and make the content of the titration vessel. Next, take an accurately weighed amount of the sample containing 1–5 mg of water, add it quickly to the vessel, and dissolve by stirring. Perform the titration to the end point under vigorous stirring. When the sample is insoluble in the anolyte, powder it quickly, and add an accurately weighed amount of the sample to the vessel. After stirring the mixture for 5–30 minutes, while protecting from atmospheric moisture, perform the titration with vigorous stirring. Determine the quantity of electricity (C) required for the production of iodine during the titration, and calculate the content (%) of the water in the sample.

### 3.3.4 Viscosity measurement

The dynamic viscosity of synthesized polyols was determined using a digital VR 3000 Myr viscometer (Figure 3.6) at 25±0.1ºC. The procedure is as follow: the selected suitable size of spindle was submerged carefully in the sample vessel to avoid bubbles forming under its bottom surface. The level the sample should be higher than the immersion point of spindle and the shaft of spindle should not be knocked against the sides of sample container. After that, the polyols sample started to measure its viscosity by selection the spindle speed first. The stable flow conditions are reached quickly and the correct value of viscosity was read within few seconds.

**Figure 3.6** VR 3000 Myr viscometer used for viscosity measurement of polyols.

### 3.3.5 Fourier transform infrared spectroscopy

FTIR spectra of starting materials and PUR foam samples were collected using a Thermo Scientific Nicolet 6700 FTIR spectrometer equipped with a Smart iTR diamond attenuated total reflectance (ATR) accessory operated at 4 $cm^{-1}$ spectral resolution over the wavenumber range of 4000–650 $cm^{-1}$.

### 3.3.6 Nuclear magnetic resonance spectroscopy

The $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded in deuterated chloroform ($CDCl_3$) with tetramethylsilane (TMS) as an internal reference on a Bruker ACF 200 nuclear magnetic resonance spectrometer which operated at 400 MHz for $^{1}H$ and 100 MHz for $^{13}C$ nuclei. The chemical shifts ($\delta$) are reported in parts per million (ppm) relative to the residual $CHCl_3$ signal (7.26 ppm for $^{1}H$ NMR and 77.0 ppm for $^{13}C$ NMR).

### 3.3.7 Electrospray ionization-mass spectrometry

The components of synthesized polyols were characterized using electrospray ionization-mass spectrometry (ESI-MS). Mass spectrometry was carried out in positive ionization model on an amaZon SL Ion Trap Mass Spectrometers (Bruker Daltonics, Germany) equipped with a standard ESI source and HyStar 3.1 (Bruker Daltonics, Germany) control software. The sample was diluted in acetonitrile and then injected by direct infusion with a syringe pump at flow rate of 3.0 μL/min and using nitrogen both as nebulizer and drying gas. Ion source voltages consisted of 140 V of capillary exit and scanned mass range was about 70–1000 m/z. In order to determination of free triethanolamine, the sample was diluted in acetronotrile/0.1%formic acid solution and performed following the same condition of qualitative analysis.

## 3.4 Rigid polyurethane foam preparation

Rigid polyurethane foams from biobased polyols and commercial polyols were prepared by one-shot method, which is the very efficient mixing of all the raw materials containing two components in the short time (seconds). RPUR foams are prepared by together mixing component A (isocyanate) and component B (a blend of polyol, catalyst, and surfactant) at ambient temperature without heating. For a laboratory RPUR foam preparation, the hand mixing method sometimes called cup foaming is used mainly for developing and checking raw material systems in formulation, which produces smaller rigid foam buns. The process needs the high speed electrical stirrer, paper cups, stopwatch, and solvent for cleaning mixing blade (acetone).

Firstly, polyols, surfactant, catalyst, and blowing agent were premixed in a 700 mL paper cup with mechanical stirrer at 2000 rpm until they become homogeneous. Subsequently, a calculated amount of PMDI was added rapidly into the resulting mixture and continued stirred for 15 s at the same speed. The foam was allowed to rise and set freely at ambient condition. The overall RPUR foaming process is presented in Figure 3.7.

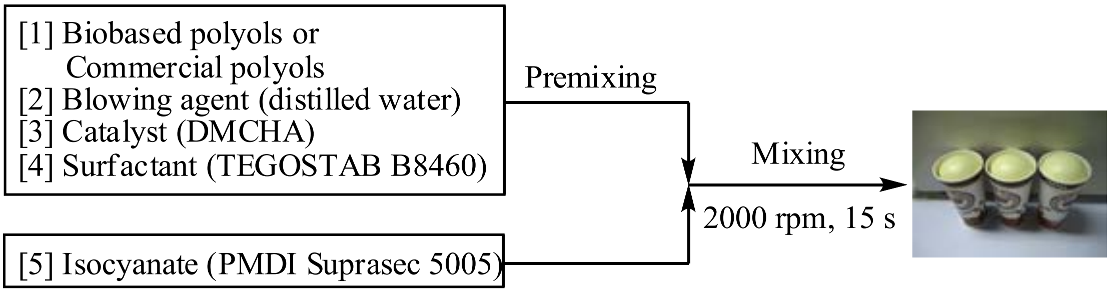


**Figure 3.7** Laboratory RPUR foaming process.

During foam generation, the foaming profile including cream time, gel time, tack free time, and rise time were recorded by a digital stopwatch. After free-rise foaming had been completed, the foams were cured at room temperature for 48 hours before physical and mechanical properties testing. All samples were prepared at least three replicates.

The effects of reactive starting materials i.e. PMDI content (NCO index), DMCHA catalyst, blowing agent (distilled water), and surfactant contents on the reaction time and density were examined. The proportions of starting materials were calculated relate to 100 parts by weight (pbw) of polyols, shown in Table 3.3. To evaluate the optimal formulation, the final RPUR foams have been produced with desired density at 40–45 kg/m$^3$.

**Table 3.3** Water-blown RPUR foams formulation

| Ingredients | Amount (pbw[a]) |
|---|---|
| Polyols | 100 |
| Biobased polyols | |
| Commercial polyols | |
| Catalyst (DMCHA) | 0.25–2.0 |
| Blowing agent (distilled water) | 1.0–5.0 |
| Surfactant (TEGOSTAB® B8460) | 1.5–3.5 |
| PMDI (Suprasec® 5005) | NCO index[b] 100–250 |

[a] The amount of ingredients were calculated relate to parts per 100 wt% of polyols.

[b]NCO index refers to the excess amount of PMDI used over the theoretical equivalent amount that is required, expressed in percentage terms. The calculation of PMDI used in formulation is shown in APPENDIX C.

## 3.5 Foam properties measurement

### 3.5.1 Density

The apparent density of foams can be evaluate as the weight of cellular materials in air per unit volume of sample, after all foaming surface have been cut off, according to ASTM D 1622–08. The test specimens are generally cubic rectangular shape with dimension of 30 × 30 × 30 mm (Figure 3.11). The specimen is measured dimension using a vernier caliper and accurately weighed on a balance, which calculating its density as follows:

$$\text{Density (kg/m}^3\text{)} = \frac{\text{Sample weight}}{\text{Volume}}$$

The average of five measurements was taken to report.

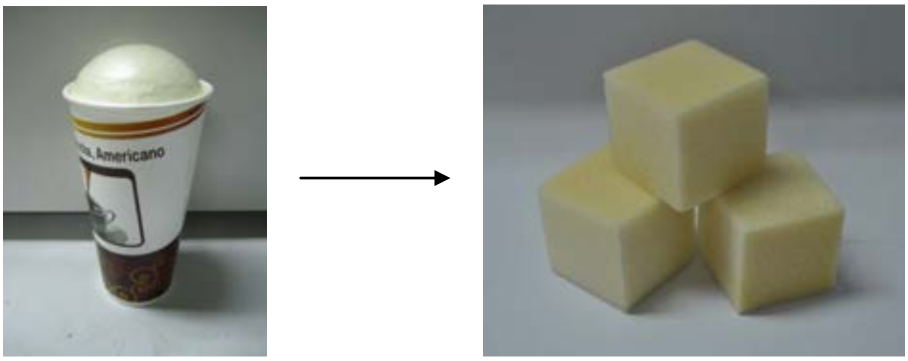


**Figure 3.9** Sample preparation for foam density measurement.

### 3.5.2 Compressive testing

Compressive tests of foams in parallel and perpendicular to the foam rise direction were performed using a Lloyd LRX universal testing machine. The dimension of the foam specimens was 30 × 30 × 30 mm (width × length × thickness). The rate of crosshead movement was fixed at 2.54 mm/min and the preload cell used was 0.1000 N. The compressive strength at 10% deformation of its original thickness was calculated and the average value of three specimens was reported.

### 3.5.3 Scanning electron microscope

The cellular structure of foams was observed using Hitachi S-4800 scanning electron microscope (SEM). The small portion of foams were cut and sliced carefully with sharp blade and stuck onto aluminum stubs. Then the samples were sputter-coated with gold before scanning under an accelerating voltage of 20 kV.

### 3.5.4 Thermal properties

#### 3.6.4.1 Thermogravimetric analysis (TGA)

The percentage weight loss and thermal degradation characteristics of RPUR foam samples were examined by thermogravimetric analysis (TGA) using Mettler Toledo TGA/SDTA 851$^{e}$. The initial amount of test samples was approximately 2–20 mg. The samples were heated from ambient to 800ºC at a heating rate of 10ºC/min under a nitrogen gas atmosphere.

#### 3.5.4.2 Thermal constant analyzer

The room temperature thermal conductivity was performed using the Hot Disk Thermal Constant Analyzer (TCA) TPS2500 (Hot Disk AB) with 50 × 50 × 20 mm (width × length × thickness) of sample size. Disk type was Kapton Insulation (sensor No. C7577, radius = 2.001 mm). Three measurements were made for each study and the average was reported.

# CHAPTER IV

# RESULTS AND DISCUSSION

## Rigid polyurethane foams from vegetable oil-based polyols

### 4.1 Synthesis and characterization of biopolyols

Hairy basil seed oil biopolyol (HBOB), sesame seed oil biopolyol (SSOB), and pumpkin seed oil biopolyol (POB) could be synthesized from hairy basil seed oil (HBO), sesame seed oil (SSO), and pumpkin seed oil (PO) by two steps reaction as shown in Figure 4.1. Due to the high content of unsaturated moieties in HBO, SSO and PO, they can be simply modified at unsaturated units to introduce multiple OH groups by firstly hydroxylation reaction with commonly used oxidizing agents such as peroxy acids. For this study, peroxyformic acids were generated by the reactions of formic acid with hydrogen peroxide to react at double bonds position of fatty acid chains. The occurring epoxide intermediates could be opened ring subsequently under strong acidic condition to form OH groups [15]. The OH number of all hydroxylated HBO, SSO and PO, was approximately 84–107 mg KOH/g which was unsuitable for RPUR foam preparation. After that, the alcoholysis reaction of hydroxylated HBO, SSO and PO with triethanolamine was carried out to increase their OH number. The synthesized biopolyols, namely HBOB, SSOB, and POB, composed mainly of triglyceride monoester containing the variation of hydroxylated fatty acid chains and a probably distribution of diesters, trimesters, fatty acid oligomer, and unreacted triethanolamine [8, 17, 56]. The resulting biopolyols did not require any further purification before used. Because of their hygroscopic in nature, they should be stored in an airtight container.

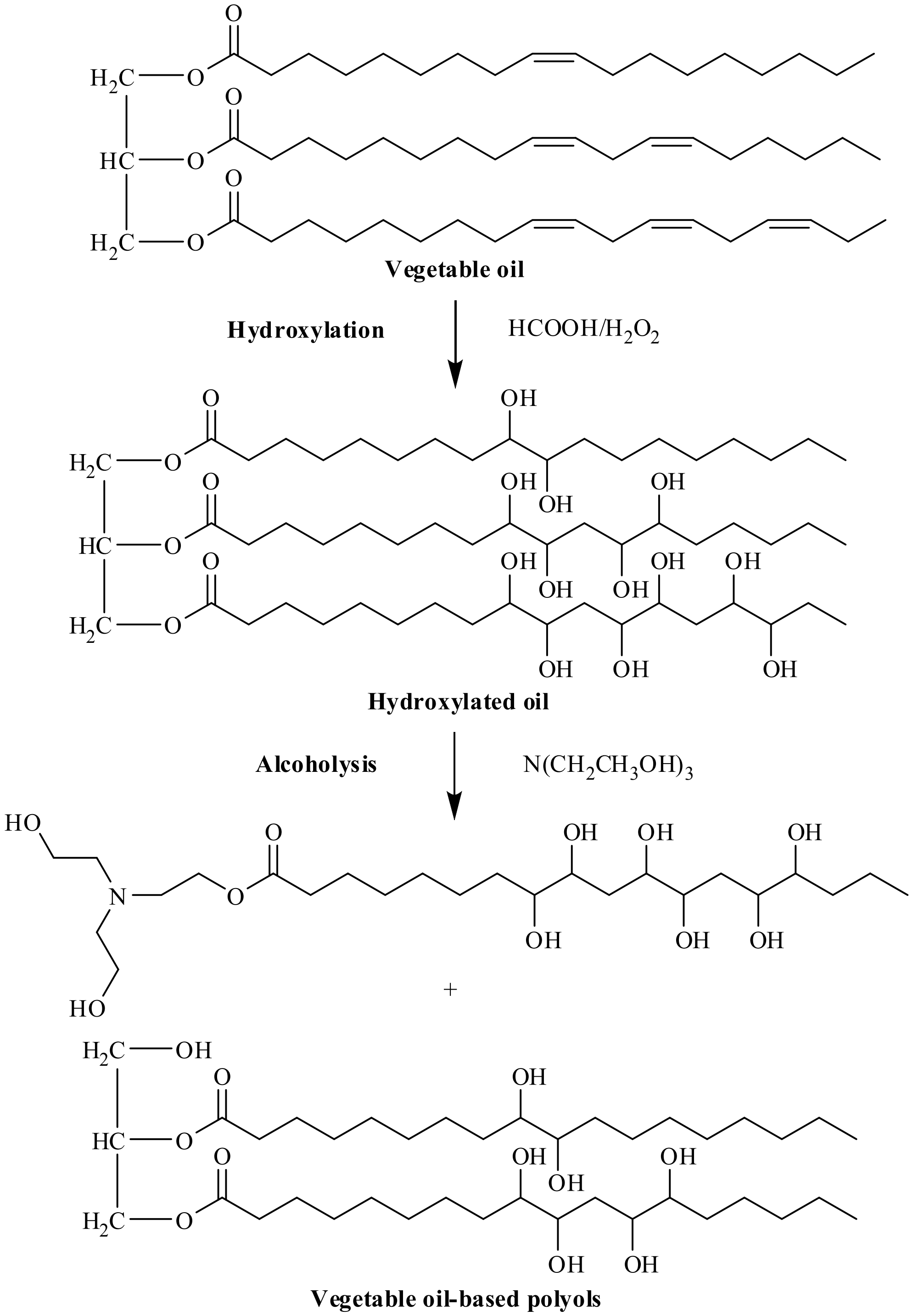


**Figure 4.1** The idealized synthesis route for preparation of vegetable oil-based polyols.

Table 4.1 shows the characteristics of unmodified and modified vegetable oils. Based on the unsaturated fatty acid composition, HBOB, SSOB, and POB had the OH value of 383, 351, and 340 mg KOH/g, respectively, which could be used with typical required for RPUR foam preparation. The viscosity of synthesized products was increased after the first and second modification since the increase of OH groups generates the strong inter- and intramolecular interaction. Furthermore, the higher viscosity of alcoholyzed products might have resulted from lithium hydroxystearate presenting in the reaction mixture. Generally, this lithium soap has been used as a thickening agent for grease production [69]. HBOB has the highest viscosity because of the highest OH number. Conversely, the viscosity of POB is lower than that of SSOB. Moreover, the trend of acid value and water content of all modified seed oils was raising up due to the synthetic process occurred under acidic condition and the presenting water as the byproduct [15, 19].

**Table 4.1** Physico-chemical properties of unmodified and modified vegetable oils

| | | HBO | SSO | PO |
|---|---|---|---|---|
| Unmodified | Color (visual) | Light yellow | Light blown | Dark green |
| | Viscosity (at 25ºC, cP) | 123±6 | 136±3 | 160±6 |
| | Acid value (mg KOH/g) | 8.23±0.05 | 7.23±0.18 | 2.13±0.14 |
| | Water content (wt%) | 0.10 | 0.08 | 0.09 |
| Hydroxylation | Color (visual) | Yellow | Brown | Dark green |
| | Viscosity (at 25ºC, cP) | 8620±16 | 7302±19 | 6722±19 |
| | OH number (mg KOH/g) | 106.82±1.51 | 85.64±0.91 | 84.25±1.04 |
| | Acid value (mg KOH/g) | 17.80±0.45 | 16.30±0.18 | 10.27±0.16 |
| | Water content (wt%) | 0.42 | 0.38 | 0.80 |
| Alcoholysis | Color (visual) | Brown | Brown | Dark green |
| | Viscosity (at 25ºC, cP) | 13314±30 | 11278±29 | 9862±47 |
| | OH number (mg KOH/g) | 382.51±1.84 | 351.03±3.84 | 340.24±6.80 |
| | Acid value (mg KOH/g) | 11.97±0.14 | 10.29±0.21 | 5.37±0.19 |
| | Water content (wt%) | 1.31 | 0.53 | 0.83 |

### 4.1.1 Fourier transform infrared spectroscopy of biopolyols

The ATR-IR spectroscopy was used for qualitative identification of the chemical reaction of the polyols formation by the assignments of the major signals of unmodified vegetable oils and modified seed oils. Since IR spectra of all neat, hydroxylated, and alcoholyzed seed oils were the similar characteristics, only the ATR-IR data of HBO is presented in Figure 4.2. The ATR-IR data of SSO and PO are shown in APPENDIX A (Figure A1 and A2, respectively).

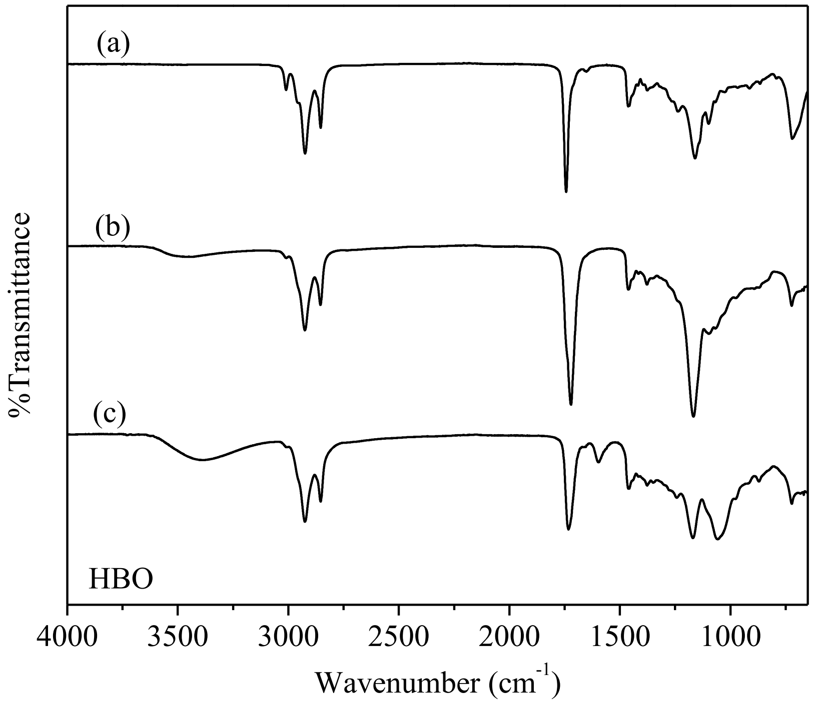


**Figure 4.2** ATR-IR spectra of unmodified and modified vegetable oils (a) hairy basil seed oil (HBO), (b) hydroxylated HBO and (c) alcoholyzed hydroxylated HBO (HBOB).

From the IR spectrum of virgin HBO (Figure 4.2a), the main peaks of triglyceride functional groups could be clearly observed. The peaks at 2925, 2853, and 1459 cm$^{-1}$ were attributed to the asymmetric, symmetric C–H stretching and C–H bending vibration of $-CH_2-$ groups, respectively. The strong signal at 1740 cm$^{-1}$ was assigned to C=O stretch of triglyceride ester groups. The weak absorption band (a shoulder) at 3014 $cm^{-1}$ corresponded to C–H stretching of aliphatic C=C–H group, whereas the very small peak at 1649 $cm^{-1}$ was attributed to C=C stretching vibration in *cis* conformation. Moreover, the C–O stretch of ester groups could be observed at 1164 $cm^{-1}$.

After modification, the most important difference is the presence of a broad band around 3300–3500 $cm^{-1}$ indicating an increase in hydroxyl groups by chemical reaction in agreement with higher OH numbers especially after alcoholysis. For hydroxylated HBO, the very small absorption peak of double bonds at 3014 and 1649 $cm^{-1}$ were found, while the hydroxyl band was presented as shown in Figures 4.2b and 4.2c. It indicated that an unsaturated position in fatty acid chains was almost completely functionalized. Additionally, the characteristic peak of secondary hydroxyl group was shown in hydroxylated HBO at around 1099 $cm^{-1}$ region. Furthermore, the ester carbonyl peak of modified HBO appeared broader and shifted from 1740 $cm^{-1}$ to 1720–1730 $cm^{-1}$, probably due to the esters and acids generated during chemical process.

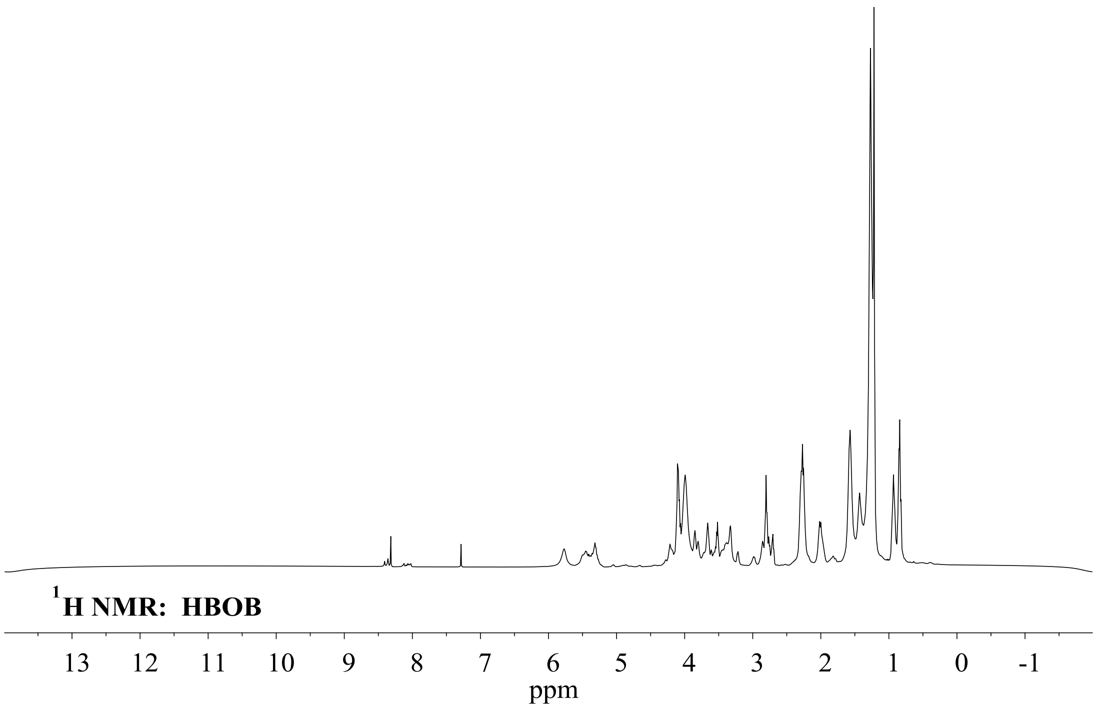
When the alcoholysis reaction with triethanolamine was carried out, the obtained biopolyols was the mixture of various esters of triglycerides. In addition, at signal 1596 $cm^{-1}$ corresponded to the amides of fatty acids that were occurred by aminolysis side reaction of triglyceride with triethanolamine [15, 19]. Besides, the band at 1057 $cm^{-1}$ appeared in alcoholyzed HBO arising from C–O stretching vibration of triethanolamine.

However, there was clearly no research that studied and reported the amount of free triethanolamine presenting in the obtained polyols. Therefore, the remaining triethanolamine in the synthesized polyols was firstly confirmed and determined in this study using electrospray ionization-mass spectrometry. Furthermore, free triethanolamine decreased the foaming times and increased the compressive strength of RPUR foams prepared from these vegetable oils-based polyols [70].

### 4.1.2 Nuclear magnetic resonance spectroscopy of biopolyols

The chemical structures of the obtained biopolyols were characterized using $^{1}H$ NMR and $^{13}C$ NMR analysis. Due to the synthesized products without purification were used as polyols for RPUR foam production, therefore their $^{1}H$ NMR and $^{13}C$ NMR spectra represented the characteristics of the main functional groups presenting in these biopolyols. The $^{1}H$ NMR and $^{13}C$ NMR spectra of resulting HBOB, SSOB, and POB in $CDCl_3$ are presented in Figures 4.3–4.5.

In the HBOB sample (Figure 4.3), the presence of signals at chemical shift ($\delta$) 5.40 ppm in $^{1}H$ NMR and at 125–135 ppm in $^{13}C$ NMR were assigned to the remaining unsaturated fatty acid (CH=CH) in polyols. Moreover, the small signals above $\delta$ 8.40 ppm in $^{1}H$ NMR and at 170–172 ppm in $^{13}C$ NMR corresponded to the acid groups. In Figures 4.3–4.5, SSOB and POB polyols had the same characteristic as HBOB polyols but the lower signal of olefinic protons was found. These NMR data gave the characteristics of resulting polyols agreeing with that identified by FTIR analysis.



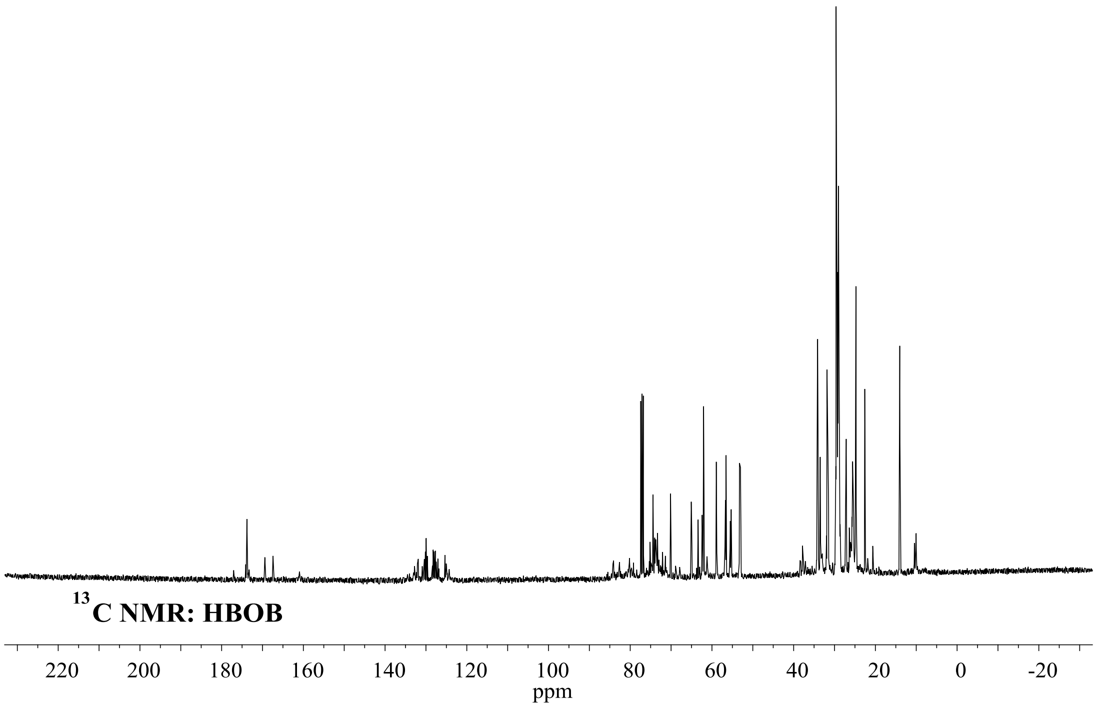


**Figure 4.3** $^1$H NMR and $^{13}$C NMR spectra in $CDCl_3$ of hairy basil seed oil-based polyol (HBOB).

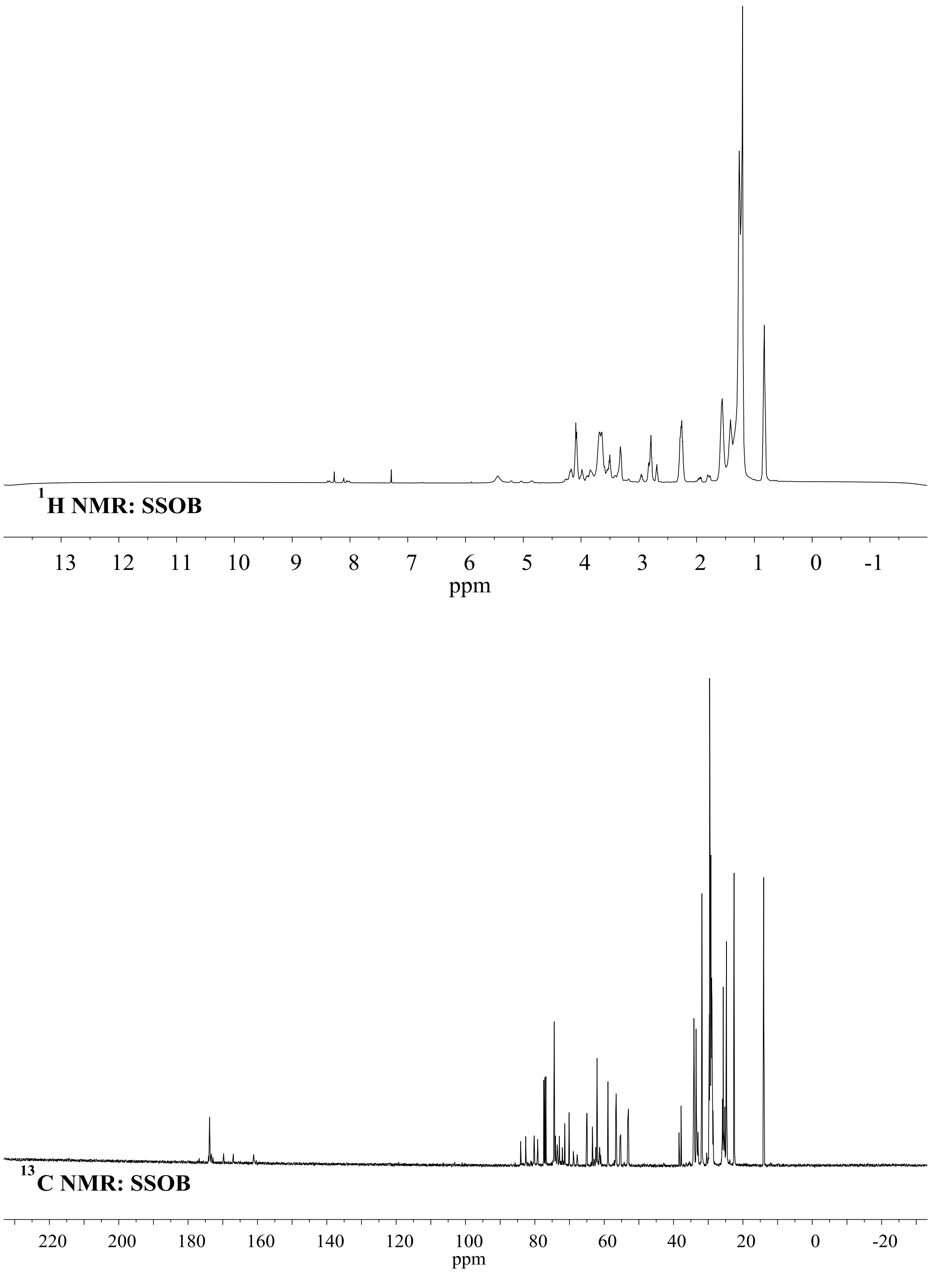


**Figure 4.4** $^1$H NMR and $^{13}$C NMR spectra in $CDCl_3$ of sesame seed oil-based polyol (SSOB).

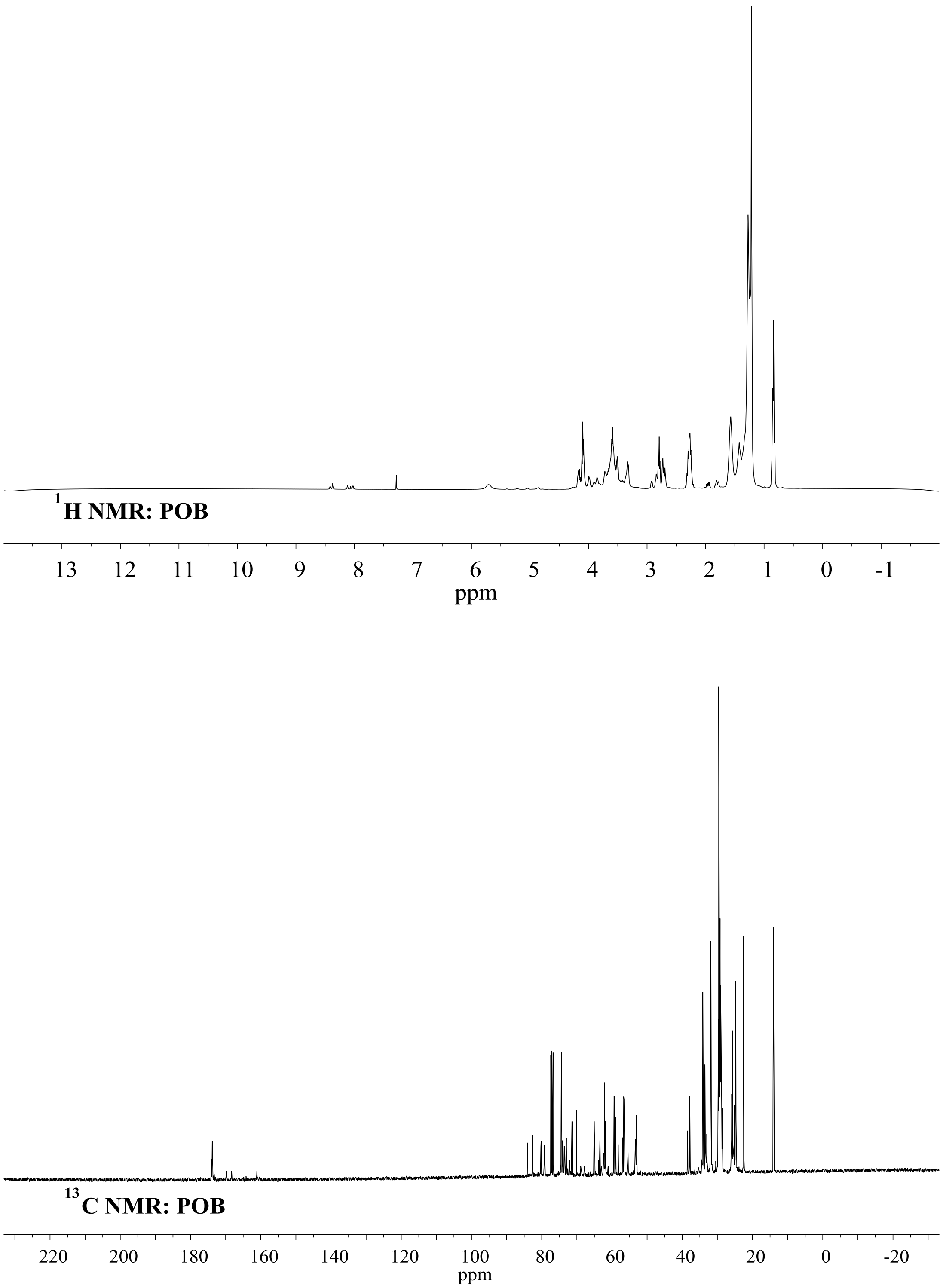


**Figure 4.5** $^1$H NMR and $^{13}$C NMR spectra in $CDCl_3$ of pumpkin seed oil-based polyol (POB).

### 4.1.3 Electrospray ionization-mass spectrometry of biopolyols

#### 4.1.3.1 Qualitative analysis of synthesized biopolyols

The synthesized vegetable oil-based polyols for rigid polyurethane foam preparation did not any purified before used and the foaming process and foam properties could be affected from the various components presenting in these biopolyols. Therefore, the obtained biopolyols were characterized to identify the individual structural components using electrospray ionization-mass spectrometer (ESI-MS) in positive ionization mode. Figure 4.6 represents the full scanned mass spectra of HBOB, SSOB, and POB, respectively and their extended spectra in the mass range 70–300, 300–550, and 550–850 m/z are shown in APPENDIX B (Figures B1-B3). The observed mass profiles of the major peaks are summarized in Table 4.2.

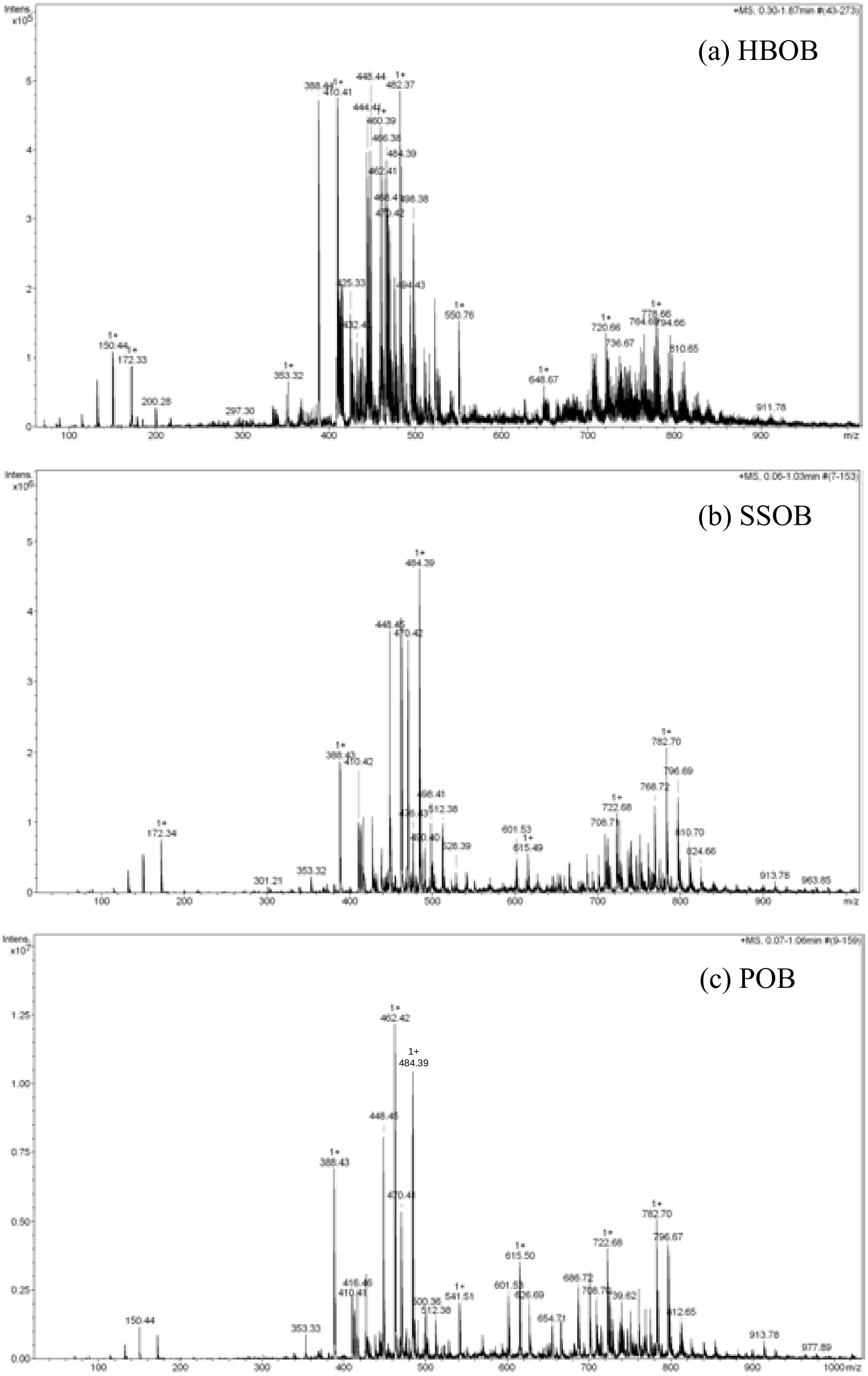


**Figure 4.6** The positive ion ESI-MS spectra of synthesized vegetable oil-based polyols scanned at 70–1000 m/z, (a) hairy basil seed oil-based polyol, (b) sesame seed oil-based polyol, and (c) pumpkin seed oil-based polyol, respectively.

**Table 4.2** The main structural components in synthesized vegetable oil-based polyols identified by ESI-MS in positive ionization mode

| Structure | Calculated mass | | Observed mass detected in synthesized biopolyols | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | HBOB | | SSOB | | POB | |
| | $[M+H]^+$ | $[M+Na]^+$ | $[M+H]^+$ | $[M+Na]^+$ | $[M+H]^+$ | $[M+Na]^+$ | $[M+H]^+$ | $[M+Na]^+$ |
| Esters with triethanolamine | | | | | | | | |
| Monoester-C(16:0)* | 388.34 | 410.32 | 388.44 | 410.41 | 388.43 | 410.42 | 388.43 | 410.41 |
| Monoester-C(18:0) | 416.37 | 438.36 | 416.45 | 438.43 | 416.46 | 438.44 | 416.46 | 438.43 |
| Monoester-C(18:1) | 414.36 | 436.34 | 414.43 | 436.41 | - | - | - | - |
| Monoester-C(18:2) | 412.34 | 434.31 | 412.43 | 434.40 | - | - | - | - |
| Monoester-C(18:0)-diol | 448.36 | 470.35 | 448.44 | 470.42 | 448.45 | 470.42 | 448.44 | 470.41 |
| Monoester-C(18:1)-diol | 446.35 | 468.33 | 446.42 | 468.41 | - | - | - | - |
| Monoester-C(18:2)-diol | 444.33 | 466.31 | 444.41 | 466.38 | - | - | - | - |
| Monoester-C(18:0)-tetraol $-H_2O$ | 462.34 | 484.32 | 462.41 | 484.39 | 462.41 | 484.39 | 462.42 | 484.39 |
| Monoester-C(18:1)-tetraol $-H_2O$ | 460.33 | 482.31 | 460.39 | 482.37 | - | - | - | - |
| Monoester-C(18:0)-hexaol $-H_2O$ | 494.43 | 516.31 | 494.43 | 516.37 | - | - | - | - |
| Monoester-C(18:0)-hexaol $-2H_2O$ | 476.32 | 498.30 | 476.42 | 498.38 | - | - | - | - |

*C(m:n); m = number of carbon atom in fatty acid chain, n = number of double bond remaining in fatty acid chain.

**Table 4.2** The main structural components in synthesized vegetable oil-based polyols identified by ESI-MS in positive ionization mode (continued)

| Structure | Calculated mass | | Observed mass detected in synthesized biopolyols | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | HBOB | | SSOB | | POB | |
| | $[M+H]^+$ | $[M+Na]^+$ | $[M+H]^+$ | $[M+Na]^+$ | $[M+H]^+$ | $[M+Na]^+$ | $[M+H]^+$ | $[M+Na]^+$ |
| Esters with triethanolamine | | | | | | | | |
| Diester-C(16:16:0)** | 626.57 | 648.55 | 626.68 | 648.66 | 626.69 | - | 626.69 | - |
| Diester-C(16:18:0) | 654.60 | 676.58 | 654.72 | 676.70 | 654.70 | - | 654.71 | 676.69 |
| Diester-C(18:18:0) | 682.63 | 704.62 | 682.68 | 704.67 | - | - | - | - |
| Diester-C(16:18:0)-diol | 686.59 | 708.57 | 686.69 | 708.68 | 686.73 | 708.71 | 686.72 | 708.70 |
| Diester-C(16:18:0)-tetraol –$H_2O$ | 700.57 | 722.55 | 700.67 | 722.66 | 700.70 | 722.68 | 700.70 | 722.68 |
| Diester-C(16:18:1)-tetraol –$H_2O$ | 698.56 | 720.54 | 698.68 | 720.65 | - | - | - | - |
| Diester-C(18:18:0)-diol | 714.62 | 736.61 | 714.71 | 736.67 | 714.75 | 736.73 | 714.75 | 736.71 |
| Diester-C(18:18:2)-diol | 710.61 | 732.57 | 710.69 | 732.70 | - | - | - | - |
| Diester-C(18:18:0)-tetraol | 746.61 | 768.60 | 746.68 | 768.68 | 746.75 | 768.72 | 746.74 | 768.71 |
| Diester-C(18:18:0)-tetraol –$H_2O$ | 728.60 | 750.59 | 728.68 | 750.69 | 728.71 | 750.71 | 728.70 | 750.71 |
| Diester-C(18:18:1)-tetraol | 744.60 | 766.58 | 744.68 | 766.69 | - | - | - | - |

**C(x:y:z); x = number of carbon atom in 1st fatty acid chain, y = number of carbon atom in 2nd fatty acid chain, and z = number of double bond remaining in fatty acid chain.

**Table 4.2** The main structural components in synthesized vegetable oil-based polyols identified by ESI-MS in positive ionization mode (continued)

| Structure | Calculated mass | | Observed mass detected in synthesized biopolyols | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | HBOB | | SSOB | | POB | |
| | $[M+H]^+$ | $[M+Na]^+$ | $[M+H]^+$ | $[M+Na]^+$ | $[M+H]^+$ | $[M+Na]^+$ | $[M+H]^+$ | $[M+Na]^+$ |
| <u>Esters with triethanolamine</u> | | | | | | | | |
| Diester-C(18:18:1)[**]-tetraol $-H_2O$ | 726.59 | 748.60 | 726.69 | 748.70 | - | - | - | - |
| Diester-C(18:18:2)-tetraol | 742.58 | 764.56 | 742.68 | 764.69 | - | - | - | - |
| Diester-C(18:18:2)-tetraol $-H_2O$ | 724.58 | 746.55 | 724.63 | 746.68 | - | - | - | - |
| Diester-C(18:18:3)-tetraol | 740.56 | 762.55 | 724.63 | 762.67 | - | - | - | - |
| Diester-C(18:18:0)-hexaol | 778.60 | 800.59 | 778.66 | - | 778.72 | - | - | - |
| Diester-C(18:18:0)-hexaol $-H_2O$ | 760.59 | 782.57 | 760.68 | 782.69 | 760.72 | 782.70 | 760.72 | 782.70 |
| Diester-C(18:18:1)-hexaol $-H_2O$ | 758.58 | 780.56 | 758.67 | 780.69 | - | - | - | - |
| Diester-C(18:18:3)-hexaol | 772.56 | 794.54 | 762.88 | 794.66 | - | - | - | - |
| Diester-C(18:18:3)-hexaol $-H_2O$ | 754.55 | 776.53 | 754.66 | 776.66 | - | - | - | - |
| Diester-C(18:18:0)-octaol $-H_2O$ | 792.58 | 814.56 | 792.69 | 814.67 | - | - | - | - |
| Diester-C(18:18:0)-octaol $-2H_2O$ | 774.57 | 796.55 | 774.67 | 796.67 | 774.70 | 796.69 | 774.70 | 796.67 |

[**] C(x:y:z); x = number of carbon atom in 1st fatty acid chain, y = number of carbon atom in 2nd fatty acid chain, and z = number of double bond remaining in fatty acid chain.

**Table 4.2** The main structural components in synthesized vegetable oil-based polyols identified by ESI-MS in positive ionization mode

| Structure | Calculated mass | | Observed mass detected in synthesized biopolyols | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | HBOB | | SSOB | | POB | |
| | $[M+H]^+$ | $[M+Na]^+$ | $[M+H]^+$ | $[M+Na]^+$ | $[M+H]^+$ | $[M+Na]^+$ | $[M+H]^+$ | $[M+Na]^+$ |
| <u>Esters with triglyceride</u> | | | | | | | | |
| Monoglyceride-C(16:0)* | 331.28 | 353.27 | - | 353.32 | - | 353.32 | - | 353.32 |
| Monoglyceride-C(18:0) | 359.32 | 381.30 | - | - | - | - | - | 381.35 |
| Monoglyceride-C(18:0)-diol | 391.31 | 413.29 | - | 413.38 | - | 413.36 | - | 413.35 |
| Monoglyceride-C(18:0)-tetraol –$H_2O$ | 405.28 | 427.27 | - | - | - | 427.33 | - | 427.33 |
| Monoglyceride-C(18:1)-tetraol –$H_2O$ | 403.27 | 425.25 | - | 425.33 | - | - | - | - |
| Diglyceride-C(16:16:0)** | 569.51 | 591.50 | 569.49 | - | 569.55 | - | 569.53 | - |
| Diglyceride-C(16:18:0) –$H_2O$ | 579.53 | 601.52 | - | - | - | 601.53 | - | 601.53 |
| Diglyceride-C(16:18:2) | 593.51 | 615.50 | - | - | - | 615.49 | - | 615.50 |
| Diglyceride-C(16:18:0)-diol | 629.53 | 651.52 | - | - | - | 651.54 | - | - |

*C(m:n); m = number of carbon atom in fatty acid chain, n = number of double bond remaining in fatty acid chain.

**C(x:y:z); x = number of carbon atom in 1st fatty acid chain, y = number of carbon atom in 2nd fatty acid chain, and z = number of double bond remaining in fatty acid chain.

**Table 4.2** The main structural components in synthesized vegetable oil-based polyols identified by ESI-MS in positive ionization mode

| Structure | Calculated mass | | Observed mass detected in synthesized biopolyols | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | HBOB | | SSOB | | POB | |
| | $[M+H]^+$ | $[M+Na]^+$ | $[M+H]^+$ | $[M+Na]^+$ | $[M+H]^+$ | $[M+Na]^+$ | $[M+H]^+$ | $[M+Na]^+$ |
| Esters with triglyceride | | | | | | | | |
| Diglyceride-C(18:18:0)**-tetraol –$H_2O$ | 643.51 | 665.50 | - | 665.55 | - | 665.60 | - | 665.61 |
| Diglyceride-C(18:18:0)-tetraol | 689.56 | 711.54 | - | - | - | 711.66 | - | 711.66 |
| Diglyceride-C(18:18:1) –tetraol | 687.54 | 709.52 | - | 709.67 | - | - | - | - |
| Diglyceride-C(18:18:2) –tetraol | 685.52 | 707.51 | - | 707.63 | - | - | - | - |
| Diglyceride-C(18:18:3) –tetraol | 683.51 | 705.49 | - | 705.65 | - | - | - | - |
| Diglyceride-C(18:18:0)-hexaol | 703.53 | 725.52 | - | 725.66 | - | 725.63 | - | 725.63 |
| Diglyceride-C(18:18:1)-hexaol | 701.52 | 723.50 | - | 723.62 | - | - | - | - |
| Diglyceride-C(18:18:2)-hexaol | 699.50 | 721.49 | - | 721.61 | - | - | - | - |
| Diglyceride-C(18:18:0)-octaol –$2H_2O$ | 717.51 | 739.50 | - | 739.63 | - | 739.61 | - | 739.62 |

**C(x:y:z); x = number of carbon atom in 1st fatty acid chain, y = number of carbon atom in 2nd fatty acid chain, and z = number of double bond remaining in fatty acid chain.

From ESI-MS data of the obtained biopolyols, the disappearance of glycerol peaks at $[M + Na]^+$, m/z 115) was observed. It indicated that these biopolyols synthesized from the alcoholysis of hydroxylated seed oils and triethanolamine had the variety of species including mainly mono- and diester containing the variation of hydroxylated fatty acid chains as presented in Figure 4.7. HBOB sample had the various esters with the uncompleted and completed hydroxylation at unsaturated carbon atom in fatty acid chain due to the virgin hairy basil seed oil had the high content of α-linolenic acid (54.26%). Additionally, the esters of triglyceride and the unreacted triethanolamine were detected in all polyol systems.

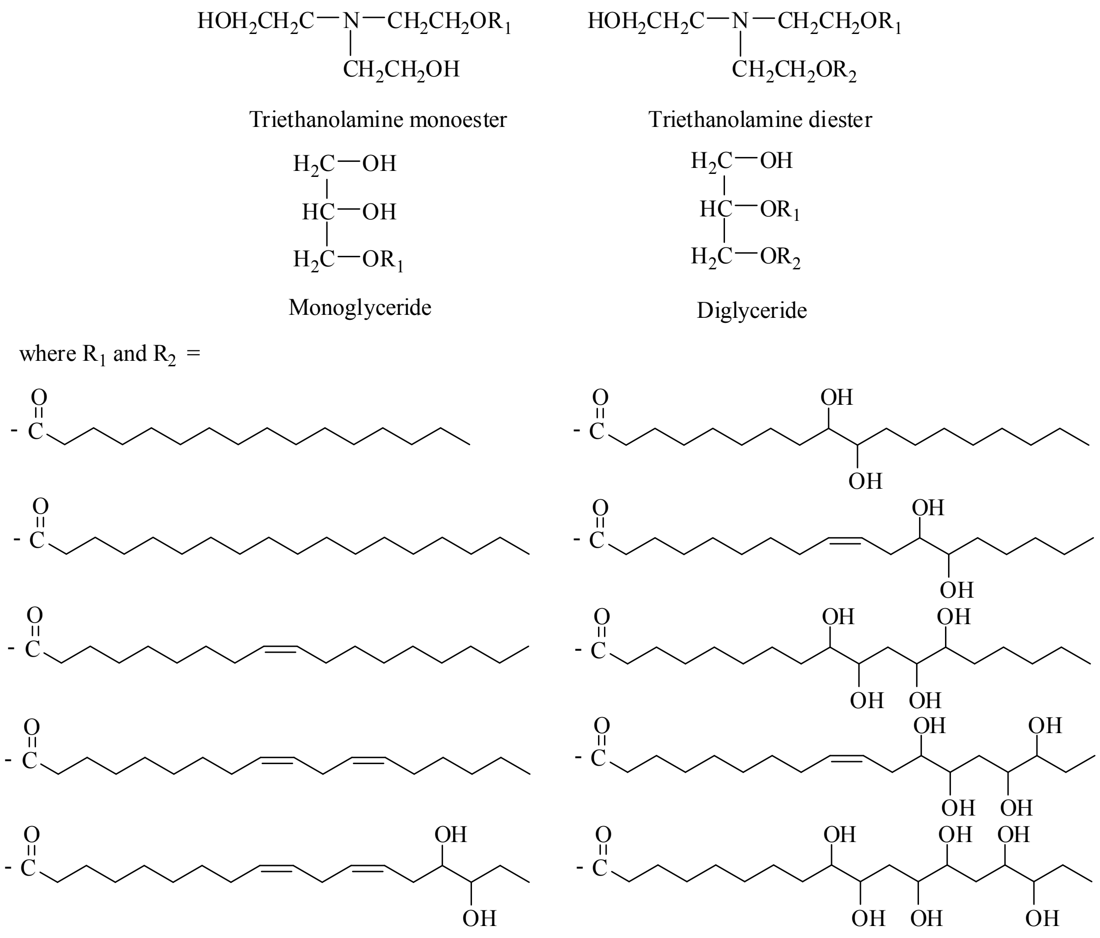


**Figure 4.7** The structures of esters with triethanolamine and triglyceride mostly presenting in synthesized vegetable oil-based polyols.

#### 4.1.3.2 Quantitative analysis of free triethanolamine presenting in biopolyols

In PUR foam system, isocyanates could react with any active hydrogen compounds mainly including polyols, water, and amines. From ESI-MS data, the presence of free triethanolamine was significantly detected that shown in Figure 4.8. Triethanolamine is the one in synthesized polyols which affected the properties of RPUR foams. It reduced the foaming time because it could act as catalyst for PUR foam system [70]. Moreover, it could be used as crosslink agent that provided the RPUR foams with high compressive strength. Therefore, the quantitative analysis of triethanolamine remaining in biopolyols (HBOB, SSOB, and POB) was studied and calculated from total mass spectra of triethanolamine peaks at $[M + H]^+$, m/z 150, $[M + Na]^+$, m/z 172, and $[M + K]^+$, m/z 188.

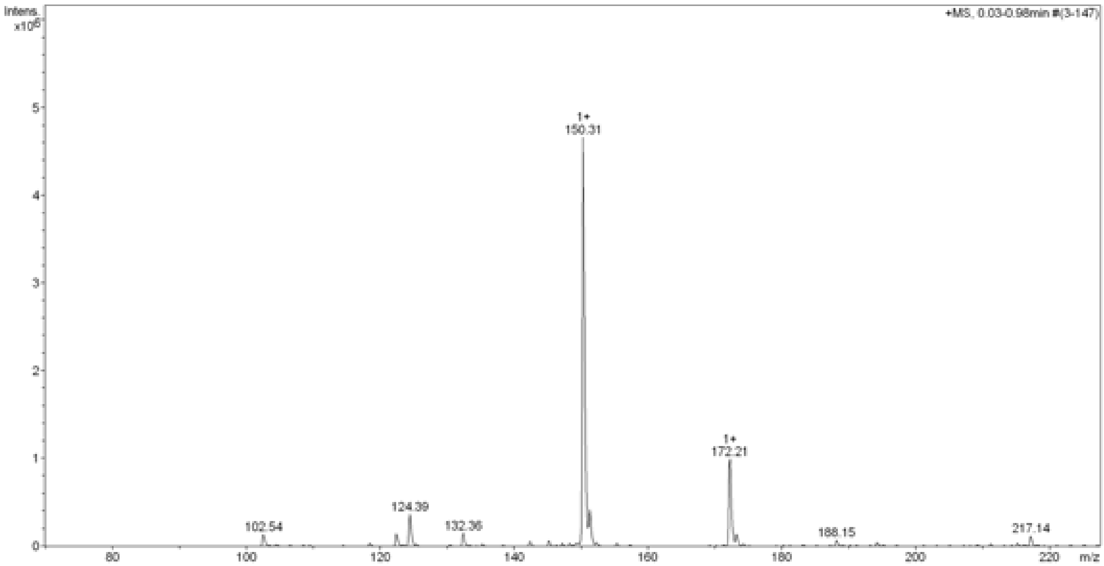


**Figure 4.8** The positive ion ESI-MS spectrum of triethanolamine.

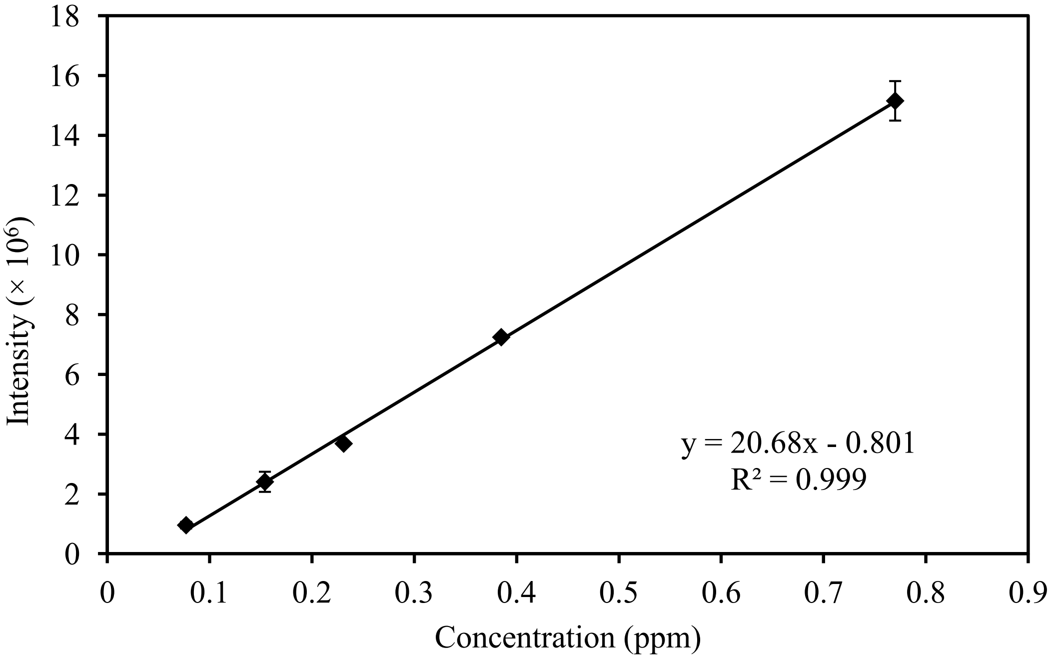


**Figure 4.9** The calibration curve of triethanolamine from ESI-MS data in a concentration range of 0.5–5.0 mg/L.

Figure 4.9 illustrates the calibration curve of triethanolamine from ESI-MS data and the amount of free triethanolamine in biopolyol samples are presented in Table 4.3. From Table 4.3, the amount of unreacted triethanolamine in the HBOB was relatively high. SSOB and POB had the lower content of free triethanolamine. That significantly affected to the foaming time and foam properties. Therefore, the further study should evaluate and optimize the triethanolamine content that used for synthesized polyols in the alcoholysis step.

**Table 4.3** The amount of unreacted triethanolamine in vegetable oil-based poyols detected by ESI-MS

| Vegetable oil-based polyols | Amount of free triethanolamine (wt% of polyol) |
|---|---|
| Hairy basil seed oil (HBOB) | 5.07±0.29 |
| Sesame seed oil (SSOB) | 1.95±0.19 |
| Pumpkin seed oil (POB) | 0.52±0.01 |

## 4.2 External appearance of rigid polyurethane (RPUR) foams from vegetable oil-based polyols (HBOB, SSOB, and POB)

To test the formation for vegetable oil-based PUR foams, the RPUR foams were prepared using starting material and resulting products from each reaction step. The external appearance of foams was the primary key parameter to further study. From Figure 4.10, it was found that the RPUR foams preparing from neat vegetable oils (HBO, SSO and PO) and hydroxylated HBO, SSO and PO showed the undesired appearance such as brittleness, shrinkage, and less uniform foam due to its less OH number. While the RPUR foams from alcoholized products (HBOB, SSOB and POB) exhibited the good appearance. Therefore, it confirmed that after the alcoholysis of hydroxylated oils provided a suitable OH number for RPUR foam preparation.

(a) Neat vegetable oils (HBO, SSO, and PO) (b) Hydroxylated HBO, SSO, and PO

(c) Alcoholized hydroxylated oil (HBOB, SSOB and POB)

**Figure 4.10** External appearance of RPUR foams prepared from (a) neat vegetable oil, (b) hydroxylated oils, and (c) alcololized oils.

## 4.3 Preparation of rigid polyurethane foams from vegetable oil-based polyols (HBOB, SSOB and POB)

First of all, the RPUR foams from HBOB, SSOB and POB were prepared according to a typical RPUR formulation comprising 100 parts by weight (pbw) of polyols, 2.0–3.0 pbw of water, 0.05–1.0 pbw of catalyst, and 2.5 pbw of surfactant which have been used to produce RPUR foams in our laboratory [57–61]. The isocyanate index (NCO index) of 100, 150, and 200 were used to screen the practical formulation in order to further study the effects of raw materials on the foaming behaviors and foam density. The resulting RPUR foams should provide a good appearance that mentioned before and the density were in a range 40–50 kg/m$^3$ as well as the reaction time (cream time, gel time, tack free time, and rise time) should not be too short for hand mixing method with good reproducibility. Table 4.4 shows the preliminary results of RPUR foams preparation from hairy basil oil-based foams. The PUR foams from pumpkin and sesame seed oil-based polyols are shown in Tables 4.5 and 4.6, respectively.

At NCO index of 100, all PUR foams showed shrinkage after cutting for a few days which was not suitable for further study of mechanical properties. When using 2.0 pbw of water, the reaction times were too short. On the other hand, the variable reaction times were presented at the small amount of catalyst. From these preliminary results, it indicated that the practical formulation used for RPUR foams from our vegetable oil-based formulation consisted of 100 pbw of polyols (HBOB, SSOB and POB), 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant.

**Table 4.4** The reaction time and density of RPUR foams prepared from hairy basil seed oil biopolyol (HBOB)

| Parameters[*] | NCO index | Reaction time (s) | | | | Density (kg/m$^3$) | External appearance |
|---|---|---|---|---|---|---|---|
| | | Cream time | Gel time | Tack free time | Rise Time | | |
| $H_2O$ 3.0 pbw<br>Catalyst 1.0 pbw | HBOB-100 | 18±1 | 25±1 | 141±2 | 122±3 | 28.42±0.29 | shrinkage |
| | HBOB-150 | 25±1 | 37±2 | 176±2 | 152±2 | 37.18±0.14 | goodness |
| | HBOB-200 | 30±2 | 44±2 | 240±2 | 213±3 | 44.53±0.25 | goodness |
| $H_2O$ 2.0 pbw<br>Catalyst 1.0 pbw | HBOB-100 | 13±2 | 19±4 | 129±3 | 104±5 | 32.41±1.01 | shrinkage |
| | HBOB-150 | 22±2 | 32±4 | 158±2 | 119±2 | 42.61±1.29 | goodness |
| | HBOB-200 | 26±1 | 36±4 | 210±6 | 169±6 | 47.74±0.81 | goodness |
| $H_2O$ 3.0 pbw<br>Catalyst 0.5 pbw | HBOB-100 | 19±3 | 34±3 | 226±5 | 185±3 | 30.71±0.42 | shrinkage |
| | HBOB-150 | 28±2 | 45±3 | 251±10 | 208±7 | 39.99±0.65 | goodness |
| | HBOB-200 | 34±2 | 59±5 | 330±8 | 273±6 | 49.55±0.30 | goodness |
| $H_2O$ 2.0 pbw<br>Catalyst 0.5 pbw | HBOB-100 | 13±1 | 31±2 | 215±4 | 174±4 | 34.38±0.35 | goodness |
| | HBOB-150 | 25±2 | 42±3 | 237±5 | 194±5 | 44.82±0.50 | goodness |
| | HBOB-200 | 34±2 | 57±3 | 293±7 | 268±6 | 55.75±0.56 | brittleness |

[*] RPUR formulation comprising 100 pbw of HBOB, 2.0–3.0 pbw of water, 0.05–1.0 pbw of catalyst, and 2.5 pbw of surfactant at NCO index as 100, 125, and 150.

**Table 4.5** The reaction time and density of RPUR foams prepared from sesame seed oil biopolyol (SSOB)

| Parameters* | NCO index | Reaction time (s) | | | | Density ($kg/m^3$) | External appearance |
|---|---|---|---|---|---|---|---|
| | | Cream time | Gel time | Tack free time | Rise Time | | |
| $H_2O$ 3.0 pbw<br>Catalyst 1.0 pbw | SSOB-100 | 14±1 | 24±2 | 127±3 | 107±2 | 27.74±0.17 | shrinkage |
| | SSOB-150 | 21±1 | 34±2 | 165±3 | 136±2 | 37.74±0.27 | shrinkage |
| | SSOB-200 | 25±1 | 43±1 | 224±2 | 175±2 | 43.01±0.13 | goodness |
| $H_2O$ 2.0 pbw<br>Catalyst 1.0 pbw | SSOB-100 | 13±1 | 19±2 | 100±5 | 78±6 | 31.93±0.55 | shrinkage |
| | SSOB-150 | 18±1 | 27±2 | 141±4 | 117±4 | 39.00±0.56 | goodness |
| | SSOB-200 | 21±1 | 39±2 | 193±6 | 147±6 | 47.60±0.53 | goodness |
| $H_2O$ 3.0 pbw<br>Catalyst 0.5 pbw | SSOB-100 | 17±1 | 26±2 | 183±5 | 151±4 | 30.44±0.36 | shrinkage |
| | SSOB-150 | 23±1 | 40±2 | 221±3 | 189±2 | 37.53±0.34 | goodness |
| | SSOB-200 | 29±2 | 51±2 | 303±4 | 258±5 | 46.71±0.45 | goodness |
| $H_2O$ 2.0 pbw<br>Catalyst 0.5 pbw | SSOB-100 | 15±1 | 25±2 | 166±5 | 147±3 | 34.23±0.40 | shrinkage |
| | SSOB-150 | 22±1 | 35±2 | 203±2 | 181±3 | 41.10±0.14 | goodness |
| | SSOB-200 | 26±1 | 50±2 | 278±5 | 246±4 | 51.87±0.37 | goodness |

* RPUR formulation comprising 100 pbw of SSOB, 2.0–3.0 pbw of water, 0.05–1.0 pbw of catalyst, and 2.5 pbw of surfactant at NCO index as 100, 150, and 200.

**Table 4.6** The reaction time and density of RPUR foams prepared from pumpkin seed oil biopolyol (POB)

| Parameters[*] | NCO index | Reaction time (s) | | | | Density (kg/m$^3$) | External appearance |
|---|---|---|---|---|---|---|---|
| | | Cream time | Gel time | Tack free time | Rise Time | | |
| $H_2O$ 3.0 pbw<br>Catalyst 1.0 pbw | POB-100 | 15±1 | 23±2 | 124±2 | 103±2 | 25.92±0.13 | shrinkage |
| | POB-150 | 21±1 | 32±2 | 156±2 | 124±2 | 33.97±0.13 | shrinkage |
| | POB-200 | 24±1 | 43±2 | 218±2 | 166±2 | 42.51±0.21 | goodness |
| $H_2O$ 2.0 pbw<br>Catalyst 1.0 pbw | POB-100 | 12±1 | 18±2 | 67±4 | 70±3 | 29.26±0.23 | shrinkage |
| | POB-150 | 16±1 | 25±2 | 130±7 | 107±5 | 36.00±0.66 | shrinkage |
| | POB-200 | 18±1 | 35±4 | 187±5 | 152±6 | 39.00±0.33 | goodness |
| $H_2O$ 3.0 pbw<br>Catalyst 0.5 pbw | POB-100 | 19±1 | 29±3 | 176±4 | 146±4 | 28.43±0.33 | shrinkage |
| | POB-150 | 24±2 | 37±2 | 217±4 | 172±5 | 33.97±0.13 | shrinkage |
| | POB-200 | 28±1 | 52±3 | 296±3 | 251±2 | 43.44±0.30 | goodness |
| $H_2O$ 2.0 pbw<br>Catalyst 0.5 pbw | POB-100 | 15±1 | 25±2 | 67±3 | 142±6 | 32.67±0.39 | shrinkage |
| | POB-150 | 19±1 | 33±2 | 214±4 | 167±5 | 39.00±0.22 | goodness |
| | POB-200 | 24±2 | 41±8 | 285±3 | 243±5 | 45.00±0.33 | goodness |

[*] RPUR formulation comprising 100 pbw of POB, 2.0–3.0 pbw of water, 0.05–1.0 pbw of catalyst, and 2.5 pbw of surfactant at NCO index as 100, 150, and 200.

In order to optimize the formulation for vegetable oil-based RPUR foam preparation, the effects of the reactive starting materials contents on the foaming behavior and foam density were studied by varying NCO index, blowing agent, catalyst, and surfactant contents based on the formulation that mentioned before. For example, the NCO index was varied, while the other parameters were fixed as 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant.

## 4.4 Study on the effects of reactive starting material contents on foaming behavior and foam density

### 4.4.1 Effects of NCO index on reaction time and foam density

On the urethane formation chemistry, one NCO group of polyisocyanate reacts with one OH group of polyols. The stoichiometric NCO/OH molar ratio equals 1.0, referred as 100 of NCO index. In practically, the higher NCO index was required to making RPUR foams. When using water as blowing agent, the excess NCO groups react with water under highly exothermic reaction to release carbon dioxide gas to make bubbles in RPUR matrix. The rigidity of PUR foam is also occurred owing to the addition crosslink networks as polyisocyanurates (PIR), allophanate, and biuret tend to increase in the PUR systems [27].

To study the effect of NCO index, the calculated amount of PMDI was used at varying NCO indices from 100 to 250, the water, catalyst, and surfactant levels be fixing at 3.0, 1.0, and 2.5 pbw, respectively and their appearance was shown in Figure 4.11. The reaction times of RPUR foams prepared from three vegetable oil biopolyols (HBOB, SSOB, POB) were compared with those prepared from two commercial polyols (Raypol$^{®}$ 8360 and Raypol$^{®}$ 4218) in Table 4.7. It was found that as NCO index further increased, the reaction times were longer. The reaction time of the control foams made from Raypol$^{®}$ 8360 are shorter than those of Raypol$^{®}$ 4218 and biopolyols. The incidence could be attributed to primary OH groups displayed in Raypol$^{®}$ 8360 polyols and it has less OH number. Whereas Raypol$^{®}$ 4218 and biopolyols comprises mostly secondary OH groups. It is known that the reactivity of primary OH groups with isocyanate is higher about 10 times than similar polyols with secondary OH groups [2]. In addition, HBOB-based foams with the highest OH number are the longest reaction times than SSOB- and POB-based foams. Since the amount of PMDI used for preparing RPUR foams was calculated relative to the OH number of polyols [2], the equivalent weight of polyols is lower with higher OH number and the higher PMDI content is required for foam production. Furthermore, the increasing NCO index not only increased the reaction times but also increased the density of foam because of the higher amount of PMDI using in formulation. Nevertheless, the optimal NCO index was utilized with the desired density of RPUR foams (40–45 kg/m$^3$) as well as the good appearance and performance of water-blown RPUR foams. At the high level of NCO content, the friability and brittleness of the resulting foams were found because of the additional network formation, and the solubility of foaming chemicals was poor [27]. Therefore, the suitable PMDI level for HBOB-, SSOB-, POB- and Raypol® 8360-based foams systems were performed with NCO index at 175 while the Raypol® 4218-based foam accomplished this goal with 150 of NCO index.

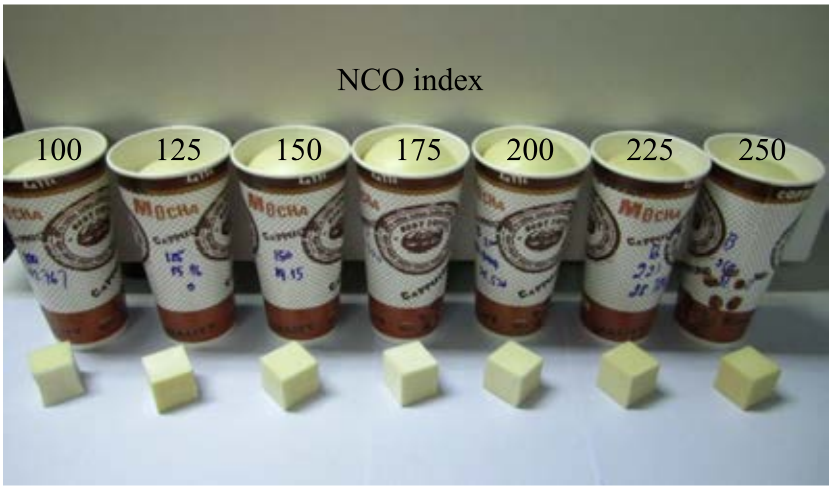


**Figure 4.11** The external appearance of HBOB-based foams prepared at NCO indexes of 100–250, 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant.

**Table 4.7** Effects of isocyanate index on reaction time and density of RPUR foams prepared at NCO indexes of 100–250, 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant

| NCO index* | Reaction time (s) | | | | Density (kg/m$^3$) | External appearance |
|---|---|---|---|---|---|---|
| | Cream time | Gel time | Tack free time | Rise Time | | |
| HBOB-100 | 19±1 | 26±1 | 139±2 | 121±4 | 28.39±0.17 | shrinkage |
| HBOB-125 | 21±1 | 31±1 | 156±2 | 138±1 | 32.55±0.42 | shrinkage |
| HBOB-150 | 24±1 | 36±1 | 176±2 | 150±2 | 36.63±0.42 | goodness |
| HBOB-175 | 26±1 | 40±1 | 211±2 | 175±4 | 42.41±0.17 | goodness |
| HBOB-200 | 29±1 | 44±1 | 238±2 | 205±4 | 45.12±0.47 | goodness |
| HBOB-225 | 32±2 | 49±1 | 283±3 | 228±3 | 48.81±0.48 | goodness |
| HBOB-250 | 35±1 | 55±1 | 338±3 | 273±5 | 53.72±0.53 | goodness |
| SSOB-100 | 16±1 | 22±1 | 128±3 | 106±3 | 26.73±0.29 | shrinkage |
| SSOB-125 | 19±1 | 28±1 | 144±3 | 120±4 | 30.64±0.45 | shrinkage |
| SSOB-150 | 21±1 | 33±1 | 161±3 | 138±2 | 34.99±0.42 | shrinkage |
| SSOB-175 | 23±2 | 37±1 | 188±4 | 156±4 | 40.77±0.34 | goodness |
| SSOB-200 | 25±1 | 42±1 | 217±3 | 171±2 | 43.44±0.42 | goodness |
| SSOB-225 | 27±1 | 46±2 | 262±3 | 202±3 | 46.87±0.28 | goodness |
| SSOB-250 | 30±2 | 52±2 | 321±3 | 245±5 | 51.67±0.30 | goodness |
| POB-100 | 16±1 | 21±2 | 123±3 | 102±3 | 26.16±0.33 | shrinkage |
| POB-125 | 18±1 | 26±2 | 138±4 | 112±4 | 29.51±0.35 | shrinkage |
| POB-150 | 20±1 | 31±1 | 158±2 | 128±3 | 34.19±0.34 | shrinkage |
| POB-175 | 22±1 | 36±1 | 181±2 | 145±4 | 40.16±0.40 | goodness |
| POB-200 | 24±1 | 40±1 | 216±5 | 165±4 | 42.81 ± 0.32 | goodness |
| POB-225 | 26±1 | 44±1 | 258±2 | 192±3 | 45.43 ± 0.29 | goodness |
| POB-250 | 29±1 | 50±1 | 309±3 | 231±4 | 49.82 ± 0.34 | goodness |

[*] A calculation of PMDI used in formulation is shown in APPENDIX D (Tables D4-D6).

**Table 4.7** Effects of isocyanate index on reaction time and density of RPUR foams prepared at NCO indexes of 100–250, 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant (continued)

| NCO index[*] | Reaction time (s) | | | | Density (kg/m$^3$) | External appearance |
|---|---|---|---|---|---|---|
| | Cream time | Gel time | Tack free time | Rise Time | | |
| 8360-100 | 13±1 | 20±1 | 92±2 | 55±1 | 25.81±0.32 | shrinkage |
| 8360-125 | 15±1 | 23±1 | 120±1 | 64±1 | 30.41±0.42 | goodness |
| 8360-150 | 16±1 | 24±1 | 136±4 | 70±2 | 33.87±0.31 | goodness |
| 8360-175 | 17±1 | 26±2 | 152±2 | 90±3 | 39.21±0.43 | goodness |
| 8360-200 | 18±1 | 32±2 | 175±3 | 109±2 | 42.85±0.40 | brittleness |
| 8360-225 | 20±1 | 36±1 | 205±4 | 127±2 | 44.94±0.17 | brittleness |
| 8360-250 | 22±1 | 41±1 | 235±4 | 160±2 | 48.04±0.27 | brittleness |
| 4218-100 | 23±1 | 31±1 | 174±1 | 146±2 | 37.54±0.46 | goodness |
| 4218-125 | 25±1 | 35±1 | 187±2 | 151±2 | 40.12±0.18 | goodness |
| 4218-150 | 28±1 | 40±1 | 205±3 | 176±4 | 43.34±0.43 | goodness |
| 4218-175 | 32±1 | 44±1 | 242±3 | 186±3 | 45.68±0.37 | goodness |
| 4218-200 | 34±1 | 50±2 | 288±3 | 216±4 | 49.25±0.25 | goodness |
| 4218-225 | 36±1 | 55±1 | 323±2 | 232±3 | 53.77±0.48 | brittleness |
| 4218-250 | 42±1 | 61±1 | 364±1 | 260±1 | 59.92±0.64 | brittleness |

[*] A calculation of PMDI used in formulation is shown in APPENDIX D (Tables D2-D3).

### 4.4.2 Effects of blowing agent contents on reaction time and foam density

Table 4.8 and Figure 4.12 show the effect of distilled water content on the reaction profile and foam density. The distilled water content was varied from 1.0 to 5.0 pbw at NCO index as 175 and the control amount of 1.0 pbw of catalyst and 2.5 pbw of surfactant. In these results, the reaction times were slower with the rising of water contents. Since water is one of active hydrogen component that reacted with isocyanate and used for foam formulation calculation, the actual amount of PMDI is increased with the increase of water quantity. At high water content, the density of foams was reduced due to a lot of heat was produced from the highly exothermic reaction between water and isocyanate so too much carbon dioxide was released and decreased the foam volume. At the water content 4.0 and 5.0 pbw, the resulting foams exhibited shrinkage after curing. Therefore, the optimal water content was manipulated on the provided proper density. In addition to the vegetable oil-based polyols had a high viscous liquid; therefore the heterogeneous system of PUR foam components were occurred with the adding high amount of water.

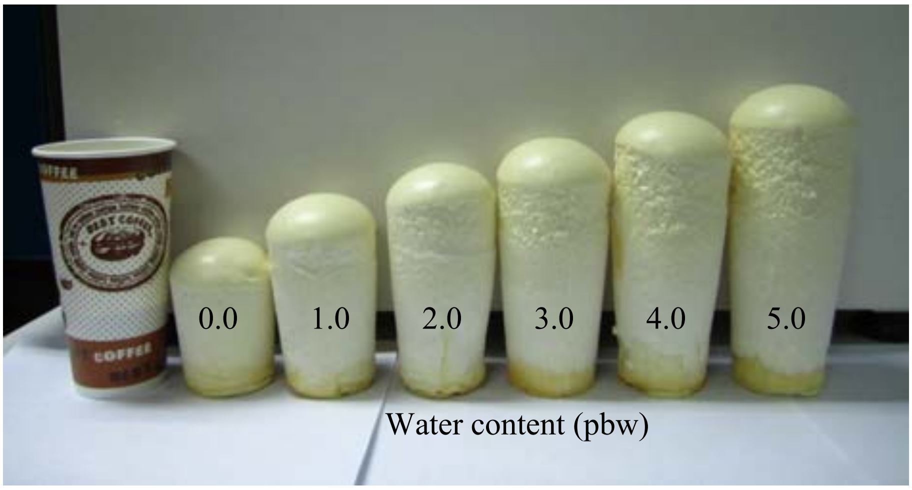


**Figure 4.12** The external appearance of HBOB-based foams prepared at varying water content of 1.0–5.0 pbw, NCO index of 175, 1.0 pbw of catalyst, and 2.5 pbw of surfactant.

**Table 4.8** Effects of blowing agent (water) contents on reaction time and density of RPUR foams prepared at varying water content of 1.0–5.0 pbw, NCO index of 175, 1.0 pbw of catalyst, and 2.5 pbw of surfactant

| | Parameters* | Amount of Distilled Water (pbw) | | | | |
|---|---|---|---|---|---|---|
| | | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
| HBOB | Cream time (s) | 20±2 | 24±1 | 26±1 | 27±1 | 28±2 |
| | Gel time (s) | 34±1 | 37±2 | 40±1 | 42±1 | 45±1 |
| | Tack free time (s) | 187±4 | 205±3 | 211±2 | 235±3 | 268±4 |
| | Rise time (s) | 148±3 | 165±4 | 175±4 | 189±3 | 204±4 |
| | Density (kg/m$^3$) | 47.73±0.25 | 45.06±0.13 | 42.41±0.17 | 39.97±0.13 | 35.22±0.21 |
| SSOB | Cream time (s) | 20±1 | 21±1 | 23±1 | 25±1 | 27±1 |
| | Gel time (s) | 31±1 | 35±1 | 37±1 | 40±1 | 42±1 |
| | Tack free time (s) | 138±4 | 162±3 | 188±4 | 196±3 | 212±3 |
| | Rise time (s) | 110±2 | 139±3 | 156±4 | 166±4 | 186±4 |
| | Density (kg/m$^3$) | 45.73±0.41 | 42.49±0.43 | 40.77±0.34 | 37.15±0.13 | 33.93±0.28 |
| POB | Cream time (s) | 17±1 | 21±1 | 22±1 | 24±1 | 25±1 |
| | Gel time (s) | 30±1 | 34±1 | 36±1 | 39±1 | 42±1 |
| | Tack free time (s) | 132±3 | 159±4 | 181±2 | 190±2 | 203±6 |
| | Rise time (s) | 101±3 | 131±4 | 145±4 | 156±4 | 177±3 |
| | Density (kg/m$^3$) | 44.51±0.30 | 41.37±0.49 | 40.16±0.40 | 36.78±0.24 | 32.73±0.33 |

* A calculation of PMDI used in formulation is shown in APPENDIX D (Tables D4-D6).

**Table 4.8** Effects of blowing agent (water) contents on reaction time and density of RPUR foams prepared at varying water content of 1.0–5.0 pbw, NCO index of 175, 1.0 pbw of catalyst, and 2.5 pbw of surfactant (continued)

| | Parameters[*] | Amount of Distilled Water (pbw) | | | | |
|---|---|---|---|---|---|---|
| | | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
| Raypol® 8360 | Cream time (s) | 13±1 | 16±1 | 17±1 | 18±1 | 20±1 |
| | Gel time (s) | 22±1 | 25±1 | 27±1 | 29±1 | 32±2 |
| | Tack free time (s) | 119±1 | 140±2 | 152±2 | 163±5 | 181±4 |
| | Rise time (s) | 71±5 | 78±2 | 90±3 | 99±4 | 116±4 |
| | Density (kg/m$^3$) | 43.69±0.45 | 41.79±0.39 | 39.21±0.43 | 34.90±0.44 | 30.41±0.33 |
| Raypol® 4218 | Cream time (s) | 26±1 | 29±1 | 32±1 | 34±1 | 35±1 |
| | Gel time (s) | 38±1 | 42±1 | 44±1 | 46±1 | 48±2 |
| | Tack free time (s) | 200±4 | 221±4 | 242±3 | 261±3 | 285±4 |
| | Rise time (s) | 133±4 | 168±2 | 186±3 | 203±3 | 222±5 |
| | Density (kg/m$^3$) | 51.86±0.23 | 47.87±0.31 | 45.68±0.37 | 42.43±0.36 | 38.30±0.17 |

[*] A calculation of PMDI used in formulation is shown in APPENDIX D (Tables D2-D3).

### 4.4.3 Effects of catalyst contents on reaction time and foam density

The influence of catalyst levels on the reaction time and the density of foams were examined by the variation of catalyst level in the range 0.25–2.00 pbw (Figure 4.13) under a condition of NCO index as 175, distilled water and surfactant content as 3.0 and 2.5 pbw, respectively. DMCHA was selected as foaming catalyst for this work. It is widely used for RPUR foam manufacturing. From Table 4.9, it is noticed that reaction time decreased with an enhancement of catalyst level. As the results, it is noted that DMCHA acts as a dual function catalyst which accelerates strongly gelling reaction and balancing blowing reaction [1]. This data was supported by the effect of blowing agent on the reaction times that mentioned before. Moreover, the foam density was decreased with the increasing catalyst level. The adjustment of catalyst level could promote the reaction rate; however, the foam cell was not uniform and hard to control the foaming process with the high catalyst dosage. Therefore, a level 1.0 pbw of DMCHA catalyst was used for making foams which was also to solve the reaction delay by the reaction of free acids in system with base (amine) catalyst [51].

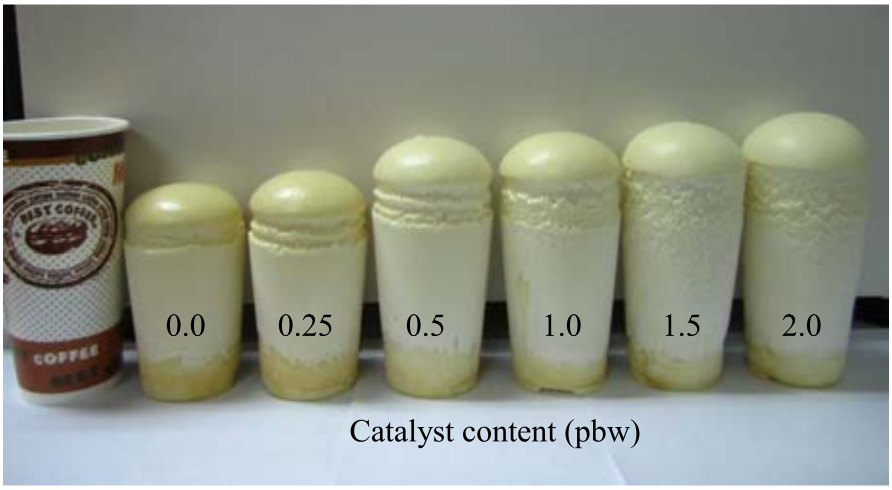


**Figure 4.13** The external appearance of HBOB-based foams prepared at varying catalyst content at 0.25–2.0 pbw, NCO index of 175, 3.0 pbw of water, and 2.5 pbw of surfactant.

**Table 4.9** Effects of catalyst (DMCHA) contents on reaction time and density of RPUR foams prepared at varying catalyst content at 0.25–2.0 pbw, NCO index of 175, 3.0 pbw of water, and 2.5 pbw of surfactant

| | Parameters* | Amount of DMCHA (pbw) | | | | |
|---|---|---|---|---|---|---|
| | | 0.25 | 0.50 | 1.00 | 1.50 | 2.00 |
| HBOB | Cream time (s) | 31±1 | 29±1 | 26±1 | 24±1 | 20±1 |
| | Gel time (s) | 48±1 | 43±1 | 40±1 | 35±1 | 30±1 |
| | Tack free time (s) | 294±3 | 235±4 | 211±2 | 180±3 | 141±4 |
| | Rise time (s) | 224±4 | 193±4 | 175±4 | 153±2 | 108±2 |
| | Density (kg/m$^3$) | 45.88±0.21 | 43.27±0.16 | 42.41±0.17 | 38.92±0.14 | 39.26±0.20 |
| SSOB | Cream time (s) | 28±1 | 25±1 | 23±1 | 21±1 | 18±1 |
| | Gel time (s) | 45±1 | 41±1 | 37±1 | 32±2 | 28±1 |
| | Tack free time (s) | 273±4 | 228±2 | 188±4 | 155±4 | 128±2 |
| | Rise time (s) | 194±2 | 174±2 | 156±4 | 133±4 | 86±2 |
| | Density (kg/m$^3$) | 44.54±0.27 | 42.02±0.25 | 40.77±0.34 | 37.54±0.46 | 33.99±0.12 |
| POB | Cream time (s) | 27±1 | 24±1 | 22±1 | 19±1 | 16±1 |
| | Gel time (s) | 44±1 | 40±1 | 36±1 | 32±1 | 27±1 |
| | Tack free time (s) | 262±2 | 211±5 | 181±2 | 149±4 | 112±3 |
| | Rise time (s) | 188±4 | 165±3 | 145±4 | 131±3 | 76±2 |
| | Density (kg/m$^3$) | 43.37±0.19 | 41.25±0.21 | 40.16±0.40 | 36.13±0.11 | 33.20±0.18 |

[*] A calculation of PMDI used in formulation is shown in APPENDIX D (Tables D4-D6).

**Table 4.9** Effects of catalyst (DMCHA) contents on reaction time and density of RPUR foams prepared at varying catalyst content at 0.25–2.0 pbw, NCO index of 175, 3.0 pbw of water, and 2.5 pbw of surfactant (continued)

| | Parameters* | Amount of DMCHA (pbw) | | | | |
|---|---|---|---|---|---|---|
| | | 0.25 | 0.50 | 1.00 | 1.50 | 2.00 |
| Raypol® 8360 | Cream time (s) | 17±1 | 19±1 | 17±1 | 18±1 | 19±1 |
| | Gel time (s) | 27±1 | 29±1 | 27±1 | 27±1 | 29±1 |
| | Tack free time (s) | 153±4 | 154±3 | 152±2 | 156±4 | 157±3 |
| | Rise time (s) | 84±4 | 90±4 | 90±3 | 91±2 | 93±2 |
| | Density (kg/m$^3$) | 39.41±0.33 | 40.12±0.13 | 39.21±0.43 | 39.68±0.37 | 40.86±0.34 |
| Raypol® 4218 | Cream time (s) | 31±1 | 31±1 | 32±1 | 31±1 | 32±2 |
| | Gel time (s) | 42±1 | 44±1 | 44±1 | 43±2 | 45±1 |
| | Tack free time (s) | 243±3 | 242±2 | 242±3 | 240±4 | 242±4 |
| | Rise time (s) | 185±4 | 184±3 | 186±3 | 183±4 | 187±3 |
| | Density (kg/m$^3$) | 44.70±0.22 | 45.25±0.26 | 45.68±0.37 | 45.58±0.40 | 46.40±0.33 |

[*] A calculation of PMDI used in formulation is shown in APPENDIX D (Tables D2-D3).

### 4.4.4 Effects of surfactant contents on foaming behavior and foam density

Furthermore, the effect of the surfactant content was investigated. With the different surfactant level at 1.5–3.5 pbw among the quantity of the other parameters be fixed, the surfactant content had no significant effect on either the foaming behavior or foam density as revealed in Table 4.10. The sufficient amount of surfactant could reduce surface tension between incompatible foaming ingredients such as hydrophobic polyols, hydrophilic blowing agent and catalyst in mixing step. However, the main function of polysiloxane surfactant was to stabilize foam cells during gas bubble nucleation in polymer matrix and controlled closed cell content [1–2]. The excess surfactant level could act as plasticizer function; hence the proper quantity of surfactant was used to obtain the desired rigidity of foams [50].

**Table 4.10** Effects of surfactant contents on reaction time and density of RPUR foams prepared at varying surfactant (TEGOSTAB® B8460) content at 1.5–3.5 pbw, NCO index of 175, 3.0 pbw of water, and 1.0 pbw of catalyst

| | Parameters[*] | Amount of TEGOSTAB® B8460 (pbw) | | | | |
|---|---|---|---|---|---|---|
| | | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 |
| HBOB | Cream time (s) | 24±1 | 25±1 | 26±1 | 26±1 | 28±1 |
| | Gel time (s) | 40±1 | 41±1 | 40±1 | 42±1 | 44±1 |
| | Tack free time (s) | 208±3 | 211±4 | 211±2 | 217±2 | 220±2 |
| | Rise time (s) | 173±3 | 173±3 | 175±4 | 175±3 | 179±3 |
| | Density ($kg/m^3$) | 40.93±0.21 | 42.30±0.15 | 42.41±0.17 | 42.95±0.33 | 44.88±0.14 |
| SSOB | Cream time (s) | 22±1 | 22±1 | 23±1 | 25±1 | 25±1 |
| | Gel time (s) | 35±1 | 36±1 | 37±1 | 39±1 | 40±1 |
| | Tack free time (s) | 186±3 | 184±3 | 188±4 | 194±2 | 190±4 |
| | Rise time (s) | 157±3 | 154±3 | 156±4 | 165±4 | 158±2 |
| | Density ($kg/m^3$) | 40.11±0.13 | 39.64±0.32 | 40.77±0.34 | 42.26±0.46 | 39.97±0.26 |
| POB | Cream time (s) | 22±1 | 24±1 | 22±1 | 23±1 | 24±1 |
| | Gel time (s) | 35±1 | 37±1 | 36±1 | 38±2 | 37±2 |
| | Tack free time (s) | 182±3 | 184±3 | 181±2 | 184±4 | 188±2 |
| | Rise time (s) | 143±3 | 147±2 | 145±4 | 143±4 | 148±2 |
| | Density ($kg/m^3$) | 39.02±0.30 | 40.23±0.11 | 40.16±0.40 | 41.14±0.13 | 41.48±0.28 |

[*] A calculation of PMDI used in formulation is shown in APPENDIX D (Tables D4-D6).

**Table 4.10** Effects of surfactant contents on reaction time and density of RPUR foams prepared at varying surfactant (TEGOSTAB® B8460) content at 1.5–3.5 pbw, NCO index of 175, 3.0 pbw of water, and 1.0 pbw of catalyst (continued)

| | Parameters[*] | Amount of TEGOSTAB® B8460 (pbw) | | | | |
|---|---|---|---|---|---|---|
| | | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 |
| Raypol® 8360 | Cream time (s) | 17±1 | 19±1 | 17±1 | 18±1 | 19±1 |
| | Gel time (s) | 27±1 | 29±1 | 27±1 | 27±1 | 29±1 |
| | Tack free time (s) | 153±4 | 154±3 | 152±2 | 156±4 | 157±3 |
| | Rise time (s) | 84±4 | 90±4 | 90±3 | 91±2 | 93±2 |
| | Density (kg/m$^3$) | 39.41±0.33 | 40.12±0.13 | 39.21±0.43 | 39.68±0.37 | 40.86±0.34 |
| Raypol® 4218 | Cream time (s) | 31±1 | 31±1 | 32±1 | 31±1 | 32±2 |
| | Gel time (s) | 42±1 | 44±1 | 44±1 | 43±2 | 45±1 |
| | Tack free time (s) | 243±3 | 242±2 | 242±3 | 240±4 | 242±4 |
| | Rise time (s) | 185±4 | 184±3 | 186±3 | 183±4 | 187±3 |
| | Density (kg/m$^3$) | 44.70±0.22 | 45.25±0.26 | 45.68±0.37 | 45.58±0.40 | 46.40±0.33 |

[*] A calculation of PMDI used in formulation is shown in APPENDIX D (Tables D2-D3).

### 4.4.5 The optimal formulation of vegetable oil based-RPUR foams

Based on the earlier relevant results, the formulation for three vegetable oil-based RPUR foam production was judiciously optimized on several parameters. Hence, the seed oil-based foam processing in this work was NCO index as 150–160 and premixing 100 pbw of polyol system with distilled water, DMCHA catalyst, and surfactant contents at 3.0, 1.0 and 2.5 pbw, respectively (Table 4.11). The external appearance of prepared three vegetable oil-based RPUR foams was shown in Figure 4.14.

**Table 4.11** The optimal formulation of water-blown RPUR foams prepared from vegetable oil-based polyols

| Ingredients | Part by weight (pbw) |
|---|---|
| Vegetable oil-based polyols | 100 |
| Catalyst (DMCHA) | 1.0 |
| Blowing agent (distilled water) | 3.0 |
| Surfactant (TEGOSTAB® B8460) | 2.5 |
| PMDI (Suprasec® 5005) | NCO index 150–160 |

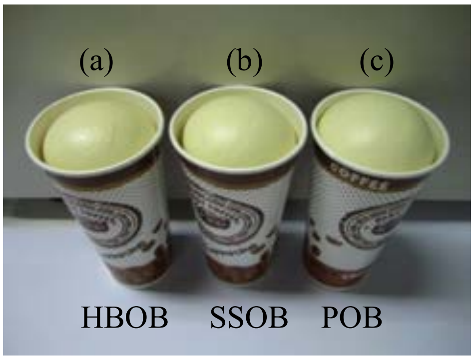


**Figure 4.14** The external appearance of vegetable oil-based RPUR (a) HBOB foam, (b) SSOB foam, and (c) POB foam prepared at NCO index of 150–160, 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant.

## 4.5 Characterizations of rigid polyurethane foams from vegetable oil-based polyols

The ATR-IR spectra of main starting materials and resulting biopolyol-based RPUR foams are shown in Figures 4.15a and 4.15b. It was worth noting that broad hydroxyls band at 3300–3500 $cm^{-1}$ (Figure 4.15b) and free carbonyl groups vibration peak at 1733 $cm^{-1}$ in HBOB polyol decreased, while the presence of characteristics absorption peaks of urethane and urea linkages was observed in RPUR foam (Figure 4.15c). The peaks at 3345 and 1711 $cm^{-1}$ were attributed to N–H stretching and C=O stretching vibration, respectively whereas, the signals at 1505 and 1215 $cm^{-1}$ were assigned according to N–H bending and C–N–H asymmetric stretches of urethane and urea groups. Additionally, the characteristic bands at 2270 $cm^{-1}$ region that presented in RPUR foam corresponded to an unreacted –N=C=O group. Moreover, the isocyanurate network formation by additional additional trimerization of isocyanates could be observed as two peaks at 1594 and 1412 $cm^{-1}$ that associating with the Ar–H and C–N isocyanurate [10, 51, 61].

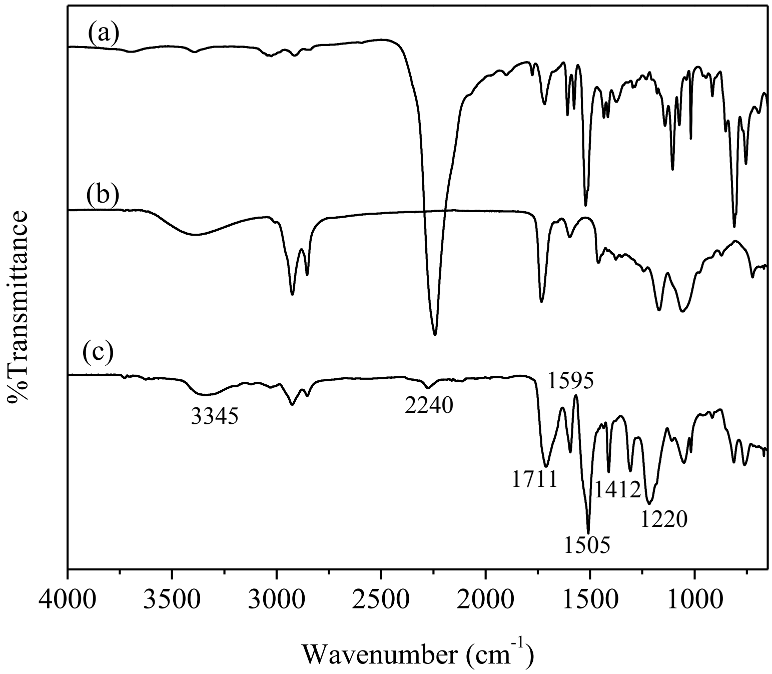


**Figure 4.15** ATR-IR spectra of starting materials and RPUR foam (a) PMDI, (b) HBOB polyol, and (c) HBOB-RPUR foam.

### 4.5.1 Isocyanate conversion of RPUR foams

From ATR-IR spectra shown in Figure 4.15a, it was observed that the characteristic bands around 2270–2275 $cm^{-1}$ region corresponded to free isocyanate groups and its intensity was reduced when reacted with polyols. Therefore, the polymerization of polymeric MDI and synthesized biopolyols and additional polymerization were investigated by ATR-IR spectroscopy in the term of NCO conversion. Figure 4.16 presents the ATR-IR spectra of HBOB based-foams in the varied NCO index ranging 100–250, an increase in free NCO absorption intensity could be observed in RPUR foam systems with the rising of NCO index used. The ATR-IR spectra of SSOB, POB, Raypol® 4218, and Raypol® 8360 based-foams show in APPENDIX E (Figures E1-E4). The main IR bands of RPUR foams are shown in Table 4.12.

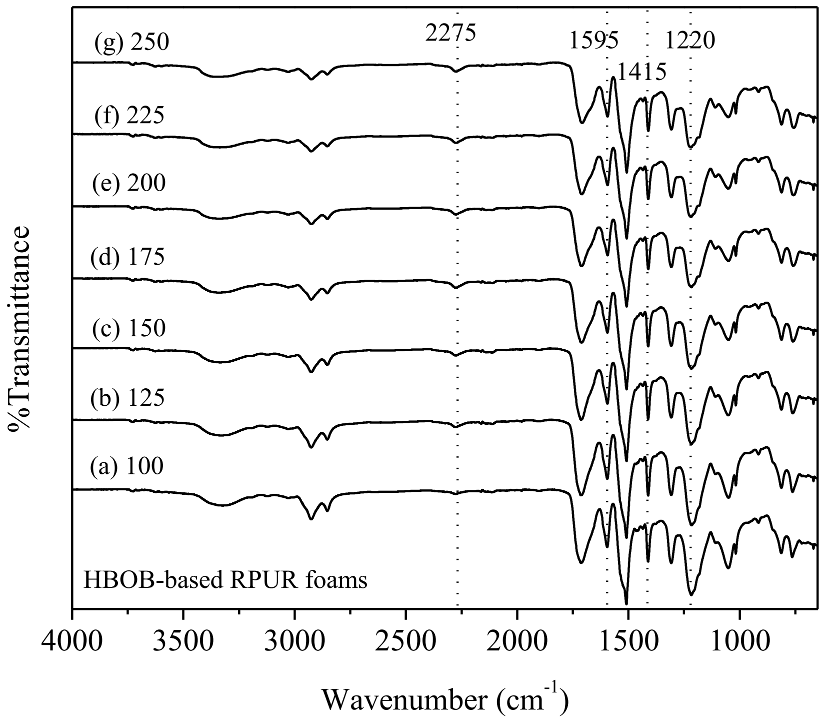


**Figure 4.16** ATR-IR spectra of HBOB-based RPUR foams prepared at NCO indexes of 100–250, 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant.

**Table 4.12** The main IR bands of rigid polyurethane foam system [62–63]

| Wavenumber ($cm^{-1}$) | Functional group |
|---|---|
| 2270–2275 | N=C=O asymmetric stretching (free isocyanate) |
| 1702–1735 | C=O stretching (urethane, urea, amide, allophanate, and biuret) |
| 1594–1595 | Ar–H (phenyl) |
| 1509–1510 | N–H bending (urethane) |
| 1410–1412 | C–N stretching (isocyanurate) |
| 1217–1225 | C–O stretching (urethane) |

NCO conversion defined as the %yields of polymerized products occurred in RPUR foam system that could be measured from the ratio of the IR peak area of remaining NCO at time after polymerization to the IR peak area of initial NCO used, which calculated from equation below [62–63]:

$$\%\text{NCO conversion} = \left(1 - \frac{\text{NCO}^{t}}{\text{NCO}^{i}}\right) \times 100$$

where $\text{NCO}^{t}$ is the area of free NCO absorption peak at time t and $\text{NCO}^{i}$ is the area of free NCO absorption peak at the initial time. The quantity of free NCO peak area of RPUR foams were normalized by aromatic ring absorption peak at 1595 $cm^{-1}$. The IR bands at 2275 $cm^{-1}$ (NCO), 1595 $cm^{-1}$ (Ar–H ), 1415 $cm^{-1}$ (isocyanurate) and 1220 $cm^{-1}$ (urethane) were used to calculate NCO conversion [62–63]. The calculation method of NCO conversion is shown in Appendix E.

Table 4.13 represents the NCO conversion of biopolyols RPUR foams (HBOB, SSOB, and POB) and commercial RPUR foams (Raypol® 8360 and Raypol® 4218) prepared at NCO indexes of 100–250, 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant. It indicated that the NCO conversion of RPUR foams from biopolyols slightly decreased (99.7–99.8%) by the increase of NCO index, whereas the NCO conversion of commercial RPUR foams was decreased in the range of 97.0–99.8%. Moreover, the trimerization of excess isocyanates in all RPUR foam systems which observed from PIR:PUR ratio could be slightly occurred.

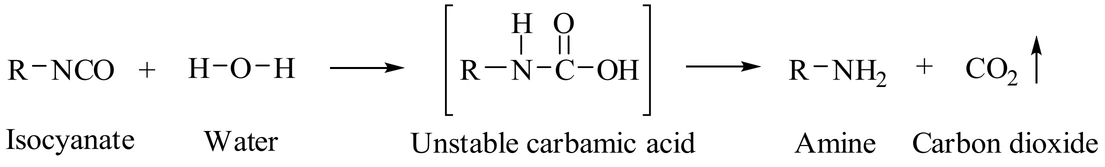
**Table 4.13** NCO conversion of RPUR foams prepared at the NCO indexes of 100–250 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant

| NCO index | NCO conversion (%) | PIR/PUR |
|---|---|---|
| HBOB-100 | 99.90 | 0.1303 |
| HBOB-125 | 99.82 | 0.1560 |
| HBOB-150 | 99.80 | 0.1622 |
| HBOB-175 | 99.77 | 0.1683 |
| HBOB-200 | 99.74 | 0.1754 |
| HBOB-225 | 99.72 | 0.1783 |
| HBOB-250 | 99.71 | 0.1857 |
| SSOB-100 | 99.92 | 0.1270 |
| SSOB-125 | 99.86 | 0.1309 |
| SSOB-150 | 99.79 | 0.1654 |
| SSOB-175 | 99.76 | 0.1699 |
| SSOB-200 | 99.72 | 0.1865 |
| SSOB-225 | 99.70 | 0.2027 |
| SSOB-250 | 99.69 | 0.2113 |
| POB-100 | 99.94 | 0.1246 |
| POB-125 | 99.84 | 0.1355 |
| POB-150 | 99.78 | 0.1423 |
| POB-175 | 99.75 | 0.1491 |
| POB-200 | 99.74 | 0.1543 |
| POB-225 | 99.73 | 0.1622 |
| POB-250 | 99.72 | 0.1635 |

**Table 4.13** NCO conversion of RPUR foams prepared at the NCO indexes of 100–250 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant (continued)

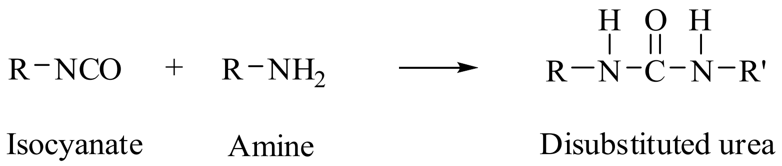
| NCO index | NCO conversion (%) | PIR/PUR |
|---|---|---|
| Raypol$^{®}$ 8360-100 | 99.85 | 0.1195 |
| Raypol$^{®}$ 8360-125 | 99.68 | 0.1380 |
| Raypol$^{®}$ 8360-150 | 99.39 | 0.1798 |
| Raypol$^{®}$ 8360-175 | 99.13 | 0.1821 |
| Raypol$^{®}$ 8360-200 | 98.16 | 0.2395 |
| Raypol$^{®}$ 8360-225 | 97.87 | 0.2961 |
| Raypol$^{®}$ 8360-250 | 97.00 | 0.3661 |
| Raypol$^{®}$ 4218-100 | 99.82 | 0.1864 |
| Raypol$^{®}$ 4218-125 | 99.71 | 0.2126 |
| Raypol$^{®}$ 4218-150 | 99.54 | 0.2273 |
| Raypol$^{®}$ 4218-175 | 99.18 | 0.2473 |
| Raypol$^{®}$ 4218-200 | 98.93 | 0.2625 |
| Raypol$^{®}$ 4218-225 | 98.61 | 0.2819 |
| Raypol$^{®}$ 4218-250 | 98.25 | 0.3119 |

The NCO conversion of RPUR foam from biopolyols was more than the commercial ones probably due to the presence of free carboxylic acid (acid value 5.37–11.97 mg KOH/g) and high water content (0.53–1.31 wt%) in synthesized biopolyols provided the addition reaction between isocyanates and both active hydrogen compounds. The presence of bound water in synthesized biopolyols can be react with isocyanates to generate $CO_2$ gas and amine as shown in the equation below [1, 27]:



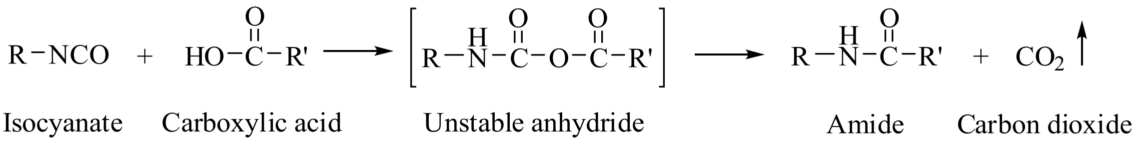
$$R{-}NCO + H{-}O{-}H \longrightarrow \left[ R{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}OH \right] \longrightarrow R{-}NH_2 + CO_2\uparrow$$

Additionally, the amine further reacts rapidly with other isocyanate groups and generates a disubstituted urea resulting in a crosslinking network as presented below [1, 27]:



$$\underset{\text{Isocyanate}}{R-NCO} + \underset{\text{Amine}}{R-NH_2} \longrightarrow \underset{\text{Disubstituted urea}}{R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R'}$$

The reaction of isocyanates and free acids to produce amide and $CO_2$ is presented following equation [30]:



$$\underset{\text{Isocyanate}}{R-NCO} + \underset{\text{Carboxylic acid}}{HO-\overset{O}{\overset{\|}{C}}-R'} \longrightarrow \underset{\text{Unstable anhydride}}{\left[R-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R'\right]} \longrightarrow \underset{\text{Amide}}{R-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-R'} + \underset{\text{Carbon dioxide}}{CO_2\uparrow}$$

The reactivity of isocyanates toward carboxylic acids is lower than the one with amine, primary alcohols, and water but is higher slightly than secondary alcohols [30]. Because of the production of $CO_2$ gas from these reactions that presented above, RPUR systems prepared from biopolyols could expand to be foam without adding blowing agent (water) that presented in Figure 4.17.

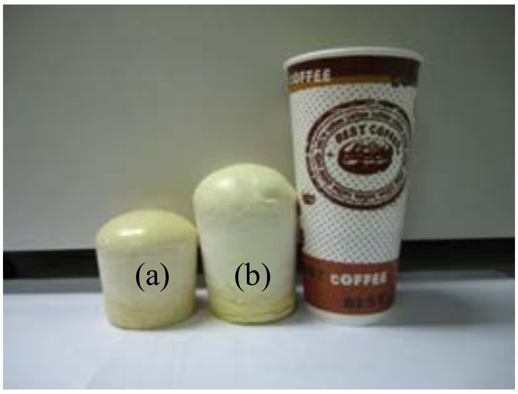


**Figure 4.17** The external appearance of RPUR foams prepared at NCO index of 100, 1.0 pbw of water, 2.5 pbw of surfactant, and without adding water: (a) Raypol® 4218 foams and (b) HBOB foams.

### 4.5.2 Physical and mechanical properties of rigid polyurethane foams from vegetable oil-based polyols

Table 4.14 shows some mechanical properties of the RPUR foams which prepared following optimal formulation. All RPUR foams were produced at density in the range of 40–45 kg/m$^3$ which giving satisfactory mechanical properties for thermal insulating applications. Typically, the compressive strength of RPUR foams with this density range is 250–300 kPa [64].

**Table 4.14** Mechanical properties of rigid polyurethane foams prepared from optimized formulations

| Polyol used to prepare RPUR foam | Density (kg/m$^3$) | Compressive strength (kPa) | |
|---|---|---|---|
| | | Parallel to foam rise direction | Perpendicular to foam rise direction |
| HBOB | 42.48±0.33 | 246.8±4.8 | 171.0±22.2 |
| SSOB | 40.84±0.33 | 240.2±17.5 | 152.2±21.3 |
| POB | 40.78±0.56 | 237.7±10.3 | 152.3±23.1 |
| Raypol® 8360 | 40.20±0.49 | 261.1±16.1 | 198.6±12.5 |
| Raypol® 4218 | 44.05±0.34 | 303.1±26.8 | 235.5±6.8 |

The compression stress-strain curves of all synthesized RPUR foams with loading both parallel and transverse direction to the foam rising are presented in Figures 4.18a and 4.18b, respectively. Each curve showing three regions related to a deformation mechanism [32, 65]. The initial linear domain at low stress associates to the elasticity of the materials resulting from cell window stretching because of trapped gas pressure and their slope is the Young's modulus. Following the long linear plateau region is observed at the stress value which does not change much. This collapse plateau corresponds to cell collapse gradually by elastic buckling of cell walls or in brittle foams depending on the nature of solid polymer and cell morphology. If the stress at the yield point presents before 10% deformation or, in the absence of yield point, the stress at 10% deformation is compressive strength [62, 66]. When the cell walls have almost completely collapse and crush, the stress level is increased rapidly through the solid polymer itself. This third domain can be referred as densification.

The compressive strength of RPUR foam samples in parallel to the foam rising were within the range of 237.7–303.1 kPa, whereas the compression in perpendicular direction was displayed from 152.2–235.5 kPa. For low density RPUR foams, the compression strength would usually dissimilar with the direction of the foam rise because of their anisotropy [2]. Raypol® 4218 based foam showed higher compressive strength than biopolyol-based foams because of its highest crosslink density. Among biopolyol-based foams, HBOB-RPUR foam showed the highest compressive properties. On the other hand, Raypol® 8360-RPUR foam presented the lowest compressive strength. Although it was known that the strength properties of cellular materials not only primary depended on their density but this phenomenon was also governed by the basis of the polyols structure. The synthesized PUR foams had a variation of degree of cross-linking which are leading to a difference of its mechanical properties [20, 51]. When using polyester polyols from vegetable oils, the fatty acid chain would act as soft segment by plasticizing effects, therefore, RPUR foam synthesized from them given the rigidity less than those of commercial polyether polyols [8, 51].

As all RPUR foam samples displayed the anisotropic in compression, it was presumed that many cells were not perfectly spherical which was confirmed by SEM. From a correlation data, it is supported that the mechanical properties of the cellular materials depend considerably on their densities and cell morphology [1–2, 51, 62].

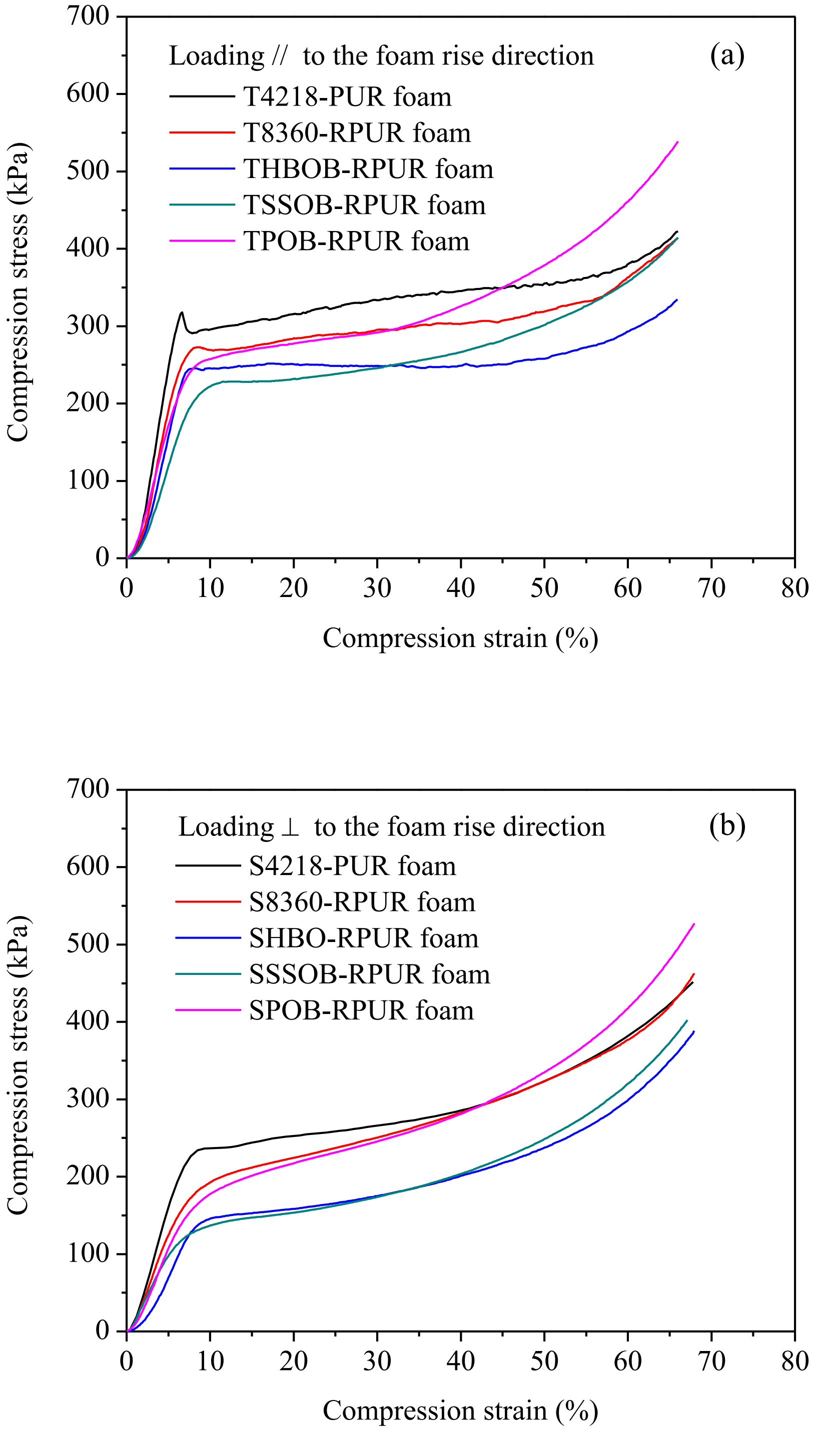


**Figure 4.18** Compression strain versus stress curves of rigid polyurethane foams with foam density ranging from 40–45 kg/m$^3$, (a) in parallel to the foam rise direction and (b) in perpendicular to the foam rise direction.

### 4.5.3 Morphology of RPUR foams

The SEM images of foam samples are shown in Figure 4.19. The structure of biopolyol-based cell foams in the free-rise direction exhibited highly uniform and mostly closed-cells. The rupture of cell membrane and some open-cells might result from cutting samples. The foam cellular structure comprised of dodecahedron-shaped cells (cell size approximately 300–400 μm) with struts (cell edges) and thin cell window films [1]. In a converse direction, the foam cells were partially elongated probably resulting from mold shape under higher temperature and gas pressure presenting in core polymer matrix during foam expansion [67].

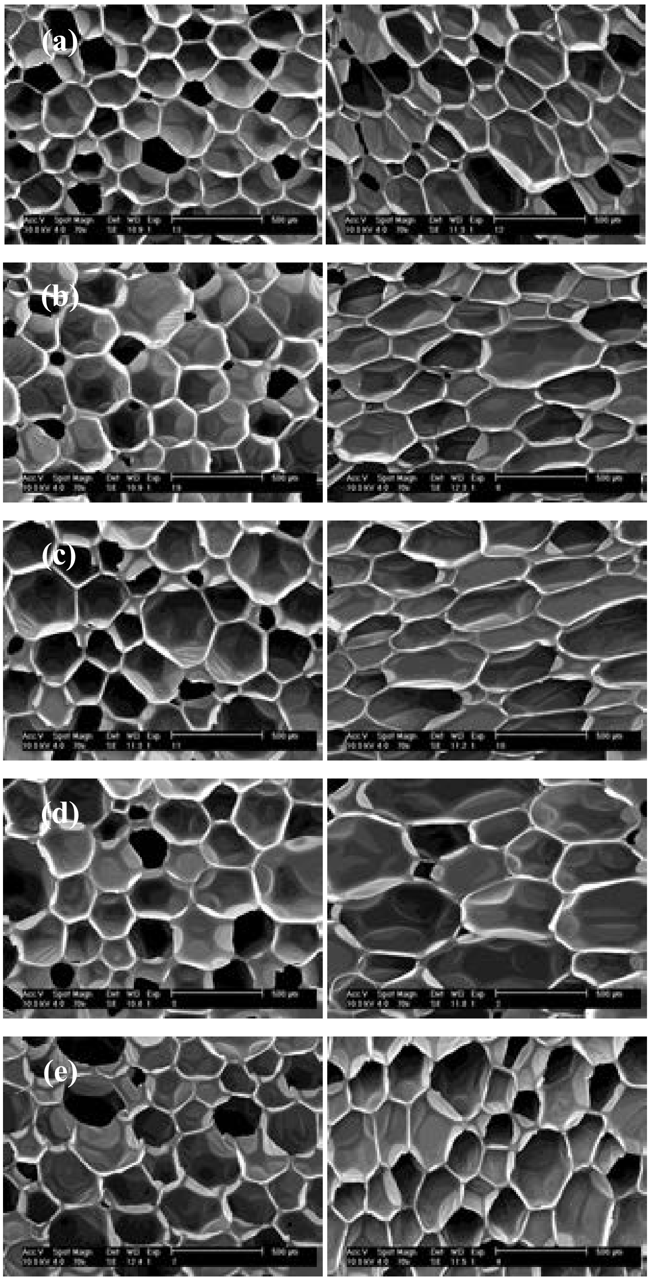


**Figure 4.19** SEM micrographs of resulting RPUR foams in top view (left) and side view (right) of foam rising direction (50×); (a) HBOB-RPUR, (b) SSOB-RPUR, (c) POB-RPUR, (d) Raypol® 4218-RPUR and (e) Raypol® 8360-RPUR foams.

### 4.5.4 Thermal properties of rigid polyurethane foams

#### 4.5.4.1 Thermal stability

Thermal stability of biopolyol-based RPUR foams and the commercial polyol-based foams which had the density 40–45 kg/m$^3$ was investigated by TGA performed under nitrogen atmosphere. TGA and their derivative (DTG) curves are presented in Figure 4.20. The DTG curves revealed two distinct degradation stages. The initial decomposition temperature at 5% weight loss of all biopolyols-based RPUR foams was observed at approximately 257.5–258.3°C and the first decomposition stage ($T_{max}$) in the range of 300–330ºC was associated to the degradation of thermally unstable urethane linkage. The second weight loss stage ($T_{max}$) occurred approximately 425–470ºC correlating to the decomposition of polyols chains, that could be depend on polyols structures and different internal cross-linking in polymer networks [10, 20, 50]. For biopoyols-based RPUR foams, HBO-RPUR foam was thermally more stable than the others because of its higher cross-linking density with higher OH number.

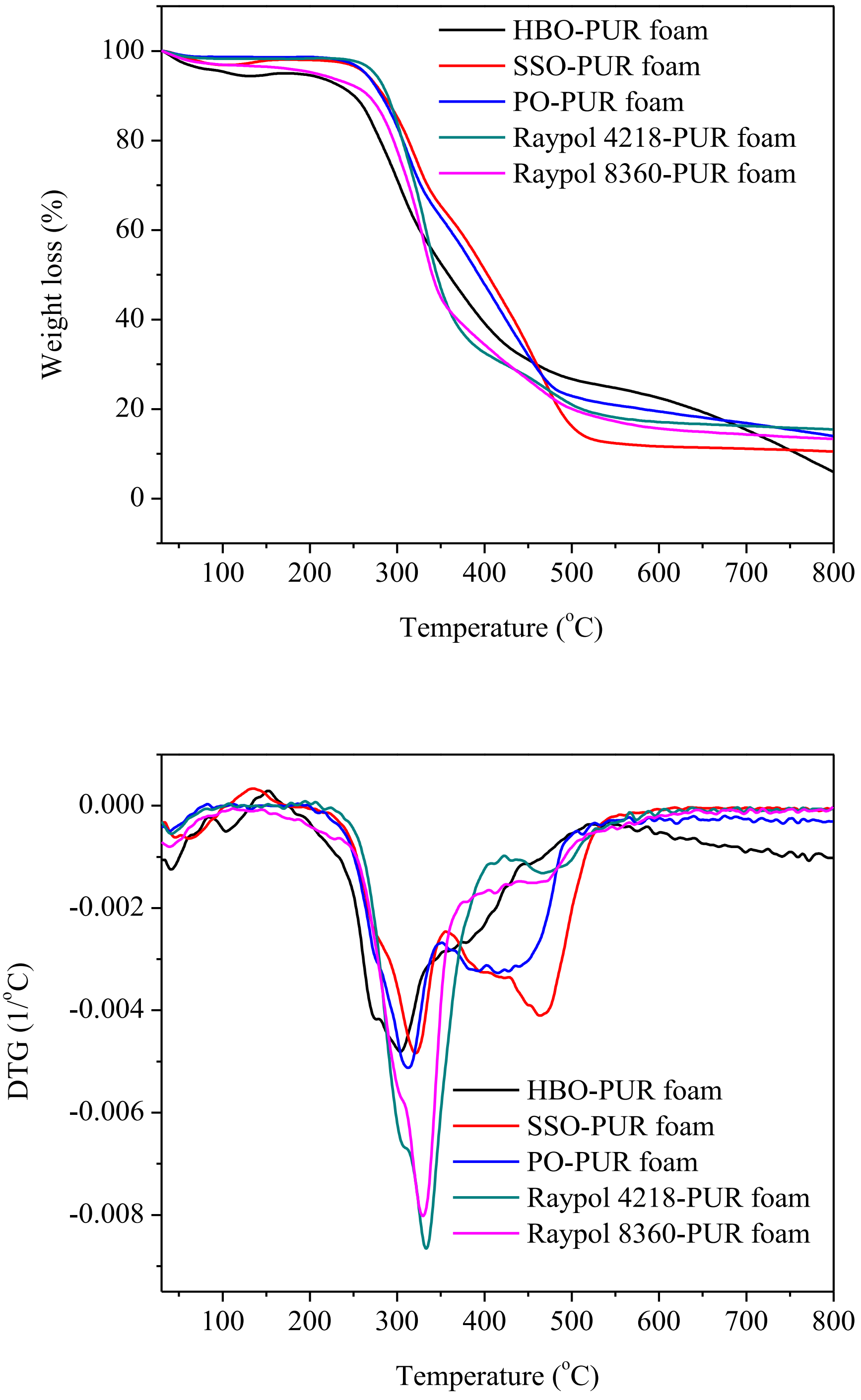


**Figure 4.20** TGA thermograms and their derivative (DTG) curves of rigid polyurethane foams at the heating rate of 10°C/min under $N_2$ atmosphere

#### 4.5.4.2 Thermal conductivity

The room temperature thermal conductivity of synthesized RPUR foams was represented in Table 4.15. It was known that the total thermal conductivity of PUR foams consisted of the heat transfer between gas and polymer solid phase. Their thermal conductivity is relatively low because of small solid contents in the foam materials about 3–10% of the total volume [1]. Therefore their insulation performance was mainly governed by the conduction of trapped gas types and foam density. When using water as a green blowing agent, the foam cells were formed by the resulting $CO_2$ gas which had a slightly higher gaseous thermal conductivity than conventional hydrocarbon such as HCFC, HFC, and cyclopentane, etc [1–2]. For low density RPUR foam (30–50 kg/m$^3$), the thermal conductivity was controlled by gas conduction. Therefore an increasing foam density within this range was caused by an increase in the content of small cells per unit volume that contributed a decrease in the thermal conductivity [1]. The thermal conductivity value of the prepared water-blown RPUR foams with density 40–45 kg/m$^3$ was in the range of 0.0330–0.0368 W/mK that was higher than idealized RPUR foams (0.020–0.030 W/mK) probably due to the long post curing period.

**Table 4.15** Thermal conductivity of RPUR foams with density 40–45 kg/m$^3$

| RPUR foam prepared from | Thermal conductivity (W/mK) |
|---|---|
| HBOB | 0.0331±0.0002 |
| SSOB | 0.0342±0.0001 |
| POB | 0.0339±0.0001 |
| Raypol® 8360 | 0.0330±0.0001 |
| Raypol® 4218 | 0.0368±0.0003 |

# CHAPTER V

# CONCLUSION

## 5.1 Vegetable oil-based polyols for rigid polyurethane foam preparation

A bio-based polyols from vegetable oils including hairy basil seed oil (HBO), sesame seed oil (SSO), and pumpkin seed oil (PO) has been completely synthesized by simple hydroxylation following alcoholysis reaction. The hydroxylated seed oils were firstly synthesized by peroxyformic acid and then the alcoholysis reaction of the hydroxylated seed oils with triethanolamine in the presence of lithium hydroxide as a catalyst was carried out. The resulting polyols exhibited the OH number in the range of 340–383 mg KOH/g and a relative high viscosity (9862–13314 cP), which were suitable used as polyols for RPUR foam preparation comparable to the commercial polyols (polyethers/polyesters specification: OH no. = 300–600 mg KOH/g, acid no. = 0.20 mg KOH/g, and viscosity at 25°C = 2000–50000 cP). FTIR data was used to confirm the formation of polyols. The properties of vegetable oil-based polyols in this research compared with those from the other literatures, which synthesized by hydroxylation following alcoholysis reaction, are summarized in Table 5.1.

**Table 5.1** Comparison of vegetable oil-based polyols properties

| Reference | Source | OH number (mg KOH/g) | Acid number (mg KOH/g) | Viscosity at 25°C (cP) |
|---|---|---|---|---|
| Hu *et al*. [15] | rape seed oil | 367 | 0.14 | 1600 |
| Moisiewicki *et al*. [19] | tung oil | 434 | 53.1 | a paste like consistency |
| Veronese *et al*. [20] | soybean oil | 477 | 2.16 | 2187 |
| This research | hairy basil seed oil | 382.51 | 11.97 | 13314 |
| | sesame seed oil | 351.03 | 10.29 | 11278 |
| | pumpkin seed oil | 340.24 | 5.37 | 9862 |

## 5.2 Rigid polyurethane foam prepared from vegetable oil-based polyols

The synthesized biopolyols based on hairy basil seed oil (HBOB), sesame seed oil (SSOB), and pumpkin seed oil (POB) have been used as polyols for RPUR foam preparation. In foam processing, the variation of starting material contents displayed a relative effect to foaming behavior and their density. An increase in NCO index and distilled water level resulted in the longer reaction time, the foam density at higher NCO index was raised gradually that contrast to the water content effect. As the catalyst level increasing, the reaction time was reduced with a slight decrease in density of foam. However, the amount of surfactant had no significant effect on either the foaming behavior or foam density.

The water blown RPUR foams from these biopolyols were successfully prepared using the optimized formulation comprising 100 pbw of polyols, 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant at NCO index as 150–160. Within optimal formulation, vegetable oil-based RPUR foams had the density in the range of 40–45 kg/m$^3$ and displayed the satisfactory mechanical and thermal performance. However, the proper PUR formulations could be manipulated to produce the desired material applications. Due to the synthesized seed oil-based polyols were the mixture of several species especially the high content of water and triethanolamine, therefore the RPUR foam formulation was optimized carefully. In calculation step, all active hydrogen compounds in premixed polyol systems were used to calculate relative to isocyanate used.

Additionally, the cellular structure of seed oil-based foams presented anisotropy in polygonal shaped-cells. From the detail experimental data, it is indicated that the obtained RPUR foams from these seed oil-based polyols exhibited behaviors slightly comparable to those of the commercial foams, but also possessed the potential and favorable economics as a renewable resources for RPUR foam preparation.

The comparison of RPUR foam systems prepared from three biopolyols and plant oil-based polyols in the other literatures are concluded in Table 5.2.

**Table 5.2** Comparison of rigid polyurethane foams prepared from plant oil-based polyols and commercial polyols

| | Hu *et al*. [15] | Stirna *et al.* [17] | Veronese *et al*. [20] | This research |
|---|---|---|---|---|
| RPUR foam formulation | | | | |
| Polyol (pbw) | Rape seed oil-based polyol (100) | Rape seed oil-based polyol/ polyester (80:20) | Soybean oil-base polyol (100) | Hairy basil seed oil-based polyol (100) |
| Blowing agent (pbw) | Water + HCFC (29) | Water (3.2) | Water (1.4) + pentane (4.1) | Water (3.0) |
| Catalyst (pbw) | LB (3.13) + SFC (1.00) | Potassium oleate (2.0) + dimethylethanolamine (2.0) | DMCHA (0.6) | DMCHA (1.0) |
| Surfactant (pbw) | Silicone B8462 (3.72) | Silicone (1.5) | Silicone B8460 (3.7) | Silicone B8460 (2.5) |
| Isocyanate (pbw) | NCO index = 180<br>PMDI (246) | NCO index = 170<br>PMDI | NCO index = 120<br>MDI (163) | NCO index = 150<br>PMDI (241) |
| RPUR foaming behavior | | | | |
| Cream time (s) | 24 | 25 | - | 26 |
| Gel time (s) | 64 | 42 | - | 40 |
| Tack free time (s) | 122 | - | - | 211 |
| RPUR foam properties | | | | |
| Density (kg/m$^3$) | 40.8 | 66 | 49 | 42 |
| // Compressive strength (kPa) | 178 | 410 | 170 | 247 |
| Thermal conductivity (W/mK) | 0.025 | 0.035 | - | 0.0331 |

**Table 5.2** Comparison of rigid polyurethane foams prepared from plant oil-based polyols and commercial polyols (continued)

| | This research | | | |
|---|---|---|---|---|
| RPUR foam formulation | | | | |
| Polyol (pbw) | Sesame seed oil-based polyol (100) | Pumpkin seed oil-based polyol (100) | Commercial sucrose-based polyether, Raypol® 4218 (100) | Commercial phthalate-based polyester, Raypol® 8360 (100) |
| Blowing agent (pbw) | Water (3.0) | Water (3.0) | Water (3.0) | Water (3.0) |
| Catalyst (pbw) | DMCHA (1.0) | DMCHA (1.0) | DMCHA (1.0) | DMCHA (1.0) |
| Surfactant (pbw) | Silicone B8460 (2.5) | Silicone B8460 (2.5) | Silicone B8460 (2.5) | Silicone B8460 (2.5) |
| Isocyanate (pbw) | NCO index = 160<br>PMDI (228) | NCO index = 160<br>PMDI (224) | NCO index = 150<br>PMDI (227) | NCO index = 175<br>PMDI (232) |
| RPUR foaming behavior | | | | |
| Cream time (s) | 23 | 22 | 28 | 17 |
| Gel time (s) | 37 | 36 | 40 | 26 |
| Tack free time (s) | 188 | 181 | 205 | 152 |
| RPUR foam properties | | | | |
| Density ($kg/m^3$) | 41 | 40 | 43 | 40 |
| // Compressive strength (kPa) | 240 | 238 | 261 | 303 |
| Thermal conductivity (W/mK) | 0.0342 | 0.0339 | 0.0368 | 0.0330 |

## 5.2 Suggestion for further study

Due to te synthesized polyols were the mixture of various species including mono-, diesters, triethanolamine, free acids, and water. We strongly suggest that

- the raw materials and the obtained products should be characterized by LC-MS,
- the water in final products after alcoholysis needs to remove by vacuum distillation,
- the storage life of polyols needs to study, and
- the RPUR foam formulation should be optimized carefully based on the active hydrogen compounds presenting in polyol system.

# REFERENCES

[1] Lee, S. T. and Ramesh, N. S. *Polymeric foams: mechanisms and materials*. FL: CRC Press, 2004.

[2] Woods, G. *The ICI Polyurethanes Book,* 2nd Edition. The Netherlands: John Wiley & Sons, 1990.

[3] Lligadas, G., Ronda, J. C., Galià, M., and Càdiz, V. Plant oils as platform chemicals for polyurethane synthesis: current state-of-the art. *Biomacromolecules* 11 (2010): 2825–2835.

[4] Sharma, V. and Kundu, P. P. Condensation polymers from natural oils. *Prog. Polym. Sci*. 33 (2008): 1199–1215.

[5] Petrović, Z. S. Polyurethane from vegetable oils. *Polym. Rev.* 48 (2008): 109–155.

[6] Sooksai, S. and Noitang, S. Extraction of oil from hairy basil (*Ocimum spp.)* seeds and swelling properties of mucilage from seed residues. *Research reports: Chulalongkorn University Intellectual Repository,* 2007.

[7] Petrović, Z. S., Zlatanić, A., Lava, C. C., and Sinadinović-Fišher, C. Epoxidation of soybean oil in toluene with peroxoacetic and peroxoformic acids – kinetics and side reactions. *Eur. J. Lipid. Sci. Technol*. 104 (2002): 293–299.

[8] Zlatanić, A., Lava, C. C., Zhang, W., and Petrović, Z. S. Effect of structure on properties of polyols and polyurethane based on different vetetable oils. *J. Appl. Polym. Sci. Part B: Polym. Phys*. 42 (2004): 809–819.

[9] Okieimen, F. E., Pavithran, C., and Bakare, I. O. Epoxidation and hydroxylation of rubber seed oil: one-pot multi-step reactions. Eur. *J. Lipid. Sci. Technol*. 107 (2005): 330–336.

[10] Bandyopadhyay-Ghosh, S., Ghosh, S. B., and Sain, M. Synthesis of soy-polyol by two step continuous route and development of soy-based polyurethane foam. *J. Polym. Environ.* 18 (2010): 437–442.

[11] Petrović, Z. S., Guo, A., Javni, I., Cvetković, I., and Hong, D. P. Polyurethane networks from polyols obtained by hydroformylation of soybean oil. *Polym. Int*. 57 (2008): 275–281.

[12] Tran, P., Graiver, D., and Narayan, R. Ozone-mediated polyol synthesis from soybean oil. *J. Am. Oil. Chem. Soc*. 82 (2005): 653–659.

[13] Petrović, Z. S., Zhang, W., and Javni I. Structure and properties of polyurethanes prepared from triglyceride polyols by ozonolysis. *Biomacromolecules* 6 (2005): 713–719.

[14] Kong, X. and Narine, S. S. Physical properties of polyurethane plastic sheets produced from polyols from canola oil. *Biomacromolecules* 8 (2007): 2203–2209.

[15] Hu, Y. H., Gao, Y., Wang, D. N., Hu, C. P., Zu, S., Vanoverloop, L., and Randall, D. Rigid polyurethane foam prepared from a rape seed oil based polyol. *J. Appl. Polym. Sci*. 84 (2002): 591–597.

[16] Tanaka, R., Hirose, S., and Hatakeyama, H. Preparation and characterization of polyurethane foams using palm oil-based polyol. *Bioresour. Technol.* 99 (2008): 3810–3816.

[17] Stirna, U., Cabulis, U., and Beverte, I. Water-blown polyisocyanurate foams from vegetable oil polyols. *J. Cell. Plast.* 44 (2008): 139–160.

[18] Bakare, I. O., Pavithran,C., Okieimen, F. E., and Pilla, C. K. S. Synthesis and characterization of rubber-seed-oil-based polyurethanes. *J. Appl. Polym. Sci.* 109 (2008): 3292–3301.

[19] Mosiewicki, M. A., Casado, U., Marcovich, N. E., and Aranguren, M. I. Polyurethanes from tung oil: polymer characterization and composites. *Polymer. Eng. Sci.* 49 (2009): 685–692.

[20] Veronese, V. B., Menger, R. K., de C. Forte, M. M., and Petzhold, C. L. Rigid polyurethane foam based on modified vegetable oil. *J. Appl. Polym. Sci.* 120 (2011): 530–537.

[21] Otey, F. H., Zagoren, B., Bennett, F. L., and Mehltretter, C. L. Preparation and properties of glycol glycoside polyethers for rigid polyurethane foams. *I&EC Prod. Res.* 4 (1965): 224–227.

[22] Desai, S. D., Patel, J. V., and Sinha, V. K. Polyurethane adhesive system from biomaterial-based polyol for bonding wood. *Int. J. Adhes. Adhes.* 23 (2003): 393–399.

[23] Mishra, D. and Sinha, V. K. Value-based polymer precursors from paper waste and its application in polyurethane foams. *J. Cell. Plast.* 46 (2010): 15–29.

[24] Kricheldorf, H. R., Nuyken O., and Swift, G. *Handbook of polymer synthesis.* 2nd Edition. NY: CRC Press, 2004.

[25] Lee, S.-T., Park, C. B., and Ramesh, N. S. *Polymeric foams: technology and science of polymeric foams.* Boca Raton, FL: CRC Press, 2007.

[26] Methylene diphenyl diisocyanate (MDI), toluene diisocyanate (TDI) and polyurethane market (2011–2016) by marketsandmarkets.com [Online]. Available from: http://www.marketsandmarkets.com/Market-Reports/mdi-tdi-polyurethane-market-381.html [July, 2011].

[27] Ashida, K., *Polyurethane and related foams: chemistry and technology*. Boca Raton, FL: CRC Press, 2007.

[28] Pentrakoon, D. *An introduction to plastic foams.* Bangkok, Thailand: Chulalongkorn University Press, 2005.

[29] Sourcebook of technologies for protecting the ozone layer: flexible and rigid foams by United Nations Environment Programme [Online]. Available from: http://www.unep.fr/ozonaction/information/mmcfiles/1350-e.pdf [September, 1996].

[30] Ionescu, M. *Chemistry and technology of polyols for polyurethanes*. The United Kingdom: Rapra Technology, 2005.

[31] Thomson, T. *Polyurethanes as specialty chemicals: principles and applications*. Boca Raton, FL: CRC Press, 2005.

[32] Randall, D. and Lee S. *The Huntsman Polyurethanes Book.* The United Kingdom: John Wiley & Sons, 2002.

[33] Eaves, D. *Handbook of Polymer Foams*. The United Kingdom: Rapra Technology, 2004.

[34] Shahidi, F. *Bailey's Industrial oil and fat products.* 6th Volume set, 6th Edition. NJ: Wiley & Sons, 2005.

[35] American Society for Testing Materials; Standard test methods for testing polyurethane raw materials: Determination of the isocyanate content of aromatic isocyanate, ASTM (D 5155–07); *ASTM*: West Conshohocken, PA, 2007.

[36] American Society for Testing Materials; Standard test methods for testing polyurethane raw materials: Determination of hydroxyl mumbers of polyols, ASTM (D 4274–05); *ASTM*: West Conshohocken, PA, 2005.

[37] American Society for Testing Materials; Standard test methods for polyurethane raw materials: Determination of acid and alkalinity numbers of polyols, ASTM (D 4662–03); *ASTM*: West Conshohocken, PA, 2003.

[38] Thermal insulation materials made of rigid polyurethane foam (PUR-PIR) PU Europe report No. 1., October, 2006.

[39] American Society for Testing Materials; Standard test methods for apparent density of rigid cellular plastics, ASTM (D 1622–08); *ASTM*: West Conshohocken, PA, 2008.

[40] Lee, S.-T. and Scholz, D. *Polymeric foams: technology and developments in regulation, process, and products.* Boca Raton, FL: CRC Press, 2009.

[41] Erhan, S. Z. *Industrial uses of vegetable oils*. IL: ACOS Press, 2005.

[42] Mohanty, A. K., Misra, M., and Drzal, L. T. *Natural fibers, biopolymers, and biocomposites*. Boca Raton, FL: CRC Press, 2005.

[43] Singh, B. P. *Industrial crops and uses*. The United Kingdom: CAB International, 2010.

[44] Chantarakul, N. Preparation of modified glutinous starch and low density polyethylene blends. Science Program in Applied Polymer Science and Textile Technology. *Faculty of Science, Chulalongkorn University*, 2004.

[45] Kumar, P. P., Paramashivappa, R., Vithayathil, P. J., Subba Rao, P. V., and Srinivasa Rao, A. Process for isolation of cardanol from technical cashew (*Anacardium occidentale* L.) nut shell liquid. *J. Agric. Food Chem.* 50 (2002): 4705–4708.

[46] Bhunia1, H. P., Jana1, R. N., Basak, A., Lenka, S., and Nando, G. B. Synthesis of polyurethane from cashew nut shell liquid (CNSL), a renewable resource. *J. Polym. Sci. Part A.: Polym. Chem.* 36 (1998): 391–400.

[47] Suresh, K. I. and Kishanprasad, V. S. Synthesis, structure, and properties of novel polyols from cardanol and developed polyurethanes. *Ind. Eng. Chem. Res. 44* (2005): 4504–4512.

[48] Suresh, K. I. and Kishanprasad, V. S. Process for preparing polyurethane polyol and rigid foam thereform. *U.S. Patent* 7,244,772 B2. 2007, Jul. 17.

[49] Reese, J. R., Moore, M. N., Wardius, D. S., and Hager, S. L. Novel polyether polyols based on cashew nutshell liquid, a process for the production of these polyether polyols, flexible foams produced from these polyether polyols, and the process for the production of these foams. *US patent* 2008/0139685 A1. 2008, Jul. 12.

[50] Guo, A., Javni, I., and Petrović, Z. S. Rigid polyurethane foams based of soybean oil. *J. Appl. Polym. Sci.* 77 (2000): 467–473.

[51] Narine, S. S., Kong, X., Bouzidi, L., and Sporns, P. Physical properties of polyurethanes produced from polyols from seed oils: II. Foams. *J. Amer. Oil. Chem. Soc.* 84 (2007): 65–72.

[52] Chuayjuljit, S., Maungchareon, A., and Saravari, O. Preparation and properties of palm oil-based rigid polyurethane nanocomposite foams. *J. Reinf. Plast. Compos.* (2008): 1–8.

[53] Yao, Y., Yoshioka, M., and Shiraishi, N. Water-absorbing polyurethane foams from liquefied starch. *J. Appl. Polym. Sci.* 60 (1996): 1939–1949.

[54] Ge, J., Zhohg, W., Guo, Z., Li, W., and Sakai, K. Biodegradable polyurethane materials from bark and starch. I. Highly resilient foams. *J. Appl. Polym. Sci.* 77 (2000): 2575–2580.

[55] Kim, D.-H., Kwon, O.-J., Yang, S.-R., Park, J.-S., and Chun, B. C. Structural, thermal, and mechanical properties of polyurethane foams prepared with starch as the main component of polyols. *Fiber Polym.* 8 (2007): 249–256.

[56] Monteavaro, L. L., da Silva, E. O., Costa, A. P. O., Samios, D., Gerbase, A. E., and Petzhold, C. L. Polyurethane networks from formiated soy polyols: synthesis and mechanical characterization. *J. Am. Oil. Chem. Soc.* 82 (2005): 365–371.

[57] Pengjam, W. Preparation of rigid polyurethane foam catalyzed by Cu-amine and Mn-amine complexes. Science program in Petrochemistry and Polymer Science. *Faculty of Science, Chulalongkorn University*, 2009.

[58] Pomsook, J. Preparation of rigid polyurethane foam using mixed metal complexes and ethylenediamine as catalysts. Science program in Petrochemistry and Polymer Science. *Faculty of Science, Chulalongkorn University*, 2010.

[59] Promnimit, R. Preparation of rigid polyurethane foams using mixed metal complexes and pentaethylenehexamine as catalyst. Science program in Petrochemistry and Polymer Science. *Faculty of Science, Chulalongkorn University*, 2011.

[60] Ruangsri, M. Preparation of rigid polyurethane foams using mixed metal complexes and tetraethylenepentamine as catalysts. Science program in Petrochemistry and Polymer Science. *Faculty of Science, Chulalongkorn University*, 2011.

[61] Modesti, M. and Lorenzetti, A. An experimental method for evaluating isocyanate conversion and rimer formationin polyisocyanate-polyurethane foams. *Eur. Polym. J.* 37 (2001): 949–954.

[62] Chaffanjon, P., Grisgby, R. A., Rister, E. L., and Zimmerman, R. L. Used of real-time FTIR to characterize kinetics of amine catalysts and to develop new grades for various polyurethane applications, including low emission catalysts. *J. Cell. Plast.* 39(2003): 187–210.

[63] Raffel, B. and Loevenich, C. J. High throughput screening of rigid polyisocyanurate foam formulations: quantitative characterization of isocyanate yield via the adiabatic temperature method. *J. Cell. Plast.* 42*(*2006): 17–47.

[64] Oertel, G. Polyurethane Handbook: chemistry-raw materials-processing-application -properties; 2nd Edition; *Hanser Pubishers*, NY, 1985.

[65] Saint-Michel, F., Chazeau, L., Cavaillé, J.-Y., and Chabert, E. Mechanical properties of high density polyurethane foams I. effect of the density. *Compos. Sci. Tech.* 66 (2006): 2700–2708.

[66] American Society for Testing Materials; Standard test methods for compressive properties of rigid cellular plastics, ASTM (D 1621–04a); *ASTM*: West Conshohocken, PA, 2004.

[67] Hawkins, M. C., O'Toole, B., and Jackovich D. Cell morphology and mechanical properties of rigid polyurethane foam. *J. Cell. Plast.* 41 (2005): 267–285.

[68] Valero, M. F., Pulido, J. E., Hernández, J. C., Posada, J. A., and Ramírez, A. Preparation and properties of polyurethanes based on castor oil chemically modified with yucca starch glycoside. *J. Elastom. Plast.* 41 (2009): 223–244.

[69] Pehler, R. C. C., Whiteman, J. R. , and Witte Jr., A. C. Lithium soap grease additive. *US patent* 4536308. 1985, Aug. 20.

[70] Xue, H.-J., Ding X.-J., Li H.-B., Wu H.-L., and Tang B. Effect of triethanolamine on properties of rigid polyurethane foam. *China Plastics Industry*. 2008.

# APPENDICES

# APPENDIX A

## ATR-IR spectra of unmodified and modified vegetable oils

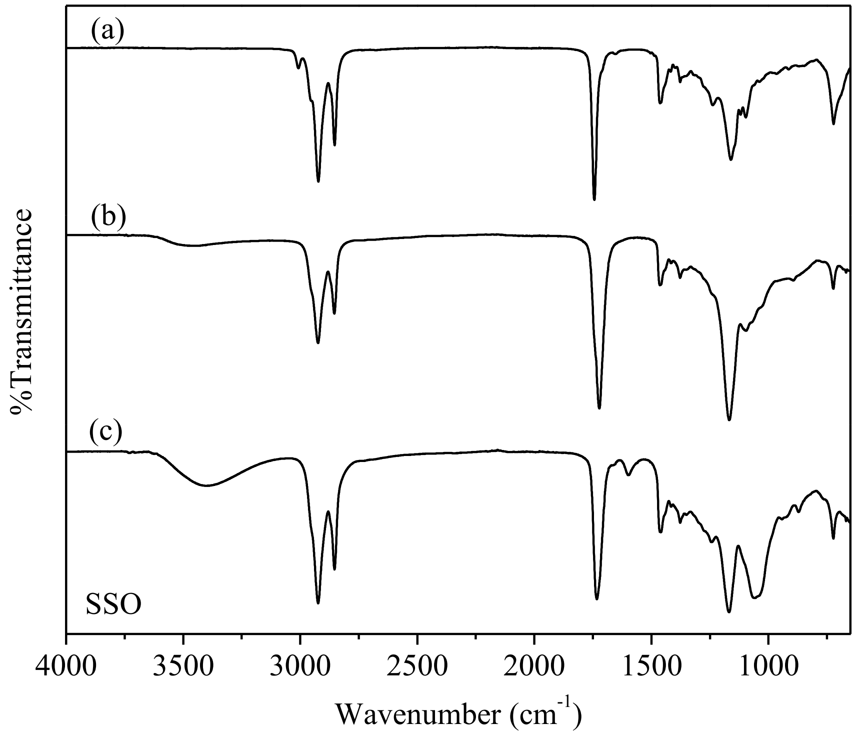


**Figure A1** ATR-IR spectra of unmodified and modified vegetable oils (a) sesame seed oil (SSO), (b) hydroxylated SSO and (c) alcoholyzed hydroxylated SSO (SSOB).

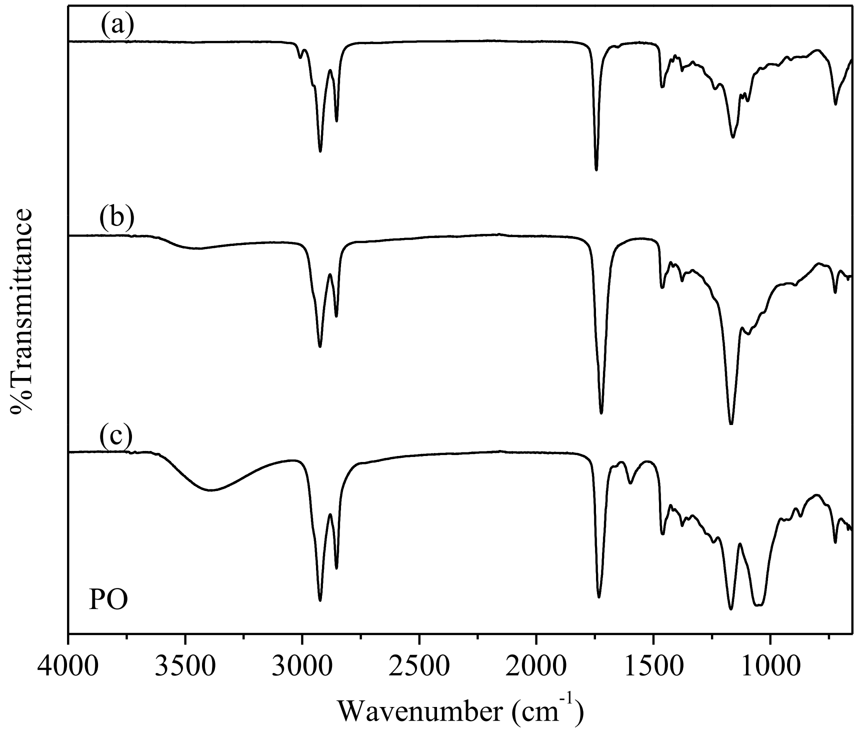


**Figure A2** ATR-IR spectra of unmodified and modified vegetable oils (a) pumpkin seed oil (PO), (b) hydroxylated PO and (c) alcoholyzed hydroxylated PO (POB).

# APPENDIX B

## The positive positive ion ESI-MS spectra of synthesized biopolyols

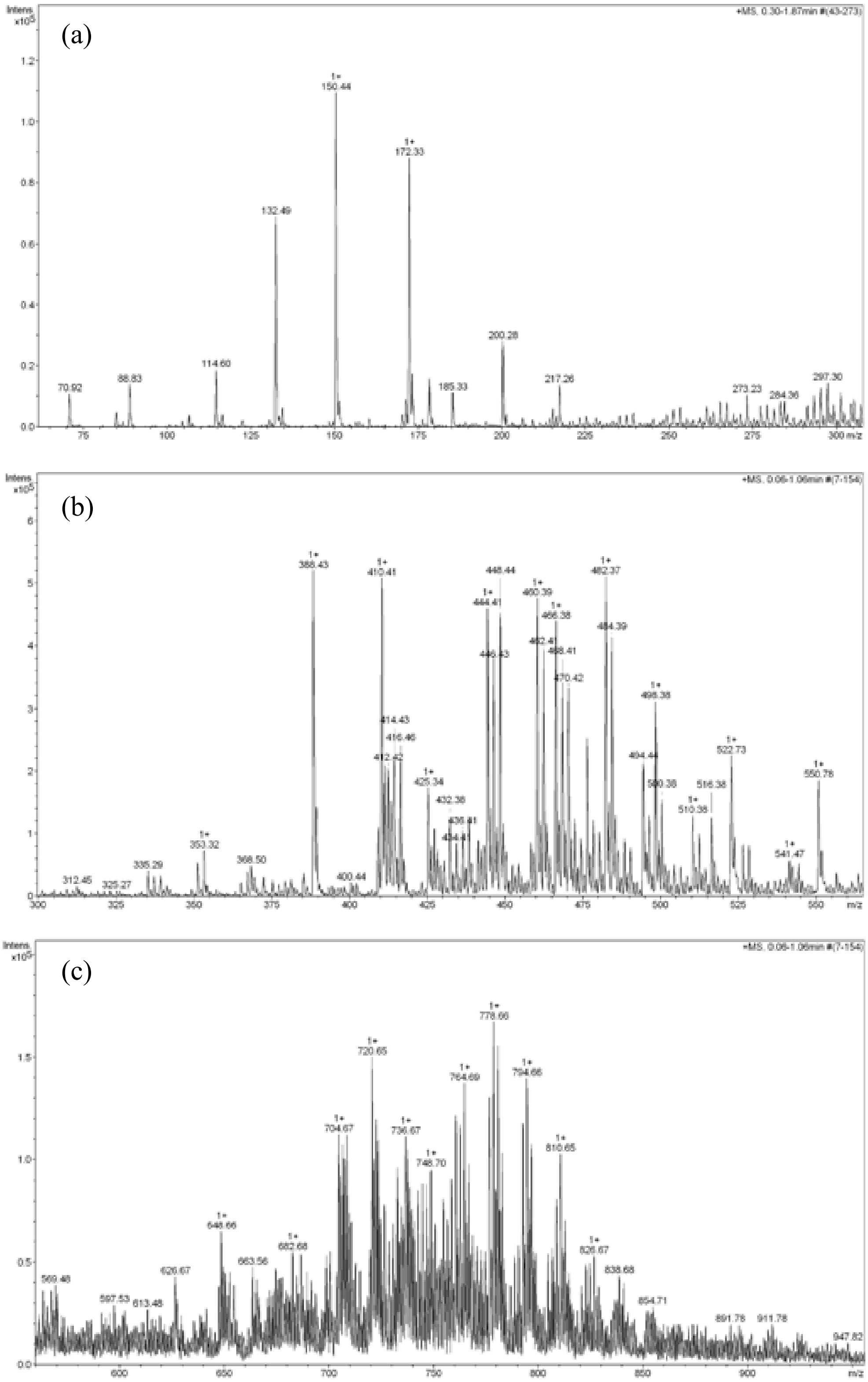


**Figure B1** The positive ion ESI-MS spectra of hairy basil seed oil-based polyols which extended mass range (a) 70–300, (b) 300–550, and (c) 550–850 m/z, respectively.

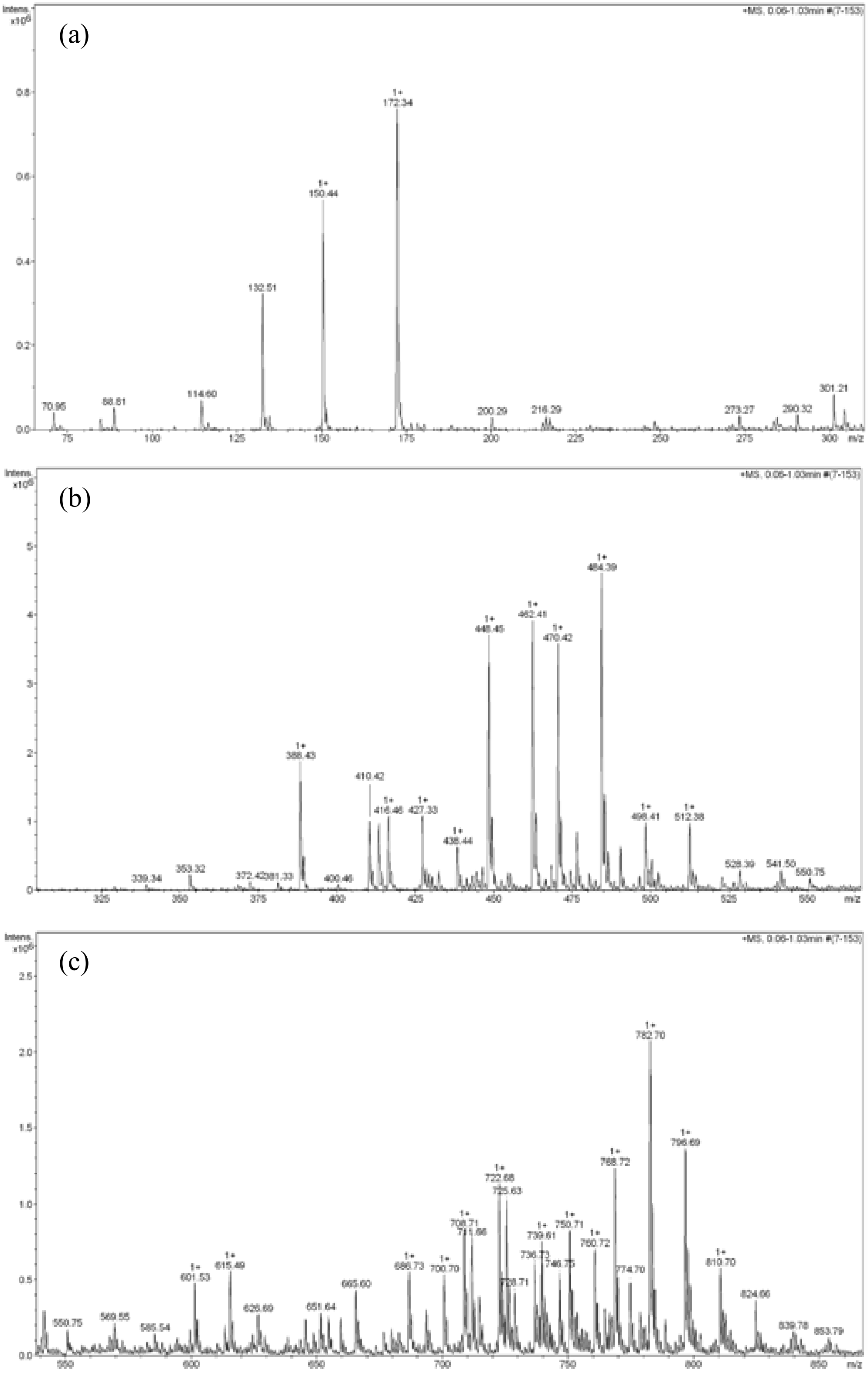


**Figure B2** The positive ion ESI-MS spectra of sesame seed oil-based polyols which extended mass range (a) 70–300, (b) 300–550, and (c) 550–850 m/z, respectively.

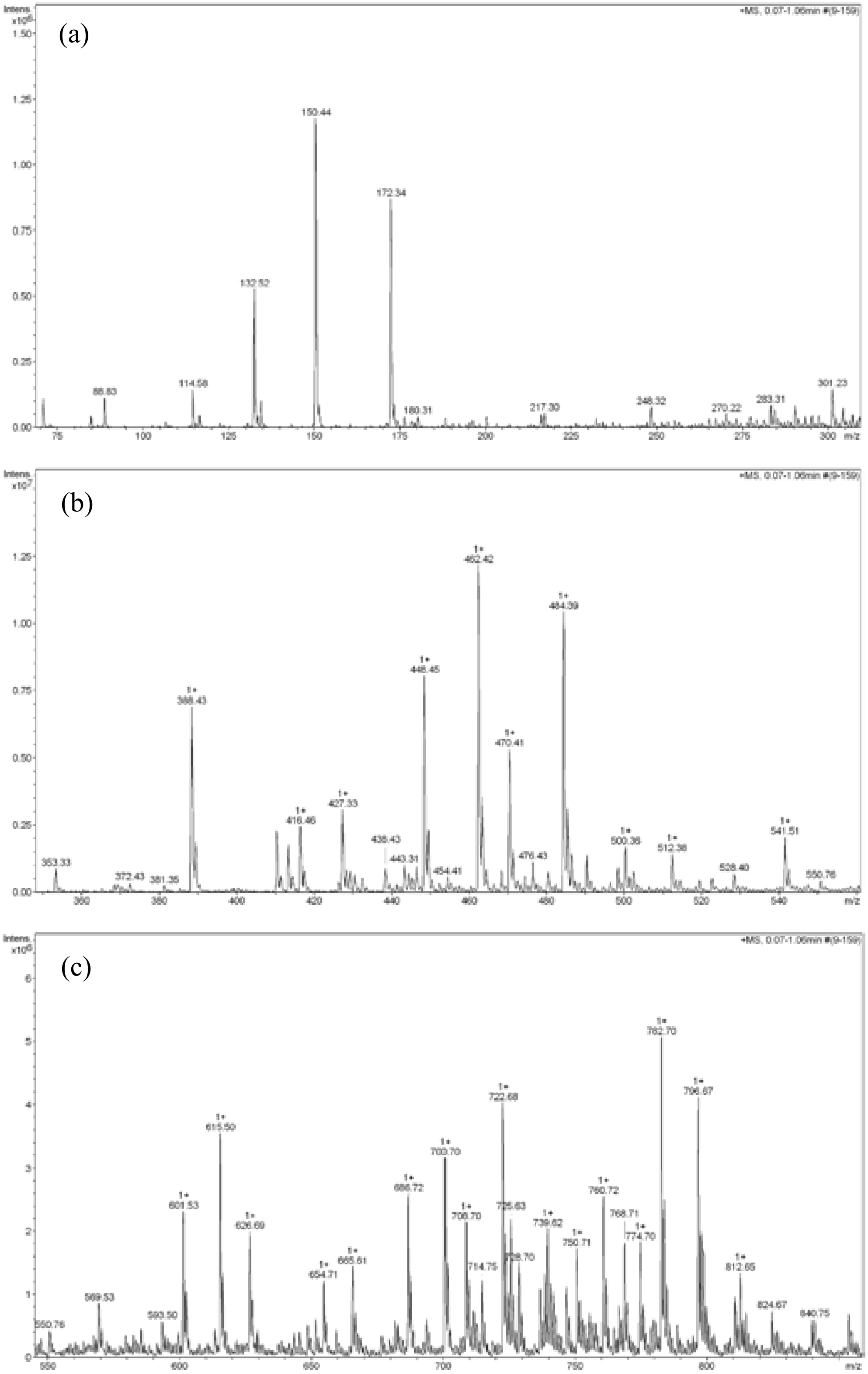
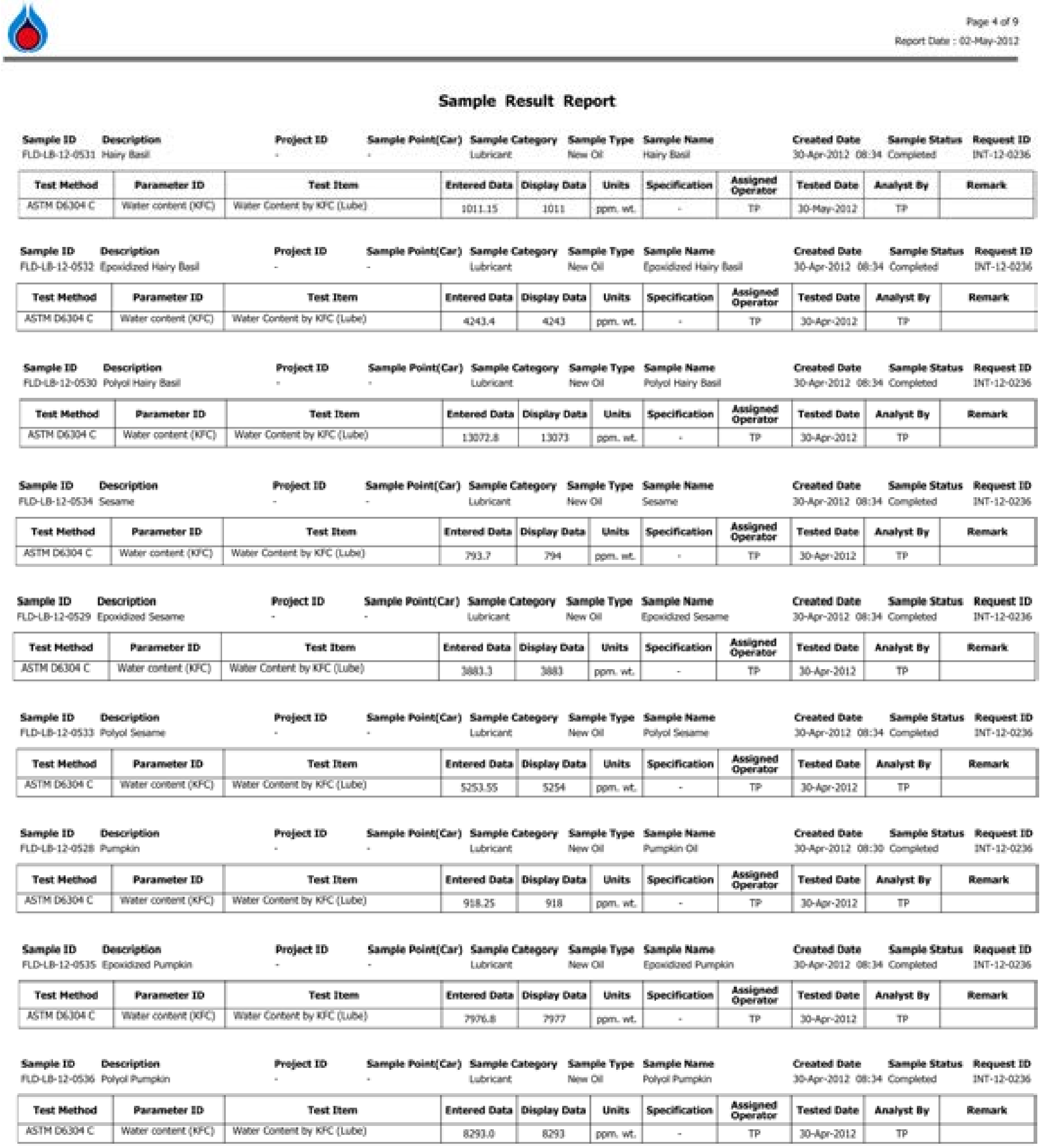


**Figure B3** The positive ion ESI-MS spectra of pumpkin seed oil-based polyols which extended mass range (a) 70–300, (b) 300–550, and (c) 550–850 m/z, respectively.

# APPENDIX C

## The water content data of unmodified and modified vegetable oils



Page 4 of 9
Report Date : 02-May-2012

## Sample Result Report

| Sample ID | Description | Project ID | Sample Point(Car) | Sample Category | Sample Type | Sample Name | Created Date | Sample Status | Request ID |
|---|---|---|---|---|---|---|---|---|---|
| FLD-LB-12-0531 | Hairy Basil | - | - | Lubricant | New Oil | Hairy Basil | 30-Apr-2012 08:34 | Completed | INT-12-0236 |

| Test Method | Parameter ID | Test Item | Entered Data | Display Data | Units | Specification | Assigned Operator | Tested Date | Analyst By | Remark |
|---|---|---|---|---|---|---|---|---|---|---|
| ASTM D6304 C | Water content (KFC) | Water Content by KFC (Lube) | 1011.15 | 1011 | ppm. wt. | - | TP | 30-May-2012 | TP | |

| Sample ID | Description | Project ID | Sample Point(Car) | Sample Category | Sample Type | Sample Name | Created Date | Sample Status | Request ID |
|---|---|---|---|---|---|---|---|---|---|
| FLD-LB-12-0532 | Epoxidized Hairy Basil | - | - | Lubricant | New Oil | Epoxidized Hairy Basil | 30-Apr-2012 08:34 | Completed | INT-12-0236 |

| Test Method | Parameter ID | Test Item | Entered Data | Display Data | Units | Specification | Assigned Operator | Tested Date | Analyst By | Remark |
|---|---|---|---|---|---|---|---|---|---|---|
| ASTM D6304 C | Water content (KFC) | Water Content by KFC (Lube) | 4243.4 | 4243 | ppm. wt. | - | TP | 30-Apr-2012 | TP | |

| Sample ID | Description | Project ID | Sample Point(Car) | Sample Category | Sample Type | Sample Name | Created Date | Sample Status | Request ID |
|---|---|---|---|---|---|---|---|---|---|
| FLD-LB-12-0530 | Polyol Hairy Basil | - | - | Lubricant | New Oil | Polyol Hairy Basil | 30-Apr-2012 08:34 | Completed | INT-12-0236 |

| Test Method | Parameter ID | Test Item | Entered Data | Display Data | Units | Specification | Assigned Operator | Tested Date | Analyst By | Remark |
|---|---|---|---|---|---|---|---|---|---|---|
| ASTM D6304 C | Water content (KFC) | Water Content by KFC (Lube) | 13072.8 | 13073 | ppm. wt. | - | TP | 30-Apr-2012 | TP | |

| Sample ID | Description | Project ID | Sample Point(Car) | Sample Category | Sample Type | Sample Name | Created Date | Sample Status | Request ID |
|---|---|---|---|---|---|---|---|---|---|
| FLD-LB-12-0534 | Sesame | - | - | Lubricant | New Oil | Sesame | 30-Apr-2012 08:34 | Completed | INT-12-0236 |

| Test Method | Parameter ID | Test Item | Entered Data | Display Data | Units | Specification | Assigned Operator | Tested Date | Analyst By | Remark |
|---|---|---|---|---|---|---|---|---|---|---|
| ASTM D6304 C | Water content (KFC) | Water Content by KFC (Lube) | 793.7 | 794 | ppm. wt. | - | TP | 30-Apr-2012 | TP | |

| Sample ID | Description | Project ID | Sample Point(Car) | Sample Category | Sample Type | Sample Name | Created Date | Sample Status | Request ID |
|---|---|---|---|---|---|---|---|---|---|
| FLD-LB-12-0529 | Epoxidized Sesame | - | - | Lubricant | New Oil | Epoxidized Sesame | 30-Apr-2012 08:34 | Completed | INT-12-0236 |

| Test Method | Parameter ID | Test Item | Entered Data | Display Data | Units | Specification | Assigned Operator | Tested Date | Analyst By | Remark |
|---|---|---|---|---|---|---|---|---|---|---|
| ASTM D6304 C | Water content (KFC) | Water Content by KFC (Lube) | 3883.3 | 3883 | ppm. wt. | - | TP | 30-Apr-2012 | TP | |

| Sample ID | Description | Project ID | Sample Point(Car) | Sample Category | Sample Type | Sample Name | Created Date | Sample Status | Request ID |
|---|---|---|---|---|---|---|---|---|---|
| FLD-LB-12-0533 | Polyol Sesame | - | - | Lubricant | New Oil | Polyol Sesame | 30-Apr-2012 08:34 | Completed | INT-12-0236 |

| Test Method | Parameter ID | Test Item | Entered Data | Display Data | Units | Specification | Assigned Operator | Tested Date | Analyst By | Remark |
|---|---|---|---|---|---|---|---|---|---|---|
| ASTM D6304 C | Water content (KFC) | Water Content by KFC (Lube) | 5253.55 | 5254 | ppm. wt. | - | TP | 30-Apr-2012 | TP | |

| Sample ID | Description | Project ID | Sample Point(Car) | Sample Category | Sample Type | Sample Name | Created Date | Sample Status | Request ID |
|---|---|---|---|---|---|---|---|---|---|
| FLD-LB-12-0528 | Pumpkin | - | - | Lubricant | New Oil | Pumpkin Oil | 30-Apr-2012 08:30 | Completed | INT-12-0236 |

| Test Method | Parameter ID | Test Item | Entered Data | Display Data | Units | Specification | Assigned Operator | Tested Date | Analyst By | Remark |
|---|---|---|---|---|---|---|---|---|---|---|
| ASTM D6304 C | Water content (KFC) | Water Content by KFC (Lube) | 918.25 | 918 | ppm. wt. | - | TP | 30-Apr-2012 | TP | |

| Sample ID | Description | Project ID | Sample Point(Car) | Sample Category | Sample Type | Sample Name | Created Date | Sample Status | Request ID |
|---|---|---|---|---|---|---|---|---|---|
| FLD-LB-12-0535 | Epoxidized Pumpkin | - | - | Lubricant | New Oil | Epoxidized Pumpkin | 30-Apr-2012 08:34 | Completed | INT-12-0236 |

| Test Method | Parameter ID | Test Item | Entered Data | Display Data | Units | Specification | Assigned Operator | Tested Date | Analyst By | Remark |
|---|---|---|---|---|---|---|---|---|---|---|
| ASTM D6304 C | Water content (KFC) | Water Content by KFC (Lube) | 7976.8 | 7977 | ppm. wt. | - | TP | 30-Apr-2012 | TP | |

| Sample ID | Description | Project ID | Sample Point(Car) | Sample Category | Sample Type | Sample Name | Created Date | Sample Status | Request ID |
|---|---|---|---|---|---|---|---|---|---|
| FLD-LB-12-0536 | Polyol Pumpkin | - | - | Lubricant | New Oil | Polyol Pumpkin | 30-Apr-2012 08:34 | Completed | INT-12-0236 |

| Test Method | Parameter ID | Test Item | Entered Data | Display Data | Units | Specification | Assigned Operator | Tested Date | Analyst By | Remark |
|---|---|---|---|---|---|---|---|---|---|---|
| ASTM D6304 C | Water content (KFC) | Water Content by KFC (Lube) | 8293.0 | 8293 | ppm. wt. | - | TP | 30-Apr-2012 | TP | |

# APPENDIX D

## NCO Index calculation

**NCO Index calculation of biopolyols from vegetable oils**

Calculation the parts by weight (pbw) of pure PMDI (Suprasec® 5005), Molar mass = 366.99, functionality = 2.7 at an isocyanate index 100, 125, 150, 175, 200 and 250 required to react with the following formulation:

**Table D1** Formulations of RPUR foams

| Formulation (pbw) | Part by weight |
|---|---|
| Polyols | 100.0 |
| [1] Raypol® 4218 (OH No. = 438.93 mg KOH/g) | |
| [2] Raypol® 8360 (OH No. = 460.12 mg KOH/g) | |
| [3] Hairy basil oil-based-polyol (OH No. = 382.51 mg KOH/g) | |
| [4] Sesame oil based-polyol (OH No. = 351.03 mg KOH/g) | |
| [5] Pumpkin oil based-polyol (OH No. = 340.24 mg KOH/g) | |
| Catalysts | 0.5 |
| Surfactant | 2.5 |
| Blowing agent (distilled $H_2O$, MW = 18 g/mole, functionality = 2) | 1.0–5.0 |
| PMDI (Suprasec® 5005), NCO indexes of 100–250 | ? |

**<u>Example 1:</u> PMDI used to react with Raypol® 4218 (OH number = 438.93 mg KOH/g) at NCO index = 100, water = 1.0 pbw.**

$$\text{Equivalent weight of Raypol 4218} = \frac{56.1}{\text{OH no.}} \times 1000$$

$$\text{Equivalent weight of Raypol 4218} = \frac{56.1}{438.93} \times 1000 = 127.81$$

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

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

$$\text{Number of equivalent in formulation} = \frac{\text{parts by weight (pbw)}}{\text{equivalent weight}}$$

Equivalent in the above formulation:

$$\text{Polyol (Raypol 4218)} = \frac{100}{127.81} = 0.782$$

$$\text{Water (blowing agent)} = 1\text{pbw ; Water} = \frac{1.0}{9.0} = 0.111$$

$$\text{Total equivalent weight} = 0.893$$

For stoichiometric equivalence, PMDI pbw is total equivalent × equivalent weight because PMDI reacts with polyol and water.

Thus:

$$\text{PMDI (pbw)} = 0.893 \times \frac{\text{PMDI molar mass}}{\text{functionality}}$$

$$= 0.893 \times \frac{366.99}{2.7}$$

$$= 121.38$$

**Notes:** 121.38 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

$$\text{Isocyanate actual} = \frac{121.38}{100} \text{ x } 100 = 121.38$$

Isocyanate index 125

$$\text{Isocyanate actual} = \frac{121.38}{100} \text{ x } 125 = 151.73$$

Isocyanate index 150

$$\text{Isocyanate actual} = \frac{121.38}{100} \text{ x } 150 = 182.37$$

Isocyanate index 175

$$\text{Isocyanate actual} = \frac{121.38}{100} \text{ x } 175 = 212.42$$

Isocyanate index 200

$$\text{Isocyanate actual} = \frac{121.38}{100} \text{ x } 200 = 242.76$$

Isocyanate index 225

$$\text{Isocyanate actual} = \frac{121.38}{100} \text{ x } 225 = 273.11$$

Isocyanate index 250

$$\text{Isocyanate actual} = \frac{121.38}{100} \times 250 = 303.45$$

**Table D2** The actual amount of PMDI used to react with Rapol 4218 at varying NCO index 100–250, different quantity of blowing agent content at 1.0–5.0 pbw, 1.0 pbw of catalyst, and 2.5 pbw of surfactant

| Blowing agent (pbw) | NCO Index | | | | | | |
|---|---|---|---|---|---|---|---|
| | 100 | 125 | 150 | 175 | 200 | 225 | 250 |
| 1 | 121.38 | 151.73 | 182.37 | 212.42 | 242.76 | 273.11 | 303.45 |
| 2 | 136.47 | 170.59 | 204.71 | 238.82 | 272.94 | 307.06 | 341.18 |
| 3 | 151.55 | 189.43 | 227.32 | 265.21 | 303.10 | 340.99 | 378.88 |
| 4 | 166.64 | 208.30 | 249.96 | 291.62 | 333.28 | 374.94 | 416.60 |
| 5 | 181.86 | 227.33 | 272.79 | 318.26 | 363.72 | 409.19 | 454.65 |

**<u>Example 2:</u> PMDI used to react with Raypol® 8360 (OH number = 460.12 mg KOH/g) at NCO index = 100, water = 1.0 pbw.**

$$\text{Equivalent weight of Raypol 8360} = \frac{56.1}{\text{OH no.}} \times 1000$$

$$\text{Equivalent weight of Raypol 8360} = \frac{56.1}{360.12} \times 1000 = 155.78$$

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

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

$$\text{Number of equivalent in formulation} = \frac{\text{parts by weight (pbw)}}{\text{equivalent weight}}$$

Equivalent in the above formulation:

$$\text{Polyol (Raypol 8360)} = \frac{100}{155.78} = 0.642$$

$$\text{Water (blowing agent)} = \text{1pbw} ; \text{Water} = \frac{1.0}{9.0} = 0.111$$

$$\text{Total equivalent weight} = 0.753$$

For stoichiometric equivalence, PMDI pbw is total equivalent × equivalent weight because PMDI reacts with polyol and water.

Thus:

$$\text{PMDI (pbw)} = 0.753 \times \frac{\text{PMDI molar mass}}{\text{functionality}}$$

$$= 0.753 \times \frac{366.99}{2.7}$$

$$= 102.35$$

**Notes:** 102.35 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

$$\text{Isocyanate actual} = \frac{102.35}{100} \times 100 = 102.35$$

Isocyanate index 125

$$\text{Isocyanate actual} = \frac{102.35}{100} \times 125 = 127.94$$

Isocyanate index 150

$$\text{Isocyanate actual} = \frac{102.35}{100} \times 150 = 153.53$$

Isocyanate index 175

$$\text{Isocyanate actual} = \frac{102.35}{100} \times 175 = 179.11$$

Isocyanate index 200

$$\text{Isocyanate actual} = \frac{102.35}{100} \times 200 = 204.70$$

Isocyanate index 225

$$\text{Isocyanate actual} = \frac{102.35}{100} \times 225 = 230.29$$

Isocyanate index 250

$$\text{Isocyanate actual} = \frac{102.35}{100} \times 250 = 255.88$$

**Table D3** The actual amount of PMDI used to react with Rapol® 8360 at varying NCO index 100–250, different quantity of blowing agent content at 1.0–5.0 pbw, 1.0 pbw of catalyst, and 2.5 pbw of surfactant

| Blowing agent (pbw) | NCO Index | | | | | | |
|---|---|---|---|---|---|---|---|
| | 100 | 125 | 150 | 175 | 200 | 225 | 250 |
| 1 | 102.35 | 127.94 | 153.53 | 179.11 | 204.70 | 230.29 | 255.88 |
| 2 | 117.44 | 146.80 | 176.16 | 205.52 | 234.88 | 264.24 | 293.60 |
| 3 | 132.52 | 165.65 | 198.78 | 231.91 | 265.04 | 298.11 | 331.30 |
| 4 | 147.61 | 184.51 | 221.42 | 258.32 | 295.22 | 332.12 | 369.03 |
| 5 | 162.83 | 203.53 | 244.25 | 284.95 | 325.66 | 366.37 | 407.08 |

<u>Example 3</u>: **PMDI used to react with hairy basil seed oil-based polyol (OH number = 382.51 mg KOH/g) at NCO index = 100, water = 1.0 pbw.**

$$\text{Equivalent weight of HBOB} = \frac{56.1}{\text{OH no.}} \times 1000$$

$$\text{Equivalent weight of HBOB} = \frac{56.1}{382.51} \times 1000 = 146.66$$

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

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

$$\text{Number of equivalent in formulation} = \frac{\text{parts by weight (pbw)}}{\text{equivalent weight}}$$

Equivalent in the above formulation:

$$\text{Polyol (HBOB)} = \frac{100}{146.66} = 0.682$$

$$\text{Water (blowing agent)} = 1\text{pbw} ;\ \text{Water} = \frac{1.0}{9.0} = 0.111$$

$$\text{Total equivalent weight} = 0.793$$

For stoichiometric equivalence, PMDI pbw is total equivalent × equivalent weight because PMDI reacts with polyol and water.

Thus:

$$\text{PMDI (pbw)} = 0.793 \times \frac{\text{PMDI molar mass}}{\text{functionality}}$$

$$= 0.793 \times \frac{366.99}{2.7}$$

$$= 107.78$$

**Notes:** 107.78 defines the isocyanate quantity at 100 index

Where:

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

Thus:

Isocyanate index 100

$$\text{Isocyanate actual} = \frac{107.78}{100} \text{ x } 100 = 107.78$$

Isocyanate index 125

$$\text{Isocyanate actual} = \frac{107.78}{100} \text{ x } 125 = 134.73$$

Isocyanate index 150

$$\text{Isocyanate actual} = \frac{107.78}{100} \text{ x } 150 = 161.67$$

Isocyanate index 175

$$\text{Isocyanate actual} = \frac{107.78}{100} \text{ x } 175 = 188.62$$

Isocyanate index 200

$$\text{Isocyanate actual} = \frac{107.78}{100} \text{ x } 200 = 215.56$$

Isocyanate index 225

$$\text{Isocyanate actual} = \frac{107.78}{100} \text{ x } 225 = 242.51$$

Isocyanate index 250

$$\text{Isocyanate actual} = \frac{107.78}{100} \times 250 = 269.45$$

**Table D4** The actual amount of PMDI used to react with hairy basil seed oil-based polyol at varying NCO index 100–250, different quantity of blowing agent content at 1.0–5.0 pbw, 1.0 pbw of catalyst, and 2.5 pbw of surfactant

| Blowing agent (pbw) | NCO Index | | | | | | |
|---|---|---|---|---|---|---|---|
| | 100 | 125 | 150 | 175 | 200 | 225 | 250 |
| 1 | 107.78 | 134.73 | 161.67 | 188.62 | 215.56 | 242.51 | 269.45 |
| 2 | 122.87 | 153.59 | 184.31 | 215.02 | 245.74 | 276.46 | 307.18 |
| 3 | 137.96 | 172.45 | 206.94 | 241.43 | 275.92 | 310.41 | 344.90 |
| 4 | 153.05 | 191.31 | 229.58 | 267.84 | 306.10 | 344.36 | 382.63 |
| 5 | 168.27 | 210.34 | 252.41 | 294.47 | 336.54 | 378.61 | 420.68 |

**Example 4: PMDI used react with sesame seed oil-based polyol (OH number = 351.03 mg KOH/g) at NCO index = 100, water = 1.0 pbw.**

$$\text{Equivalent weight of SSOB} = \frac{56.1}{\text{OH no.}} \times 1000$$

$$\text{Equivalent weight of SSOB} = \frac{56.1}{351.03} \times 1000 = 159.82$$

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

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

$$\text{Number of equivalent in formulation} = \frac{\text{parts by weight (pbw)}}{\text{equivalent weight}}$$

Equivalent in the above formulation:

$$\text{Polyol (SSOB)} = \frac{100}{159.82} = 0.626$$

$$\text{Water (blowing agent)} = 1\text{pbw} ; \text{Water} = \frac{1.0}{9.0} = 0.111$$

$$\text{Total equivalent weight} = 0.737$$

For stoichiometric equivalence, PMDI pbw is total equivalent × equivalent weight because PMDI reacts with polyol and water.

Thus:

$$\text{PMDI (pbw)} = 0.737 \times \frac{\text{PMDI molar mass}}{\text{functionality}}$$

$$= 0.737 \times \frac{366.99}{2.7}$$

$$= 100.17$$

**Notes:** 100.17 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

$$\text{Isocyanate actual} = \frac{100.17}{100} \times 100 = 100.17$$

Isocyanate index 125

$$\text{Isocyanate actual} = \frac{100.17}{100} \times 125 = 125.21$$

Isocyanate index 150

$$\text{Isocyanate actual} = \frac{100.17}{100} \times 150 = 150.26$$

Isocyanate index 175

$$\text{Isocyanate actual} = \frac{100.17}{100} \times 175 = 175.30$$

Isocyanate index 200

$$\text{Isocyanate actual} = \frac{100.17}{100} \times 200 = 200.34$$

Isocyanate index 225

$$\text{Isocyanate actual} = \frac{100.17}{100} \times 225 = 225.38$$

Isocyanate index 250

$$\text{Isocyanate actual} = \frac{100.17}{100} \times 250 = 250.43$$

**Table D5** The actual amount of PMDI used to react with sesame seed oil-based polyol at varying NCO index 100 – 250, different quantity of blowing agent content at 1.0 – 5.0 pbw, 1.0 pbw of catalyst, and 2.5 pbw of surfactant

| Blowing agent (pbw) | NCO Index | | | | | | |
|---|---|---|---|---|---|---|---|
| | 100 | 125 | 150 | 175 | 200 | 225 | 250 |
| 1 | 100.17 | 125.21 | 150.26 | 175.30 | 200.34 | 225.38 | 250.43 |
| 2 | 115.26 | 144.08 | 172.89 | 201.71 | 230.52 | 259.34 | 288.15 |
| 3 | 130.35 | 162.94 | 195.53 | 228.11 | 260.70 | 293.29 | 325.88 |
| 4 | 145.44 | 181.80 | 218.16 | 254.52 | 290.88 | 327.24 | 363.60 |
| 5 | 160.66 | 200.83 | 240.99 | 281.16 | 321.32 | 361.49 | 401.65 |

**<u>Example 5</u>: PMDI used to react with pumpkin seed oil-based polyol (OH number = 340.24 mg KOH/g) at NCO index = 100, water = 1.0 pbw.**

$$\text{Equivalent weight of PO} = \frac{56.1}{\text{OH no.}} \times 1000$$

$$\text{Equivalent weight of PO} = \frac{56.1}{340.24} \times 1000 = 164.88$$

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

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

$$\text{Number of equivalent in formulation} = \frac{\text{parts by weight (pbw)}}{\text{equivalent weight}}$$

Equivalent in the above formulation:

$$\text{Polyol (POB)} = \frac{100}{164.88} = 0.607$$

$$\text{Water (blowing agent)} = 1\text{pbw ; Water} = \frac{1.0}{9.0} = 0.111$$

$$\text{Total equivalent weight} = 0.718$$

For stoichiometric equivalence, PMDI pbw is total equivalent × equivalent weight because PMDI reacts with polyol and water.

Thus:

$$\text{PMDI (pbw)} = 0.718 \times \frac{\text{PMDI molar mass}}{\text{functionality}}$$

$$= 0.718 \times \frac{366.99}{2.7}$$

$$= 97.59$$

**Notes:** 97.59 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

$$\text{Isocyanate actual} = \frac{97.59}{100} \times 100 = 97.59$$

Isocyanate index 125

$$\text{Isocyanate actual} = \frac{97.59}{100} \times 125 = 121.99$$

Isocyanate index 150

$$\text{Isocyanate actual} = \frac{97.59}{100} \times 150 = 146.39$$

Isocyanate index 175

$$\text{Isocyanate actual} = \frac{97.59}{100} \times 175 = 170.78$$

Isocyanate index 200

$$\text{Isocyanate actual} = \frac{97.59}{100} \times 200 = 195.18$$

Isocyanate index 225

$$\text{Isocyanate actual} = \frac{97.59}{100} \times 225 = 219.58$$

Isocyanate index 250

$$\text{Isocyanate actual} = \frac{97.59}{100} \times 250 = 243.08$$

**Table D6** The actual amount of PMDI used to react with pumpkin seed oil-based polyol at varying NCO index 100–250, different quantity of blowing agent content at 1.0–5.0 pbw, 1.0 pbw of catalyst, and 2.5 pbw of surfactant

| Blowing agent (pbw) | NCO Index | | | | | | |
|---|---|---|---|---|---|---|---|
| | 100 | 125 | 150 | 175 | 200 | 225 | 250 |
| 1 | 97.59 | 121.99 | 146.39 | 170.78 | 195.18 | 219.58 | 243.98 |
| 2 | 112.68 | 140.85 | 169.02 | 197.19 | 225.36 | 253.53 | 281.70 |
| 3 | 127.77 | 159.71 | 191.66 | 223.58 | 255.54 | 287.48 | 319.43 |
| 4 | 142.85 | 178.56 | 214.28 | 249.99 | 285.70 | 321.41 | 357.13 |
| 5 | 158.08 | 197.60 | 237.12 | 276.64 | 316.16 | 355.68 | 395.2 |

# APPENDIX E

## ATR-IR spectra of RPUR foams for NCO conversion calculation

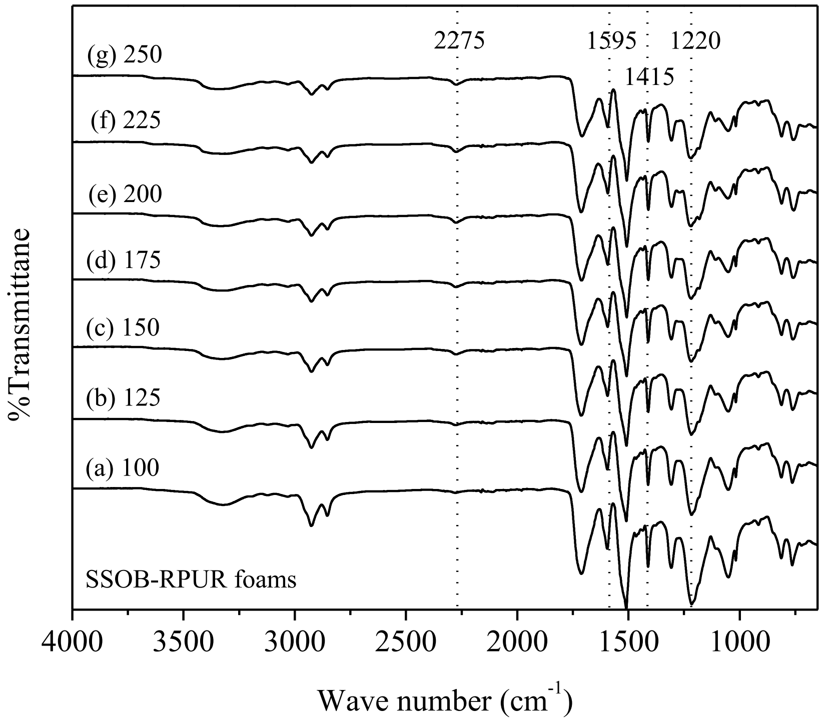


**Figure E1** ATR-IR spectra of SSOB-based RPUR foams prepared at NCO index of 100–250, 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant.

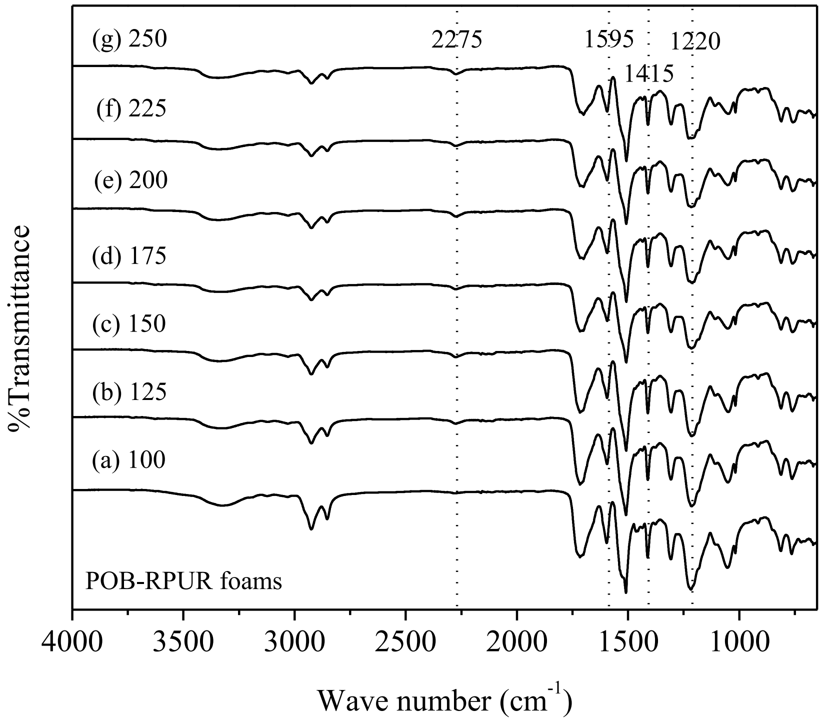


**Figure E2** ATR-IR spectra of POB-based RPUR foams prepared at NCO index of 100–250, 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant.

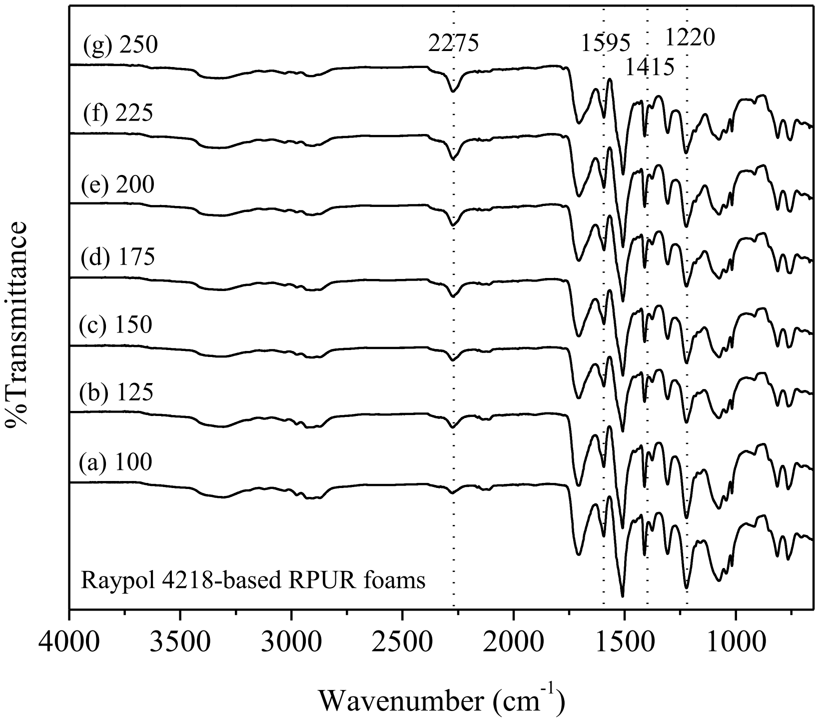


**Figure E3** ATR-IR spectra of Raypol® 4218-based RPUR foams prepared at NCO index of 100–250, 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant.

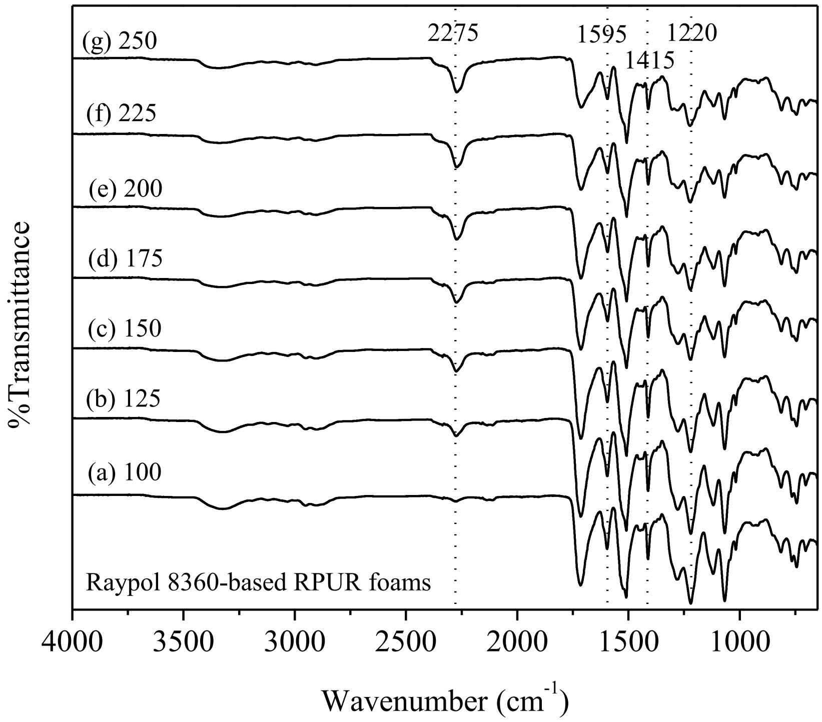


**Figure E3** ATR-IR spectra of Raypol® 8360-based RPUR foams prepared at NCO index of 100–250, 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant.

**Calculation of NCO Conversion**

The NCO conversion can be calculated by FTIR method, defined as the ratio between isocyanate peak area at time t and isocynate peak at time 0, following equation:

$$\text{Isocyanate conversion (\%)} = \left[ 1 - \frac{\text{NCO}^t}{\text{NCO}^i} \right] \text{x } 100$$

Where:

$\text{NCO}^t$ is the area of isocyanate absorbance peak area at time t

$\text{NCO}^i$ is the area of isocyanate absorbance peak area at time 0.

Quantity of free NCO in RPUR foams were normalized by aromatic ring absorption band at 1595 $\text{cm}^{-1}$.

**Table E1** Free NCO absorbance peak area in PMDI (Suprasec® 5005) from ATR-IR

| PMDI (Suprasec® 5005) spectra | NCO Absorbance peak area Normalized @ 1.0 Ar-H peak area |
|---|---|
| 1 | 98.132 |
| 2 | 98.095 |
| 3 | 98.203 |
| Average ($\text{NCO}^i$) ; ATR-IR | 98.143 |

**Example:** Calculate the conversion of isocyanate ($\alpha$) and PIR/PUR of RPUR foams prepared from HBOB at NCO index of 100 that shown in Table D2

**Conversion of Isocyanate (%)**

Data at **Table E1**

Absorbance peak area of initial NCO = 98.1 = $NCO^i$

The data from **Table E2** at NCO index 100, absorbance peak area of free NCO was normalized by aromatic quantity:

Absorbance peak area of final NCO = 0.649 = NCO

Thus:

$$\text{conversion of isocyanate (\%)} = \left[ 1- \frac{NCO^t}{NCO^i} \right] \text{x } 100$$

$$= \left[ 1- \frac{0.10}{98.1} \right] \text{x } 100$$

% NCO conversion = 99.898

**PIR/PUR**

Absorbance peak area of PIR (polyisocyanate) = 3.285

Absorbance peak area of PUR (polyurethane) = 25.029

Thus:

$$\text{PIR/PUR} = \frac{3.285}{25.029} = 0.130$$

**Table E2** NCO conversion of HBOB-based RPUR foams prepared at NCO index of 100 – 250, 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant

| NCO index | Peak area | | | | | NCO conversion (%) | PIR/PUR |
|---|---|---|---|---|---|---|---|
| | NCO 2275 cm$^{-1}$ | Ar-H 1595 cm$^{-1}$ | PIR 1415 cm$^{-1}$ | PUR 1220 cm$^{-1}$ | NCO$^{f}$ (Ar-H=1.0) | | |
| 100 | 0.649 | 6.475 | 3.285 | 25.209 | 0.100 | 99.898 | 0.130 |
| 125 | 1.150 | 6.671 | 3.920 | 25.125 | 0.172 | 99.824 | 0.156 |
| 150 | 1.218 | 6.073 | 3.600 | 22.188 | 0.201 | 99.320 | 0.162 |
| 175 | 1.300 | 5.814 | 3.437 | 20.417 | 0.223 | 97.773 | 0.168 |
| 200 | 1.278 | 5.043 | 3.040 | 17.328 | 0.253 | 99.742 | 0.175 |
| 225 | 1.457 | 5.330 | 3.192 | 17.899 | 0.273 | 99.721 | 0.178 |
| 250 | 1.626 | 5.657 | 3.434 | 18.489 | 0.287 | 99.707 | 0.185 |

**Table E3** NCO conversion of SSOB-based RPUR foams prepared at NCO index of 100 – 250, 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant

| NCO index | Peak area | | | | | NCO conversion (%) | PIR/PUR |
|---|---|---|---|---|---|---|---|
| | NCO 2275 cm$^{-1}$ | Ar-H 1595 cm$^{-1}$ | PIR 1415 cm$^{-1}$ | PUR 1220 cm$^{-1}$ | NCO$^{f}$ (Ar-H=1.0) | | |
| 100 | 0.530 | 6.936 | 3.584 | 28.227 | 0.076 | 99.922 | 0.127 |
| 125 | 0.750 | 5.357 | 2.892 | 21.169 | 0.140 | 99.857 | 0.131 |
| 150 | 1.090 | 5.248 | 3.066 | 18.537 | 0.208 | 99.788 | 0.165 |
| 175 | 1.167 | 5.053 | 2.979 | 17.539 | 0.231 | 99.764 | 0.170 |
| 200 | 1.453 | 5.483 | 3.239 | 17.367 | 0.265 | 99.729 | 0.187 |
| 225 | 1.644 | 5.644 | 3.327 | 16.415 | 0.291 | 99.703 | 0.202 |
| 250 | 1.613 | 5.361 | 3.596 | 17.020 | 0.301 | 99.693 | 0.211 |

**Table E4** NCO conversion of POB-based RPUR foams prepared at NCO index of 100 – 250, 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant

| NCO index | Peak area | | | | | NCO conversion (%) | PIR/PUR |
|---|---|---|---|---|---|---|---|
| | NCO 2275 cm$^{-1}$ | Ar-H 1595 cm$^{-1}$ | PIR 1415 cm$^{-1}$ | PUR 1220 cm$^{-1}$ | NCO$^{f}$ (Ar-H=1.0) | | |
| 100 | 0.359 | 6.178 | 2.935 | 23.559 | 0.058 | 99.941 | 0.125 |
| 125 | 0.851 | 5.457 | 2.929 | 21.169 | 0.156 | 99.841 | 0.136 |
| 150 | 1.194 | 5.583 | 2.843 | 19.982 | 0.214 | 99.782 | 0.142 |
| 175 | 1.225 | 5.030 | 2.613 | 17.529 | 0.242 | 99.753 | 1.491 |
| 200 | 1.244 | 4.866 | 2.520 | 16.332 | 0.256 | 99.739 | 0.154 |
| 225 | 1.443 | 5.522 | 2.593 | 15.982 | 0.261 | 99.733 | 0.162 |
| 250 | 1.345 | 4.980 | 2.604 | 15.924 | 0.270 | 99.724 | 0.163 |

**Table E5** NCO conversion of Raypol 8360 RPUR foams prepared at NCO index of 100 – 250, 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant

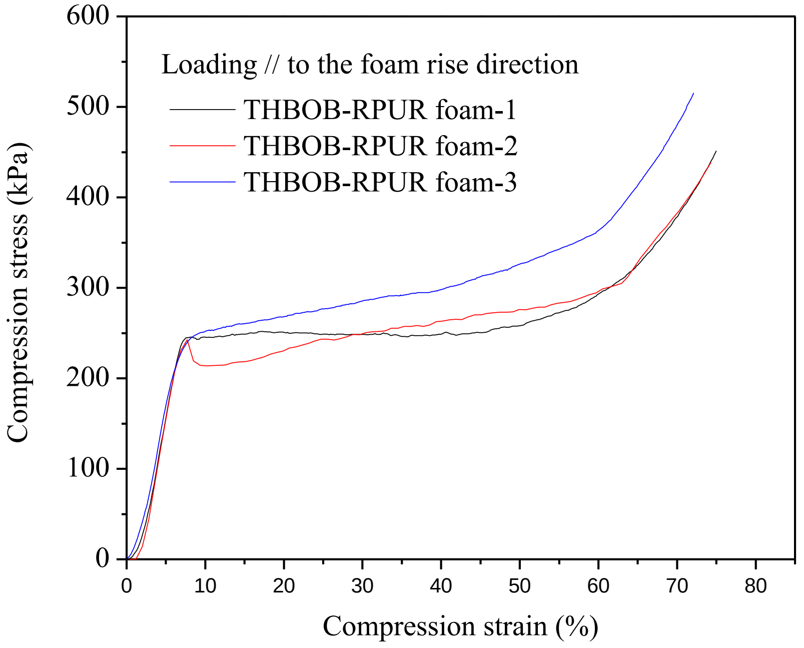
| NCO index | Peak area | | | | | NCO conversion (%) | PIR/PUR |
|---|---|---|---|---|---|---|---|
| | NCO 2275 cm$^{-1}$ | Ar-H 1595 cm$^{-1}$ | PIR 1415 cm$^{-1}$ | PUR 1220 cm$^{-1}$ | NCO$^{f}$ (Ar-H=1.0) | | |
| 100 | 0.604 | 4.031 | 2.015 | 16.864 | 0.150 | 99.847 | 0.120 |
| 125 | 0.873 | 2.830 | 2.346 | 16.994 | 0.309 | 99.685 | 0.138 |
| 150 | 1.268 | 2.125 | 3.023 | 20.224 | 0.597 | 99.391 | 0.150 |
| 175 | 1.231 | 1.437 | 3.784 | 20.782 | 0.857 | 99.127 | 0.182 |
| 200 | 1.823 | 1.007 | 5.214 | 21.754 | 1.810 | 98.155 | 0.240 |
| 225 | 1.635 | 0.783 | 5.751 | 19.424 | 2.086 | 97.871 | 0.296 |
| 250 | 1.248 | 0.425 | 8.223 | 22.467 | 2.938 | 99.005 | 0.366 |

**Table E6** NCO conversion of Raypol 4218 RPUR foams prepared at NCO indexes of 100 – 250, 3.0 pbw of water, 1.0 pbw of catalyst, and 2.5 pbw of surfactant

| NCO index | Peak area | | | | | NCO conversion (%) | PIR/PUR |
|---|---|---|---|---|---|---|---|
| | NCO 2275 cm$^{-1}$ | Ar-H 1595 cm$^{-1}$ | PIR 1415 cm$^{-1}$ | PUR 1220 cm$^{-1}$ | NCO$^{f}$ (Ar-H=1.0) | | |
| 100 | 0.699 | 4.006 | 4.515 | 24.228 | 0.174 | 99.822 | 0.186 |
| 125 | 0.901 | 3.125 | 3.216 | 15.125 | 0.288 | 99.706 | 0.212 |
| 150 | 0.902 | 2.013 | 4.603 | 20.249 | 0.448 | 99.542 | 0.227 |
| 175 | 1.724 | 2.165 | 5.437 | 21.987 | 0.796 | 99.188 | 0.247 |
| 200 | 1.989 | 1.888 | 5.210 | 19.848 | 1.054 | 98.926 | 0.263 |
| 225 | 1.756 | 1.287 | 4.289 | 15.215 | 1.364 | 98.609 | 0.281 |
| 250 | 1.934 | 1.129 | 6.234 | 19.988 | 1.713 | 98.254 | 0.311 |

# APPENDIX F

## Compression strain versus stress curves of rigid polyurethane foams



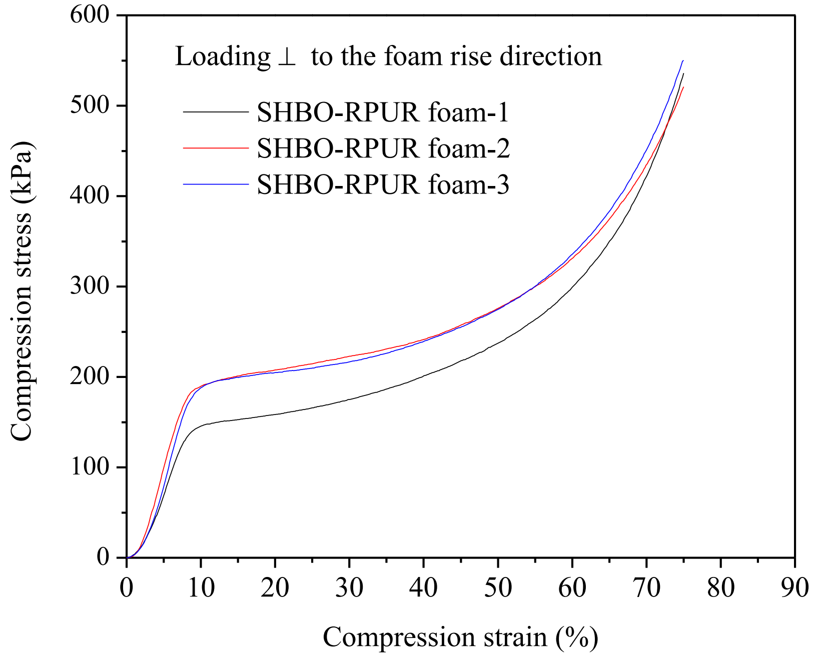


**Figure F1** Compression strain versus stress curves of hairy basil seed oil-based RPUR foams in parallel and perpendicular to the foam rise direction with foam density ranging from 40–45 kg/m$^3$.

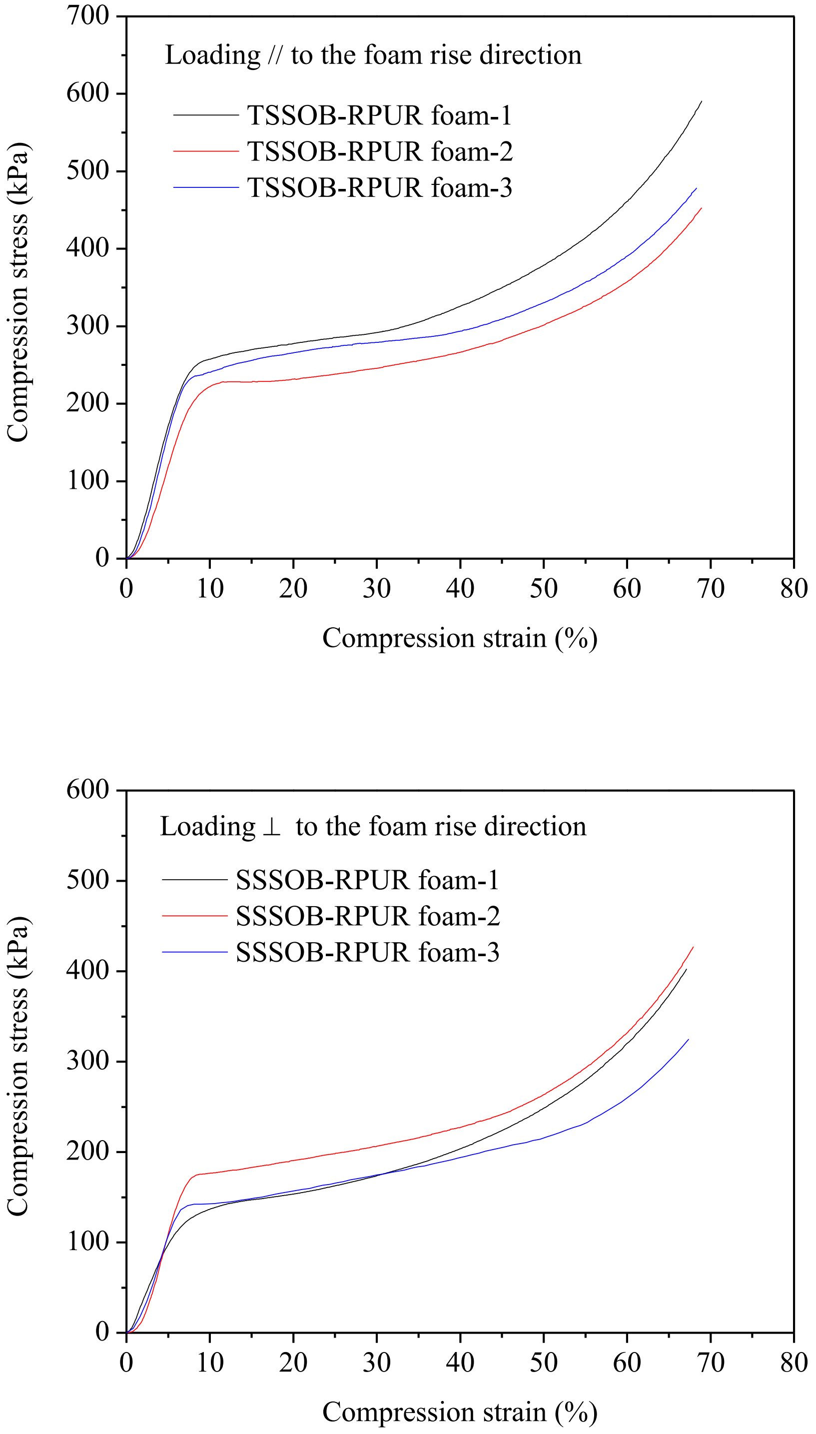
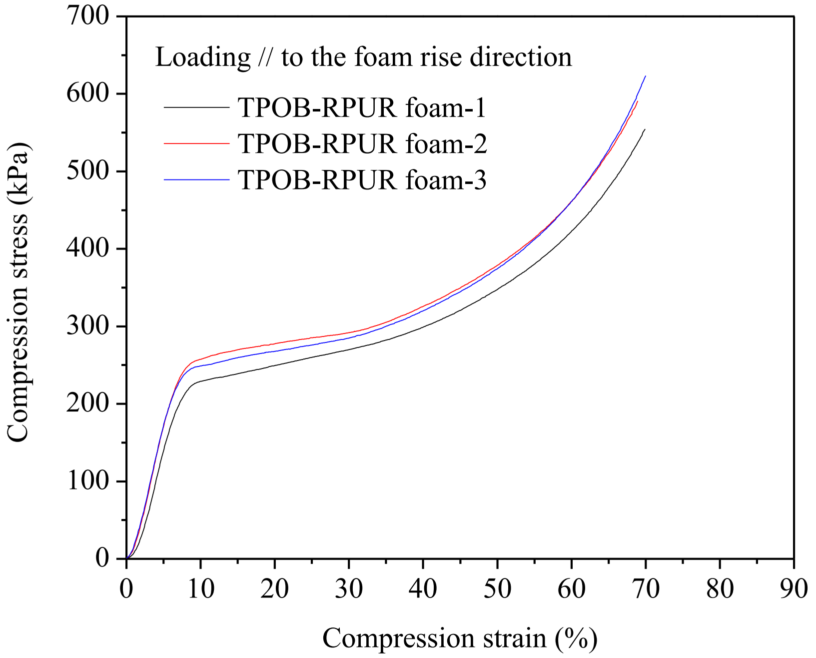


**Figure F2** Compression strain versus stress curves of sesame seed oil-based RPUR foams in parallel and perpendicular to the foam rise direction with foam density ranging from 40–45 kg/m$^3$.



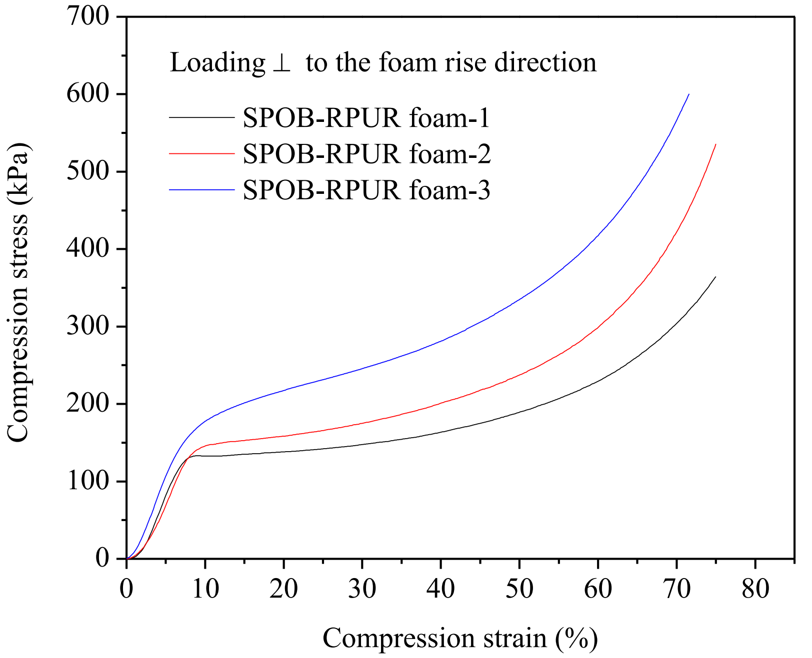
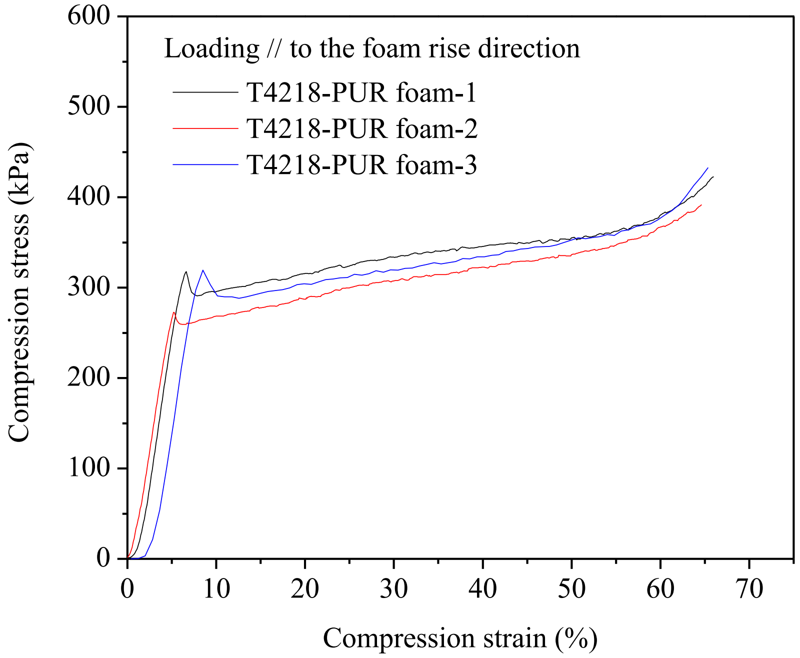


**Figure F3** Compression strain versus stress curves of pumpkin seed oil-based RPUR foams in parallel and perpendicular to the foam rise direction with foam density ranging from 40–45 kg/m$^3$.



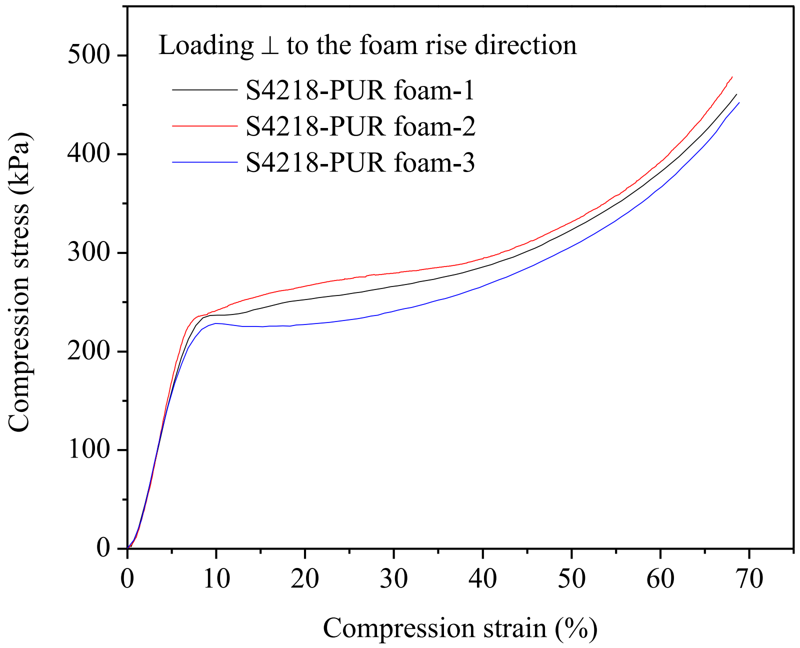
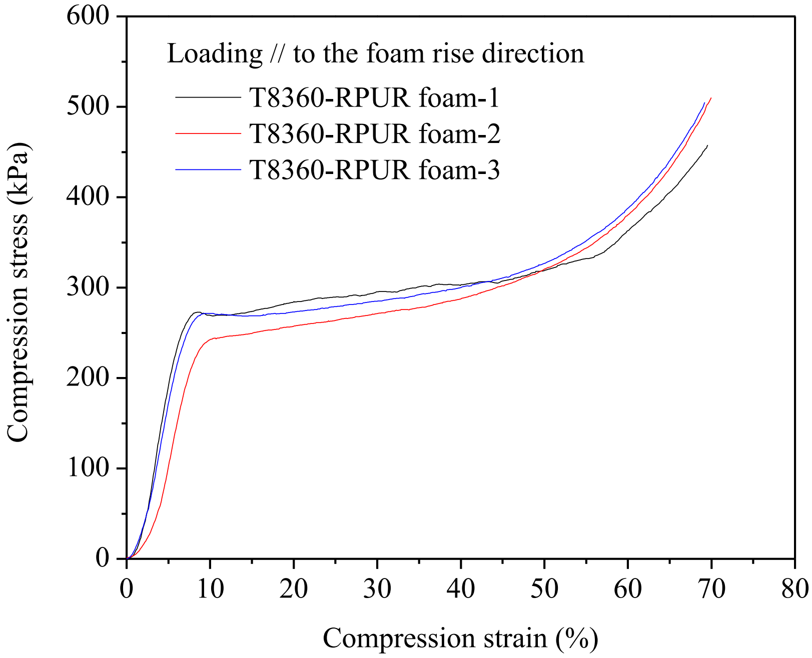


**Figure F4** Compression strain versus stress curves of Raypol® 4218-based RPUR foams in parallel and perpendicular to the foam rise direction with foam density ranging from 40–45 kg/m$^3$.



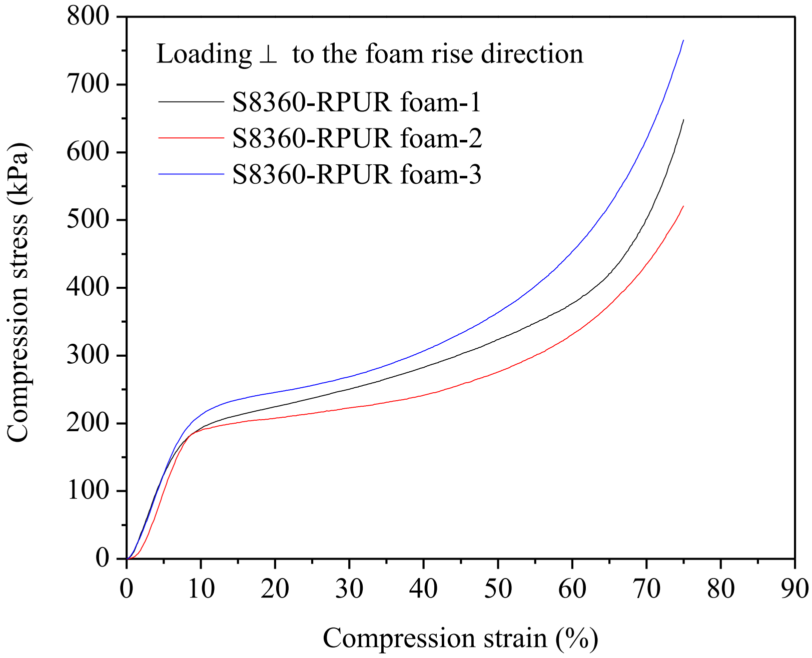


**Figure F4** Compression strain versus stress curves of Raypol® 8360-based RPUR foams in parallel and perpendicular to the foam rise direction with foam density ranging from 40–45 kg/m$^3$.

# APPENDIX G

## Thermal conductivity data of rigid polyurethane foams

| Samples | Condition Used | | Thermal Properties | Measurement Results | Average | S.D. |
|---|---|---|---|---|---|---|
| | Out Put of Power (W) | Measuring time (s) | | | | |
| **5. "HB175"** | 0.003 | 5 | **Thermal Conductivity** (W / m K) | 0.0330<br>0.0330<br>0.0334 | **0.0331** | 0.0002 |
| | | | **Thermal Diffusivity** (mm$^2$ /s) | 0.4679<br>0.4705<br>0.4579 | **0.4654** | 0.0067 |
| | | | **Specific Heat** (MJ/m$^3$ K) | 0.0705<br>0.0702<br>0.0729 | **0.0712** | 0.0015 |
| **6. "P175"** | 0.003 | 5 | **Thermal Conductivity** (W / m K) | 0.0338<br>0.0339<br>0.0339 | **0.0339** | 0.0001 |
| | | | **Thermal Diffusivity** (mm$^2$ /s) | 0.4825<br>0.4600<br>0.4515 | **0.4646** | 0.0161 |
| | | | **Specific Heat** (MJ/m$^3$ K) | 0.0701<br>0.0737<br>0.0751 | **0.0730** | 0.0026 |
| **4. "BS175"** | 0.003 | 5 | **Thermal Conductivity** (W / m K) | 0.0342<br>0.0342<br>0.0343 | **0.0342** | 0.0001 |
| | | | **Thermal Diffusivity** (mm$^2$ /s) | 0.4154<br>0.4371<br>0.4203 | **0.4243** | 0.0114 |
| | | | **Specific Heat** (MJ/m$^3$ K) | 0.0822<br>0.0783<br>0.0815 | **0.0807** | 0.0021 |

| Samples | Condition Used | | Thermal Properties | Measurement Results | Average | S.D. |
|---|---|---|---|---|---|---|
| | Out Put of Power (W) | Measuring time (s) | | | | |
| **8. "Paypol4218-150"** | 0.003 | 5 | **Thermal Conductivity** (W / m K) | 0.0371<br>0.0366<br>0.0367 | **0.0368** | 0.0003 |
| | | | **Thermal Diffusivity** ($mm^2$ /s) | 0.4504<br>0.4299<br>0.4175 | **0.4326** | 0.0166 |
| | | | **Specific Heat** ($MJ/m^3$ K) | 0.0824<br>0.0852<br>0.0879 | **0.0852** | 0.0028 |
| **9. "Paypol8360-175"** | 0.003 | 5 | **Thermal Conductivity** (W / m K) | 0.0332<br>0.0330<br>0.0331 | **0.0330** | 0.0001 |
| | | | **Thermal Diffusivity** ($mm^2$ /s) | 0.3958<br>0.4009<br>0.4034 | **0.4000** | 0.0039 |
| | | | **Specific Heat** ($MJ/m^3$ K) | 0.0840<br>0.0823<br>0.0820 | **0.0828** | 0.0011 |

**หมายเหตุ:**

1. Thermal conductivity is a measure of the ability to transmit heat through the material.
2. Thermal conductivity is a measure of transient heat flow and is defined as the thermal conductivity divided by the product of specific heat times density.
3. Specific heat is the quantity of heat needed to raise the temperature of a unit mass of the substance 1 degree of temperature.
4. Hot Disk Thermal Constant Analyzer (Hot Disk AB)

| | | |
|---|---|---|
| Reproducibility | - Thermal Conductivity | ±2% |
| | - Thermal Diffusivity | ±5% |
| | - Specific Heat | ±7% |

ศูนย์เทคโนโลยีโลหะและวัสดุแห่งชาติ
สำนักงานพัฒนาวิทยาศาสตร์และเทคโนโลยีแห่งชาติ
114 อุทยานวิทยาศาสตร์ประเทศไทย ถนนพหลโยธิน ตำบลคลองหนึ่ง อำเภอคลองหลวง
จังหวัดปทุมธานี 12120 โทรศัพท์ 0 2564 6500 โทรสาร 0 2564 6501-5
National Metal and Materials Technology Center
National Science and Technology Development Agency
114 Thailand Science Park, Phahonyothin Road, Klong 1, Klong Luang, Pathumthani 12120 Thailand.
Tel. +66 2564 6500 Fax. +66 2564 6501-5 http://www.mtec.or.th

# VITAE

Name: Miss Paweena Ekkaphan

Date of birth: February 14, 1982

Address: 29 Moo 3, Donka subdistrict, U Thong district, Suphanburi province, Thailand, 72160.

University Education: Bachelor's degree of Science Program in Chemistry, Faculty of Science, Chulalongkorn University, 2000–2004.

Master's degree of Science Program in Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, 2004–2007.

Doctor of Philosophy Program in Petrochemistry, Faculty of Science, Chulalongkorn University, 2007–2012.

Conference attendance: Oral presentation "Preparation of polyurethane foams from seed oils" at The 1st National Research Symposium on Petroleum, Petrochemicals, and Advanced Materials and The 16th PPC Symposium on Petroleum, Petrochemicals, and Polymers in The Montien Hotel Bangkok, Bangkok, Thailand.

Poster presentation "Rigid polyurethane foams from seed oils" at 7th International Symposium on Advanced Materials in Asia-Pacific (7th ISAMAP) and JAIST International Symposium on Nano Technology 2010 (NT2010) in Japan Advanced Institute of Science and Technology (JAIST), Nomi, Ishikawa, Japan.