ผลของชนิดสารเพิ่มเสถียรภาพทางความร้อนต่อความสามารถในการนำกลับมาใช้ใหม่ของพีวีซีสำหรับงานท่อ

นายอรัญ อัศวโกสินชัย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2557

EFFECTS OF TYPES OF HEAT STABILIZERS ON RECYCLING ABILITY OF POLY(VINYL CHLORIDE) FOR PIPE APPLICATION

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2014

Thesis Title	EFFECTS OF TYPES OF HEAT STABILIZERS ON RECYCLING ABILITY OF POLY(VINYL CHLORIDE) FOR PIPE APPLICATION
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อรัญ อัศวโกสินชัย : ผลของชนิดสารเพิ่มเสถียรภาพทางความร้อนต่อความสามารถในการนำกลับมาใช้ใหม่ของพีวีซีสำหรับงานท่อ (EFFECTS OF TYPES OF HEAT STABILIZERS ON RECYCLING ABILITY OF POLY(VINYL CHLORIDE) FOR PIPE APPLICATION) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร.ศราวุธ ริมดุสิต, 160 หน้า.

พอลิไวนิลคลอไรด์หรือพีวีซีเป็นพอลิเมอร์ที่มีความสำคัญยิ่งชนิดหนึ่งในเชิงอุตสาหกรรม ในประเทศไทยมากกว่า 50% ของพีวีซีถูกใช้ในการทำผลิตภัณฑ์ท่อชนิดต่างๆ อย่างไรก็ตามธรรมชาติของพีวีซีจำเป็นต้องมีการเติมสารเพิ่มเสถียรภาพทางความร้อนร่วมด้วยเสมอเนื่องจากพีวีซีเกิดการสลายตัวทางความร้อนได้ง่าย สารเพิ่มเสถียรภาพทางความร้อนชนิดสารประกอบตะกั่ว เป็นสารที่นิยมใช้กับพีวีซี แต่มีองค์ประกอบเป็นโลหะหนักที่เป็นพิษต่อสิ่งมีชีวิตและสิ่งแวดล้อม ทำให้ถูกจำกัดการใช้งานมากขึ้น โดยสารที่นิยมนำมาใช้ทดแทนสารประกอบตะกั่วคือ สารประกอบแคลเซียม/ซิงค์ซึ่งปลอดภัยต่อสิ่งมีชีวิตมากกว่า แต่สารกลุ่มนี้มีข้อด้อยในการใช้งานที่สำคัญคือประสิทธิภาพในการเพิ่มเสถียรภาพทางความร้อนแก่พีวีซีที่ต่ำกว่าสารประกอบตะกั่ว ในปัจจุบันได้มีการวิจัยและพัฒนาสารเพิ่มเสถียรภาพทางความร้อนชนิดสารอินทรีย์ Organic Based Stabilizer หรือ OBS) ที่ปราศจากสารประกอบโลหะ และบางชนิดสกัดได้จากพืชหรือพืชสมุนไพร สารกลุ่มนี้จึงค่อนข้างปลอดภัยต่อผู้บริโภคเมื่อเทียบกับสารทั้งสองกลุ่มข้างต้น ดังนั้นในงานวิจัยนี้จึงมีวัตถุประสงค์หาสารเพิ่มเสถียรภาพชนิดสารอินทรีย์มาแทนสารประกอบตะกั่วและแคลเซียม/ซิงค์ โดยเฉพาะเพื่อใช้ในการขึ้นรูปท่อพีวีซี ในงานวิจัยนี้ได้ทำการทดสอบประสิทธิภาพการเพิ่มเสถียรภาพทางความร้อนและคุณสมบัติต่างๆ ที่สำคัญในพีวีซีของสารเพิ่มเสถียรภาพทางความร้อนชนิดสารอินทรีย์ ประกอบด้วยอนุพันธ์ของสารยูราซิล และสารยูจีนอล เปรียบเทียบกับสารเพิ่มเสถียรภาพทางความร้อนที่มีการใช้งานในอุตสาหกรรมชนิดสารประกอบตะกั่ว และสารประกอบแคลเซียมและซิงค์ และสารประกอบอินทรีย์สำเร็จรูปที่มีจำหน่ายเชิงการค้า โดยทำการขึ้นรูปชิ้นงานด้วยเครื่องบดผสมแบบสองลูกกลิ้งและเครื่องอัดไฮดลอลิก และทำการทดสอบสมบัติต่างๆ จากการทดลองพบว่าสารเพิ่มเสถียรภาพทางความร้อนชนิดสารอินทรีย์คืออนุพันธ์ของสารยูราซิลและสารยูจีนอล สามารถขึ้นรูปได้ง่ายกว่าสารเพิ่มเสถียรภาพทางความร้อนชนิดสารประกอบตะกั่ว และสารประกอบแคลเซียมและซิงค์ และสารประกอบอินทรีย์สำเร็จรูป นอกจากนี้สารเพิ่มเสถียรภาพทางความร้อนชนิดสารอินทรีย์ชนิดคืออนุพันธ์ของสารยูราซิลและสารยูจีนอลมีคุณสมบัติในการรับแรงดึงและดัดโค้งที่ดีกว่าสารเพิ่มเสถียรภาพทางความร้อนเชิงการค้าทั้ง 3 ชนิดข้างต้น การเปลี่ยนแปลงสีของพีวีซีเมื่อได้รับความร้อนถือเป็นปัจจัยที่สำคัญในการเปรียบเทียบความสามารถของสารเพิ่มเสถียรภาพทางความร้อน โดยพีวีซีที่เติมอนุพันธ์ของสารยูราซิลจะพบว่าหลังการขึ้นรูปสีของพีวีซีไม่มีการเปลี่ยนแปลงมากนัก และสามารถทนต่อการเปลี่ยนแปลงสีได้นานถึง 50 นาทีเมื่อได้รับความร้อนที่อุณหภูมิ 180°c ในด้านการรีไซเคิล พบว่าพีวีซีที่เติมสารเพิ่มเสถียรภาพทางความร้อนเชิงการค้า สามารถขึ้นรูปได้อย่างต่ำ 5 ครั้ง ในขณะที่พีวีซีที่เติม อนุพันธ์ของสารยูราซิลสามารถขึ้นรูปได้อย่างต่ำ 4 ครั้ง ส่วนพีวีซีที่เติมยูจินอลไม่สามารถขึ้นรูปซ้ำได้เนื่องจากสีชิ้นงานที่เข้มขึ้นมาก นอกจากนี้ในการขึ้นรูปซ้ำไม่เกิน 3 รอบ พบว่าไม่มีผลกระทบต่อคุณสมบัติทางกลของพีวีซีในทุกระบบยกเว้นระบบของยูจีนอล ทั้งนี้สารอินทรีย์ชนิดอนุพันธ์ของสารยูราซิลมีศักยภาพและความปลอดภัยในการใช้เป็นสารเพิ่มเสถียรภาพทางความร้อนสำหรับพีวีซี เพื่อใช้ทดแทนสารประกอบตะกั่วคือ สารประกอบแคลเซียม/ซิงค์ได้เป็นอย่างดี นอกจากนี้ยังพบว่าหากใช้อนุพันธ์ของสารยูราซิลร่วมกับสารยูจีนอลในอัตราส่วน 1:1 จะส่งผลให้เกิดสภาวะเสริม ในด้านสมบัติการเพิ่มเสถียรภาพทางความร้อนในพีวีซีเมื่อเทียบกับการใช้สารอินทรีย์ตัวใดตัวหนึ่งเพียงชนิดเดียว

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ลายมือชื่อ อ.ที่ปรึกษาหลัก ______________________________

5570577121 : MAJOR CHEMICAL ENGINEERING

KEYWORDS: POLY(VINYL CHLORIDE) / HEAT STABILIZER / ORGANIC BASED STABILIZER

ARAN ASAWAKOSINCHAI: EFFECTS OF TYPES OF HEAT STABILIZERS ON RECYCLING ABILITY OF POLY(VINYL CHLORIDE) FOR PIPE APPLICATION. ADVISOR: ASSOC. PROF. SARAWUT RIMDUSIT, Ph.D., 160 pp.

Poly(vinyl chloride) or PVC is a well-known commodity plastic because of its versatility, low cost and long life cycle. In Thailand, water pipe is a major product of PVC. However, PVC is known to degrade at elevated temperature. Without the discovery of heat stabilizers, PVC was not an industrially useful polymer. In practice, lead stabilizers are used to improve the decomposition temperature in order to obtain high-quality PVC products. But they are limited as stabilizers because of their toxicity. Initiative of limiting lead consumption has led to the development of alternative stabilizers. Calcium/zinc stabilizers are typical nontoxic heat stabilizers, however, Ca/Zn stabilizers have some disadvantages in their long-term stability. Whereas, organic based stabilizers (OBS) are new technology providing environmentally friendly stabilization for rigid PVC pipe applications. This research aims to suggest suitable organic based stabilizers to substitute conventional lead stabilizer as well as Ca/Zn stabilizer for PVC pipe. In this research, uracil derivative and eugenol compare with commercial heat stabilizer i.e. lead stabilizer, Ca/Zn stabilizer and commercial organic based stabilizer in their efficiency as heat stabilizer or important PVC properties. The PVC samples was processed by two-roll mills and compression molder at 180ºC. From the results, uracil derivative and eugenol were found to be more readily fused with PVC than commercial heat stabilizers. From mechanical testing, PVC stabilized with uracil derivative and eugenol showed higher tensile and flexural properties than other samples. In addition, PVC stabilized with uracil derivative provided relatively low thermal discoloration by maintaining original white color of PVC at temperature of 180°C up to 50 minutes. From recycle ability, PVC stabilized with commercial stabilizers could processed up to at least 5 cycles. However, PVC stabilized with uracil derivative was found to be able to withstand the processing cycle up to 4 cycles. Whereas PVC stabilized with eugenol was able to undergo only one cycle. Thus, it is clearly seen that uracil derivative showed high potential use as a safe and effective organic based heat stabilizer for PVC to substitute lead or Ca/Zn stabilizer. Moreover, Synergistic behavior in thermal stability of PVC was also observed when mixture of eugenol and uracil derivative at 1:1 mass ratio.

Department:	Chemical Engineering	Student's Signature	....
Field of Study:	Chemical Engineering	Advisor's Signature	....
Academic Year:	2014		

ACKNOWLEDGEMENTS

I wish to express my deep appreciation to my advisor, Assoc. Prof. Dr. Sarawut Rimdusit for his kindness, invaluable supervision, guidance, advice, and encouragement throughout the course of this study and editing of this thesis.

My sincere gratitude is to Dr. Varun Taepaisitphongse, Assoc. Prof. Siriporn Damrongsakkul and Asst. Prof. Dr. Chanchira Jubsilp for their instructive advices as my thesis committee.

This research is financially supported by Vinythai Public Company Limited, Bangkok, Thailand. I also wish to thank Ms. Dusita Kolaka, Ms. Nada Sroysaard, Ms. Pinyaporn Veerapradit and all staffs in Quality Control and Customer Development Department (QCD) of Vinythai Plant for their helpful and invaluable advices on instrumentation used in this work.

Additionally, I would like to acknowledge my senior colleagues especially Ms. Manunya Okhawilai for her assistance and useful comments on my thesis. Everyone in Polymer Engineering Laboratory, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University is highly appreciated for his/her invaluable discussion and friendly encouragement.

Finally, I would like to affectionately give my gratitude to my family for their wholehearted understanding, patience, and encouragement throughout my entire study.

CONTENTS

Page

THAI ABSTRACT iv

ENGLISH ABSTRACT v

ACKNOWLEDGEMENTS vi

CONTENTS vii

LIST OF FIGURES xi

LIST OF TABLES xviii

CHAPTER I INTRODUCTION 1

- 1.1 General Introduction 1
- 1.2 Objectives 3
- 1.3 Scope of the study 3
- 1.4 Procedure of the study 4

CHAPTER II THEORY 5

- 2.1 Poly(vinyl chloride) (PVC) 5
  - 2.1.1 Properties of PVC 6
  - 2.1.2 Applications of PVC 8
  - 2.1.3 PVC Pipes 8
- 2.2 Thermal Degradation of PVC 9
- 2.3 Heat Stabilizers for Poly(vinyl chloride) 11
  - 2.3.1 Classification of PVC Stabilizers 11
  - 2.3.2 History of the Use of PVC Pipe Stabilizers 13
  - 2.3.3 Major Types of PVC Heat Stabilizers 13

CHAPTER III LITERATURE REVIEWS 17

Page

CHAPTER IV EXPERIMENTAL 30

4.1 Materials 30

4.2 Methodology 31

4.2.1 PVC Dryblend Preparation 31

4.2.2 PVC Processing 32

4.2.3 Recycling Preparation of PVC Stabilized with Various Stabilizers 33

4.3 Characterizations of PVC Stabilized with Heat Stabilizers 33

4.3.1 Processing Characterization 33

4.3.1.1 Fusion of PVC Compounds Using a Torque Rheometer 33

4.3.2 Physical Properties 34

4.3.3 Mechanical Characterization 37

4.3.4 Thermal Characterization 38

CHAPTER V RESULTS AND DISCUSSION 42

5.1 Effect of Commercial Lead, Calcium Zinc (Ca/Zn) and Organic Based Stabilizers on Rheological Properties and Static Thermal Stability on PVC Resin 42

5.1.1 Effect of Commercial Lead, Calcium Zinc and Organic Based Stabilizers on Rheological Property on PVC Resin 42

5.1.2 Effect of Commercial Lead, Calcium Zinc and Organic Based Stabilizers on Static Thermal Stability on PVC Resin 47

5.1.3 Thermogravimetric Analysis (TGA) of Commercial Organic Stabilizers. 49

5.2 Effect of DAU, Eugenol and DAU/Eugenol Mixture Stabilizers on Static Thermal Stability and Mechanical Property of Rigid PVC 51

5.2.1 Static Thermal Stability of PVC Stabilized with Eugenol 51

Page

5.2.2 Static Thermal Stability of PVC Stabilized with DAU 52

5.2.3 Tensile Properties of PVC Stabilized with DAU 53

5.2.4 Effect of Processing Temperatures for PVC Stabilized with DAU and Eugenol Stabilizers 54

5.2.5 PVC Stabilized with DAU/Eugenol Mixtures...56

5.3 Properties of PVC Stabilized with Various Heat Stabilizers (at a Fixed Stabilizer Content of 3 phr) 59

5.3.1 Effects of Types of Heat Stabilizers on Fusion Behaviors of PVC Stabilized with Various Heat Stabilizers (at a Fixed Content 3 phr) 59

5.3.2 Thermogravimetric Analysis (TGA) of PVC Stabilized with Various Types of Heat Stabilizers 60

5.3.3 Static Thermal Stability of PVC Stabilized with Various Heat Stabilizers 61

5.3.4 Dynamic Mechanical Analysis of PVC Stabilized with Various Types of Heat Stabilizers at a Fixed Content 3 phr 62

5.4 Effects of Repeated Processing and Various Types of Heat stabilizers..........64

5.4.1 Effects of Repeated Processing on Density of PVC Stabilized with Various Types of Heat Stabilizers...64

5.4.2 Effects of Repeated Processing on Color Change of PVC Stabilized with Various Types of Heat Stabilizers...65

5.4.3 Effects of Repeated Processing Cycles on FTIR Spectra of PVC Stabilized with Various Types of Heat Stabilizers...................................67

5.4.4 Effects of Repeated Processing on Tensile Property of PVC Stabilized with Various Types of Heat Stabilizers...68

5.4.5 Effects of Repeated Processing on Flexural Property of PVC Stabilized with Various Types of Heat Stabilizers...69

Page

5.4.6 Effects of Repeated Processing on Izod Impact Property of PVC Stabilized with Various Types of Heat Stabilizers....................................70

5.4.7 Effects of Repeated Processing on Gelation of PVC Stabilized with Various Types of Heat Stabilizers...71

5.4.8 Effects of Repeated Processing on Heat Distortion Temperature of PVC Stabilized with Various Types of Heat Stabilizers 74

CHAPTER VI 107

CONCLUSIONS 107

REFERENCES 109

APPENDIX... 115

VITA.. 160

LIST OF FIGURES

FIGURE PAGE

2.1 Structures of vinyl chloride monomer and poly(vinyl chloride) 5

2.2 a) PVC resin, b) PVC granule 6

2.3 PVC pipe, a major PVC product in the market 8

2.4 Thermal degradation of PVC 9

2.5 Allylic chlorine atom 9

2.6 Initiation of dehydrochlorination and elimination of HCl and simultaneous formation of conjugated double bonds 10

2.7 Wavelength of absorbed light in visible region vs. number of conjugated double bonds in polyene 10

2.8 Mechanism of PVC thermal stabilization by a primary stabilizer 12

2.9 Mechanism of epoxidized compound by a secondary stabilizer in practice, both stabilizers are to be used together as the primary stabilizers 12

2.10 Example of Dibasic lead stabilizer 14

2.11 Calcium stearate heat stabilizer 15

2.12 a) Methyl tin mercaptan and b) Dibutyl tin maleate (DBTM) 16

2.13 a) Eugenol and b) 1,3-Dimethyl-6-aminouracil 16

3.1 Dehydrochlorination rate of rigid PVC, in air, at 180°C, in presence of 2 g of the investigated stabilizers per 100 g of PVC 17

3.2 Mechanism of eugenol as primary stabilizer 18

3.3 Influences of the stabilizers (2 phr) on dynamic stability time of PVC at 180°C 18

3.4 Thermogravimetric analysis of PVC stabilized with CZ, DTU, DAU, MAU and MATU. 20
3.5 Mechanism of uracil derivatives as secondary stabilizer. 21
3.6 Rate of dehydrochlorination of rigid PVC at 180°C, in air, in the presence of various concentrations of Poly(glycidyl methacrylate). 24
3.7 Effect of lead and Ca/Zn stabilizers on elongation at break vs. number of extrusion cycles. 25
3.8 The extrusion pressure and elongation at break, as a function of number of extrusions. 26
3.9 FTIR spectra of a commercial rigid PVC samples heated at 180°C at 0-7 hours. 27
3.10 DSC thermograms of compression molded PVC compounds exhibiting area A and area B due to fusion........ 29
4.1 High speed mixer: Plasmec Turbomixer 10L with cooler 31
4.2 Two-roll mills and compression molder........ 32
4.3 Fritsch pulverisette 15 cutting mill........ 33
4.4 Brabender (torque rheometer)........ 34
4.5 Mathis Thermotester........ 35
4.6 UL-94 vertical test........ 41
5.1 Torque rheometer process curves of PVC_{lead} at 180°C 75
5.2 Torque rheometer process curves of $PVC_{Ca/Zn}$ (PRD5549:Chem)........ 75
5.3 Torque rheometer process curves of $PVC_{Ca/Zn}$ (M78NP:Sunace)........ 76
5.4 Torque rheometer process curves of $PVC_{Ca/Zn}$ (M964NP:Sunace)........ 76
5.5 Torque rheometer process curves of $PVC_{Ca/Zn}$ (M162P:Siam)........ 77
5.6 Torque rheometer process curves of PVC with OBS from Chemson........ 77
5.7 Torque rheometer process curves of PVC with OBS from Sunace........ 78

5.8 Color change of PVC resin using lead stabilizers (3 phr) at 180°C in air (Strips were automatically moved out of the box at 5 mm/min). 79

5.9 Color change of PVC resin using Ca/Zn stabilizers (3 phr) at 180°C in air (Strips were automatically moved out of the box at 5 mm/min). 79

5.10 Color change of PVC resin using commercial OBS stabilizers (3 phr) at 180°C in air 79

5.11 TGA thermograms of commercial organic stabilizers in nitrogen atmosphere: Sunace OBS (■), Chemson OBS (▲)... 80

5.12 Derivative TGA thermograms of commercial organic stabilizers in nitrogen atmosphere: Sunace OBS (■), Chemson OBS (▲). 80

5.13 TGA thermograms of commercial organic based stabilizers in oxygen atmosphere: Sunace OBS (■), Chemson OBS (▲)... 81

5.14 Derivative TGA thermograms of commercial organic based stabilizers in oxygen atmosphere: Sunace OBS (■), Chemson OBS (▲). 81

5.15 Color change of PVC resin using a eugenol as a stabilizer at 180°C in air (Strips were automatically moved out of the chamber at 1 mm/min)........... 82

5.16 Color change of PVC resin with titanium dioxide (2 phr) and various eugenol contents as stabilizer at 180°C in air (Strips were automatically moved out of the heating chamber at 1 mm/min). 82

5.17 Color change of PVC stabilized with various DAU contents (1-4 phr) at 180°C in air (Strips were automatically moved out of the heating chamber at 1 mm/min)... 82

5.18 Tensile stress-strain curves of PVC stabilized with various DAU contents: 1 phr (■), 2 phr (◆), 3 phr (●) and 4 phr (▲). 83

5.19 Color change of PVC resin mixed with 3 phr of eugenol and 3 phr of DAU as a stabilizer with various processing temperature at 150, 160 and 170°C under air atmosphere 83

5.20 Color change of the PVC stabilized with eugenol/DAU mixtures at DAU contents. (Strips were automatically moved out of the box at 1 mm/min at 180°C under air atmosphere) 84

5.21 Color change of the PVC stabilized with eugenol/DAU mixtures at DAU contents. (Strips were automatically moved out of the box at 1 mm/min at 150°C under air atmosphere). 85

5.22 Effects of types of heat stabilizers in PVC resin on storage modulus: $\mathrm{PVC}_{\mathrm{DAU\ 3\ phr}}$ (■), $\mathrm{PVC}_{\mathrm{DAU\ 1.5\ phr,\ eugenol\ 1.5\ phr}}$ (●) and $\mathrm{PVC}_{\mathrm{eugenol\ 3\ phr}}$ (▲) 85

5.23 Effects of types of heat stabilizers in PVC resin on tan δ $\mathrm{PVC}_{\mathrm{DAU\ 3\ phr}}$ (■), $\mathrm{PVC}_{\mathrm{DAU\ 1.5\ phr,\ eugenol\ 1.5\ phr}}$ (●) and $\mathrm{PVC}_{\mathrm{eugenol\ 3\ phr}}$ (▲)........ 86

5.24 Thermogravimetric analysis of the rigid PVC stabilized with various stabilizers: neat PVC (×),$\mathrm{PVC}_{\mathrm{lead}}$ (■), $\mathrm{PVC}_{\mathrm{Ca/Zn}}$ (◆), $\mathrm{PVC}_{\mathrm{OBScomm}}$ (●), $\mathrm{PVC}_{\mathrm{DAU}}$ (▲) and $\mathrm{PVC}_{\mathrm{eugenol}}$ (▼)........ 87

5.25 Color change of the PVC stabilized with lead, Ca/Zn, OBScomm, DAU and eugenol at 3 phr as a function of time at 180°C. 87

5.26 Effects of types of heat stabilizers in PVC resin on storage modulus: commercial PVC from local Thai company (◣), $\mathrm{PVC}_{\mathrm{lead}}$ (■), $\mathrm{PVC}_{\mathrm{Ca/Zn}}$ (◆), $\mathrm{PVC}_{\mathrm{OBScomm}}$ (●), $\mathrm{PVC}_{\mathrm{DAU}}$ (▲) and $\mathrm{PVC}_{\mathrm{eugenol}}$ (▼)........ 88

5.27 Effects of types of heat stabilizers in PVC resin on tan δ: commercial PVC from local Thai company (◣), $\mathrm{PVC}_{\mathrm{lead}}$ (■), $\mathrm{PVC}_{\mathrm{Ca/Zn}}$ (◆), $\mathrm{PVC}_{\mathrm{OBScomm}}$ (●), $\mathrm{PVC}_{\mathrm{DAU}}$ (▲) and $\mathrm{PVC}_{\mathrm{eugeno}}$l (▼). 88

5.28 UL-94 vertical test of PVC stabilized with lead stabilizer 89

5.29 UL-94 vertical test of PVC stabilized with calcium/zincstabilizer........ 89

5.30 UL-94 vertical test of PVC stabilized with commercial OBS stabilizer 90

5.31 UL-94 vertical test of PVC stabilized with DAU 90

5.32 UL-94 vertical test of PVC stabilized with eugenol 91

5.33 Effects of repeated processing cycles on density of PVC with various heat stabilizers: PVClead (■), $\text{PVC}_{\text{Ca/Zn}}$ (◆), $\text{PVC}_{\text{OBScomm}}$ (●), PVC_{DAU} (▲) and $\text{PVC}_{\text{eugenol}}$ (▼). 92

5.34 Effects of repeated processing cycles on color change of PVC with various heat stabilizers: PVClead (■), $\text{PVC}_{\text{Ca/Zn}}$ (◆), $\text{PVC}_{\text{OBScomm}}$ (●), PVC_{DAU} (▲) and $\text{PVC}_{\text{eugenol}}$ (▼). 92

5.35 Effects of repeated processing cycles on yellow index of PVC with various heat stabilizers: PVClead (■), $\text{PVC}_{\text{Ca/Zn}}$ (◆), $\text{PVC}_{\text{OBScomm}}$ (●), PVC_{DAU} (▲) and $\text{PVC}_{\text{eugenol}}$ (▼). 93

5.36 Effects of repeated processing cycles of FTIR spectra of PVC stabilized with lead stabilizers: 1st processing cycle (■), 3rd processing cycle (◆) and 5th processing cycle (●). 94

5.37 Effects of repeated processing cycles of FTIR spectra of PVC stabilized with Ca/Zn stabilizers: 1st processing cycle (■), 3rd processing cycle (◆) and 5th processing cycle (●). 95

5.38 Effects of repeated processing cycles of FTIR spectra of PVC stabilized commercial OBS stabilizers: 1st processing cycle (■), 3rd processing cycle (◆) and 5th processing cycle (●). 96

5.39 Effects of repeated processing cycles of FTIR spectra of PVC stabilized with DAU stabilizers: 1st processing cycle (■), 2nd processing cycle (◆) and 3rd processing cycle (●). 97

5.40 Effects of repeated processing cycles on tensile strength of PVC with various heat stabilizers: PVClead (■), $PVC_{Ca/Zn}$ (◆), $PVC_{OBScomm}$ (●), PVC_{DAU} (▲) and $PVC_{eugenol}$ (▼). 98

5.41 Effects of repeated processing cycles on tensile modulus of PVC with various heat stabilizers: PVClead (■), $PVC_{Ca/Zn}$ (◆), $PVC_{OBScomm}$ (●), PVC_{DAU} (▲) and $PVC_{eugenol}$ (▼). 99

5.42 Effects of repeated processing cycles on flexural strength of PVC with various heat stabilizers: PVClead (■), $PVC_{Ca/Zn}$ (◆), $PVC_{OBScomm}$ (●), PVC_{DAU} (▲) and $PVC_{eugenol}$ (▼). 100

5.43 Effects of repeated processing cycles on flexural modulus of PVC with various heat stabilizers:PVClead (■), $PVC_{Ca/Zn}$ (◆), $PVC_{OBScomm}$ (●), PVC_{DAU} (▲) and $PVC_{eugenol}$ (▼).. 101

5.44 Effects of repeated processing cycles on Izod impact of PVC with various heat stabilizers:PVClead (■), $PVC_{Ca/Zn}$ (◆), $PVC_{OBScomm}$ (●), PVC_{DAU} (▲) and $PVC_{eugenol}$ (▼).. 102

5.45 DSC thermograms of PVC stabilized with various types of heat stabilizer (1st cycle): PVClead (green line), PVCCa/Zn (red line), PVCOBScomm (dark blue line), PVCDAU (blue line) and PVCeugenol (pink line). 103

5.46 DSC thermograms of PVC stabilized lead at number of processing cycles 1st cycle (red line), 2nd cycle (dark blue line), 3rd cycle (blue line), 4th cycle (grey line) and 5th cycle (pink line). 103

5.47 DSC thermograms of PVC stabilized Ca/Zn at number of processing cycles 1st cycle (red line), 2nd cycle (dark blue line), 3rd cycle (green line), 4th cycle (grey line) and 5th cycle (blue line). 104

5.48 DSC thermograms of PVC stabilized OBS at number of processing cycles 1st cycle (dark blue line), 2nd cycle (blue line), 3rd cycle (green line), 4th cycle (pink line) and 5th cycle (brown line) 104

5.49 DSC thermograms of PVC stabilized DAU at different number of processing cycles 1st cycle (blue line), 2nd cycle (black line) and3rd cycle (dark blue line). 105

5.50 Effects of repeated processing cycles on degree of gelation of PVC with heat stabilizers: PVClead (■), PVCCa/Zn (◆), PVCOBScomm (●), PVCDAU (▲) and PVCeugenol (▼). 105

5.51 Effects of repeated processing cycles on heat distortion temperature of PVC with various heat stabilizers: PVClead (■), PVCCa/Zn (◆), PVCOBScomm (●), PVCDAU (▲) and PVCeugenol (▼). 106

LIST OF TABLES

TABLE PAGE

2.1 Properties of PVC resin 7

3.1 Extent of discoloration of thermally degraded rigid PVC at 180°C, in air, in presence of 2 wt% of the investigated stabilizers as a function of degradation time 18

3.2 TGA results of stabilized PVC 20

3.3 Formulation and result of color measurement of Un-plasticized PVC (Rigid) 21

3.4 Induction period (Ts) as a function of type of the investigated N-phenyl -3-substituted-5-pyrazolone derivatives acting as thermal stabilizers for rigid PVC, at 180°C, in air 22

3.5 Extent of discoloration of thermally degraded rigid PVC, at 180°C, in presence of 2 wt% of investigated stabilizers as a function of degradation time 23

3.6 Effect of repeated extrusion on various properties of PVC resin with Ca/Zn stabilizer 26

4.1 Table 4.1 Composition and price of each ingredient 31

4.2 Three material classification in Ul-94.Vertical Test 40

5.1 Effects of types of heat stabilizers on major parameters in the plastograms of PVC. 78

5.2 Various properties of PVC with various heat stabilizers. 84

5.3 Effects of types of heat stabilizers on key parameters in plastograms. 86

5.4 Effects of repeated processing cycle on color of PVC with various heat stabilizers. 92

CHAPTER I

INTRODUCTION

1.1 General Introduction

Poly(vinyl chloride) (PVC) is a well-known commodity plastic which production is the third largest in the world after polyethylene and polypropylene [1]. The world production of PVC has been approximately estimated to be 40 million tons in 2012. It is a cost-competitive polymer with broad spectrum of properties (rigid, semi-flexible, flexible) and is utilized in various construction applications including water, sewage, or drainage pipes and in many extruded profiles [2]. In Thailand, water pipe is a major product of PVC application and it generally uses lead compound as a heat stabilizer.

Technically, however, PVC is known to degrade at high temperature and gives off hydrochloric acid that in turn accelerates the thermal degradation process [3]. The number of the conjugated double bonds formed during the process determines the level of color in the sample ranging from yellow, orange, red, brown, and black [4]. The decomposition by-product, HCL, can also deteriorate mechanical, thermal as well as physical properties of the polymer [5]. Without the discovery of heat stabilizers, PVC was not an industrially useful polymer due to its prone to thermal decomposition at elevated temperature mentioned above.

In practice, commercial heat stabilizers of PVC pipe such as lead stabilizers and calcium zinc stabilizers are used to improve the decomposition temperature in order to obtain high-quality PVC products. Although basic lead stabilizers have high efficiency stabilization, they are limited as stabilizers applied in PVC on account of their toxicity [6]. In 2003, certain European environment regulations limited the use of lead in the production of PVC pipe. In the 2007-2012, lead stabilizer consumption in Europe decreased by 76,364 tons and the continent will phase out the use of lead in the production of PVC pipe in 2015 [7].

Initiative of limiting lead consumption has led to the development of alternative stabilizers in the last ten years [8]. These include calcium/zinc based products for profiles and sewage or drainage pipes and organic based products for drinking water pipes and pipes. Some metal soaps such as calcium stearate/zinc stearate are typical nontoxic heat stabilizers for PVC [9], however, calcium and zinc stabilizers have some disadvantages in their long-term stability [10]. Whereas, organic based stabilizers are new technology providing environmentally friendly stabilization for rigid PVC pipe applications and of major interest both academically and industrially.

One organic stabilizer widely known in organic based heat stabilizer for PVC is uracil derivatives [11]. There are several literatures that confirm that uracil derivatives have good efficiency to suppress thermal degradation of PVC [12, 13]. Another organic stabilizer is eugenol which is a main component (80 wt.%) of clove oil. It is widely used in perfumes, antioxidants, and drugs, and taste items [14]. Eugenol is an organic compound bearing a multifunctional group which can intervene with the chain degradative products resulting from the thermal treatment of poly(vinyl chloride), together with the fact that it is a safe material, it has been investigated for the stabilizing efficiency against the thermal degradation of PVC [4].

In this research, 3 classes of heat stabilizers (lead compound, calcium/zinc compound and organic stabilizers) are evaluated and their efficiencies will be compared based on the effects on thermal properties (HDT, degradation temperature), mechanical properties (flexural and tensile test), physical properties (density, color change) and recycle ability of rigid. Organic based heat stabilizers with a potential to replace toxic classes of lead and Ca/Zn systems will be proposed and evaluated.

1.2 Objectives

1. To investigate using organic thermal stabilizer (nontoxic) instead of lead compound or calcium/zinc compound for poly(vinylchloride) processing in pipe applications.
2. To systematically study the effects of organic heat stabilizer contents on thermal stability of the poly(vinylchloride).
3. To investigate the effects on recycling ability of poly(vinylchloride) stabilized with 3 types of heat stabilizer.
4. To determine other essential thermal, mechanical and physical properties of recycled poly(vinylchloride) pipes from 3.

1.3 Scope of the study

1. Prepare the PVC compound based on filler e.g. calcium carbonate) and heat stabilizers, e.g. lead stabilizer, mixed metal as Calcium/Zinc stabilizer (Ca/Zn), and organic stabilizers, e.g. eugenol, derivative uracil and commercial organic based stabilizer (OBS).
2. Find thermal stability (HDT, degradation temperature and transition temperature), mechanical properties (flexural and tensile test), and some physical properties (density, color stability) as well as gelation of each heat stability-filled PVC sample using:
    - Mechanical properties (INSTRON: flexural and tensile)
    - Dynamic mechanical analysis (DMA: Tg and storage modulus)
    - Thermogravimetric analysis (TGA: Td and char residue)
    - Differential scanning calorimetry (DSC: Tg and gel behaviors)
    - Color spectrophotometry (Color change)
    - Fourier transform infrared spectroscopy (FTIR: degradation behaviors)
    - Flammability (UL-94)

3. Study the PVC stabilized with various types of heat stabilizers at recycling processing (up to 5 recycle times). Evaluate the essential thermal mechanical and physical properties from 2.

1.4 Procedure of the study

1. Reviewing related literature.
2. Preparation of chemicals and equipment for using in this research.
3. Preparation of PVC compound and recycled PVC compound and heat stabilizers, e.g. lead stabilizer, mixed metal as Calcium/Zinc stabilizer (Ca/Zn), and organic stabilizer, e.g. eugenol and derivative uracil and commercial organic based stabilizer (OBS).
4. Recycle PVC compound stabilized with various types of heat stabilizers.
5. Determination of thermal and mechanical properties of PVC as follows:
    - Mechanical properties (INSTRON: flexural and tensile)
    - Dynamic mechanical analysis (DMA: Tg and storage modulus)
    - Thermogravimetric analysis (TGA: Td and char residue)
    - Differential scanning calorimetry (DSC: Tg and gel behaviors)
    - Color spectrophotometry (Color change)
    - Fourier transform infrared spectroscopy (FTIR: degradation behaviors)
    - Flammability (UL-94)
6. Analysis of the experimental results.
7. Preparation of the final report.

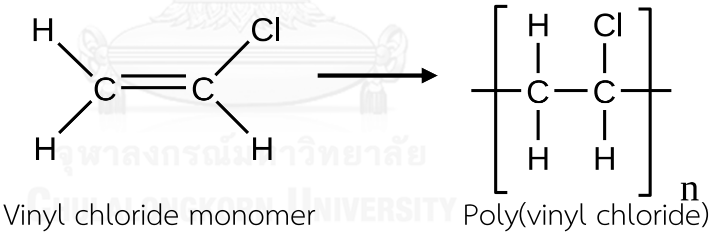
CHAPTER II

THEORY

2.1 Poly(vinyl chloride) (PVC)

Poly(vinyl chloride), commonly abbreviated as PVC, is the third-most widely produced plastics, after polyethylene and polypropylene. PVC products can be rigid or flexible, opaque or transparent, and insulating or conducting [15].

PVC is thermoplastic and has chemical and physical structure that makes it broad spectrum of properties. It (often referred to as vinyl) is polymerized commercially by free-radical polymerization of vinyl chloride with several techniques such as suspension, emulsion and micro-suspension processes. PVC is made commercially at several molecular weights, depending on its intended applications.



Vinyl chloride monomer Poly(vinyl chloride)

Figure 2.1 Structures of vinyl chloride monomer and poly(vinyl chloride).

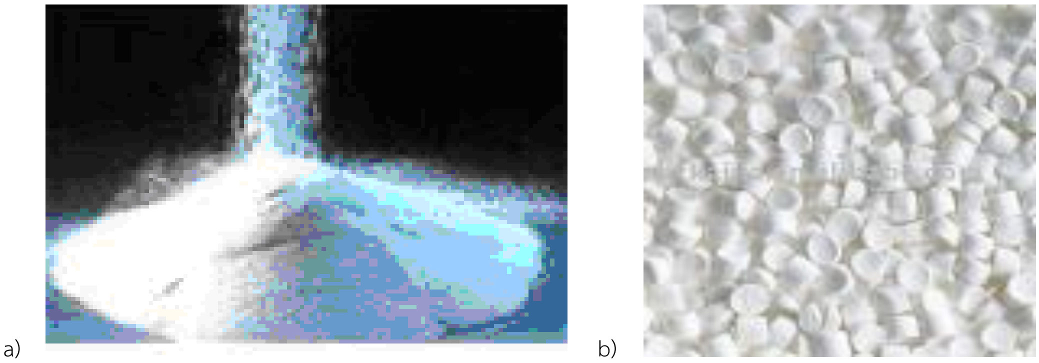


Figure 2.2 a) PVC resin b) PVC granule [16]

2.1.1 Properties of PVC

PVC has excellent dimensional stability, outstanding resistance to weathering, fungi, water and alcohols, good resistance to acid, alkalis, fats and petroleum hydrocarbons, good dielectric properties, inherently flame resistance, extreme cost effective in comparison to other plastics with a high degree of versatility in end-use and processing possibilities such as extrusion, injection, or foam processing [17]. It is durable, easily maintained, and can be produced in a large range of colors. Moreover, the advantage of PVC is that it can be blended with a wide range of additives to improve stability, cost, stiffness and softening point. It is easy to modify or add various types of additives such as plasticizers, impact modifiers, pigments, lubricants, heat stabilizers, UV stabilizers, antioxidants and so forth into PVC, to enhance or broaden its properties. It can also be blended with various polymers such as acrylonitrile butadiene styrene (ABS), acrylonitrile styrene acrylate (ASA), acrylic, polymethyl methacrylate (PMMA), ethylene vinyl acetate (EVA), chlorinated polyethylene (CPE), ethylene propylene diene monomer rubber (EPDM), nitrile rubber etc. [17].

Table 2.1: Properties of PVC resin [18].

Properties	ASTM Test Method	Units	PVC
Physical			
Density	D792	g/cm^3	1.42
Water Absorption	D570	%	0.06
Rockwell Hardness	D785	R Scale	115
Mechanical			
Tensile Modulus	D638	GPa	2.8
Yield Strength	D638	MPa	52
Flexural Modulus	D790	GPa	3.3
Yield Strength	D790	MPa	88
Izod Impact	D256	J/m	53
Thermal			
Vicat Softening Point	D1525	℃	83
Heat Deflection Temperature	D648	℃	82
Flammability	D635	-	Self-Extinguishing
Flammability	UL94	-	V-0
Electrical			
Volume Resistivity	D257	ohm/cm	5.4×10^{15}
Dielectric Constant	D150	60 Hz	3.19
Dielectric Strength	D149	V/mm	544
Chemical			
Chemical Resistance	D1784	-	Class B

2.1.2 Applications of PVC

The relatively low cost, highly biological and chemical resistance of PVC as well as the outstanding workability have resulted in it being used in a wide variety of applications. It is used for sewage pipes and other pipe applications where cost or vulnerability to corrosion limits the use of metal pipes. With the addition of impact modifiers and stabilizers, it has become a key material for window and door frame products. By adding plasticizers, it can become flexible enough to be used in cabling applications as a wire insulator, etc.

2.1.3 PVC Pipes

Roughly half of the PVC resin manufactured annually in the world is used for producing pipes for municipal and industrial applications [6]. Its light weight, cost-competitive and low maintenance make it highly attractive for various works. However, it must be carefully installed and bedded to prevent longitudinal cracking [19]. Additionally, PVC pipes can be fused together using various solvent cements, or heat-fused (butt-fusion process, similar to joining HDPE pipe) to create permanent joints that are virtually impervious to leakage [19].

Figure 2.3: PVC pipe, a major PVC product in the market [20].

2.2 Thermal Degradation of PVC

Thermal degradation is a process which the action of heat or high temperature causes a loss in physical, mechanical, or electrical properties of the material. In the case of PVC, its thermal degradation occurs via autocatalytic dehydrochlorination reaction or zipper elimination reaction with the subsequent formation of conjugated double bonds in the main chains [21-24] that indicated in Figure 2.4. When the first HCl molecule is lost from the PVC chain to form an unsaturated allylic chloride structure, this allylic structure (Figure 2.5) will enable the next loss of an HCl molecule and the repeated process will lead to the chain or zip dehydrochlorination. Typically, HCl from the elimination reaction is detected from 70°C up to 330°C [3] while traces of benzene have been reported at the temperature range of 150 – 160°C [5] and at 200-360°C, about 15% (weight/weight) of the polyene is converted to benzene due to the intermolecular cyclization reaction of polyene segments [25].

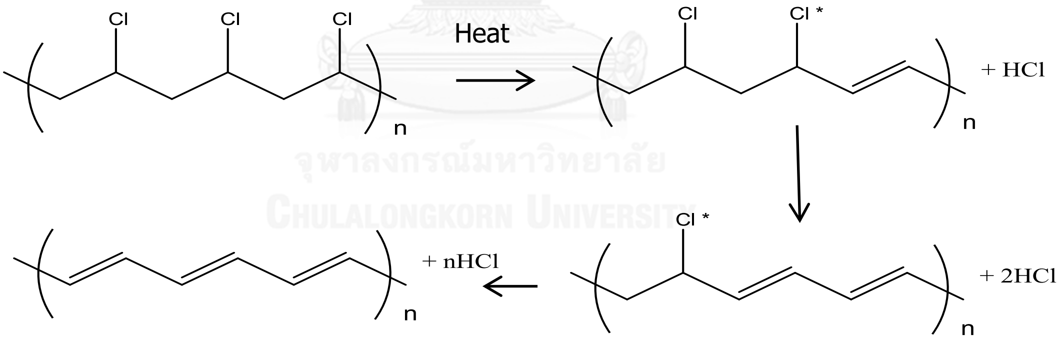


Figure 2.4: Thermal degradation of PVC [22].

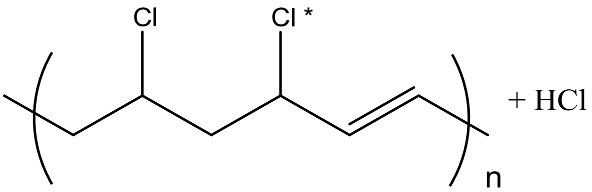


Figure 2.5: (*) Allylic chlorine atom [22].

In principle, thermal degradation process of PVC involves three major steps: 1) initiation of dehydrochlorination, 2) elimination of HCl and simultaneous formation of conjugated double bonds (Figure 2.6) and, lastly, 3) termination of dehydrochlorination process. Color change from the degradation process has been attributed to the formation of conjugated polyene sequence of 5 to 25 double bonds and can be detected by a spectroscopic technique as seen in Figure 2.7 [26-29]. The exact mechanism of the thermal decomposition of PVC is still controversial but it is generally accepted that the evolution of HCl via a chain reaction called zipper elimination or unzipping process [5].

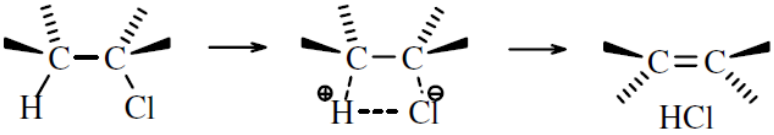


Figure 2.6: Initiation of dehydrochlorination and elimination of HCl and simultaneous formation of conjugated double bonds [30].

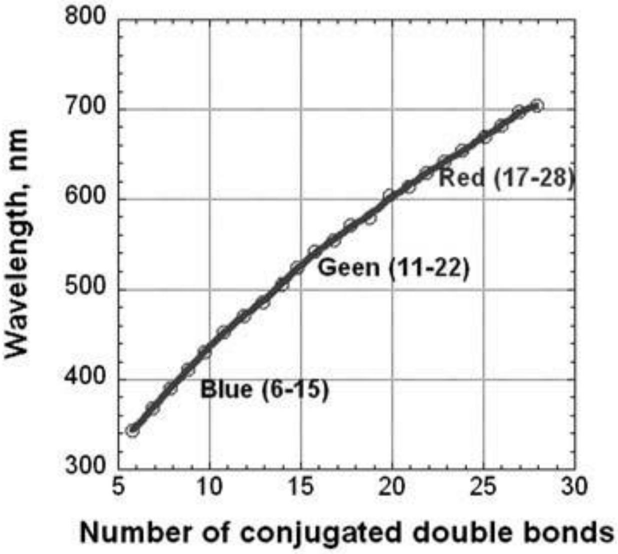


Figure 2.7: Wavelength of absorbed light in visible region vs. number of conjugated double bonds in polyene [29].

2.3 Heat Stabilizers for Poly(vinyl chloride)

To solve those thermal degradation problems, suitable heat stabilizers have been incorporated in PVC to stabilize or prolong its mechanical and thermal integrity. The stabilizer is a substance which removes labile chlorine groups, prevents oxidation, absorbs HCl, and terminates the growth of polyene sequences, all without generating any HCl salts which are Lewis acids that accelerate degradation. It must be a highly reactive material which can function rapidly at low levels without adversely affecting processing or any aesthetic property of the PVC products. All heat stabilizers stabilize PVC through one or more of the following mechanisms: the substitution of labile chlorides with stable ligands, the neutralization of HCl, the addition of double bonds, the prevention of oxidation, the complex of degradation antagonists, and the deactivation of free radicals [31]. An ideal stabilizer should provide good initial color, clarity, long term stability, weather ability and processing ability. The additive should be completely compatible with PVC, non-volatile, odorless, nontoxic and inexpensive [8].

2.3.1 Classification of PVC Stabilizers

PVC stabilizers can be classified according to their modes of action as follows:

1. Primary stabilizers are the types of stabilizers that function by mainly reacting with allylic chloride atoms which are the intermediates in the chain unzipping degradation thus inhibiting further dehydrochlorination as depicted in Figure 2.8. Since the process should be faster than the chain propagation reaction, it requires a very active nucleophile. However, it is necessary that the reactivity of the nucleophile should not be too high to be able to react with the secondary chlorine of the PVC chain, a process which will quickly exhaust the stabilizer. In principle, the effective stabilizer should have a Lewis acid character to enable complex formation with the chlorine atoms PVC [31].

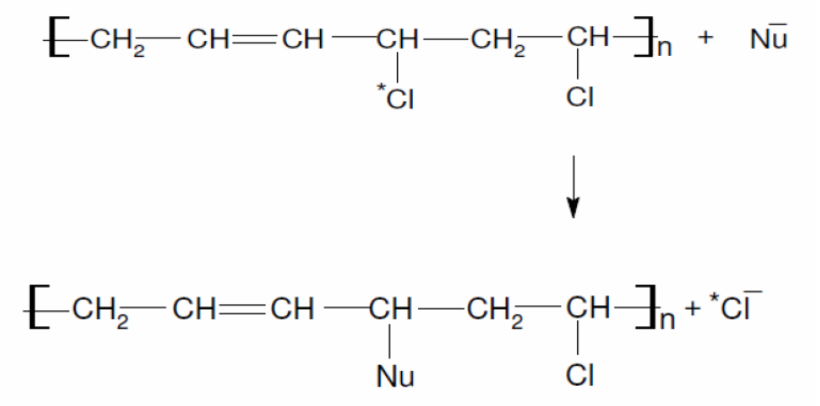


Figure 2.8: Mechanism of PVC thermal stabilization by a primary stabilizer [27].

2. Secondary stabilizer primarily acts by scavenging the HCl/Cl radical generated during the thermal degradation process. HCl is a known catalyst to accelerate the initiation and the propagation reactions of the thermal degradation reaction [32]. Theoretically, the free radical scavenging cannot completely stop the degradation process as it is a diffusion controlled mechanism. However, the HCl scavenging has been reported to substantially reduce the rate of thermal degradation and to considerably retard the degradation process that eventually leads to PVC blackening [33]. Epoxidized compound is one of secondary stabilizer [30] as depicted in Figure 2.9.

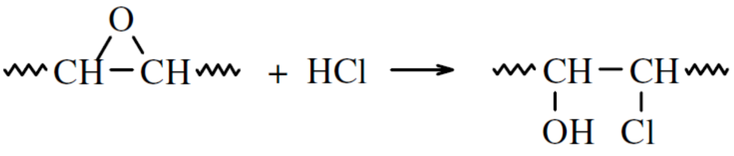


Figure 2.9: Mechanism of epoxidized compound by a secondary stabilizer [30].

In practice, both stabilizers are to be used together as the primary stabilizers are strong Lewis acid reacting with HCl that catalyzes the initiation and propagation of PVC degradation. The secondary stabilizers should be present in the formulation to react with the HCl to protect the primary stabilizers [8]

2.3.2 History of the Use of PVC Pipe Stabilizers

Clarence Parks and Garland Jennings of BF Goodrich, during 1951-1952, discovered that PVC with rubber impact modifiers was suitable for making a piping system with fast production for mine sweepers requested by the US Navy. The use of lead stabilizer in this pipe was rejected by the Navy and replaced by dibutyltin di-2-ethylhexylthoglycolate and antimony trimercaptide thermal stabilizers proposed by Elliott Weinberg of Metals & Thermite Corporation. This event began the US piping industry. In Thailand, PVC pipe is considered to be the leading PVC products in the market. A need to be able to recycle the PVC pipe is thus necessary for PVC waste management in this country. This could not be done without the use of suitable heat stabilizers for PVC pipe.

2.3.3 Major Types of PVC Heat Stabilizers

The main classes of thermal stabilizers of PVC in current use are lead salts, metal soaps, and organo-tin compounds. Some of these additives are toxic, environmental pollution, and/or high cost. Though metal soaps and organo-tin stabilizers are safer than lead salts, their stabilization effects are generally lower than those of lead salts. Recently calcium and zinc soaps of some seed oils had been reported to be safe thermal stabilizers of PVC. Due to environmental awareness worldwide, non-toxic and environmentally friendly thermal stabilizers are actively developed and replaced the traditional stabilizers above. Thermal stabilizers of PVC should possess the capacity to absorb and neutralize HCL evolved during its degradation, an ability to replace or displace active or labile substituent groups such as tertiary and allylic chlorine atoms, a capacity to give pro-degradant substances such as heavy metal chlorides, an ability to modify chain reactions by interrupting conjugated polyene formation and inhibiting HCl formation. In addition, they should be colorless, compatible with and non-migrating from PVC. The additive should be cost-competitive, non-toxic, tasteless and negligible effect on polymer's physical and rheological characteristics [34].

2.3.3.1 Lead Stabilizers

Lead stabilizers are the oldest, the least expensive, and by far the most widely used PVC heat stabilizers. In 2000, it constitutes more than 50% by volume of the PVC heat stabilizers used in the world. However, in the US, lead-based stabilizers represent less than 15% of the market due to the environmental concerns with lead. In Europe, the use of lead stabilizer in PVC is to be terminated completely in 2015 [7]. This kind of heat stabilizer is outstanding in terms of long term heat stability, excellent electrical properties due to an ability to form water insoluble chlorides, and low unit cost. The major drawbacks of lead stabilizers include their inherent opacity, their tendency to stain when exposed to sulfur, and their cumulative toxicity [34].

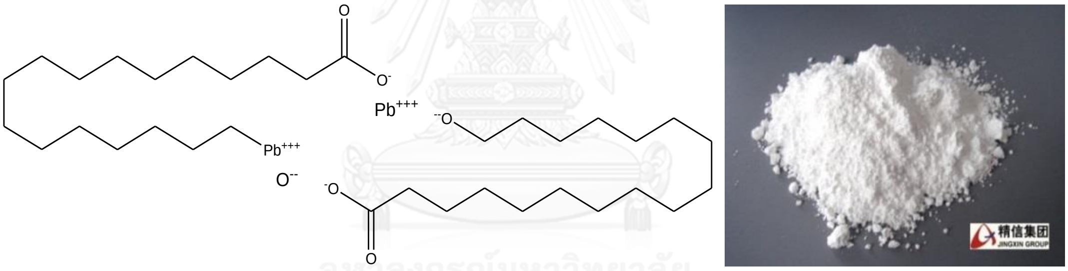


Figure 2.10: Example of Dibasic lead stabilizer [35]

2.3.3.2 Mixed Metal Stabilizers

Mixed metal stabilizers rely on the interaction of at least two different types of metal salts with PVC and with each other in their stabilization mechanism. Mixed metal stabilizers are named according to their principal primary metal salts or soaps they contain e.g. barium/cadmium types, barium/cadmium/zinc types, barium/zinc types and calcium/zinc types. They are available in solids, liquids or paste forms. This type of heat stabilizer is the major type used in flexible PVC. They are expected to replace significant amount of lead based stabilizers in Europe over the next decade in flexible or rigid PVC applications. These stabilizers are much more reliant on the use of synergists than either lead or organotin stabilizers and often contain over 50% by weight of synergists i.e. phosphite esters, epoxy esters, polyols, hydrotalcites, and zeolites which function primarily as scavengers for HCl and acidic metal chlorides. These stabilizers normally require less lubricant to process as a result of the presence of metal soaps in their compositions. The principal weakness of mixed metals as heat stabilizers is related to their difficulty to be used. The users must rely on the technical support from the suppliers [34].

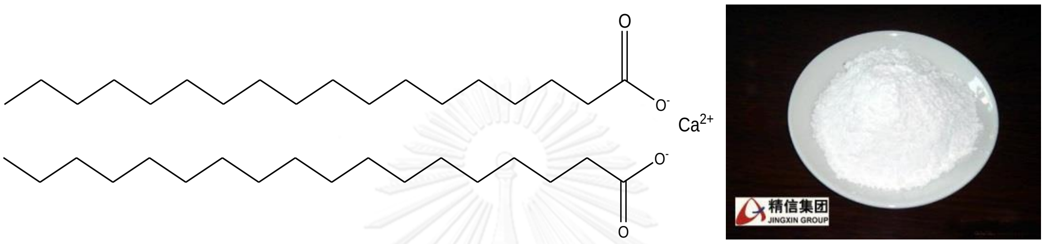


Figure 2.11: Calcium stearate heat stabilizer [20]

2.3.3.3 Organo-tin Stabilizers

Organo-tin stabilizers are the preferable stabilizer for clear rigid PVC applications. They are the stabilizer of choice in North America for all rigid PVC pipe and profile applications [36]. Organo-tin liquid stabilizers are highly miscible with PVC and approach the solvency of primary plasticizers. Thus, the use of tin stabilizers often requires more lubricant than lead or mixed metal stabilizers. They are the most effective and the most expensive, on a unit basis, of all the commercial primary stabilizers for PVC [36]. The quantity as low as 0.5 wt% can be used to stabilize rigid PVC as a result of their inherent compatibility with PVC. The strengths of organo-tin mercaptides are their high efficiency and excellent clarity. The major weaknesses which limit their applications are all related to sulfur content, i.e. odor, light stability, and sulfur staining problems. The advantages of organo-tin carboxylates are their light stability, long-term low temperature stability, and their clarity. Their shortcomings are their relatively high cost compared to mixed metal stabilizers [34].

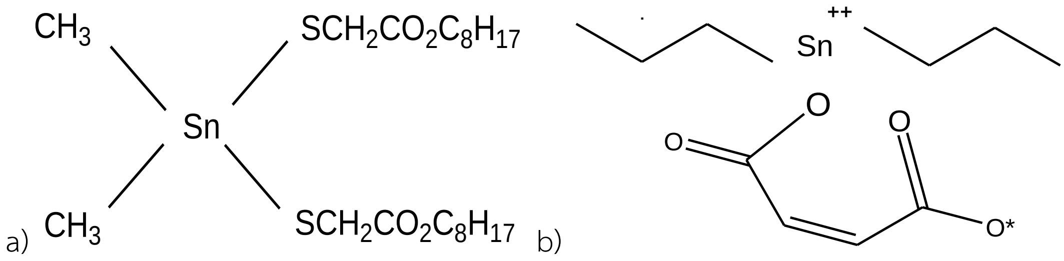


Figure 2.12: a) Methyl tin mercaptan and b) Dibutyl tin maleate (DBTM) [7]

2.3.3.4 Organic Stabilizers

The majority of thermal stabilizers of PVC such as lead salts, some metal carboxylates and some organo-tin are highly toxic thus causes severe environmental problems. Consequently, extensive research on non-toxic, environmentally friendly, and economically viable heat stabilizers for PVC has been performed particularly in the stabilizing efficiency of organic thermal stabilizers or non-heavy metal stabilizers such as N-substituted maleimides [37], barbituric acid (BA), thiobarbituric acid (TBA) [38], sorbitol and xylitol [39], hydroxylbenzylthioethers [40], epoxidized soybean oil, poly(N-acryloylbenzhy-drazide), Vanillin–Schiff's bases, poly(hexamethylene adipate), poly(ethylene adipate), anthraquinone, 4-allyl-2-methoxy-phenol (eugenol), uracil derivatives, etc. [8]. Among these stabilizers, eugenol and uracil derivatives have been reported to exhibit highly promising characteristics as heat stabilizers for rigid PVC applications [3,9].

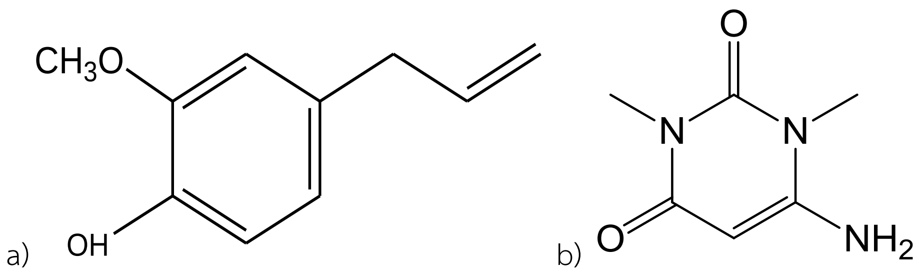


Figure 2.13: a) Eugenol and b) 1,3-Dimethyl-6-aminouracil.

CHAPTER III

LITERATURE REVIEWS

M.W. Sabaa and R.R. Mohamed [4] studied eugenol (4-allyl-2-methoxyphenol) as a thermal stabilizer for rigid PVC and compared the results with some of the common reference stabilizers such as dibasic lead carbonate, calcium–zinc soap and octyltin mercaptide. The stabilizing efficiency of PVC heat stabilizers were evaluated by the evolved HCl gas and color change of sample in air at 180°C. From their results, eugenol was reported to exhibit higher thermal stability value (Ts) than those reference stabilizers (almost about three times) that means high stabilizing efficiency and very good color retention when compared with other reference stabilizers as clearly seen in Figure 3.1 with the values tabulated in Table 3.1.

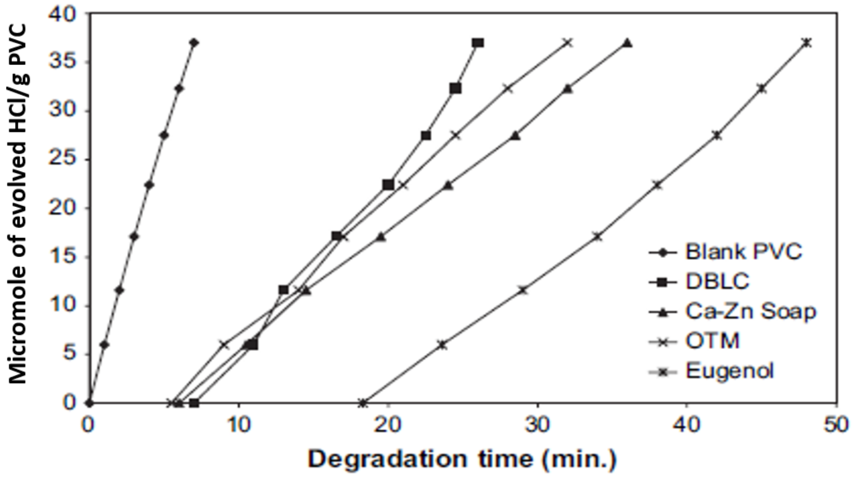


Figure 3.1 Dehydrochlorination rate of rigid PVC, in air, at 180°C, in presence of 2 g of the investigated stabilizer per 100 g of PVC (2 phr) [4].

Table 3.1: Extent of discoloration of thermally degraded rigid PVC at 180°C, in air, in presence of 2 phr of the investigated stabilizers as a function of degradation time [4].

Types of stabilizers	Color at 0 min	Color at 15 min	Color at 25 min	Color at 35 min	Color at 45 min
Blank PVC	White	Light	brown	Dark brown	Black
DBLC	White	Light brown	Brown Dark	Brown Dark	Brown
Ca/Zn soap	White	Orange	Light brown	Dark brown	Dark brown
OTM	Cream	Light green	Green	Dark green	Dark green
Eugenol	White	White	White	Yellow	Yellow

Moreover, a possible stabilization mechanism of eugenol when reacted with PVC was through a crosslinking of eugenol to give more gelation on PVC resin as depicted in Figure 3.2.

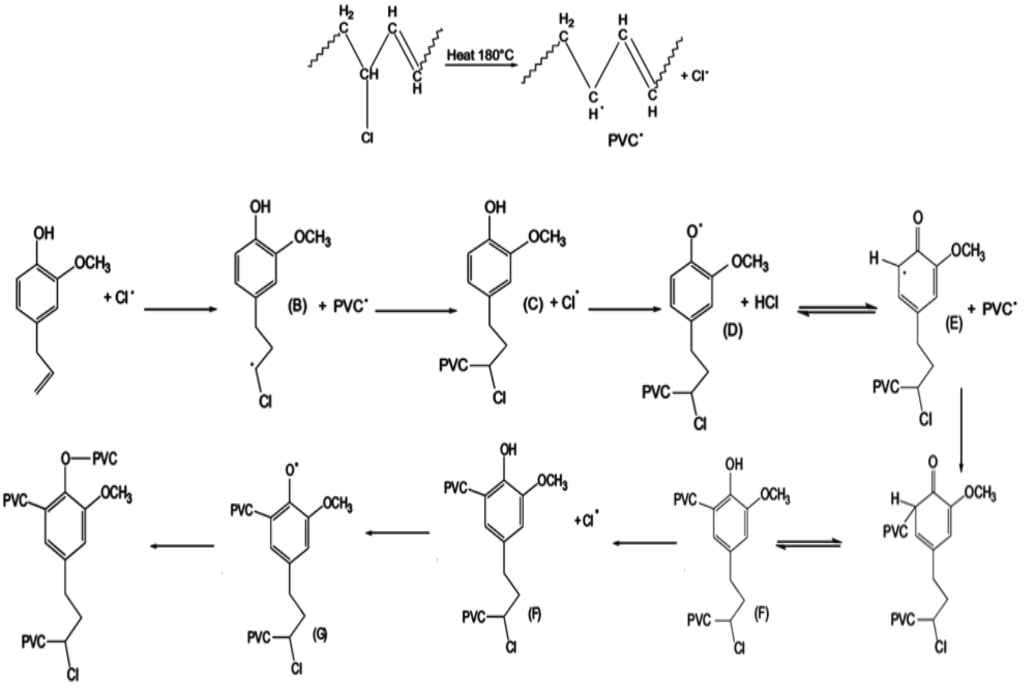


Figure 3.2 Mechanism of eugenol as primary stabilizer [4].

X. Xu, S. Chen, W. Tang, Y. Qu and X. Wang [12] studied uracil derivatives, i.e. N, N-dimethyl-6-amino-uracil (DAU), N-methyl-6-amino-uracil (MAU) and N-monomethyl-6-amino-thiouracil (MATU) as a thermal stabilizer for rigid PVC and compared the results with calcium zinc stabilizer (CZ) and diphenylthiourea (DTU). The stabilizing efficiency of PVC heat stabilizers were evaluated by the dynamic stability time of PVC and thermogravimetric analysis of sample in air at 180°C. From their results, DAU, MAU and MATU was reported to exhibit higher thermal stability value (Ts) than CZ and DTU that means high stabilizing efficiency as clearly seen in Figure 3.3.

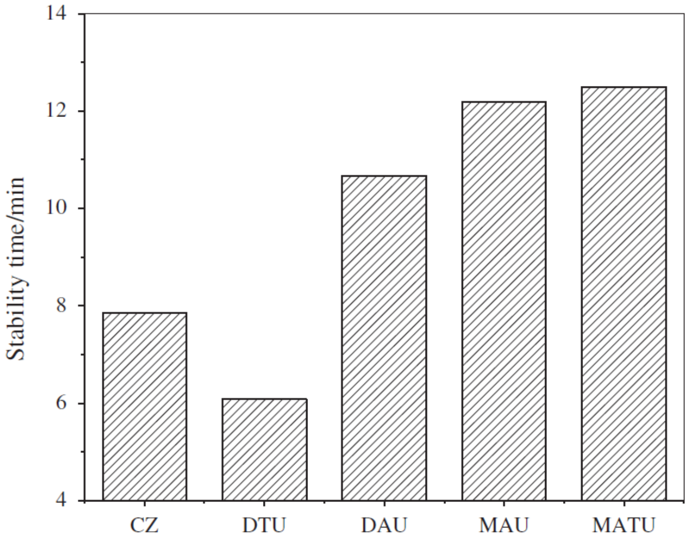


Figure 3.3: Influences of the stabilizers (2 phr) on dynamic stability time of PVC at 180°C in air [12].

The thermal behavior of uracil derivatives was characterized by TGA at a constant heating rate of 10°C/min as seen in Figure 3.4. Table 3.2 summarized the initial decomposition temperature (IDT) and percent residue yield at 200°C obtained for these stabilizers. It could be observed that all of them were relatively stable at temperature up to 200°C with a weight loss less than 3%. Thermal weight loss was one of the important factors used to evaluate utilization rate of a stabilizer [39]. Thus, uracil derivatives, i.e. DAU, MAU, MATU, help improve thermal stabiliziation against thermal degradation of PVC.

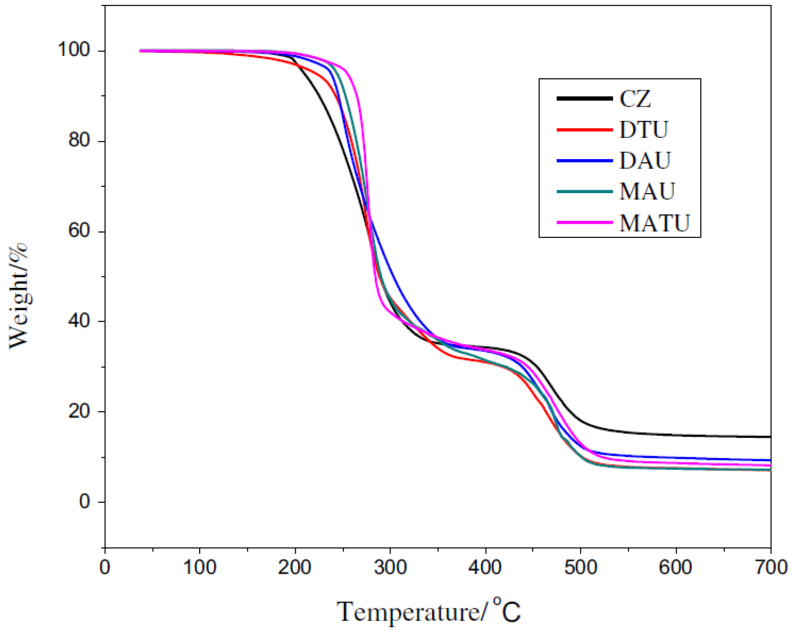


Figure 3.4 Thermogravimetric analysis of PVC stabilized with CZ, DTU, DAU, MAU and MATU [12].

Table 3.2 TGA results of stabilized PVC [12].

Stabilizers	IDT(°C)	% Weight loss at 200°C	% Residue at 700 °C
CZ	202	3	14
DTU	188	4	7
DAU	209	2	9
MAU	215	1	7
MATU	221	1	8

Furthermore, an excellent synergistic effect could be obtained when the model compound MATU combined with zinc stearate ($ZnSt_2$) in different mass ratios, and the initial color and long-term stability of PVC products were remarkably improved. Moreover, a possible stabilization mechanism of uracil derivatives as secondary stabilizer when reacted with PVC as depicted in Figure 3.5.

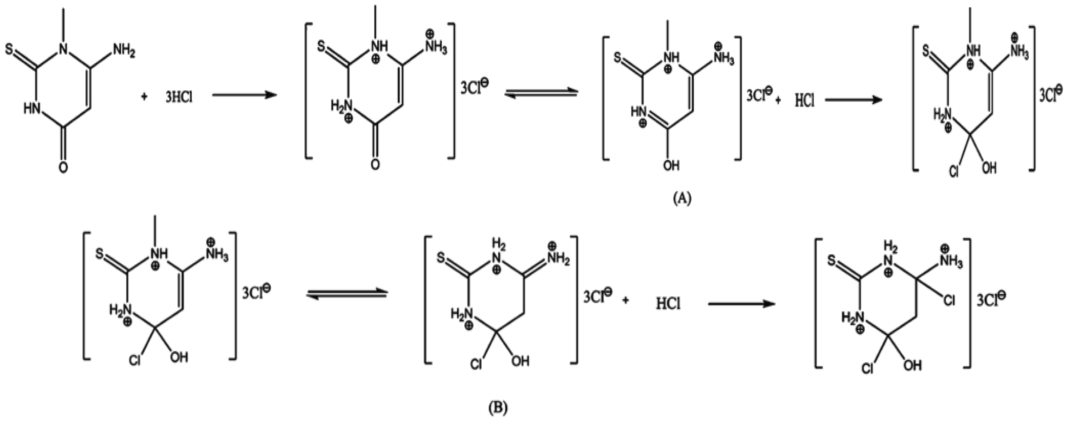


Figure 3.5 Mechanism of uracil derivatives as secondary stabilizer [12].

T. Hopfman, H. Friedrich, K. Kuhn and W. Wehner [10] studied uracil derivative product as heat stabilizer. The formulation and result of color measurement of Un-plasticized PVC (Rigid) indicated 1,3-dimethyl-6-aminouracil improve color of PVC in Table 3.3. The results indicated addition small amounts of 1,3-Dimethyl-6-aminouracil can improve PVC color.

Table 3.3 Formulation and result of color measurement of rigid PVC [10].

PVC K value 67 (Shin Etsu 6704)	100	100	100
Zeolite A	1	1	1
Calcium stearate	0.4	0.4	0.4
paraffin Wax	0.6	0.6	0.6
polyethylene Wax	0.6	0.6	0.6
oxidized polyethylene Wax	0.1	0.1	0.1
1,3-Dimethyl-6-aminouracil	-	0.1	0.2
Color measurement: yellowness Index	red-violet	31	26

M.W. Sabaa, E.H. Oraby, A.S. Abdel-Naby and R.R. Mohamed [41] studied a use of 1-phenyl-3-methyl-4-cinnamal-2-pyrazolin-5-one (PMCP), 1-phenyl-3-amino-4-cinnamal-2-pyrazolin-5-one (PACP), 1-phenyl-3-methyl-2-pyrazolin-5-one (PMP), 1-phenyl-3-amino-pyrazolin-5-one (PAP), 1-phenyl-3-methyl-4-benzal-2-pyrazolin-5-one (PMBP), 1-phenyl-3-amino-4-benzal-2-pyrazolin-5-one (PABP), 1-phenyl-3-methyl-4-crotonal-2-pyrazolin-5-one (PMCrP), 1-phenyl-3-amino-4-crotonal-2-pyrazolin-5-one (PACrP), 1-phenyl-3-methyl-4-acryloyl-2-pyrazolin-5-one (PMAP), 1-phenyl-3-amino-4-acryloyl-2-pyrazolin-5-one (PAAP), 1-phenyl-3-methyl-4-salicyloyl-2-pyrazolin-5-one (PMSP) and 1-phenyl-3-salicyloyl-amino-2-pyrazolin-5-one (PSAP) as a thermal stabilizer for rigid PVC. These stabilizers have been reported to provide higher thermal stability value than those from reference heat stabilizers i.e.DBLC, CaSt/ZnSt and octyl-tin, compared at the fixed amount of the additives of 2 wt%. However, in terms of color stability, these types of organic based heat stabilizers were observed to be inferior to eugenol stabilizer but are superior to eugenol in term of thermal stability i.e. providing longer induction period (Ts).

Table 3.4: Induction period (Ts) as a function of type of the investigated N-phenyl-3-substituted-5-pyrazolone derivatives acting as thermal stabilizers for rigid PVC, at 180°C, in air [41].

Code names	Induction period (Ts) (min)	Code names	Induction period (Ts) (min)
PVC	0	PMCP	53
DBLC	7	PACP	47
Ca/Zn	6	PMCrP	33
n-OTM	5.5	PACrP	29
PMP	23	PMAP	31
PAP	17	PAAP	25
PMBP	29	PMSP	32

Table 3.5: Extent of discoloration of thermally degraded rigid PVC, at 180°C, in presence of 2 wt% of some of the investigated stabilizers as a function of degradation time [41].

Type of stabilizer	Color of PVC stabilized with heat stabilizer			
	0 min	15 min	25 min	35 min
Blank PVC	White	Light brown	Dark brown	Black
DBLC	White	Very light brown	Light brown Dark	Brown
Ca/Zn soap	White	Light yellow Dark	yellow Light	Brown
n-OTM	Pale yellow	Very light grey	Light grey	Dark grey
PMP	White	Light yellow	Dark yellow	Very dark yellow
PAP	White	Very pale yellow	Light yellow	Dark yellow
PMCP	Pale yellow	Very light yellow	Very light yellow	Light brown
PACP	Pale yellow	Very light yellow	Dark yellow	Light brown

M.W. Sabaa, Z.R. Farag and N.A. Mohamed [42] studied the thermal degradation behavior of poly(vinyl chloride) (PVC) in presence of poly(glycidyl methacrylate) (PGMA) had been studied using continuous potentiometric determination of the evolved HCl gas from the degradation process from one hand and by evaluating the extent of discoloration of the degraded samples from the other. Moreover, the efficiency of blending PGMA with dibasic lead carbonate (DBLC) conventional thermal stabilizer and a probable radical mechanism for the effect of PGMA on the thermal stabilization of PVC had also been investigated as seen in Figure 3.6.

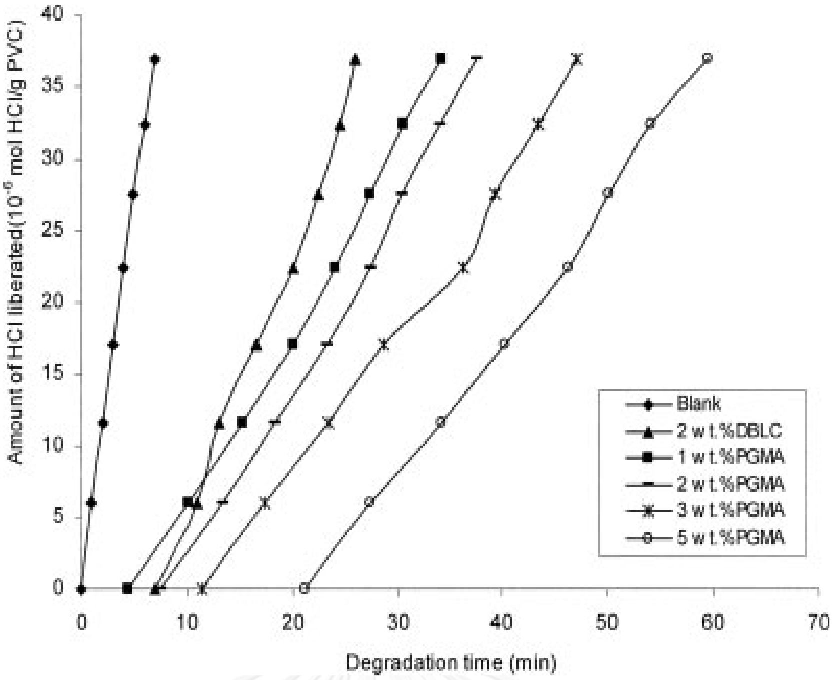


Figure 3.6: Rate of dehydrochlorination of rigid PVC at 180°C, in air, in the presence of various concentrations of Poly(glycidyl methacrylate) [42].

A.S. Ditta, A.J. Wilkinson, G.M. McNally, and W.R. Murphy [43] examined the effect of thermal degradation of PVC on its mechanical properties using lead stabilizer and Ca/Zn stabilizer. The effects of number of extrusion cycles of the PVC on its major properties were investigated. It was seldom found that thermal degradation significantly affected mechanical properties of PVC. Whereas stabilization prevented excessive damage which may cause noticeable changes in the sample mechanical properties as depicted in Figure 3.7. When PVC was stabilized with lead stabilizer which offers very long protection, then elongation at break only initially decreased because morphological changes affected mechanical properties. This was followed by elongation increase. PVC stabilized with calcium/zinc stabilizer reacted initially in the same manner but then elongation decreased substantially because catalytic influence of $ZnCl_2$ rapidly increased deterioration rate.

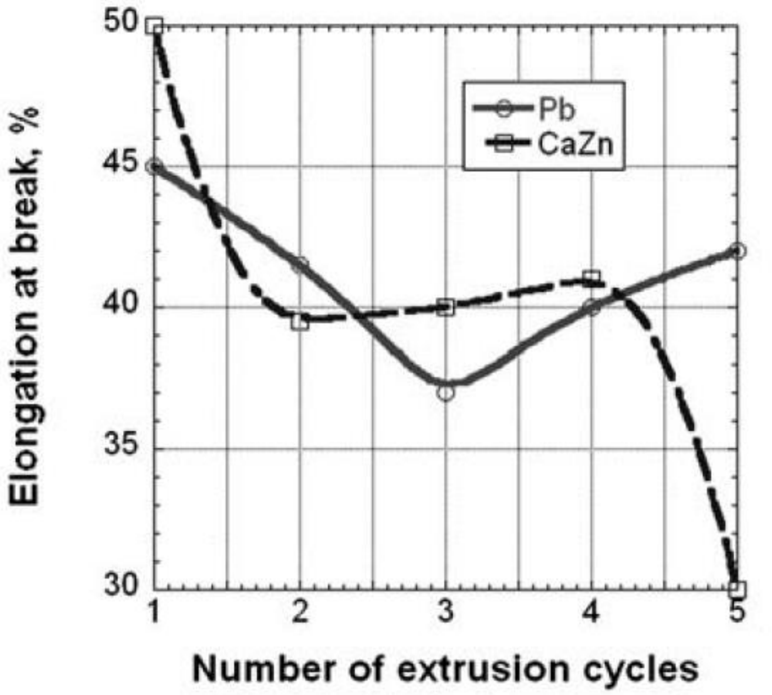


Figure 3.7: Effect of lead and Ca/Zn stabilizers on elongation at break vs. number of extrusion cycles [43].

N. Yarahmadi, I. Jakubowicz, and T. Gevert [44] investigated PVC profiles based on Ca/Zn stabilizer. The profiles were re-extruded by twin screw extruder, from one to five times without adding new additives. The material was characterized after each extrusion. They observed some improvement of mechanical properties after the second extrusion. This was explained by an increase in the degree of gelation of the PVC material. The properties were decreased with further re-extrusion of the samples. The main color change due to repeated extrusion was towards red (a) and a change in greyness (L) as a result of thermal dehydrochlorination as shown in Table 3.6. The elongation at break result indicated in Figure 3.8. The activation energies of the thermal degradation process were also determined for the material after each re-extrusion and were found to decrease with an increasing number of extrusions.

Table 3.6: Effect of repeated extrusion on various properties of PVC resin with Ca/Zn stabilizer [44].

Property	1st Extrusion	2nd Extrusion	3rd Extrusion	4th Extrusion	5th Extrusion
Color change:					
L*	95.7	95.5	95.3	95.1	94.9
a*	0.1	0	-0.2	-0.3	-0.1
b*	1.7	2	2.3	2.7	3.0
Gloss	56.6	63.6	66.3	63.8	62.3
Tensile strength (MPa)	42	45	45	44	43

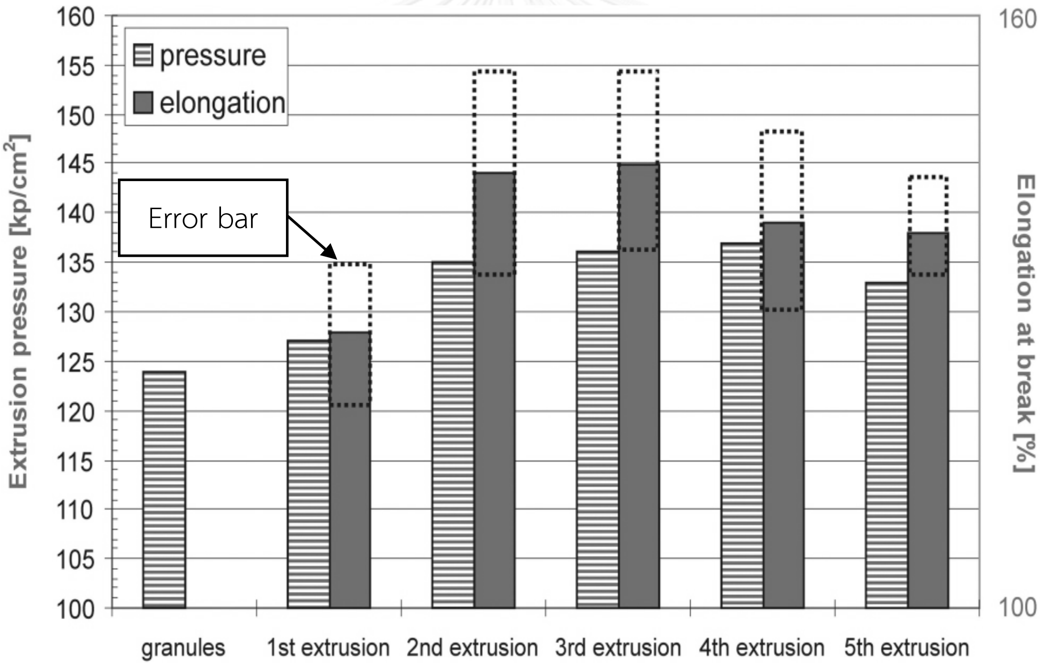


Figure 3.8: The extrusion pressure and elongation at break, as a function of number of extrusions [44].

M. Celina, D. K. Ottesen, K. T. Gillen amd R. L. Clough [45] investigated degradation behavior of PVC by FTIR. PVC degrades primarily via hydrogen chloride elimination in a free radical process that results in the formation of highly conjugated structures (polyene sequences). In their work, a commercial rigid PVC sample was held at 180°C; the observed FTIR spectral change of PVC with time were shown in Figure 3.7. There are general decrease such as C-H bands (1430 and 1242 cm^{-1}), C-C vibrations (962 and possibly 1090 cm^{-1}) and C-Cl bands (685 and 614 cm^{-1}). The increase around 1600 cm^{-1} was expected, since it correlated with polyene sequences due to dehydrochlorination. It is, however, important to note that this was also accompanied by a strong carbonyl growth, indicating additional oxidative degradation.

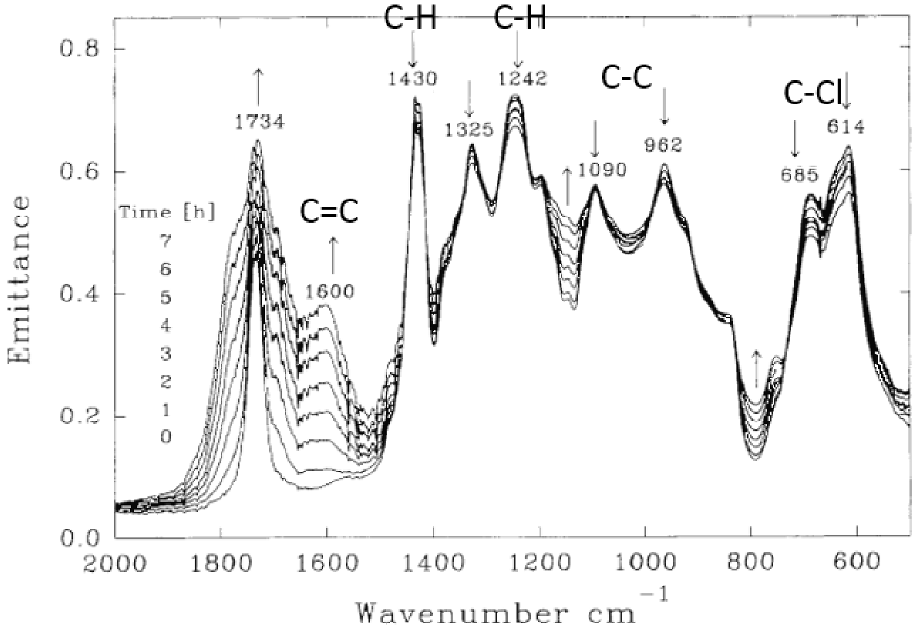


Figure 3.9. FTIR spectra of a commercial rigid PVC samples heated at 180°C at 0-7 hours [45]

M. Gilbert and J. C. Vyvoda [46] studied gelation behavior of PVC via differential scanning calorimety (DSC) as presented in Figure 3.8. When PVC was heated during processing, the smaller grains (crystallites) generally melt first. During melting, the grains tended to fuse together forming a new secondary structure (a partially-gelled state). These changes were usually referred to as gelation. The level of gelation depended on the processing temperatures, with higher temperatures yielding a higher degree of gelation. This behavior was crucial to the quality of the PVC products as the level of gelation was an important factor in determining the mechanical strength and fracture behavior of the final products. From the figure, they reported that the first transition found between 80-90°C represented the glass transition temperature (Tg) of the PVC. Furthermore, area A, which was an endothermic response, represented the melting temperature of the partially gelled crystallites. Area B, on the other hand, represented the melting of crystallites that did not gel during the processing of the PVC part. Finally, the inflection point observed between areas A and B indicated the processing temperature. From the Figure, it could be clearly seen that with increasing the processing temperature, area A was increased while the corresponding area B was decreased and finally disappears suggesting complete gelation in the PVC sample.

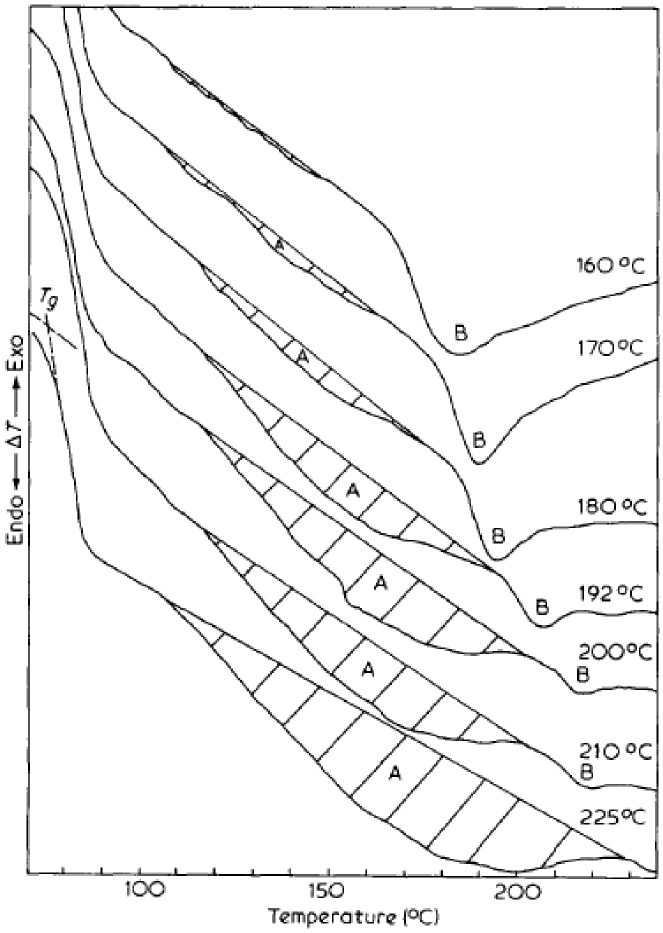


Figure 3.10: DSC thermograms of compression molded PVC compounds exhibiting area A and area B due to fusion [46].

CHAPTER IV

EXPERIMENTAL

4.1 Materials

Suspension grade PVC with K-value of 66 which is for pipe and other extrusion profile applications was kindly obtained from Vinythai Public Company Limited., Thailand. The additives used in PVC compound comprises of calcium carbonate as filler whereas lead compound, calcium/zinc compound and other three types of organic compounds are used as heat stabilizers. Calcium carbonate and lead compound were provided by Vinythai Public Company Limited., Thailand whereas calcium/zinc compound (PRD5549, CZ78NP, CZ964NP and CZ162P) and commercial organic based stabilizers were supported by Sunace Co., Ltd. Singapore, Chemson Co., Ltd., China and Siam Stabilizer Co., Ltd., Thailand. Eugenol and 1,3-dimethyl-6-amino-uracil (DAU) (organic compound stabilizer) were purchased from Aldrich Ltd., Germany. The costs of PVC with DAU and Eugenol were higher than the PVC with lead and Ca/Zn stabilizer as indicated in Table 4.1. It was because DAU and Eugenol which were single component were not optimized in economic. The additional of hydrotalsite as absorbing HCl, 1,3-Diketone as displacing labile chlorides, phosphite esters as multifunctional and precipitated calcium carbonate as filler [34] are included in the PVC formulation in order to reduce cost or improve heat stability.

Table 4.1 Composition and price of each ingredient.

Ingredient		Composition		Price (Baht/kg)	Price of PVC_{lead} (Baht/kg)	Price of $PVC_{Ca/Zn}$ (Baht/kg)	Price of PVC_{DAU} (Baht/kg)	Price of $PVC_{Eugenol}$ (Baht/kg)
		(g)	(wt%)					
PVC (k=66)		100	88.50	30 [47]	26.6	26.6	26.6	26.6
Calcium carbonate		10	8.85	2 [47]	0.2	0.2	0.2	0.2
Heat stabilizer	Lead	3	2.65	55 [47]	1.5	-	-	-
	Ca/Zn			80 [47]	-	2.1	-	-
	DAU			180 [48]	-	-	4.6	-
	Eugenol			200 [47]	-	-	-	5.3
Total		113	100	-	28.3	28.9	31.4	32.1

4.2 Methodology

4.2.1 PVC Dryblend Preparation

PVC resin and 2 additives were blended in a high speed mixer model Plasmec Turbomixer 100L at Vinythai Public Company Limited (Rayong, Thailand). The mixing process consisted of two mixing tanks, operating with 2 steps of hot and cold mixers as following details:

Hot Mixing Step

- Add PVC resin and solid additives into the mixer.
- Stir at high speed (1200 rpm) until the temperature was 110°C.
- Discharge to a cold mixer.

Cold Mixing Step

- The hot dryblend was cooled by cooling water at temperature of 15-20°C.
- Stir until the temperature of dryblend was decreased to 35°C.
- Discharge to a container.

Figure 4.1: High speed mixer: Plasmec Turbomixer 10L with cooler.

4.2.2 PVC Processing

PVC dryblend was processed by two-roll mills with 0.125 mm gap at temperatures of 180°C for 3 minutes to yield a homogeneous sample. The two-roll mills at Vinythai Public Company Limited (Rayong, Thailand) were also shown in Figure 4.2. The total amount of material loading on two-roll mills should not exceed 300 g. The obtained sample was preheated at 180°C for 200 s and then pressed into sheet by compression molding at 180°C and pressure of 150 bars for 30 s. The compression-molded sheets were then cut into test pieces for further property evaluations.

Figure 4.2: Two-roll mills and compression molder

4.2.3 Recycling Preparation of PVC Stabilized with Various Stabilizers

PVC stabilized with various stabilizers samples after processed by two-roll mills and compressed by compression molder was cut by using cutting mills (Model:Fritsch pulverisette 15 cutting mill) as shown in Figure 4.3. The PVC stabilized with various stabilizers samples were cut at speed 3000 rpm to reduce the size to 3-7 mm. Then, the cut sample (reduced size) was fed into the two-roll mills and further compressed by the compression molder as noted in section 4.2,2. This process was repeated up to 5 times.

Figure 4.3: Fritsch pulverisette 15 cutting mill

4.3 Characterizations of PVC Stabilized with Heat Stabilizers

4.3.1 Processing Characterization

4.3.1.1 Fusion of PVC Compounds Using a Torque Rheometer

The fusion characteristics of PVC dryblend (55 g of sample amount) were studied by Brabender kneader (Plasti–Corder Pl) and processed in the chamber at wall temperatures (T_{Ch}) of 180°C. Rotational speed of the screw was 60 rpm. The real temperature of the compound was determined by the resistance temperature device

(RTD) situated between the rotors, directly in the kneaded PVC compound, and isolated from the walls of the chamber.

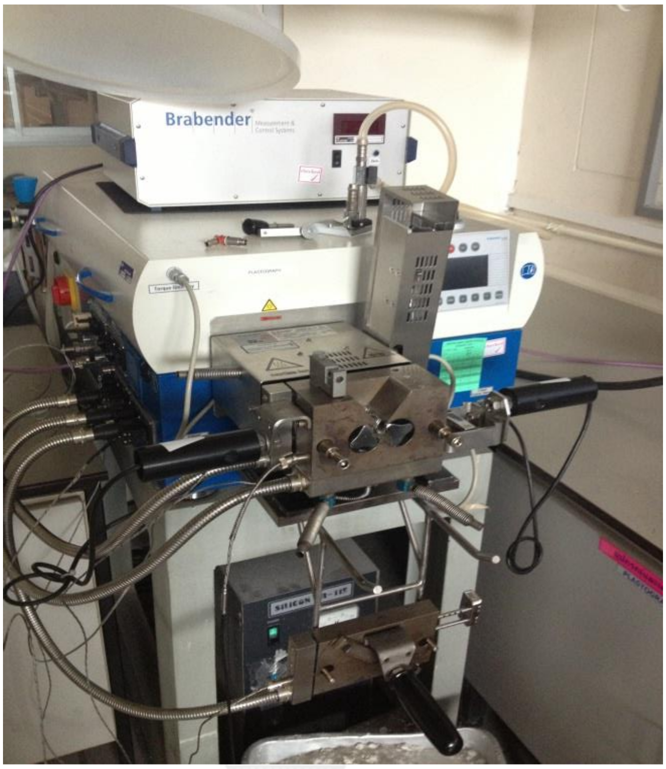


Figure 4.4: Brabender (torque rheometer)

4.3.2 Physical Properties

4.3.2.1 Density Measurement

The density of the PVC specimen was measured by a water displacement method according to ASTM D792. The dimension of the specimen was 20 mm x 35 mm x 4 mm. All specimens were weighed in air and in water at given temperature. The density was calculated from the following equation:

$$\rho = \left(\frac{A}{A-B}\right) \times \rho_0$$

Where ρ = Density of the specimen (g/cm^3),

A = Weight of the specimen in air (g)

B = Weight of the specimen in demineralized water (g)

ρ_0 = Density of demineralized water at the given temperature (g/cm^3).

4.3.2.2 Discoloration Test (Static Thermal Stability)

PVC dry blend obtained by two-roll mills in section 4.2.2 with thickness 1.0 mm was cut into 1.5 cm × 30 cm strips. These strips were put in Mathis thermotester (Figure 4.5) at 180°C and hold for 5 min. Strips were then automatically moved out of the box at 1 mm/min. The effect of the stabilizers was evaluated by the comparisons of visual color differences of the heated PVC strips.

Figure 4.5: Mathis Thermotester

4.3.2.3 Color Change Measurement

This test method resulted from the consolidation of separately published methods for instrumental evaluation of color differences. The total difference, ΔE_{ab}^*, between two colors each given in terms of lightness (L*) and chromaticity coordinate (a* and b*) is calculated following ASTM D 2244 by Ultrascan Pro (Hunter Lab, USA) which measures both reflected and transmitted color and meets CIE (International Commission on Illumination):

$$\Delta E_{ab}^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

The magnitude, ΔE_{ab}^*, gives no indication of the character of the difference since it does not indicate the relative quantity and direction of hue, saturation, and lightness differences. The direction of the color difference is described by the magnitude and algebraic signs of the component ΔL^*, Δa^* and Δb^*.

$$\Delta L^* = L_1^* - L_0^*,\ \Delta a^* = a_1^* - a_0^*,\ \Delta b^* = b_1^* - b_0^*$$

Where L_0^*, a_0^* and b_0^* refer to the initial values, and L_1^*, a_1^* and b_1^* refer to the final values of a specimen. The signs of the components ΔL^*, Δa^* and Δb^* have the following approximate meanings:

$+\Delta L^*$= lighter, $-\Delta L^*$ = darker

$+\Delta a^*$ = redder (less green), $-\Delta a^*$ = greener (less red)

$+\Delta b^*$ = yellower (less blue), $-\Delta b^*$= bluer (less yellow)

4.3.2.4 Fourier Transform Infrared (FTIR) Spectral Analysis

The chemical structures of PVC stabilized with each heat stabilizers in each processing were studied by FT-IR spectroscopic technique. FTIR spectrums were recorded on a Spectrum GX FTIR spectrometer from Perkin Elmer instrument at a resolution of 4 cm^{-1}, in transmittance mode with the frequency range of 2000 to 400 cm^{-1}. The samples were prepared by mixed with KBr.

4.3.3 Mechanical Characterization

4.3.3.1 Tensile Property Measurement

Tensile properties were measured by a Universal Testing Machine (Instron Instrument, model 5567) according to ISO 527-2. The test specimens were a dumbbell shape with a thickness as 3 mm. They were tested using a crosshead speed of 5 mm/min with the pre-load of 150 N giving a straight tensile force. The tensile modulus defined as the ratio of stress to strain which was determined from the initial slope of the stress-strain curve whereas the tensile strength is the ultimate stress. Eight PVC specimens from each stabilizer were tested and the average values were reported.

4.3.3.2 Flexural Property Measurement

Flexural modulus and flexural strength of the PVC specimens were measured by a Universal Testing Machine (Instron Instrument, model 5567) according to ASTM D790. Three-point bending test was carried out at room temperature at the crosshead speed of 1.2 mm/min with the support span of 48 mm. The dimension of the specimen was 4 mm×12.7 mm×64 mm. Five specimens from each heat stabilizers were examined and the average values were reported.

4.3.3.3 Notched Izod Impact Property Measurement

Notched Izod Impact is a single point test that measures a materials resistance to impact from a swinging pendulum. Izod impact is defined as the kinetic energy needed to initiate fracture and continue the fracture until the specimen is broken. The specimen is clamped into the pendulum impact test fixture with the notched side facing the striking edge of the pendulum. The pendulum is released and allowed to strike through the specimen. Izod Impact strength of the specimens was obtained by Impact Tester (Yasuda) according to ASTM D256. The dimension of the test specimen was 12.7 mm×60 mm×3.2 mm and the depth under the notch of the specimen was 10.7 mm.

4.3.4 Thermal Characterization

4.3.4.1 Thermogravimetric Analysis (TGA)

Degradation temperature of samples, i.e. commercial organic based stabilizers and PVC filled with each heat stabilizers were measured on a thermogravimetric analyzer (TGA 1, Mettler Toledo, Germany). Samples were heated from room temperature to 800°C in a ceramic pan at a rate of 10°C/min in nitrogen or oxygen atmospheres. The sample weight was measured to be approximately 8-15 mg. Weight loss of the samples was measured as a function of temperature. Values for residues were taken at the end of the main decomposition step.

4.3.4.2 Differential Scanning Calorimetry (DSC)

Thermal history of PVC sample after processing was measured by DSC (Perkin Elmer DSC 8000). The sample weight was approximately 15-25 mg. The temperature was equilibrated at 30°C and the samples were heated from 30 to 230°C with the heating rate of 10°C/min. Nitrogen gas flow rate was maintained at 50 ml/min. These conditions follow international standard (ISO 18373-1) which is suitable for all types of rigid PVC pipes.

4.3.4.3 Dynamic Mechanical Analysis (DMA)

Viscoelastic properties of PVC stabilized with various heat stabilizers were examined by a dynamic mechanical analyzer (NETZSCH, DMA242). The dimension of the specimen was rectangular with 50 mm length, 10 mm width, and 2 mm thickness. The three point bending mode of deformation was used under a test temperature range from 30°C to 150°C with a heating rate of 2 °C/min. The test amplitude and frequency were 30μm and 1Hz, respectively. The glass transition temperature was taken as the temperature of the maximum in the loss modulus and the loss tangent plots.

4.3.4.4 Heat Distortion Temperature (HDT)

Heat distortion temperature is defined as the temperature at which a standard test bar deflected a specified distance under the load applied at its center to give maximum stress. It is used to determine short-term heat resistance. It distinguishes between materials that are able to sustain light loads at high temperatures and those that lose their rigidity over a narrow temperature range. The specimen was placed under the deflection measuring device. The specimen was then immersed in a silicone oil with a means of raising the temperature at 120°C/h or 2 ± 0.2°C/min until they deflected 0.25 mm following ASTM D648. This temperature was recorded as the deflection temperature under flexural load of the test specimen.

4.3.4.5 UL-94 Vertical Test

UL-94 test includes three classifications i.e. V-0, V-1 and V-2. These test were performed on vertical testing apparatus as shown in Figure 4.6. These test used 5 specimens (120 mm x 12 mm x 3 mm). The specimen was placed in a holder in a vertical position where the lower end of specimen is contacted by a flame for 10 seconds thus initiating burning. A second ignition was made after self-extinguishing of the flame at the sample for 10 seconds. The burning process is characterized by the times t_1 and t_2 pertaining to the two burning steps. The parameter t_1 and t_2 denote the time between removing the methane flame and self-extinguishing of the sample. Moreover, it is always noted whether drips from the sample are released or drips make absorbent cotton flame during the burning times t_1 and t_2. If $t_1 + t_2$ were less than 10 second with no dripping, it would be considered a V-0 material. In addition,V-1 and V-2 condition could be listed in Table 4.2.

Table 4.2 Three material classification in Ul-94.Vertical Test

V-0	Burning stops within 10 seconds ($t_1 + t_2$) after two applications of ten seconds each of a flame to a test bar. NO flaming drips are allowed.
V-1	Burning stops within 60 seconds ($t_1 + t_2$) after two applications of ten seconds each of a flame to a test bar. NO flaming drips are allowed.
V-2	Burning stops within 60 seconds ($t_1 + t_2$) after two applications of ten seconds each of a flame to a test bar. Flaming drips are allowed.

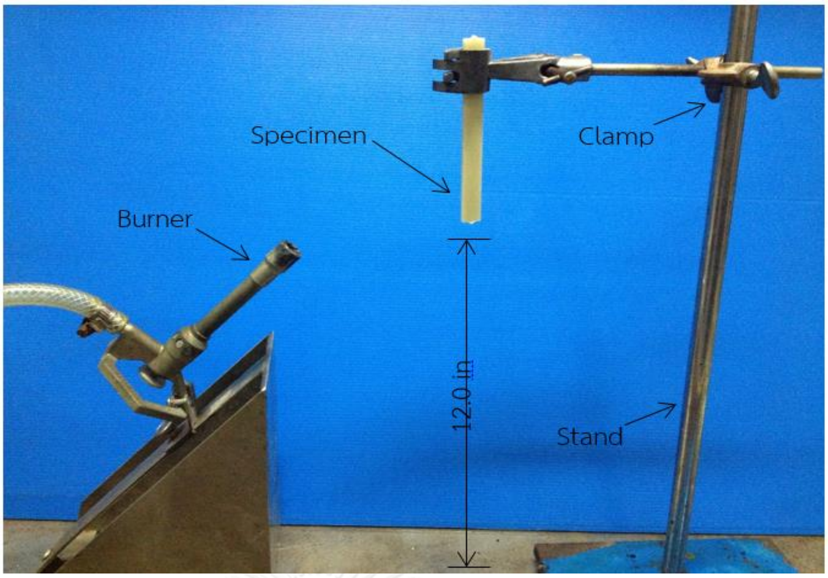


Figure 4.6: UL-94 vertical test

CHAPTER V

RESULTS AND DISCUSSION

5.1 Effect of Commercial Lead, Calcium Zinc (Ca/Zn) and Organic Based Stabilizers on Rheological Properties and Static Thermal Stability on PVC Resin

In this work, the effect of types of commercial heat stabilizer such as lead stabilizer (from Sunace Co., Ltd), Ca/Zn stabilizers (from Sunace Co., Ltd, Chemson Co., Ltd. and Siam Stabilizer Co., Ltd.) and organic based stabilizer (OBS) (from Sunace Co., Ltd, Chemson Co., Ltd) on rheological properties via plastograms obtained from fusion test and static thermal stability through color change measurement of PVC resin were investigated. The experimental results can be summarized as follows.

5.1.1 Effect of Commercial Lead, Calcium Zinc and Organic Based Stabilizers on Rheological Property on PVC Resin

5.1.1.1 Major Characteristics of PVC Plastogram obtained from a Torque Rheometer

A typical torque rheometer process curves or plastograms, recorded with Brabender measuring mixer, was presented in Figures 5.1-5.6. The red line in the plots was a real sample temperature whereas the blue line in each plot was mixing torque as a function of mixing time. After the loading stage, a significant increase of the torque was observed (point A) with a simultaneous decrease of the temperature measured in the chamber. Next, a decrease of the torque with its minimum at point B was detected. After that the torque rheometer process curve passed through an inflection point G and reached the maximum at point X. At this time, the temperature of the processed PVC slightly increased to the nominate value. Usually, at point G and X, an increase in the temperature was observed. After point X, a slight decrease and stabilization of the torque was seen (point E), whereas the temperature between points X and E remained relatively constant [49].

The value of the minimum torque (point B) of processed PVC compound was related to the momentary equilibrium state between sliding of breaking PVC grain, and increasing degree of PVC gelation. It was expected that the degree of gelation increased with the rising temperature and shear rate. However, the processing of the compound in a Brabender measuring mixer, during time when the torque minimum was attained, was sufficient to accomplish partial gelation of the PVC. The gelation degree, for the PVC composition, was generally temperature and shearing rate dependent. Therefore, it should not be concluded that the gelation starts first after reaching the minimum of torque as explained by Tomaszewska and coworkers [49].

Point G in the plot was the transitory stage between the minimum and the maximum of torque and was visible as an inflection point on the torque curve. An increase of the torque value at point G suggested a significant transformation of the PVC morphology which was occur in the gelled polymeric material [50].

The maximum torque or fusion torque (M_X) is the torque which occurs at point X on the torque curve, whereas the time to reach point X is fusion time (abbreviated t_X) [51]. Chen and coworkers claimed that at this peak position, a material reaches an effectively void-free state and starts to melt at the interface between the compacted material and the hot metal surface [52]. The fusion percolation threshold is defined as the torque difference between B and X. Point X was found to have been caused by compaction and by the onset of fusion. On the contrary, an increase in the torque to its maximum value can be attributed to the gelation of both agglomerates and primary PVC particles [51]. Moreover, the real temperature corresponding to the torque at point X is designated as fusion temperature or the temperature of the full fusion of a PVC compound. In this work, the fusion temperature was about 190-195^{o}C.

The equilibrium state of torque (Point E) corresponds to the time when the melt becomes homogeneous. As a consequence, the equilibrium between the heat of the friction and the temperature of the chamber is achieved. An increase in the chamber temperature and shear rate typically leads to shorten time of reaching equilibrium and a decrease of torque value at point E [53].

The rise of the processing temperature leads to a reduction of the viscosity of the liquid, amorphous phase, and therefore the remaining grains may effortlessly translocate. As a result, a decrease in the friction may be observed, and M_X decreases with the temperature. This effect is confirmed by the lower resistance of the processed PVC compound against rotating blades. The lowering of the viscosity should be accompanied by an increase in the flow rate value. However, for samples processed to point X, a decrease in the flow rate value frequently observed, which is attributed to the progressive occurrence of PVC gelation. That is an intensive formation of a physical network of secondary crystallites probably dominates in this stage of the kneading [50].

5.1.1.2 Plastogram of PVC with Lead Stabilizer

Typical plastograms of PVC resin filled with lead stabilizer (PVC_{lead}) in this work exhibited a fusion time and maximum torque as depicted in Figure 5.1. From the figure, the maximum torque represented by point X (M_X) in the blue curve was found to be 31.3 Nm/min and the fusion time corresponded with M_X was 330 s.

5.1.1.3 Plastogram of PVC with Calcium Zinc Stabilizers

Brabender test results, i.e. plastograms at 180°C of the PVC resin filled with four types of the calcium zinc stabilizers (Ca/Zn) were plotted in Figures 5.2-5.5. In this work, 4 sample groups of the rigid PVCs filled with Ca/Zn, i.e. the PVC resin filled with Ca/Zn from Chemson Co., Ltd. (abbreviated PVC_{CZ} (PRD5549:Chem)), the rigid PVC filled with Ca/Zn from Sunace Co., Ltd. (abbreviated PVC_{CZ} (M78NP:Sunace) and PVC_{CZ} (M964NP:Sunace)), the PVC resin filled with Ca/Zn from Siam Stabilizer Co., Ltd. (abbreviated PVC_{CZ} (M162P:Siam)) were evaluated. In Figure 5.2, the maximum torque (M_X) and fusion time (t_X) of PVC_{CZ} (PRD5549:Chem) sample was approximately 32.1 Nm/min (point X in the blue curve) and 462 s, respectively, while those of the PVC_{CZ} (M78NP:Sunace) sample was about 31.3 Nm/min and 648 s, respectively, as displayed in Figure 5.3. Figure 5.4 showed the obtained plastogram of the PVC_{CZ} (M964NP:Sunace) sample. The M_X and t_X was found to be 33.5 Nm/min and 564 s, respectively, while those of the PVC_{CZ} (M162P:Siam) was about 43.3 Nm/min and 222 s, respectively, as showed in Figure 5.5.

As described above, it can be seen that the lowest fusion time of the PVC resin added with the Ca/Zn stabilizers was observed in the PVC_{CZ} (M162P:Siam) sample. Therefore, the PVC_{CZ} (M162P:Siam) sample tended to be easier to process when compared to the processing ability of the PVC_{CZ} (PRD5549:Chem), PVC_{CZ} (M78NP:Sunace) and PVC_{CZ} (M964NP: Sunace) samples. From the figure, the trend in increasing torque after 8 minutes in the rigid PVC filled with M162P stabilizer from Siam stabilizer Co., Ltd was noticed while this characteristic was not seen in the PVC_{CZ} (PRD5549:Chem), PVC_{CZ} (M78NP:Sunace), and PVC_{CZ} (M964NP:Sunace) samples. This behavior may correspond to the degradation of the sample i.e. the char formation. Therefore, from the experimental results, the Ca/Zn stabilizer, i.e. the PRD5549, from Chemson Co., Ltd was selected to be the most suitable Ca/Zn stabilizer for the rigid PVC in this study because of the obtained lower fusion time at the temperature of 180°C than that of others without showing a sign of thermal degradation as seen in the M612P/PVC system.

5.1.1.4 Plastogram of PVC with Organic Based Stabilizers

Brabender test results of PVC resin filled with organic based stabilizers (OBS) from Chemson Co., Ltd. (PVC_{OBS}:Chem) and from Sunace Co., Ltd (PVC_{OBS}:Sunace) were compared at a wall temperature of a mixing chamber of 180°C as seen in Figure 5.6 and Figure 5.7, respectively. In Figure 5.6, the maximum torque (M_X) and fusion time (t_X) of the PVC_{OBS}:Chem sample was reported to be 23.3 Nm/min (represented by point X in blue line in Figure 5.6) and 1144 s, respectively. While, in Figure 5.7, the PVC_{OBS}:Sunace sample showed the MX and tx to be 26.7 Nm/min and 586 s, respectively. As the results, the PVC resin filled with organic based stabilizer from Sunace Co., Ltd (PVC_{OBS}:Sunace showed a lower fusion time than that of the rigid PVC filled with organic based stabilizer from Chemson Co., Ltd (PVC_{OBS}:Chem). Consequently, the incorporation of an organic based stabilizer from Chemson Co., Ltd into the PVC resin could be processed more easily when compared to an addition of the organic based stabilizer from Sunace Co., Ltd due to the lower mixing torque at the same test condition (180°C).

Furthermore, the maximum torque and the fusion time values of the PVC resin filled with various heat stabilizers obtained from the plastograms in Figure 5.1 to Figure 5.7 were also summarized in Table 5.1. From the table, the PVC resin filled with each OBS stabilizers tended to exhibit lower fusion torque and longer fusion time than those of the PVC resin filled with lead stabilizer and with all types of calcium zinc stabilizers.

5.1.2 Effect of Commercial Lead, Calcium Zinc and Organic Based Stabilizers on Static Thermal Stability on PVC Resin

To test heat stabilizing effectiveness, static thermal stability (through oven testing) by an observation of the changed appearance of the samples at constant elevated temperatures as a function of time for rigid PVC samples with different heat stabilizers, i.e. commercial lead stabilizer (lead), commercial calcium/zinc stabilizers (Ca/Zn) and commercial organic based stabilizers (OBS) were investigated.

5.1.2.1 Effect of Lead Stabilizers on Static Thermal Stability of Rigid PVC

Static thermal stability result revealed by examining color change at 180°C as a function of time of the rigid PVC strips filled with commercial lead stabilizers, processing by two roll mills at 180°C for 3 min, is shown in Figure 5.8. It could be seen that the change in color of the rigid PVC strips. PVC stabilized with lead stabilizer could maintain original white color until 30 min and then gradual change in color from light yellow to brown in 30 – 160 min that showed relatively long term stability of commercial lead stabilizer.

5.1.2.2 Effect of Ca/Zn Stabilizers on Static Thermal Stability of Rigid PVC

Static thermal stability result revealed by examining color change at 180°C as a function of time of the rigid PVC strips filled with various types of commercial calcium zinc stabilizers, processing by two roll mills at 180°C for 3 min, is shown in Figure 5.9. It could be seen that the change in color of the rigid PVC strips filled with the Ca/Zn stabilizers, i.e. PVC_{CZ} (PRD5549:Chem), PVC_{CZ} (M78NP:Sunace), PVC_{CZ} (M964NP:Sunace) and PVC_{CZ} (M162P:Siam) were observed after holding in Mathis thermotester for 10 min. From the figure, the discoloration time of the PVC_{CZ} (M78NP:Sunace) strip is about 12 min and then the color drastically change from light yellow to brown. For the PVC_{CZ}

(PRD5549:Chem) strip, the discoloration time was about 7 min and then the color changes to light yellow. The discoloration time of the PVC_{CZ} (M964NP:Sunace) was about 6 min, then the color changes from light yellow to light brown, while that of the PVC_{CZ} (M162P:Siam) strip was only about 4 min. However, the color change of PVC_{CZ} (M162P:Siam) was from light brown to dark brown. Therefore, the PVC_{CZ} (M78NP:Sunace) sample showed the significantly greater static thermal stability when compared to the other PVC resin filled with Ca/Zn stabilizers.

In principle, PVC color change was primarily due to the formation of conjugated double bonds from polyene during thermal degradation of the polymer. The calcium and zinc stabilizers had been incorporated in PVC to stabilize or prolong its thermal integrity. Strongly basic carboxylates derived from calcium are an effective HCl scavenger whereas zinc exhibits stronger Lewis acid characteristics and could not only scavenge HCl but also could substitute carboxylate for the allylic chlorine atoms and thus terminates the growth of the polyene sequences [34].

5.1.2.3 Effect of Commercial Organic Based Stabilizers on Static Thermal Stability of Rigid PVC

Static thermal stability results via the change in color performed at 180°C as a function of time of PVC resin with various types of commercial organic based stabilizers, i.e. PVC_{OBS}:Chem and PVC_{OBS}:Sunace, processing by two roll mills at 190°C for 8 min, were shown in Figure 5.10. From the figure, It could be seen that the PVC_{OBS}:Sunace strip after holding in Mathis thermotester 10 min showed the discoloration time to be longer than that of PVC_{OBS}:Chem, i.e. 20 min for the PVC_{OBS}:Sunace and 8 min for PVC_{OBS}:Chem. In addition, after discoloration time of each PVC filled with both OBS stabilizer, the PVC_{OBS}:Sunace exhibited a change in the color from pale yellow to yellow at 48 min, while the change in the color of the PVC_{OBS}:Chem was from yellow to dark brown. As a consequence, the PVC_{OBS}:Sunace sample provides a better static thermal stability when compared to the PVC_{OBS}:Chem sample comparing at a fixed amount of the heat stabilizers of 3 phr.

Organic stabilizer has many key ingredients that can suppress degradation processes of PVC. For example, epoxidized compounds are reported to be able to accept HCl [34]. Uracil derivatives were reported to show greater stabilizing efficiency compared to traditional Ca/Zn stabilizers at the same concentration in PVC samples. This is attributed to the ability of these compounds to substitute the labile chlorine atoms in PVC molecules and can absorb HCl released during the degradation of the PVC sample [12].

5.1.3 Thermogravimetric Analysis (TGA) of Commercial Organic Stabilizers

TGA is an analytical technique used to determine a material's degradation behavior and its fraction of volatile components by monitoring the weight change that occurs as a function of increasing temperature at a constant heating rate or as a function of time.

5.1.3.1 Thermogravimetric Analysis of Commercial Organic Stabilizers in Nitrogen

Thermal degradation behavior of commercial organic stabilizers was presented in Figure 5.11 in nitrogen atmosphere. The line (■) in the plots is OBS from Sunace Co., Ltd whereas the line (▲) is OBS from Chemson Co., Ltd. The temperature at 5% weight loss was one parameter to determine thermal stability of the material. From the figure, we found that the temperatures at 5% weight loss of OBS from Sunace Co., Ltd and Chemson Co., Ltd were 80°C and 290°C, respectively. Moreover, the solid residue of OBS from Sunace Co., Ltd and Chemson Co., Ltd were 25% and 28%, respectively.

Furthermore, derivative TGA thermograms of the commercial OBS are shown in Figure 5.12. From the figure, we can see that OBS from Sunace Co., Ltd had an ingredient that exhibits mass loss at 80°C and the major component of this OBS shows mass loss at 460°C, while the major component of the OBS from Chemson Co., Ltd also provides sharp mass loss at about the same temperature, i.e. 460°C. Therefore, it is possible that the main component of both OBS might be similar.

5.1.3.2 Thermogravimetric Analysis of Commercial Organic Stabilizers in Oxygen

Thermal degradation behavior of commercial organic stabilizers is presented in Figure 5.13 in oxygen atmosphere. The line (■) in the plots is OBS from Sunace Co., Ltd whereas the line (▲) is OBS from Chemson Co., Ltd. From the figure, we found that the temperature at 5% weight loss of OBS from Sunace Co., Ltd and Chemson Co., Ltds was 80°C and 260°C, respectively, whereas the solid residue of OBS from Sunace Co., Ltd and Chemson Co., Ltd was 24% and 28%, respectively. This suggests the presence of inorganic filler in both commercial OBSs.

Furthermore, derivative TGA thermograms are shown in Figure 5.14. From the figure, the OBS from Sunace Co., Ltd showed the major ingredients to be vaporized or decomposed at 80°C, 320°C, 350°C, and 450°C, while the OBS from Chemson Co., Ltd displayed the mass loss temperature at 320°C, 350°C, and 450°C. It is likely that these OBSs comprise of mixtures of chemicals and fillers. However, we can observe that the main component was degraded at about the same temperature of 450°C. Therefore, it is possible that the main component might be similar but the Sunace’s OBS consists of smaller molecule as one key component in its formulation. The TGA results in oxygen are also consistent with those performed in nitrogen atmosphere.

5.2 Effect of DAU, Eugenol and DAU/Eugenol Mixture Stabilizers on Static Thermal Stability and Mechanical Property of Rigid PVC

In this section, the properties, i.e. static thermal stability and mechanical of the PVC stabilized with DAU, eugenol and their mixtures have been investigated. The optimal content and processing temperature of the stabilized PVC was considered via the static thermal stability.

5.2.1 Static Thermal Stability of PVC Stabilized with Eugenol

Static thermal stability results after holding in Mathis thermotester for 10 min of PVC resin with two contents of eugenol stabilizer, i.e. 2 and 4 phr, processing by two roll mills at 160°C for 3 min, performed at 180°C as a function of time are shown in Figure 5.15. As seen in the figure, an addition of the eugenol stabilizer at 2 and 4 phr into the PVC resin showed a similar color change pattern, i.e. from brown to dark brown in 25 min and then the samples turned to dark brown beyond that.

To improve the discoloration time of the PVC resin filled with a eugenol stabilizer, the incorporation of titanium dioxide (TiO_2) at 2 phr as a white pigment at different eugenol contents into the PVC resin was investigated as displayed in Figure 5.16. After the processing the $PVC_{eugenol}$ filled with TiO_2 by two roll mills at 160°C for 3 minutes, the color of the strip remained whiter when compared with that of the PVC strip without adding TiO_2 as similarly reported in PVC/lead/TiO_2 [54]. Moreover, the static thermal stability measured via the change in color of all $PVC_{eugenol}$ strips filled with 2 phr of the TiO_2 are exhibited in Figure 5.16. From the figure, we can see that the color change of all $PVC_{eugenol}$ filled with 2 phr of the TiO_2 pigment are negligible within the first 30 min and then the change in the color from white to light brown was observed. Therefore, the addition of the TiO_2 pigment can substantially help reduce the change in color of the $PVC_{eugenol}$.

5.2.2 Static Thermal Stability of PVC Stabilized with DAU

Static thermal stability results after holding in Mathis thermotester for 10 min of PVC resin stabilized with various DAU contents, i.e. 1, 2, 3 and 4 phr, processing by two roll mills at 170°C for 3 min, performed at 180°C as a function of time are shown in Figure 5.17. As seen in the figure, the addition the DAU at 1, 2, 3 and 4 phr into the PVC resin showed the similar color change, i.e. from original color to brown in 50 min.

The samples color turned brown to black with an addition of 1 phr of the DAU faster than 2, 3 and 4 phr of the DAU as seen in the figure. It was noted that the addition of DAU at 2-4 phr showed similar efficiency though better than the addition only of 1 phr. Therefore, the optimal content of the DAU in the PVC resin were suggested to be 2 phr. In addition, we can see that an incorporation of the DAU stabilizer into the PVC resulted in a better retardancy of the color change of the PVC than the PVC stabilized with the eugenol stabilizer.

Furthermore, the static thermal stability via the color change characteristic of the PVC stabilized with the DAU stabilizer, which was a single organic component, is compared to that of the PVC stabilized with the commercial one pack PVC stabilizers, i.e. lead, Ca/Zn and OBS at a fixed content of 3 phr which is the quantity recommended by the producers as seen in Appendix D. Therefore, in preparing our future PVC samples, all heat stabilizers used will be added at a fixed amount of 3 phr and the properties will be compared.

5.2.3 Tensile Properties of PVC Stabilized with DAU

PVC samples stabilized with various contents of DAU, i.e. 1, 2, 3 and 4 phr were processed by two-roll mills at temperatures of 170°C for 3 min to yield a homogeneous sample. The obtained samples was then preheated for 200s and then pressed into a thick sheet by a compression molder at 180°C and at a pressure of 150 bars for 30s. The compression-molded sheets were then cut into test pieces for tensile test.

Tensile stress versus tensile strain curves of the heat stabilized PVC samples are depicted in Figure 5.18. From the figure, tensile strength is the maximum tensile stress in the curve whereas tensile modulus of each sample was computed from the initial slope of the stress-strain curves before loss elasticity. Moreover, elongation at break is tensile strain when the sample brakes.

From the table, tensile strength of the PVC stabilized with DAU at various contents at 1, 2, 3 and 4 phr were about 51.3, 56.3, 56.0 and 55.6 MPa, respectively, and the tensile modulus of stabilized PVC samples were determined to be 1.42, 1.61, 1.65, and 1.64 GPa, respectively. The PVC stabilized with DAU at 1 phr showed the tensile strength values somewhat lower than that of the PVC stabilized with DAU at 2, 3 and 4 phr contents. The phenomenon confirmed the optimal amount of the DAU to be about 2 phr as already observed in the Mathis thermotesting in the previous section. In other words, to add only 1 phr of DAU in PVC is not sufficient to prevent its thermal degradation. As a consequence, partial degradation on the PVC sample was expected causing the observed lower mechanical properties.

5.2.4 Effect of Processing Temperatures for PVC Stabilized with DAU and Eugenol Stabilizers

5.2.4.1 Effect of Processing Temperatures from 150°C to 180°C on the color change of PVC Stabilized with DAU and Eugenol Stabilizers

PVC stabilized with DAU (PVC_{DAU}) and PVC stabilized with eugenol ($PVC_{eugenol}$) at a fixed stabilizer content of 3 phr was prepared and evaluated. Each PVC stabilized with DAU and eugenol was processed by two roll mills at 150°C, 160°C and 170°C for 3 min, respectively. Static thermal stability performed isothermally at 180°C as a function of time, conducted on a Mathis thermotester, of the above PVC samples is presented in Figure 5.19. As seen in the figure, the discoloration of the PVC_{DAU} samples processed at the temperature of 150°C, 160°C and 170°C for 3 min showed a similar color change pattern. That is all PVC_{DAU} samples changed their color from white to yellow within 50 min of the heat treatment and then the color of the samples changed from yellow to dark in 105 min. In a case of the $PVC_{eugenol}$ samples, we can see that the sample processed at the temperature of 160°C and 170°C showed greater color change than that processed at the temperature of 150°C, which maintained its brown color longer than the samples processed at higher temperatures. Though the color change of eugenol-stabilized PVC seems to be more severe than those stabilized with the DAU, its effect is considered to be substantial to the thermal stability of unstabilized PVC which cannot be processed to form any test specimen. From these results, it can be concluded that eugenol can clearly function as a heat stabilizer for the PVC though its effect on thermal stability of PVC in term of color change retardation is significantly lower than the DAU. Therefore, the processing conditions to prepare the PVC stabilized with DAU and eugenol stabilizers can be from 150°C for 3 min. Such low temperature of 150°C cannot be used to process PVC with lead, Ca/Zn as well as commercial OBS systems. This is one of the positive aspect of using DAU and eugenol as PVC heat stabilizer compared to the commercial ones i.e. the lower processing temperature.

5.2.4.2 Effects of Different Processing Temperature between 150°C and 180°C on Properties of PVC Stabilized with Eugenol and DAU

Effects of different processing temperature between 150°C and 180°C on properties of PVC stabilized with eugenol and DAU at a fixed content of 3 phr are summarized in Table 5.2. From the table, degrees of gelation of the PVC stabilized with DAU i.e. at processing temperature of 150°C and 180°C, were approximately 11.4 and 75.6% respectively. In case of PVC stabilized with eugenol i.e. at processing temperature of 150°C and 180°C, the degrees of gelation were approximately 22.4 and 89.8 % respectively. According to the results, degree gelation of PVC decreased when the processing temperature decreased because processing temperature significantly affected fusion behavior of PVC as discussed by Gilbert and Vyvoda that the decrease of processing temperature systematically lowered degree of gelation in PVC resin as the temperature used in lower than the melting temperature of the PVC crystallites [46].

However, the processing temperature between 150°C and 180°C was found to show negligible effect on flexural strength and flexural modulus of PVC stabilized with those stabilizers. These results indicated that degree of gelation i.e. between 10 to 20% and 70 to 90%, showed trivial effect on flexural properties of the PVC.

In addition, after processing, color change of PVC stabilized with eugenol was expectedly found to be lighter when processing temperature decreased from 180°C to 150°C. This is due to the lower rate of thermal degradation at low temperature. Whereas, color of PVC stabilized with DAU was about the same when processing temperature decreased from 180°C to 150°C. This is due to the fact that DAU is highly effective in maintaining the initial color of PVC even at high temperature of 180°C.

Lowering the temperature to 150°C was found to show almost the same effect of color change. This experiment suggests the benefit of using eugenol and uracil as both chemicals provide lower processing temperature compared to the other three commercial heat stabilizers thus more energy saving in PVC processing.

5.2.5 PVC Stabilized with DAU/Eugenol Mixtures

The mechanisms for eugenol as primary heat stabilizer and DAU as secondary heat stabilizer for PVC had been reported by Sabaa [4] and Xu [12], respectively. It was also suggested that the primary stabilizers, particularly, strong Lewis acids can react with HCl while the secondary stabilizers can scavenge the released HCl and help protect the primary stabilizers [33].

5.2.5.1 Static Thermal Stability of PVC Stabilized with Eugenol/DAU Stabilizer Mixtures at a Fixed Content 3 phr

The mechanisms for eugenol as primary heat stabilizer and DAU as secondary heat stabilizer for PVC had been reported by Sabaa [4] and Xu [12], respectively. It was also suggested that the primary stabilizers, particularly, strong Lewis acids can react with HCl while the secondary stabilizers can scavenge the released HCl and help protect the primary stabilizers [33]. The change in color as a function of time of PVC stabilized with eugenol/DAU mixtures at a fixed amount of 3 phr at various mixing ratios between eugenol and DAU processed by two roll mills at 150°C for 3 min was also conducted by Mathis thermotester at 180°C as seen in Figure 5.20. From the figure, the color of PVC stabilized with 3 phr of eugenol (3:0) changed immediately from white to light pink color and turned to be brown within 20 min whereas the PVC stabilized with 3 phr of DAU sample showed more gradual color change from white to yellow color and turned to brown in 50 min. Interestingly, it can be observed that the use of eugenol/DAU mixture can further enhance the color stability of the PVC. That is some sign of synergistic behavior of the use of eugenol/DAU mixture as heat stabilizers for

PVC was observed. Moreover, all PVC/(eugenol/DAU) samples with 1.0-2.0 phr of the DAU revealed no color changed in the thermotester for up to 50 min. This characteristic may be due to the complementary effect of eugenol as a primary heat stabilizers to inhibit polyene sequences formation of PVC while the DAU may function as a secondary heat stabilizer to retard the degradation process that eventually lead to PVC blackening thus the observed synergistic effect above.

In order to confirm synergistic effect on color change (i.e. thermal stability) of the specimen as a function of time of PVC stabilized with eugenol/DAU mixtures at a fixed amount of 3 phr and at various mixing ratios, the testing temperature of Mathis thermotester was reduced from 180°C to 150°C and the results are illustrated in Figure 5.21. The change in color of PVC with reduced temperature was evidently observed as a much prolonged time of the color change of the specimens, resulting from the lower rate of degradation at low temperature. From the figure, the color of PVC stabilized with 3 phr of eugenol (3:0) changed rapidly from white to light brown color and turned to brown within 70 min whereas the PVC stabilized with 3 phr of DAU sample showed more gradual color change from white to yellow color and turned to brown in 130 min. Interestingly, it can be observed that the use of eugenol/DAU mixture can further enhance the color stability of the PVC. That is a characteristic of synergistic behavior of the use of eugenol/DAU mixture as heat stabilizers for PVC. Moreover, all PVC/(eugenol/DAU) samples with 1.5-2.0 phr of the DAU revealed no color changed up to 150 min suggesting the best long term stability based on this mixed OBS systems.

5.2.5.2 Dynamic Mechanical Analysis of PVC Stabilized with Eugenol/DAU Stabilizer Mixtures at a Fixed Content of 3 phr

Dependence of storage modulus on temperature of PVC stabilized with Eugenol/DAU stabilizer mixtures is shown in Figure 5.22. According to the results, storage modulus at 30°C of the PVC stabilized with various ratios of Eugenol/DAU mixtures was similar with the value of about 3 GPa. However, storage modulus of PVC was different in the rubbery plateau region. That is rubbery plateau modulus of PVC was found to increase when quantity of eugenol in the mixture increased. This phenomenon is attributed to a function of eugenol to crosslink PVC molecules via its unsaturated bond or hydroxyl group as suggested by Sabaa and Mohamed [4].

The glass transition temperature (Tg) assigned to the maximum of tan δ of the PVC stabilized with Eugenol/DAU mixtures can be also determined from the plots of tan δ against temperature on dynamic mechanical analysis (DMA) curves as shown in Figure 5.23. The glass transition temperatures of PVC (DAU 3 phr), PVC (DAU 1.5 phr, eugenol 1.5 phr) and PVC (eugenol 3 phr) were determined to be approximately 89, 94 and 100°C respectively. Increasing DAU contents in the mixture can enhance glass transition temperature. In other words, eugenol can act as PVC plasticizer by reducing the Tg of PVC.

5.3 Properties of PVC Stabilized with Various Heat Stabilizers (at a Fixed Stabilizer Content of 3 phr)

Properties of PVC stabilized with various types of commercial heat stabilizers that are multi-component stabilizers or one pack stabilizers i.e. lead stabilizer (Sak-sf86-ns) from Sunace Co., Ltd., calcium zinc stabilizer (Ca/Zn) (PRD 5549-1) from Chemson Co., Ltd. and organic based stabilizer (OBS) (Sak-osp4005-np) from Sunace Co., Ltd., (OBS) are used in this experiment to compare with DAU and eugenol as heat stabilizers which are a single organic component. The content in each heat stabilizer is fixed at 3 phr which provides sufficient static thermal stability in the PVC samples. The effects of types of heat stabilizers will be compared based on their processing ability (fusion test), degradation temperature, color change and thermo mechanical properties.

5.3.1 Effects of Types of Heat Stabilizers on Fusion Behaviors of PVC Stabilized with Various Heat Stabilizers (at a Fixed Content 3 phr)

Processing ability measured by a fusion test of PVC stabilized with each heat stabilizer was investigated. Fusion time and maximum torque determined from point X in the fusion curve or plastogram indicating the complete fusion of the PVC stabilized with various heat stabilizers is summarized in Table 5.3. From the table, the PVC stabilized with commercial OBS stabilizers tended to exhibit lower fusion torque and longer fusion time than those of the PVC stabilized with lead stabilizer or calcium zinc stabilizers. In the case of, eugenol- and DAU-stabilized PVC, because they fused very fast during loading, the fusion time and maximum torque cannot be detected. This behavior indicated that eugenol and DAU stabilizers can more readily fused with PVC than lead or Ca/Zn or OBS stabilizers possibly due to polar nature of DAU and eugenol.

Additionally, relatively small organic molecules of DAU and eugenol tend to dissolve more readily in PVC thus resulting in the fast fusion behavior.

5.3.2 Thermogravimetric Analysis (TGA) of PVC Stabilized with Various Types of Heat Stabilizers

TGA is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a function of increasing temperature at a constant heating rate or as a function of time.

Thermal degradation behaviors of PVC stabilized with various heat stabilizers at a fixed content of 3 phr was examined using a thermogravimetric analyzer under nitrogen atmosphere at a heating rate of 10°C/min from room temperature to 800°C as depicted in Figure 5.24. Thermal decomposition temperature and char residual values of the samples are showed in the figure. A general two-stage process of the thermal decomposition of the PVC was observed. From the literature, the first stage thermal decomposition is mainly due to the evolution of HCl whereas the second stage thermal decomposition is attributed to the cyclization of conjugated polyene sequences to form aromatic compounds [55]. Therefore, as expected for our PVC, the neat PVC showed the two stages of the thermal decomposition temperature, i.e. ~240°C at 5% weight loss and ~400°C, respectively as seen in Figure 5.24.

The incorporation of heat stabilizers, i.e. commercial lead, Ca/Zn, OBS, DAU and eugenol (fixed at 3 phr for each type) in PVC was found to substantially enhance the thermal decomposition temperature of the PVC in the first stage ($T_{d,5}$), i.e. 278°C, 278°C, 263°C, 274°C, and 260°C, respectively comparing with the value of 241°C of the as-received PVC. As a consequence, all heat stabilizers evaluated in this work can effectively improve thermal degradation temperature at 5% weight loss of the neat PVC. Moreover, we can also see that the DAU stabilizer seems to improve $T_{d,5}$ of the

PVC comparable to lead and Ca/Zn stabilizers whereas an eugenol showed the nearest efficiency comparable to the commercial OBS.

Furthermore, the solid residues of the samples at 800°C are also indicated in the figure. We can see that inorganic stabilizers, i.e. commercial lead, Ca/Zn and OBS, can increase the solid residue of the PVC. The highest solid residue belonged to the PVC stabilized with Ca/Zn (i.e. 19.1%), whereas the organic stabilizers, i.e. DAU, eugenol as well as the commercial OBS tend to provide a negligible effect on the solid residue formation of the PVC. This is due to the thermally decomposable nature of the organic based stabilizers compared to their inorganic counterparts.

5.3.3 Static Thermal Stability of PVC Stabilized with Various Heat Stabilizers

Static thermal stability of PVC samples with different heat stabilizers, i.e. commercial lead stabilizer, commercial calcium/zinc stabilizer (Ca/Zn), commercial organic based stabilizer (OBS), DAU and eugenol was investigated by an observation of the changed appearance of the sample at 180°C as a function of time. It was observed that the addition of lead, Ca/Zn, OBS, DAU and eugenol in PVC showed the difference in the discoloration time as seen in Figure 5.25. PVC stabilized with DAU effectively retained its initial white color within 50 min of the heat treatment indicating the highest short-term thermal stability compared to others. However, color of the DAU-stabilized sample immediately changed to brown within 80 min whereas PVC stabilized with lead, Ca/Zn and OBS showed a more gradual change in color within the same period of time. This phenomenon suggested the better long-term stability of the lead, Ca/Zn, or the commercial OBS comparing with the more effective short term stability of the DAU system. This is because the DAU stabilizer acts as HCl scavenger [8] that can considerably reduce the rate of degradation and avoids the very fast process that eventually causes PVC blackening [26].

5.3.4 Dynamic Mechanical Analysis of PVC Stabilized with Various Types of Heat Stabilizers at a Fixed Content 3 phr

Dependence of storage modulus on temperature of PVC stabilized with various types of heat stabilizers are shown in Figure 5.26. According to the results, storage modulus at 30°C of the PVC stabilized with heat stabilizers i.e. lead stabilizer, calcium/zinc stabilizer, organic based stabilizer, DAU and eugenol were approximately 2.88, 2.75, 2.83, 2.99 and 2.98 GPa respectively. The higher storage modulus at room temperature of the PVC stabilized with DAU and eugenol stablilizers compared to the other suggesting that the PVC stabilized with DAU and eugenol are more rigid than the others. Moreover, it is likely that lead, Ca/Zn, or commercial OBS which are one pack heat stabilizers might contain additives that can lower modulus of the PVC such as external lubricant, internal lubricant etc. As heating continued, PVC stabilized with eugenol lost their rigidity at elevated temperature more readily than PVC stabilized with lead, Ca/Zn, OBS and DAU. This greater change in slope of the modulus curve indicated higher thermal sensitivity of the material.

The glass transition temperature (Tg) assigned to the maximum of tan δ of the PVC stabilized with the heat stabilizers i.e. lead stabilizer, calcium/zinc stabilizer, organic based stabilizer, DAU and eugenol can be also determined from the plots of tan δ against temperature from dynamic mechanical analysis curves (DMA) as shown in Figure 5.27. The glass transition temperatures of the PVC stabilized with heat stabilizers, i.e. lead stabilizer, calcium/zinc stabilizer, organic based stabilizer, DAU and eugenol were determined to be approximately 99.4, 98.7, 99.8, 99.6 and 88.8°C respectively. The Tg of PVC stabilized with eugenol are the lowest because of liquid nature of eugenol at room temperature whereas the other four types showed similar glass transition temperature values. The results suggested that the excessive use of liquid type heat stabilizer might not be appropriate as this will result in the lowering of thermal properties of the sample.

5.3.5 UL-94 Vertical Test of PVC Stabilized with Various Types of Heat Stabilizers at a Fixed Content 3 phr

The fire resistant properties of PVC stabilized with each heat stabilizer types were also examined by UL-94 vertical measurement. After burning, PVC showed clearly a self-extinguishing characteristic because it contains more than 50% of chlorine. Hydrogen chloride gas generating from thermal cracking slows down the continuous combustion reaction and prevents burning progress by warding off the PVC product surface from oxygen in the air [55]. All of our PVC samples were classified as V-0, the maximum flame resistant class of UL-94 vertical rating. Thus, each heat stabilizers of 3 phr used in this experiment show negligible effect on flame-retardant properties of our PVC. These result confirmed the good flame retarding nature of PVC. The photographs of the burnt specimens under UL94 burning tests are shown in Figure 5.28-5.32. The obtained UL-94 results of our PVC samples are also consistent with the commercial PVC pipe [see Appendix E.2].

5.4 Effects of Repeated Processing and Various Types of Heat stabilizers

In this section, 5 types of heat stabilizers are used same in 5,3. The contents in each heat stabilizers are 3 phr. Each processing cycles concluded 2 steps i.e. two-roll mills at temperatures of 180°C for 3 minutes to yield a homogeneous sample and then mold compressed at the same temperature and pressure of 150 bars for 4 minutes. For repeated processing, the piece was cut by cutting mill to reduce the size then sample was fed into 2 roll mill and further compression molded. Their efficiency of repeated processing and types of heat stabilizers will be compared based on the effects on physical properties (density, color change and FTIR), mechanical properties (tensile, flexural and izod impact) and thermal properties (DSC and HDT).

5.4.1 Effects of Repeated Processing on Density of PVC Stabilized with Various Types of Heat Stabilizers

Density of the PVC stabilized with various heat stabilizers at each processing cycle are plotted in Figure 5.33. From the table, in the case of the PVC stabilized with commercial lead, Ca/Zn and OBS, It could be seen that the repeated processing cycle (up to 4 cycles) showed negligible effect on the density values of the PVC samples, i.e. 1.457-1.460 g/cm^3, 1.449-1.452 g/cm^3 and 1.447-1.451 g/cm^3 respectively. In addition, the density values of PVC stabilized with DAU was in the range of 1.452-1.456 g/cm^3 whereas the density value of PVC stabilized with eugenol was measured to be 1.447 g/cm^3. The effects of types of heat stabilizers on density give only marginally different density values because only 3 phr of the heat stabilizer was used in each PVC specimen. The obtained density values of our PVC samples are also consistent with the density of typical PVC pipe i.e. ca. 1.43 g/cm^3 [see Appendix E.1].

5.4.2 Effects of Repeated Processing on Color Change of PVC Stabilized with Various Types of Heat Stabilizers

The effects of repeated processing on the visual appearance of the samples i.e. their color change, and their corresponding $\triangle$E values due to the color change are shown in Table 5.4 and Figure 5.34 respectively. Color change is important property because it relates to chemical degradation [4]. From our results as showed in Figure 5.34, it was observed that the addition of commercial lead, Ca/Zn, OBS, DAU and eugenol in our PVC provided different color change. For PVC stabilized with commercial lead, Ca/Zn, and OBS stabilizers, we can reprocess the samples up to at least 5 cycles. However, the PVC stabilized with DAU was found to be able to withstand the processing cycles up to 4 times. Whereas PVC stabilized with eugenol was able to undergo only one processing cycle. The color change values of the PVC stabilized with commercial lead, Ca/Zn, and OBS from first processing cycle up to 5 processing cycles were measured by a spectrophometer to be 26.7 to 45.1, 31.5 to 63.6 and 29 to 46.9, respectively. In the case of PVC stabilized with DAU, the values were changed from 20 to 29.2 at the third processing cycle. Finally, the color change of PVC stabilized with eugenol was found to show the highest color change value even at one processing cycle with the value of 73.3. From the above results, it is evident that is PVC stabilized with DAU effectively retained its initial light color up to 3 cycles which is also the lowest color change value as a result of repeated processing cycles indicating the highest thermal stability compared to the others whereas PVC stabilized with commercial lead, Ca/Zn and OBS showed a greater change in color within the same period of time i.e. up to 3 cycles. In practice, the ability for the PVC sample to sustain up to 3 repeated processing cycles should be sufficient for typical applications. Also it is to be reminded that the DAU and eugenol stabilizers used in our study are single organic component stabilizers while the other three commercial heat stabilizers are formulated multi-component, one-pack heat stabilizers. From the above results, it is clearly seen that DAU, even though a single component heat stabilizer, showed high potential as a heat stabilizer for PVC. Its effectiveness as a PVC heat stabilizer should be further enhanced with the aid of co-stabilizers, or synergists etc. In the case of eugenol, it was clearly proved to be a potential organic based heat stabilizer for PVC resin but to a much lesser extent comparing with DAU.

Considering long term heat stability of the PVC, it was also observed that PVC stabilized with commercial lead and OBS effectively retained their small color change up to 4 times of reprocessing cycles indicating the highest thermal stability in terms of long term thermal stability compared to their Ca/Zn counterpart which showed the highest slope as seen in Figure 26 below. It was postulated that zinc chloride that formed in a degradation process of the PVC stabilized with Ca/Zn stabilizer, that showed in equation (1) and (2), might play a part to catalyze PVC thermal degradation process and further dehydrochlorination of the PVC thus the lower long term stability compared to the commercial lead and OBS systems [9].

$$\mathrm{PVC + ZnSt_2 \longrightarrow PVCSt + ZnClSt + ZnCL_2} \qquad (1)$$

$$\mathrm{PVC \xrightarrow{\triangle} HCl \xrightarrow{ZnSt_2} ZnClSt + HSt} \qquad (2)$$

Yellow index values (YIs) of PVC stabilized with various stabilizers are depicted in Figure 5.35. Yellowness index represented the change in color of PVC samples in terms of white color to yellow color is measured by a spectrophotometer. The higher the YI, the yellower the sample and indicates more degradation. The YIs of the PVC stabilized with commercial lead, Ca/Zn, and OBS at the first processing cycle and at the 4th reprocessing cycles were measured to be 29.5 to 71.4, 41.7 to 115.2, and 33.5 to 72.3, respectively. In the case of the PVC stabilized with DAU, the YI value was changed from 24.3 for the first processing cycle to 40.2 for the 4th processing cycle. Finally, the YI value of the PVC stabilized with eugenol even at the first processing cycle, i.e. 87.3 was found to show a higher YI value than the commercial lead and OBS at fifth processing cycle, i.e. 71.4 and 72.3, respectively suggesting the most sensitive to heat of this PVC system. Furthermore, Yellow index graph as a function of number of repeated processing cycles of the PVC stabilized with commercial lead, Ca/Zn, OBS, DAU and eugenol at 3 phr content are depicted in the figure. From the figure, we can see that trend of the yellow index of all PVC samples is relatively similar to that of the color change behavior.

5.4.3 Effects of Repeated Processing Cycles on FTIR Spectra of PVC Stabilized with Various Types of Heat Stabilizers

In this research, FTIR spectra of PVC sample stabilized with lead, calcium zinc and commercial OBS stabilizer after 1, 3 and 5 rounds of processing cycles are displayed in Figure 5.36-5.38, whereas PVC sample stabilized with DAU at 1 to 3 of processing cycles are displayed in Figure 5.39. The FTIR spectra of PVC stabilized with each type of heat stabilizer was found to be similar as a function of various processing cycles. However, PVC stabilized with calcium zinc stabilizer displayed more color change than the other three heat stabilizers thus it is the best choice for observing spectral change with FTIR investigation. From Figure 5.37, PVC stabilized with calcium zinc stabilizer from first processing cycle to 5th processing cycles showed also the same FTIR spectrum. This phenomenon suggested the effect of processing cycles up to 5 cycles provided negligible thermal degradation to the PVC stabilized with commercial heat stabilizer and up to about 3 cycles of the PVC stabilized with DAU. The result confirms the potential use of DAU as a good candidate for PVC heat stabilizer.

5.4.4 Effects of Repeated Processing on Tensile Property of PVC Stabilized with Various Types of Heat Stabilizers

Tensile strength is the maximum tensile stress in stress-strain curve and quantifies how much stress of the material will endure before failure. Higher tensile strength values indicate polymer more durability. Figure 5.40 depicts the tensile strength at each repeated processing cycles of the PVC stabilized with various heat stabilizers, i.e. commercial lead, commercial Ca/Zn, commercial OBS, DAU and eugenol. Furthermore, the numerical results of the tensile strength of the PVC stabilized with various heat stabilizers at each repeated processing cycles are also plotted in the figure. In the figure, in the case of the PVC stabilized with commercial lead, Ca/Zn and OBS, we can see that the each processing cycle up to 5 cycles showed negligible effect on the tensile strength values, i.e. 51.2-52.9 MPa, 51.9-52.3 MPa and 51.3-52.9 MPa. For the PVC stabilized with DAU and eugenol, again, no significant difference in the tensile strength value at the each processing cycle up to 3 times was observed. From the table, the tensile strength values of the PVC stabilized with DAU was in the range of 55.2-56.5 MPa. We observed tensile strength of PVC stabilized with DAU and eugenol were higher than the PVC stabilized with commercial lead, Ca/Zn and OBS. This characteristic might be due to the relatively better compatibility of eugenol and DAU heat stabilizers with PVC upon mixing compared with the heterogeneous nature of the lead, Ca/Zn and OBS stabilized with PVC. Interesting, the tensile strength values of the PVC stabilized with each heat stabilizer are in agreement with that of PVC pipes from Thai Pipe Industry Co., Ltd. (Thailand) , i.e. tensile strength = 49.1- 53.4 MPa [see Appendix E.1].

Furthermore, comparing at the 1st processing cycle, we can see that the tensile strength of the PVC stabilized with the commercial lead and OBS provided slightly lower values than those of the other heat stabilizers. This is probably due to the lower gelation of the PVC stabilized with commercial lead and commercial OBS compared with the PVC stabilized with commercial Ca/Zn, DAU and eugenol. Moreover, these results confirm that the PVC stabilized with commercial lead, Ca/Zn and OBS can potentially be recycled or reprocessed for at least up to 5 cycles while the recycling ability of the PVC stabilized with DAU was up to 3 cycles.

Tensile modulus of PVC with different types of heat stabilizers at repeated processing cycles was shown in Figure 5.41. Tensile modulus of each specimen was determined from the initial slope of the stress-strain curves before loss elasticity. No significant difference in tensile modulus of PVC with commercial lead, Ca/Zn, and OBS was observed similar to the results from tensile strength.

5.4.5 Effects of Repeated Processing on Flexural Property of PVC Stabilized with Various Types of Heat Stabilizers

Flexural strength defined as a material's ability to resist deformation under flexure load of PVC stabilized with various heat stabilizers, i.e. commercial lead, commercial Ca/Zn, commercial OBS, DAU and eugenol as a function of reprocessing cycles is plotted in Figure 5.42 and the numerical data of the flexural strength of the stabilized PVC is listed in Table 12. From the table, the flexural strength of our PVC stabilized with commercial lead, Ca/Zn and OBS was about 75.3-77.6 MPa, 77.6-79.5 MPa and 75.4-79.5 MPa, respectively. From these results, we can see that the PVC stabilized with commercial lead, Ca/Zn and OBS stabilizers can still maintain the flexural strength for the repeated processing tests up to 4 cycles. Furthermore, in case the PVC stabilized with DAU and eugenol organic stabilizers, the flexural strength values of the PVC stabilized with DAU subjected to 1 to 3 processing cycles were in the range of 78.3-80.5MPa, while that of the PVC stabilized with eugenol stabilizer that can be processed with only 1 processing cycle was about 82.5 MPa. Therefore, we can observe that the number of reprocessing cycles up to 5 cycles of the three commercial heat stabilizers showed negligible effect on the flexural strength of the stabilized PVC.

For DAU, and eugenol, the mechanical integrity was observed at up to 3 cycles and 1 cycle, respectively. Interestingly, the flexural strength values of the PVC stabilized with each heat stabilizer are in agreement with that of PVC pipes from Thai Pipe Industry Co., Ltd. (Thailand) , i.e. flexural strength = 78.5-98.1 MPa [see Property Table in Appendix E.1, E.2].

In addition, flexural modulus determined from the initial slope of the stress-strain curves before loss elasticity for the PVC with different types of heat stabilizers i.e. commercial lead, commercial Ca/Zn, commercial OBS, DAU and eugenol at repeated processing cycles in flexure mode is depicted in Figure 5.43 and the numerical flexural modulus values of each stabilized PVC at each repeated processing cycle are listed in Table 13, From the table, flexural modulus of each stabilized PVC sample at each repeated processing cycle was similar, i.e, 2.33-2.39 GPa, 2.43-2.51 GPa, 2.31-2.47 GPa, 2.42-2.46 GPa and 2.46 GPa for the PVC stabilized with commercial lead, commercial Ca/Zn, commercial OBS, DAU and eugenol, respectively. Therefore, the repeated processing cycles showed negligible effect on the flexural modulus of the PVC stabilized with each heat stabilizers, i.e. 4 cycles for commercial lead, Ca/Zn and OBS heat stabilizers; 2 cycles for DAU stabilizer and one cycle for eugenol stabilizer. The flexural modulus values in our PVC samples are also in good agreement with the value of 2.48 GPa (360,000 psi) for PVC pipe produced by Georg Fisher Co., as seen in Appendix E.2.

5.4.6 Effects of Repeated Processing on Izod Impact Property of PVC Stabilized with Various Types of Heat Stabilizers

Izod impact tests are used in studying the toughness and ability of impact resistance of the polymer materials that are factors of their ability to absorb energy during plastic deformation [56]. Impact strength values of the PVC stabilized with various types of heat stabilizers as a function of number of processing cycles are showed in Figure 5.44. From the figure, the impact strength values of the PVC stabilized with commercial heat stabilizers, i.e. lead, Ca/Zn and OBS reprocessed up to 5 cycles were in the range of 102.7-104.8 J/m, 103.8-106.3 J/m and 103.8-108.9 J/m, respectively while the impact strength values of the PVC stabilized with DAU for 3 processing cycles was calculated to be about 89.4-91.3 J/m while the impact strength value of the PVC stabilized with eugenol was found to be 91.5 J/m.

In addition, impact strength values of PVC stabilized with DAU and eugenol were determined to be lower than the three commercial heat stabilizers. This might be due to the fact that the commercial lead, Ca/Zn and OBS heat stabilizers are one-pack stabilizers or multi-component stabilizers while the DAU and eugenol heat stabilizers are a single organic component additive. The one pack systems might contain some additives that help improve energy absorption characteristics of the PVC. However, the impact strengths of PVC stabilized with both DAU and eugenol are in the range comparable to the impact strength values required for the rigid PVC as seen in Appendix E2.

5.4.7 Effects of Repeated Processing on Gelation of PVC Stabilized with Various Types of Heat Stabilizers

For our PVC stabilized with 5 different heat stabilizers, the gelation observed in DSC thermograms is shown in Figure 5.45. In this thermogram, the characteristic line of PVC stabilized with each heat stabilizer showed only minor differences i.e. $PVC_{lead,}$ and PVC_{OBS} had small additive peaks at 113^{o}C and 116°C respectively, also, the first transition of $PVC_{eugenol}$ was found to be lower than the others. That is the T_g value of PVC stabilized with eugenol is about 82°C which is lower than the T_g values of PVC stabilized with other stabilizers that possessed T_g values of approximately 90°C. The lowest T_g of PVC stabilized with eugenol was also confirmed by dynamic mechanical analysis. Additionally, percent of degree of gelation (G) of the PVC stabilized with each heat stabilizer can be calculated using the following equation [57]:

$$G = \frac{H_A}{H_A + H_B} \times 100\% \tag{3}$$

Where H_A = Net area A under the curve after subtracting any area under the curve due to additive peaks (J/g),

H_B = Net area B under the curve (J/g)

G = Percent of degree of gelation (%)

For example, percent of degree of gelation (G) of $\mathrm{PVC}_{\mathrm{lead}}$ at the first processing cycle can be determined as follow:

$$G = \frac{3.4203\ J/g}{3.4203\ J/g + 1.9257\ J/g} \times 100 \sim 64.0\ \%$$

The percent of degree of gelation of PVC stabilized with lead, CaZn, OBS, DAU and eugenol was calculated to be 64.0, 70.2, 59.0, 72.4 and 89.8 % respectively. Types of heat stabilizers therefore showed significant effects on the degree of gelation of the starting PVC. This characteristic may depend on additive formulations in each heat stabilizer that results in different ease of processing or other necessary properties of the PVC. From the experimental data, the highest degree of gelation belongs to the PVC stabilized with eugenol stabilizer, while the PVC stabilized with DAU stabilizer shows the lowest degree of gelation. Therefore, in this section, we can see another benefit of eugenol stabilizer as the processing aid additive to promote gelation in PVC besides its potential function as PVC co-stabilizer with DAU system as mentioned in Section 5.2.5.1. In addition, the processing temperatures of all stabilized PVC samples are in a range of 183-188°C from the observation in inflection point or the point between areas A and B in the DSC thermograms. The slightly greater processing temperature beyond the set point temperature of 180°C obtained from these DSC thermograms might be due to the additional heating by shear force during the PVC processing.

DSC thermograms of PVC stabilized with commercial lead, CaZn, OBS and DAU at each number of processing cycles are also displayed in Figure 5.46-5.49 respectively. It was observed that the PVC stabilized with each stabilizer in first to fifth processing cycles showed similar trends. All the gelation behaviors examined from the calculated degree of gelations are summarized in Figure 50. From the results, we can see that degree of gelation of the PVC stabilized with commercial lead, Ca/Zn, OBS and DAU tended to increase with increasing the repeated processing cycles. This is because increase of the number of the repeated processing cycles (up to 5 cycles in our case) results in the smaller grains (crystallites), remaining after each repeated processing cycle being molten. Finally, the glass transition temperature of all PVC samples were found to be unaffected by the repeating processing, thus the constant Tg was obtained as a function of processing cycles.

5.4.8 Effects of Repeated Processing on Heat Distortion Temperature of PVC Stabilized with Various Types of Heat Stabilizers

Heat distortion temperature was defined as the temperature at which a standard test bar deflected a specified distance under the load applied at its center to give maximum stresses. It was used to determine short-term heat resistance. It distinguished between materials that were able to sustain light loads at high temperatures and those that lose their rigidity over a narrow temperature range. The effects of repeated processing cycles of PVC samples on the heat distortion temperature (HDT) are shown in Figure 5.51 and the corresponding numerical values are listed in Table 16. From the results, PVC stabilized with commercial lead, Ca/Zn OBS, and DAU showed the HDT values to be about 74-76°C which is significantly higher than that of the PVC stabilized with eugenol stabilizers i.e. 65°C. This characteristic might be due to liquid nature of eugenol used that might act as PVC plasticizer thus decreases glass transition temperature (T_g) of the PVC. The trend was confirmed by dynamic mechanical analysis. Moreover, the obtained HDT values of PVC stabilized with commercial stabilizers were relatively constant in each repeated processing cycles up to 4 cycles. In case of PVC stabilized with DAU relatively constant in each repeated processing cycle up to 2 cycles. However, PVC stabilized with eugenol cannot be reprocessed therefore no result on this sample was reported at higher processing cycle.

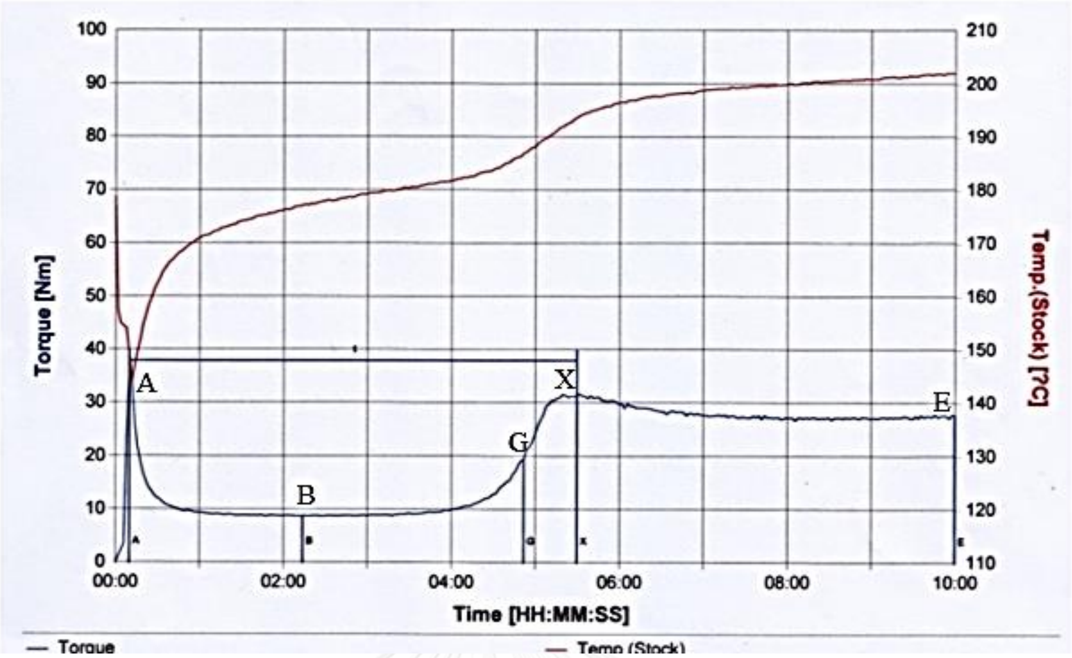


Figure 5.1: Torque rheometer process curves of PVC_{lead} at 180°C

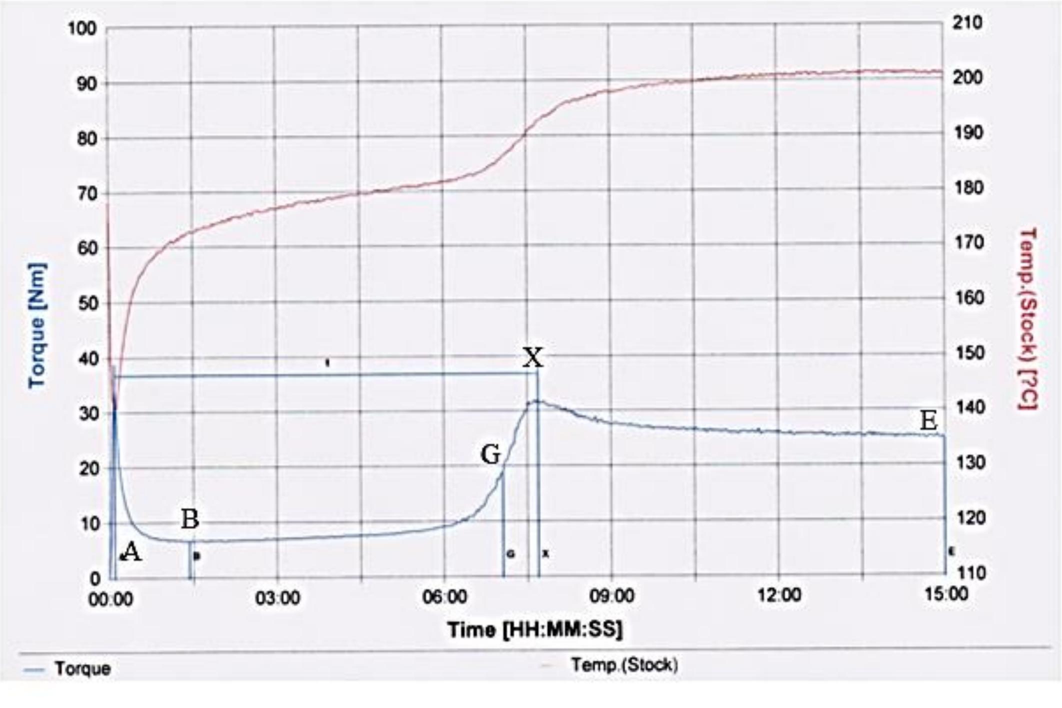


Figure 5.2: Torque rheometer process curves of $PVC_{Ca/Zn}$ (PRD5549:Chem).

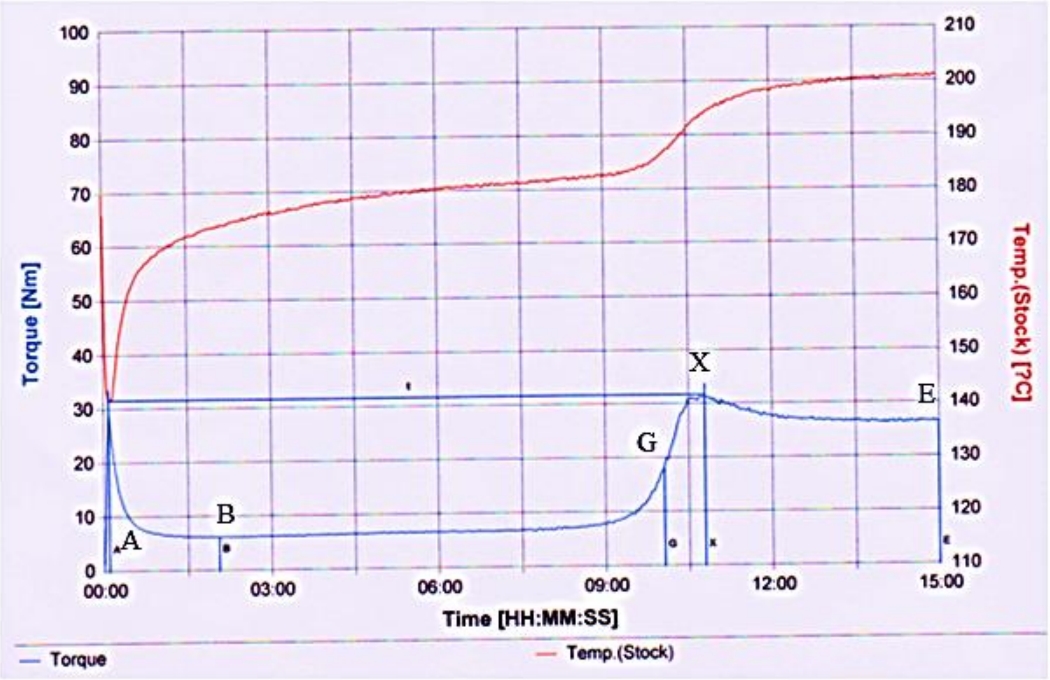


Figure 5.3: Torque rheometer process curves of $PVC_{Ca/Zn}$ (M78NP:Sunace).

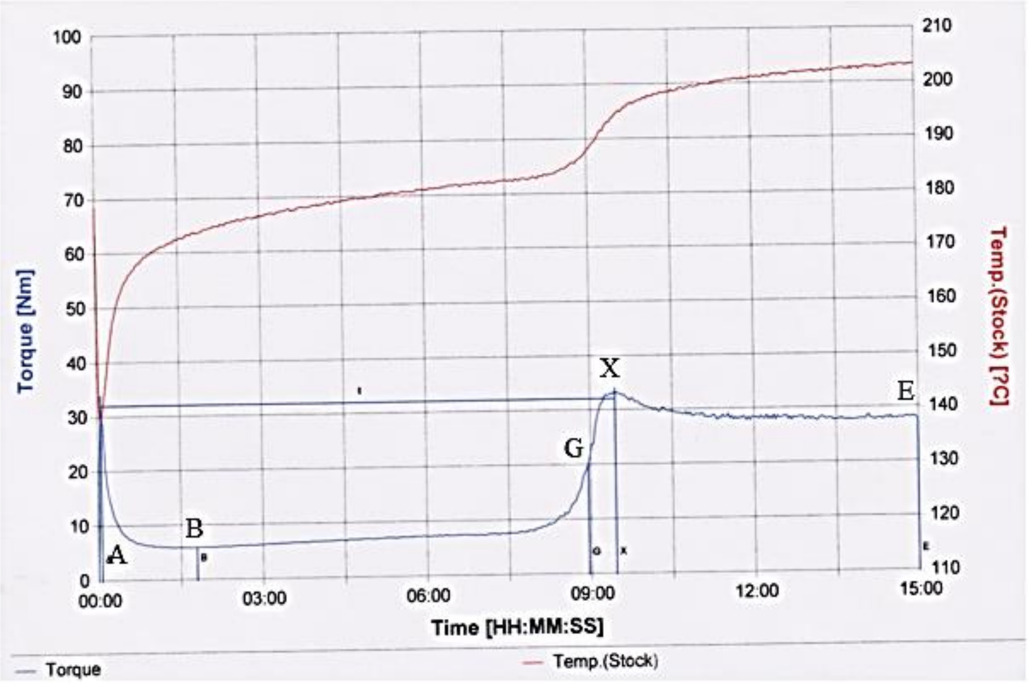


Figure 5.4: Torque rheometer process curves of $PVC_{Ca/Zn}$ (M964NP:Sunace).

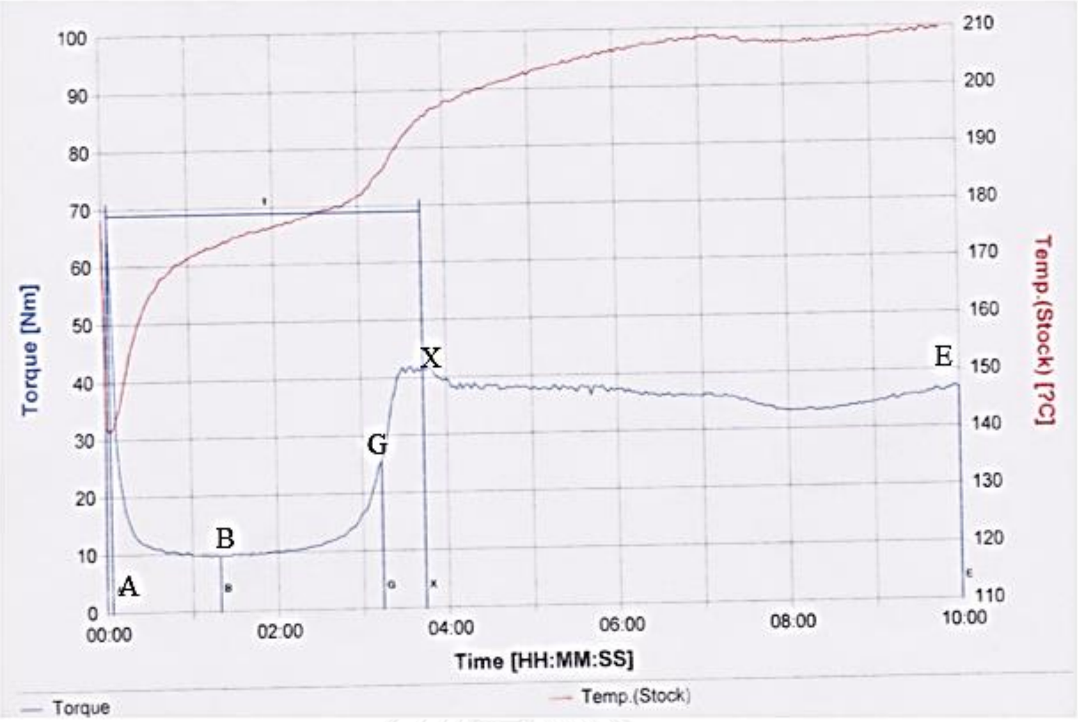


Figure 5.5: Torque rheometer process curves of $PVC_{Ca/Zn}$ (M162P:Siam).

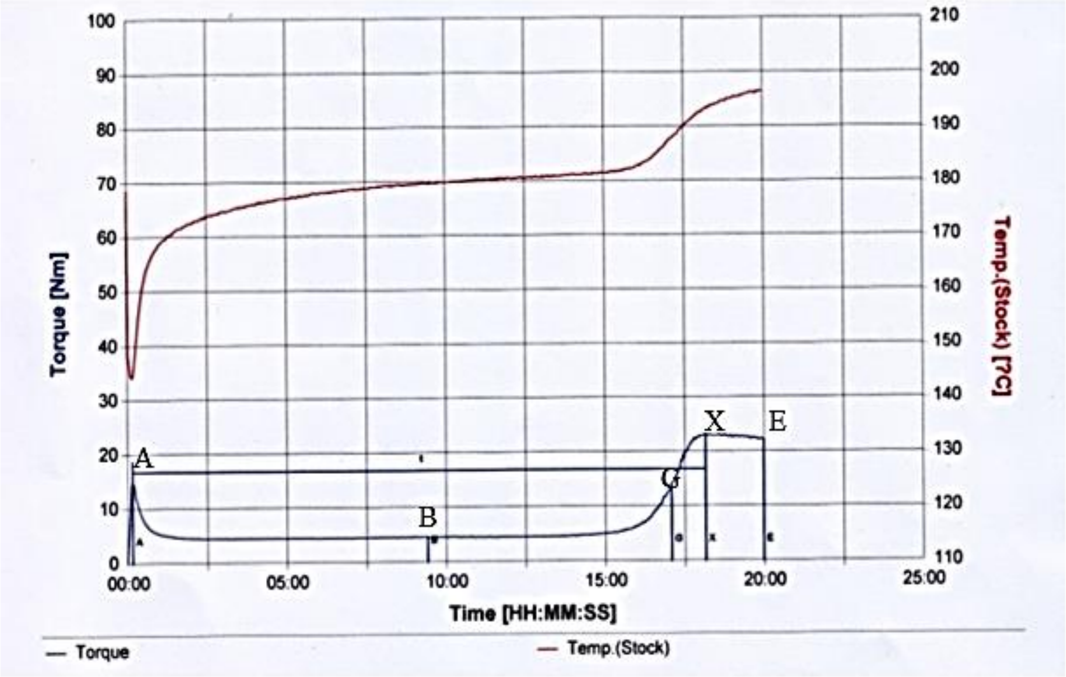


Figure 5.6: Torque rheometer process curves of PVC with OBS from Chemson.

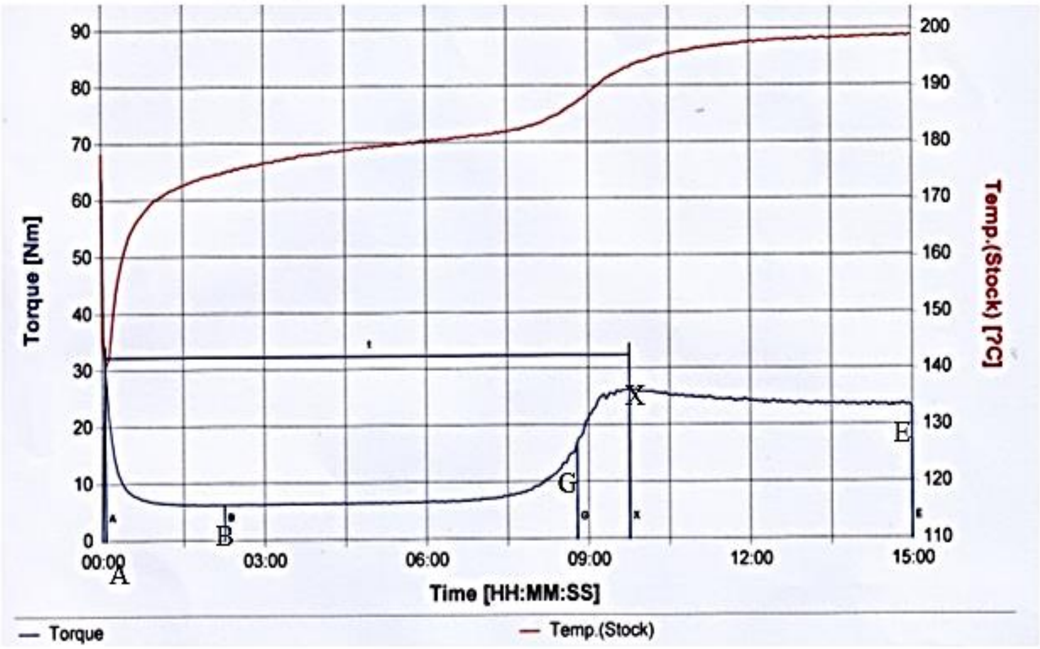


Figure 5.7: Torque rheometer process curves of PVC with OBS from Sunace.

Table 5.1: Effects of types of heat stabilizers on major parameters in the plastograms of PVC.

Samples	Stabilizer type in PVC resin	Maximum torque (Nm/min)	Fusion time (s)
1	Lead (SF86NS) from Sunace Co , Ltd.	31.3	330
2	Ca/Zn (PRD5549) from Chemson Co., Ltd.	32.1	462
3	Ca/Zn (M78NP) from Sunace Co , Ltd.	31.3	648
4	Ca/Zn (M964NP) from Sunace Co., Ltd.	33.5	564
5	Ca/Zn (M162P) from Siam stabilizer Co., Ltd.	43.3	222
6	OBS (TRX722A4) from Chemson Co., Ltd.	23.3	1144
7	OBS (OSP4005NP) from Sunace Co., Ltd	26.7	586

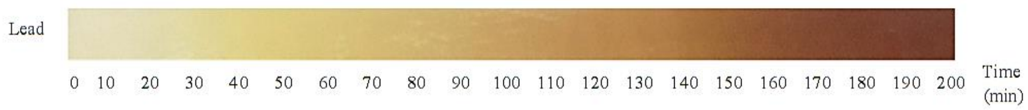


Figure 5.8: Color change of PVC resin using commercial lead stabilizers (3 phr) at 180°C in air (Strips were automatically moved out of the box at 5 mm/min).

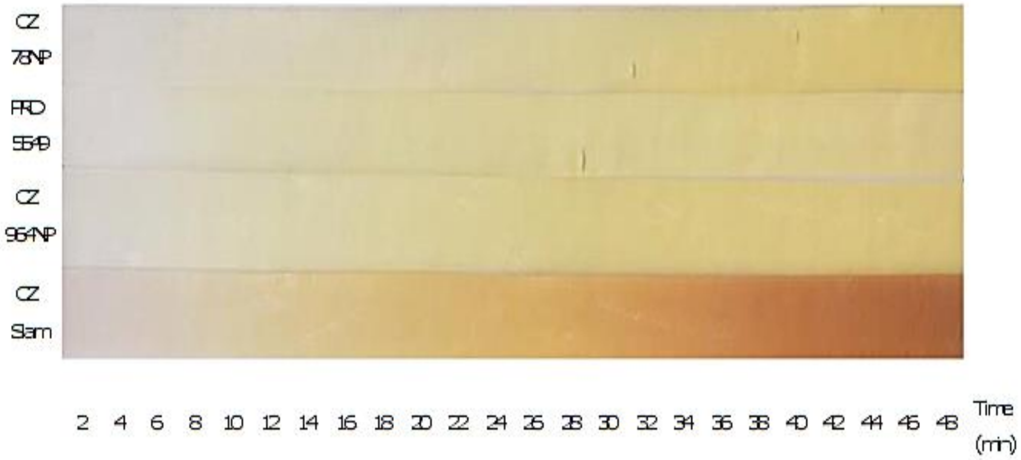


Figure 5.9: Color change of PVC resin using commercial Ca/Zn stabilizers (3 phr) at 180°C in air (Strips were automatically moved out of the box at 5 mm/min).

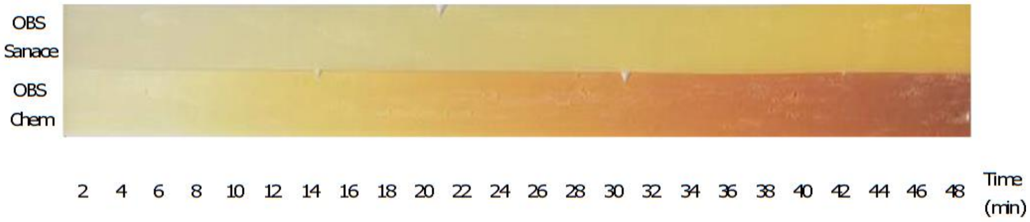


Figure 5.10: Color change of PVC resin using commercial OBS stabilizers (3 phr) at 180°C in air (Strips were automaticallymoved out of the box at 5 mm/min).

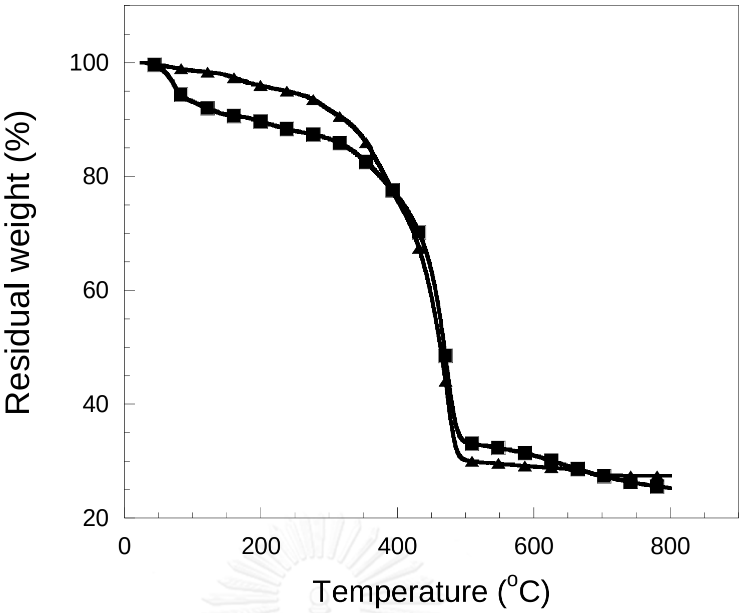


Figure 5.11: TGA thermograms of commercial organic stabilizers in nitrogen atmosphere: Sunace OBS (■), Chemson OBS (▲).

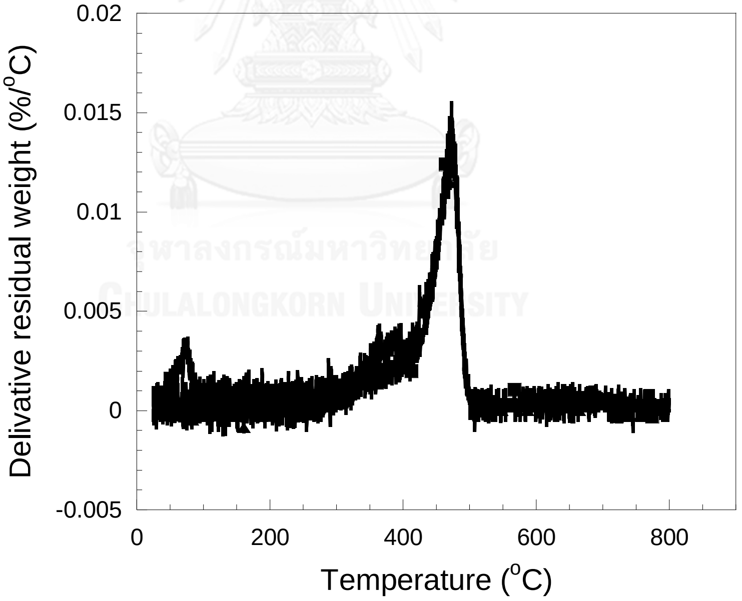


Figure 5.12: Derivative TGA thermograms of commercial organic stabilizers in nitrogen atmosphere: Sunace OBS (■), Chemson OBS (▲).

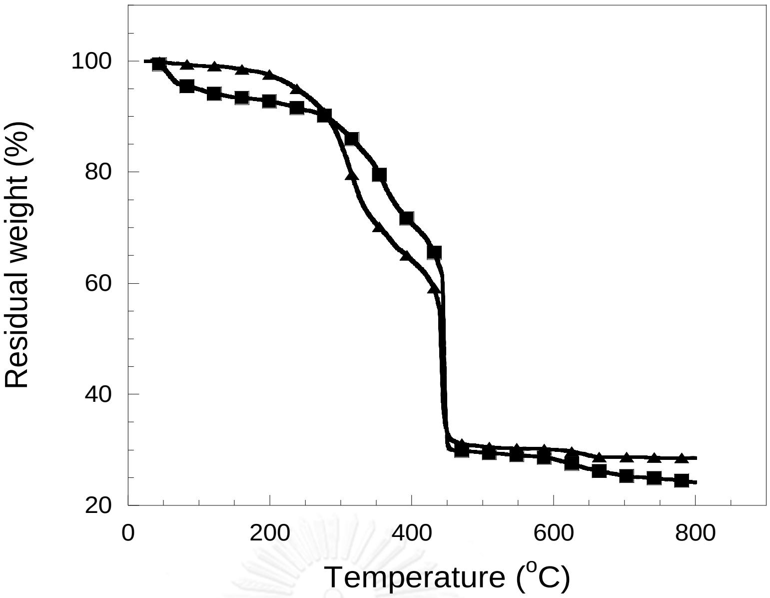


Figure 5.13: TGA thermograms of commercial organic based stabilizers in oxygen atmosphere: Sunace OBS (■), Chemson OBS (▲).

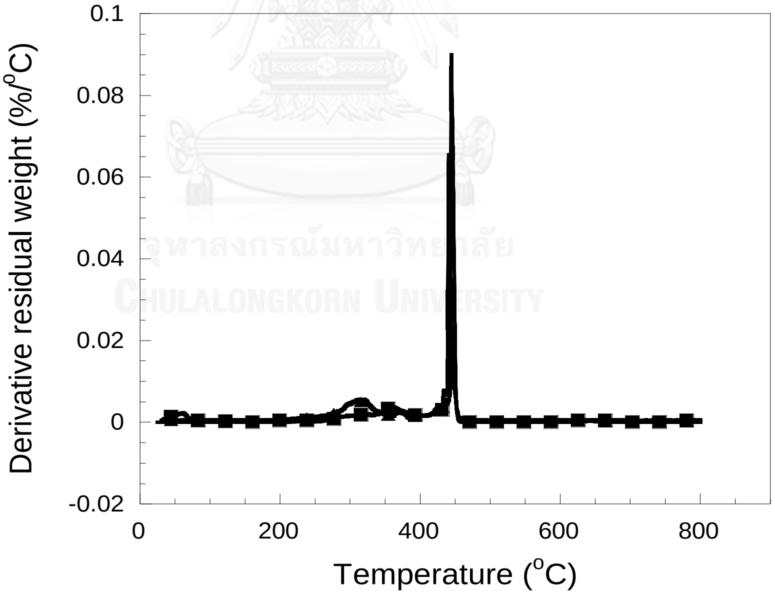


Figure 5.14: Derivative TGA thermograms of commercial organic based stabilizers in oxygen atmosphere: Sunace OBS (■), Chemson OBS (▲).

Figure 5.15: Color change of PVC resin using a eugenol as a stabilizer at 180°C in air (Strips were automatically moved out of the heating chamber at 1 mm/min).

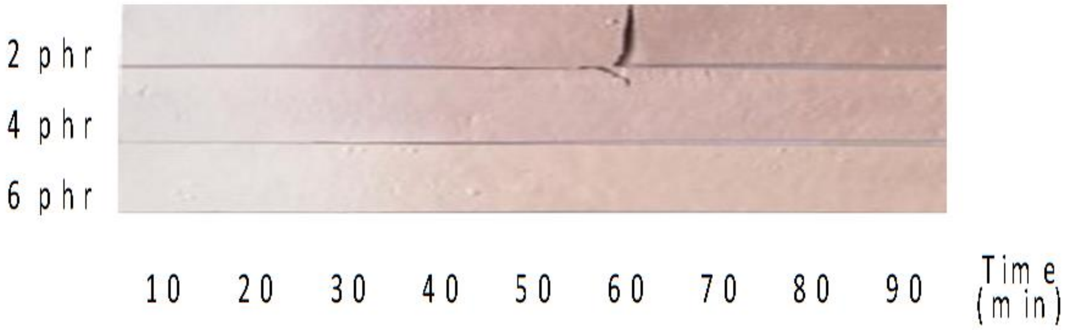


Figure 5.16: Color change of PVC resin with titanium dioxide (2 phr) and various eugenol contents as stabilizer at 180°C in air (Strips were automatically moved out of the heating chamber at 1 mm/min).

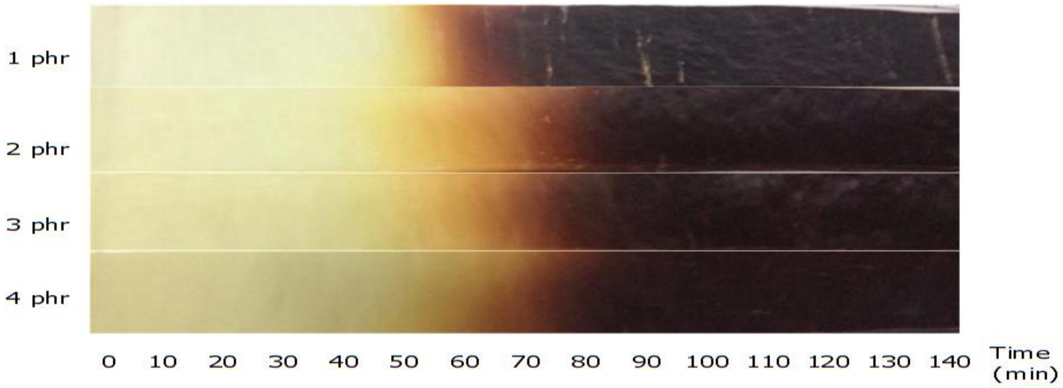


Figure 5.17: Color change of PVC stabilized with various DAU contents (1-4 phr) at 180°C in air (Strips were automatically moved out of the heating chamber at 1 mm/min).

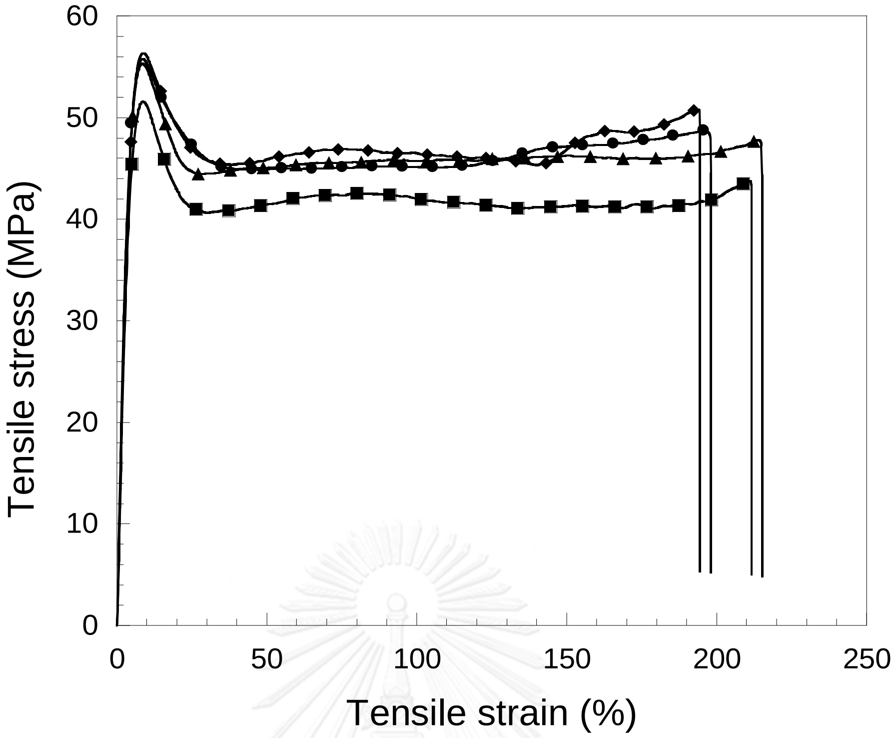


Figure 5.18: Tensile stress-strain curves of PVC stabilized with various DAU contents: 1 phr (■), 2 phr (◆), 3 phr (●) and 4 phr (▲).

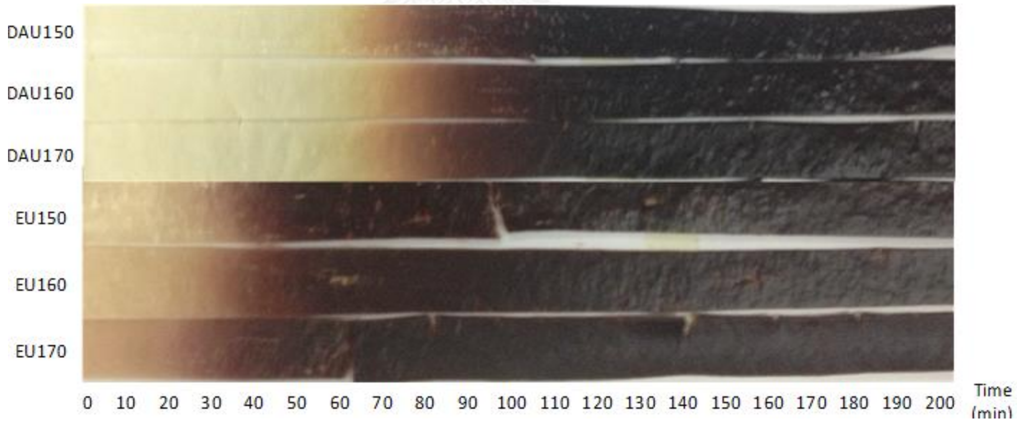


Figure 5.19: Color change of PVC resin mixed with 3 phr of eugenol and 3 phr of DAU as a stabilizer with various processing temperature at 150, 160 and 170°C under air atmosphere (Strips were automatically moved out of the box at 1 mm/min).

Table 5.2: Various properties of PVC stabilized with DAU and eugenol at processing temperature of 150°C and 180°C

Sample name	%gelation	Flexural strength (MPa)	Flexural modulus (GPa)	YI	ΔE
PVCeugenol 150°C	22.4	82.3±0.6	2.45±0.12	82.9±1.3	49.42±0.8
PVCeugenol 180°C	89.8	82.5±0.5	2.46±0.18	87.3±1.0	73.3±2.3
PVCDAU150°C	11.4	79.4±0.8	2.43±0.25	24.5±0.6	20.1±0.4
PVCDAU180°C	75.6	80.5±1.4	2.44±0.19	24.3±0.4	20.0±0.3

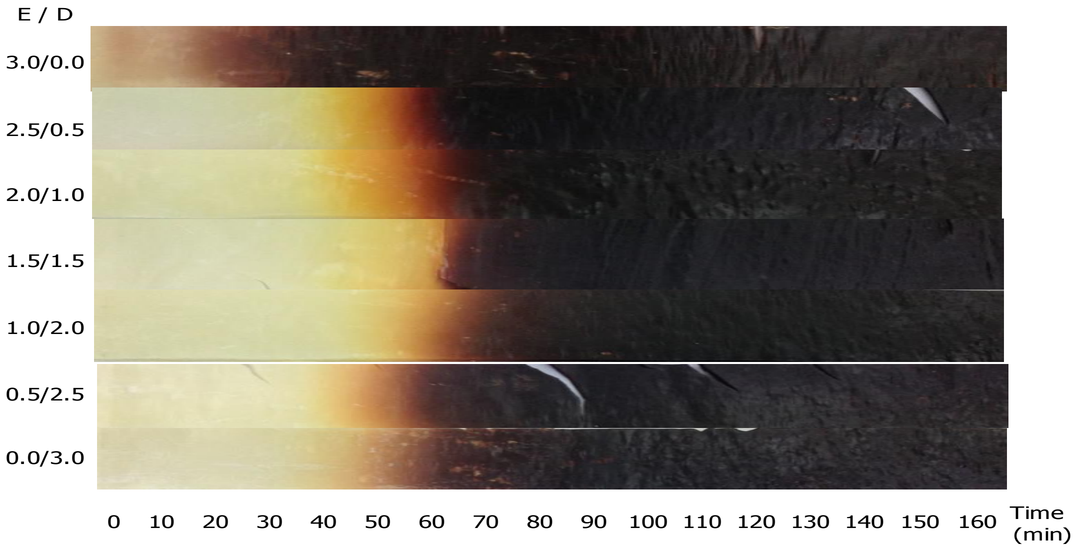


Figure 5.20: Color change of the PVC stabilized with eugenol/DAU mixtures at various DAU contents. (Strips were automatically moved out of the box at 1 mm/min at 180°C under air atmosphere). Noted: E/D is eugenol/DAU content.

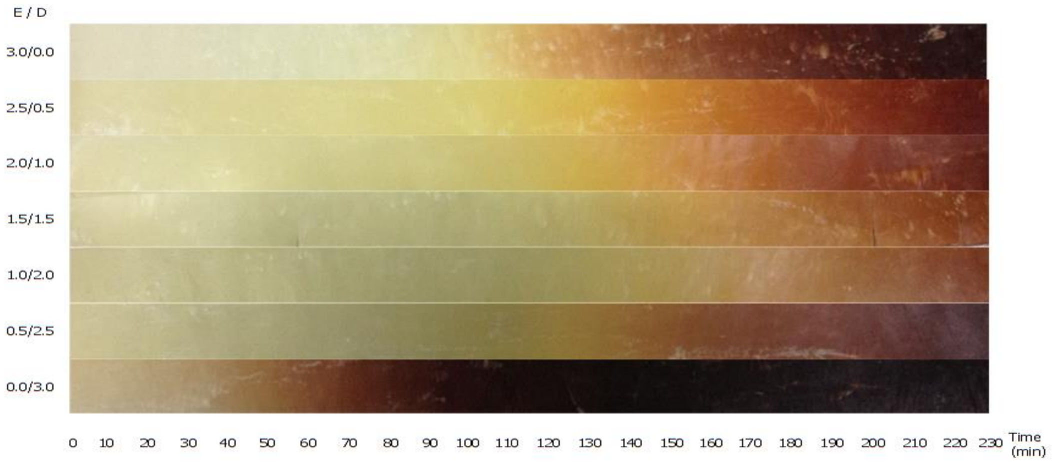


Figure 5.21: Color change of the PVC stabilized with eugenol/DAU mixtures at various DAU contents. (Strips were automatically moved out of the box at 1 mm/min at 150°C under air atmosphere). Noted: E/D is eugenol/DAU content.

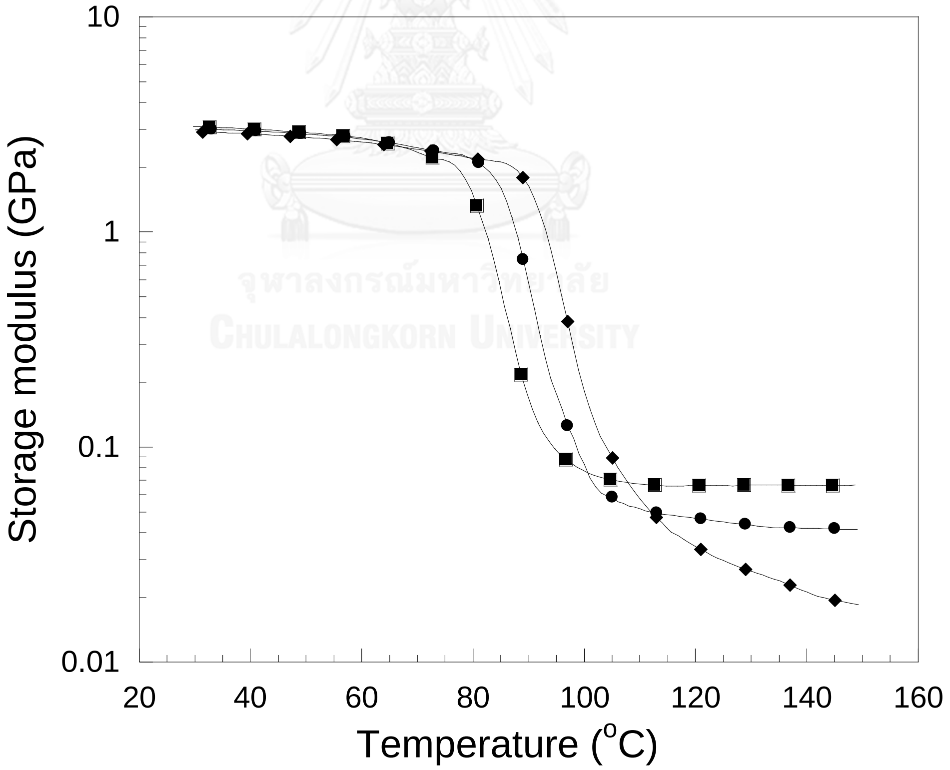


Figure 5.22: Effects of types of heat stabilizers in PVC resin on storage modulus: $\text{PVC}_{\text{DAU 3 phr}}$ (■), $\text{PVC}_{\text{DAU 1.5 phr, eugenol 1.5 phr}}$ (●) and $\text{PVC}_{\text{eugenol 3 phr}}$ (▲)

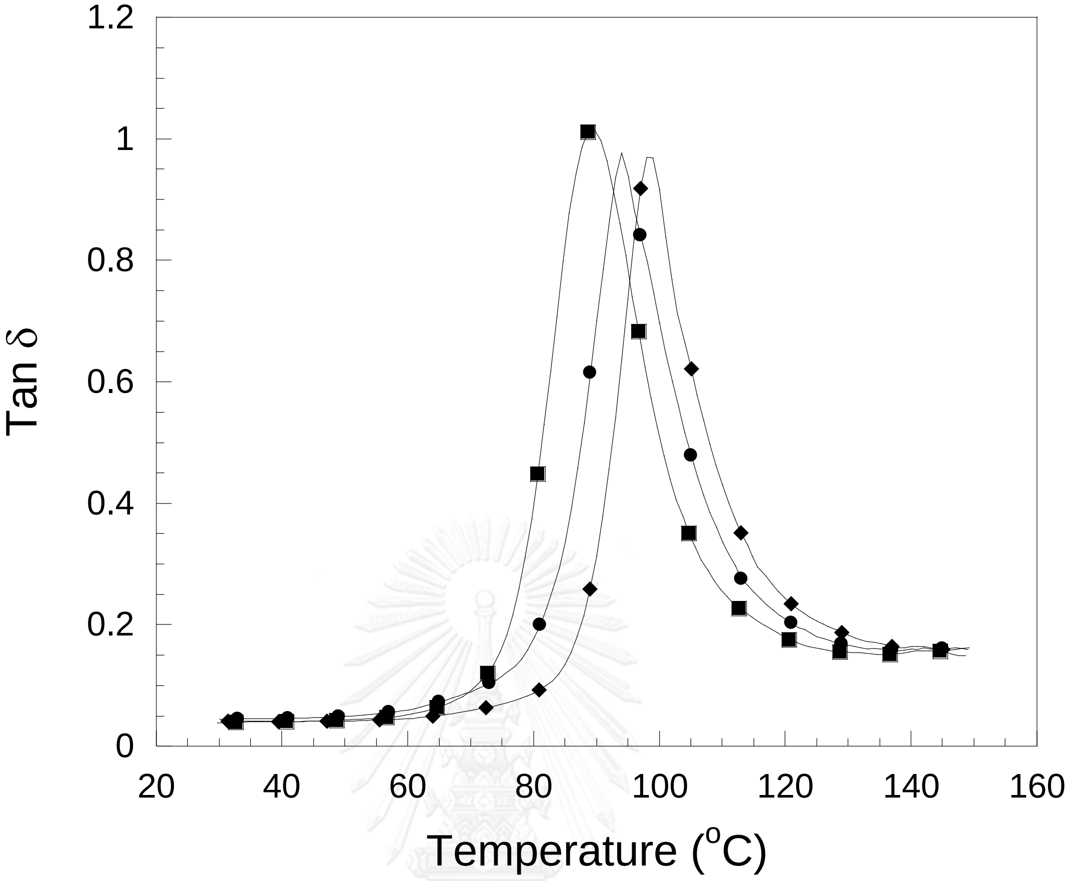


Figure 5.23: Effects of types of heat stabilizers in PVC resin on tan δ $PVC_{DAU\ 3\ phr}$ (■), $PVC_{DAU\ 1.5\ phr,\ eugenol\ 1.5\ phr}$ (●), $PVC_{DAU\ 2\ phr}$ and $PVC_{eugenol\ 3\ phr}$ (▲)

Table 5.3. Effects of types of heat stabilizers on key parameters in plastograms of PVC.

Stabilizer types in PVC resin	Maximum torque from a plastogram (point X)	
	Maximum torque (Nm/min)	Fusion time (s)
Lead	31.3	330
Calcium zinc	32.1	462
OBS	26.7	586
DAU	Immediately fused at loading stage	
Eugenol		

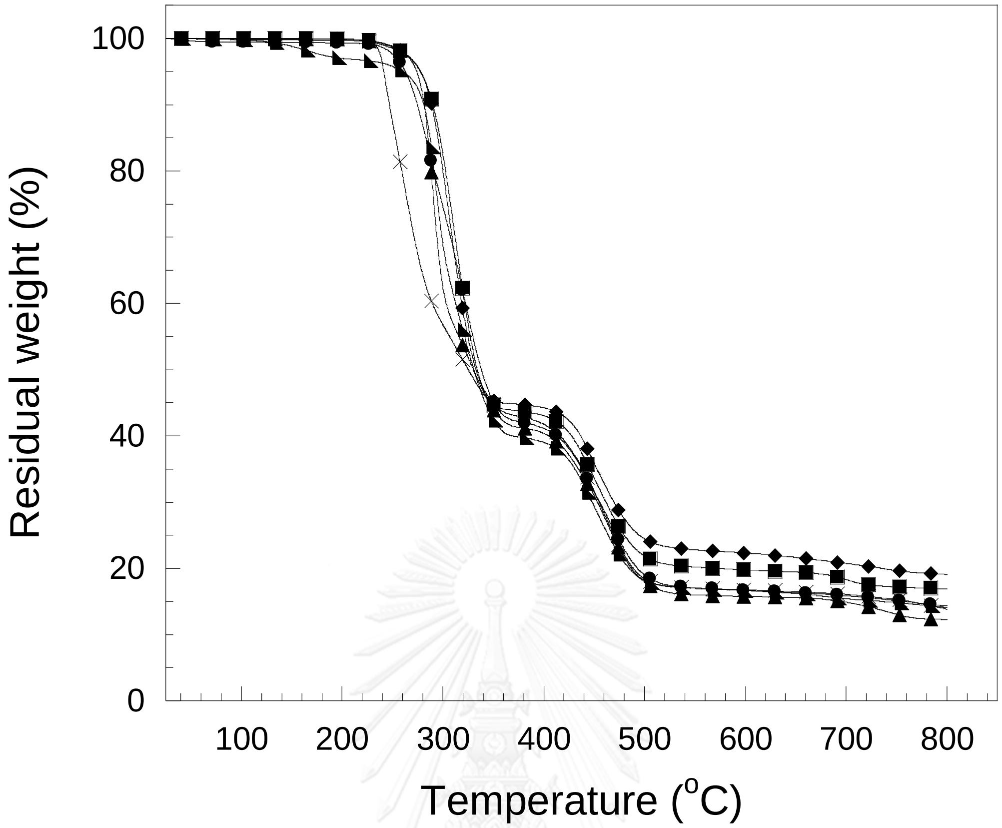


Figure 5.24: Thermogravimetric analysis of the rigid PVC stabilized with various stabilizers: neat PVC (×),PVC$_{lead}$ (■), PVC$_{Ca/Zn}$ (◆), PVC$_{OBScomm}$ (●), PVC$_{DAU}$ (▲), PVCeugenol (▼)

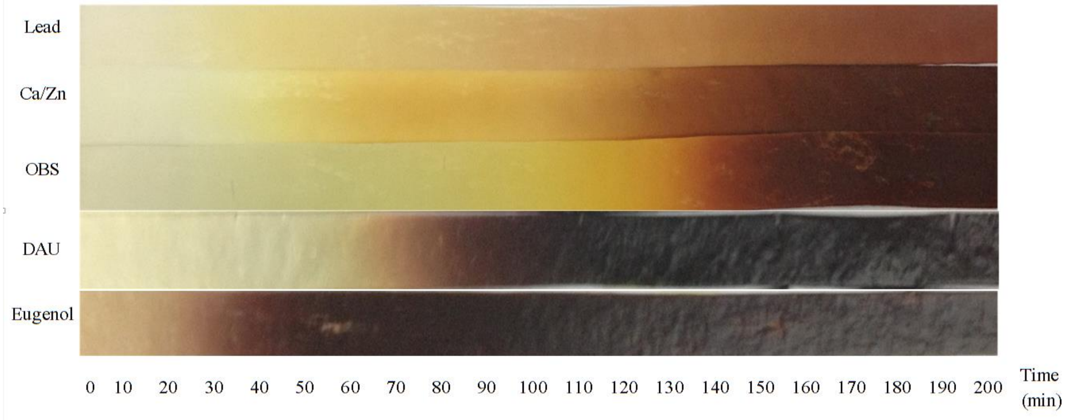


Figure 5.25. Color change of the PVC stabilized with lead, Ca/Zn, OBScomm, DAU and eugenol at 3 phr as a function of time at 180°C.

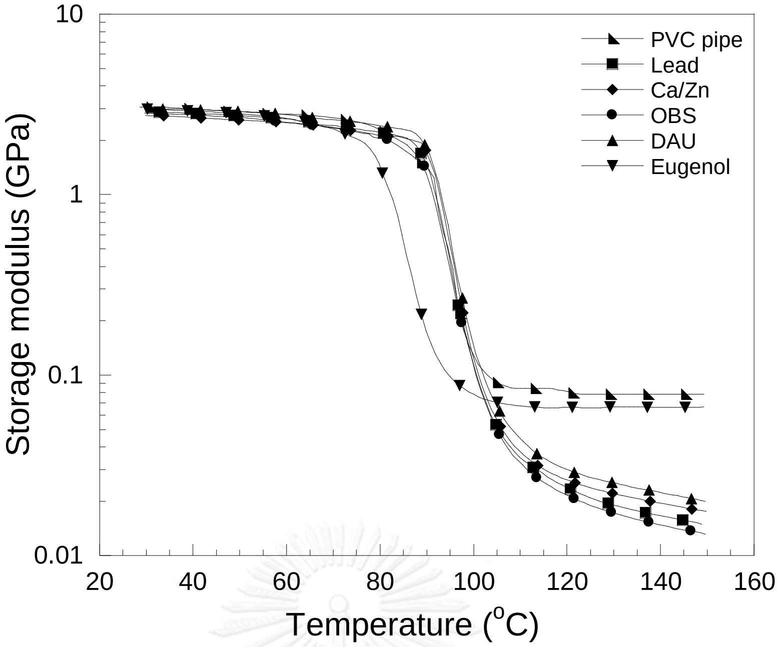


Figure 5.26: Effects of types of heat stabilizers in PVC resin on storage modulus: commercial PVC from local Thai company (◣), PVC$_{lead}$ (■), PVC$_{Ca/Zn}$ (◆), PVC$_{OBScomm}$ (●), PVC$_{DAU}$ (▲) and PVC eugenol (▼).

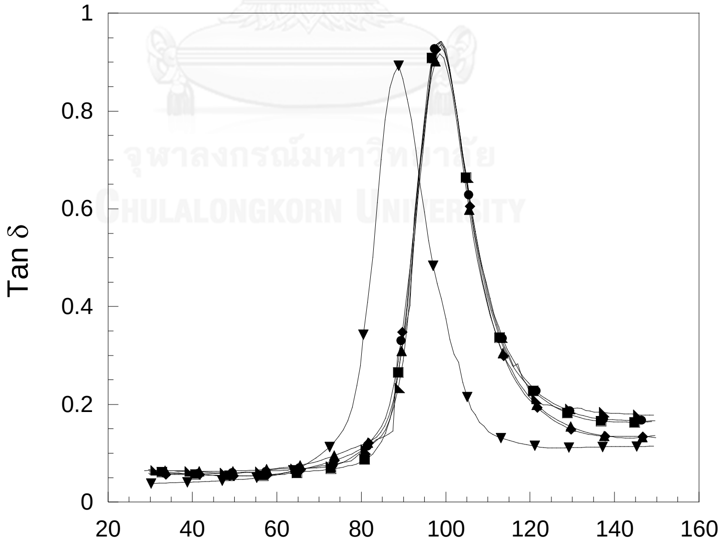


Figure 5.27: Effects of types of heat stabilizers in PVC resin on tan δ: commercial PVC from local Thai company (◣), PVC$_{lead}$ (■), PVC$_{Ca/Zn}$ (◆), PVC$_{OBScomm}$ (●), PVC$_{DAU}$ (▲) and PVC eugenol (▼).

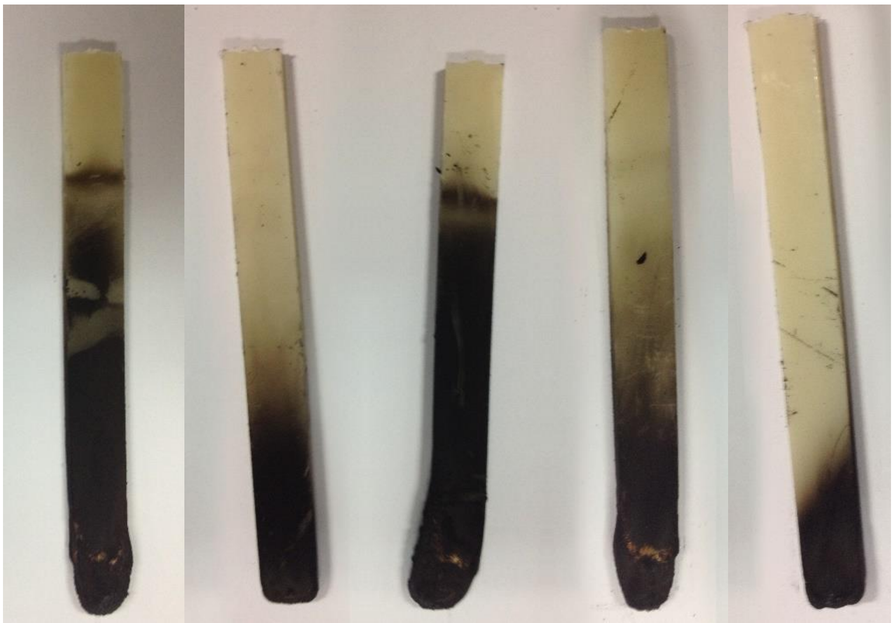


Figure 5.28: UL-94 vertical test of PVC stabilized with lead stabilizer

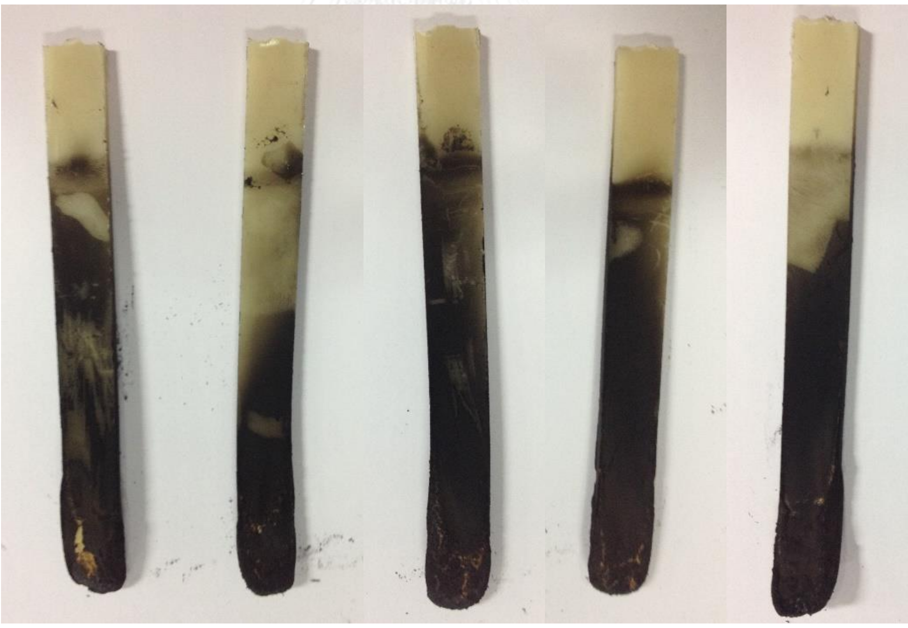


Figure 5.29: UL-94 vertical test of PVC stabilized with calcium/zinc stabilizer

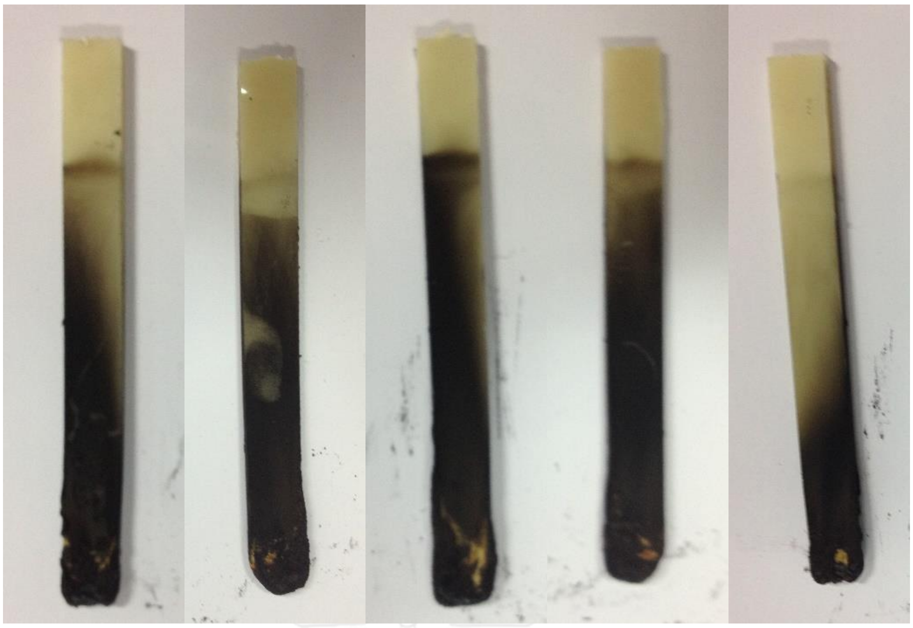


Figure 5.30: UL-94 vertical test of PVC stabilized with commercial OBS stabilizer

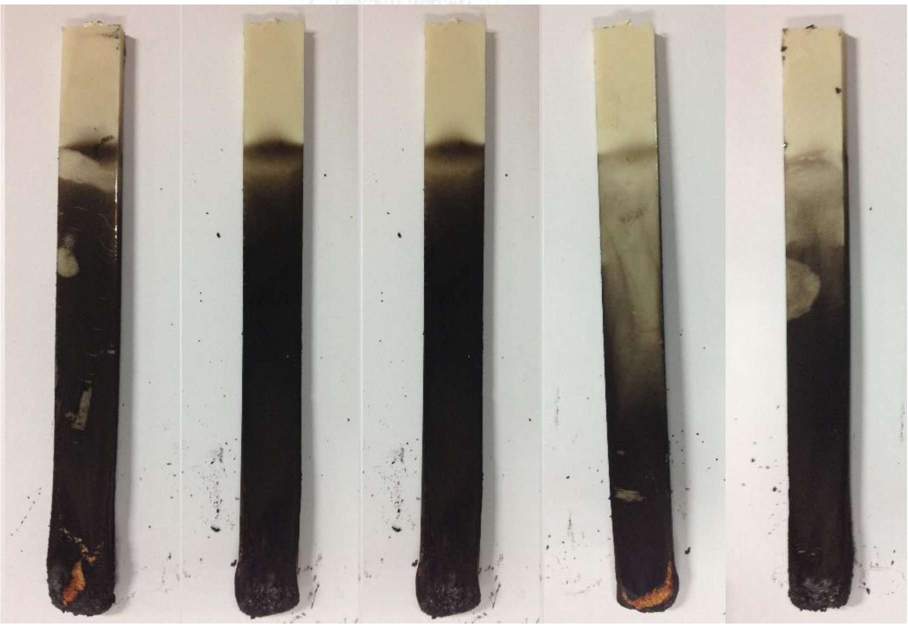


Figure 5.31: UL-94 vertical test of PVC stabilized with DAU

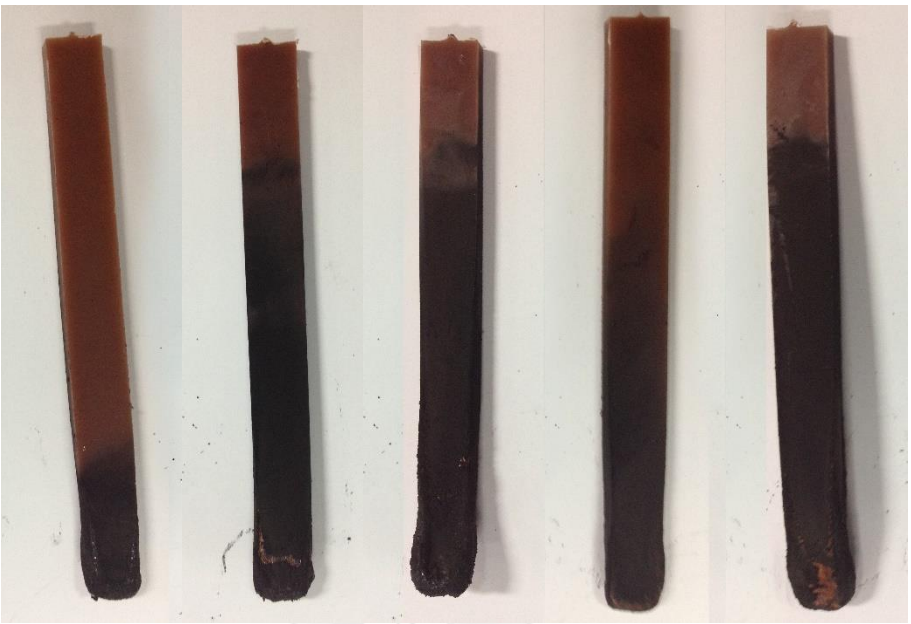


Figure 5.32: UL-94 vertical test of PVC stabilized with eugenol

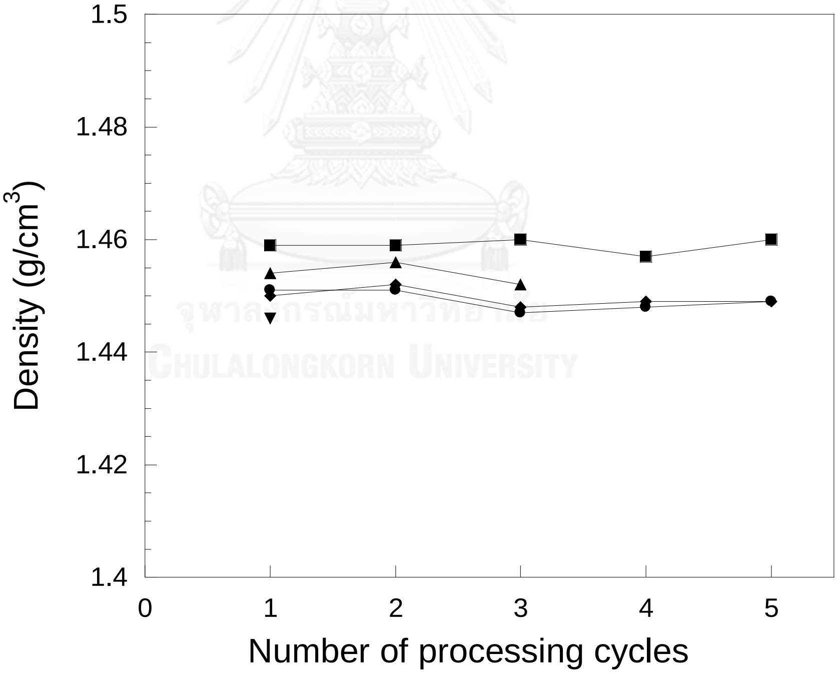
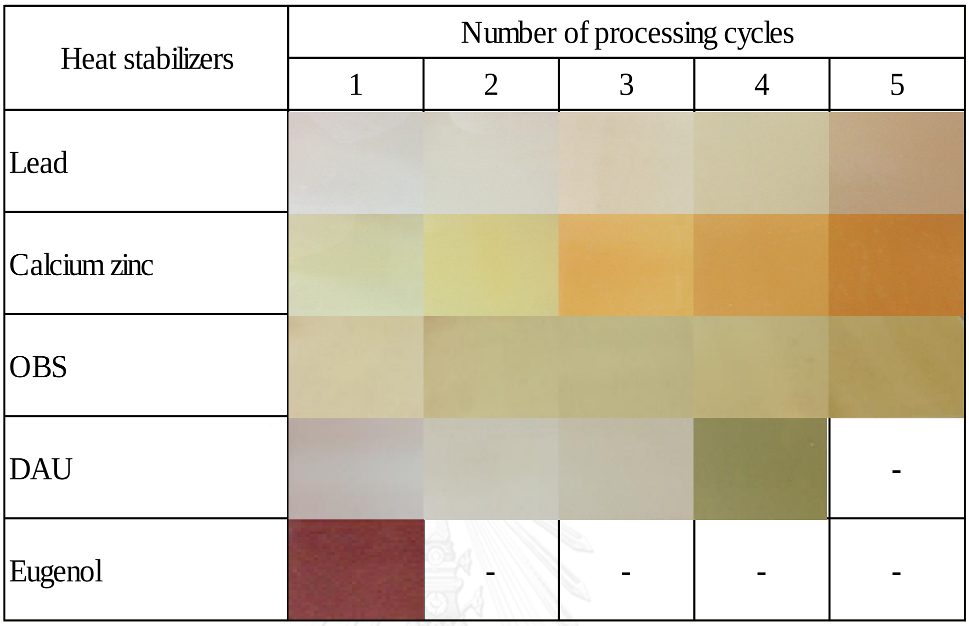


Figure 5.33: Effects of repeated processing cycles on density of PVC with various heat stabilizers: PVC_{lead} (■), $PVC_{Ca/Zn}$ (◆), $PVC_{OBScomm}$ (●), PVC_{DAU} (▲) and PVCeugenol (▼).

Table 5.4: Effects of repeated processing cycle on color of PVC with various heat stabilizers.



Heat stabilizers	Number of processing cycles				
	1	2	3	4	5
Lead					
Calcium zinc					
OBS					
DAU					-
Eugenol		-	-	-	-

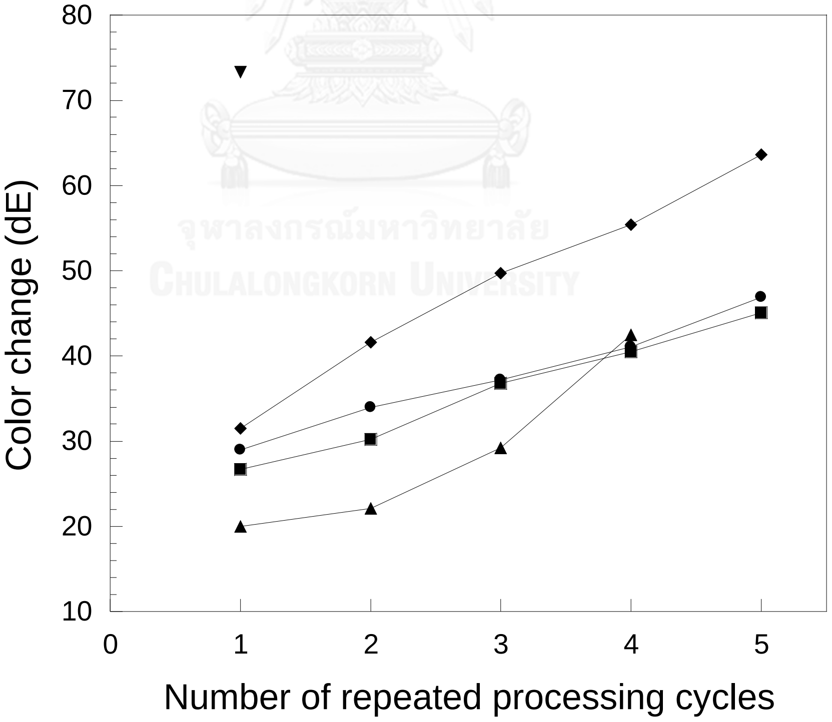


Figure 5.34: Effects of repeated processing cycles on color change of PVC with various heat stabilizers: PVC_{lead} (■), $PVC_{Ca/Zn}$ (◆), $PVC_{OBScomm}$ (●), PVC_{DAU} (▲) and PVCeugenol (▼).

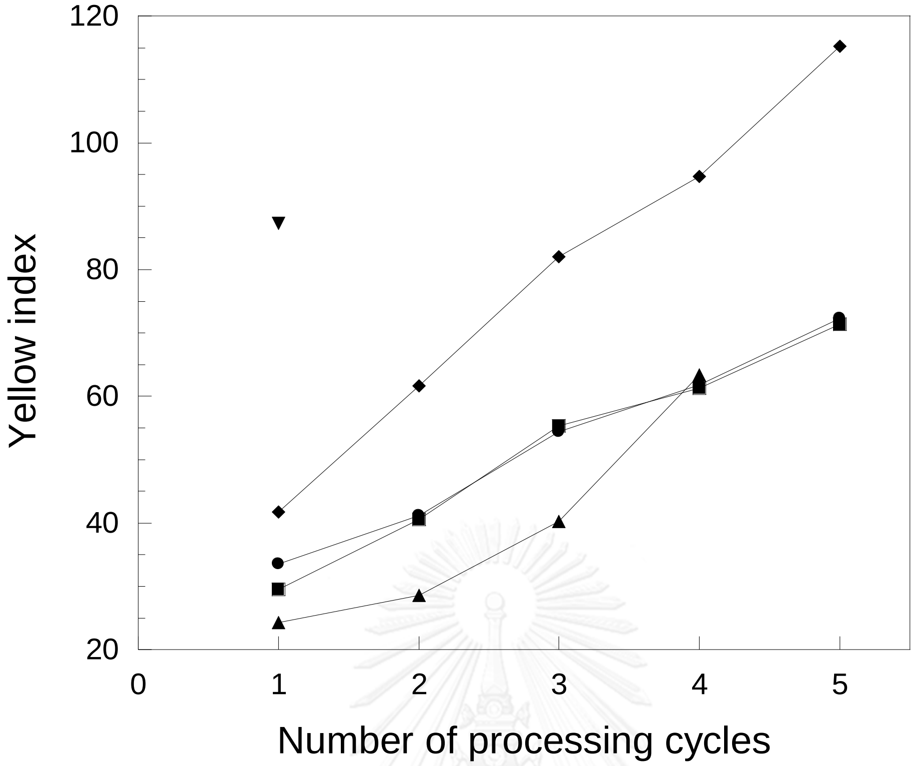


Figure 5.35: Effects of repeated processing cycles on yellow index of PVC with various heat stabilizers: PVC_{lead} (■), $PVC_{Ca/Zn}$ (◆), $PVC_{OBScomm}$ (●), PVC_{DAU} (▲) and PVCeugenol (▼).

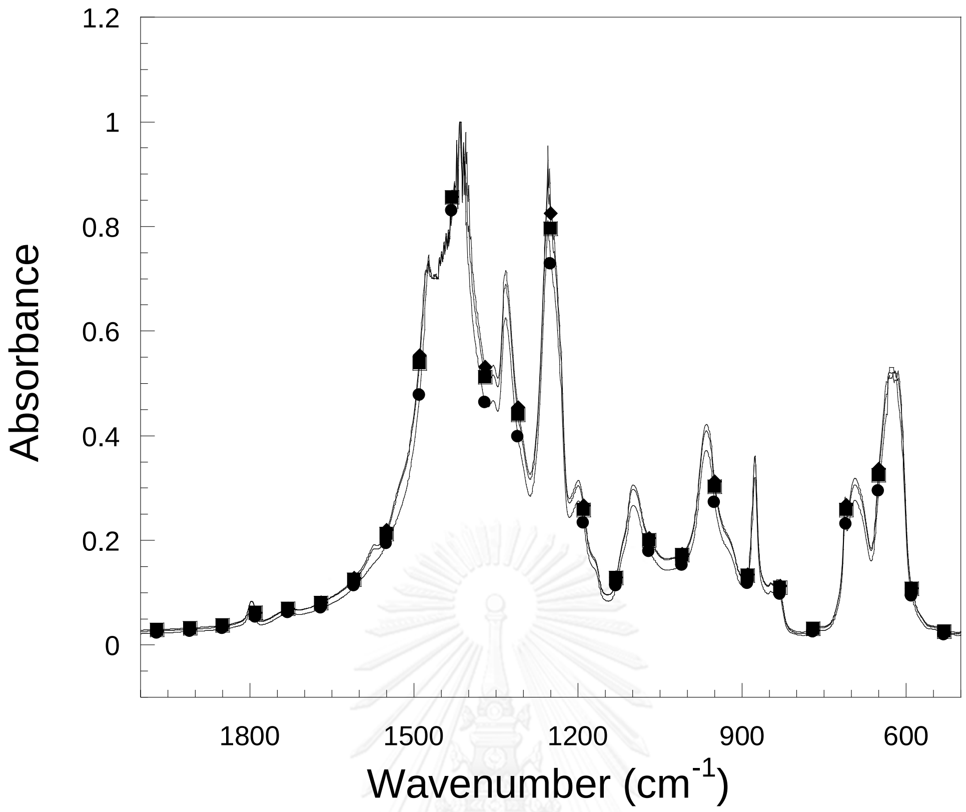


Figure 5.36. Effects of repeated processing cycles of FTIR spectra of PVC stabilized with lead stabilizers: 1st processing cycle (■), 3rd processing cycle (◆) and 5th processing cycle (●).

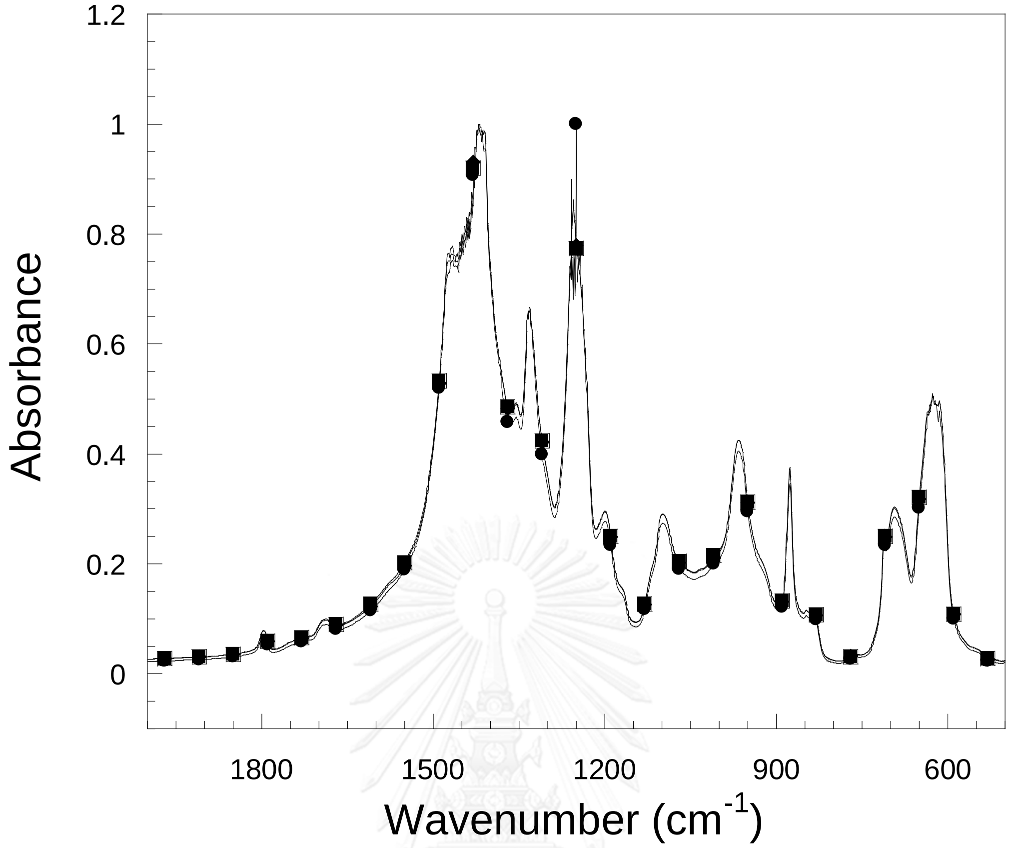


Figure 5.37. Effects of repeated processing cycles of FTIR spectra of PVC stabilized with Ca/Zn stabilizers: 1st processing cycle (■), 3rd processing cycle (◆) and 5th processing cycle (●).

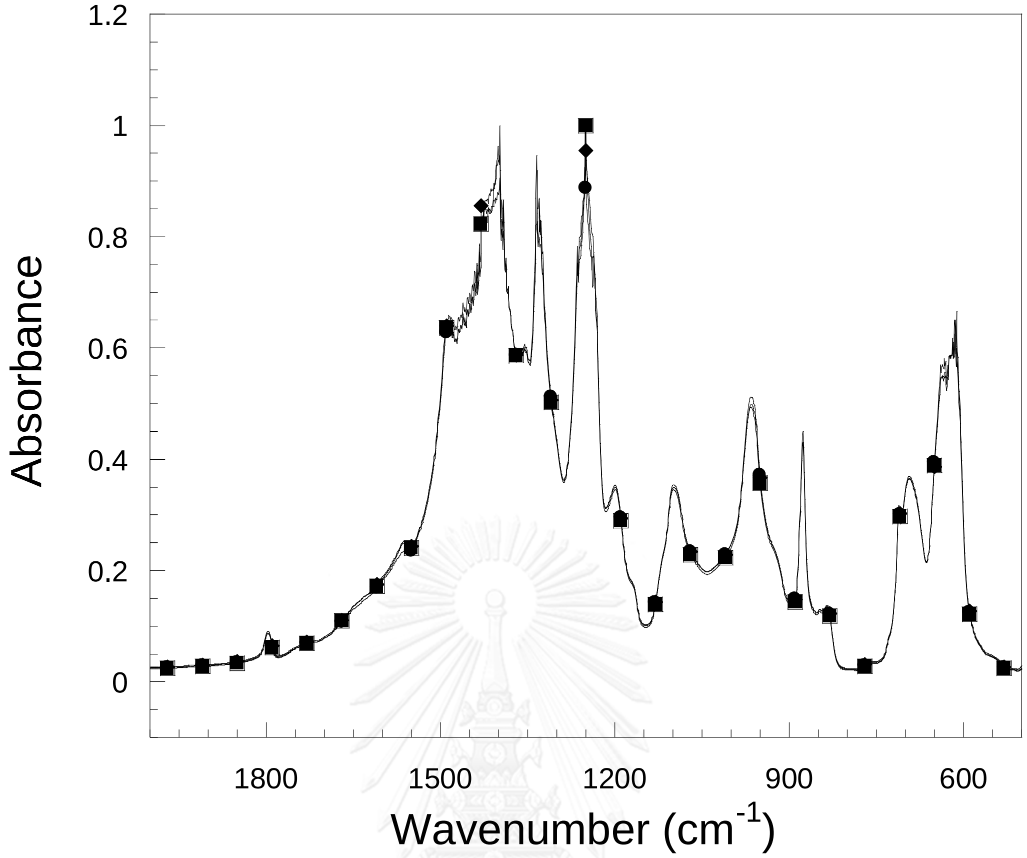


Figure 5.38. Effects of repeated processing cycles of FTIR spectra of PVC stabilized with commercial OBS stabilizers: 1st processing cycle (■), 3rd processing cycle (◆) and 5th processing cycle (●).

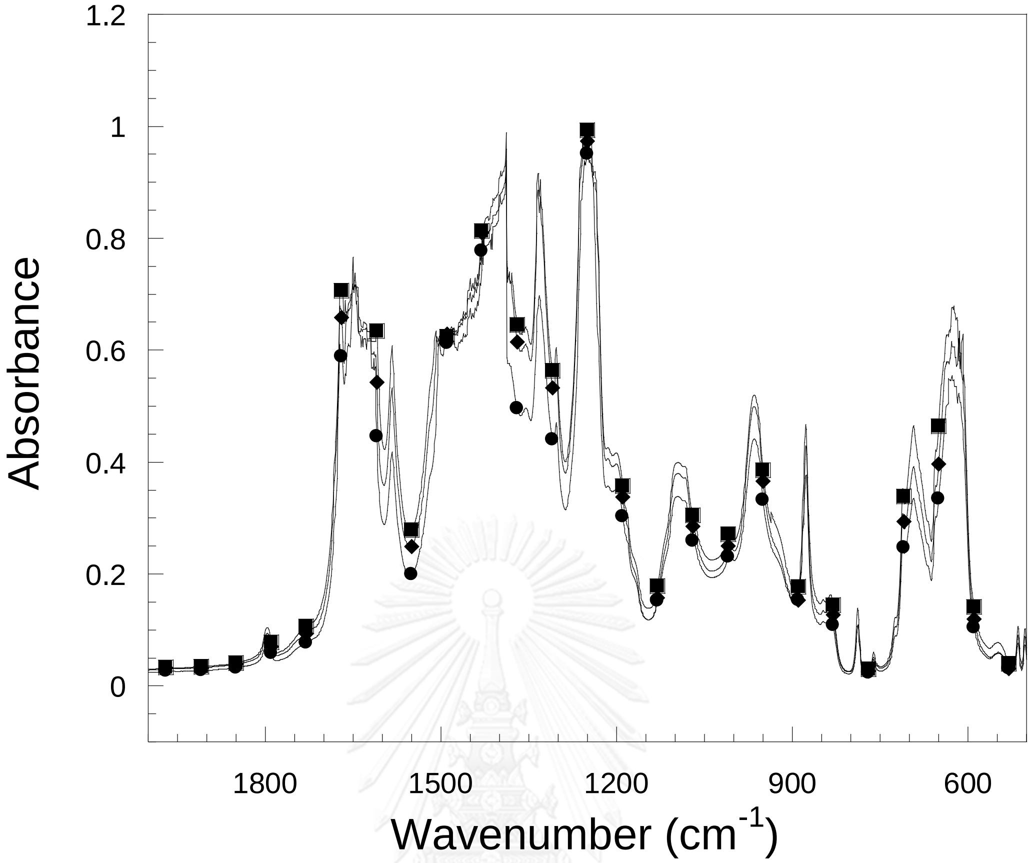


Figure 5.39. Effects of repeated processing cycles of FTIR spectra of PVC stabilized with DAU stabilizers: 1st processing cycle (■), 2nd processing cycle (◆) and 3rd processing cycle (●).

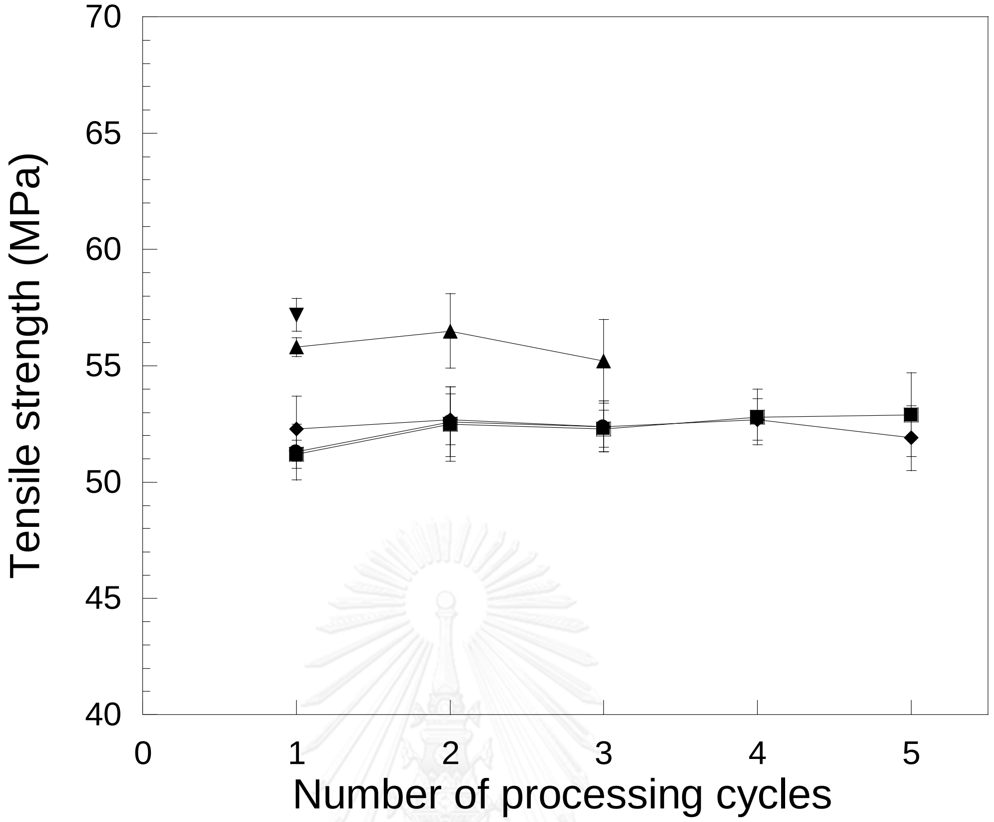


Figure 5.40: Effects of repeated processing cycles on tensile strength of PVC with various heat stabilizers: PVC_{lead} (■), $PVC_{Ca/Zn}$ (◆), $PVC_{OBScomm}$ (●), PVC_{DAU} (▲) and PVCeugenol (▼).

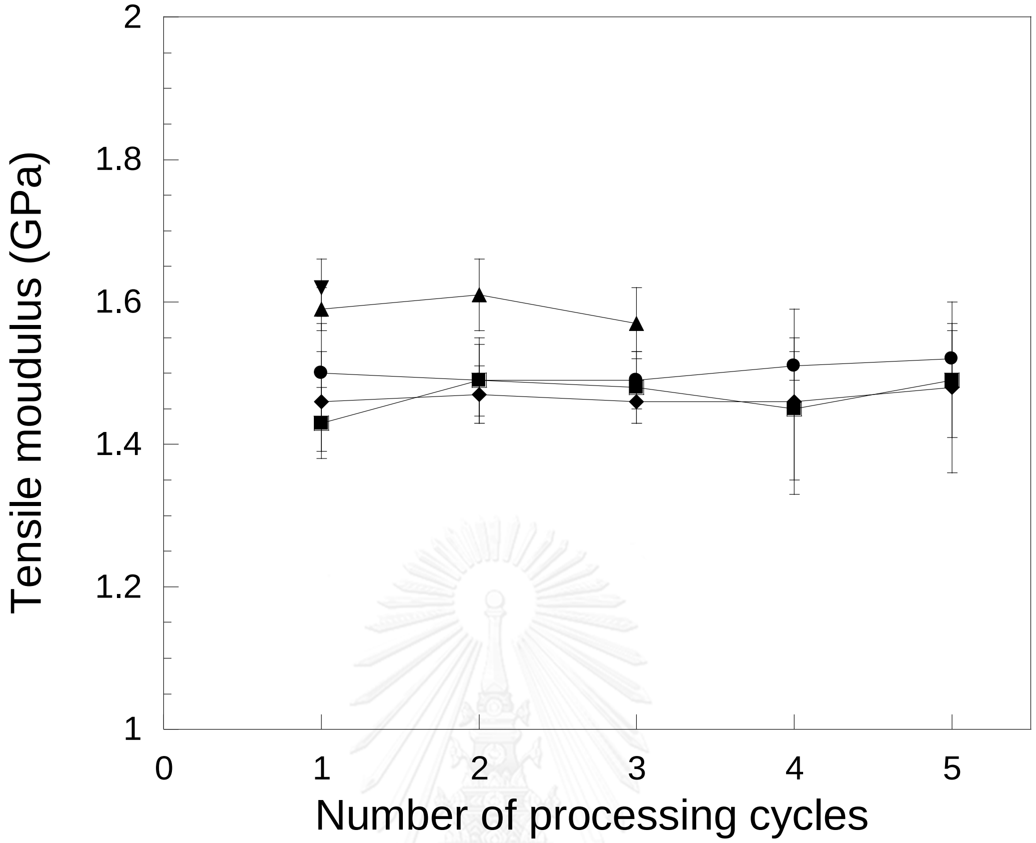


Figure 5.41: Effects of repeated processing cycles on tensile modulus of PVC with various heat stabilizers: PVC_{lead} (■), $PVC_{Ca/Zn}$ (◆), $PVC_{OBScomm}$ (●), PVC_{DAU} (▲) and PVCeugenol (▼).

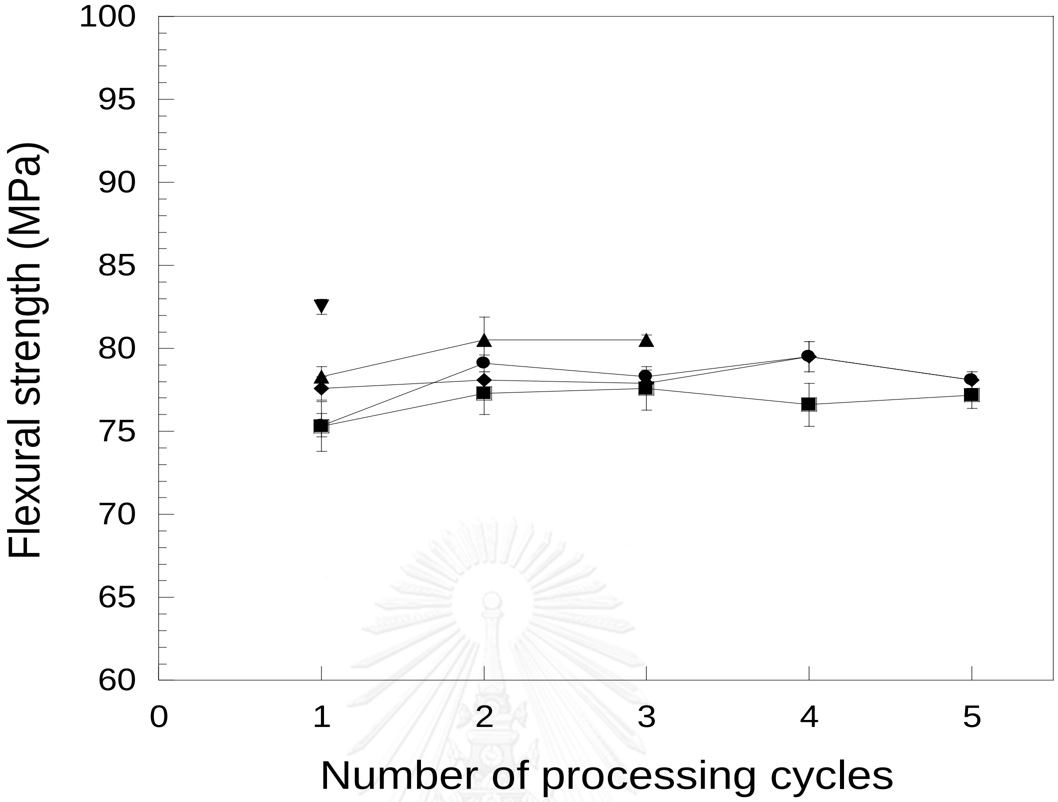


Figure 5.42: Effects of repeated processing cycles on flexural strength of PVC with various heat stabilizers: PVC_{lead} (■), $PVC_{Ca/Zn}$ (◆), $PVC_{OBScomm}$ (●), PVC_{DAU} (▲) and PVCeugenol (▼).

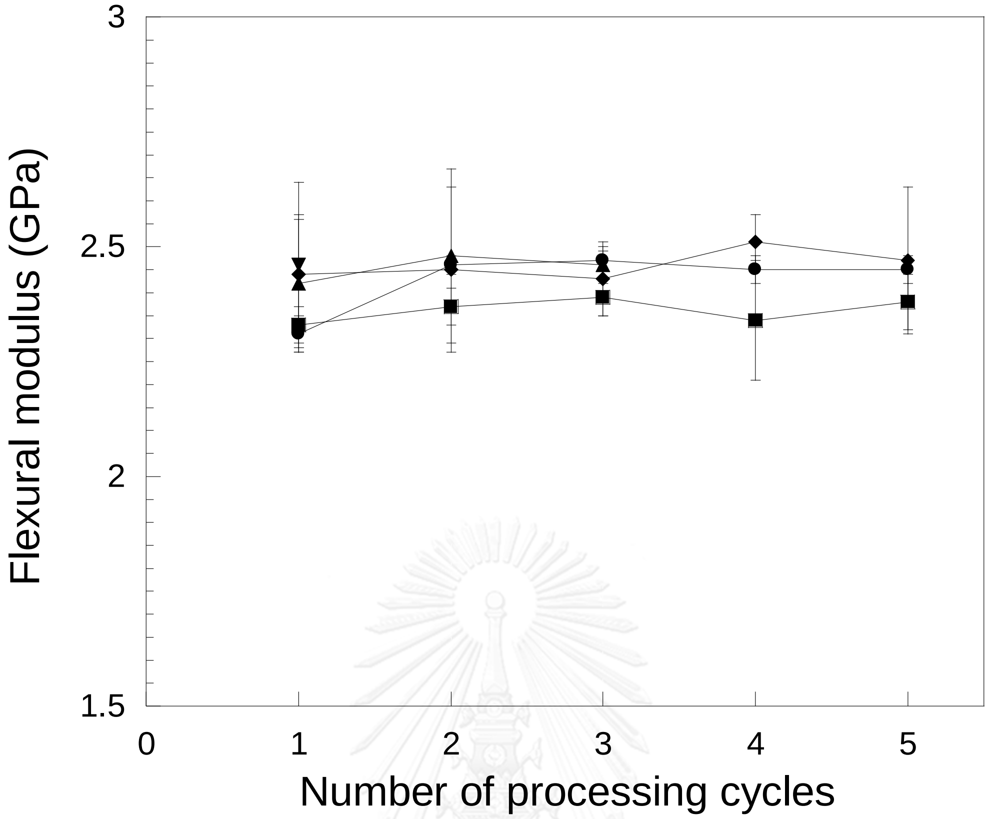


Figure 5.43: Effects of repeated processing cycles on flexural modulus of PVC with various heat stabilizers:PVC$_{lead}$ (■), PVC$_{Ca/Zn}$ (◆), PVCOBS$_{comm}$ (●), PVC$_{DAU}$ (▲) and PVC$_{eugenol}$ (▼).

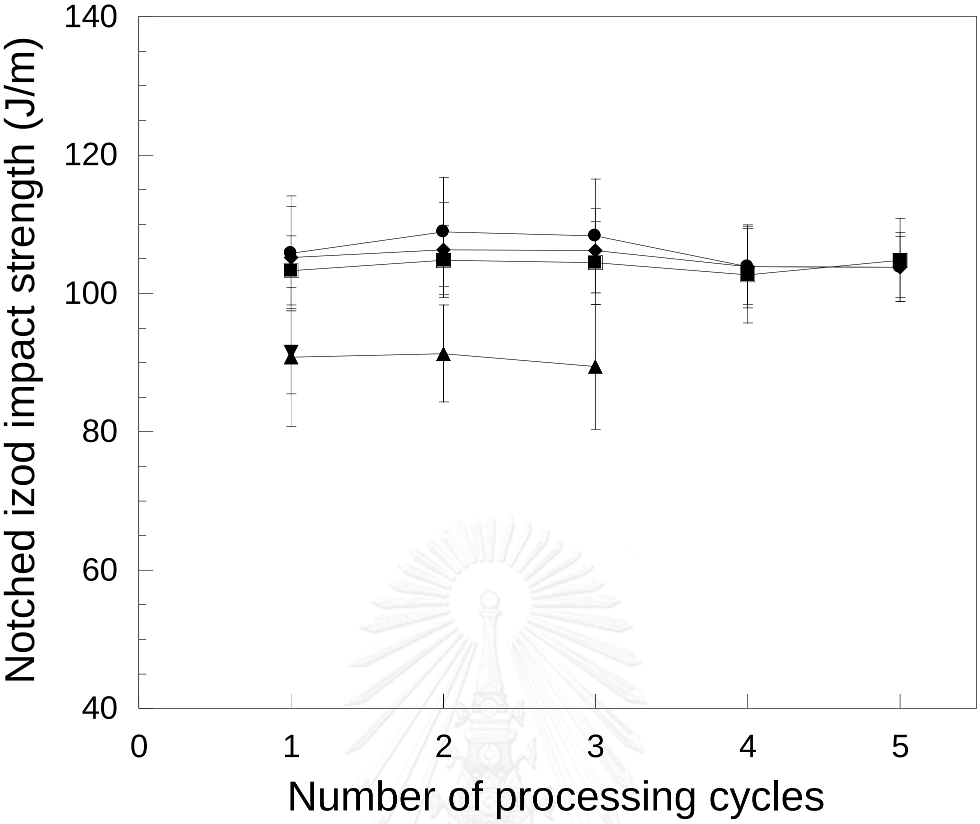


Figure 5.44: Effects of repeated processing cycles on Izod impact of PVC with various heat stabilizers:PVClead (■), PVCCa/Zn (◆), PVCOBScomm (●), PVCDAU (▲) and PVCeugenol (▼).

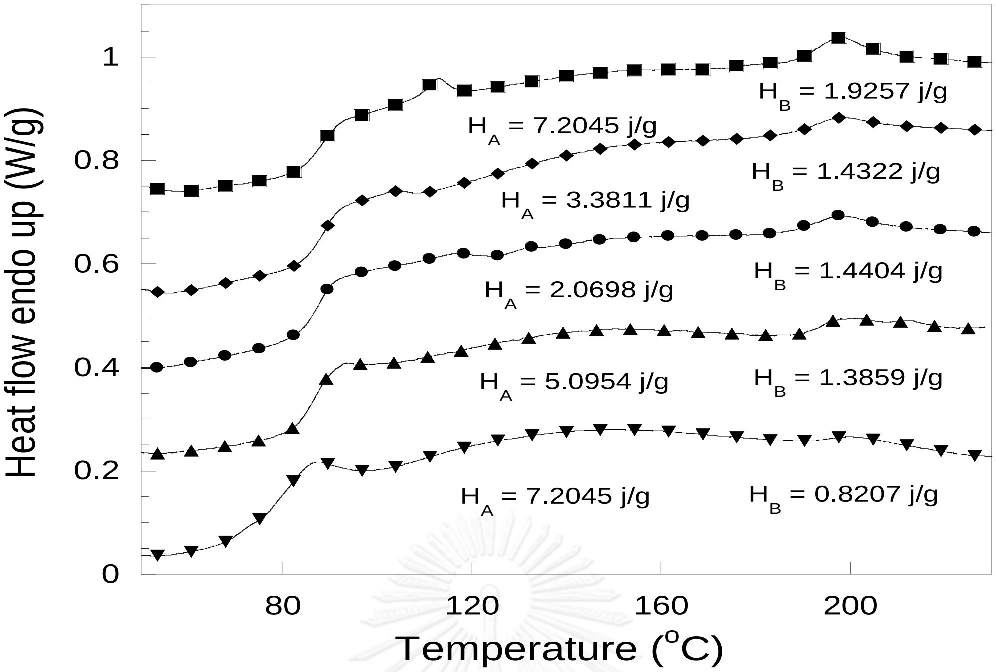


Figure 5.45: DSC thermograms of PVC stabilized with various types of heat stabilizer (1st cycle): PVC_{lead} (■), $PVC_{Ca/Zn}$ (◆), $PVC_{OBScomm}$ (●), PVC_{DAU} (▲) and $PVC_{eugenol}$ (▼).

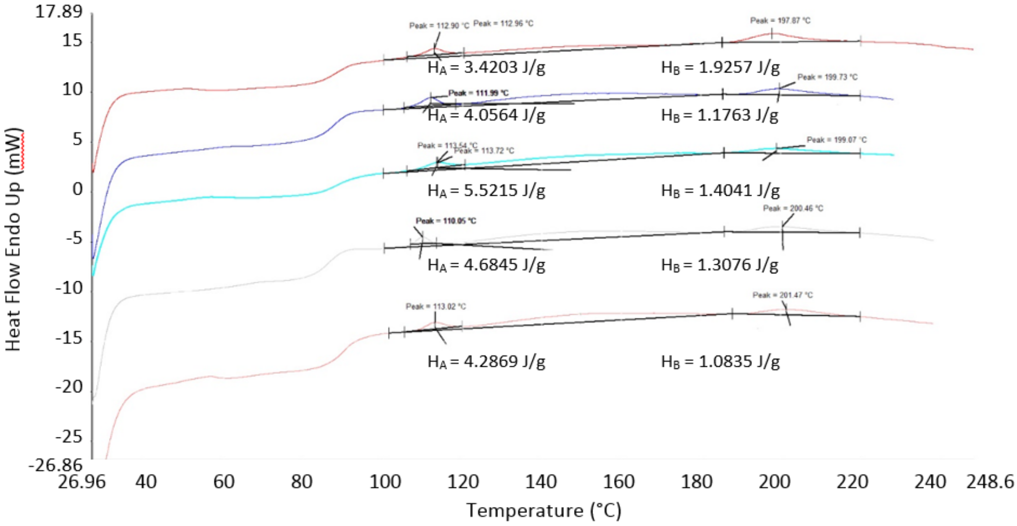


Figure 5.46: DSC thermograms of PVC stabilized lead at number of processing cycles 1st cycle (red line), 2nd cycle (dark blue line), 3rd cycle (blue line), 4th cycle (grey line) and 5th cycle (pink line).

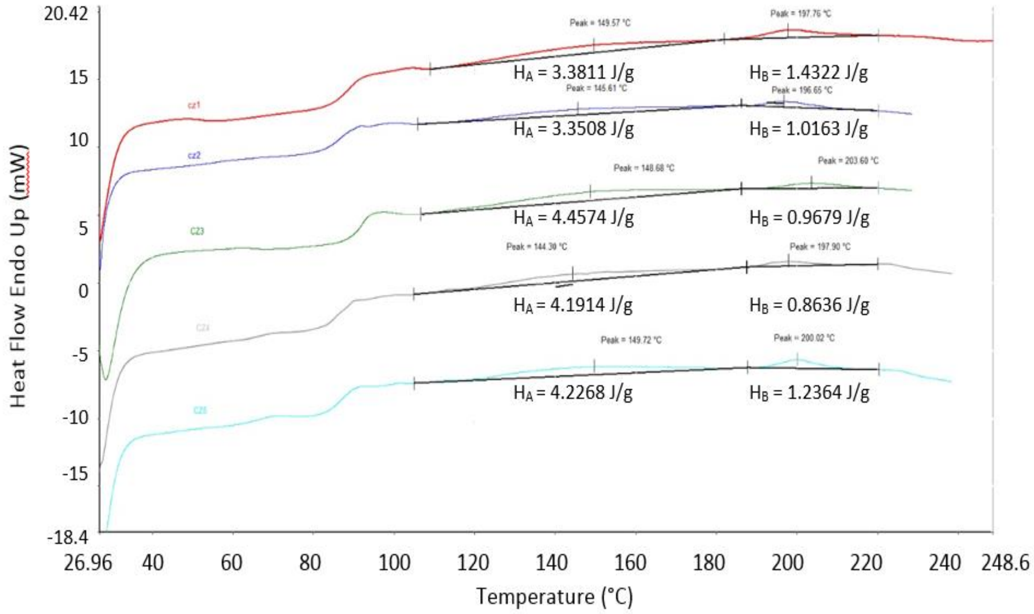


Figure 5.47: DSC thermograms of PVC stabilized Ca/Zn at number of processing cycles 1st cycle (red line), 2nd cycle (dark blue line), 3rd cycle (green line), 4th cycle (grey line) and 5th cycle (blue line).

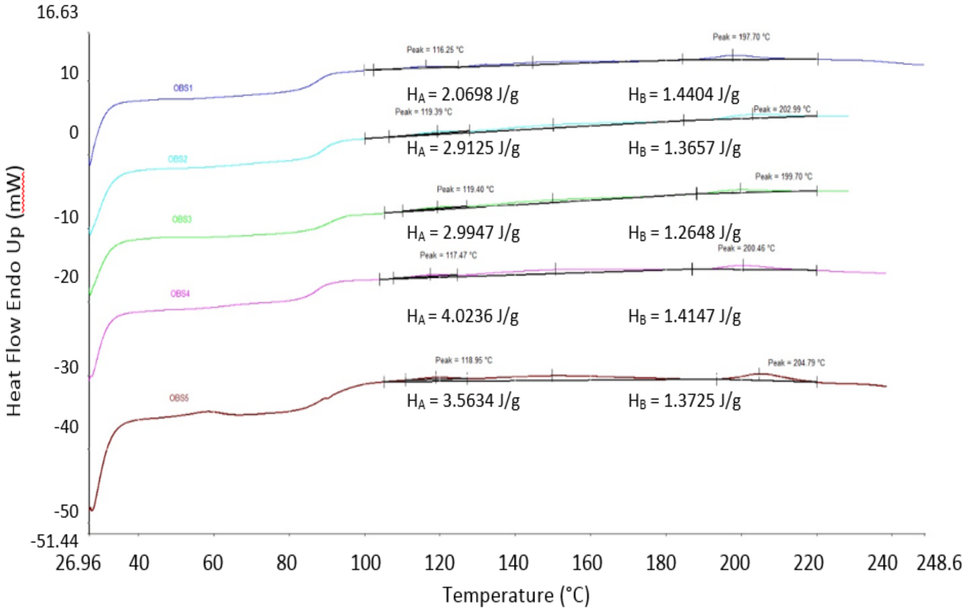


Figure 5.48: DSC thermograms of PVC stabilized OBS at number of processing cycles 1st cycle (dark blue line), 2nd cycle (blue line), 3rd cycle (green line), 4th cycle (pink line) and 5th cycle (brown line)

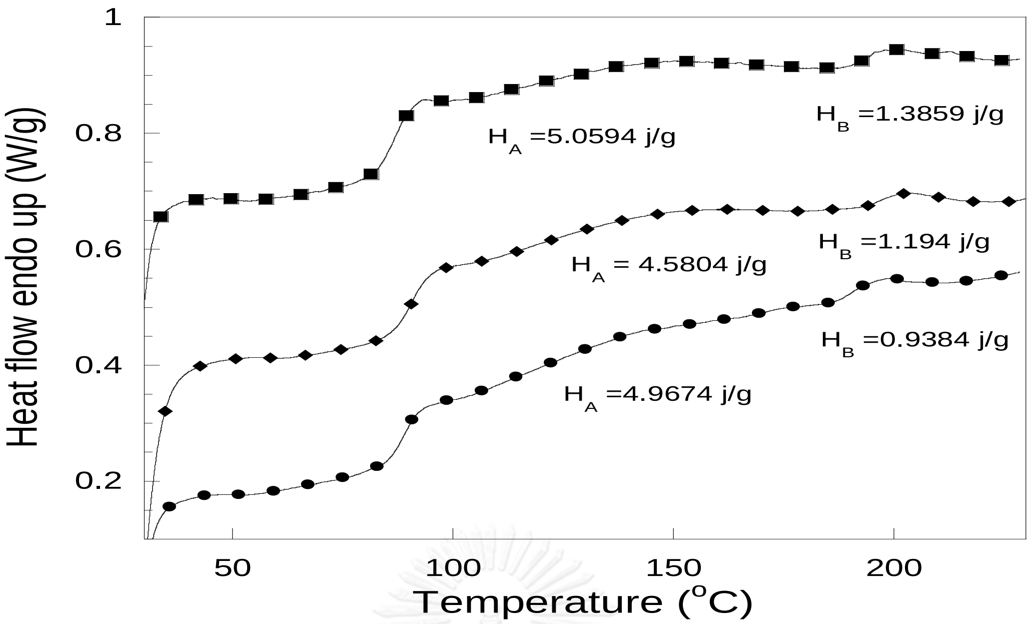


Figure 5.49: DSC thermograms of PVC stabilized DAU at different number of processing cycles 1st cycle (■), 2nd cycle (◆) and 3rd cycle (●).

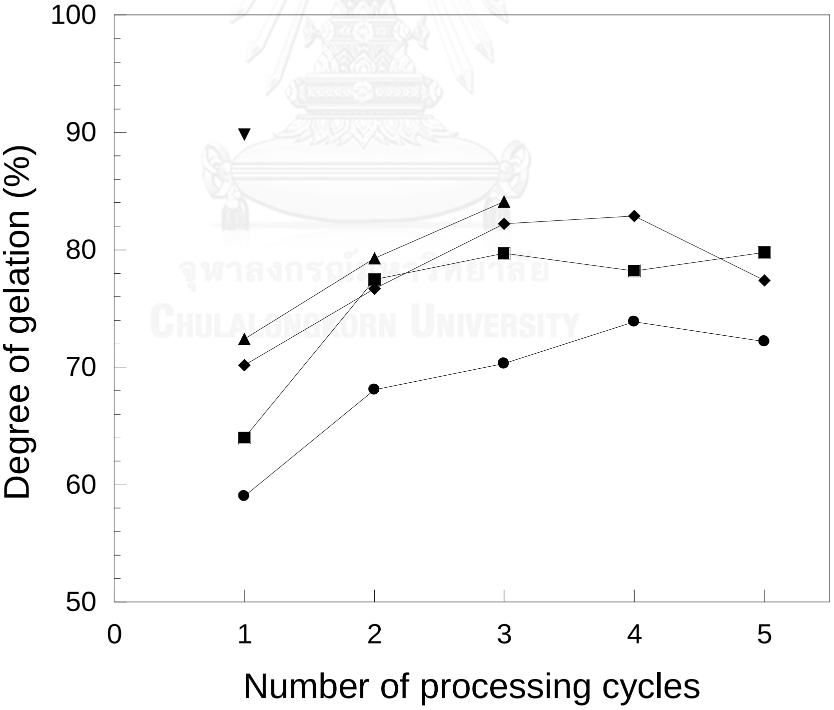


Figure 5.50: Effects of repeated processing cycles on degree of gelation of PVC with various heat stabilizers: PVC$_{lead}$ (■), PVC$_{Ca/Zn}$ (◆), PVC$_{OBS}$ (●), PVC$_{DAU}$ (▲) and PVCeugenol (▼).

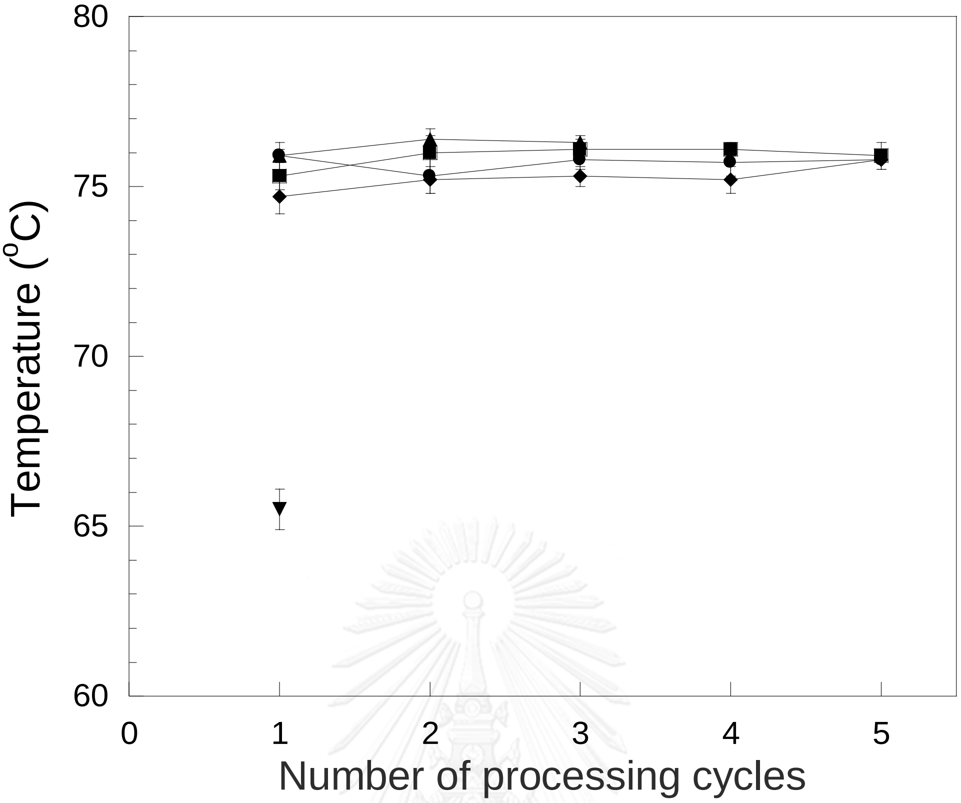


Figure 5.51: Effects of repeated processing cycles on heat distortion temperature of PVC with various heat stabilizers: PVC_{lead} (■), $PVC_{Ca/Zn}$ (◆), $PVC_{OBScomm}$ (●), PVC_{DAU} (▲) and PVCeugenol (▼).

CHAPTER VI

CONCLUSIONS

Potential organic based heat stabilizers which are non-toxic and safer in pipe application compared to traditional lead or Ca/Zn stabilizers for PVC resin are evaluated in this work. From the results, DAU and eugenol, which are, single organic component, heat stabilizers, were found to be more readily fused with PVC than commercial lead Ca/Zn and OBS stabilizers, the multi-component stabilizers, as confirmed by a fusion test. Consequently, PVC stabilized with DAU and eugenol was observed to be processable in a lower range of temperature i.e. ca. 150°C, while PVC with commercial stabilizers required higher processing temperature.

From thermogravimetric analysis, all types of heat stabilizers were able to help improve thermal degradation temperature at 5% weight loss of the neat PVC suggesting potential use of those stabilizers. In addition, PVC specimens with DAU provided relatively low thermal discoloration by maintaining original white color of PVC at temperature of 180°C up to 50 minutes suggesting its best short-term performance among those stabilizers. The glass transition temperatures of PVC stabilized with eugenol was the lowest among the others as observed from dynamic mechanical analysis curves. From mechanical testing, PVC stabilized with DAU and eugenol showed higher tensile and flexural properties while they possessed lower impact property than those of PVC with the other stabilizers. Synergistic behavior in thermal stability of PVC was also observed when mixture of eugenol and uracil derivative at 1:1 mass ratio and at a concentration of 3 phr in PVC was used.

From recycle ability test, PVC stabilized with commercial lead, Ca/Zn, and OBS stabilizers could processed up to at least 5 cycles. However, PVC stabilized with DAU was found to be able to withstand the processing cycle up to 4 cycles. Whereas PVC stabilized with eugenol was able to undergo only one processing cycle. From color change investigation, PVC stabilized with commercial lead and commercial OBS stabilizers effectively retained their small color change up to 5 times of processing cycles. Furthermore, effects of repeated processing cycle of PVC stabilized with each heat stabilizer showed negligible effect on mechanical properties at least up to 3 processing cycles except for eugenol.

From the above results, it is clearly seen that DAU showed high potential use as a safe and effective organic based heat stabilizer for PVC to substitute lead or Ca/Zn systems. Moreover, additional synergist substances such as hydrotalcite (a secondary stabilizer) or other types of primary stabilizers may be combined with DAU in order to enhance efficiency of PVC heat stability as well as to reduce cost.

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Secondary Sources

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APPENDIX

APPENDIX A

Effect of DAU, Eugenol and DAU/Eugenol Mixture Stabilizers on Static Thermal Stability and Mechanical Property of Rigid PVC.

Table A-1 Tensile properties of PVC stabilized with DAU at various DAU contents.

Sample Name	Tensile strength (MPa)	Tensile modulus (GPa)
PVC_{DAU} 1 phr	51.3±1.0	1.42±0.04
PVC_{DAU} 2 phr	56.3±1.2	1.61±0.07
PVC_{DAU} 3 phr	56.0±0.4	1.65±0.03
PVC_{DAU} 4 phr	55.6±0.9	1.64±0.05

Table A-2 Extent of discoloration of thermally degraded rigid PVC strips stabilized with eugenol/DAU mixtures at various DAU contents.

Samples	Contents (phr)		Color of PVC samples				
	Eugenol	DAU	0 min	20 min	50 min	60 min	80 min
1	3	0	Light pink	Brown	Dark brown	Dark brown	Dark brown
2	2.5	0.5	White	White	Yellow	Dark brown	Dark brown
3	2	1	White	White	Light yellow	Dark brown	Dark brown
4	1,5	1.5	White	White	White	Brown	Dark brown
5	1	2	White	White	White	Light brown	Brown
6	0.5	2.5	White	White	Brown	Dark brown	Dark brown
7	0	3	White	White	Light brown	Brown	Dark brown

* Strips were automatically moved out of the box at 1 mm/min at 180^{o}C under air atmosphere

APPENDIX B

Effect of DAU, Eugenol and DAU/Eugenol Mixture Stabilizers on Static Thermal Stability and Mechanical Property of Rigid PVC.

Table B-1 Thermal stability of PVC stabilized with various stabilizers at 3 phr contents.

Samples	T_d at 5 % weight loss (^{o}C)	Char residue (%)
PVC	241	13.9
PVC_{Lead}	278	16.9
$PVC_{Ca/Zn}$	278	19.1
PVC_{OBS}	263	14.3
PVC_{DAU}	274	12.3
$PVC_{Eugenol}$	260	14.1

APPENDIX C

Effects of Repeated Processing and Various Types of Heat stabilizers

Table C-1 Effects of repeated processing cycles on density of PVC with various heat stabilizers.

Sample name	Density of PVC samples at each processing cycle (g/cm^3)				
	1st	2nd	3rd	4th	5th
$\mathrm{PVC_{lead}}$	1.459	1.459	1.460	1.457	1.460
$\mathrm{PVC_{CZ}}$	1.450	1.452	1.448	1.449	1.449
$\mathrm{PVC_{OBS}}$	1.451	1.451	1.447	1.448	1.449
$\mathrm{PVC_{DAU}}$	1.454	1.456	1.452	-	-
$\mathrm{PVC_{eugenol}}$	1.447	-	-	-	-

Table C-2 Effects of repeated processing cycle on color change value (ΔE) of PVC with various heat stabilizers.

Sample Name	Color change (ΔE) of PVC samples at each processing cycle (g/cm^3)				
	1st	2nd	3rd	4th	5th
$\mathrm{PVC_{lead}}$	26.7±0.2	30.2±0.1	36.8±0.2	40.5±0.4	45.1±0.3
$\mathrm{PVC_{CZ}}$	31.5±0.4	41.6±1.5	49.7±0.5	55.4±0.2	63.6±1.0
$\mathrm{PVC_{OBS}}$	29.0±0.3	34.0±1.1	37.2±0.6	41.1±0.7	46.9±0.6
$\mathrm{PVC_{DAU}}$	20.0±0.3	22.1±1.1	29.2±0.2	42.5±0.3	-
$\mathrm{PVC_{eugenol}}$	73.3±2.3	-	-	-	-

Table C-3 Effects of repeated processing cycle on yellow index value (YI) of PVC with various heat stabilizers.

Sample name	Yellow index of PVC samples at each processing cycle (g/cm^3)				
	1st	2nd	3rd	4th	5th
PVC_{lead}	29.5±0.6	40.6±0.6	55.3±0.9	61.3±0.9	71.4±0.5
PVC_{CZ}	41.7±0.2	61.6±1.2	82.0±0.7	94.7±0.2	115.2±0.6
PVC_{OBS}	33.5±0.6	41.2±0.8	54.4±0.2	61.8±0.7	72.3±0.8
PVC_{DAU}	24.3±0.4	28.6±0.5	40.2±0.3	63.4±0.7	-
$PVC_{eugenol}$	87.3±1.0	-	-	-	-

Table C-4 Effects of repeated processing cycles on tensile strength of PVC with various heat stabilizers.

Sample name	Tensile strength at each processing cycle (MPa)				
	1st	2nd	3rd	4th	5th
PVC_{lead}	51.2±0.6	52.5±1.6	52.3±0.8	52.8±1.2	52.9±1.8
PVC_{CZ}	52.3±1.4	52.7±1.1	52.4±1.1	52.7±0.9	51.9±1.4
PVC_{OBS}	51.3±1.2	52.6±1.5	52.4±1.1	52.1±0.5	52.9±0.6
PVC_{DAU}	55.8±0.4	56.5±1.6	55.2±1.8	-	-
$PVC_{eugenol}$	57.2±0.7	-	-	-	-

Table C-5 Effects of repeated processing cycles on tensile modulus of PVC with various heat stabilizers.

Sample name	Tensile modulus at each processing cycle (GPa)				
	1st	2nd	3rd	4th	5th
PVC_{lead}	1.43 ±0.05	1.49±0.06	1.48±0.05	1.45±0.10	1.49±0.08
PVC_{CZ}	1.46±0.07	1.47±0.04	1.46±0.03	1.46±0.13	1.48±0.12
PVC_{OBS}	1.50±0.07	1.49±0.05	1.49±0.04	1.51±0.02	1.52±0.04
PVC_{DAU}	1.59±0.03	1.61±0.05	1.57±0.05	-	-
$PVC_{eugenol}$	1.62±0.04	-	-	-	-

Table C-6 Effects of repeated processing cycles on flexural strength of PVC with various heat stabilizers.

Sample name	Flexural strength at each processing cycle (MPa)				
	1st	2nd	3rd	4th	5th
PVC_{lead}	75.3±1.5	77.3±1.3	77.6±1.3	76.6±1.3	77.2±0.8
PVC_{CZ}	77.6±0.5	78.1±1.2	77.9±1.3	79.5±1.2	78.8±0.9
PVC_{OBS}	75. 4±0.7	79.1±0.5	78.3±0.4	79.5±0.9	78.1±0.5
PVC_{DAU}	78.3±0.6	80.5±1.4	80.5±0.3	-	-
$PVC_{eugenol}$	82.5±0.5	-	-	-	-

Table C-7 Effects of repeated processing cycles on flexural modulus of PVC with various heat stabilizers.

Sample name	Flexural modulus at each processing cycle (GPa)				
	1st	2nd	3rd	4th	5th
$\mathrm{PVC}_{\mathrm{lead}}$	2.33±0.04	2.37±0.04	2.39±0.04	2.34±0.13	2.38±0.06
$\mathrm{PVC}_{\mathrm{CZ}}$	2.44±0.12	2.45±0.18	2.43±0.08	2.51±0.06	2.47±0.16
$\mathrm{PVC}_{\mathrm{OBS}}$	2.31±0.04	2.46±0.02	2.47±0.02	2.45±0.03	2.45±0.03
$\mathrm{PVC}_{\mathrm{DAU}}$	2.42±0.15	2.44±0.19	2.46±0.04	-	-
$\mathrm{PVC}_{\mathrm{eugenol}}$	2.46±0.18	-	-	-	-

Table C-8 Effects of processing cycles on impact strength of PVC with various heat stabilizers.

Sample name	Izod impact strength at each processing cycle (J/m)				
	1st	2nd	3rd	4th	5th
$\mathrm{PVC}_{\mathrm{lead}}$	104.3±5.2	104.8±5.4	104.4±7.5	102.7±8.1	104.8±9.3
$\mathrm{PVC}_{\mathrm{CZ}}$	105.2±7.4	106.3±6.9	106.2±6.1	103.9±5.5	103.8±4.4
$\mathrm{PVC}_{\mathrm{OBS}}$	105.8±8.3	108.9±8.2	108.3±8.3	103.9±6.3	103.8±5.0
$\mathrm{PVC}_{\mathrm{DAU}}$	90.8±9.8	91.3±7.3	89.4±9.4	-	-
$\mathrm{PVC}_{\mathrm{eugenol}}$	91.5±5.7	-	-	-	-

Table C-9 Effects of repeated processing cycles on gelation of PVC with various heat stabilizers.

Sample name	Gelation of PVC samples at each processing cycle (%)				
	1st	2nd	3rd	4th	5th
PVC_{lead}	64.0	77.5	79.7	78.2	79.8
PVC_{CZ}	70.2	76.7	82.2	82.9	77.4
PVC_{OBS}	59.0	68.1	70.3	73.9	72.2
PVC_{DAU}	72.4	79.3	84.1	-	-
$PVC_{eugenol}$	89.8	-	-	-	-

Table C-10 Effects of repeated processing cycles on heat distortion temperature (HDT) of PVC with various heat stabilizers.

Sample name	HDT of PVC samples at each processing cycle (°C)				
	1st	2nd	3rd	4th	5th
PVC_{lead}	75.3±0.4	76.0±0.7	76.1±0.3	76.1±0.2	75.9±0.4
PVC_{CZ}	74.7±0.5	75.2±0.4	75.3±0.3	75.2±0.4	75.1±0.3
PVC_{OBS}	75.9±0.2	75.3±0.5	75.8±0.3	75.7±0.4	75.8±0.3
PVC_{DAU}	75.9±0.4	76.4±0.1	76.3±0.2	-	-
$PVC_{eugenol}$	65.5±0.6	-	-	-	-

APPENDIX D

Material Specification Sheets

Appendix D-1 Suspension PVC resin specification sheet

266RC

Suspension PVC resin

VINYTHAI

Siamvic

APPLICATIONS

Extrusion

- Rigid pipe

- profile

CHARACTERISTICS

Siamvic 266RC is a medium K value resin specially designed for **rigid PVC extrusion**

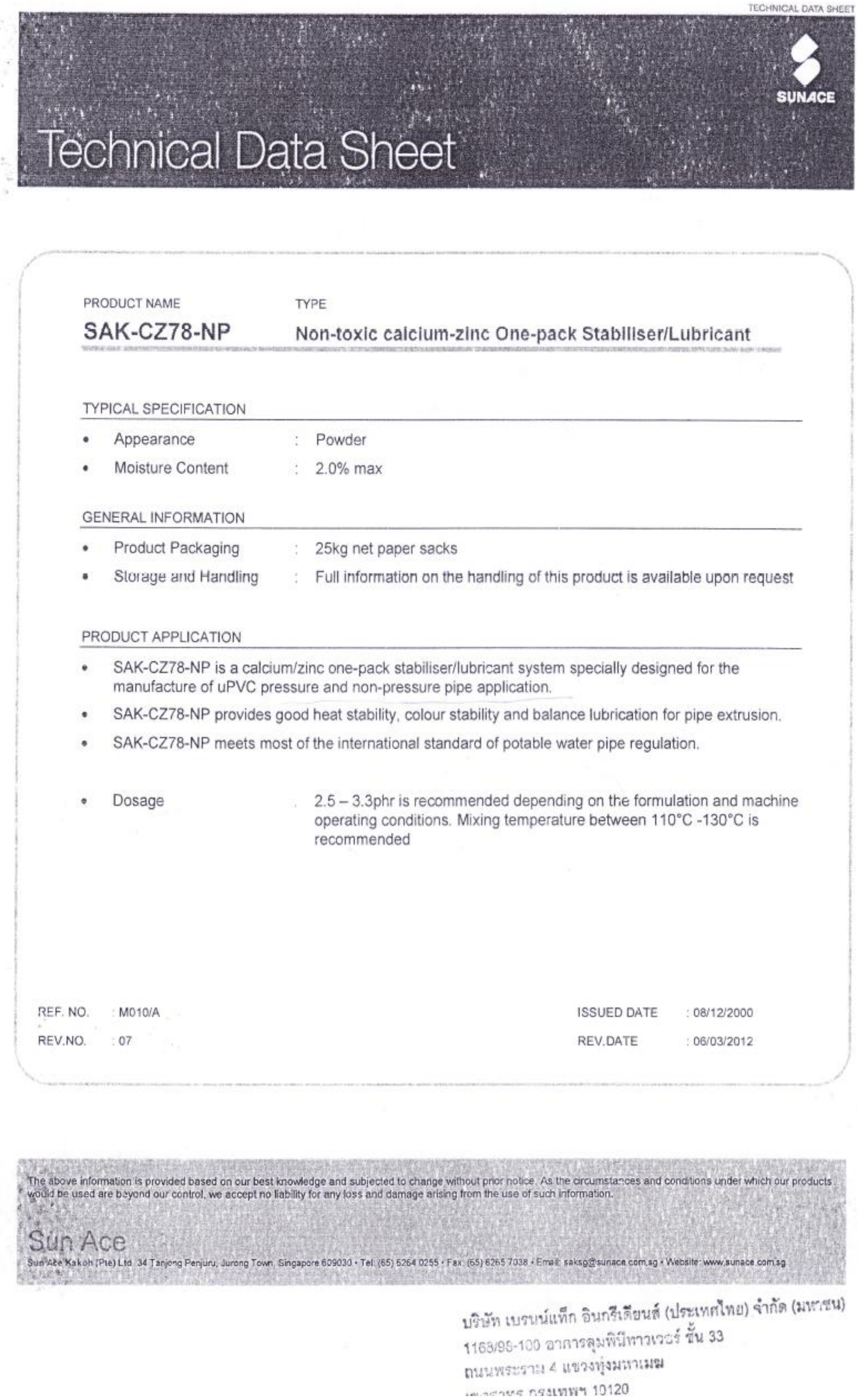
- very low dust during transportation and pneumatic filling of silos
- high bulk density
- regular feed of extruders as dry blend
- high extrusion output
- easy gelling, good mechanical properties
- compatibility with a wide range of heat stabilizers and fillers
- low uptake of moisture

Characteristics	Units	Values (*)	Standards
Viscosity index	ml/g	109	ISO 1628-2
K value (cyclohexanone)		66	ISO 1628-2
Polymerization degree		1000	JIS K6721
Apparent bulk density	kg/l	0.57	ISO 60
Volatile matter	%	<0.3	ISO 1269
Particle size			ISO 1624
on 60 mesh (0.250mm)	%	<5	
on 230 mesh (0.063mm)	%	>95	

(*) In the case of certain characteristics the values given in this data sheet are means based on a large number of individual measurements distributed around the means in a range corresponding to the normal manufacture and measurement tolerances. These values should not be considered as specifications.

All information in this document is given in good faith but without any warranty or guarantee of any kind whatsover, whether implied or expressed. Freedom from patent rights must not be assumed. National or local regulation on industrial safety and hygiene are applicable in all cases; in no case can we accept any responsibility for failure to observe such regulations.

Appendix D.2: Calcium-zinc one pack (SAK-CZ78-NP) specification sheet.



TECHNICAL DATA SHEET

SUNACE

Technical Data Sheet

PRODUCT NAME

SAK-CZ78-NP

TYPE

Non-toxic calcium-zinc One-pack Stabiliser/Lubricant

TYPICAL SPECIFICATION

- Appearance : Powder
- Moisture Content : 2.0% max

GENERAL INFORMATION

- Product Packaging : 25kg net paper sacks
- Storage and Handling : Full information on the handling of this product is available upon request

PRODUCT APPLICATION

- SAK-CZ78-NP is a calcium/zinc one-pack stabiliser/lubricant system specially designed for the manufacture of uPVC pressure and non-pressure pipe application.
- SAK-CZ78-NP provides good heat stability, colour stability and balance lubrication for pipe extrusion.
- SAK-CZ78-NP meets most of the international standard of potable water pipe regulation.

- Dosage : 2.5 – 3.3phr is recommended depending on the formulation and machine operating conditions. Mixing temperature between 110°C -130°C is recommended

REF. NO. : M010/A

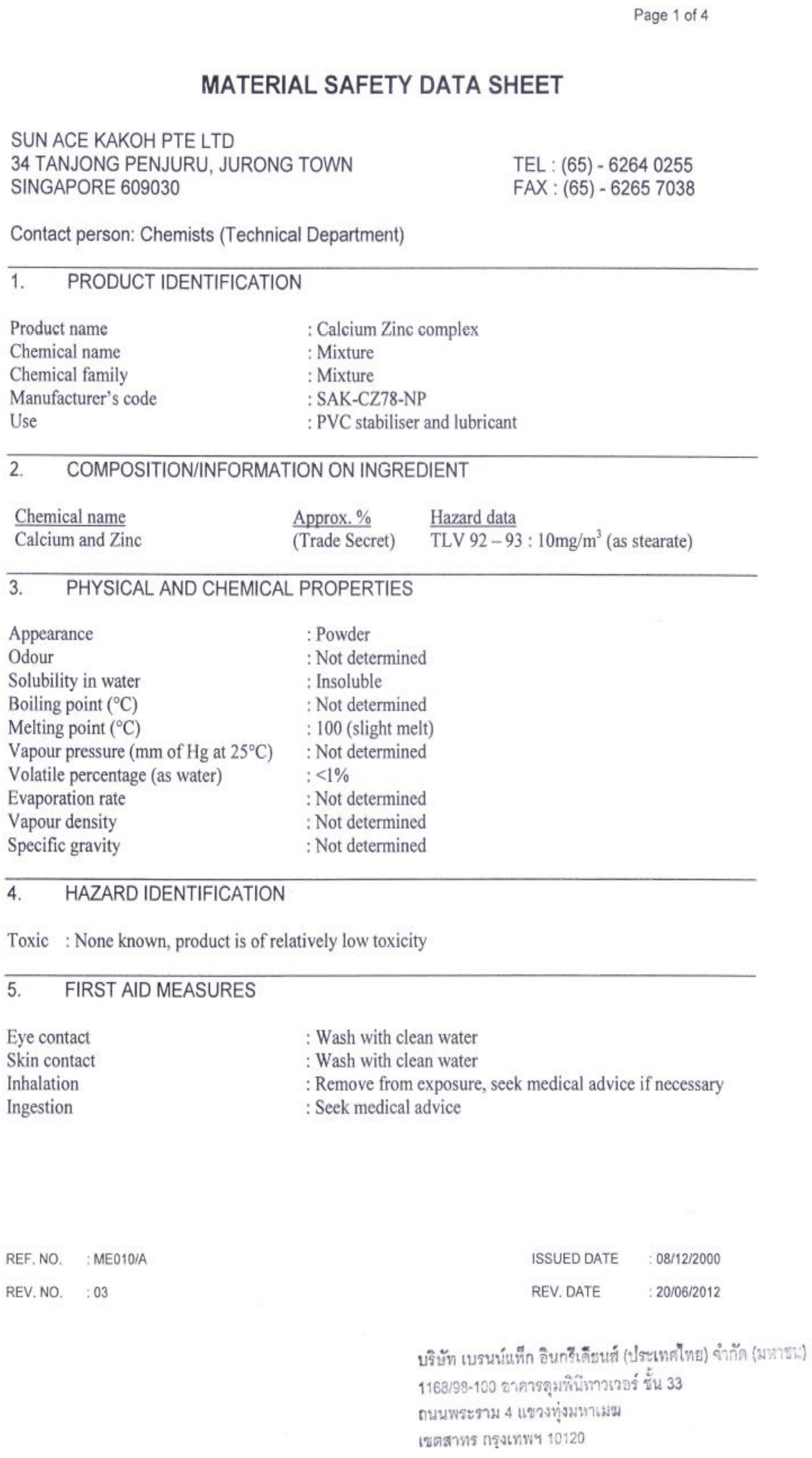
REV.NO. : 07

ISSUED DATE : 08/12/2000

REV.DATE : 06/03/2012

Sun Ace
Sun Ace Kakoh (Pte) Ltd. 34 Tanjong Penjuru, Jurong Town, Singapore 609030 • Tel: (65) 6264 0255 • Fax: (65) 6265 7038 • Email: saksg@sunace.com.sg • Website: www.sunace.com.sg

บริษัท เบรนน์แท็ก อินกรีเดียนส์ (ประเทศไทย) จำกัด (มหาชน)
1168/95-100 อาคารลุมพินีทาวเวอร์ ชั้น 33
ถนนพระราม 4 แขวงทุ่งมหาเมฆ
เขตสาทร กรุงเทพฯ 10120



MATERIAL SAFETY DATA SHEET

SUN ACE KAKOH PTE LTD
34 TANJONG PENJURU, JURONG TOWN
SINGAPORE 609030
TEL : (65) - 6264 0255
FAX : (65) - 6265 7038

Contact person: Chemists (Technical Department)

1. PRODUCT IDENTIFICATION

Product name : Calcium Zinc complex
Chemical name : Mixture
Chemical family : Mixture
Manufacturer's code : SAK-CZ78-NP
Use : PVC stabiliser and lubricant

2. COMPOSITION/INFORMATION ON INGREDIENT

Chemical name	Approx. %	Hazard data
Calcium and Zinc	(Trade Secret)	TLV 92 – 93 : 10mg/m^3 (as stearate)

3. PHYSICAL AND CHEMICAL PROPERTIES

Appearance : Powder
Odour : Not determined
Solubility in water : Insoluble
Boiling point (°C) : Not determined
Melting point (°C) : 100 (slight melt)
Vapour pressure (mm of Hg at 25°C) : Not determined
Volatile percentage (as water) : <1%
Evaporation rate : Not determined
Vapour density : Not determined
Specific gravity : Not determined

4. HAZARD IDENTIFICATION

Toxic : None known, product is of relatively low toxicity

5. FIRST AID MEASURES

Eye contact : Wash with clean water
Skin contact : Wash with clean water
Inhalation : Remove from exposure, seek medical advice if necessary
Ingestion : Seek medical advice

บริษัท เบรนน์แท็ก อินกรีเดียนส์ (ประเทศไทย) จำกัด (มหาชน)
1168/98-100 อาคารลุมพินีทาวเวอร์ ชั้น 33
ถนนพระราม 4 แขวงทุ่งมหาเมฆ
เขตสาทร กรุงเทพฯ 10120

6. FIRE FIGHTING MEASURES

Flash point	: Not determined
Auto ignition temperature	: Not determined
Flammable limit (%)	: Not determined
Fire & explosion hazards	: Zinc oxide, calcium oxide and carbon monoxide
Extinguishing media	: Foam, dry powder and CO_2
Special fire fighting procedure	: Avoid high pressure spray; this may cause spattering and spread the fire. Avoid dust cloud which forms explosion hazard. Firemen should equip with safety protective equipment

7. ACCIDENTAL RELEASE MEASURES

Spillage	: Remove by vacuum cleaner, or cover with damp sand or saw dust if sweep

8. HANDLING AND STORAGE

Handling	: Open packaging bag carefully, avoid spillage, wash hand after handling
Storage	: Store in cool, dry place. Ground all equipment containing material. Avoid exposure to sunlight and keep away from food & beverage.

9. EXPOSURE CONTROL/PERSON PROTECTION

Exposure limit	: 10mg/m^3 (TWA1992-93 as stearate)
Ventilation	: Use adequate ventilation to prevent dust and comply with TLV
Personal protective	
Respiratory	: Dust respirator
Eye	: Recommended but not essential
Gloves	: Recommended
Clothing	: Overall or dust cloth, change daily

10. STABILITY AND REACTIVITY

Stability	: Stable under normal condition of storage & transport
Incompatibility (material to avoid)	: Can react with strong acids
Hazardous decomposition products	: Zinc oxide, calcium oxide and carbon monoxide
Hazardous polymerisation	: Will not occur

บริษัท เบรนน์แท็ก อินกรีเดียนส์ (ประเทศไทย) จำกัด (มหาชน)
1168/93-100 อาคารลุมพินีทาวเวอร์ ชั้น 33
ถนนพระราม 4 แขวงทุ่งมหาเมฆ
10120

11. TOXICOLOGICAL INFORMATION

Acute toxicity
LD50 oral : No information
LD50 dermic : No information
Chronic toxicity : Not determined.

Further toxicological information
Eye contact : May cause irritation
Skin contact : May cause irritation
Inhalation : May cause irritation of the respiratory system
Ingestion : May cause moderate gastrointestinal discomfort if swallowed. Large dose may cause abdominal spasms and diarrhea.

12. ECOLOGYICAL INFORMATION

Mobility : No information
Bioaccumulation : No information
Biodegradability : No information

13. DISPOSAL CONSIDERATION

Disposal : Dispose to local regulation and act

14. TRANSPORATION INFORMATION

UN no. : Not available
T.D.G. Classification : Not classified
Packing group : Not classified
Special shipping instructions : Not available

15. REGULATORY INFORMATION

Classification : Not classified
Risk phrases : R22 – Harmful if swallowed
Safety phrases : S44 – If you feel unwell, seek medical advice
S28 – After contact with skin, wash immediately with plenty of water and soap.

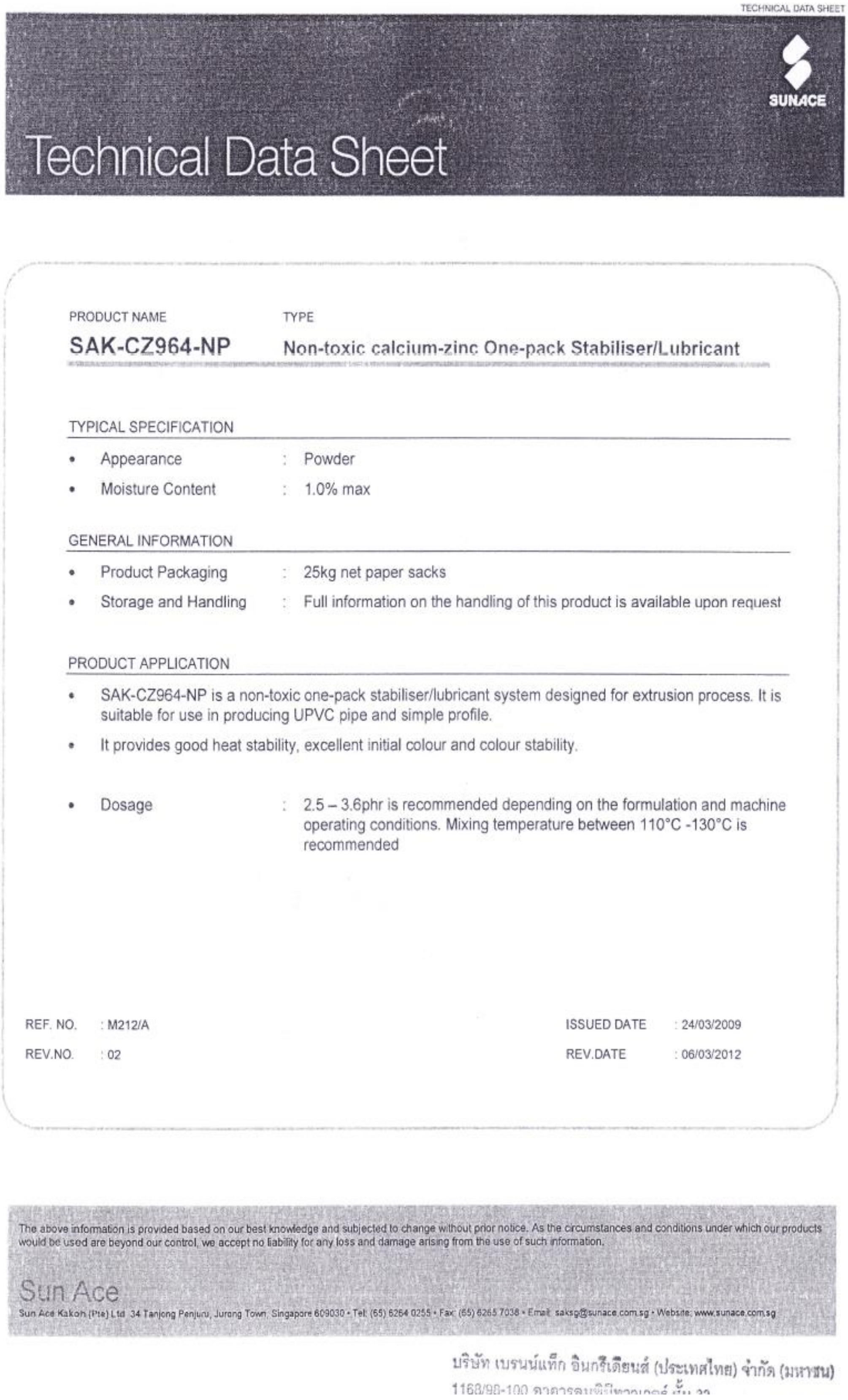
Other regulations, restrictions and prohibiting stipulations
: Handle in accordance with good industrial hygiene and safety practice.

บริษัท เบรนท์แท็ก อินกรีเดียนส์ (ประเทศไทย) จำกัด (มหาชน)
1168/98-100 อาคารลุมพินีทาวเวอร์ ชั้น 33
ถนนพระราม 4 แขวงทุ่งมหาเมฆ

16. OTHER INFORMATION

None

Appendix D.3: Calcium-zinc one pack (SAK-CZ964-NP) specification sheet.



TECHNICAL DATA SHEET

SUNACE

Technical Data Sheet

PRODUCT NAME	TYPE
SAK-CZ964-NP	**Non-toxic calcium-zinc One-pack Stabiliser/Lubricant**

TYPICAL SPECIFICATION

- Appearance : Powder
- Moisture Content : 1.0% max

GENERAL INFORMATION

- Product Packaging : 25kg net paper sacks
- Storage and Handling : Full information on the handling of this product is available upon request

PRODUCT APPLICATION

- SAK-CZ964-NP is a non-toxic one-pack stabiliser/lubricant system designed for extrusion process. It is suitable for use in producing UPVC pipe and simple profile.
- It provides good heat stability, excellent initial colour and colour stability.

- Dosage : 2.5 – 3.6phr is recommended depending on the formulation and machine operating conditions. Mixing temperature between 110°C -130°C is recommended

REF. NO. : M212/A
REV.NO. : 02
ISSUED DATE : 24/03/2009
REV.DATE : 06/03/2012

Sun Ace

Sun Ace Kakoh (Pte) Ltd 34 Tanjong Penjuru, Jurong Town, Singapore 609030 • Tel: (65) 6264 0255 • Fax: (65) 6265 7038 • Email: saksg@sunace.com.sg • Website: www.sunace.com.sg

บริษัท เบรนน์แท็ก อินกรีเดียนส์ (ประเทศไทย) จำกัด (มหาชน)
1168/98-100 อาคารลุมพินีทาวเวอร์ ชั้น

MATERIAL SAFETY DATA SHEET

SUN ACE KAKOH PTE LTD
34 TANJONG PENJURU, JURONG TOWN
SINGAPORE 609030

TEL : (65) - 6264 0255
FAX : (65) - 6265 7038

Contact person: Chemists (Technical Department)

---

1. PRODUCT IDENTIFICATION

Product name : Calcium Zinc complex
Chemical name : Mixture
Chemical family : Mixture
Manufacturer's code : SAK-CZ964-NP
Use : PVC stabiliser and lubricant

---

2. COMPOSITION/INFORMATION ON INGREDIENT

Chemical name	Approx. %	Hazard data
Calcium and Zinc	(Trade Secret)	TLV 92 – 93 : 10mg/m^3 (as stearate)

---

3. PHYSICAL AND CHEMICAL PROPERTIES

Appearance : Powder
Odour : Not determined
Solubility in water : Insoluble
Boiling point (°C) : Not determined
Melting point (°C) : 100 (slight melt)
Vapour pressure (mm of Hg at 25°C) : Not determined
Volatile percentage (as water) : < 2 %
Evaporation rate : Not determined
Vapour density : Not determined
Specific gravity : Not determined

---

4. HAZARD IDENTIFICATION

Toxic : None known, product is of relatively low toxicity

---

5. FIRST AID MEASURES

Eye contact : Wash with clean water
Skin contact : Wash with clean water
Inhalation : Remove from exposure, seek medical advice if necessary
Ingestion : Seek medical advice

[illegible]แท็ก อินกรีเดียนส์ (ประเทศไทย) จำกัด (มหาชน)
11[illegible]/93-100 อาคารลุมพินีทาวเวอร์ ชั้น 33
ถนนพระราม 4 แขวงทุ่งมหาเมฆ

6. FIRE FIGHTING MEASURES

Flash point : Not determined
Auto ignition temperature : Not determined
Flammable limit (%) : Not determined
Fire & explosion hazards : Zinc oxide, calcium oxide and carbon monoxide
Extinguishing media : Foam, dry powder and CO_2
Special fire fighting procedure : Avoid high pressure spray; this may cause spattering and spread the fire. Avoid dust cloud which forms explosion hazard. Firemen should equip with safety protective equipment

7. ACCIDENTAL RELEASE MEASURES

Spillage : Remove by vacuum cleaner, or cover with damp sand or saw dust if sweep

8. HANDLING AND STORAGE

Handling : Open packaging bag carefully, avoid spillage, wash hand after handling
Storage : Store in cool, dry place. Ground all equipment containing material. Avoid exposure to sunlight and keep away from food & beverage.

9. EXPOSURE CONTROL/PERSON PROTECTION

Exposure limit : $10 mg/m^3$ (TWA1992-93 as stearate)
Ventilation : Use adequate ventilation to prevent dust and comply with TLV

Personal protective
- Respiratory : Dust respirator
- Eye : Goggle recommended but not essential
- Gloves : Recommended
- Clothing : Overall or dust cloth, change daily

10. STABILITY AND REACTIVITY

Stability : Stable under normal condition of storage & transport
Incompatibility (material to avoid) : Can react with strong acids
Hazardous decomposition products : Zinc oxide, calcium oxide and carbon monoxide
Hazardous polymerisation : Will not occur

11. TOXICOLOGICAL INFORMATION

Acute toxicity
LD50 oral : No information
LD50 dermic : No information
Chronic toxicity : Not determined

Further toxicological information
Eye contact : May cause irritation
Skin contact : May cause irritation
Inhalation : May cause irritation of the respiratory system
Ingestion : May cause moderate gastrointestinal discomfort if swallowed. Large dose may cause abdominal spasms and diarrhea.

12. ECOLOGYICAL INFORMATION

Mobility : No information
Bioaccumulation : No information
Biodegradability : No information

13. DISPOSAL CONSIDERATION

Disposal : Dispose to local regulation and act

14. TRANSPORATION INFORMATION

UN no. : Not classified
T.D.G. Classification : Not classified
Packing group : -
Special shipping instructions : -

15. REGULATORY INFORMATION

Classification : Not classified
Risk phrases : R22 – Harmful if swallowed
Safety phrases : S44 – If you feel unwell, seek medical advice
S28 – After contact with skin, wash immediately with plenty of water and soap.

Other regulations, restrictions and prohibiting stipulations
: Handle in accordance with good industrial hygiene and safety practice.

บริษัท เบรนน์แท็ก อินกรีเดียนส์ (ประเทศไทย) จำกัด (มหาชน)
1168/98-100 อาคารลุมพินีทาวเวอร์ ชั้น 33
ถนนพระราม 4 แขวงทุ่งมหาเมฆ

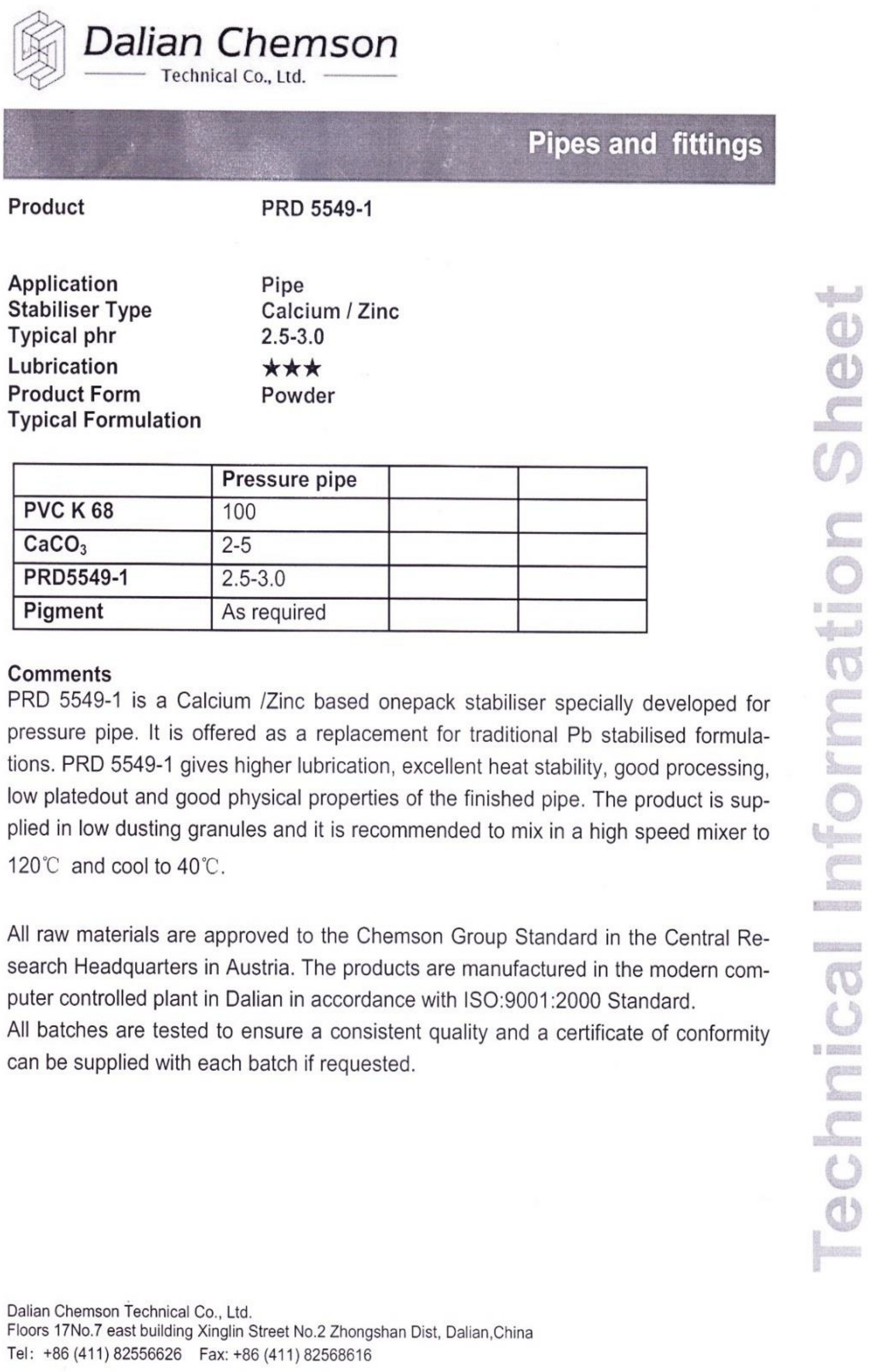
16. OTHER INFORMATION

None

"To the best of our knowledge the information contained herein is correct at the time of writing, and it is subject to change without prior notice. All chemicals may present unknown health hazards and should be used with caution. Although certain hazards are described herein, we cannot guarantee that these are the only hazards which exist. Final determination of suitability of the chemical is the sole responsibility of the user. Users of any chemical should satisfy themselves that the conditions and methods of use assure that the chemical is used safely.

No warranty expressed or implied is made as to the accuracy, completeness of the information contained herein."

Appendix D.4: Calcium-zinc one pack (PRD 5549-1) specification sheet.



Dalian Chemson
Technical Co., Ltd.

Pipes and fittings

Technical Information Sheet

Product	**PRD 5549-1**
Application	Pipe
Stabiliser Type	Calcium / Zinc
Typical phr	2.5-3.0
Lubrication	★★★
Product Form	Powder
Typical Formulation	

	Pressure pipe		
PVC K 68	100		
$CaCO_3$	2-5		
PRD5549-1	2.5-3.0		
Pigment	As required		

Comments

PRD 5549-1 is a Calcium /Zinc based onepack stabiliser specially developed for pressure pipe. It is offered as a replacement for traditional Pb stabilised formulations. PRD 5549-1 gives higher lubrication, excellent heat stability, good processing, low platedout and good physical properties of the finished pipe. The product is supplied in low dusting granules and it is recommended to mix in a high speed mixer to 120℃ and cool to 40℃.

All raw materials are approved to the Chemson Group Standard in the Central Research Headquarters in Austria. The products are manufactured in the modern computer controlled plant in Dalian in accordance with ISO:9001:2000 Standard.
All batches are tested to ensure a consistent quality and a certificate of conformity can be supplied with each batch if requested.

Dalian Chemson Technical Co., Ltd.
Floors 17No.7 east building Xinglin Street No.2 Zhongshan Dist, Dalian,China
Tel：+86 (411) 82556626 Fax: +86 (411) 82568616

Figure D.5: Calcium-zinc one pack (MCZ-102P) specification sheet.

บริษัท สยามสเตบิไลเซอร์สแอนด์เคมิคอลส์ จำกัด
SIAM STABILIZERS AND CHEMICALS CO., LTD.
ชั้น 16 อาคารรัจนาการ 183 ถนนสาทรใต้ แขวงยานนาวา เขตสาทร กรุงเทพฯ 10120 โทร : (02) 676-6000 ต่อ 5161-5166 สายตรง (02) 6766550-1 โทรสาร : (02) 676-6050
16th Fl. Rajanakarn Bldg., 183 South Sathorn Rd., Sathorn, Bangkok Thailand 10120 Tel : (02) 676-6000 Ext. 5161-5166 Direct (02) 6766550-1 Fax : (02) 676-6050

CERTIFICATE OF ANALYSIS

May 30, 2013

PRODUCT NAME : STABINEX MCZ-102P

REF NO. NL-QC-149/2013

CUSTOMER NAME : คุณอรัญ อัศวโกสินชัย
(นิสิตภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย)

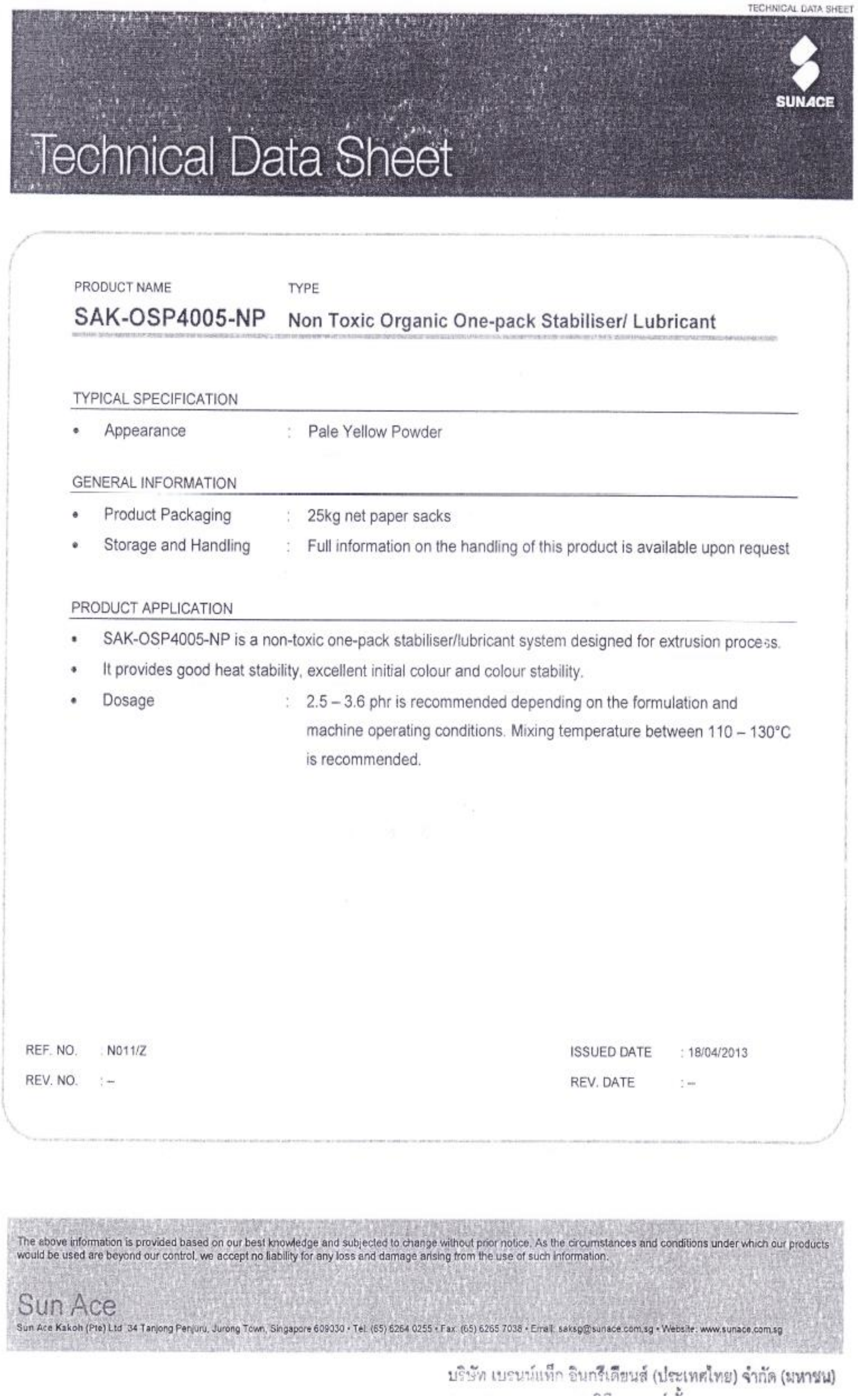
DESCRIPTION	SPECIFICATION	TEST METHOD	RESULT OF ANALYSIS			
LOT NO.			CJN005	-	-	-
QUANTITY(kgs.)			5	-	-	-
		SSC METHOD				
APPEARANCE	WHITE POWDER	WI-QC-032	PASS	-	-	-
MOISTURE (%)	< 3.0	WI-QC-001	0.4	-	-	-
BULK DENSITY (gm/ml)	0.30 - 0.70	WI-QC-003	0.44	-	-	-

SIAM STABILIZERS AND CHEMICALS CO., LTD.
SSC PASSED SSC
QUALITY CONTROL

CHEMIST

โรงงาน เลขที่ 5 ถนนปกรณ์สงเคราะห์ราษฎร์ ต.มาบตาพุด อ.เมือง จ.ระยอง 21150 โทร. (038) 683450-53 โทรสาร (038) 683449
Factory 5 Pakorn Songkhro Rat Rd., T. Map Ta Phut, A. Muang, Rayong Thailand 21150 Tel. (038) 683450-53 Fax. (038) 683449
]

Appendix D.6: Organic based stabilizer from Sunace Co., Ltd. (SAK-OSP4005-NP) specification sheet.



TECHNICAL DATA SHEET

SUNACE

Technical Data Sheet

PRODUCT NAME

SAK-OSP4005-NP

TYPE

Non Toxic Organic One-pack Stabiliser/ Lubricant

TYPICAL SPECIFICATION

- Appearance : Pale Yellow Powder

GENERAL INFORMATION

- Product Packaging : 25kg net paper sacks
- Storage and Handling : Full information on the handling of this product is available upon request

PRODUCT APPLICATION

- SAK-OSP4005-NP is a non-toxic one-pack stabiliser/lubricant system designed for extrusion process.
- It provides good heat stability, excellent initial colour and colour stability.
- Dosage : 2.5 – 3.6 phr is recommended depending on the formulation and machine operating conditions. Mixing temperature between 110 – 130°C is recommended.

REF. NO. : N011/Z

REV. NO. : –

ISSUED DATE : 18/04/2013

REV. DATE : –

Sun Ace

Sun Ace Kakoh (Pte) Ltd 34 Tanjong Penjuru, Jurong Town, Singapore 609030 • Tel. (65) 6264 0255 • Fax. (65) 6265 7038 • Email: saksg@sunace.com.sg • Website: www.sunace.com.sg

บริษัท เบรนน์แท็ก อินกรีเดียนส์ (ประเทศไทย) จำกัด (มหาชน)

MATERIAL SAFETY DATA SHEET

SUN ACE KAKOH PTE LTD
34 TANJONG PENJURU, JURONG TOWN
SINGAPORE 609030

TEL : (65) - 6264 0255
FAX : (65) - 6265 7038

Contact person: Chemists (Technical Department)

1. PRODUCT IDENTIFICATION

Product name : Organic based complex
Chemical name : Mixture
Chemical family : Mixture
Manufacturer's code : SAK-OSP4005-NP
Use : PVC stabilizer/booster

2. COMPOSITION/INFORMATION ON INGREDIENT

Chemical name	Approx. %	Hazard data
Organic compound	(Trade Secret)	No information

3. PHYSICAL AND CHEMICAL PROPERTIES

Appearance : Powder
Odour : Not determined
Solubility in water : Insoluble
Boiling point (°C) : Not determined
Melting point (°C) : 100°C (partial melt)
Vapour pressure (mm of Hg at 25°C) : Not determined
Evaporation rate : Not determined
Vapour density : Not determined
Specific gravity : Not determined

4. HAZARD IDENTIFICATION

Toxic : None known, product is of relatively low toxicity

5. FIRST AID MEASURES

Eye contact : Wash with clean water
Skin contact : Wash with clean water
Inhalation : Remove from exposure, seek medical advice if necessary
Ingestion : Seek medical advice

REF. NO. : N011/Z
REV. NO. : --

ISSUED DATE : 18/04/2013
REV. DATE : --

บริษัท เบรนน์แท็ก อินกรีเดียนส์ (ประเทศไทย) จำกัด (มหาช
1163/98-100 อาคารจุมพินีทาวเวอร์ ชั้น 33

6. FIRE FIGHTING MEASURES

Flash point : Not determined
Auto ignition temperature : Not determined
Flammable limit (%) : Not determined
Fire & explosion hazards : carbon monoxide
Extinguishing media : Foam, dry powder and CO_2
Special fire fighting procedure : Avoid high pressure spray; this may cause spattering and spread the fire. Avoid dust cloud which forms explosion hazard. Firemen should equip with safety protective equipment

7. ACCIDENTAL RELEASE MEASURES

Spillage : Remove by vacuum cleaner, or cover with damp sand or saw dust if sweep

8. HANDLING AND STORAGE

Handling : Open packaging bag carefully, avoid spillage, wash hand after handling
Storage : Store in cool, dry place. Ground all equipment containing material. Avoid exposure to sunlight and keep away from food & beverage.

9. EXPOSURE CONTROL/PERSON PROTECTION

Exposure limit : No information
Ventilation : Use adequate ventilation to prevent dust
Personal protective
    Respiratory : Dust respirator
    Eye : Recommended but not essential
    Gloves : Recommended
    Clothing : Overall or dust cloth, change daily

10. STABILITY AND REACTIVITY

Stability : Stable under normal condition of storage & transport
Incompatibility : Can react with strong acids and strong reducing agents
Hazardous decomposition products : carbon monoxide
Hazardous polymerisation : Will not occur

11. TOXICOLOGICAL INFORMATION

Acute toxicity
LD50 oral : No information
LD50 dermic : No information
Chronic toxicity : Not determined

Further toxicological information
Eye contact : May cause irritation
Skin contact : May cause irritation
Inhalation : May cause irritation of the respiratory system
Ingestion : May cause moderate gastrointestinal discomfort if swallowed. Large dose may cause abdominal spasms and diarrhea.

12. ECOLOGYICAL INFORMATION

Mobility : No information
Bioaccumulation : No information
Biodegradability : No information

13. DISPOSAL CONSIDERATION

Disposal : Dispose to local regulation and act

14. TRANSPORATION INFORMATION

UN no. : Not classified
T.D.G. Classification : Not classified
Packing group : Not classified
Special shipping instructions : Not classified

15. REGULATORY INFORMATION

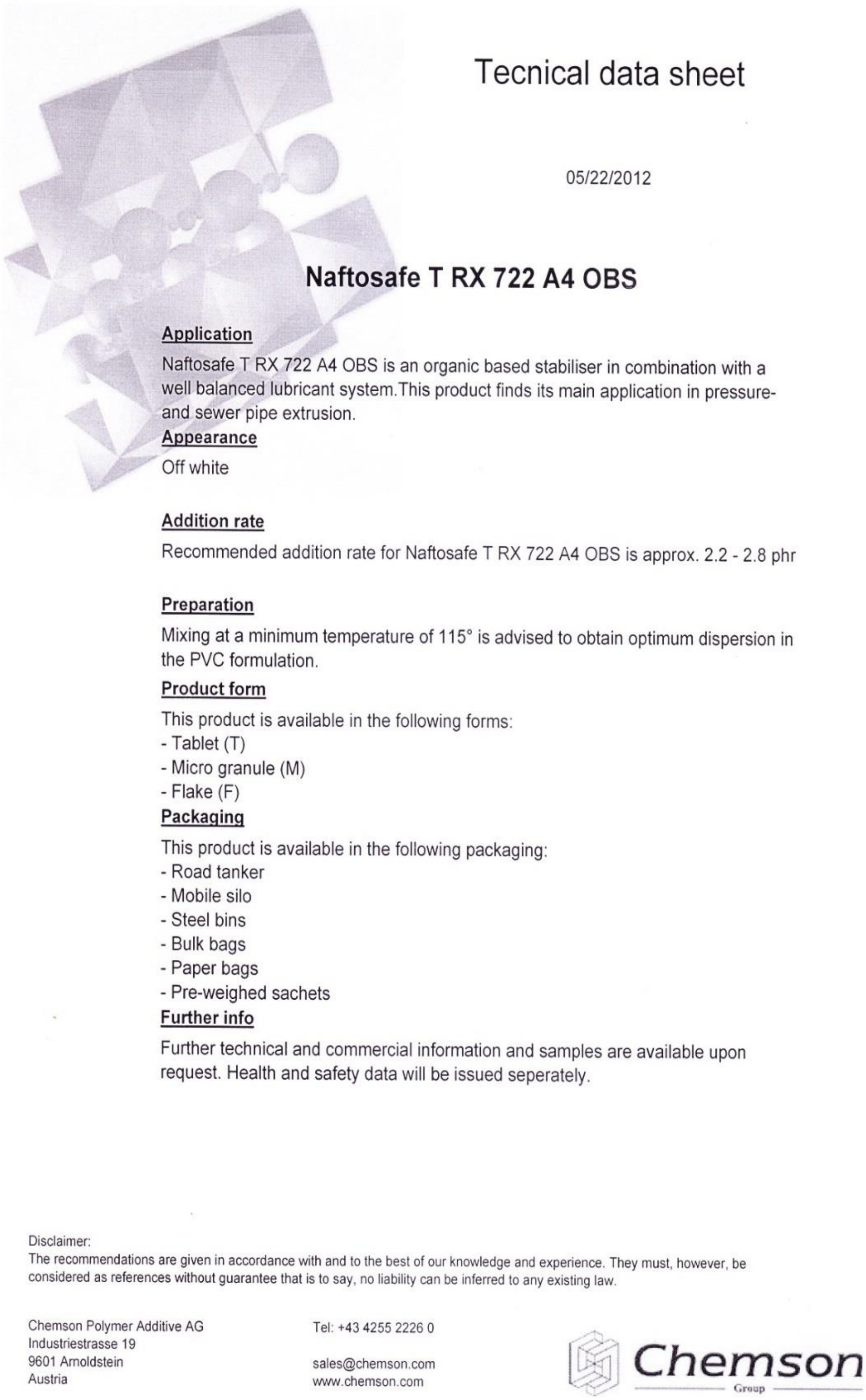
Classification : Not classified
Risk phrases : R22 – Harmful if swallowed
Safety phrases : S44 – If you feel unwell, seek medical advice
S28 – After contact with skin, wash immediately with plenty of water and soap.

Other regulations, restrictions and prohibiting stipulations
: Handle in accordance with good industrial hygiene and safety practice.

16. OTHER INFORMATION

None

Appendix D.7: Organic based stabilizer from Chemson Co., Ltd. (T RX 722 A4 OBS) specification sheet.



Tecnical data sheet

05/22/2012

Naftosafe T RX 722 A4 OBS

Application

Naftosafe T RX 722 A4 OBS is an organic based stabiliser in combination with a well balanced lubricant system.This product finds its main application in pressure- and sewer pipe extrusion.

Appearance

Off white

Addition rate

Recommended addition rate for Naftosafe T RX 722 A4 OBS is approx. 2.2 - 2.8 phr

Preparation

Mixing at a minimum temperature of 115° is advised to obtain optimum dispersion in the PVC formulation.

Product form

This product is available in the following forms:

- Tablet (T)
- Micro granule (M)
- Flake (F)

Packaging

This product is available in the following packaging:

- Road tanker
- Mobile silo
- Steel bins
- Bulk bags
- Paper bags
- Pre-weighed sachets

Further info

Further technical and commercial information and samples are available upon request. Health and safety data will be issued seperately.

Disclaimer:
The recommendations are given in accordance with and to the best of our knowledge and experience. They must, however, be considered as references without guarantee that is to say, no liability can be inferred to any existing law.

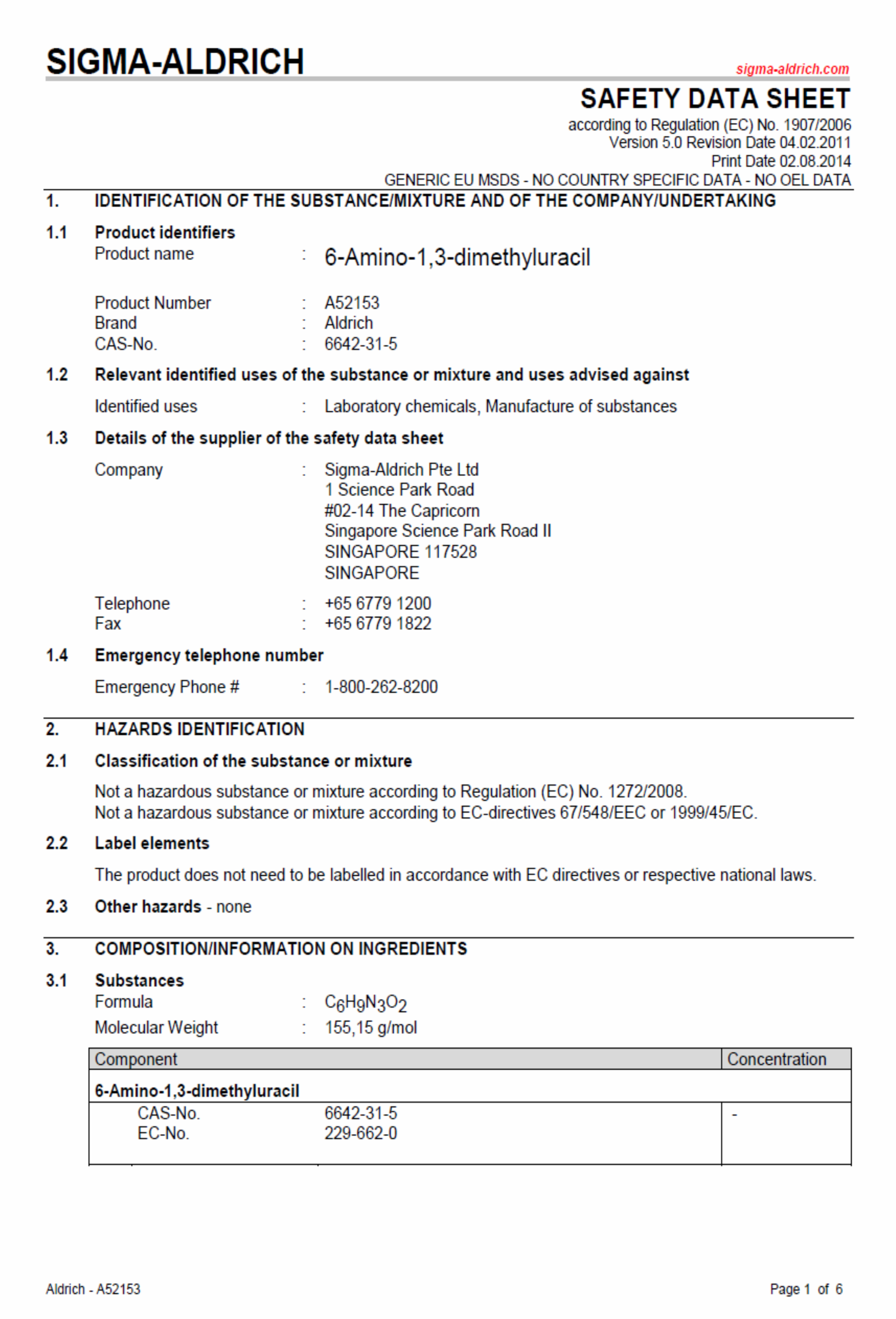
Chemson Polymer Additive AG
Industriestrasse 19
9601 Arnoldstein
Austria

Tel: +43 4255 2226 0

sales@chemson.com
www.chemson.com

Chemson
Group

Appendix D.8: 1,3 Dimethyl-6-aminouracil specification sheet.



SIGMA-ALDRICH sigma-aldrich.com

SAFETY DATA SHEET

according to Regulation (EC) No. 1907/2006
Version 5.0 Revision Date 04.02.2011
Print Date 02.08.2014
GENERIC EU MSDS - NO COUNTRY SPECIFIC DATA - NO OEL DATA

1. IDENTIFICATION OF THE SUBSTANCE/MIXTURE AND OF THE COMPANY/UNDERTAKING

1.1 Product identifiers

Product name : 6-Amino-1,3-dimethyluracil

Product Number : A52153
Brand : Aldrich
CAS-No. : 6642-31-5

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses : Laboratory chemicals, Manufacture of substances

1.3 Details of the supplier of the safety data sheet

Company : Sigma-Aldrich Pte Ltd
1 Science Park Road
#02-14 The Capricorn
Singapore Science Park Road II
SINGAPORE 117528
SINGAPORE

Telephone : +65 6779 1200
Fax : +65 6779 1822

1.4 Emergency telephone number

Emergency Phone # : 1-800-262-8200

2. HAZARDS IDENTIFICATION

2.1 Classification of the substance or mixture

Not a hazardous substance or mixture according to Regulation (EC) No. 1272/2008.
Not a hazardous substance or mixture according to EC-directives 67/548/EEC or 1999/45/EC.

2.2 Label elements

The product does not need to be labelled in accordance with EC directives or respective national laws.

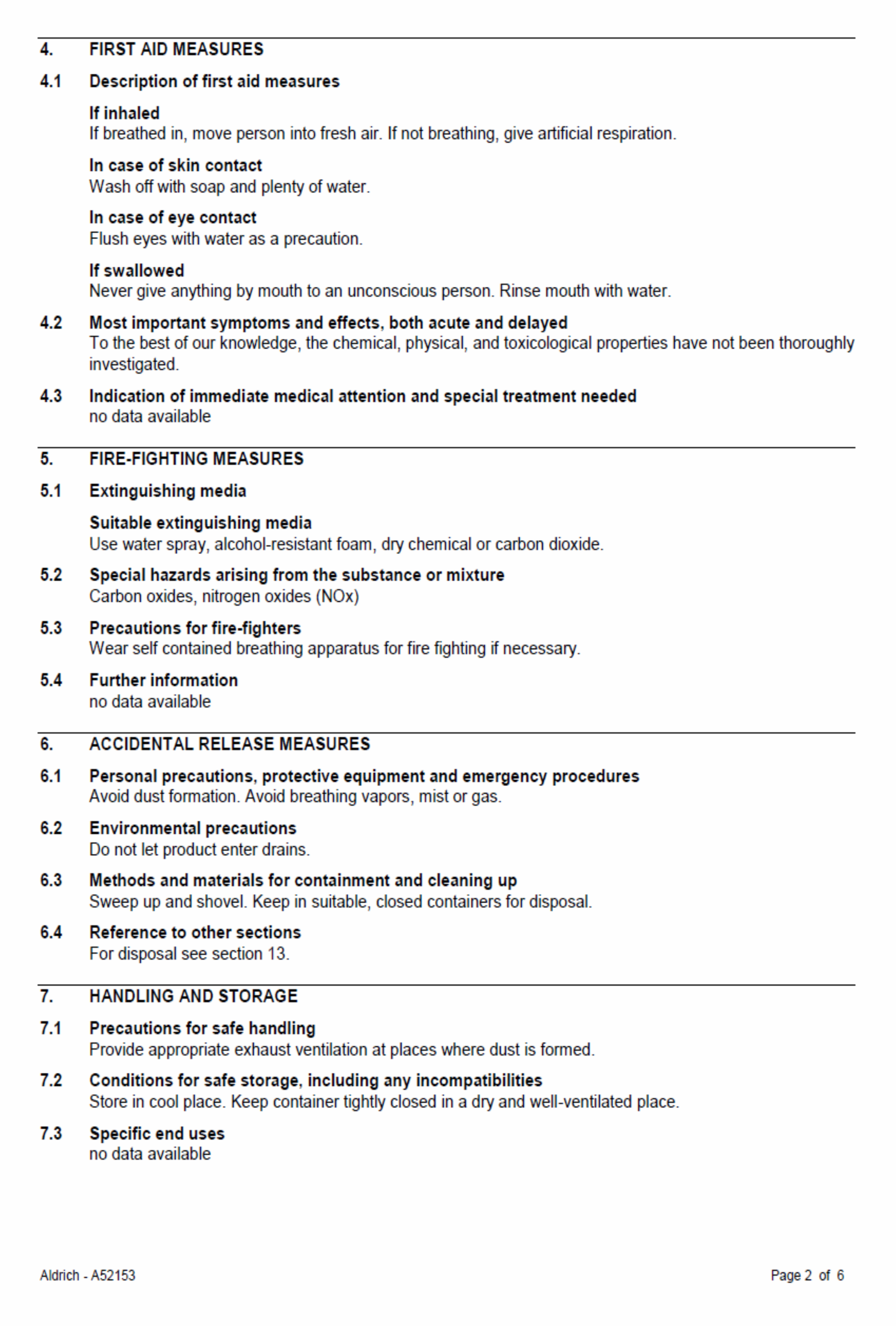
2.3 Other hazards - none

3. COMPOSITION/INFORMATION ON INGREDIENTS

3.1 Substances

Formula : $C_6H_9N_3O_2$
Molecular Weight : 155,15 g/mol

Component		Concentration
6-Amino-1,3-dimethyluracil		
CAS-No. EC-No.	6642-31-5 229-662-0	-



4. FIRST AID MEASURES

4.1 Description of first aid measures

If inhaled
If breathed in, move person into fresh air. If not breathing, give artificial respiration.

In case of skin contact
Wash off with soap and plenty of water.

In case of eye contact
Flush eyes with water as a precaution.

If swallowed
Never give anything by mouth to an unconscious person. Rinse mouth with water.

4.2 Most important symptoms and effects, both acute and delayed

To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

4.3 Indication of immediate medical attention and special treatment needed

no data available

5. FIRE-FIGHTING MEASURES

5.1 Extinguishing media

Suitable extinguishing media
Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

5.2 Special hazards arising from the substance or mixture

Carbon oxides, nitrogen oxides (NOx)

5.3 Precautions for fire-fighters

Wear self contained breathing apparatus for fire fighting if necessary.

5.4 Further information

no data available

6. ACCIDENTAL RELEASE MEASURES

6.1 Personal precautions, protective equipment and emergency procedures

Avoid dust formation. Avoid breathing vapors, mist or gas.

6.2 Environmental precautions

Do not let product enter drains.

6.3 Methods and materials for containment and cleaning up

Sweep up and shovel. Keep in suitable, closed containers for disposal.

6.4 Reference to other sections

For disposal see section 13.

7. HANDLING AND STORAGE

7.1 Precautions for safe handling

Provide appropriate exhaust ventilation at places where dust is formed.

7.2 Conditions for safe storage, including any incompatibilities

Store in cool place. Keep container tightly closed in a dry and well-ventilated place.

7.3 Specific end uses

no data available

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

8.1 Control parameters

Components with workplace control parameters

8.2 Exposure controls

Appropriate engineering controls
General industrial hygiene practice.

Personal protective equipment

Eye/face protection
Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU).

Skin protection
Handle with gloves. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.

The selected protective gloves have to satisfy the specifications of EU Directive 89/686/EEC and the standard EN 374 derived from it.

Body Protection
Choose body protection in relation to its type, to the concentration and amount of dangerous substances, and to the specific work-place., The type of protective equipment must be selected according to the concentration and amount of the dangerous substance at the specific workplace.

Respiratory protection
Respiratory protection is not required. Where protection from nuisance levels of dusts are desired, use type N95 (US) or type P1 (EN 143) dust masks. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

9. PHYSICAL AND CHEMICAL PROPERTIES

9.1 Information on basic physical and chemical properties

a)	Appearance	Form: powder Colour: off-white
b)	Odour	no data available
c)	Odour Threshold	no data available
d)	pH	no data available
e)	Melting/freezing point	Melting point/range: 295 °C - dec.
f)	Initial boiling point and boiling range	no data available
g)	Flash point	no data available
h)	Evaporation rate	no data available
i)	Flammability (solid, gas)	no data available
j)	Upper/lower flammability or explosive limits	no data available
k)	Vapour pressure	no data available
l)	Vapour density	no data available
m)	Relative density	no data available
n)	Water solubility	no data available

o)	Partition coefficient: n-octanol/water	no data available
p)	Autoignition temperature	no data available
q)	Decomposition temperature	no data available
r)	Viscosity	no data available
s)	Explosive properties	no data available
t)	Oxidizing properties	no data available

9.2 Other safety information

no data available

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10. STABILITY AND REACTIVITY

10.1 Reactivity

no data available

10.2 Chemical stability

no data available

10.3 Possibility of hazardous reactions

no data available

10.4 Conditions to avoid

no data available

10.5 Incompatible materials

no data available

10.6 Hazardous decomposition products

Other decomposition products - no data available

---

11. TOXICOLOGICAL INFORMATION

11.1 Information on toxicological effects

Acute toxicity

LD50 Oral - mouse - > 1.000 mg/kg

Skin corrosion/irritation

no data available

Serious eye damage/eye irritation

no data available

Respiratory or skin sensitization

no data available

Germ cell mutagenicity

Carcinogenicity

IARC: No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.

Reproductive toxicity

Specific target organ toxicity - single exposure

no data available

Specific target organ toxicity - repeated exposure

no data available

Aspiration hazard

no data available

Potential health effects

Inhalation	May be harmful if inhaled. May cause respiratory tract irritation.
Ingestion	May be harmful if swallowed.
Skin	May be harmful if absorbed through skin. May cause skin irritation.
Eyes	May cause eye irritation.

Signs and Symptoms of Exposure
To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

Additional Information
RTECS: YQ8755000

12. ECOLOGICAL INFORMATION

12.1 Toxicity
no data available

12.2 Persistence and degradability
no data available

12.3 Bioaccumulative potential
no data available

12.4 Mobility in soil
no data available

12.5 Results of PBT and vPvB assessment
no data available

12.6 Other adverse effects
no data available

13. DISPOSAL CONSIDERATIONS

13.1 Waste treatment methods

Product
Offer surplus and non-recyclable solutions to a licensed disposal company.

Contaminated packaging
Dispose of as unused product.

14. TRANSPORT INFORMATION

14.1 UN-Number
ADR/RID: - IMDG: - IATA: -

14.2 UN proper shipping name
ADR/RID: Not dangerous goods
IMDG: Not dangerous goods
IATA: Not dangerous goods

14.3 Transport hazard class(es)
ADR/RID: - IMDG: - IATA: -

14.4 Packaging group
ADR/RID: - IMDG: - IATA: -

14.5 Environmental hazards
ADR/RID: no IMDG Marine pollutant: no IATA: no

14.6 Special precautions for users
no data available

15. REGULATORY INFORMATION

This safety datasheet complies with the requirements of Regulation (EC) No. 1907/2006.

15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture

no data available

15.2 Chemical Safety Assessment

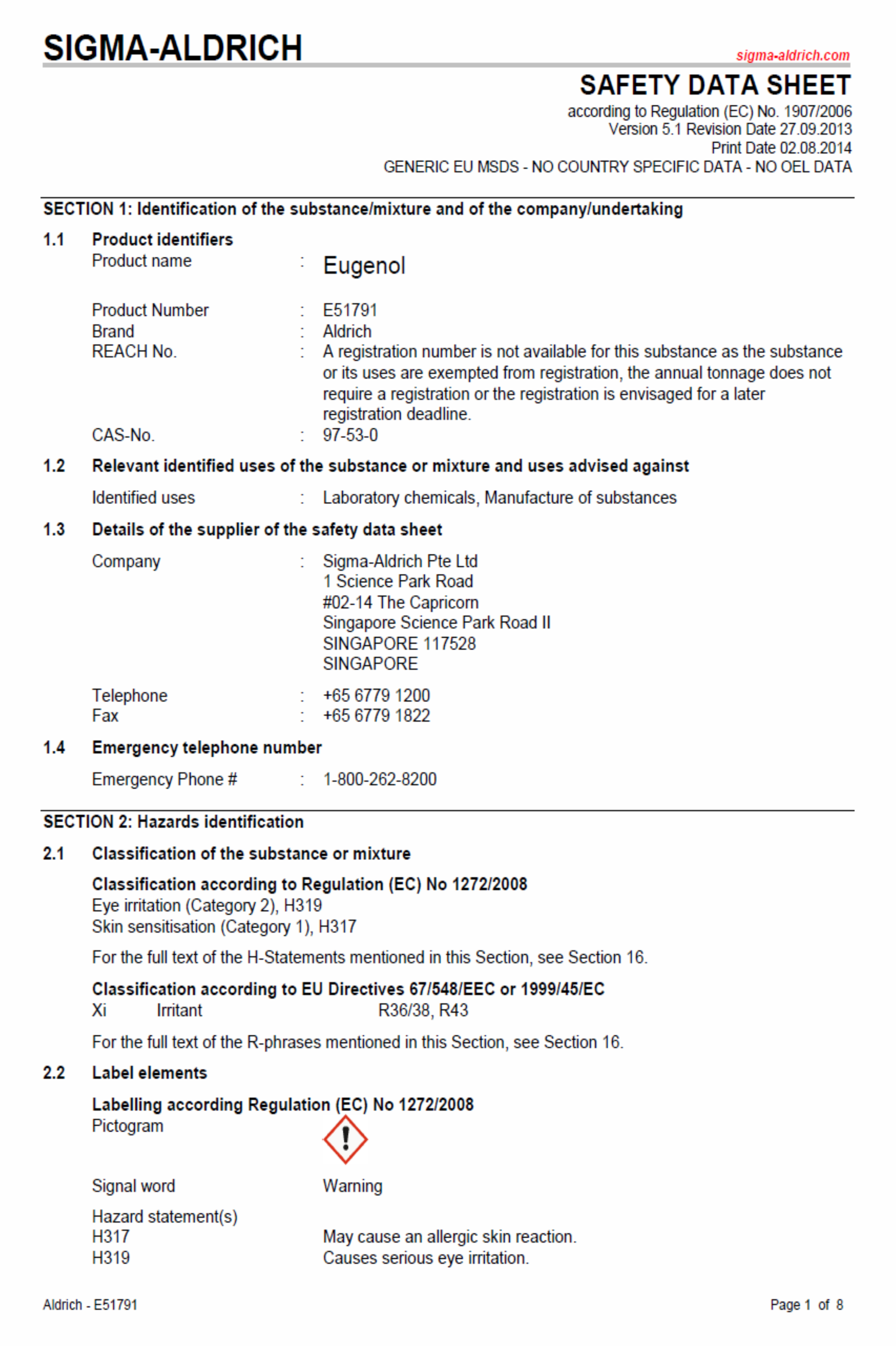
no data available

16. OTHER INFORMATION

Further information

The above information is believed to be correct but does not purport to be all inclusive and shall be used only as a guide. The information in this document is based on the present state of our knowledge and is applicable to the product with regard to appropriate safety precautions. It does not represent any guarantee of the properties of the product. Sigma-Aldrich Co., shall not be held liable for any damage resulting from handling or from contact with the above product. See reverse side of invoice or packing slip for additional terms and conditions of sale.

Appendix D.9: Eugenol specification sheet.



SIGMA-ALDRICH

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SAFETY DATA SHEET

according to Regulation (EC) No. 1907/2006
Version 5.1 Revision Date 27.09.2013
Print Date 02.08.2014
GENERIC EU MSDS - NO COUNTRY SPECIFIC DATA - NO OEL DATA

SECTION 1: Identification of the substance/mixture and of the company/undertaking

1.1 Product identifiers

Product name	: Eugenol
Product Number	: E51791
Brand	: Aldrich
REACH No.	: A registration number is not available for this substance as the substance or its uses are exempted from registration, the annual tonnage does not require a registration or the registration is envisaged for a later registration deadline.
CAS-No.	: 97-53-0

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses	: Laboratory chemicals, Manufacture of substances

1.3 Details of the supplier of the safety data sheet

Company	: Sigma-Aldrich Pte Ltd 1 Science Park Road #02-14 The Capricorn Singapore Science Park Road II SINGAPORE 117528 SINGAPORE
Telephone	: +65 6779 1200
Fax	: +65 6779 1822

1.4 Emergency telephone number

Emergency Phone #	: 1-800-262-8200

SECTION 2: Hazards identification

2.1 Classification of the substance or mixture

Classification according to Regulation (EC) No 1272/2008
Eye irritation (Category 2), H319
Skin sensitisation (Category 1), H317

For the full text of the H-Statements mentioned in this Section, see Section 16.

Classification according to EU Directives 67/548/EEC or 1999/45/EC

Xi	Irritant	R36/38, R43

For the full text of the R-phrases mentioned in this Section, see Section 16.

2.2 Label elements

Labelling according Regulation (EC) No 1272/2008

Pictogram	⚠
Signal word	Warning
Hazard statement(s)	
H317	May cause an allergic skin reaction.
H319	Causes serious eye irritation.

Precautionary statement(s)	
P280	Wear protective gloves.
P305 + P351 + P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
Supplemental Hazard Statements	none

2.3 Other hazards - none

SECTION 3: Composition/information on ingredients

3.1 Substances

Synonyms	: 2-Methoxy-4-(2-propenyl)phenol 4-Allyl-2-methoxyphenol 4-Allylguaiacol
Formula	: $C_{10}H_{12}O_2$
Molecular Weight	: 164,20 g/mol
CAS-No.	: 97-53-0
EC-No.	: 202-589-1

Hazardous ingredients according to Regulation (EC) No 1272/2008

Component		Classification	Concentration
Eugenol			
CAS-No. EC-No.	97-53-0 202-589-1	Eye Irrit. 2; Skin Sens. 1; H317, H319	<= 100 %

Hazardous ingredients according to Directive 1999/45/EC

Component		Classification	Concentration
Eugenol			
CAS-No. EC-No.	97-53-0 202-589-1	Xi, R36/38 - R43	<= 100 %

For the full text of the H-Statements and R-Phrases mentioned in this Section, see Section 16

SECTION 4: First aid measures

4.1 Description of first aid measures

General advice
Consult a physician. Show this safety data sheet to the doctor in attendance.

If inhaled
If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.

In case of skin contact
Wash off with soap and plenty of water. Consult a physician.

In case of eye contact
Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.

If swallowed
Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.

4.2 Most important symptoms and effects, both acute and delayed

The most important known symptoms and effects are described in the labelling (see section 2.2) and/or in section 11

4.3 Indication of any immediate medical attention and special treatment needed

no data available

SECTION 5: Firefighting measures

5.1 Extinguishing media

Suitable extinguishing media
Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

5.2 Special hazards arising from the substance or mixture

Carbon oxides

5.3 Advice for firefighters

Wear self contained breathing apparatus for fire fighting if necessary.

5.4 Further information

no data available

SECTION 6: Accidental release measures

6.1 Personal precautions, protective equipment and emergency procedures

Use personal protective equipment. Avoid breathing vapours, mist or gas. Ensure adequate ventilation. For personal protection see section 8.

6.2 Environmental precautions

Prevent further leakage or spillage if safe to do so. Do not let product enter drains. Discharge into the environment must be avoided.

6.3 Methods and materials for containment and cleaning up

Soak up with inert absorbent material and dispose of as hazardous waste. Keep in suitable, closed containers for disposal.

6.4 Reference to other sections

For disposal see section 13.

SECTION 7: Handling and storage

7.1 Precautions for safe handling

Avoid contact with skin and eyes. Avoid inhalation of vapour or mist.
For precautions see section 2.2.

7.2 Conditions for safe storage, including any incompatibilities

Store in cool place. Keep container tightly closed in a dry and well-ventilated place.

Store under inert gas. Air sensitive.

7.3 Specific end use(s)

A part from the uses mentioned in section 1.2 no other specific uses are stipulated

SECTION 8: Exposure controls/personal protection

8.1 Control parameters

Components with workplace control parameters

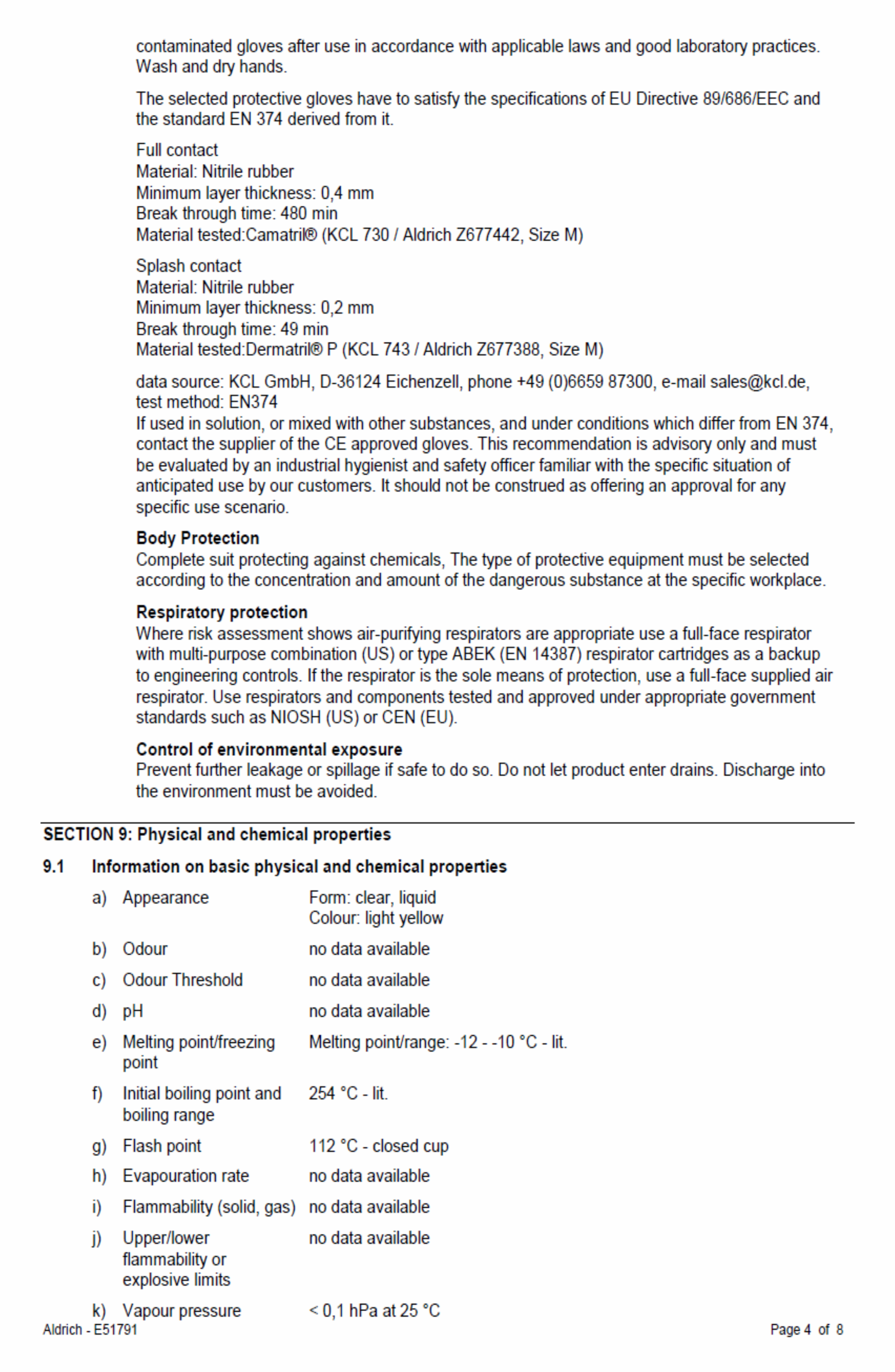
8.2 Exposure controls

Appropriate engineering controls
Handle in accordance with good industrial hygiene and safety practice. Wash hands before breaks and at the end of workday.

Personal protective equipment

Eye/face protection
Face shield and safety glasses Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU).

Skin protection
Handle with gloves. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of



contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.

The selected protective gloves have to satisfy the specifications of EU Directive 89/686/EEC and the standard EN 374 derived from it.

Full contact
Material: Nitrile rubber
Minimum layer thickness: 0,4 mm
Break through time: 480 min
Material tested:Camatril® (KCL 730 / Aldrich Z677442, Size M)

Splash contact
Material: Nitrile rubber
Minimum layer thickness: 0,2 mm
Break through time: 49 min
Material tested:Dermatril® P (KCL 743 / Aldrich Z677388, Size M)

data source: KCL GmbH, D-36124 Eichenzell, phone +49 (0)6659 87300, e-mail sales@kcl.de, test method: EN374
If used in solution, or mixed with other substances, and under conditions which differ from EN 374, contact the supplier of the CE approved gloves. This recommendation is advisory only and must be evaluated by an industrial hygienist and safety officer familiar with the specific situation of anticipated use by our customers. It should not be construed as offering an approval for any specific use scenario.

Body Protection
Complete suit protecting against chemicals, The type of protective equipment must be selected according to the concentration and amount of the dangerous substance at the specific workplace.

Respiratory protection
Where risk assessment shows air-purifying respirators are appropriate use a full-face respirator with multi-purpose combination (US) or type ABEK (EN 14387) respirator cartridges as a backup to engineering controls. If the respirator is the sole means of protection, use a full-face supplied air respirator. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

Control of environmental exposure
Prevent further leakage or spillage if safe to do so. Do not let product enter drains. Discharge into the environment must be avoided.

SECTION 9: Physical and chemical properties

9.1 Information on basic physical and chemical properties

a)	Appearance	Form: clear, liquid Colour: light yellow
b)	Odour	no data available
c)	Odour Threshold	no data available
d)	pH	no data available
e)	Melting point/freezing point	Melting point/range: -12 - -10 °C - lit.
f)	Initial boiling point and boiling range	254 °C - lit.
g)	Flash point	112 °C - closed cup
h)	Evapouration rate	no data available
i)	Flammability (solid, gas)	no data available
j)	Upper/lower flammability or explosive limits	no data available
k)	Vapour pressure	< 0,1 hPa at 25 °C

l)	Vapour density	no data available
m)	Relative density	1,067 g/cm3 at 25 °C
n)	Water solubility	no data available
o)	Partition coefficient: n-octanol/water	log Pow: 2,7
p)	Auto-ignition temperature	no data available
q)	Decomposition temperature	no data available
r)	Viscosity	no data available
s)	Explosive properties	no data available
t)	Oxidizing properties	no data available

9.2 Other safety information

no data available

SECTION 10: Stability and reactivity

10.1 Reactivity

no data available

10.2 Chemical stability

Stable under recommended storage conditions.

10.3 Possibility of hazardous reactions

no data available

10.4 Conditions to avoid

Air

10.5 Incompatible materials

Strong oxidizing agents

10.6 Hazardous decomposition products

Other decomposition products - no data available
In the event of fire: see section 5

SECTION 11: Toxicological information

11.1 Information on toxicological effects

Acute toxicity
LD50 Oral - rat - > 2.000 mg/kg
(OECD Test Guideline 423)

Skin corrosion/irritation
Skin - rabbit
Result: No skin irritation
(OECD Test Guideline 404)

Serious eye damage/eye irritation
Eyes - rabbit
Result: Irritating to eyes.
(OECD Test Guideline 405)

Respiratory or skin sensitisation
in vivo assay - mouse
May cause allergic skin reaction.
(OECD Test Guideline 429)

Germ cell mutagenicity
rat
Liver
DNA damage

mouse
lymphocyte
Mutation in mammalian somatic cells.

Hamster
Embryo
Unscheduled DNA synthesis

Hamster
Embryo
Morphological transformation.

Hamster
Embryo
Sister chromatid exchange

mouse
Micronucleus test

Carcinogenicity

Carcinogenicity - mouse - Oral
Tumorigenic:Equivocal tumorigenic agent by RTECS criteria. Liver:Tumors.

IARC: 3 - Group 3: Not classifiable as to its carcinogenicity to humans (Eugenol)

Reproductive toxicity
no data available

Specific target organ toxicity - single exposure
no data available

Specific target organ toxicity - repeated exposure
no data available

Aspiration hazard
no data available

Additional Information
RTECS: SJ4375000

To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

SECTION 12: Ecological information

12.1 Toxicity

Toxicity to fish	LC50 - Danio rerio (zebra fish) - 13 mg/l - 96 h (OECD Test Guideline 203)
Toxicity to daphnia and other aquatic invertebrates	EC50 - Daphnia - 1,13 mg/l - 48 h

12.2 Persistence and degradability

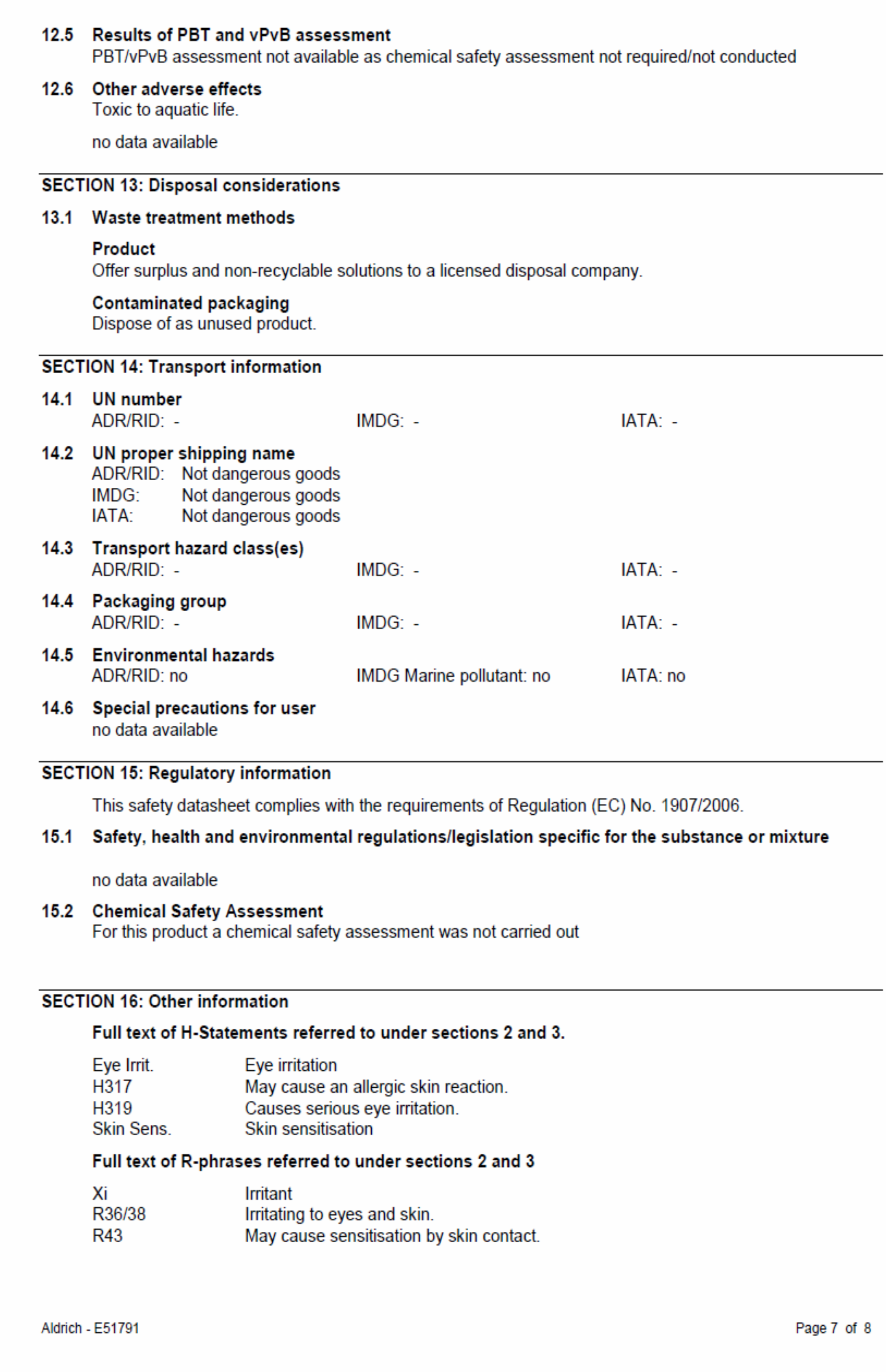
Biodegradability	Result: - Readily biodegradable. (Directive 67/548/EEC Annex V, C.4.E.)

12.3 Bioaccumulative potential

no data available

12.4 Mobility in soil

no data available



12.5 Results of PBT and vPvB assessment
PBT/vPvB assessment not available as chemical safety assessment not required/not conducted

12.6 Other adverse effects
Toxic to aquatic life.

no data available

SECTION 13: Disposal considerations

13.1 Waste treatment methods

Product
Offer surplus and non-recyclable solutions to a licensed disposal company.

Contaminated packaging
Dispose of as unused product.

SECTION 14: Transport information

14.1 UN number
ADR/RID: - IMDG: - IATA: -

14.2 UN proper shipping name
ADR/RID: Not dangerous goods
IMDG: Not dangerous goods
IATA: Not dangerous goods

14.3 Transport hazard class(es)
ADR/RID: - IMDG: - IATA: -

14.4 Packaging group
ADR/RID: - IMDG: - IATA: -

14.5 Environmental hazards
ADR/RID: no IMDG Marine pollutant: no IATA: no

14.6 Special precautions for user
no data available

SECTION 15: Regulatory information

This safety datasheet complies with the requirements of Regulation (EC) No. 1907/2006.

15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture

no data available

15.2 Chemical Safety Assessment
For this product a chemical safety assessment was not carried out

---

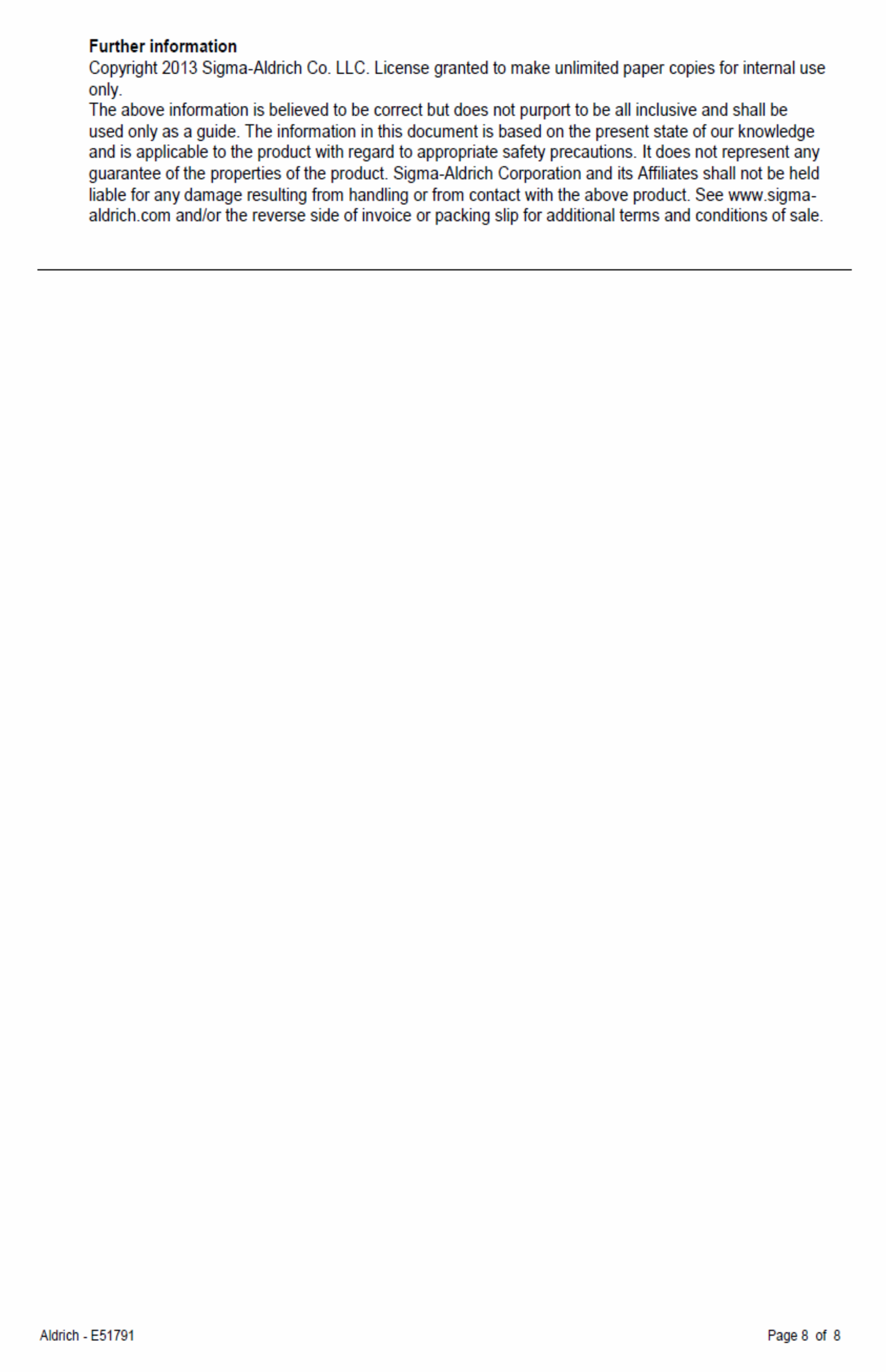
SECTION 16: Other information

Full text of H-Statements referred to under sections 2 and 3.

Eye Irrit.	Eye irritation
H317	May cause an allergic skin reaction.
H319	Causes serious eye irritation.
Skin Sens.	Skin sensitisation

Full text of R-phrases referred to under sections 2 and 3

Xi	Irritant
R36/38	Irritating to eyes and skin.
R43	May cause sensitisation by skin contact.



Further information

APPENDIX E

Properties of PVC Pipe

Appendix E-1 Physical and mechanical properties of “Thai Pipe” uPVC Pipe & Fittings

คุณสมบัติทางกายภาพและทางกล
ของท่อและอุปกรณ์ข้อต่อพีวีซี "ท่อน้ำไทย"

PHYSICAL AND MECHANICAL PROPERTIES OF "THAI PIPE" uPVC PIPE & FITTINGS

คุณสมบัติทั่วไปของท่อและอุปกรณ์ข้อต่อท่อพีวีซี "ท่อน้ำไทย"

GENERAL PROPERTIES OF "THAI PIPE" uPVC PIPE & FITTING

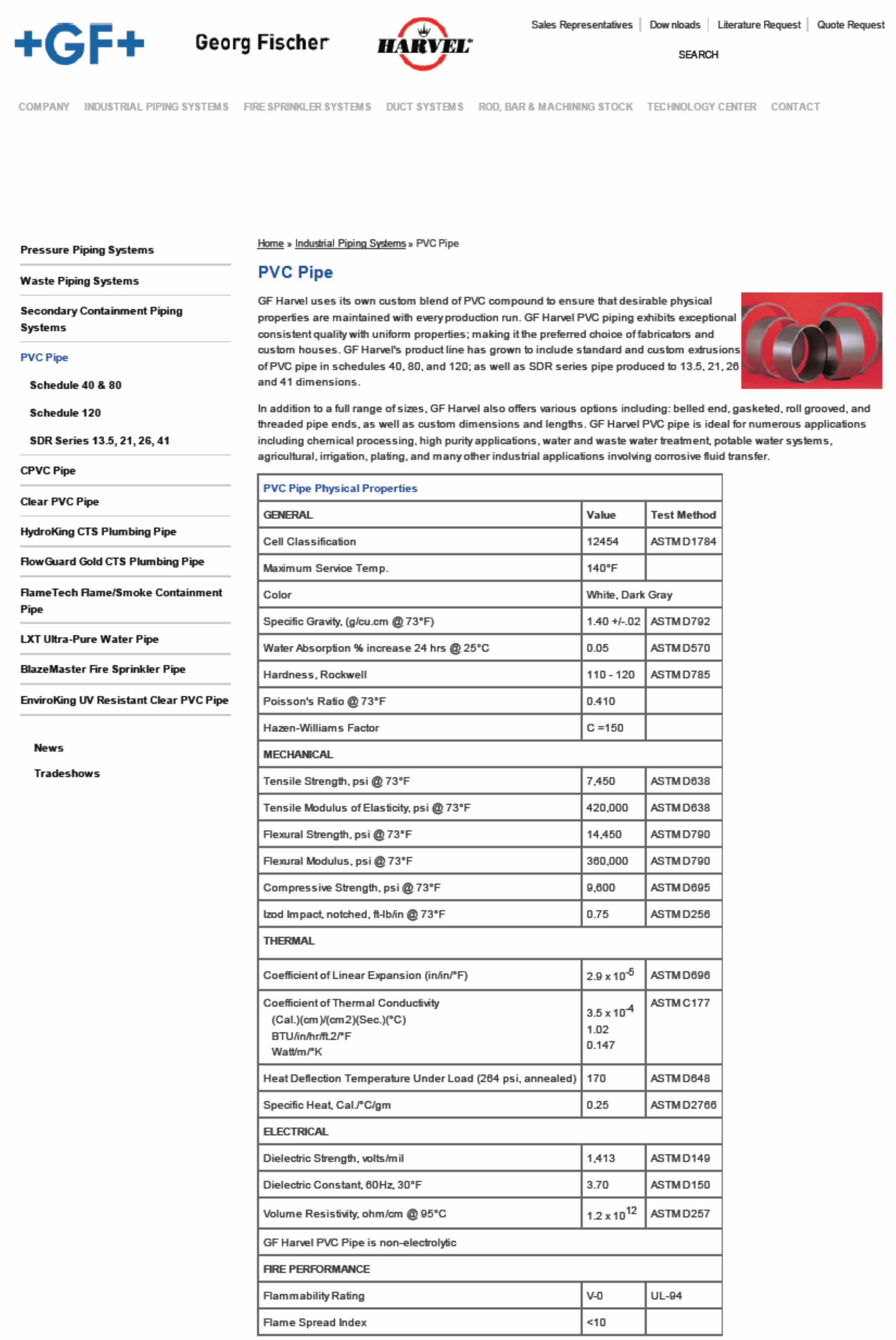
ITEM PROPERTIES	UNIT	TEST METHOD	CHARACTERISTIC VALUE
Specific Gravity	-	A.S.T.M. D792	1.43
Hardness	Rockwell R	A.S.T.M. D785	120
Water Absorption	mg/cm^2	A.S.T.M. D570	0.04 ~ 0.06
Tensile Strength	Kgf/cm^2	A.S.T.M. D638-60T	500 ~ 550
Elongation at Breaking	%	A.S.T.M. D638	100 ~ 170
Bending Strength	Kgf/cm^2	A.S.T.M. D790-59T	800 ~ 1,000
Compressive Strength	Kgf/cm^2	A.S.T.M. D695	700
Modulus of Elasticity	Kgf/cm^2	A.S.T.M. D747	2.8 ~ 3.0 x 10^4
Poisson’s Ratio	-	-	0.35 ~ 0.40
Impact Strength (charpy)	Kgf-cm/cm^2	A.S.T.M. D256-56	5.0
Coefficient of Linear Expansion	^{0}C^{-1}	A.S.T.M. D696	6 ~ 7 x 10^5
Specific Heat	Cal/g.^{0}C	-	0.20 ~ 0.28
Thermal Conductivity	Kcal/m.h. ^{0}C	-	0.12 ~ 0.14
Softening Temperature	^{0}C	A.S.T.M. D648-56	75 ~ 82
Flame Resistance	-	A.S.T.M. D635-56T	Self-extinguishing
Volume Resistivity	Ω.cm	A.S.T.M. D257-54T	3 ~ 5 x 10^{15}
Dielectric Strength	KV/mm	-	More than 40
Dielectric Power Factor	-	A.S.T.M. D150-54T	0.02
Dielectric Constant	-	A.S.T.M. D150-54T	3.2

THAI PIPE

ท่อน้ำไทย

70

Appendix E.2: Physical and mechanical properties of “Georg Fisher” PVC Pipe.



+GF+ Georg Fischer HARVEL

Sales Representatives | Downloads | Literature Request | Quote Request

SEARCH

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  - **Schedule 120**
  - **SDR Series 13.5, 21, 26, 41**
- **CPVC Pipe**
- **Clear PVC Pipe**
- **HydroKing CTS Plumbing Pipe**
- **FlowGuard Gold CTS Plumbing Pipe**
- **FlameTech Flame/Smoke Containment Pipe**
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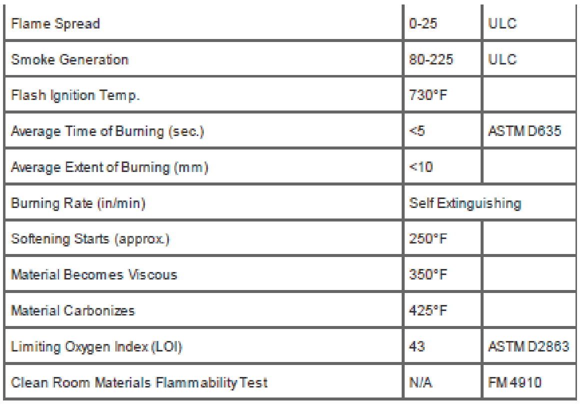
PVC Pipe

GF Harvel uses its own custom blend of PVC compound to ensure that desirable physical properties are maintained with every production run. GF Harvel PVC piping exhibits exceptional consistent quality with uniform properties; making it the preferred choice of fabricators and custom houses. GF Harvel's product line has grown to include standard and custom extrusions of PVC pipe in schedules 40, 80, and 120; as well as SDR series pipe produced to 13.5, 21, 26 and 41 dimensions.

In addition to a full range of sizes, GF Harvel also offers various options including: belled end, gasketed, roll grooved, and threaded pipe ends, as well as custom dimensions and lengths. GF Harvel PVC pipe is ideal for numerous applications including chemical processing, high purity applications, water and waste water treatment, potable water systems, agricultural, irrigation, plating, and many other industrial applications involving corrosive fluid transfer.

PVC Pipe Physical Properties

GENERAL	Value	Test Method
Cell Classification	12454	ASTM D1784
Maximum Service Temp.	140°F	
Color	White, Dark Gray	
Specific Gravity, (g/cu.cm @ 73°F)	1.40 +/-.02	ASTM D792
Water Absorption % increase 24 hrs @ 25°C	0.05	ASTM D570
Hardness, Rockwell	110 - 120	ASTM D785
Poisson's Ratio @ 73°F	0.410	
Hazen-Williams Factor	C =150	
MECHANICAL		
Tensile Strength, psi @ 73°F	7,450	ASTM D638
Tensile Modulus of Elasticity, psi @ 73°F	420,000	ASTM D638
Flexural Strength, psi @ 73°F	14,450	ASTM D790
Flexural Modulus, psi @ 73°F	360,000	ASTM D790
Compressive Strength, psi @ 73°F	9,600	ASTM D695
Izod Impact, notched, ft-lb/in @ 73°F	0.75	ASTM D256
THERMAL		
Coefficient of Linear Expansion (in/in/°F)	2.9×10^{-5}	ASTM D696
Coefficient of Thermal Conductivity (Cal.)(cm)/(cm2)(Sec.)(°C) BTU/in/hr/ft.2/°F Watt/m/°K	3.5×10^{-4} 1.02 0.147	ASTM C177
Heat Deflection Temperature Under Load (264 psi, annealed)	170	ASTM D648
Specific Heat, Cal./°C/gm	0.25	ASTM D2766
ELECTRICAL		
Dielectric Strength, volts/mil	1,413	ASTM D149
Dielectric Constant, 60Hz, 30°F	3.70	ASTM D150
Volume Resistivity, ohm/cm @ 95°C	1.2×10^{12}	ASTM D257
GF Harvel PVC Pipe is non-electrolytic		
FIRE PERFORMANCE		
Flammability Rating	V-0	UL-94
Flame Spread Index	<10	



Flame Spread	0-25	ULC
Smoke Generation	80-225	ULC
Flash Ignition Temp.	730°F	
Average Time of Burning (sec.)	<5	ASTM D635
Average Extent of Burning (mm)	<10	
Burning Rate (in/min)	Self Extinguishing	
Softening Starts (approx.)	250°F	
Material Becomes Viscous	350°F	
Material Carbonizes	425°F	
Limiting Oxygen Index (LOI)	43	ASTM D2863
Clean Room Materials Flammability Test	N/A	FM 4910

VITA

Mr. Aran Asawakosinchai was born in Chanthabuti, Thailand on August 31, 1989. He completed high school in 2008 from Benjamarachuthit Chanthaburi School and graduated Bachelor degree from the Department of Chemical Engineering, Faculty of Engineering, King Mongkut's University of Technology Thonburi, Thailand in 2012. After graduation, he continued his study for a Master's Degree of Chemical Engineering at the Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University.

Some part of this work was selected for oral presentation at the 2014 IUPAC World Polymer Congress or MACRO 2014 on July 6-11, 2014 at Chiangmai, Thailand and the Eighth International Conference on Materials Science and Technology (MSAT) on December 15-16, 2014 at Swissotel Le Concerde, Bangkok, Thailand