NOVEL BIO-BASED RUBBER OIL FROM EPOXIDIZED AND ACETYLATED CASHEW NUT SHELL LIQUID (CNSL)

IDRIS KALKAN

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENT FOR THE DEGREE OF MASTER OF SCIENCE IN POLYMER TECHNOLOGY
DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE
KING MONGKUT'S INSTITUTE OF TECHNOLOGY LADKRABANG
YEAR 2020

KMITL-2020-SC-M-014-048

NOVEL BIO-BASED RUBBER OIL FROM EPOXIDIZED AND ACETYLATED CASHEW NUT SHELL LIQUID (CNSL)

IDRIS KALKAN

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENT FOR THE DEGREE OF MASTER OF SCIENCE IN POLYMER TECHNOLOGY
DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE
KING MONGKUT'S INSTITUTE OF TECHNOLOGY LADKRABANG
YEAR 2020

KMITL-2020-SC-M-014-048

Thesis Title	Novel Bio-Based Rubber Oil from Epoxidized and Acetylated Cashew Nut Shell Liquid
Student Name	Mr. Idris Kalkan
Student ID	59605030
Degree	Master of Science (Polymer Technology)
Department	Chemistry
Faculty	Science
University	King Mongkut's Institute of Technology Ladkrabang (KMITL)
Year	2020
Thesis Advisor	Assoc. Prof. Dr. Ittipol Jangchud

Abstract

For sustainable economy, novel renewable bio-based additives, i.e., epoxidized and acylated cashew nut shell liquids (CNSLs) derived from agricultural waste have been carried out. Cardanol, one of main components of CNSLs, was used as the model. Epoxidized cardanol (EC) was carried out via peracetic acid formed in-situ in the presence of an ion exchange resin as a catalyst. Acetylated cardanol (AC) was achieved by solvent free mechanism and zinc oxide as catalyst. The oil was successfully modified as the molecular structures of EC and AC were confirmed by FTIR, ^{1}H NMR and iodine value test. Feasibilities of using the modified oils as rubber processing oil in CR, NR and CR/NR (50:50) blend were studied and compared with commercial petroleum-based naphthenic oil. Compounded rubber samples were tested for Mooney viscosity, cure characteristics, mechanical and physical properties. Rubbers with cardanol and its derivatives showed some improvements in torque results. C and especially AC indicated lower cure times and higher cure efficiencies, whereas EC showed longer cure times and lower cure efficiencies when compared to naphthenic oil. Rubbers compounded with four different oils did not reveal significant differences according to bleeding, swelling, hardness and tensile test, however, AC indicated superior antiaging properties based on shore A hardness, tensile strength, M100 and elongation at break results before

and after accelerated aging process. As a result C and AC, especially AC, have great potential to replace naphthenic oil as rubber oil, on the other hand, EC is not recommended due to cure test results.

Keywords: Cardanol, epoxidation, acetylation, natural rubber and chloroprene rubber

Acknowledgements

The author would like to express his sincere appreciation to those, who helped him during this study by any means of contribution and support.

First of all, the author would like to express his sincere gratitude to his research advisor, Assoc. Prof. Dr. Ittipol Jangchud for his continuous advices, guidance and encouragement for this study despite his very busy schedule.

The author would like to greatfully thank to committe members, Assoc. Prof. Dr. Sombat Thanawan and Assoc. Prof. Dr. Chonlada Rithvirul for taking their times to evaluate this research and give very productive feedback in order to help the project improve.

The author would like to give special thanks to his research co-advisor, Dr. Watthana Klairutsamee for his kind contributions, advices and guidance throughout the study.

The author would like to gratefully acknowledge Ms.Suppanapang Raksawong for kindly supporting this study by her experience as senior badge graduate.

The author is also grateful to Miss. Monticha Junpunya and Miss. Nopphawan Tanboriphan for their kind help and effort whenever required.

Special thanks to Science Faculty, King Mongkut's Institute of Technology Ladkrabang, especially office staff and lab technicians for their kind support and help.

Finally, the author thanks to his wife and children for being very considerate and supportive for the times he could not spare enough time because of heavy and time consuming work of research.

Mr. Idris Kalkan

Table of Contents

Page

Abstract i
Acknowledgements iii
Table of Contents iv
List of Tables vii
List of Figures viii
Abbreviations xi
Chapter 1 Introduction 1
1.1 Research Motivation 1
1.2 Objectives of the study 2
1.3 Scopes of the study 3
1.4 Benefits of the study 3
Chapter 2 Theory and Literature Reviews 4
2.1 Bio-Based Additives 4
2.2 Cashew Nut Shell Liquid (CNSL) 5
2.2.1 Components of CNSL 6
2.2.2 Decarboxylation of CNSL 7
2.2.3 Cardanol and Its Applications 8
2.3 Epoxidation of Cardanol 9
2.3.1 Functional Double Bonds of Side Chain 10
2.3.2 Peroxide/Acetic Acid 11
2.3.3 Catalyst for Epoxidation 11
2.3.4 Expectations for Epoxidation 12
2.4 Esterification of Cardanol on Phenolic Hydroxyl Groups 13
2.4.1 Acetyl Chloride 14
2.4.2 Catalyst for Acetylation 14
2.4.3 Expectations for Acetylation 15
2.5 Rubbers and Additives 15
2.5.1 Natural Rubber (NR) 15
2.5.2 Chloroprene Rubber (CR) 17

Table of Contents (Continued)

Page

2.5.3 Rubber Compounding and Additives..... 18
2.5.3.1 Vulcanization and Vulcanizing Agents..... 19
2.5.3.2 Accelerators and Activators..... 20
2.5.3.3 Fillers..... 21
2.5.3.4 Other Ingredients..... 21
2.6 Rubber Oils and Their Properties..... 21
2.7 Literature Reviews..... 23
Chapter 3 Research Methodology..... 26
3.1 Chemicals and Materials..... 27
3.2 Equipment..... 28
3.3 Cardanol Modification..... 29
3.3.1 Epoxidation of Cardanol..... 29
3.3.2 Acetylation of Cardanol..... 32
3.4 Characterization..... 35
3.5 Rubber Compounding..... 35
3.6 Rubber Testing..... 39
3.6.1 Mooney Viscosity Test..... 40
3.6.2 Cure Characteristics..... 41
3.6.3 Compress Molding..... 42
3.6.4 Swelling Test..... 43
3.6.5 Bleeding Test..... 44
3.6.6 Accelerated Aging..... 46
3.6.7 Tensile Test..... 47
3.6.8 Hardness Test..... 48
Chapter 4 Main Results and Discussions..... 49
4.1 Synthesis of cardanol derivatives..... 49
4.1.1 Characterization of EC and AC..... 50
4.1.1.1 FTIR analysis of EC and AC..... 50
4.1.1.2 Analyzing ^{1}H NMR results of EC and AC..... 53
4.1.1.3 Analyzing iodine value test results of EC and AC..... 55

Table of Contents (Continued)

Page

4.2 Effect of Cardanol and its derivatives in pure NR, pure CR and NR/CR (50:50) compounding 56
4.2.1 Effect of processing oil on torque 57
4.2.2 Mooney viscosity and cure test results 60
4.3 Effect of Cardanol and its derivatives on physical and mechanical properties of NR/CR (50:50) rubber blend 63
4.3.1 Swelling percent 63
4.3.2 Bleeding amount 65
4.3.3 Hardness 65
4.3.4 Tensile properties 66
Chapter 5 Conclusions and Suggestions 69
5.1 Conclusions 69
5.2 Suggestions 70
References 71
Appendices 76
Appendix A 77
Appendix B 79
Appendix C 81
Appendix D 82
Appendix E 84
Author Biography 85

List of Tables

Table **Page**

2.1 Components and their weight percent in unprocessed CNSL..... 6

3.1 List of chemicals for epoxidation and acetylation of cardanol..... 27

3.2 List of ingredients for rubber compounding 27

3.3 List of equipment 28

3.4 The weight ratios of chemicals used for the epoxidation reaction of cardanol.. 30

3.5 The weight and mole ratios of chemicals for the acetylation of Cardanol..... 33

3.6 Concentrations and functions of ingredients used for rubber compounding..... 36

3.7 The order and time of adding ingredients for rubber compounding by internal mixer..... 37

4.1 Some FTIR transmittance peaks for (corresponding to figure 4.3) 51

4.2 Some distinctive proton chemical shifts corresponding to figure 4.4 55

4.3 Iodine value test results and unsaturation percent of EC and AC relative to C... 56

4.4 Torque and temperature results obtained from rubber compounding by internal mixer 59

4.5 Mooney viscosity, scorch time (t_{s2}), cure time (t_{90}) and cure rate index (CRI) results of CR, NR and NR/CR (50:50) rubber formulations prepared by different processing oils: C, EC, AC and N 62

4.6 Tensile strength, elongation at break and M100 results obtained from tensile test before and after accelerated aging for NR/CR (50:50) rubber blend compounded with four different oils 67

List of Figures

Figure **Page**

2.1 Cashew Apple Fruit, Cashew Nut and Cashew Nutshell Liquid (CNSL) 5

2.2 Cross section of a row cashew nut and cashew nutshell..... 6

2.3 Components of CNSL a) anacardic acid, b) cardanol, c) cardol and d) 2-methylcardol..... 7

2.4 Decarboxylation of anacardic acid 8

2.5 The reactions of cardanol..... 9

2.6 Epoxidation of cardanol using epichlorohydrin..... 10

2.7 Epoxidation of double bond by carboxylic peracid formed in situ reaction..... 11

2.8 The formation of organic peracid and epoxidation of double bonds 11

2.9 Amberlite IR 120H ion exchange resin 12

2.10 Esterification of hydroxyl group by (a) acid anhydride and (b) acid chloride... 13

2.11 Acetylation of hydroxyl group by acetyl chloride at solvent free conditions.. 14

2.12 (a) Rubber sap liquid collection from rubber tree by tapping, (b) NR gum ready to be used for rubber compounding 16

2.13 Isoprene and natural rubber (polyisoprene) structures 16

2.14 Cis and trans structures of polyisoprene 17

2.15 Polymerization of chloroprene to form polychloroprene (Neoprene)..... 17

2.16 Polybutadiene, NR and CR differ by only circled groups in their chemical structure 18

2.17 CR (Neoprene) in gum structure and ready to be used for compounding 18

2.18 Vulcanization of NR (polyisoprene)..... 20

2.19 Vulcanization of CR (Neoprene)..... 20

3.1 Overall flowchart for research methodology 26

3.2 Left to right: Cardanol, epoxidized cardanol and acetylated cardanol 29

3.3 Epoxidation of Cardanol by peracetic acid generated in situ reaction..... 30

3.4 Experimental set up for epoxidation of cardanol..... 31

3.5 (a) Separating catalyst by filtration, (b) water and oil layers after washing, (c) separating toluene by rotary evaporator 32

3.6 Acetylation of cardanol by solvent free method..... 33

List of Figures (Continued)

Figure **Page**

3.7 Experimental set-up for acetylation of cardanol..... 34
3.8 (a) initial pH of AC, (b) final pH of AC, (c) separation of water and oil layers 35
3.9 (a) Feeding internal mixer, (b) internal mixer on progress, (c) right after opening mixer's chamber, (d) rubber just removed from internal mixer 38
3.10 (a) Rubber compounding by cut and fold method, (b) Rubber sheet ready for Mooney viscosity test, cure time test and compress molding..... 39
3.11 The overall flowchart for rubber testing 40
3.12 Pictures taken during Mooney viscosity test: (a) Specimen is placed in the Mooney viscometer, (b) Mooney Viscometer is on progress and (c) specimen after Mooney viscosity testing 41
3.13 Pictures taken during cure test (a) Specimen is placed in moving die rheometer for cure time test (b) moving die rheometer on progress and (c) specimen after cure time test..... 42
3.14 (a) mold is coated by a very thin silicon layer, (b) un-vulcanized rubber is placed in the mold, (c) specimen is ready for compress molding, (d) mold is placed inthe machine, (e) vulcanized specimen right after being removed from mold and (f) extra parts of vulcanized specimen is removed..... 43
3.15 (a) Specimens are immersed into toluene, (b) test tubes are covered by aluminum foil to prevent solvent exit and light entrance..... 44
3.16 (a) and (b) specimen is placed between steel plates inside waxed paper, (c) specimen is placed in the oven with loaded 5 kg weight on and (d) bleeding test on progress..... 46
3.17 (a) Air oven used for accelerated aging, (b) specimens for tensile test in accelerated aging process, (c) specimens for hardness test in accelerated aging process..... 47
3.18 (a) Thickness and width values entry before tensile test, (b) specimen placed in the universal testing machine, (c) tensile test on progress..... 48

List of Figures (Continued)

Figure **Page**

3.19 Running shore A hardness test 48
4.1 Structural formulas of C, EC and AC. Any change in the functional group is indicated by red color of circling 49
4.2 Left to right: EC, AC and C..... 50
4.3 FTIR results of unmodified cardanol, epoxidized cardanol and acetylated cardanol 52
4.4 Hydrohalogenation of double bond..... 53
4.5 ^{1}H NMR results of (a) unmodified-cardanol, (b) epoxidized cardanol and (c) acetylated cardanol 54
4.6 A sample torque and temperature vs. time graph belonging to rubber compounding by internal mixer 57
4.7 A sample print out from moving die rheometer machine and measurements of scorch time (t_{s2}) and 90% of cure time (t_{90}) 60
4.8 Sample cure curves for CR, NR and CR/NR (50:50) blend..... 63
4.9 Swelling test results of NR/CR (50:50) rubber formulation compounded by different processing oils: C, EC, AC and N 64
4.10 Bleeding test results of NR/CR (50:50) rubber formulation compounded by different processing oils: C, EC, AC and N..... 65
4.11 Results of Shore A hardness test before and after accelerated aging for NR/CR (50:50) rubber blend compounded with four different oils..... 66
4.12 The cure curve of rubber..... 67

Abbreviations

AC	Acetylated cardanol
ASTM	American Society for Testing and Materials
C	Cardanol
CBS	N-Cyclohexyl-2-benzothiazole sulfenamide
CR	Chloroprene rubber
CRI	Cure rate index
$CoCl_2$	Cobalt (II) chloride
$Cu(ClO_4)_2.6H_2O$	Copper(II) perchlorate hexahydrate
EC	Epoxidized cardanol
ETU	Ethlene thiourea
FTIR	Fourier-transform infrared spectroscopy
HCl	Hydrochloric acid
^1H NMR	Proton nuclear magnetic resonance
ISO	International Organization for Standardization
M100	Stress/strain modulus at 100% elongation
MgO	Magnesium oxide
N	Naphthenic oil
NR	Natural rubber
6 PPD	N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine
phr	Parts per hundred rubber
ppm	Parts per million
rpm	Revolutions per minute
t_{s2}	Scorch time
t_{90}	Time required for 90% of cure
ZnO	Zinc oxide
$ZrOCl_2.8H_2O$	Zirconyl chloride octahydrate

Chapter 1

Introduction

1.1 Research motivation

Fossil fuels have been the main resources for many applications in daily life. Globally, nearly 15 billion tons of fossil fuels are used every year, which means the reservoirs won't last long [44]. More than 300 million tons of global plastic consumption uses almost 10% of overall petroleum consumption [2]. Over 10 million tons of by products are released to the nature every year by different ways, such as volatility, as industrial waste, non-recoverable usage etc., which has great impact on nature's balance by causing contamination, toxicity, global warming and such problems [3, 19, 21].

Forecasted depletion within next few decades and hazardous effects of fossil fuels have made people look for renewable resources. There have been numerous studies and researches on finding alternatives in different areas to petroleum products, which would not only help protecting nature, but also diminish and eventually end the dependence on the crude oil and the other fossil resources [2, 3, 4].

Bio-renewable resources and the usage of agricultural wastes or byproducts as resource gain a great importance because of the concerns raised above and sufficiency economics. For this reason many projects and researches have been run, such as producing biodiesel by using animal wastes, using resin of pine trees for coating purposes and using urushiol, canola oil, soybean oil, Cashew Shell Nut Liquid (CNSL) and many other vegetable oils or their derivatives as additive or main component in different applications [3, 14]. Among all these alternatives, non-edible resources are preferred over the edible ones since consuming edible resources will affect feedstocks [19, 24].

Although native to Brazil, cashew nut tree may grow in Asia Pacific region and so that in Thailand. Being highly valuable owing to the precious cashew nut, the plant provides a byproduct liquid called Cashew Shell Nut Liquid (CNSL), which is a non-edible mixture of oils and one of the most promising renewable bio-based resources.

CNSL has a very high potential of being resource to many applications as alternative to petroleum products. With the phenolic ring and unsaturated alkyl side chain in its chemical structure, CNSL gives many other application possibilities than only being used as wood coating right after extracting from nutshell or being burnt for heat within the nutshell [2-4, 27].

According to Malaysian Rubber Export Promotion Council (MREPC), Yearly global rubber production is around 29 million tons. Considering processing oil content is 5-20 phr for rubber compounding, the oil required is 1.5-6.0 million tons, which is quite big amount. Providing all of this oil from fossil fuel resources would have huge negative consequences on fossil fuel reserves and environment because of the reasons mentioned above. Being a bio renewable resource and a very strong candidate to replace petroleum, CNSL and its derivatives will be used as processing oil for CR, NR and NR/CR (50:50) rubber blend compounding and will be compared with a petroleum based commercial oil. Cardanol, one of CNSL components, was used as model compound for CNSL. Cardanol was modified by two different methods, epoxidation and acetylation, to be used for the comparative study mentioned above.

This study is hoped to be a good contribution to the works and efforts have been made to support sufficiency economics and developing bio-renewable resources alternative to fossil fuels in order to protect nature and help to solve environmental problems.

1.2 Objectives of the study

1) To synthesize novel processing oils for rubber compounding by epoxidation and acetylation of cardanol, model compound for CNSL
2) To comparatively study the feasibilities of cardanol and its derivatives with a petroleum based commercial oil as bio-based additives in NR, CR and their blends.

1.3 Scopes of the study

1) Study the epoxidation and acetylation of cardanol
2) Compounding different NR/CR (50:50) rubber formulas by using cardanol derivatives and a petroleum based commercial oil.
3) Study the effect of processing oil on cure characteristics of previously compounded NR/CR (50:50) rubber formulas.
4) Study the effect of processing oil on mechanical properties of previously compounded NR/CR (50:50) rubber formulas by tensile, hardness and swelling tests.
5) Study the effect of processing oil on heat deterioration of previously compounded NR/CR (50:50) rubber formulas by applying accelerated ageing method.

1.4 Benefits of the study

By this study, it was expected to find out whether modified CNSL could be used for CR, NR and NR/CR (50:50) blend as processing oil, as well as, the success of methods for epoxidation and acetylation of Cardanol, which was used as model compound for CNSL. The performances of cardanol and its epoxidized and acetylated forms were compared to these of petroleum based commercial oil, naphthenic oil. It was hoped to contribute sufficiency economics by using an agricultural waste and help to protect environment by producing an alternative to petroleum based commercial products.

Chapter 2

Theory and Literature Reviews

2.1 Bio-based additives

Fossil fuels, such as petroleum, charcoal and natural gas, are resources, which cannot be renewed owing to the fact that it takes millions of years to be formed. Bio renewable resources, however, are by products or wastes from plants or animals that can be reformed in a cycle to replace the used amount.

The high importance of renewable resources is because of three main reasons: The first is that the finiteness of the most common and most used resource, fossil fuels, which is considered to used up within 50 to 80 years make people look for alternatives to decrease dependence on this. The second one is environmental concern due to the hazardous effects of fossil fuels on nature such as global warming, contaminations and toxicity. The third reason is to save cost so as to support sufficiency economics by using renewable agricultural and feedstock breeding by products or wastes.

Bio renewable resources have a big variety in nature. Forests for wood, cellulose and heat energy; wool, cotton and silk for fiber; animal skin for coating; resin of some trees for coating and as row material for some applications; animal fat, organs and extracted chemicals for bio diesel, cosmetic and medical purposes; vegetable oils for lubrication, additive or row material for many application are just a few examples among various.

Among these examples, vegetable and plant oils have attracted a big attention especially in polymer technology because of the variety of chemical reaction possibilities coming from their functionality owing to the unsaturation and some other functional groups, such as hydroxyl, carbonyl, carboxyl, in their chemical structures. These chemical structures give the advantage of utilizing them without modification or modifying by epoxidation, esterification, decarboxylation and so on.

Urushiol, Soybean oil, palm oil, canola oil, castor oil, linseed oil and CNSL are just few of many which have been the subjects of many projects for the purpose of

replacing petroleum based commercial products due to environmental and economic concerns.

2.2 Cashew nutshell liquid (CNSL)

Being native to Brazil, Cashew nut tree, Anacardium Occidentale L., has been taken to and now growing in many other countries including India, Vietnam, Nigeria, Mozambique, Kenya and Thailand. Although it is the origin for this tree, Brazil is no longer the leading country in cashew nut production [2-6].

Figure 2.1 Cashew apple fruit, cashew nut and cashew Nutshell Liquid (CNSL) [1].

Cashew apple fruit and cashew nut are the primarily harvested products of cashew nut tree (Figure 2.1). There is a non-edible byproduct called cashew nutshell liquid (CNSL), a dark reddish-brown and viscous liquid as well as irritant to the skin, in the shell of cashew nut. Making up around 25% of the total nut's weight, this liquid can be extracted from the shell by cold extraction action press, solvent extraction, thermal-mechanical process (hot oil process at 190°C) and supercritical fluid extraction methods. The global production of CNSL is around 300,000 tons per year. [2, 3, 25]

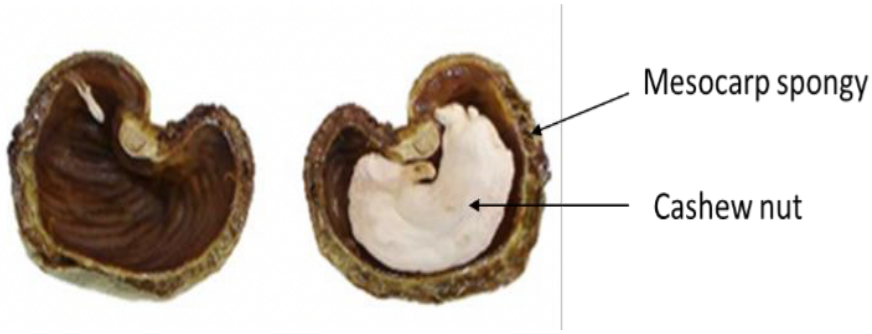


Figure 2.2 Cross section of a row cashew nut and cashew nutshell. [2]

CNSL is mixture of several oils, which commonly have a phenolic ring and a long 15-carbon side carbon chain at meta position. Owing to the functional hydroxyl group and unsaturation in the side chain, CNSL has a big potential for the variety of the chemical reactions and this the reason why it has attracted big attention to be used as bio renewable resource. It has a wide range of utilization, a few examples of which are: Additive and monomer for polymers, lubricant, adhesive, biofuel, coating, varnishing, anti-termite, pesticide and fungicidal [2, 3, 5, 8, 9].

2.2.1 Components of CNSL

CNSL consists of several liquids or oils having a phenolic aromatic ring and a fifteen-carbon unsaturated side chain at beta position in common. The similarity in their chemical structures make them miscible and, of course, difficult to be separated by simple separation techniques. Column chromatography is a very common technique to separate CNSL to its components. In unprocessed CNSL, there are four main components, which are anacardic acid, cardol, cardanol and 2-methyl cardol [2-9].

Table 2.1 Components and their weight percent in unprocessed CNSL

Cashew Nutshell Liquid (CNSL)

Component	**Composition (wt%)**
Anacardic Acid	70-77
Cardol	15-20
Cardanol	1-9
2-Methyl Cardol	1-4

Although the unsaturated side chain consists of fifteen carbons, its unsaturation level varies as saturated (5-8%), monoene (48-49%), diene (16-17%) and triene (29-30%). [2, 3]

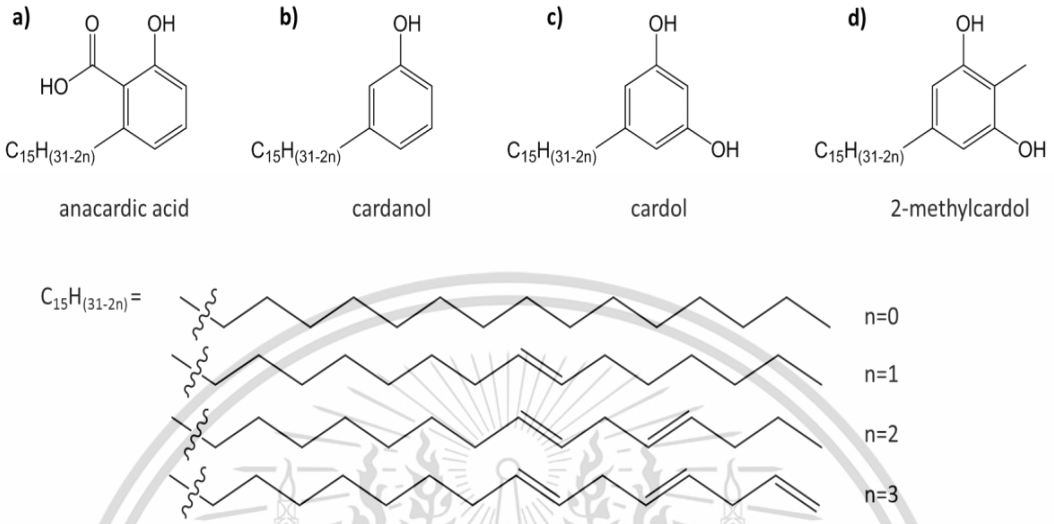


Figure 2.3 Components of CNSL a) anacardic acid, b) cardanol, c) cardol and d) 2-methylcardol. [3]

Anacardic acid is the component giving acidity and so that skin irritancy. It is the most abundant in the row CNSL, however it is sensitive to heat and its abundancy decreases dramatically when CNSL is extracted at high temperatures. cardol has the second highest weight percent in CNSL and it is structural isomer of urushiol oil. Despite of its low percentage, cardanol has attracted the biggest attention, since it goes through the similar reactions of phenol due to the structural similarity and its abundancy can be increased up to 85% by a simple process called decarboxylation of CNSL or anacardic acid. 2-Methylcardol is found as small traces in the mixture and has not been drawn too much attention yet. [2-9, 16]

2.2.2 Decarboxylation of CNSL

While the main component of row CNSL is anacardic acid (up to 77%), technical grade CNSL hardly contains anacardic acid. The reason for this is that the extraction of CNSL is run at high temperatures, 140°C -180°C, and this causes a chemical process called decarboxylation. During decarboxylation, the carboxyl group of anacardic acid is removed as carbon dioxide and anacardic acid turns into cardanol.

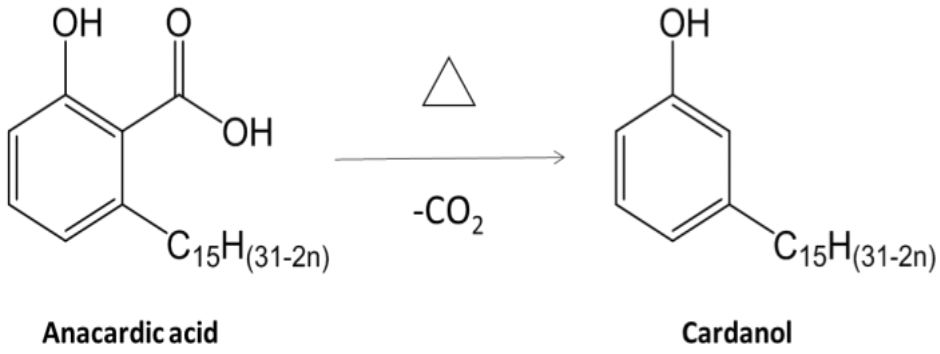


Figure 2.4 Decarboxylation of anacardic acid

Cardanol is one of the list abundant compounds in row CNSL, however, its weight percentile reaches up to 90% after decarboxylation reaction, which is shown in Figure 2.4. Decarboxylation of cardanol starts when temperature increases over 100°C, but the optimum temperature and heating time should be determined, because polymerization also takes place as the temperature increases. It has been reported by Raksawong, et al., that the conditions for the highest cardanol yield in decarboxylation process is 160°C for 30 minutes of heating under nitrogen atmosphere. [1, 2]

2.2.3 Cardanol and Its applications

In the technical CNSL, cardanol is the major component. This makes it ideal for being model compound to be studied in many projects as in this research. Cardanol's chemical structure differs from that of phenol by only a 15-C long side chain at meta-position. The side chain, as in CNSL, is a mixture of four components having different levels of saturation, which are saturated, monoene, diene and triene. [2, 3]

Although not miscible with water, since cardanol has polar (phenolic hydroxyl) and non-polar (side chain) ends, it is soluble in many organic solvents including methanol, ethanol, acetic acid, hexane, benzene, toluene, xylene, ethyl acetate and chloroform. The chemical structure of cardanol has mainly three functional parts, which are phenolic hydroxyl group, aromatic ring and unsaturated alkyl side chain. Because of the similarity in chemical structures, cardanol undergoes the same chemical reaction as phenol does, but reasonably with less reactivity because of the steric effect of the long alkyl chain.

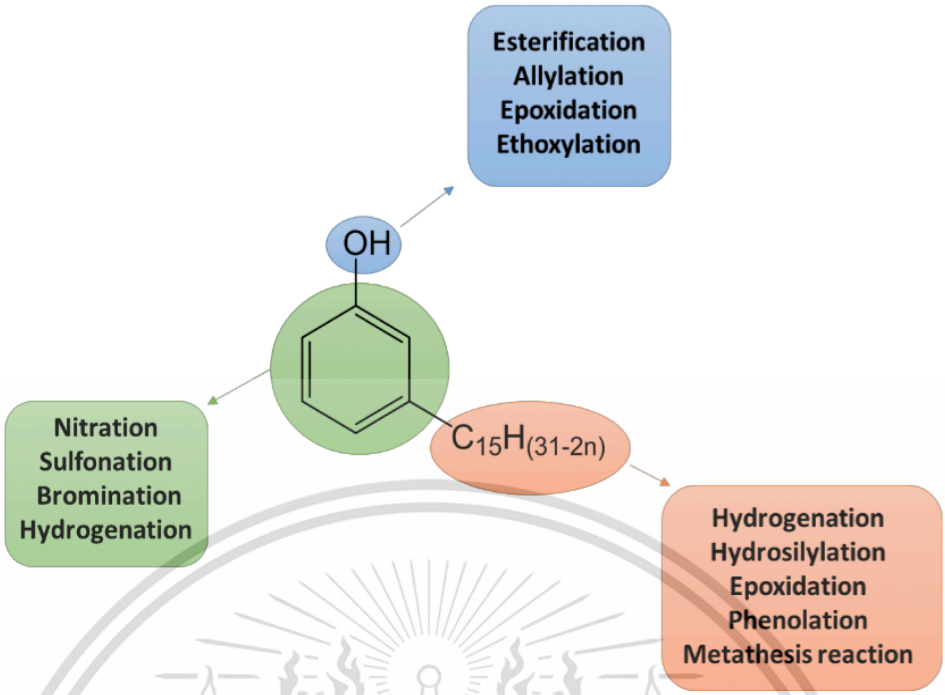


Figure 2.5 The reactions of cardanol [2].

Cardanol may undergo esterification, epoxidation, allylation and ethoxylation by its hydroxyl group. Its structure can be altered by nitration, sulfonation, halogenation and hydrogenation reactions of aromatic ring. It may, as well, be modified by nitration, sulfonation, hydrogenation, halogenation, hydroxylation, epoxidation, phenolation, polymerization and metathesis reaction of double bonds in the side chain (Figure 2.5) [3, 5].

The overmentioned big variety of chemical modification possibilities for cardanol gives it a very wide range of studies and makes it a very valuable alternative to phenol and petroleum products. As a result, Cardanol is utilized in many applications such as monomers, plasticizer, surfactant, curing agents, antioxidants, lubricants, etc. [2, 3, 5, 9, 11].

2.3 Epoxidation of cardanol

The bio-renewable oils mostly preferred to be modified before used in polymer applications in order to improve compatibility, miscibility, viscosity, cure properties, adsorption, and so on. The efficiency of cardanol too, increases when modified by some reactions through two main functional parts, phenolic hydroxyl group and double bonds in the alkyl chain. One of the most common modifications that have

been used is, no doubt, epoxidation. Epoxidation can be achieved through both phenolic hydroxyl group and unsaturation in the side chain. For the epoxidation of phenolic hydroxyl group, using epichlorohydrin is the mostly applied method (Figure 2.6) [16, 17, 28, 29].

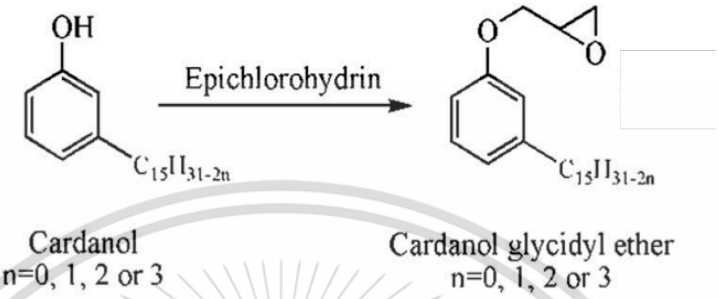


Figure 2.6 Epoxidation of cardanol using epichlorohydrin

Since another modification is desired on phenolic hydroxyl group, epoxidation of unsaturation in the side alkyl chain will be studied rather than that of hydroxyl group.

2.3.1 Functional double bonds of side chain

As abovementioned, the double bonds in the unsaturated side chain has the potential to go through hydrogenation, halogenation, hydroxylation, polymerization, metathesis and epoxidation reactions. The degree of unsaturation can be measured by Iodine Value Test. At the end of the epoxidation, iodine value is expected to be low, since the lower the iodine value means lower unsaturation, thus the higher epoxidation.

Epoxidation of double bonds in the side chain, can be performed by carboxylic peracid formed *in situ* reaction. Formic acid, acetic acid and benzoic acid are the most commonly used carboxylic acids with hydrogen peroxide. In order to catalyze the reaction, acids, such as Sulfuric acid, phosphoric acid, nitric acid etc. can be chosen for a homogeneous system, and more frequently, catalysts like IR 120H ion exchange resin and lipase may be selected for a heterogeneous system [1, 5, 8, 10-13, 15-24, 26, 28-31].

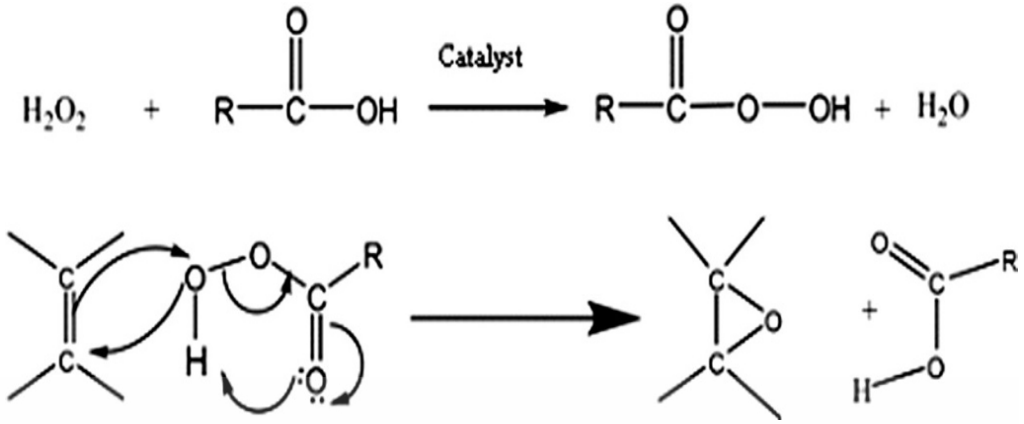


Figure 2.7 Epoxidation of double bond by carboxylic peracid formed in situ reaction.

2.3.2 Peroxide/acetic acid

As indicated in Figure 2.8, *In situ* epoxidation process happens in two simultaneous steps: The first is the organic peracid, such as per formic, per acetic, per benzoic etc., formation by hydrogen peroxide and an organic acid; the second is the epoxidation of double bonds [26].

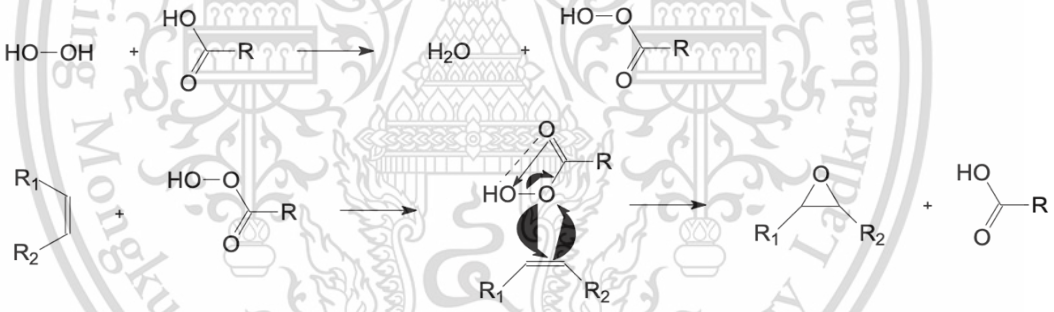


Figure 2.8 The formation of organic peracid and epoxidation of double bonds [31].

In many researches, Glacial acetic acid has been preferred as organic acid for peracid generated *in situ* epoxidation reaction of unsaturation in the side chain of cardanol as well as that of many vegetable oils including soybean oil, canola oil, castor oil, palm oil etc. Being abundant and safe to environment, acetic acid is easily utilized with hydrogen peroxide to form peracetic acid during the epoxidation process [24].

2.3.3 Catalyst for epoxidation

Mainly two groups of catalysts are used for peracid formed *in situ* epoxidation reactions: One includes mineral acids like sulfuric acid, phosphoric acid, nitric acid etc.

and the other includes an ion exchange resin, such as IR 120H or an enzyme like lipase. The second option has an advantage over the first one, because separation of catalyst is much easier and mostly done by a simple filtration, however preferring mineral acids would require more complex methods to be taken out of the mixture like neutralization [24, 26, 27].

Amberlite, IR 120H ion exchange resin is, obviously, the most popular catalyst and is very frequently chosen for carboxylic peracid formed *in situ* epoxidation reactions. It shows high efficiency owing to be separated by a simple cloth or a paper depending on the reactant types and to be reused [10-13, 15-24, 26-31].

Figure 2.9 Amberlite IR 120H ion exchange resin

IR 120H ion exchange resin is safe to environment; it is even used in water purifying systems.

2.3.4 Expectations for epoxidation

As previously mentioned, the main reason to modify cardanol, CNSL and the other renewable bio resources vegetable oils is to improve compatibility and the functionality. It has been reported that the cure characteristics, plasticizing character, antioxidative property and some other properties of cardanol improve by epoxidation for the applications in PVC, rubber and some other polymers, moreover the monomer efficiency improves too by epoxidation for its polymerization [1, 8, 10, 11, 13].

2.4 Esterification of cardanol on phenolic hydroxyl groups

Esterification is generally considered as the product made by the reaction of an alcohol with a carboxylic acid and an ester is described by the general formula, R-COOR'. Although not an alcohol, phenol and cardanol may go through reactions yielding their esters. The reaction, in this case will be called as esterification. Depending on the group added to phenolic hydroxyl, the reaction can be named more specifically, for example, it will be called as acetylation, if the added group is acetate, or will be called benzoylation, if the added group is benzoate [10-12, 25, 32-36].

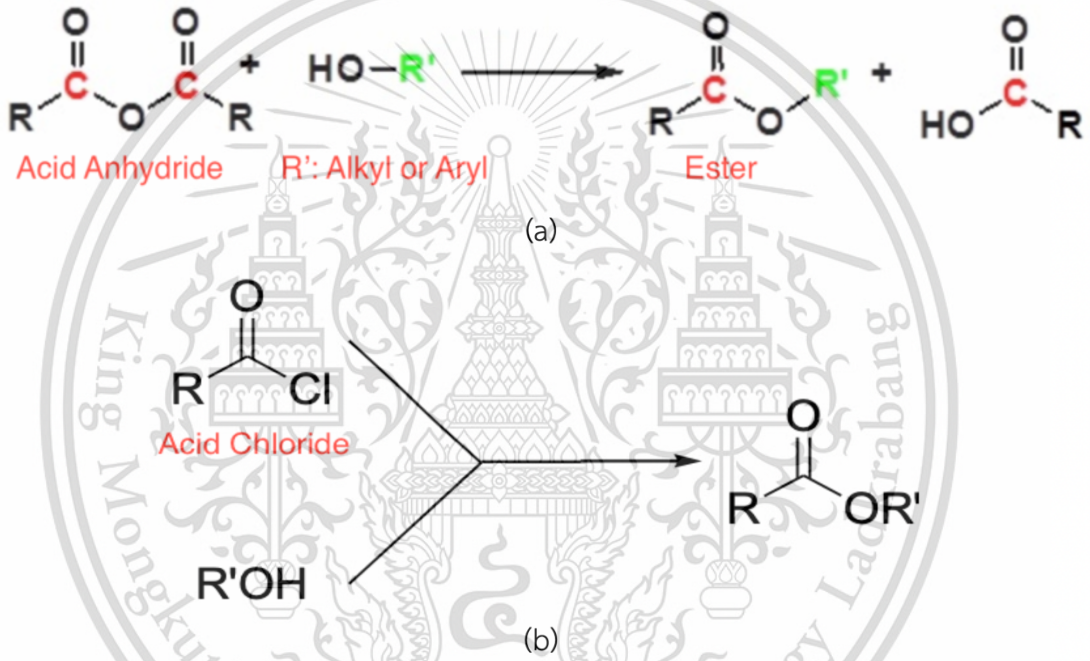


Figure 2.10 Esterification of hydroxyl group by (a) acid anhydride and (b) acid chloride

Like phenol, cardanol may undergo epoxidation, etherification, ethoxylation, allylation, as well as, esterification. Recently, as preferred in this research, a new method has been developed as alternative to the conventional esterification methods. This new method is called as 'solvent free method', which means no solvent is used and reactants are just mixed with a catalyst, then stirred at specific conditions. By solvent free technique, the reactions take place in milder conditions, higher yields are obtained in a shorter reaction time with a lower cost [32-36, 43].

2.4.1 Acetyl chloride

As shown in Figure 2.10, esterification can be achieved by either an acid anhydride or an acid halide (acyl halide). Acid halides are much more reactive than acid anhydrides, so can give high yields in much shorter reaction time, but of course, they must be handled very carefully because of their high reactivity and toxicity. Especially, water must be avoided, since acid halides react even with the humidity in the air producing a strong acid, hydrogen halide.

In fact, Acid chlorides, such as acetyl chloride, benzoyl chloride, etc., are dominantly used among acid halides. In this research acetyl chloride was selected to esterify cardanol by solvent free technique [32-35, 43].

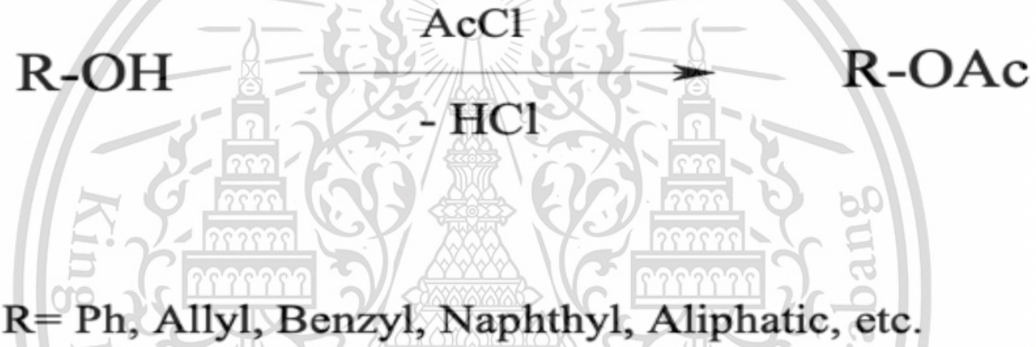


Figure 2.11 Acetylation of hydroxyl group by acetyl chloride at solvent free conditions.

Acetyl chloride is, as well, very reactive and has no water tolerance. It reacts vigorously with water yielding acetic acid and hydrochloric acid. It is also highly reactive to organic solvents having hydroxyl groups like alcohols and phenolic compounds and reacts in the way shown in Figure 2.11.

2.4.2 Catalyst for acetylation

In order to save time and cost, catalysts are very much preferred in a very wide range of chemical reactions. Acetylation reaction of cardanol takes place much more slowly than that alcohols and phenol due to the steric effect of long side chain, so a suitable catalyst has to be chosen for this reaction too. ZnO, $CoCl_2$, $ZrOCl_2.8H_2O$, $Cu(ClO_4)_2.6H_2O$ are a few examples for catalysts that have been utilized in solvent free acetylation reactions. Co and Cu like metals have toxic effects on environment and

from Zn and Zr, thinking both are environment friendly, the more abundant and economic one, ZnO, would be a very good candidate as catalyst for acetylation of cardanol, as it was preferred in this study [32-35, 43].

2.4.3 Expectations for acetylation

In this research, acetylation of cardanol was studied as an alternative modification to epoxidation. The performance of acetylated cardanol's performance as processing oil in CR, NR and NR/CR (50:50) rubber blend was expected to be observed and compared with that of unmodified cardanol and epoxidized cardanol, as well as a petroleum based commercial oil.

It was also expected to see and compare the effects of two main modification methods, epoxidation and acetylation on the torque during compounding, as well as mechanical, cure, antiaging antibleeding properties of rubber.

2.5 Rubbers and additives

Rubbers are elastomers, group of polymers with high elasticity, low Young's modulus and high yield strain. Rubbers have a wide area of usage, i.e. tires, footwear, clothing, adhesives, coating, insulating. They are mostly classified as natural rubber and synthetic rubbers, such as styrene-butadiene rubber (SBR), butadiene rubber, ethylene-propylene rubber, nitrile rubber, silicone rubber, chloroprene rubber, etc. Since natural rubber and chloroprene rubber were used in this study, these two types will be focused on next.

2.5.1 Natural rubber (NR)

Natural rubber, also called India rubber or caoutchouc, is an elastomer made of a liquid, latex, obtained from rubber tree.

(a) (b)

Figure 2.12 (a) Rubber sap liquid collection from rubber tree by tapping, (b) NR gum ready to be used for rubber compounding.

The way to get sticky-white color latex is simply a bleeding of rubber tree through a cut given on the bark (tapping). Rubber sap liquid is, then, refined to be row NR to be used for rubber compounding. The chemical name for NR is polyisoprene [41]. The monomer and polymer structures of NR are given in Figure 2.13.

Figure 2.13 Isoprene and natural rubber (polyisoprene) structures.

As seen in Figure 2.14, there are two possible geometrical isomer structures for isoprene, which are cis-isoprene and trans-isoprene. It has been seen that for NR, cis structure exists rather than trans structure. Since NR consists of all cis molecules, it is called as stereoregular and due to this reason, it can crystallize on stretching [41].

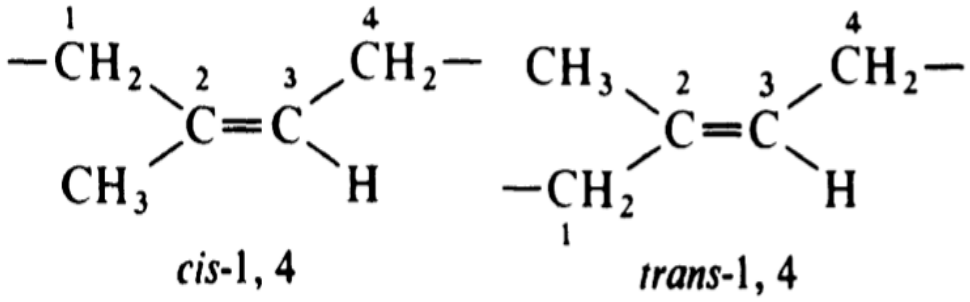


Figure 2.14 Cis and trans structures of polyisoprene [41].

Natural rubber cannot be used with its row structure, owing to insufficient physical and mechanical properties due to no crosslinking between polymer chains. For this reason, the necessary crosslink density must be provided, as well as some other ingredients, such as fillers, antioxidants, lubricants, plasticizers must be added for desired mechanical and physical properties and also in order to protect against outside factors.

2.5.2 Chloroprene rubber (CR)

Polychloroprene (CR), also called as neoprene, is one of the oldest synthetic elastomers. CR is made by the polymerization reaction of chloroprene (Figure 2.15).

Figure 2.15 Polymerization of chloroprene to form polychloroprene (Neoprene). [41]

Although it is mostly considered as chlorinated form of polybutadiene and chemically named 2-chloro butadiene, considering one hydrogen atom in butadiene is replaced by a chlorine atom, some other call it chlorinated natural rubber, because if methyl group in NR is changed to be chlorine, CR structure comes into existence [41, 42]. The differences and similarities are shown in Figure 2.16.

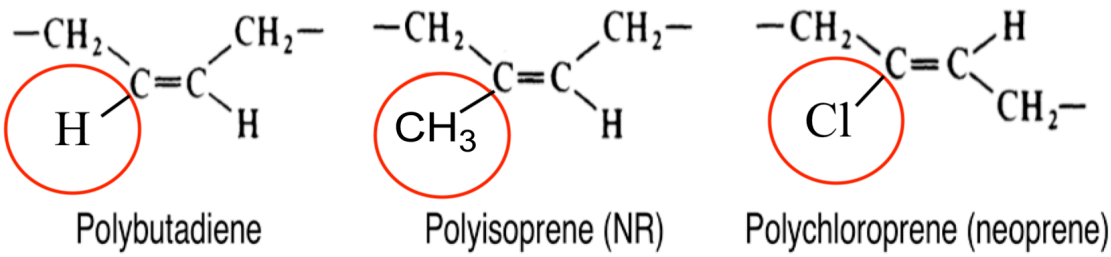


Figure 2.16 Polybutadiene, NR and CR differ by only circled group in their chemical structure. [41]

CR is almost completely made of trans structure and because of this fact it has sufficient regularity in its structure, therefore it, as well, crystallize on stretching and shows high gum tensile. It is used in pure gum form in many applications [41].

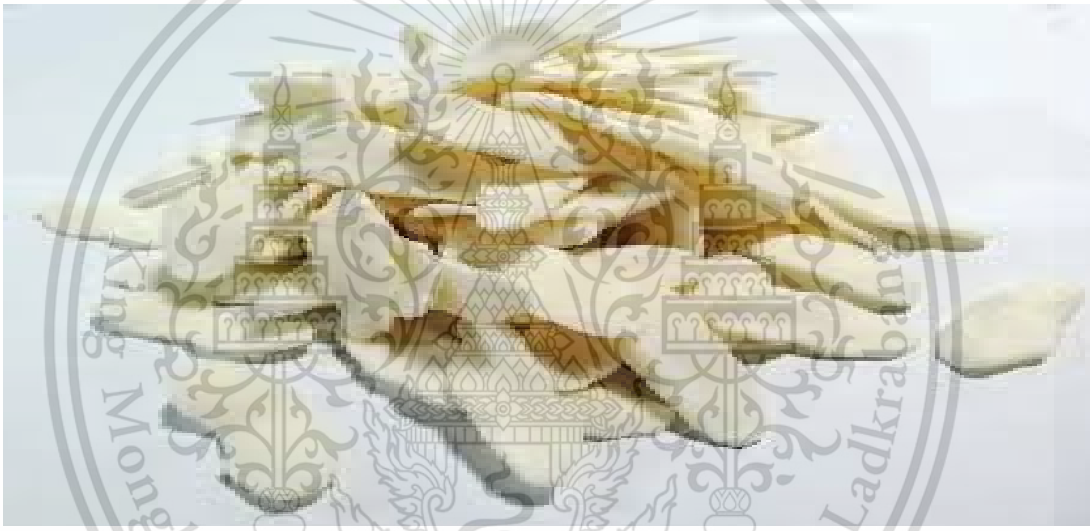


Figure 2.17 CR (Neoprene) in gum structure and ready to be used for compounding.

Although not recorded superior in any category of properties, CR is preferred because it shows very good balanced properties. It is better than NR in antiaging and heat properties, but lower than NR in tensile properties. There is another point which should not be overlooked: The density difference between NR and CR, which are 0.92 kg/L and 1.24 kg/L respectively [41, 42].

2.5.3 Rubber compounding and additives

Rubber compounding or formulation refers to the process that some chemicals are added to the raw rubber for desired physical, chemical and mechanical properties. Mixing must be good enough in order to get sufficient distribution and dispersion. There are mainly two types of mixers for rubber compounding: Internal (Bunbury) and

external mixers. In case of internal mixer, the mixing takes place in a closed chamber by the shear action between mixing rotors and chamber wall. External mixers do not have a mixing chamber, instead shear action is provided by two-roll mills turning on opposite directions [41].

The list of chemicals to be added is called as recipe. The ingredients totally depend on the desired properties and the conditions that the rubber will be used at. The common ingredients are vulcanizing agents, lubricants, activators, accelerators, antioxidants, fillers, etc.

2.5.3.1 Vulcanization and vulcanizing agents

After compounding, Rubber is not yet ready to show desired mechanical properties due to no crosslinking between its molecule chains. Vulcanization ends up with cross links between long chains causing three-dimensional structures, as a result, soft and weak rubber will be turned into strong elastomer which is no longer soluble in solvents and more durable against deteriorations caused by heat, light, oxidation, etc. Vulcanization can be achieved by various techniques such as compress molding, injection molding, open cures, microwave vulcanization. [41]

Vulcanization agents, or cross-linking agents, are the chemical providing crosslink between polymer chains in vulcanization. Sulfur is used mostly if the rubber contains unsaturated sections. There are some other vulcanizing agents other than sulfur, such as organic peroxides for saturated rubbers, dinitrosobenzene for butyl rubber and metal oxides for CR (neoprene). Selenium and tellerium can be used instead of sulfur [41].

As seen in Figure 2.18, vulcanization of NR involves opening of double bonds and formation of crosslinks over sulfur atoms. Sulfur acts as vulcanizing agent, however the process requires an activator and an accelerator too.

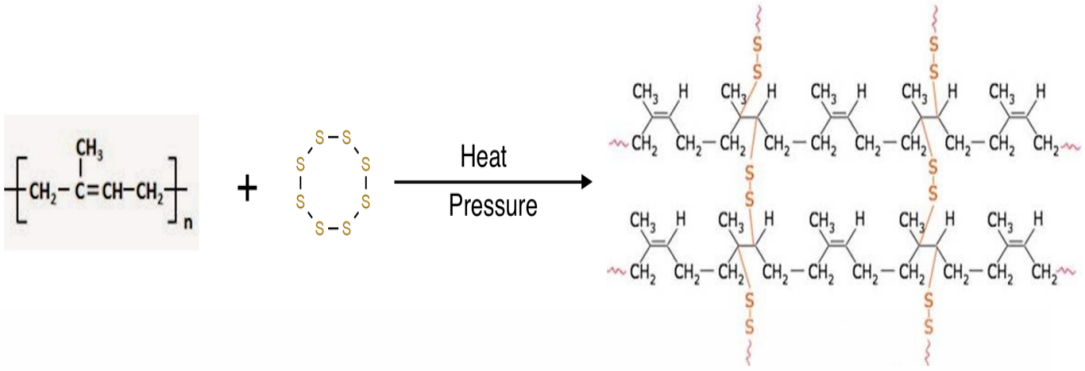


Figure 2.18 Vulcanization of NR (polyisoprene)

As indicated in Figure 2.19, CR (neoprene), as overmentioned, is not vulcanized by sulfur but metal oxides, i.e. magnesium oxide and zinc oxide. Unlike the vulcanization of NR, the vulcanization process of CR necessitates the removal of chlorine and interlinking of chains over these segments.

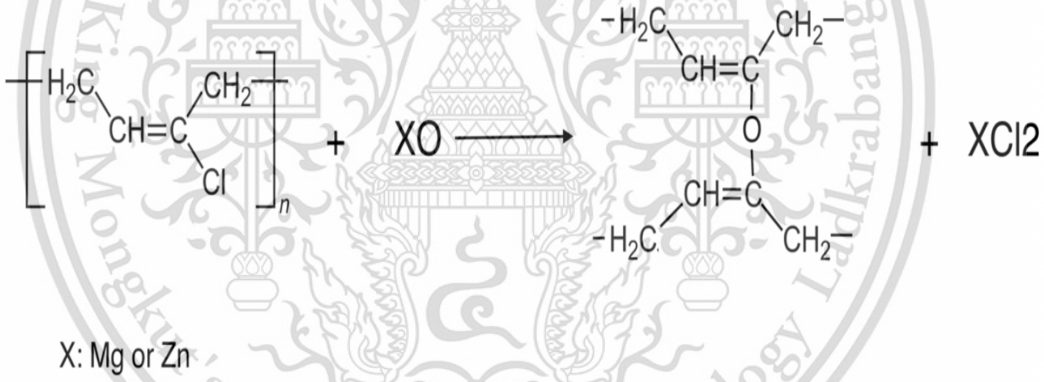


Figure 2.19 Vulcanization of CR (Neoprene)

2.5.3.2 Accelerators and activators

Accelerators are organic chemical ingredients for rubber to increase cure rate, decrease cure time and as a result improve physical properties. sulfenamides, thiazoles, thiurams, dithiocarbamates, and guanidines are some of examples that can be given for accelerators [41, 42].

Activators activate accelerators at the beginning of the cure and increase their efficiencies. Zinc oxide and stearic acid are most commonly used activators in many different rubber applications. This, of course, does not mean that they have only one

function in vulcanization, for example, while acting as activator for the vulcanization of NR, zinc oxide acts as vulcanizing agent for the vulcanization of CR [41, 42].

2.5.3.3 Fillers

Fillers are the additives, which are used to reinforce the rubber. Reinforcement fillers help increase tensile strength, tear resistance, abrasion resistance, as well as, decrease the cost. Although the carbon-black is the most commonly used filler, clay, calcium carbonate, ground coal, silica, silicate can be used too depending on the purpose [41, 42].

2.5.3.4 Other Ingredients

There are numerous types of rubber additives, for example antioxidants, antiozonants, flame retardants, age-resistors, softeners, colorants, odorants, dusting agents, homogenizing agents, blowing agents, abrasives, coupling agents, antistatic agents, processing aids and so on. As mentioned before, the recipe depends on where and at what conditions the rubber will be utilized, of course, unnecessary additives should be avoided to save cost [41, 42].

2.6 Rubber Oils and Their Properties

Rubber oils are used as processing aids, which reduce viscosity, improve processability, increase dispersion of filler, which as a result, help improve physical and mechanical properties. Rubber oil is not supposed to interfere with cure time and Mooney viscosity, which is related to molecular weight of rubber.

There are mainly three types of rubber oils, which are paraffinic, naphthenic and aromatic oils as petroleum-based oils. Vegetable oils have become alternatives to petroleum-based ones as rubber oils.

Paraffinic oils are colorless, odorless and transparent liquids. They are mixtures of long chain aliphatic hydrocarbons and obtained by distillation of crude oil. They have low reactivity due to being saturated and high boiling point. They have wide range of applications, such as lubricant, fuel, chemical in the production of some medicines, cosmetics and colorants. Paraffinic oils are preferred for long-aging applications because of their low volatility and better UV stability.

Naphthenic oils are refined from petroleum distillates. They have low aromatic and paraffinic content and composed of saturated hydrocarbons having cyclic structure. When compared to paraffinic oil with the same number of carbon atoms, naphthenic oils have higher volatility, lower viscosity, better dielectric properties and lower pour point. Therefore, naphthenic oils are preferred for good insulation and low temperature applications, as well as for lower cost concerns.

Aromatic oils include aromatic rings in their structures. They have dark colors and are used for the products, where color is not a concern. They are preferred for applications at tough conditions, for example tires, tubes, hoses, etc. Because of the unsaturation in their aromatic structure, they may have some adverse effects with other ingredients, especially when peroxide cure technique is used for vulcanization. Toxicity concern is the highest with aromatic oils.

Vegetable oils have recently been an important alternative to petroleum-based commercial oils. The unsaturation and functional groups in their chemical structures let them be modified easily in order to increase compatibility. Soybean oil, canola oil, linseed oil, palm oil, cashew nutshell liquid and many other vegetable oils have been used as plasticizer and processing oil in PVC, rubber and other polymer applications.

2.7 Literature reviews

McNutt, J. et. al. [4], This is a review study to evaluate the performances of modified vegetable oils by esterification, epoxidation, etc. to be used a bio lubricant as alternative to mineral lubricant oils. The suggested method for epoxidation is carboxylic peracid formed *in situ* reaction by using H_2O_2 and acetic acid. As a result of studies, the modified vegetable oils considered to have high potential of replacing mineral lubricants.

Sookyung, U. et. al. [12], This work uses 2, 5 and 10 phr of CNSL and decarboxylated CNSL as plasticizers in natural rubber compounding. Then cure characteristics, physical properties and thermal-mechanical behaviors of rubber formulations are tested to be used for comparative study of oil performances as plasticizers in rubber compounding. The results showed that CNSL performed much better than decarboxylated CNSL in terms of crosslink formation, cure rate, activation energy in cure kinetics and torque difference.

Raksawong S. et al. [13], the study works on epoxidation of CNSL and cardanol to be used as processing oil in natural rubber compounding. Epoxidation is achieved by peracetic acid generated *in situ* reaction by using H_2O_2 and glacial acetic acid as peracetic acid generator and an ion exchange resin, IR 120H, as catalyst. Decarboxylated CNSL, unmodified cardanol and epoxidized forms of CNSL and cardanol are used separately as processing oil for rubber compounding. Mooney viscosities, cure characteristics, swelling behaviors, bleeding and mechanical properties are tested and compared with these of petroleum based commercial oil, paraffinic oil. According to the results, rubber formula with epoxidized cardanol showed the best performance in terms of cure characteristics, tensile properties and antiaging behavior.

Lee, S. et. al. [22], In this research, cardanol is modified by two steps. At first step, it is acetylated by using acetic anhydride and next epoxidized by organic peracid generated *in situ* reaction by using H_2O_2 and formic acid as performic acid generator. Then Acetylated cardanol, epoxidized acetylated cardanol, and epoxidized soybean oil and di-2-ethylhexyl phthalate, a petroleum-based plasticizer, were used as plasticizers for PVC. Then the performances of modified cardanols compared with these of epoxidized soybean oil and petroleum-based plasticizer by running tensile,

thermogravimetric, thermal aging and leaching tests. The results reveled that epoxidized acetylated cardanol showed superior behavior when compared with the commercial plasticizer, although it weakened the interaction between PVC chains.

Campanella, A. et. al. [26], This study works on degradation of oxirane rings of epoxidized vegetable oils. First, the refined soybean oil is epoxidized by using peracetic acid generated *in situ* reaction mechanism, in which glacial acetic acid and were H_2O_2 used as per acetic acid generator and IR 120H ion exchange resin as catalyst. Then the effects of acetic acid, hydrogen peroxide and ion exchange resin on oxirane ring degradation were comparatively studied. It was seen that the most effecting factor on oxirane ring opening was the surface protons of ion exchange resin.

Mungroo, R. et. al. [30], In this work, epoxidation of canola oil was studied. Organic peracid formed *in situ* reaction method was used for epoxidation of unsaturation in the structure of canola oil. The main objective of study was to compare the efficiencies of two organic acids, formic acid and acetic acid. H_2O_2 and organic acid were used as carboxylic peracid generator and IR 120H ion exchange resin was picked as catalyst. The results showed that acetic acid performs better than formic acid at 65 ^{o}C with the mole ratio of H_2O_2/acetic acid/unsaturation: 1.5/1/0.5 and using catalyst as much as 22% of oil weight.

Anbu, N. et. al. [33], In this study, a new method, “Solvent Free Method”, is applied for acetylation of alcohols, phenols, amines and thiols. The difference between this new method and the conventional ones is that no solvent and catalyst is used. Acetylation is achieved by using acetic anhydride and substrate only. The results showed that acetylation with solvent and catalyst free method takes place in milder condition, in shorter reaction time and with higher percent yield.

Hosseini, M. et. al. [34], In this study, esterification of alcohols and phenols is achieved by solvent free method and ZnO used as catalyst. In the method, substrate and ZnO are mixed with either an acid anhydride or an acid chloride and stirred. It was reported that with acid chloride, the reaction time is much shorter.

Tamaddon, F. et. al. [35], In this work, acetylation of many alcohol and phenolic compounds, including methanol, ethanol, phenol and naphthol, were achieved by solvent free method, where ZnO was picked as catalyst. Acetyl chloride was used for acetylation. Phenolic hydroxyl/acetyl chloride: 1/1.2 was used as mole ratio where catalyst was 10% in total moles at room temperature. Much shorter reaction time and higher acetylation ratio were achieved by this method than conventional methods.

Chapter 3

Research methodology

In this research, cardanol, as model compound for CNSL, was modified to be used as processing oil for pure NR, pure CR and NR/CR (50:50) rubber blend. The modification was performed in two different ways: Epoxidation and acetylation. The reason for modifications is to see the effects of modifications of cardanol on its performance as processing aid in pure NR, pure CR and NR/CR (50:50) rubber compounding.

The characterizations of cardanol and its derivatives were achieved by FTIR, ^{1}H NMR and iodine value test. Then CR, NR and NR/CR (50:50) rubber blend formulations were prepared by using cardanol, epoxidized cardanol, acetylated cardanol and naphthenic oil, a petroleum based commercial oil. For each rubber formulation Mooney behavior was tested by Mooney Viscosimeter. Next, the cure characteristics of rubber formulations were tested by cure elastomer. After this step, the process continued only for NR/CR (50:50) rubber blend formulations. Preparing vulcanized samples, preparing suitable specimens for testing, swelling test, bleeding test, accelerated aging, hardness and tensile tests were done respectively.

The chart flow for overall methodology is given below in Figure 3.1.

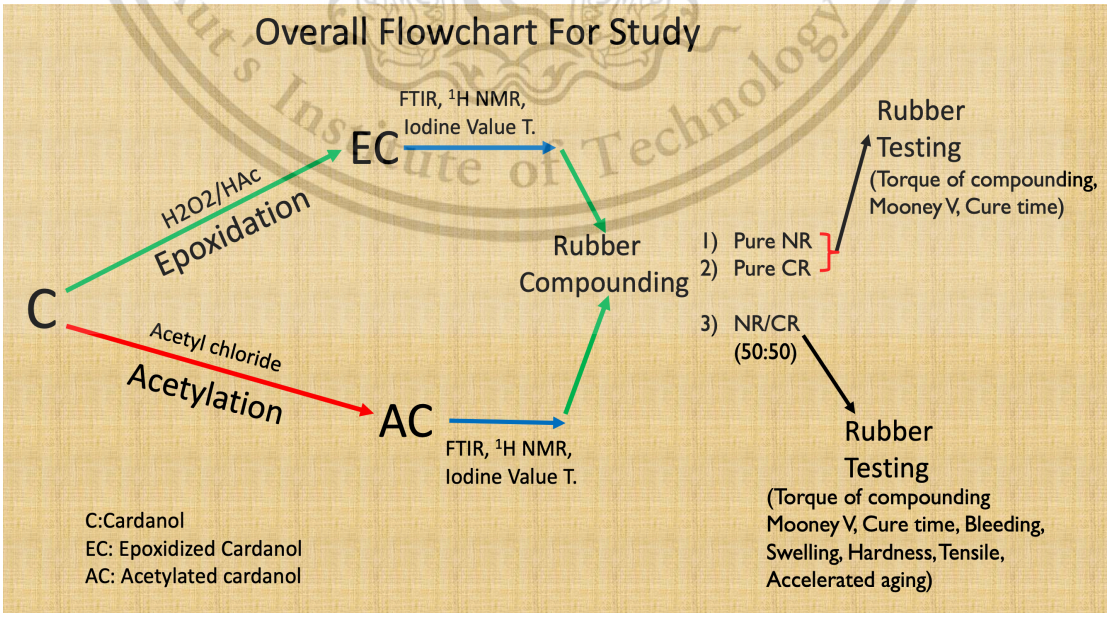


Figure 3.1 Overall flowchart for research methodology

3.1 Chemicals and materials

Table 3.1 List of chemicals for epoxidation and acetylation of cardanol.

Chemical	Manufacturer
Cardanol	Vertex Chemicals (Thailand)
Hydrogen peroxide (40%)	Carlo Erba (France)
Glacial acetic acid (99.8%)	Carlo Erba (France)
Toluene (99.5%)	Carlo Erba (France)
IR 120H ion exchange resin	Acros Organics (France)
Acetyl chloride (98%)	Acros Organics (France)
Zinc oxide (99.5%)	Global Chemicals (Thailand)
Ethyl acetate (99.8%)	Carlo Erba (France)
Sodium chloride (99.5%)	Loba Chemie (Thailand)
Sodium bicarbonate (99.3%)	Loba Chemie (Thailand)

Table 3.2 List of ingredients for rubber compounding.

Ingredients	Manufacturer
Natural rubber (NR)	Thaihua Rubber (Thailand)
Chloroprene (CR)	Denka (Japan)
ZnO	Global Chemicals (Thailand)
MgO	Global Chemicals (Thailand)
Stearic acid	PT. Cisadane Raya Chemicals
Carbon black	Global Chemicals (Thailand)
Processing oil	N: Global Chemicals (Thailand)
6 PPD	General Quimica S. A. (Spain)
ETU	General Quimica S. A. (Spain)
CBS	General Quimica S. A. (Spain)
Sulfur	Sahapaisal Industry (Thailand)

3.2 Equipment

Table 3.3 List of equipment

Equipment	Model	Manufacturer
Electric heater	RCT Basic	IKA Works, Inc.
Analytical balances	ML204	Mettler Toledo Co., Ltd.
Rotary evaporator	N-N Series	Tokyo Rikakikai Co., Ltd.
Compression molding		
Two-roll mill	LRM150	Labtech engineering Co., Ltd.
Mooney viscometer	SMV-201	Shimadzu Co., Ltd.
Moving die rheometer, MDR	II F 150	Nichigo Shoji Co., Ltd.
Universal testing machine, UTM	QC-536M1	Cometech testing machines Co., Ltd.
Hot air oven	UF 260	Memmert Gmbh + Co., Ltd.
Durometer hardness tester Shore A type	TECLOCK GS-719N	ATSD Fars P Co., Ltd.
Overhead stirrer	EURO-ST D	IKA Works, Inc.
Fourier transform infrared spectrometer, FTIR	Model NICOLET 6700	Thermo Fisher Scientific Inc.
Proton nuclear magnetic resonance spectrometer, ^{1}H NMR	JNM-ECZ500R/S1	Jeol Co., Ltd.
Oil bath		
Glassware		
Universal indicator		
Filter cloth		

3.3 Cardanol modification

Cardanol was modified by two methods separately: 1) Epoxidation through unsaturated sections of side chain. 2) Acetylation through phenolic hydroxyl group. Unmodified cardanol, epoxidized cardanol and acetylated cardanol are shown in Figure 3.2

Figure 3.2 Left to right: Cardanol, epoxidized cardanol and acetylated cardanol

3.3.1 Epoxidation of cardanol

Epoxidation of cardanol was performed by peracetic acid generated in situ reaction, in which, the formation of per acetic acid from hydrogen peroxide and acetic acid takes place simultaneously with the epoxidation of double bonds in the side chain of cardanol.

For the epoxidation of cardanol, hydrogen peroxide and glacial acetic acid generate peracetic acid for in situ reaction. Toluene is utilized as solvent and IR 120H ion exchange resin catalyzes the reaction. The overall reaction for epoxidation of cardanol is given in Figure 3.3.

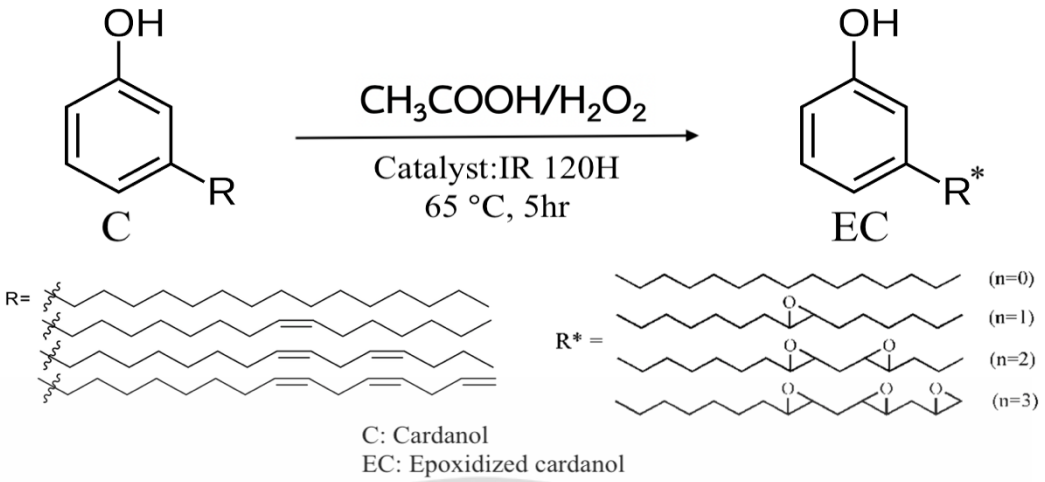


Figure 3.3 Epoxidation of Cardanol by peracetic acid generated in situ reaction. [15]

Using the weights in the Table 3.4 or other weights keeping the same weight ratios as in the table, the procedure that was followed is given below:

Table 3.4 The weight ratios of chemicals used for the epoxidation reaction of cardanol. [13]

Chemical	The Function of Chemical	The weight (grams)
Cardanol	Substrate to be Epoxidized	100
Toluene	Solvent	100
Hydrogen Peroxide (30%)	Oxygen Resource for Epoxidation	156.5
Glacial Acetic Acid	Generates Peracetic Acid with H_2O_2	27.6
IR 120H Ion Exchange Resin	Catalyst	22

The experimental set up used or epoxidation of cardanol was as in Figure 3.4.

Procedure for epoxidation of cardanol:

1. Place the weighed amounts of cardanol, toluene, glacial acetic acid and amberlite IR 120H ion exchange resin in a three necked round bottom flask.
2. Use a heater equipped with thermostat and use water bath instead of oil.

3. Connect mechanical stirrer, condenser and nitrogen gas container to the reactor and stir the mixture for 30 minutes under nitrogen atmosphere.
4. Add hydrogen peroxide very slowly, control the temperature at 65 °C and let the reaction continue for 5 hours.
5. After the reactor cools down to room temperature, separate the catalyst by filtration.
6. Wash the filtered liquid with $NaHCO_3$ solution using separatory funnel in order to neutralize remaining acetic acid. Each time wait for the layers of water and oil are separated and remove the water.
7. Separate toluene by rotary evaporator at suitable temperature and pressure for toluene

Figure 3.4 Experimental set up for epoxidation of cardanol

The biggest difficulty was to control temperature. The reaction is exothermic and especially after 50 °C reaction too fast and it is too hard to control temperature at 65°C. In order to resolve the problem, first, water bath was preferred instead of oil, since the reaction temperature is less than the boiling point of water and water has much bigger heat capacity, which would help temperature increase more slowly. Second, temperatures of both inside reactor and water bath were measured simultaneously for better temperature control.

The problems during washing the epoxidized cardanol were the risk of overflowing mixture during neutralization of acetic acid by sodium bicarbonate solution due to the carbon dioxide formation and long waiting time for separation of water and oil layers.

Below, in Figure 3.5, some pictures taken during purification of epoxidized cardanol are shown.

(a) (b) (c)

Figure 3.5 (a) Separating catalyst by filtration, (b) water and oil layers after washing, (c) separating toluene by rotary evaporator.

3.3.2 Acetylation of cardanol

Acetylation of cardanol was achieved by 'Solvent Free Acetylation' method, which requires no solvent usage and has many advantages over the solvent used conventional methods. The advantages of solvent free method are much shorter reaction time, higher yield percent and purity and lower cost when compared to the conventional methods [33, 34, 35].

Although both acid anhydrides and acid chlorides can be used for acetylation process, acetyl chloride was preferred for this study, since acetylation with acid chlorides are much faster than that with acid anhydrides [33, 34, 35]. This actually shows high reactivity of acid chlorides and, of course, necessitates more safety precautions. Acetyl chloride reacts with water vigorously to produce acetic acid and hydrochloric acid, so water was avoided very strictly.

The overall reaction for the acetylation of cardanol is shown in Figure 3.6.

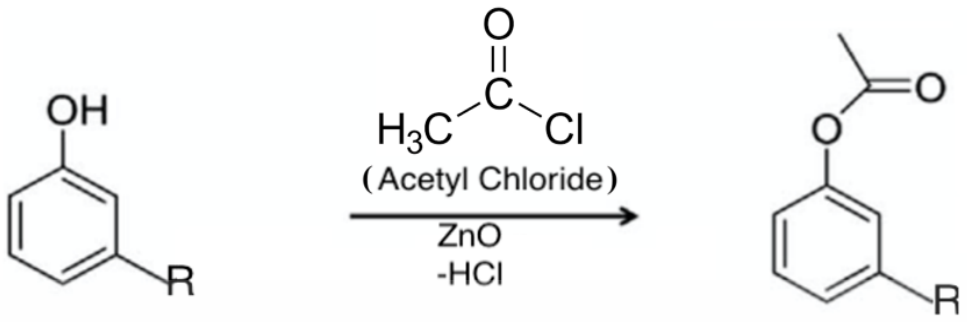


Figure 3.6 Acetylation of cardanol by solvent free method

The mole ratios of 1:1.5:0.3, as shown in Table 3.5 were chosen for cardanol, acetyl chloride and zinc oxide respectively based on the suggested information from the literature review [35].

Table 3.5 The weight and mole ratios of chemicals for the acetylation of Cardanol [35].

Chemical	The Function of Chemical	The weight (grams)	The mole
Cardanol	Substrate to be acetylated	300	1
Acetyl chloride	Acetylating agent	117.7	1.5
Zinc oxide	Catalyst	24.4	0.3

For the acetylation of cardanol, the following procedure was followed:

1. Use a three necked round bottom reactor equipped with a mechanical stirrer, a condenser and a nitrogen resource. The reactor should be placed inside a water bath for temperature control and must remain in a hood during the reaction because of the HCl production.
2. Put the calculated amount of cardanol and ZnO in the reactor and start mechanical stirrer.
3. Add the calculated amount of acetyl chloride dropwise and very slowly by using a separatory funnel and be very careful to avoid overflowing.
4. After acetyl chloride addition, let the reaction continue for 30 minutes.
5. Let the reactor cool down to room temperature and separate ZnO by filtration.

6. Wash the liquid obtained from the reaction with sodium bicarbonate solution to neutralize HCl and remaining acetyl chloride and after that wash with distilled water to remove remaining sodium bicarbonate.
7. Use ethyl acetate for easier separation of oil and water layers.
8. Evaporate the remaining water and ethyl acetate by rotary evaporator at suggested pressure and temperature for water and ethyl acetate.

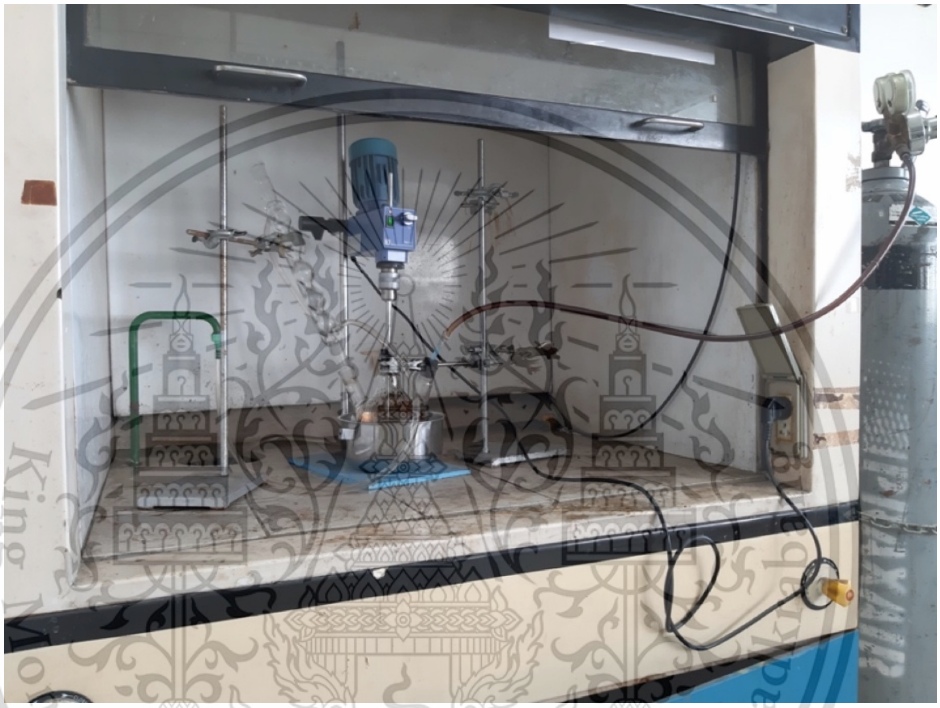


Figure 3.7 Experimental set-up for acetylation of cardanol.

The reaction of ethyl acetate with the phenolic hydroxyl of cardanol was so fast that the reactor was vulnerable to overflowing. For this reason, the addition of acetyl chloride was very slow, which took around half an hour. The presence of HCl was observed very easily by its distinctive odor and using universal pH test strips. Neutralizing HCl by sodium bicarbonate solution was handled carefully with more dilute solution, since carbon dioxide production would cause blowing up in closed container or overflowing in open container. Using ethyl acetate helped separation of oil and water layers by decreasing oil density to go up faster and giving a milky color to water for clearer separation. Some pictures related to the purification of AC is given in Figure 3.8.

(a) (b) (c)

Figure 3.8 (a) initial pH of AC, (b) final pH of AC, (c) separation of water and oil layers

3.4 Characterization

The characterization of EC and AC was achieved by FTIR, ^{1}H NMR and Iodine Value tests. The reason was to find out evidences of changes in the functional phenolic hydroxyl and unsaturation in the side alkyl chain of cardanol. For FTIR test the samples were used in their original forms, for ^{1}H NMR, however, chloroform was chosen as solvent after it was confirmed that cardanol and its derivatives were soluble in chloroform. FTIR and ^{1}H NMR was used to prove the presence or disappearance of phenolic hydroxyl groups, oxirane rings, acetate groups and double bonds. Iodine Value test helped to compare unsaturation of C, EC and AC. The results will be discussed in chapter 4.

3.5 Rubber compounding

Three groups of rubber formulations were prepared: Pure CR, Pure NR and NR/CR (50:50) blend. For each type, four rubber formulations, which differ only by the processing oil used, were prepared by using unmodified cardanol, epoxidized cardanol, acetylated cardanol and naphthenic oil, which is petroleum based commercial oil. The ingredients used for rubber formulations and their concentrations were as given below in the Table 3.6.

Table 3.6 Concentrations and functions of ingredients used for rubber compounding.

Ingredient	Pure CR	Pure NR	NR/CR (50:50)	Function
	Concentration (phr)			
Chloroprene (CR)	100	0	50	Synthetic Rubber
Natural Rubber (NR)	0	100	50	Natural Rubber
ZnO	5	5	5	Activator of vulcanization
MgO	1	1	1	Activator of vulcanization for CR
Stearic Acid	2	2	2	Activator, dispersing agent, plasticizer and lubricant
Carbon Black	50	50	50	Filler
Processing Oil	5	5	5	Processing oil
6 PPD	1	1	1	Antioxidant
ETU	1	1	1	Curing accelerator
CBS	0.5	0.5	0.5	Primary accelerator
Sulfur	1	1	1	Vulcanizing agent

As processing oil C, EC, AC and naphthenic oil were used for compounding of each rubber formulation respectively, so four formulations, which differed only by processing oil were prepared for each pure CR, pure NR and NR/CR (50:50) blend.

The rubber compounding was done by internal mixer followed by two-roll external mill rubber compounding machine. To minimize the differences of preparing four formulas, the total compounding time, the time and order of each ingredient addition were controlled. The compounding was done by the following procedure:

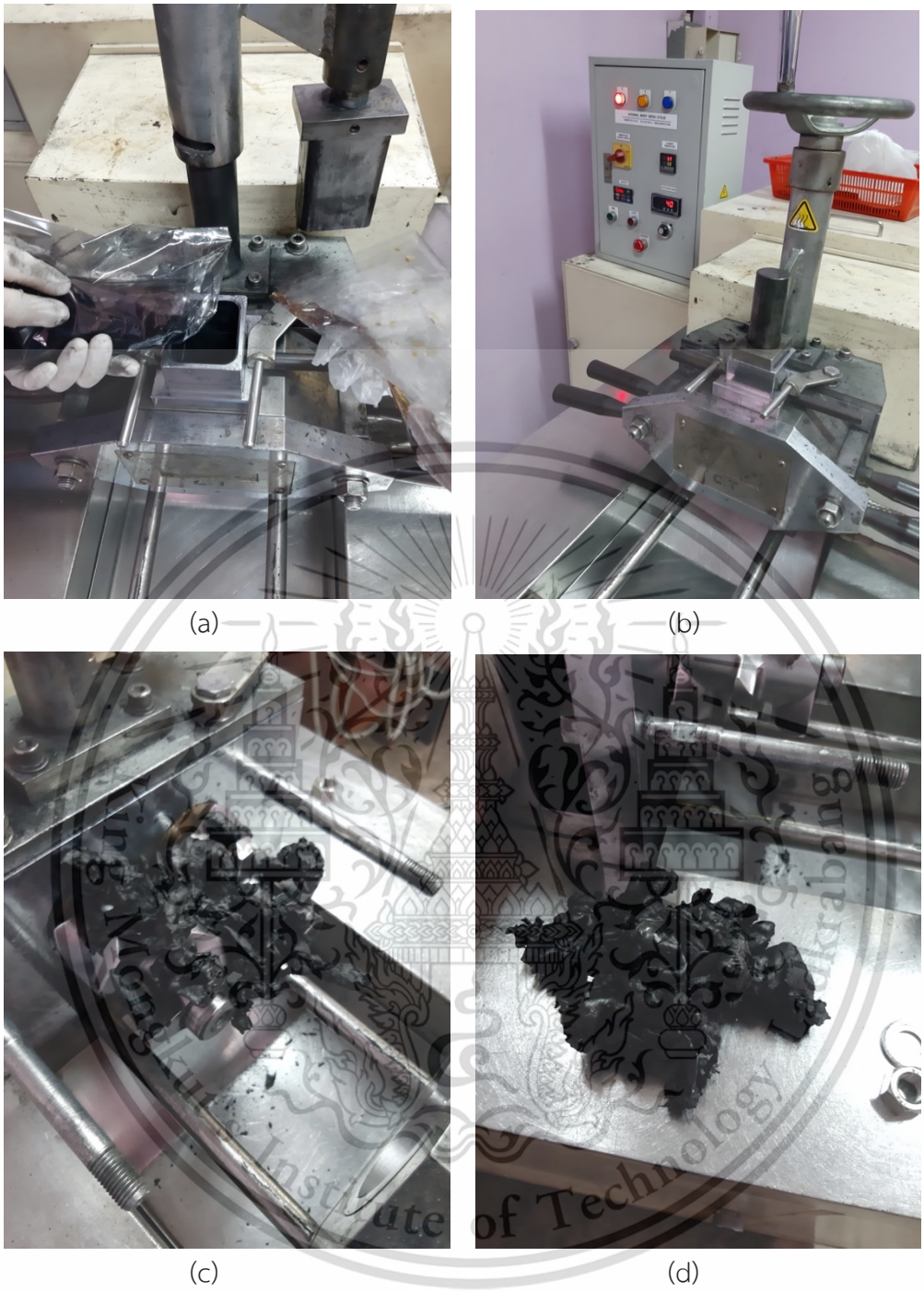
1. Turn on the internal mixer and computer. Set temperature to 50 ℃ and rotor speed to 40 rpm.
2. Do the calibration each time before starting the compounding.
3. Add the ingredients in the following order and time given in the Table 3.6 and shown in Figure 3.9.

4. Record time, temperature and torque data for each formulation.
5. Mix each formulation by cut and fold method for three minutes using external two-roll mixer and prepare proper sheets to be used for Mooney viscosity and cure time measurements as shown in Figure 3.10.

Table 3.7 The order and time of adding ingredients for rubber compounding by internal mixer.

Order	Ingredients	Mixing time (min)
1	Rubber	3
2	Carbon-Black and processing oil	6
3	Stearic acid, zinc oxide and 6 PPD	1
4	ETU and CBS	2
5	Magnesium oxide and sulfur	2
Total mixing time by internal mixer: 14 min		

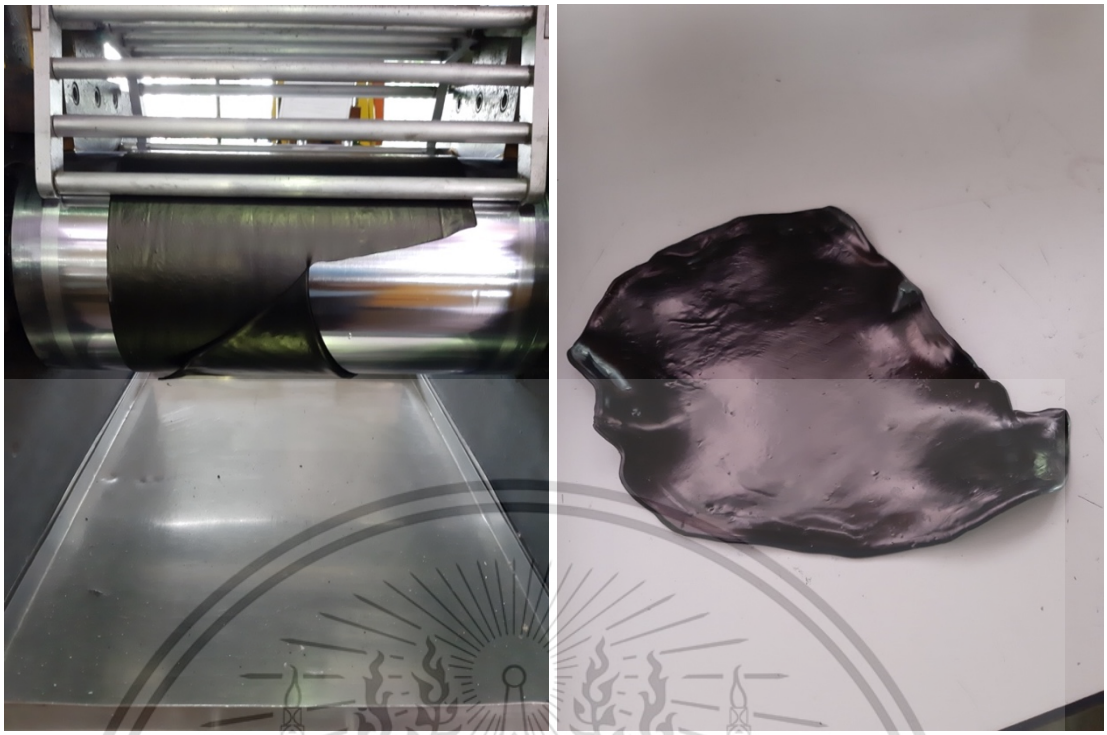
Before figuring out the procedure given above, a few times of failures were encountered. At first, all of the ingredients were added together, which caused a very high temperature increase, although the machine has air cooling system. The temperature raised to 140 °C, which ended up with vulcanization. When the procedure above was applied, there still was temperature increase, however it was kept under 100 °C.



(a) (b)

(c) (d)

Figure 3.9 (a) Feeding internal mixer, (b) internal mixer on progress, (c) right after opening mixer chamber, (d) rubber just removed from internal mixer.



(a) (b)

Figure 3.10 (a) Rubber compounding by cut and fold method, (b) Rubber sheet ready for Mooney viscosity test, cure time test and compress molding.

To minimize the errors in data, each compounding was repeated three times and average data were used for analyzing.

3.6 Rubber testing

Rubber tests before vulcanization were studied for all three rubber formulation types: Pure NR, pure CR and NR/CR (50:50) rubber blend. Vulcanization and the physical and mechanical tests for vulcanizates were run only for NR/CR (50:50) rubber blend. The overall flowchart for rubber testing is shown in Figure 3.11.

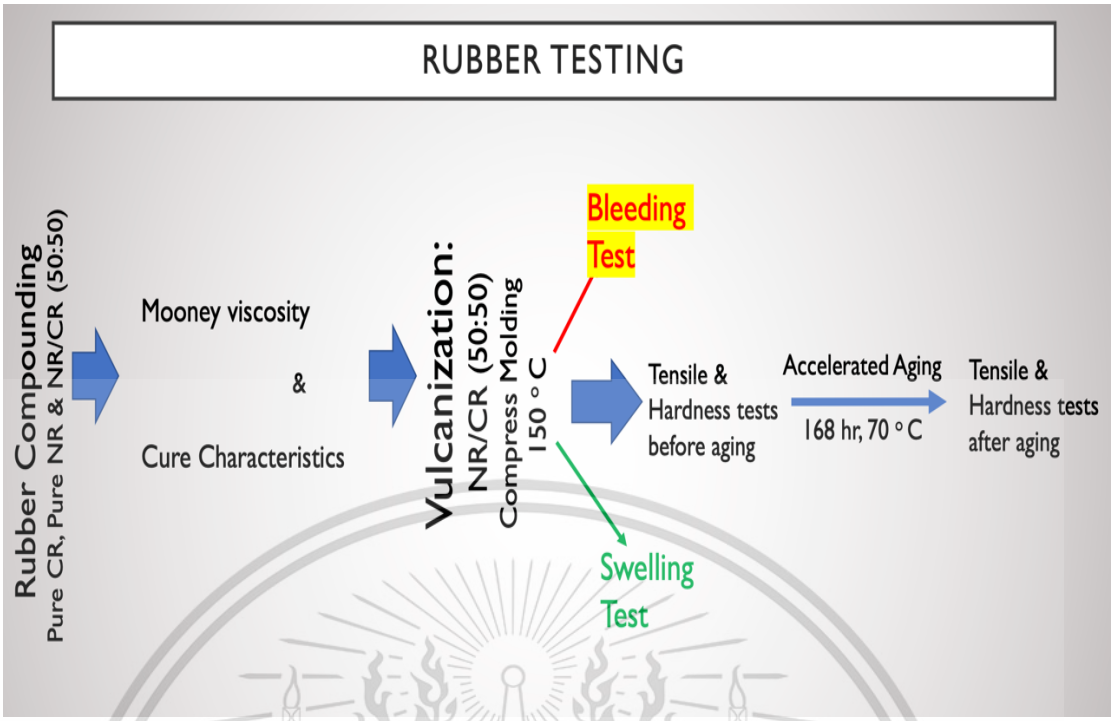
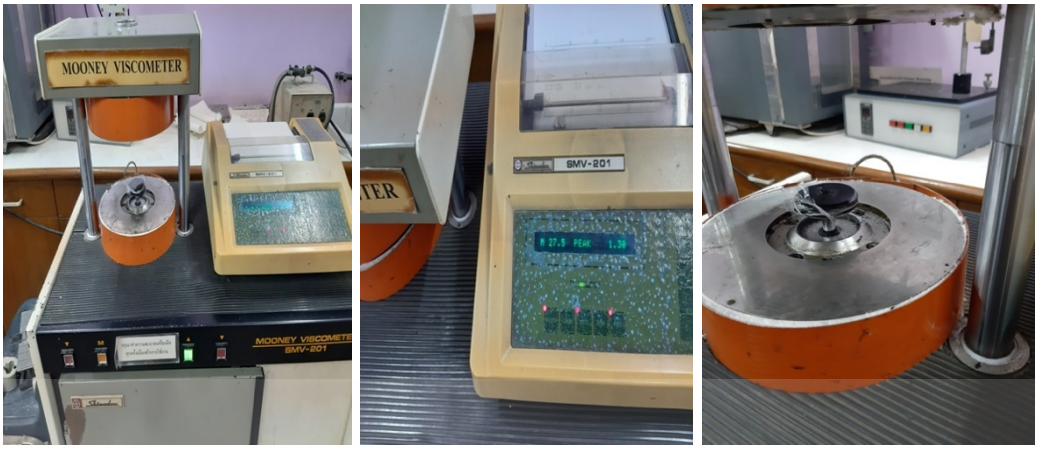


Figure 3.11 The overall flowchart for rubber testing.

3.6.1 Mooney viscosity test

Mooney test was performed according to ASTM D1646 at 100 ℃. Mooney viscometer, SMV-201 model was used, and Mooney viscosity values were recorded. The viscosity reflects the molecular weight of un-vulcanized rubber, so rubber formulas prepared should have very close Mooney viscosity values. The main purpose here was to control all other factors including molecular weight, so that we can compare the performances of overmentioned four different processing oils.

As previously mentioned, one formula of each oil (C, EC, AC and N) for pure NR, pure CR and NR/CR (50:50) blend was prepared three times. Mooney viscosity test was run for each formulation and the results were recorded. Some pictures related to Mooney viscosity test are shown in Figure 3.12.



(a) (b) (c)

Figure 3.12 Pictures taken during Mooney viscosity test: (a) Specimen is placed in the Mooney viscometer, (b) Mooney Viscometer is on progress and (c) specimen after Mooney viscosity testing.

3.6.2 Cure characteristics

Cure characteristics of four rubber formulas were measured by Moving Die Rheometer according to ASTM D5289 at 150 °C. Compounded rubber formulations were kept waiting for 1 day for the reason that distribution of ingredients still continues after compounding and reaches to the equilibrium within this waiting time. After the waiting time, cure test was run for each formulation. Cure time and scorch time values were recorded, then using these data cure rate index (CRI) values were calculated by using the formula below for each and every rubber formula.

$$\mathrm{CRI} = \frac{100}{\text{cure time} - \text{scorch time}}$$

For every time, cure test continued until the slope of curve for cure rate is zero. Then cure time and scorch time were measured.

Cure times obtained here were used for vulcanization process as well as for the understanding if the processing oil interfered with the curing process. Some pictures belonging to cure test are shown below in Figure 3.13.

(a) (b) (c)

Figure 3.13 Pictures taken during cure test (a) specimen is placed in moving die rheometer for cure time test (b) moving die rheometer on progress and (c) specimen after cure time test.

3.6.3 Compress molding

The vulcanized samples of 12 x 12 x 0.2 cm^3 size was prepared using standard steel molds by compress molding method at 150 °C, at least 24 hours after compounding according to ASTM D4703.

The temperature of compress molding machine was set to 150 °C, the preheating time was set as 1 minute and heating time for each formula was set according to the result obtained from cure test. The steel mold was coated by a very thin layer of silicon oil, the necessary amount of un-vulcanized rubber was placed inside mold and the mold was placed in the compress molding machine. At the end of heating time the mold was removed from machine and after cooled down, the vulcanized rubber was removed; extra parts were cut out by scissors and the sample was spared for specimen preparation to be used for the following tests. Some pictures for compress molding process are shown in Figure 3.14.

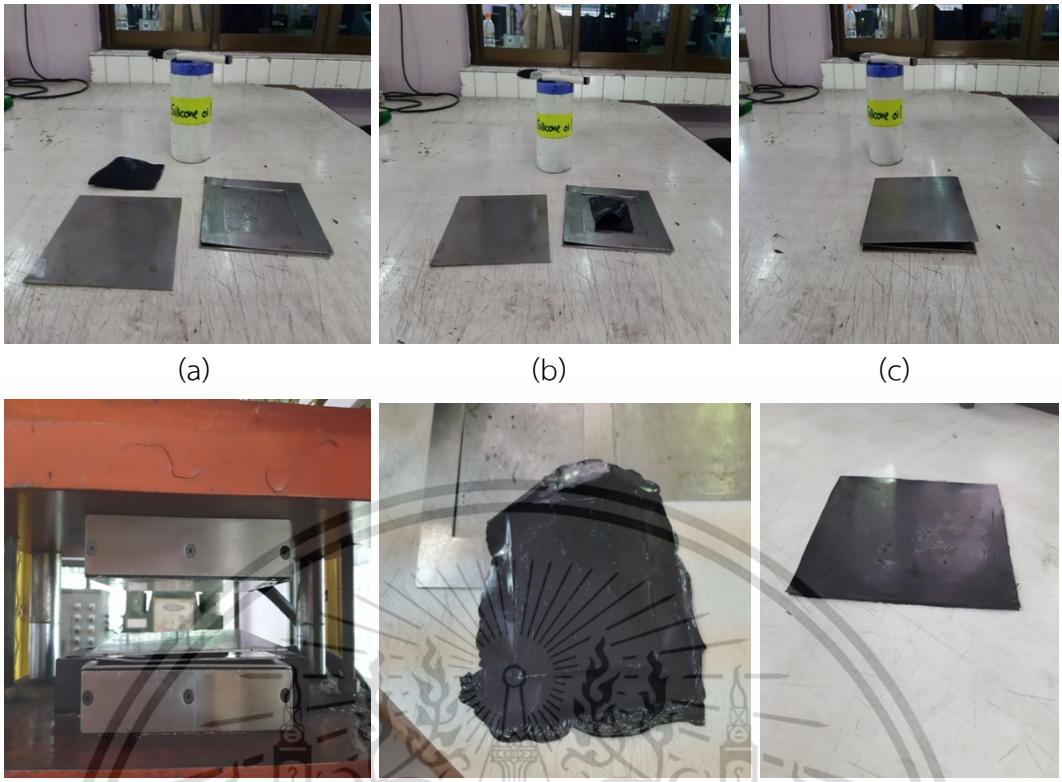


Figure 3.14 (a) mold is coated by a very thin silicon layer, (b) un-vulcanized rubber is placed in the mold, (c) specimen is ready for compress molding, (d) mold is placed in the machine, (e) vulcanized specimen right after being removed from mold and (f) extra parts of vulcanized specimen is removed

3.6.4 Swelling test

In order to observe swelling behaviors of rubber formulas, swelling test was run according to ISO 1817. Toluene was chosen as a solvent and the following procedure was followed:

1. Prepare 7 test specimens having the size of 1 x 1 x 0.2 cm^3 for each rubber formula
2. Prepare 7 test tubes for each rubber formula and label them.
3. Weigh each sample with 4 decimal points, place in the test tube and record the measured weight with the label of test tube. Repeat this for all samples of four rubber formulas.
4. Pour toluene on to sample and cover all sides of test tubes by aluminum foil so as to protect from light and solvent exit.
5. Keep the samples in solvent for 96 hours.

6. After waiting time complete, uncover each test tube, take out the specimen, measure the weight and record data.

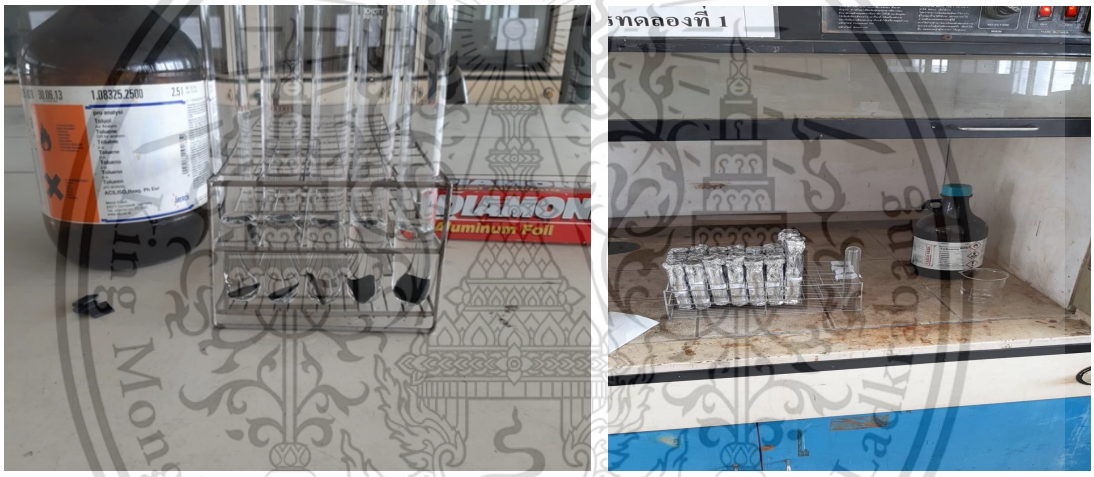
7. Use the following formula to calculate swelling%

$$Swelling\% = \frac{(W2 - W1)}{W1} 100$$

W1: Weight of sample before being exposed to toluene

W2: Weight of sample after swelling

Crosslink density and swelling % are inversely proportional, which means bigger swelling % is a result of lower crosslink density. Figure 3.15 shows the covered test tubes keeping rubber samples immersed to toluene.



(a) (b)

Figure 3.15 (a) Specimens are immersed into toluene, (b) test tubes are covered by aluminum foil to prevent solvent exit and light entrance.

3.6.5 Bleeding test

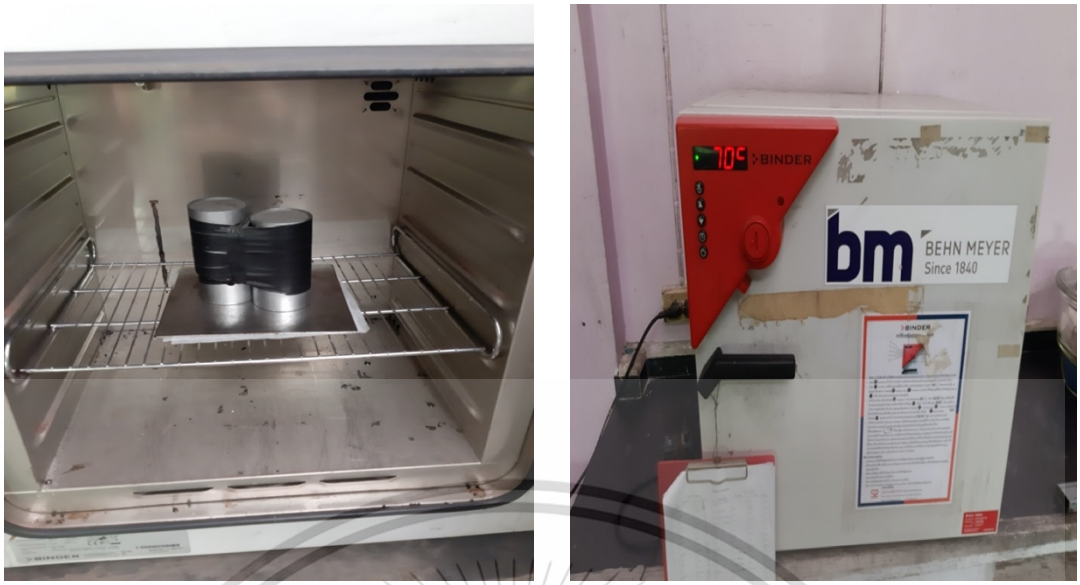
Bleeding is migration of liquid in a polymer formula to the surface. In case of rubber formulas that was prepared in this study, bleeding is the movement of processing oil, since it was the only liquid at the test conditions, so by bleeding test, we actually tested the tendency of processing oil to migrate out of NR/CR (50:50) rubber blend. Although not the only criteria, the bleeding amount may give idea about the compatibility of oil with rubber.

The bleeding test was performed according to ISO 177. The following procedure was followed for bleeding test:

1. Prepare 5 specimens of each rubber formula with the size 5 x 5 x 0.2 cm^3, label them with a suitable marker.
2. Weigh them and record data using 4 decimal points.
3. Prepare sandwich like system for each specimen. The outer most will be two steel plates, one step inside will be wax paper sheets next to the steel plates and at the center, specimen will be placed. Repeat this for all specimens.
4. Place each specimen in the oven, load 5 kg of weight on the top, after finishing all, set temperature to 70 °C and keep for 24 hours.
5. After 24 hours, take the samples out, wait until cools down to room temperature, then wipe each sample's surface gently with a paper towel, measure the weight and record the data. Repeat this for all specimens.

The decrease in weight of specimen is the amount of oil moved out. According to ISO 177, if the discharged liquid is up to 0.45 gram, it is not bleeding, but if more than 0.45 gram it is considered to be bleeding. Some pictures belonging to bleeding test are shown in Figure 3.16.

(a) (b)



(c) (d)

Figure 3.16 (a) and (b) specimen is placed between steel plates inside waxed paper, (c) specimen is placed in the oven with loaded 5 kg weight on and (d) bleeding test on progress.

3.6.6 Accelerated aging

Heat deterioration of rubber formulas was observed by "Accelerated Aging Test", so that the abilities of different processing oils to help rubber against aging was compared. The Accelerated Aging test was run in an oven allowing air circulation at 70 °C for 168 hours according to ASTM D573. The tensile and hardness tests were run before and after aging, which helped us see the change in mechanical properties during aging process.

C-type dumbbell specimens for tensile test and rectangle test specimens for hardness test were prepared. Then placed in an air oven as shown in Figure 3.17, and every two days changed to be upside down to allow homogeneous contact with air and heat. At the end of 168 hours, specimens were removed from the oven to be tested.

(a) (b) (c)

Figure 3.17 (a) Air oven used for accelerated aging, (b) specimens for tensile test in accelerated aging process, (c) specimens for hardness test in accelerated aging process.

3.6.7 Tensile test

Tensile properties were tested before and after accelerated aging process by a universal testing machine at the speed of 500 mm/min according to ASTM D412. Data was recorded before and after aging as tensile strength, max elongation at break and stress/strain modulus at 100% elongation (M100). The following procedure was followed:

1. Prepare 20 pieces of C-type dumbbell specimens for each rubber formula.
2. For each rubber formula, spare 10 specimens for accelerated aging process and use the remaining 10 specimens for tensile test before accelerated aging.
3. Measure width and thickness of each specimen by micrometer caliper, since these values must be entered before tensile test each time.
4. Test each specimen using universal testing machine and record data for tensile strength, maximum elongation at break and M100.
5. Repeat the same procedure for the 10 samples of each rubber formula that went through aging process after aging process.

Some pictures taken during tensile test are shown in Figure 3.18.

(a) (b) (c)

Figure 3.18 (a) Thickness and width values entry before tensile test, (b) specimen placed in the universal testing machine, (c) tensile test on progress.

3.6.8 Hardness test

Shore A hardness test was applied to samples of four rubber formulas by shore hardness tester according to ASTM D2240 before and after aging. Hardness test was repeated 10 times for each rubber formula in order to minimize errors.

Durometer hardness tester Shore A type, TECLOCK GS-719N model tester was used. Five kg of weight was loaded, each time specimen was placed in the tester, and pushed up to the dart and held for 15 seconds until hardness value became stable as shown in Figure 3.19.

Figure 3.19 Running shore A hardness test.

Chapter 4

Main results and discussions

This research studied synthesis of epoxidized cardanol and acetylated cardanol to be used as processing aid in pure CR, pure NR and NR/CR (50:50) rubber compounding. After rubber compounding, Mooney viscosity, cure behavior, bleeding, swelling, tensile and hardness tests were run in order to comparatively study performances of unmodified cardanol, epoxidized cardanol, acetylated cardanol and naphthenic oil as processing aid and to see if these oils have any effect on rubber formulations' cure characteristics, physical and mechanical properties.

4.1 Synthesis of cardanol derivatives

Cardanol was modified by two methods separately: Epoxidation and acetylation. Epoxidation and acetylation were achieved on two different sections of cardanol molecule. Epoxidation was aimed to achieve on unsaturation parts of long side chain; whereas, acetylation was planned to achieve on phenolic hydroxyl of cardanol. Figure 4.1 shows the changes taking place in functional groups of cardanol by circling the functional groups on their structural formulas.

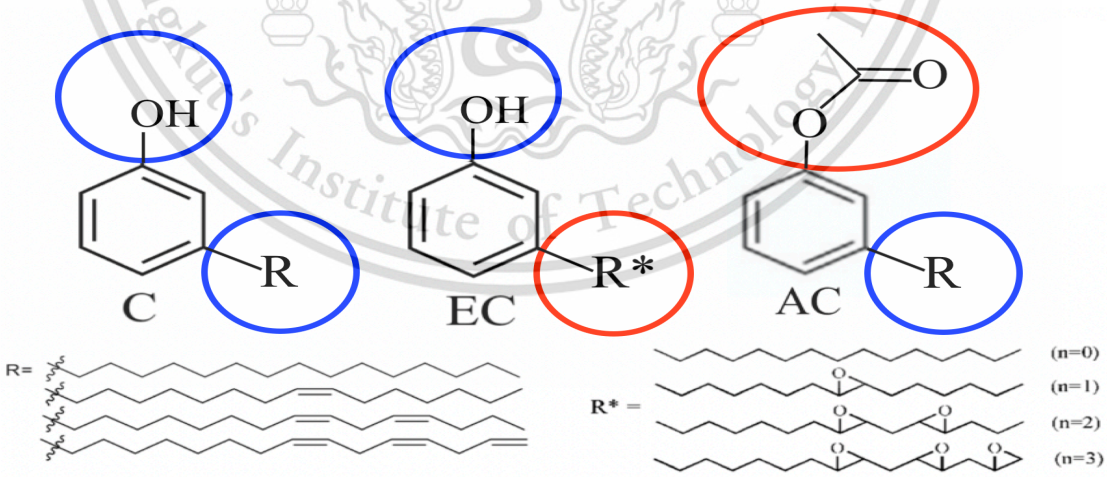


Figure 4.1 Structural formulas of C, EC and AC. Any change in the functional group is indicated by red color of circling.

Cardanol and its derivatives have their own distinctive odors. Cardanol has reddish color, while acetylated cardanol has dark brownish and epoxidized cardanol

has very dark brownish-red colors as shown in Figure 4.2. While viscosities of C and AC are quite similar as part of pouring experience, EC is much more viscous than C and AC and requires spoon to be poured.

Figure 4.2 Left to right: EC, AC and C

Fourier-transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and iodine value test were run to prove that first, the overmentioned modifications took place and second, these modifications have been realized on the sections as planned. FTIR, ^{1}H NMR and iodine value test results of EC and AC were compared with these of unmodified-cardanol in order to see if the modifications were achieved as aimed or not.

4.1.1 Characterization of EC and AC

4.1.1.1 FTIR analysis of EC and AC

FTIR results of C and EC and AC are given below in Figure 4.3 (a). The results of EC and AC are compared with that of C in order to discuss the changes from unmodified C to EC and AC. Table 4.1 could be helpful for analyzing the peaks, since it includes some distinctive peaks for some functional groups.;

Epoxidation should take place by breaking down pi bonds in the side chain of cardanol and forming oxirane rings. Phenolic hydroxyl should not change during epoxidation. The broad peak at 3340 cm^{-1} belonging to O-H stretching of phenolic hydroxyl group proves that phenolic hydroxyl was not affected while

epoxidation reaction took place. The peak at 3008 cm^{-1} as a result of C-H stretching of alkene gets much smaller for EC, which is an evidence that unsaturation of the side chain of EC decreases. A new peak for EC at 1735 cm^{-1}, which is not seen for C, indicates the formation of ketonic carbonyl group at side chain. The presence of carbonyl group in the alkyl chain indicates that not all of unsaturation is turned into epoxy groups (oxirane rings). The new peak at around 825 cm^{-1} is an evidence for the formation of oxirane rings. The peaks for C-H stretching of side chain at 2923 cm^{-1} and 2853 cm^{-1}, C=C stretching of aromatic ring at around 1590 cm^{-1}, C-H bending of side chain at 1455 cm^{-1}, 780 cm^{-1} and around 690 cm^{-1} are common for C and EC.

Table 4.1 Some FTIR transmittance peaks for (corresponding to Figure 4.3) [13, 15, 22, 48].

Peak	Wave number(cm^{-1})
Broad peak for O-H stretching phenolic hydroxyl	3350
Sharp peak for =C-H stretching of aliphatic chain	3007
Sharp peak for C=O stretching of acetate	1765
Sharp peak for C=O stretching of side chain	1735
Sharp peak for C-O stretching of ester group	1200
Peak for oxirane ring	Around 825

Acetylation of cardanol was aimed to be achieved through the phenolic hydroxyl group. As shown in Figure 4.1, H atom of phenolic hydroxyl group is replaced with an acetate group and side chain is not supposed to change during the acetylation reaction. First of all, as seen in Figure 4.3, disappearance of broad peak belonging to phenolic hydroxyl at around 3340 cm^{-1} and existence of new peaks resulting from C=O stretching of acetate group at 1765 cm^{-1} and C-O stretching of ester group at 1200 cm^{-1} proves the acetylation of cardanol on phenolic hydroxyl group. The peaks for C=C stretching of aromatic ring at around 1590 cm^{-1}, C-H stretching of side chain at 2924 cm^{-1} and 2853 cm^{-1}, and C-H bending of side chain at 1455 cm^{-1}, 780 cm^{-1} and around 690 cm^{-1} are common for A and AC. The very weak peaks between 2000-1650 cm^{-1} belong to C-H bending of aromatic ring and common for all C, EC and AC.

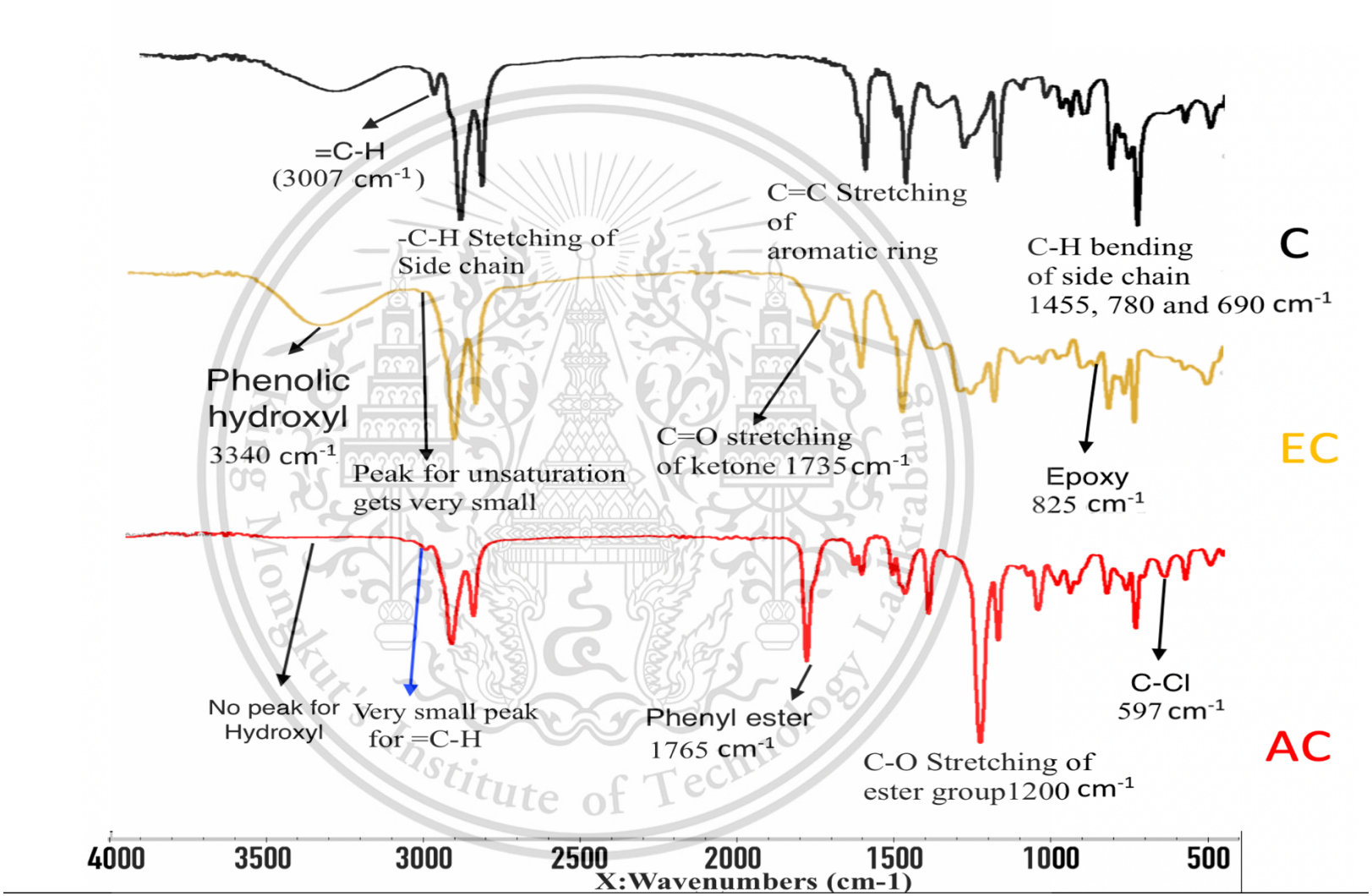


Figure 4.3 FTIR results of unmodified cardanol, epoxidized cardanol and acetylated cardanol

Unfortunately, the peak, which is present for C and represents the unsaturation in the side chain at 3007 cm^{-1} gets very small for AC. This actually shows that the unsaturation of alkyl chain decreased during the acetylation reaction. The new peak at 597 cm^{-1} seems to be the answer for why unsaturation decreased for AC. This peak belongs to C-Cl stretching, which tells us that the HCl produced as byproduct during acetylation reaction reacted with the double bonds of aliphatic chain, which is known as addition reaction of halo acids to alkenes or hydrohalogenation of alkenes, as seen in Figure 4.4, which easily takes place at room temperature [51]. In this case, if unsaturation must be protected during the acetylation, another acetylating agent should be preferred instead of acetyl chloride. Acetyl chloride was picked because of a short reaction time provided by its high chemical reactivity; however, the by-production of hydrochloric acid must be taken into the consideration if there are functional groups of substrates having potential to react with byproduct.

Figure 4.4 Hydrohalogenation of double bond [51]

4.1.1.2 Analyzing ^{1}H NMR results of EC and AC

Proton NMR results are given in Figure 4.5 for C, EC and AC. The Table 4.2 includes some distinctive peaks for C, EC and AC. The peaks at 7.1-7.3 ppm, 6.6-6.8 ppm, 5.4 ppm and 2.0 ppm belong to H atoms of aromatic ring, phenolic hydroxyl group, vinyl (-C=C-H) and allyl (=C-CH_3) respectively. The peaks belonging to vinyl at 5.4 ppm and allyl at 2.0 ppm for C gets much smaller for EC, which can be explained by saturation of double bonds in aliphatic chain by the formation of oxirane rings. On the other hand, the new peaks belonging to epoxy groups for EC at 2.9-3.2 ppm prove the formation of oxirane rings in the side chain. The peaks at 6.6-6.8 ppm show that phenolic hydroxyl is protected during epoxidation reaction. Some common peaks of aromatic ring, secondary alkyl (R-CH_2-R) and primary alkyl (R-CH_3) at 7.1-7.3 ppm, 1.2-1.6 ppm and 0.9 ppm respectively are visible as expected.

As seen in in Figure 4.5, the peak at 6.6 ppm, which belongs to phenolic hydroxyl, disappears for AC proving that hydroxyl group disappears during the acetylation process. A new peak at 2.3 ppm belonging to methyl connected to carbonyl group (-CO-CH_3) is found in the results of AC, which shows the formation of acetate group. The peaks as a result of vinylic hydrogen at 5.4 ppm becomes very small for AC, which means that the side chain of AC is more saturated. This result is actually consistent with FTIR results, as it was mentioned in the section 4.1.1.1 that the aliphatic chain had become more saturated during the acetylation reaction. And the peaks of aromatic ring, secondary alkyl (R-CH_2-R) and primary alkyl (R-CH_3) at 7.1-7.3 ppm, 1.2-1.6 ppm and 0.9 ppm respectively are also visible for AC.

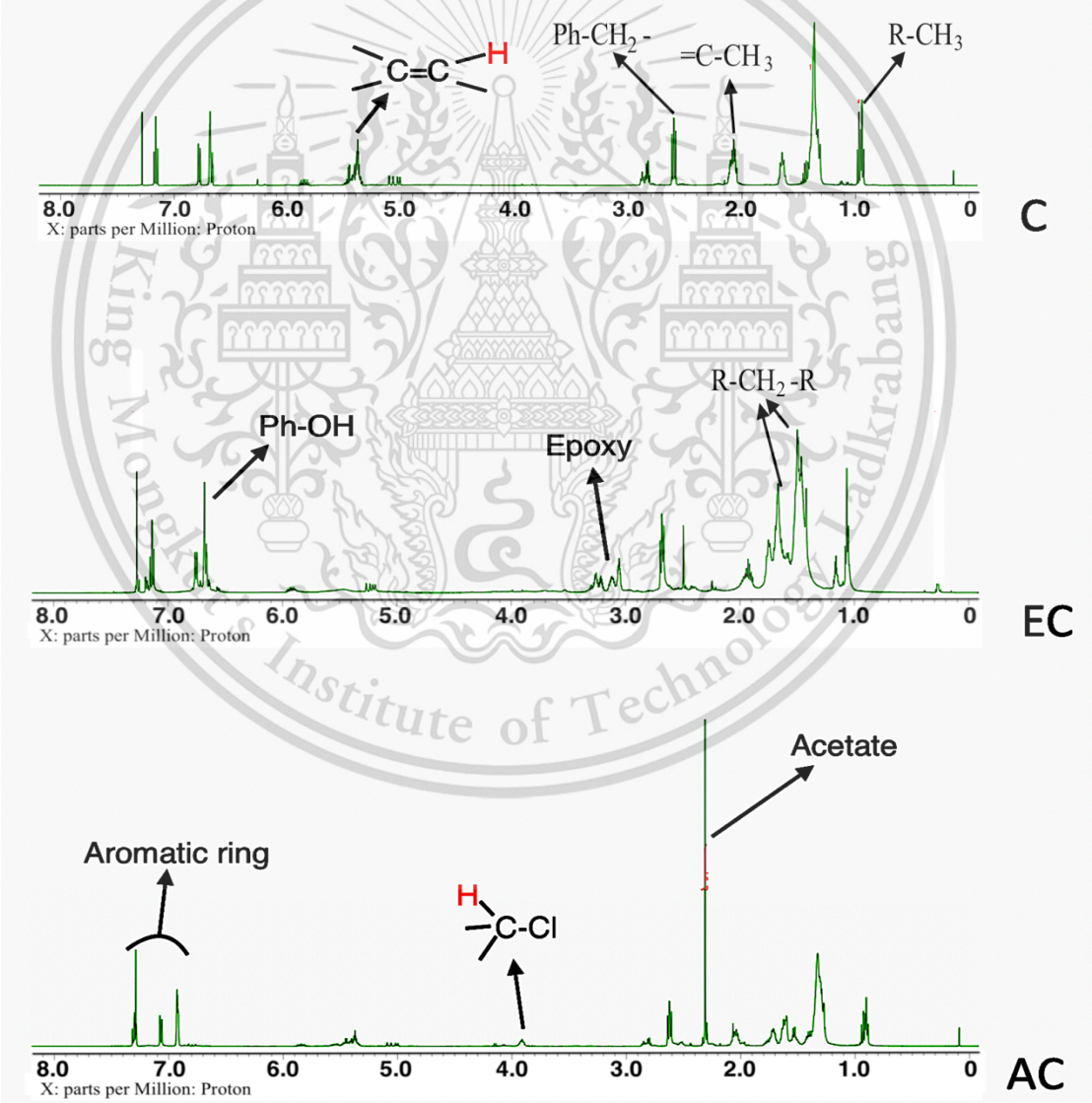


Figure 4.5 ^{1}H NMR results of unmodified-cardanol, epoxidized cardanol and acetylated cardanol.

Table 4.2 Some distinctive proton chemical shifts corresponding to Figure 4.5 [13, 15, 19, 22, 24, 49, 50].

Peak	Proton chemical shift (ppm)
Phenolic hydroxyl	4.0-7.0
Epoxy	2.0-3.0
Vinylic hydrogen (=CH-)	4.5-6.5
Allylic hydrogen (=C-CH-)	1.6-2.2
Ketonic carbonyl	2.0-2.4
-CO-CH_3	2.0-2.3

For both modifications of cardanol, epoxidation and acetylation, the results of FTIR and ^{1}H NMR are consistent with each other and prove that modification reactions took place on the functional groups as expected. The results are consistent for the fact that side chain is saturated during acetylation as a side effect of HCl's addition reaction with the double bonds.

4.1.1.3 Analyzing iodine value test results of EC and AC

Iodine value test was applied to C, EC and AC in order to monitor the unsaturation of side chain during both epoxidation and acetylation reactions. EC and AC are derived from C and the unsaturation mentioned here is the double bonds, which are present within the long 15-carbon chain attached to the aromatic ring at meta position. Initially it was expected that unsaturation should vanish during epoxidation since oxirane rings form after breaking the pi bonds and unsaturation should not be affected during acetylation inasmuch as acetate replaces the hydrogen atom of phenolic hydroxyl.

Iodine value result is given in gram of iodine consumed during the test per 100 g substrate. It is, in fact, the amount of iodine reacted with the unsaturation of substrate, therefore iodine value is directly proportional with the unsaturation level, which means the more unsaturated the substrate is, the more the iodine value will be. If iodine value indicates the level of unsaturation and if the unsaturation level of C is taken as 100%, then the relative unsaturation levels of EC and AC can be

calculated by using the formula below. Table 4.3 shows unsaturation percentages of EC and AC relative to C.

$$Relative\ Unsaturation\% = \frac{(Iodine\ Value\ of\ Modified\ Substrate)}{(Iodine\ Value\ of\ C)} * 100$$

Table 4.3 Iodine value test results and unsaturation percent of EC and AC relative to C.

Substrate	Iodine Value (g Iodine/100 g substrate)	Relative Unsaturation%
C	233	100.0
EC	104	44.6
AC	70	30.0

According to the results shown in the Table 4.3, we may calculate the percentile for maximum epoxidation by using the following formula:

$$Max.\ Epoxidation\ \% = 100\ \% - Relative\ unsaturation\ \%\ of\ EC$$

Using this formula, we see that the epoxidation% is 63.4, which can be considered as the maximum success of epoxidation reaction.

As also given in Table 4.3, relative unsaturation of AC is 30% of C. As overmentioned, it should have been 100% since the acetylation took place on phenolic hydroxyl group. It was mentioned in 4.1.1.1 and 4.1.1.2 that according to the FTIR and ^{1}H NMR results, saturation took place in the side chain. Considering that the relative unsaturation of AC is 30% of C, 70% of initial unsaturation has reacted with HCl.

4.2 Effect of cardanol and its derivatives in pure NR, pure CR and NR/CR (50:50) compounding

As mentioned before three different rubbers were used for compounding, which are: CR, NR and NR/CR (50:50) blend. For each type all ingredients were the

same but 4 different oils, C, EC, AC and N were used separately to compare their effect on rubber formulations, so that four formulations were obtained for each rubber. The order of adding ingredients and timing for rubber compounding are shown in Table 3.6, in chapter 3.

4.2.1 Effect of processing oil on torque

Torque and temperature vs. time data were obtained from the internal mixer. Figure 4.6 shows a sample torque and temperature vs. time graph.

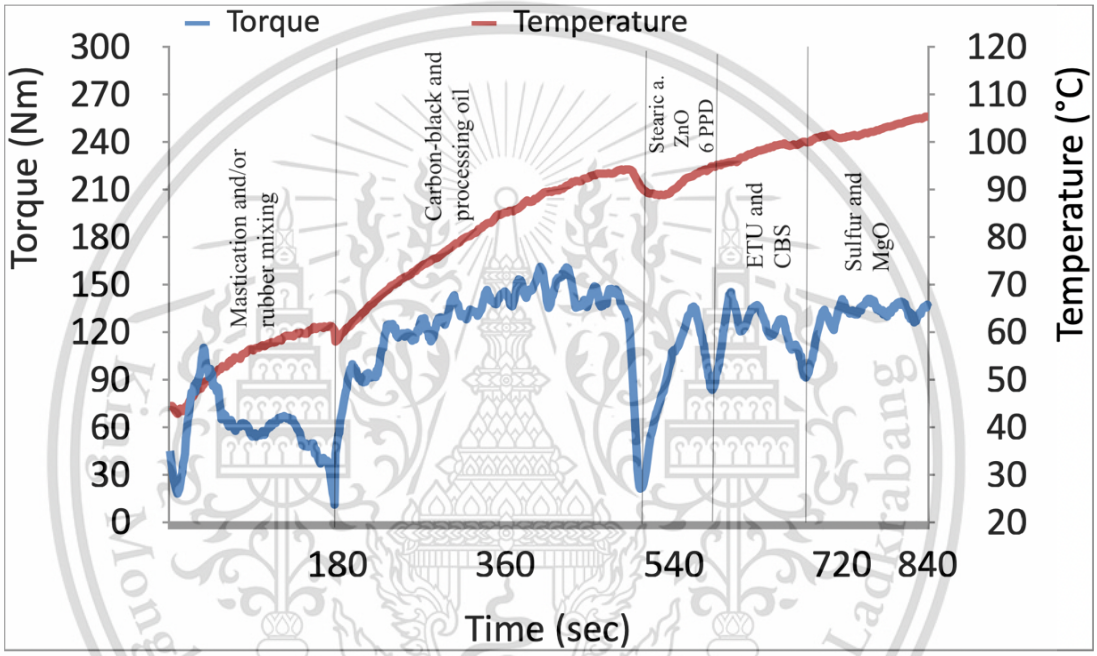


Figure 4.6 A sample torque and temperature vs. time graph belonging to rubber compounding by internal mixer.

Torque goes to minimum at the times of adding ingredients, because the feed door is opened, which causes the pressure decrease by providing extra room. At all times, the maximum torque was observed after adding the filler, carbon-black, which increases viscosity. The processing oil is added with carbon-black since the maximum torque is reached here. The performances of processing oil can be observed either by comparing the maximum torque values or the average torque values for the same type of rubber formulation. Either ways, the processing oil that the lower torque is obtained will be considered to be more suitable processing oil, due to the fact that a good processing oil decreases viscosity ending up with smaller shear force and so that smaller torque.

Two types of data were recorded during rubber compounding by internal mixer: Torque and temperature. Torque is directly proportional to the shear force, which means for the higher shear force, the bigger torque value is obtained. Temperature increase should be minded as well, since temperatures over 100 °C are not safe for rubber as vulcanization starts over 100 °C, which means crosslinking before the desired time. The internal mixer machine that was used for this study has air cooling system that cannot keep temperature at the set value. For high shear force, temperature may easily go over 100 °C ending up with spoiled rubber as a result of vulcanization took place inside the mixing chamber. That is why torque and temperature were observed and used together during the analysis of processing oils' performances. The temperature and torque results of rubber compounding by internal mixer are shown below in Table 4.4.

It can be revealed from Table 4.4 that among CR formulations by four different oils, lower maximum and average torque results are obtained from compounding with modified C derivatives, AC and EC as processing oil, than compounding with C and N. compounding with AC provided the lowest average and 'maximum torque' values where compounding with N yielded the highest. It can be said that there is not much difference between maximum torque values of four CR formulations, however if average torque matters for energy consumption, then average torque of AC is considerably lower than that of N.

Compounding CR with AC shows the lowest maximum temperature value. The interesting point here is that although had the biggest average and maximum torque values, N revealed the lowest temperature value and EC indicated one of lowest average and 'maximum torque' results, however its temperature result is the highest among CR formulations. Higher temperature decreases viscosity resulting in decreasing torque. However, as previously mentioned, high temperatures are not preferred for rubber compounding. In this case torque results should be considered together with temperature results.

Table 4.4 Torque and temperature results obtained from rubber compounding by internal mixer.

Oil	Rubber	Cumulative Torque (Nm)	Average Torque (Nm)	Max Torque (Nm)	Max Temp (°C)
C	CR	92,484	110.1	173.8	105.3
	NR	79,632	94.8	172.9	93.7
	NR/CR (50:50)	80,556	95.9	153.4	94.2
EC	CR	87,780	104.5	166.3	109.2
	NR	76,860	91.5	149.8	100.6
	NR/CR (50:50)	84,588	100.7	161.0	102.2
AC	CR	85,092	101.3	165.4	105.6
	NR	73,332	87.3	152.3	98.5
	NR/CR (50:50)	86,016	102.4	169.0	97.6
N	CR	98,028	116.7	177.1	101.4
	NR	80,640	96.0	166.2	94.8
	NR/CR (50:50)	76,020	90.5	145.6	97.9

According to the data acquired from NR compounding with four different processing oils, EC and AC have relatively lower average and 'maximum torque' values. Temperature results, however, indicate that NR compounding with EC and AC yielded higher temperature when compared to C and N.

Results that were obtained from the compounding NR/CR (50:50) rubber blend formulations with four different processing oils show that N has the lowest average and 'maximum torque' values. EC and AC have high torque results. C has the lowest temperature result and relatively lower torque results to EC and AC.

Among three rubber formulations, in general, CR and NR have the highest and lowest torque values respectively. Considering that all other ingredient types and amounts were fixed for three rubber formulations, this should be the effect of rubber type. Higher torque is the result of bigger shear force, which means bigger viscosity. It is molecular interactions that determine viscosity. NR is expected to have bigger molecular weight than CR, since it is naturally occurring and CR is a synthetic rubber,

thus it should be polarity of molecules to be dominating factor for intermolecular interactions. The chlorine atom in the structure of CR, as shown in Figure 2.15, Chapter 2, makes CR gains polarity causing higher interactions between molecules ending up with higher viscosity.

Based on data recorded for temperature, CR showed higher values, although NR and NR/CR (50:50) blend indicated similar results. The reason could be that higher viscosity of CR causes higher shear force, which increases temperature more.

4.2.2 Mooney viscosity and cure test results

The data acquired from Mooney viscosity and cure tests are shown in Table 4.5 and Figure 4.7 is given as sample for t_{s2} and t_{c90} measurements. Normally, processing oils are not supposed to have effect on Mooney behavior or cure characteristics, however considering steric effect of long carbon chain and reaction capacity of unsaturation in the side chain may cause some changes.

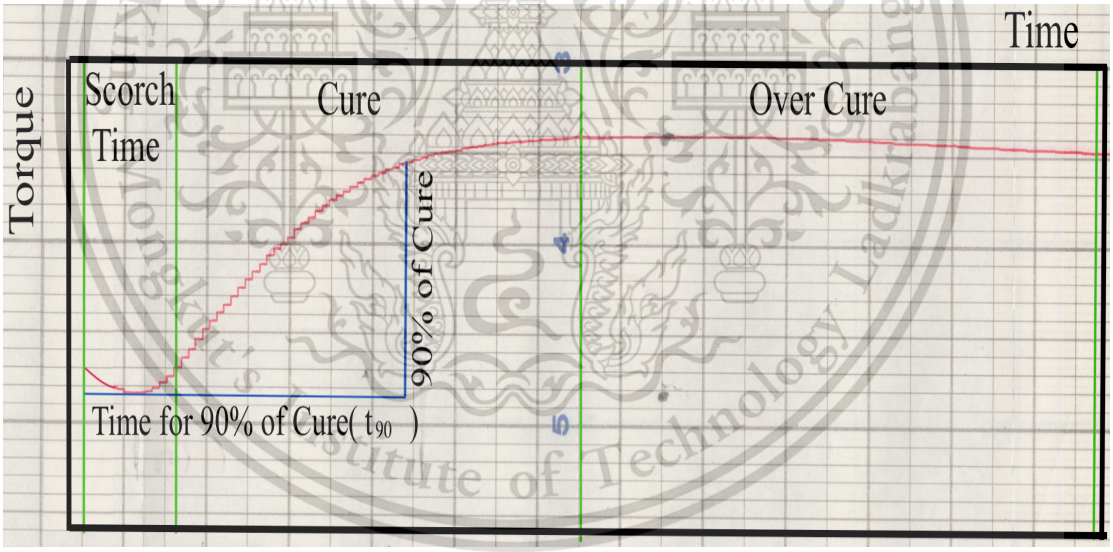


Figure 4.7 A sample print out from moving die rheometer machine and measurements of scorch time (t_{s2}) and 90% of cure time (t_{c90}).

According to the results shown in the Table 4.5, it can be said that processing oils did not have effect on Mooney viscosities of rubber formulations, since the results are quite alike. Mooney viscosity value is determined by the molecular weight of un vulcanized rubber, so considering the molecular structures of processing oils, there does not seem a way to change the molecular size of rubber by processing oil.

The changes in the results, scorch time (t_{s2}), cure time (t_{c90}) and cure rate index (CRI), indicates that processing oils did change cure characteristics. The shortest scorch time was reached by C in CR compounding and EC in NR compounding with 0.75 minute, and the longest scorch time was obtained as 1.75 minutes for AC in NR formulation. For the rest, the scorch time values are close to each other. Scorch time is the time passes until cure starts after the test is started, so the mechanism of vulcanization and the reactivity of processing oil should be the factors causing differences between scorch times. In general, it can be seen that scorch times are longer for AC and N when compared with C and EC, so the chemical structures should be the dominating factor affecting scorch times. The unsaturation level of C and oxirane rings of EC make them reactive during cure process. The unsaturation of C behaves like the one in NR and can join vulcanization, the oxirane rings of EC, on the other hand, may undergo degradation reaction, then may react with double bonds of NR. AC, on the other hand, may not be able to join crosslinking since its unsaturation is much less than C.

Cure times, as can be seen from t_{c90} data, are generally shorter for formulation compounded with C. This could be because of the relatively higher unsaturation of C. Its double bonds may join vulcanization by a very similar mechanism as NR because of the similarity in unsaturation. As also it is seen in the Table 4.5, cure times for rubber formulations compounded with EC are longer than others for all formulations, which may be because of the longer time requirement for oxirane ring opening and bond formation with double bonds in NR.

Table 4.5 Mooney viscosity, scorch time (t_{s2}), cure time (t_{c90}) and cure rate index (CRI) results of CR, NR and NR/CR (50:50) rubber formulations prepared by different processing oils: C, EC, AC and N.

Rubber Formulation	Processing Oil	Mooney Viscosity	t_{s2} (min)	t_{c90} (min)	CRI (min^{-1})
CR	C	26.5	0.75	10	10.81
	EC	27.3	1.25	16	6.78
	AC	24.8	1.75	11.5	10.26
	N	25.6	1.5	12	9.52
NR	C	29.5	1	4	33.33
	EC	30.9	0.75	5	23.53
	AC	27.2	1.25	4.25	33.33
	N	31.7	1.25	4.5	30.77
NR/CR (50:50)	C	26.0	1	7	16.67
	EC	26.5	1	8.5	13.33
	AC	23.0	1.25	6.5	19.05
	N	25.4	1	6.5	18.18

CRI, as mentioned in Chapter 3, is calculated by: $100/(t_{c90}-t_{s2})$. It is known that time and speed are inversely proportional, therefore using CRI may help us understand the cure rate.

As also seen in Figure 4.8, cure times are the longest for CR formulations and the shortest for NR formulations, in other words, CRI results are the biggest for NR formulations and the smallest for CR formulations. This should be due to the different crosslinking mechanisms of CR and NR as it was spoken in Chapter 2, Section 2.5.3.1. It probably takes longer time for the vulcanization mechanism, which involves removing Cl atom by MgO and linking through points that Cl was removed, than the

vulcanization mechanism of NR, which includes breaking the pi bond of double bond and linking over the sulfur atoms.

Figure 4.8 Sample cure curves for CR, NR and CR/NR (50:50) blend

4.3 Effect of cardanol and its derivatives on physical and mechanical properties of NR/CR (50:50) rubber blend

4.3.1 Swelling percent

Swelling percent results acquired from swelling test is shown in Figure 4.9. The calculation of percent is relative to the initial dry weight of vulcanized rubber specimens. C and N shows quite similar swelling percent results to each other and

lower than these of EC and AC. Although EC has the highest swelling percent, it is just slightly higher than that of AC.

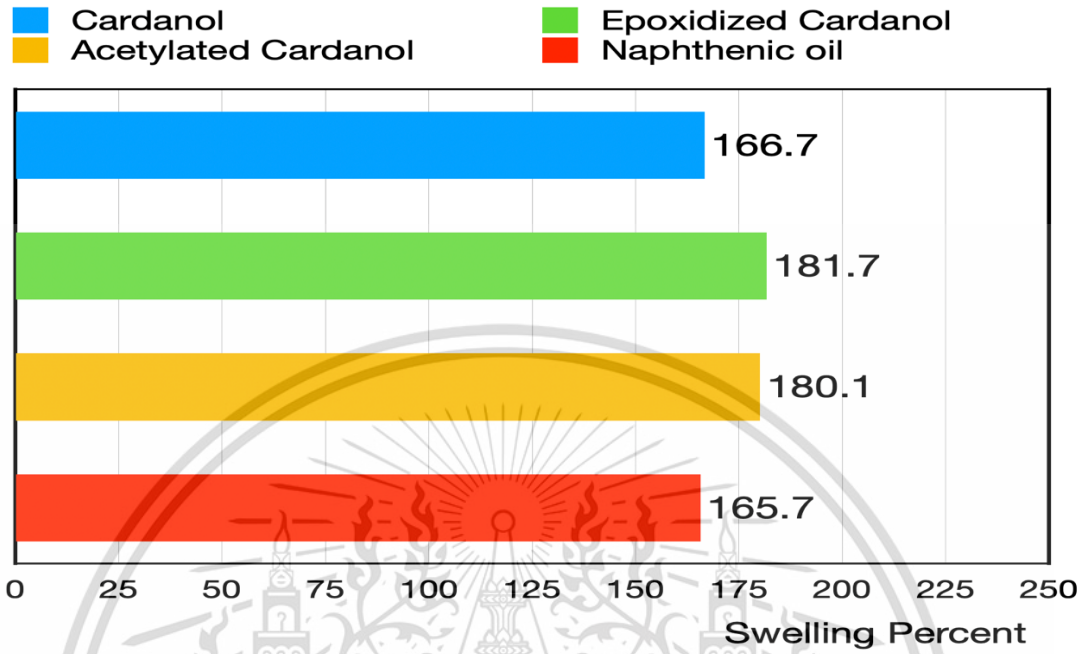


Figure 4.9 Swelling test results of NR/CR (50:50) rubber formulation compounded by different processing oils: C, EC, AC and N.

Swelling percent is inversely proportional to the crosslink density. Crosslink formation takes place as a result of the vulcanization process. Better mechanical and physical properties necessitate higher crosslink density, so desired result here should be lower swelling percent. Normally, processing oils are not supposed to interfere with the crosslink formation, but the difference in the swelling percent results for different processing oils indicates actually that some of oils somehow interfered. It is not big surprise that C, EC and AC affected crosslink formation during vulcanization due to the steric effect of their long side chain. But the answer is required for why results are not similar for all C, EC and AC. The answer should be within the unsaturation levels discussed in 4.1.1.3, iodine value test results. C has relatively much higher unsaturation level when compared to EC and AC. The unsaturation of long side chain looks like the unsaturation of NR and C may undergo vulcanization by the same process as NR, which may result in crosslink between its aliphatic chain with NR, thus lower swelling. AC and EC, on the other hand, have much lower unsaturation level meaning that much fewer double bonds of long side chain to join crosslink with NR, which ends up with more

swelling. And finally, since N does not have long side chain causing steric effect, the crosslink density is relatively higher when it is used as processing oil.

4.3.2 Bleeding amount

The bleeding test results are shown in Figure 4.10. According to the ISO 177 standards, if the amount of oil migrated at the end of the test time is 0.45 g or more, it is accepted as bleeding, if less than 0.45 g, then it is not in the bleeding range.

According to the bleeding test results, the measured amounts of oils migrated at the end of testing time are almost the same and much less than 0.45 g, the lower limit for bleeding, therefore it can be said that no bleeding for any of these four processing oils.

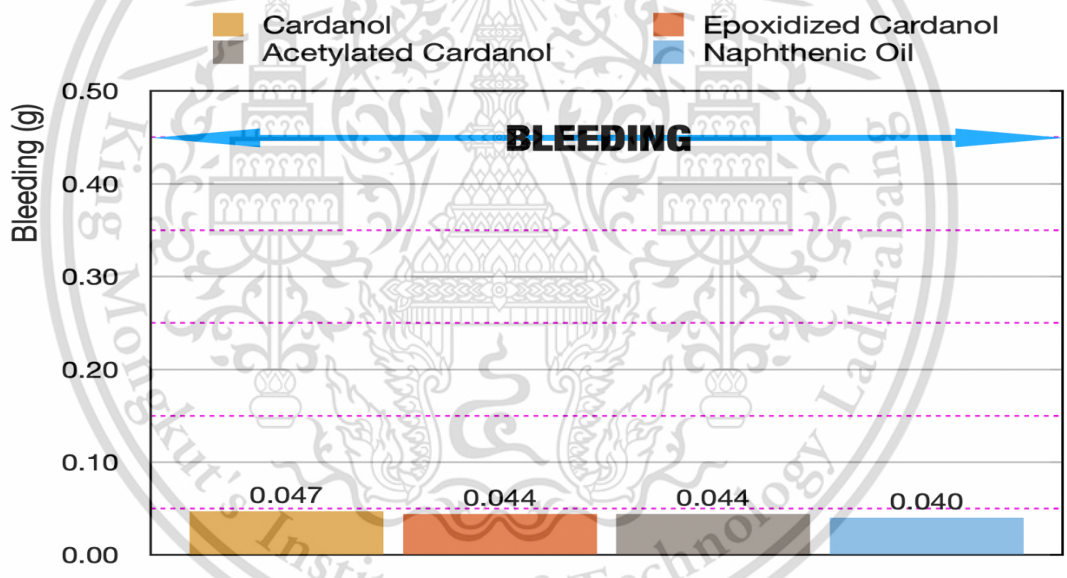


Figure 4.10 Bleeding test results of NR/CR (50:50) rubber formulation compounded by different processing oils: C, EC, AC and N.

4.3.3 Hardness

Shore A hardness test results of NR/CR (50:50) rubber blend compounded with four different oils before and after accelerated aging are given below in Figure 4.11. According to the chart, C and AC have got very similar and lower results, where EC and N indicated results alike, but slightly higher for both before and after accelerated aging process.

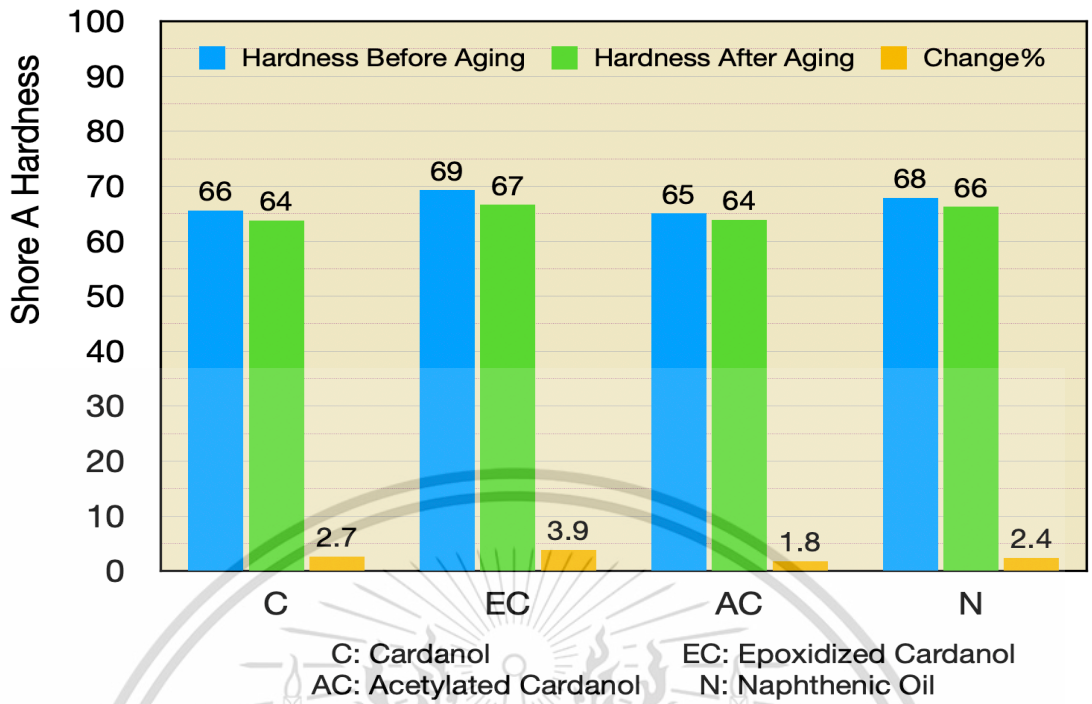


Figure 4.11 Results of Shore A hardness test before and after accelerated aging for NR/CR (50:50) rubber blend compounded with four different oils.

Although EC and N show slightly higher hardness results for both before and after accelerated aging process, the results for all four oils are very close to each other. The effect of accelerated aging on hardness, too, look very near to each other for all four processing oils.

4.3.4 Tensile properties

Data for tensile strength before and after aging for vulcanized NR/CR (50:50) rubber compounded with four different processing oils are given below in Table 4.6. Three types of data were recorded during tensile test: Tensile strength, elongation at break and stress/strain modulus at 100% elongation (M100). Tensile tests were run before and after accelerated aging in order get opinion about antiaging properties of the rubbers during accelerated aging process, in which they were exposed to the oxidation in air oven at elevated temperatures.

Table 4.6 Tensile strength, elongation at break and M100 results obtained from tensile test before and after accelerated aging for NR/CR (50:50) rubber blend compounded with four different oils.

Oil	Tensile strength (MPa)			Elongation at break (%)			M100 (MPa)		
	Before aging	After aging	Change %	Before aging	After aging	Change %	Before aging	After aging	Change %
C	13.4	15.5	15.7	321	314	2.2	2.94	3.74	27.2
EC	14.21	15.45	8.7	397	350	11.8	2.65	3.56	34.3
AC	13.01	13.68	5.1	305	285	6.6	3.2	3.68	15.0
N	14.68	15	2.2	334	276	17.4	3.26	4.41	35.3

Tensile strength, elongation at break and M100 results look quite similar in general for four processing oils. Rubber with EC shows slightly better results in tensile strength and elongation at break. Rubber with N seems to be the most affected by accelerated aging in terms of elongation at break and M100 results since it showed the biggest changes when compared to the cardanol and its derivatives. C and AC, especially AC, indicated lower changes during accelerated aging process for hardness, tensile strength, M100 and elongation at break results. Since C and AC have aromatic ring in its structure, they may be acting as antioxidant, so as to help decrease degradation of rubber [52].

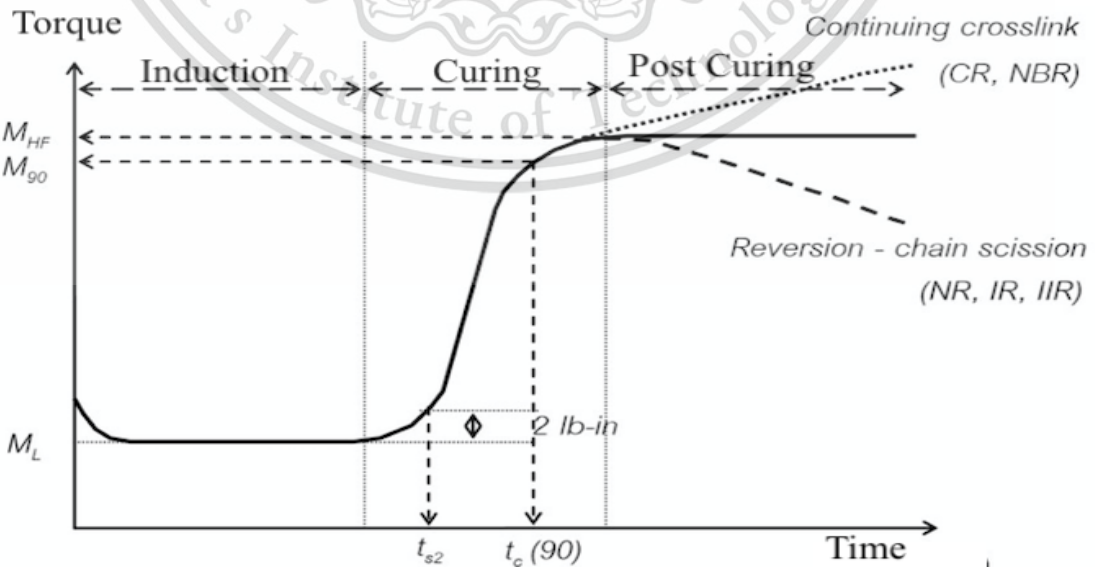


Figure 4.12 The cure curve of rubber.

When the results in Table 4.6 and Figure 4.11 are evaluated together, it can be interpreted that crosslink density increased for all samples during accelerated aging because tensile strength and M100 values increased, and elongation at break results decreases for all samples. This means the samples continued curing during accelerated aging process as shown in Figure 4.12, since they did not get maximum curing owing to the fact that t_{c90} times applied during compress molding. At the surface, however, chain scission should be taking place during aging resulting to softening, due to the fact that hardness decreased for all samples after aging.

Chapter 5

Conclusions and suggestions

5.1 Conclusions

Cardanol was modified by two different methods: Epoxidation and acetylation. Epoxidation and acetylation were planned to be achieved on double bonds of long side chain at meta position and phenolic hydroxyl respectively. It was proved by characterization tests, FTIR, ^{1}H NMR and iodine value test, that epoxidation and acetylation were achieved and took place at the desired sections. According to iodine value test results, around 63% of unsaturation were epoxidized. Although the acetylation occurred through phenolic hydroxyl as desired, a side effect too happened, which is the saturation of aliphatic chain. The iodine value test results revealed that about 70% of double bonds in AC's aliphatic chain were saturated by HCl, byproduct of acetylation by acetyl chloride.

Cardanol, its derivatives, EC and AC, and a petroleum based commercial oil, naphthenic oil, were used as processing oil for the compounding of three different rubber formulations, CR, NR and NR/CR (50:50). EC and AC showed lower torque results when compared to C and N for CR and NR compounding, where the torque results for N were lowest for NR/CR (50:50) compounding. Although N indicated better temperature results, C and AC got close results to that of N. EC, on the other hand indicated the highest temperature results.

Mooney viscosity results did not reveal much differences between C, C derivatives and N, therefore it can be said that processing oils have no effect on molecular weight of un-vulcanized rubber.

As of cure results, scorch times were shorter for C and EC, whereas C and AC showed high CRI results, which means rubber formulations compounded with C or AC cure faster, which could be due to the longer time requirement for oxirane ring opening and joining crosslinking for EC.

Although not big differences, AC and EC absorbed more solvent during the swelling test, which can be explained by having lower crosslink density due to the

steric effect of long side chain. This steric effect was avoided for C most probably because its relatively high unsaturation contributing to the vulcanization.

Bleeding test results showed that the migrated amounts of oils out of rubber were almost the same and under the lower limit of the standard.

Hardness test results before and after accelerated aging, as well did not show accountable differences between four processing oils.

Tensile results, as well, for both before and after accelerated aging process did not indicate important differences, although EC showed slightly better tensile strength and elongation at break results.

Among four processing oils, N showed the worst antiaging properties according to the M100 and elongation at break data. AC, however, showed generally lower change percentages for hardness, tensile strength, M100 and elongation at break results during aging.

In general, it can be said that C and AC, especially AC, can be alternatives to N as processing oil for rubber compounding, on the other hand, EC is not recommended to replace N due to longer cure time and lower CRI results.

5.2 Suggestions

5.2.1 Work must be repeated with decarboxylated CNSL instead of cardanol.

5.2.2 More studies with different rubbers, i.e. NBR, should be done.

5.2.3 As acetylating agent, an acid anhydride should be preferred instead of acid chloride if the unsaturation is to be protected.

5.2.4 For comparative studies, paraffinic and/or aromatic oils can be selected next time, since they are used commercially too.

5.2.5 More oil loadings should be studied to have clearer ideas about migrating amounts of oils.

References

1. Ritchie, H. and Roser, M. 2017. 'Fossil Fuels', Our World In Data.
2. Ecotricity 2020 "When Will Fossil Fuels Run out?". [online]. Available: https://www.ecotricity.co.uk/our-green-energy/energy-independence/the-end-of-fossil-fuels.
3. 'Difunctional Monomers Starting from Cashew Nut Shell Liquid (CNSL) and High Performance Polymers Therefrom. 2020. | NCL Library, Pune', http://krclib.ncl.res.in/library/content/difunctional-monomers-starting-cashew-nut-shell-liquid-cnsl-and-high-performance-polymers.
4. McNutt, J. and He, Q. (Sophia). 2016. 'Development of biolubricants from vegetable oils via chemical modification', Journal Of Industrial And Engineering Chemistry, 36: 1–12.
5. Borugadda, V. B. and Goud, V. V. 2014. 'Epoxidation of Castor Oil Fatty Acid Methyl Esters (COFAME) as a Lubricant base Stock Using Heterogeneous Ion-exchange Resin (IR-120) as a Catalyst', Energy Procedia, 54: 75–84.
6. Puchot, L. 2016. 'Cardanol: a bio-based building block for new sustainable and functional materials'.
7. Mohapatra, S. and Nando, G. B. 2014. 'Cardanol: a green substitute for aromatic oil as a plasticizer in natural rubber', RSC Adv., 4 (30): 15406–15418.
8. Caillol, S. 2018. 'Cardanol: A promising building block for biobased polymers and additives', Current Opinion In Green And Sustainable Chemistry, 14: 26–32.
9. Kuraińska, M., Beneš, H., Prociak, A., Trhlíková, O., Walterová, Z., and Stochlińska, W. 2019. 'Investigation of epoxidation of used cooking oils with homogeneous and heterogeneous catalysts', Journal of Cleaner Production, 236: 117615.
10. Jaillet, F., Darroman, E., Ratsimihety, A., Auvergne, R., Boutevin, B., and Caillol, S. 2014. 'New biobased epoxy materials from cardanol: New biobased epoxy materials from cardanol', European Journal of Lipid Science and Technology, 116 (1): 63–73.
11. Lubi, M. C. and Thachil, E. T. 2000. 'Cashew nut shell liquid (CNSL) - a versatile monomer for polymer synthesis', Designed Monomers And Polymers, 3 (2): 123–153.

12. Sookyung, U., Thitithammawong, A., Nakason, C., Pakhathirathien, C., and Thaijaroen, W. 2018. 'Effects of Cashew Nut Shell Liquid and Its Decarboxylated Form on the Properties of Natural Rubber', Journal Of Polymers And The Environment, 26 (8): 3451–3457.
13. Raksawong, S. and Jangchud, I. 2017. 'New Bioadditives from Modified Cashew Nut Shell Liquid (CNSL) for Natural Rubber', 5.
14. Greco, A., Ferrari, F., and Maffezzoli, A. 2019. 'Mechanical properties of poly(lactid acid) plasticized by cardanol derivatives', Polymer Degradation And Stability, 159: 199–204.
15. Liu, Z., Chen, J., Knothe, G., Nie, X., and Jiang, J. 2016. 'Synthesis of Epoxidized Cardanol and Its Antioxidative Properties for Vegetable Oils and Biodiesel', ACS Sustainable Chemistry & Engineering, 4 (3): 901–906.
16. Telascrêa, M., Leão, A. L., Ferreira, M. Z., Pupo, H. F. F., Cherian, B. M., and Narine, S. 2014. 'Use of a Cashew Nut Shell Liquid Resin as a Potential Replacement for Phenolic Resins in the Preparation of Panels – A Review', Molecular Crystals And Liquid Crystals, 604 (1): 222–232.
17. Unnikrishnan, K. P. and Thachil, E. T. 2008. 'Synthesis and Characterization of Cardanol-Based Epoxy Systems', Designed Monomers And Polymers, 11 (6): 593–607.
18. Greco, A., Ferrari, F., Del Sole, R., and Maffezzoli, A. 2018. 'Use of cardanol derivatives as plasticizers for PVC: Cardanol derived PVC plasticizers', Journal Of Vinyl And Additive Technology, 24: E62–E70.
19. Chen, J., Liu, Z., Jiang, J., Nie, X., Zhou, Y., and Murray, R. E. 2015. 'A novel biobased plasticizer of epoxidized cardanol glycidyl ether: synthesis and application in soft poly(vinyl chloride) films', RSC Advances, 5 (69): 56171–56180.
20. Kanehashi, S., Yokoyama, K., Masuda, R., Kidesaki, T., Nagai, K., and Miyakoshi, T. 2013. 'Preparation and characterization of cardanol-based epoxy resin for coating at room temperature curing', Journal Of Applied Polymer Science, 130 (4): 2468–2478.
21. Li, X., Nie, X., Chen, J., and Wang, Y. 2017. 'Preparation of epoxidized cardanol butyl ether as a novel renewable plasticizer and its application for poly(vinyl chloride): Epoxidized cardanol butyl ether as novel renewable plasticizer', Polymer International, 66 (3): 443–449.

22. Lee, S., Park, M. S., Shin, J., and Kim, Y.-W. 2018. 'Effect of the individual and combined use of cardanol-based plasticizers and epoxidized soybean oil on the properties of PVC', Polymer Degradation And Stability, 147: 1–11.
23. Greco, A., Brunetti, D., Renna, G., Mele, G., and Maffezzoli, A. 2010. 'Plasticizer for poly(vinyl chloride) from cardanol as a renewable resource material', Polymer Degradation And Stability, 95 (11): 2169–2174.
24. Rigoussen, A., Raquez, J.-M., Dubois, P., and Verge, P. 2019. 'A dual approach to compatibilize PLA/ABS immiscible blends with epoxidized cardanol derivatives', European Polymer Journal, 114: 118–126.
25. Monono, E. M., Haagenson, D. M., and Wiesenborn, D. P. 2015. 'Characterizing the epoxidation process conditions of canola oil for reactor scale-up', Industrial Crops And Products, 67: 364–372.
26. Campanella, A. and Baltanás, M. A. 2007. 'Degradation of the oxirane ring of epoxidized vegetable oils in a liquid–liquid–solid heterogeneous reaction system', Chemical Engineering And Processing: Process Intensification, 46 (3): 210–221.
27. Milchert, E., Malarczyk-Matusiak, K., and Musik, M. 2016. 'Technological aspects of vegetable oils epoxidation in the presence of ion exchange resins: a review', Polish Journal Of Chemical Technology, 18 (3): 128–133.
28. de Haro, J. C., Izarra, I., Rodríguez, J. F., Pérez, Á., and Carmona, M. 2016. 'Modelling the epoxidation reaction of grape seed oil by peracetic acid', Journal Of Cleaner Production, 138: 70–76.
29. Sienkiewicz, A. M. and Czub, P. 2016. 'The unique activity of catalyst in the epoxidation of soybean oil and following reaction of epoxidized product with bisphenol A', Industrial Crops And Products, 83: 755–773.
30. Mungroo, R., Pradhan, N. C., Goud, V. V., and Dalai, A. K. 2008. 'Epoxidation of Canola Oil with Hydrogen Peroxide Catalyzed by Acidic Ion Exchange Resin', Journal Of The American Oil Chemists' Society, 85 (9): 887–896.
31. Madankar, C. S., Dalai, A. K., and Naik, S. N. 2013. 'Green synthesis of biolubricant base stock from canola oil', Industrial Crops And Products, 44: 139–144.
32. Kim, J. R. and Sharma, S. 2012. 'The development and comparison of bio-thermoset plastics from epoxidized plant oils', Industrial Crops And Products, 36 (1): 485–499.

33. Researchgate. 2020. “Acetylation of Alcohols, Amines, Phenols, Thiols under Catalyst and Solvent-Free Conditions”. [online]. Available: https://www.researchgate.net/publication/334378952_Acetylation_of_Alcohols_Amines_Phenols_Thiols_under_Catalyst_and_Solvent-Free_Conditions.
34. Hosseini-Sarvari, M. 2012. ‘Greener Solvent-Free Reactions on ZnO’, Green Chemistry - Environmentally Benign Approaches, InTech.
35. Tamaddon, F., Amrollahi, M. A., and Sharafat, L. 2005. ‘A green protocol for chemoselective O-acylation in the presence of zinc oxide as a heterogeneous, reusable and eco-friendly catalyst’, Tetrahedron Letters, 46 (45): 7841–7844.
36. Kazemi, M., Sanchez-Mendoza, A., and Ghobadi, M. 2019. ‘Solvent-Free Acylation of Alcohols, Phenols, Thiols and Amines’, 8.
37. More, P. E., Bandgar, B. P., and Kamble, V. T. 2012. ‘Zinc oxide as a regioselective and heterogeneous catalyst for the synthesis of chalcones at room temperature’, Catalysis Communications, 27: 30–32.
38. Mulla, S. A. R., Inamdar, S. M., Pathan, M. Y., and Chavan, S. S. 2012. ‘Highly Efficient Cobalt (II) Catalyzed O-Acylation of Alcohols and Phenols under Solvent-Free Conditions’, Open Journal Of Synthesis Theory And Applications, 01 (03): 31–35.
39. Rubber. 2020 “A Simple Introduction”. [online]. Available: http://www.explainthatstuff.com/rubber.html.
40. Morton, M. 1999. ‘Rubber Technology’, Springer Netherlands, Dordrecht.
41. ‘Rubber Technology: Compounding and Testing for Performance’ 2009. 2nd ed. Ed., Hanser Publishers ; Hanser Gardner Publications, Munich : Cincinnati, Ohio, USA, 567.
42. Rodthongkum, M. L. 2000. ‘MODIFICATION OF NATURAL RUBBER WITH CASHEW NUT SHELL LIQUID’, 160.
43. Polymer database. 2020. “Sulfur Vulcanization”. [online]. Available: https://polymerdatabase.com/polymer%20chemistry/Vulcanization.html.
44. RUBBER TECHNOLOGY. 2020. “Ingredients, Activators, Fillers”. [online]. Available: http://www.goodyearrubber.com/custom-rubber-manufacturing-knowledge-center/rubber-technology-compounding-ingredients.
45. 6.RUBBER COMPOUNDING TECHNOLOGY-FINAL.Ppt. 2020. “Natural Rubber Polyethylene”. [online]. Available: **https://www.scribd.com/doc/293097559/6-RUBBER-COMPOUNDING-TECHNOLOGY-FINAL-ppt**.

46. Alexander, M. 2008. ‘Applications of cardanol in rubber processing’, 34.
47. Borenius, P. 2018. ‘Bio-based and Renewable Plasticizers in Rubbers and Elastomers’.
48. CHEMISTRY LIBRETEXTS. 2020. "Infrared Spectroscopy Absorption Table". [online]. Available: https://chem.libretexts.org/Bookshelves/Ancillary_Materials/Reference/Reference_Tables/Spectroscopic_Parameters/Infrared_Spectroscopy_Absorption_Table.
49. UNIVERSITY OF PUGET SOUND. 2020. "H-NMR Shift Ranges". [online]. Available: http://www2.ups.edu/faculty/hanson/Spectroscopy/NMR/HNMRshift.html
50. Ma, S., Liu, X., Fan, L., Jiang, Y., Cao, L., and Tang, Z. 2014 "Synthesis and Properties of a Bio-Based Epoxy Resin with High Epoxy Value and Low Viscosity", ChemSusChem.
51. Rawn, J. D. and Ouellette, R. J. 2018. "Organic Chemistry Sutructure, Mechanism, Synthesis", Second. Ed., ***John Fedor***, 125 London Wall, London EC2Y 5AS, United Kingdom.
52. Rodrigues, F. H. A. and Feitosa, J. P. A. 2006. "Antioxidant Activity of Cashew Nut Shell Liquid (CNSL) Derivatives on the Thermal Oxidation of Synthetic cis-1,4-Polyisoprene", ***J. Braz. Chem. Soc.***, 8.

Appendices

Appendix A

Mooney viscosity and cure time

Table A.1 Mooney viscosity, scorch time and cure time results for CR, NR and NR/CR (50:50) blend formulations

Rubber	Processing Oil	Repeat	Mooney Viscosity	t_{s2} (min)	t_{c90} (min)
CR	C	1	26.8	0.75	9.5
		2	26.9	0.50	11.0
		3	25.8	0.75	10.0
CR	EC	1	27.4	1.50	17.0
		2	27.3	1.25	16.0
		3	27.1	1.25	15.5
CR	AC	1	25.3	1.75	11.5
		2	24.7	1.50	12.0
		3	24.5	1.75	11.0
CR	N	1	25.6	1.50	12.0
		2	25.6	1.50	13.0
		3	25.7	1.50	12.0
NR	C	1	29.7	1.00	4.0
		2	29.4	1.00	4.0
		3	29.4	1.10	4.0
NR	EC	1	30.9	0.75	4.25
		2	30.9	0.75	6.00
		3	30.8	0.90	4.00

Table A.1 (continued)

Rubber	Processing Oil	Repeat	Mooney Viscosity	t_{s2} (min)	t_{c90} (min)
NR	AC	1	27.6	1.25	4.25
		2	27.0	1.25	4.25
		3	27.1	1.25	4.50
NR	N	1	31.8	1.25	4.50
		2	31.8	1.50	4.50
		3	31.5	1.25	5.00
NR/CR (50:50)	C	1	26.5	0.75	7.00
		2	25.9	1.00	6.00
		3	25.5	1.00	7.00
NR/CR (50:50)	EC	1	26.7	1.00	8.75
		2	26.3	1.00	8.50
		3	26.6	1.00	8.50
NR/CR (50:50)	AC	1	23.0	1.25	6.75
		2	23.0	1.25	6.50
		3	23.1	1.25	6.50
NR/CR (50:50)	N	1	25.1	1.00	6.75
		2	25.4	1.00	6.50
		3	25.8	1.00	6.50

Appendix B

Swelling test results

Table B.1 Swelling test results for NR/CR (50:50) formulation with different processing oils

Swelling Test Results for NR/CR (50:50) Formulation

Processing Oil	Repeat	Weight Before Swelling (gram)	Weight After Swelling (gram)
C	1	0.2998	0.7842
	2	0.2822	0.7538
	3	0.2824	0.7588
	4	0.2956	0.7877
	5	0.3030	0.8072
	6	0.2880	0.7736
	7	0.3108	0.8338
EC	1	0.3174	0.8897
	2	0.2848	0.8070
	3	0.3092	0.8718
	4	0.2774	0.7864
	5	0.2988	0.8361
	6	0.3088	0.8634
	7	0.2880	0.8159

Table B.1 (Continued)

Processing Oil	Repeat	Weight Before Swelling (gram)	Weight After Swelling (gram)
AC	1	0.2458	0.6818
	2	0.2590	0.7309
	3	0.2482	0.6934
	4	0.2460	0.6908
	5	0.2534	0.7136
	6	0.2456	0.6883
	7	0.2524	0.7042
N	1	0.2918	0.7821
	2	0.2864	0.7458
	3	0.2726	0.7305
	4	0.2552	0.6852
	5	0.2756	0.7447
	6	0.2946	0.7501
	7	0.2640	0.7140

Appendix C

Bleeding test results

Table C.1 Bleeding test results for NR/CR (50:50) formulation with different processing oils

Bleeding Test Results for NR/CR (50:50) Formulation

Processing Oil	Repeat	Initial Weight (gram)	Final Weight (gram)
C	1	0.2998	0.7842
	2	0.2822	0.7538
	3	0.2824	0.7588
	4	0.2956	0.7877
	5	0.303	0.8072
EC	1	7.5385	7.4906
	2	7.5282	7.4774
	3	6.9884	6.9403
	4	6.8110	6.7639
	5	7.0649	7.0185
AC	1	6.3463	6.3021
	2	6.9020	6.8561
	3	6.3092	6.2676
	4	6.7340	6.6898
	5	7.0502	7.0072
N	1	6.7321	6.6911
	2	7.1521	7.1078
	3	6.8267	6.7853
	4	6.7661	6.7257
	5	6.9953	6.9535

Appendix D

Hardness test results

Table D.1 Shore A test results for NR/CR (50:50) formulation with different processing oils before and after accelerated aging.

Shore A Test Results for NR/CR (50:50) Formulation

Processing Oil	Repeat	Before Aging	After Aging
C	1	65	63.5
	2	65	64
	3	66	65
	4	66	64.5
	5	65	64.5
	6	65	64
	7	66.5	63.5
	8	66	62
	9	65.5	64
	10	65.5	63
EC	1	68	66.5
	2	70	65.5
	3	69.5	65
	4	69	66.5
	5	70.3	67
	6	69.5	68.5
	7	68.5	67.5
	8	69	68
	9	70	64
	10	69	67.5

Table D.1 (Continued)

Processing Oil	Repeat	Before Aging	After Aging
AC	1	65.5	64
	2	65	64.5
	3	64.5	65
	4	64.5	64
	5	65.5	64
	6	65.5	63
	7	64.5	63.5
	8	65	63
	9	65.5	65
	10	65	63
N	1	68.5	67.5
	2	67.5	68
	3	68	65.5
	4	68	66.5
	5	67	67
	6	67.5	67
	7	68.5	64
	8	68	64.5
	9	68	66
	10	68	66.5

Appendix E

Tensile test results

Table E.1 Tensile test results for NR/CR (50:50) formulation with different processing oils before and after accelerated aging.

Processing oil	Repeat	Tensile strength (MPa)		Elongation at break (%)		M100 (MPa)	
		Before aging	After aging	Before aging	After aging	Before aging	After aging
C	1	13.73	14.31	319.07	300.53	3.01	3.61
	2	13.88	15.18	316.9	300.73	3.02	3.89
	3	11.59	16.53	303.29	344.71	2.69	3.61
	4	12.89	16.4	325.18	336.62	2.79	3.66
	5	12.9	14.52	318.08	290.28	2.87	3.84
	6	14.7	16.1	337.21	328.73	3.09	3.6
	7	12.73	15.69	322.22	315.52	2.74	3.78
	8	13.61	15.18	321.24	295.41	2.98	3.95
EC	1	14.32	15.11	415.89	341.75	2.53	3.57
	2	14.39	15.84	403.47	375.67	2.6	3.39
	3	13.27	13.2	374.09	308.82	2.63	3.44
	4	14.27	16.15	402.29	361.86	2.59	3.66
	5	15.19	16.44	421.42	364.62	2.67	3.58
	6	14.11	15.95	379.81	350.03	2.78	3.73
AC	1	13.32	9.61	304.08	221.65	3.23	3.48
	2	11.8	12.22	290.87	268.78	2.98	3.48
	3	14.5	13.73	335.44	271.74	3.11	3.87
	4	12.95	16.74	308.42	335.04	3.12	3.82
	5	12.06	15.02	313.75	307.63	2.84	3.76
	6	13.41	14.75	280.02	305.46	3.93	3.69
N	1	15.75	15.51	373.5	275.09	3.11	4.45
	2	11.82	15.41	278.25	276.28	3.23	4.58
	3	15.5	16.94	349.64	317.89	3.2	4.22
	4	14.11	15.08	308.42	282.78	3.4	4.23
	5	15.41	13.87	338.2	258.92	3.25	4.4
	6	15.48	13.13	356.14	242.36	3.35	4.55

Author Biography

Name	Mr. Idris Kalkan
Date of birth	20 September 1976
Address	10/2 Chaloem Phrakiat R.9, Soi 67, Prawet, Bangkok 10250
Education	1999 Bachelor of Education in Chemistry GPA 2.42 Middle East Technical University 2020 Master of Science Polymer Technology GPA 3.12 King Mongkut's Institute of Technology Ladkrabang
Scholarship	Scholarship from King Mongkut's Institute of Technology Ladkrabang for oral presentation at Pure and Applied Chemistry International Conference 2020 (PACCON 2020)

Academic Publication

1. Idris Kalkan, Watthana Klairutsamee, Ittipol Jangchud. 2020. "Novel bio-based rubber oil from epoxidized and acetylated cashew nutshell liquid." The Proceedings of Pure and Applied Chemistry International Conference 2020 (PACCON 2020), Impact Forum, Muangthong Tani, Bangkok, Thailand, pp. 230-235.