STUDY ON LAMINATED NATURAL RUBBER (NR) LATEX BASED FILMS FOR MOULD CLEANING APPLICATION

by

MUFIDAH BINTI MD SIDEK

Thesis submitted in fulfillment of the requirements

for the degree of

Master of Science

October 2015

ACKNOWLEDGEMENTS

First of all, I would like to express my deep and special thanks to my supervisor, Associate Professor Dr. Azura binti A. Rashid, who has supported me for her guidance, patience and kindness, continuous support and as well as inspiration during the period of my master degree study.

I also would like to gratefully thanks to Professor Dr. Hanafi bin Ismail, Dean of School of Materials and Mineral Resources Engineering, USM, for his concern and help during my study.

I also thankful to all staff and technicians from School of Materials and Mineral Resources Engineering, USM, especially technicians of Latex laboratory and Rubber laboratory for their kindness and willingness to help me to complete my project, and thanks to all friends from Post Graduates Student Club School of Materials and Mineral Resources Engineering, USM for their supported. Special thanks to my best friends Siti Zuliana Salleh and Nor Azaniza Abdul Mutalib for helping me a lot during my journey.

Last but not least, I would like to express my deepest appreciation to my beloved parents, Md Sidek bin Yaacob and Aminah binti Muhammad and my dear husband, Muhammad bin Sauddin who loved, supported, motivated all the way and encouraged me in everything I do. I would like to thank my beloved siblings for giving me moral support, happiness and love. I thank them with my deepest heart. This thesis is dedicated to them and my daughter Wardatul Jannah bt Muhammad.

Mufidah Md Sidek

October 2015

TABLE OF CONTENTS

Acknowledgements	ii
Table of Contents	iii
List of Tables	ix
List of Figures	xi
List of Abbreviations	xvii
List of Symbols	xviii
Abstrak	xix
Abstract	xx
CHAPTER 1 - INTRODUCTION	
1.1 Overview	1
1.2 Problem Statement	2
1.3 Objectives of The Study	5
1.4 Scope of Work	6
CHAPTER 2 - LITERATURE REVIEW	
2.1 Natural Rubber	7
2.1.1 Classification of Natural Rubber	8
2.1.2 Natural Rubber (NR) Latex	8
2.2 Nitrile Butadiene Rubber (NBR)	10
2.2.1 Nitrile Butadiene Rubber (NBR) Latex	11
2.3 Waste Latex	12
2.4 Recycle Process	15

2.5 Latex Compounding Ingredients 18

2.5.1 Surface Active Agents (Surfactants) 19

2.5.1.1 Emulsifiers 19

2.5.1.2 Dispersing Agent 20

2.5.1.3 Wetting Agent and Thickneners 20

2.5.2 Liquid Phase Modifier 21

2.5.2.1 Stabilizer 21

2.5.2.2 Gelling Agents 22

2.5.3 Rubber Phase Modifier 22

2.5.3.1 Vulcanizing Agent 22

2.5.3.2 Accelerator 23

2.5.3.3 Activator 24

2.5.3.4 Antioxidant 25

2.6 Cleaning Agent 26

2.6.1 Monoethanolamine (MEA) 28

2.6.2 Di-(3-aminopropyl) ether of diethylene glycol (DCA221) 29

2.7 Latex Compounding and Curing 31

2.8 Maturation Process 32

2.9 Product Formation 33

2.9.1 Latex Dipping 33

2.9.2 Casting 35

2.10 Compression Moulding 36

2.11 Lamination 38

2.12 Mould Cleaning Process 39

2.12.1 Mould Cleaning using Blasting Technique 40

2.12.2 Mould Cleaning using Bath Technique 40

2.12.3 Mould Cleaning using Dry Rubber Compound Techniques 41

CHAPTER 3 - METHODOLOGY

3.1 Introduction 43

3.2 Materials 43

3.2.1 Latex 43

3.2.2 Cleaning Agent 44

3.2.2.1 Monoethanolamine (MEA) 44

3.2.2.2 Di-(3-Aminopropyl) Ether of Diethylene Glycol (DCA221) 44

3.2.3 Compounding Ingredients 44

3.2.4 Solvent 44

3.2.5 Coagulant 45

3.3 Equipments 45

3.4 Preparation of NR latex films 45

3.4.1 Latex Compounding 45

3.4.1.1 Fresh Latex 45

3.4.1.2 Sample for different cleaning agent and different loading of cleaning agent 46

3.4.1.3 Sample for NBR Latex Cleaning Compound 47

3.4.2 Sample Preparation 48

3.4.2.1 Preparation of NR latex Film for Tensile Test via Dipping Process 48

3.4.2.2 Preparation of Laminated NR latex and Laminated NBR Latex Films via Casting 48

3.4.2.3 Laminated NR latex Films Preparation for Tensile Test via Casting 49

3.4.2.4 Sample Preparation for Cleaning Effectiveness Test 51

3.4.2.5 Compression Moulding 52

3.5 Characterization 53

3.5.1 Curing Characteristics 53

3.5.2 Mechanical properties 55

3.5.2.1 Tensile Properties 55

3.5.2.2 Tear Properties 55

3.5.3 Swelling Test and Cross Linking Density Measurement 56

3.5.4 Fourier Transform Infrared (FTIR) Spectroscopy 57

3.5.5 Thermogravimetric Analysis (TGA) 58

3.5.6 Morphology 58

3.5.6.1 Optical Microscopy Analysis 58

3.5.6.2 Stereo Zoom Microscopy Analysis 58

3.6 Overall Research Work 59

CHAPTER 4 - RESULTS AND DISCUSSION

4.1 Introduction 61

4.2 Effect of the Different Types of Cleaning Agent on Film Properties 61

4.2.1 Tensile Properties 61

4.2.2 Tear Properties 64

4.2.3 Swelling Properties and Crosslink Density Measurement 65

4.2.4 Morphological Evaluation 67

4.2.5 Fourier Transform Infrared (FTIR) 68

4.3 Effect of Different Loading of Cleaning Agent on NR Latex Film Properties 69

4.3.1 Tensile Properties 69

4.3.2 Tear Properties 71

4.3.3 Swelling Index and Crosslink Density Analysis 72

4.3.4 Morphological Evaluation 74

4.3.5 Fourier Transform Infrared (FTIR) Analysis 75

4.3.6 Thermogravimetric Analysis (TGA) 76

4.4 Effect of Different Thickness of Core Layer at Different Moulding Temperature 78

4.4.1 Cure Characteristic 78

4.4.1.1 Torque Minimum and Maximum 78

4.4.1.2 Scorch Time (t_2) and Cure Time (t_{90}) 82

4.4.2 Tensile Properties 84

4.4.3 Swelling Properties and Crosslink Density of NR latex Laminated Films 88

4.4.4 Morphological Properties of NR Latex Laminated Films 91

4.5 Tensile Properties for Different Thickness of NR latex Laminated Films and NBR Latex Laminated Films 93

4.5.1 Tensile Test for Different Thickness NR latex Laminated Films 93

4.5.2 Tensile Test for Different Thickness NBR Latex Laminated 95

Films

4.6 Cleaning Effectiveness Test 99

4.6.1 Laminated NR latex Film Using WNR Latex Film as a Core Layer. 100

4.6.2 Laminated NBR Latex Film Using WNBR Latex Film as a Core Layer. 106

CHAPTER 5 - CONCLUSIONS AND FUTURE WORKS

5.1 Conclusions 111

5.2 Future Works 115

REFERENCES 116

APPENDICES

LIST OF TABLES

		Page
Table 2.1	Composition and physical properties of natural rubber (NR) latex	9
Table 2.2	Components of cleaning agents and their main tasks	28
Table 3.1	List of materials used for compounding process	44
Table 3.2	Equipments used in the research	45
Table 3.3	Formulation for fresh natural rubber (NR) latex	46
Table 3.4	Formulation for fresh nitrile butadiene rubber (WNBR) latex	46
Table 3.5	Formulation for NR latex cleaning compound with different cleaning agent (TA) and different loading of MEA cleaning agent (TB).	47
Table 3.6	Formulation for NBR latex cleaning compound	48
Table 3.7	Wet weight of each layer of NR latex laminated films	50
Table 3.8	Wet weight of each layer of NR latex sample before drying	52
Table 3.9	Wet weight of each layer of NBR Latex sample before drying	52
Table 3.10	Sample for different NR latex laminated thickness film at different temperature.	53
Table 3.11	The frequencies of functional group	71
Table 4.1	Thermal degradation of NR latex film with different	77

loading of MEA cleaning agent

LIST OF FIGURES

		Page
Figure 1.1	Malaysian domestic consumption of NR in 2013	3
Figure 2.1	Structure of NR	7
Figure 2.2	General natural rubber types and grades	8
Figure 2.3	Chemical Structure of NBR	11
Figure 2.4	Mechanical properties of NR LATEX/PS TWL/PS blends	17
Figure 2.5	The reaction to produced MEA	29
Figure 2.6	Structure of the Diethylene Glycol Bis(3-Aminopropyl) Ether (DCA 221)	30
Figure 2.7	Schematic stages involves in latex compounding	31
Figure 2.8	Tensile strength of various types of non-irradiated lattices at maturation time variation.	33
Figure 2.9	Schematics of compression moulding process	37
Figure 2.10	Mould cleaning by using Glomold	42
Figure 3.1	The arrangement of laminated NR latex films.	49
Figure 3.2	The arrangement of NBR Latex laminated films	49
Figure 3.3	The arrangement of NR latex laminated film for tensile test	50
Figure 3.4	Latex casted (a) before drying and (b) after drying process under room temperature.	51
Figure 3.5	Cure curves for a maximum torque with reversion.	54
Figure 3.6	Dumbell shape of sample film for tensile test	55
Figure 3.7	Crescent shape of sample film for tensile test	56
Figure 3.8	Flowchart for the preparation and characterization of NR latex	60

	laminated films	
Figure 4.1	Tensile strength for different types of cleaning agent in NR latex films.	62
Figure 4.2	Elongation at break for different types of cleaning agent in NR latex films.	63
Figure 4.3	Modulus 100 and 300 for different types of cleaning agent in NR latex films	63
Figure 4.4	Tear strength for different types of cleaning agent in NR latex films	65
Figure 4.5	Swelling index for different types of cleaning agent in NR latex films	66
Figure 4.6	Crosslink density for different types of cleaning agent in NR latex films	67
Figure 4.7	Morphology of fractured surface of the film (a) control (b) MEA cleaning agent (c) DCA 221 cleaning agent.	67
Figure 4.8	FTIR analysis measurements of natural rubber with different types of cleaning agent.	69
Figure 4.9	Tensile strength for different loading of MEA cleaning agent	70
Figure 4.10	Elongation at break for different loading of MEA cleaning agent.	71
Figure 4.11	M100 and M300 for different loading of MEA cleaning agent.	71
Figure 4.12	Tear strength for different loading of MEA cleaning agent	72
Figure 4.13	Swelling index for different loading of MEA cleaning agent in NR latex films	73
Figure 4.14	Crosslink density for different loading of MEA cleaning agent	74

in NR latex films

Figure 4.15 Morphology of fractured surface of the film (a) T1 (b) T2 (c) T3 and (d) T4 75

Figure 4.16 FTIR analysis measurements of NR latex with different loading MEA cleaning agent (T1, T2, T3 and T4). 76

Figure 4.17 TGA curve of natural rubber film cured with different loading of MEA cleaning agent. 77

Figure 4.18 Torque minimum for different thickness of NR latex laminated film at different moulding temperature (120, 140, and 160°C). 80

Figure 4.19 Torque maximum for different thickness of NR latex laminated film at different moulding temperature (120, 140, and 160°C). 81

Figure 4.20 Torque difference for different thickness of NR latex laminated film at different moulding temperature (120, 140, and 160°C). 81

Figure 4.21 Scorch time (t_2) for different thickness of NR latex laminated film at different moulding temperature (120, 140, and 160°C). 83

Figure 4.22 Cure time (t_{90}) for different thickness of NR latex laminated film at different moulding temperature (120, 140, and 160°C). 83

Figure 4.23 Tensile strength for different thickness of NR latex laminated film at different moulding temperature (120, 140, and 160°C). 85

Figure 4.24 Elongation at break for different thickness of NR latex laminated film at different moulding temperature (120, 140, and 160°C). 86

Figure 4.25	M100 for different thickness of NR latex laminated film at different moulding temperature (120, 140, and 160°C).	86
Figure 4.26	M300 for different thickness of NR latex laminated film at different moulding temperature (120, 140, and 160°C). Swelling index for 10L laminated latex at different temperature.	87
Figure 4.27	Swelling index for different thickness of NR latex laminated films at different temperature (120, 140, and 160°C).	89
Figure 4.28	Crosslink density for different thickness of NR latex laminated films at different temperature (120, 140, and 160°C).	91
Figure 4.29	: Morphology of fractured surface of NR latex laminated films for sample LA at different moulding temperature (a) 120°C (b) 140°C (c) 160°C	92
Figure 4.30	Morphology of fractured surface of NR latex laminated films for sample LB at different moulding temperature (a) 120°C (b) 140°C (c) 160°C	92
Figure 4.31	Morphology of fractured surface of NR latex laminated films for sample LC at different moulding temperature (a) 120°C (b) 140°C (c) 160°C	92
Figure 4.32	Tensile strength for different thickness of NR latex laminated film	94
Figure 4.33	Elongation at break different thickness of NR latex laminated film	95

Figure 4.34	Tensile strength for different thickness of NBR latex laminated film	97
Figure 4.35	Elongation at break for different thickness of NBR latex laminated film	98
Figure 4.36	Surface of L1 under 40x magnification of optical microscope.	98
Figure 4.37	Surface of L2 under 40x magnification of optical microscope	98
Figure 4.38	Completed dry L1 sample after compression moulding	99
Figure 4.39	NR latex laminated film before compression moulding with WNR latex film as core layer.	100
Figure 4.40	Laminated latex composite before and after compression moulding with NR latex sheet as core layer.	101
Figure 4.41	Mould and LX before and after compression moulding	101
Figure 4.42	Mould and LN1 before and after compression moulding	102
Figure 4.43	Mould and LN2 before and after compression moulding	103
Figure 4.44	Mould and LN3 before and after compression moulding	103
Figure 4.45	Mould and LN4 before and after compression moulding	104
Figure 4.46	Mould and LN5 before and after compression moulding	104
Figure 4.47	Surface of NR latex laminated film after mould cleaning with optical microscope (40x magnification)	105
Figure 4.48	NBR latex laminated film before compression moulding with WNBR latex film as core layer.	106
Figure 4.49	Mould and L1 before and after compression moulding	107
Figure 4.50	Mould and L2 before and after compression moulding	107
Figure 4.51	Mould and L3 before and after compression moulding	108
Figure 4.52	Mould and L4 before and after compression moulding	108

Figure 4.53 Mould and L5 before and after compression moulding 109

Figure 4.54 Surface of laminated latex composite after mould cleaning with optical microscope (40x magnification) 110

LIST OF ABREVIATIONS

NR	Natural rubber
NR latex	Natural rubber latex
GA	Getah asli
SGA	Sisa getah asli
WNR latex	Waste natural rubber latex
NBR	Nitrile butadiene rubber
NBR latex	Nitrile butadiene rubber latex
WNBR latex	Waste nitrile butadiene rubber latex
WRL	Waste rubber latex
TSC	Total solid content
DRC	Dry rubber content
TGA	Thermogravimetric Analysis
FTIR	Fourier Transform Infrared
ACN	Acrylonitrile
ENR	Epoxidized NR
KOH	Potassium Hydroxide
TMTD	Tetramethylthiuram disulfide
DTDM	Dithiodimorpholine
ZDEC	Zinc diethyldithiocarbamate
ZDBC	Zinc di-n-butyldithiocarbamates
MEA	Monoethanolamine
DCA 221	Di-(3-aminopropyl) ether of diethylene glycol
DEG	Diethylene glycol

LIST OF SYMBOLS

g	Gram
M_w	Molecular weight
MPa	Mega Pascal
t_{s2}	Scorch time
t_{90}	Optimum curing time
M_H	Maximum torque
M_L	Minimum torque
mm	Millimeter
min	Minute
w_s	initial weight of latex film (in grams)
w_x	weight of the latex film after 48 hours swelling (in grams)
ρ	density
cm^3	centimeter per cubic
χ	interaction parameter
V_s	molecular volume of the solvent
$[X]$	crosslink density

KAJIAN FILEM BERASASKAN LATEKS GETAH ASLI (GA) BERLAMINA UNTUK KEGUNAAN PEMBERSIHAN ACUAN

ABSTRAK

Penggunaan lateks getah asli (GA) semakin meningkat kebelakangan ini menyebabkan peningkatan sisa lateks di tapak pelupusan. Ini adalah kerana sifat kompaun getah yang tidak stabil dan spesifikasi kualiti produk lateks yang ketat. Sisa buangan yang tidak digunakan dengan betul boleh menimbulkan masalah ekologi dan alam sekitar yang serius. Disebabkan masalah ini, satu percubaan telah dibuat untuk menghasilkan laminasi lateks GA dengan sisa lateks getah asli (SGA) untuk digunakan sebagai sebatian pembersih acuan menggantikan sebatian getah kering. Laminasi filem lateks disediakan dengan menyusun kepingan lateks GA (lapisan luar) dan kepingan lateks SGA (lapisan teras) secara berselang-seli. Lapisan luar mengandungi agen pencuci untuk tujuan pembersihan. Kesan jenis dan pembebanan agen pencuci yang berbeza telah dikaji. Filem lateks GA dengan agen pencuci *monoethanolamine* (MEA) mempunyai sifat mekanikal yang baik berbanding filem lateks GA dengan agen pencuci *di-(3-aminopropyl) ether of diethylene glycol* (DCA 221). Pembebanan optimum bagi agen pencuci MEA diperolehi pada 5 phr, peningkatan pembebanan MEA menyebabkan sifat mekanikal filem semakin menurun. Kesan perbezaan ketebalan lateks GA berlamina pada suhu pengacuanan yang berbeza terhadap sifat mekanikal juga dikaji. Filem berlamina dengan lapisan teras yang nipis memerlukan suhu pengacuanan yang rendah manakala filem berlamina dengan lapisan teras yang tebal memerlukan suhu pengacuanan yang tinggi untuk membentuk filem dengan sifat mekanikal yang baik. Lapisan teras memberikan filem lateks berlamina dengan sifat-sifat mekanikal yang lebih baik, tetapi nisbah lapisan teras yang berlebihan akan menyebabkan penurunan sifat-sifat tersebut. Keberkesanan pembersihan acuan, samada sebatian lateks GA atau lateks getah nitril (NBR) bergantung kepada kebolehaliran lapisan getah segar yang mempunyai agen pencuci. Keberkesanan pembersihan acuan filem berlamina lateks NBR lebih bagus berbanding filem berlamina lateks GA. Ini mungkin disebabkan kebolehaliran lateks NBR lebih baik daripada lateks GA dan lateks NBR mempunyai rintangan yang baik terhadap minyak berbanding lateks GA.

STUDY ON LAMINATED NATURAL RUBBER (NR) LATEX BASED FILMS FOR MOULD CLEANING APPLICATION

ABSTRACT

The consumption of natural rubber (NR) latex is increasing recently hence increased the waste latex in landfill. This is due to the unstable nature of the latex compound and the strict specifications in the quality of latex products. Improper use of waste latex can create serious ecological and environmental problems. Due to this problem, an attempt was made to laminate the NR latex with waste natural rubber (WNR) latex as mould cleaning compound to substitute the dry rubber compound. The latex lamination films were prepared by arranging the NR latex sheets (outer layer) alternately with WNR latex sheet (core layer). The outer layers contain the cleaning agent for cleaning purposes. Effect of different types and different loading of cleaning agent were investigated. NR latex film with monoethanolamine (MEA) cleaning agent gives the best mechanical properties compare to NR latex film with di-(3-aminopropyl) ether of diethylene glycol (DCA 221) cleaning agent. The optimum loading for MEA cleaning agent was obtained at 5 phr, the increment of MEA loading caused the mechanical properties of the NR latex film to decrease. The effect of different thicknesses of NR latex laminated film at different moulding temperature on mechanical properties of NR latex also has been studied. The laminated film with thinner core layer needed low moulding temperature while the laminated film with thicker core layer needed higher moulding temperature to form the film with good mechanical properties. The core layer gave laminated latex film with better mechanical properties, but excessive of core layer portion caused the decreased in the properties. The effectiveness of mould cleaning, either NR latex or NBR latex compound was depends on the flow ability of the fresh latex layer with mould cleaning agent. The mould cleaning effectiveness of the NBR latex laminated film is observed to be better than NR latex laminated film. It is maybe due to the flow ability of NBR latex is better than NR latex and NBR latex has good resistance to oil compare to NR latex.

CHAPTER 1

INTRODUCTION

1.1 Overview

A large number of polymer products especially rubber products are produced through moulding process. One of the major problems of moulding process is the fact that the rubber parts manufactured often stick to the mould after process. Consequently, moulds fouling are formed where deposits from previous moulding stick to the surface of the mould and these in turn cause imperfection on the next cycles of moulding process. Mould release and mould fouling have serious implications to the polymer industry in terms of limiting the production rate and in an industry where 'time is money' this can represent a significant cost to the industry. Mould cleaning process is a process of removal build-up deposit or residue material on the mould surface after repeated cycles of production. It is an important process in product manufacturing in order to have good quality of finish product. Without mould cleaning process, the surface of finish product will be affected (Lindsay, 1999).

The most common used mould cleaning process is sand blasting technique (Bawa, 2006). Sand blasting is cheaper process but it takes longer period to clean the moulds and for long term application, it tends to damage the mould because of the usage of high velocity fine materials (Packham, 2002 and Golubski, 2007). As for mould cleaning compounds from dry rubber depends solely on the skill of the operators where they are mismatch in phase of compounding with crucial parts to obtain low scorch time and better dispersion of cleaning agent (Sivaprakasam, 2007 and Johnson, 2001).

Researchers and engineers are continuously studying the easiest, fastest and safety way to clean up the mould after repeated cycles of usage. Natural rubber (NR) latex has excellent strength properties (Chuayjuljit *et al*., 2009). NR latex compounds will be beneficial as a new substitute for dry rubber compound as mould cleaning because of its excellent strength properties which can attract the dirt from mould. The NR latex films through the dipping process cannot be used as mould cleaning product due to the thin film produced which stick on the mould hence difficult for cleaning processes. Hence, the lamination of NR latex film is necessary to increase its thickness and to avoid excess film on the mould surface. The utilization of waste NR latex with fresh NR latex on the lamination films will give an added value for recycling purposed.

This work focused on preparation of NR latex films as a based material for mould cleaning compound. The adhesion property between NR latex film and waste natural rubber (WNR) latex as mould cleaning compound was investigated. The NR latex lamination film was characterized and tested for its suitability and feasibility as substitute material for mould cleaning product. The comparison of cleaning effectiveness between the NR latex lamination and Nitril Butadiene rubber (NBR) latex lamination film also is carried out. The use of NR latex lamination films with WNR latex can contribute to novel materials for mould cleaning product as a green materials and easier for cleaning.

1.2 Problem Statement

Natural rubber (NR) latex has abundant industrial uses, especially in the health-care industry, such as medical gloves, condoms, catheters, baby bottle nipples, balloons, etc (Kabara *et al*., 2006). Figure 1.1 shows the statistic for Malaysian domestic consumption of NR in year 2013. The largest consumption of NR in year

2013 for rubber gloves industry is around 70%. The highest consumption of NR in production of latex products such as rubber gloves, rubber thread, latex foam and other latex products compare to the usage of NR for tyres and tubes, rubber footwear, rubber compounding/bands/sheeting and other rubber products. The high consumption of NR latex products contributes to higher latex wastes either in solid form or liquid form from latex glove manufacturing which indirectly increased the waste disposal problems.

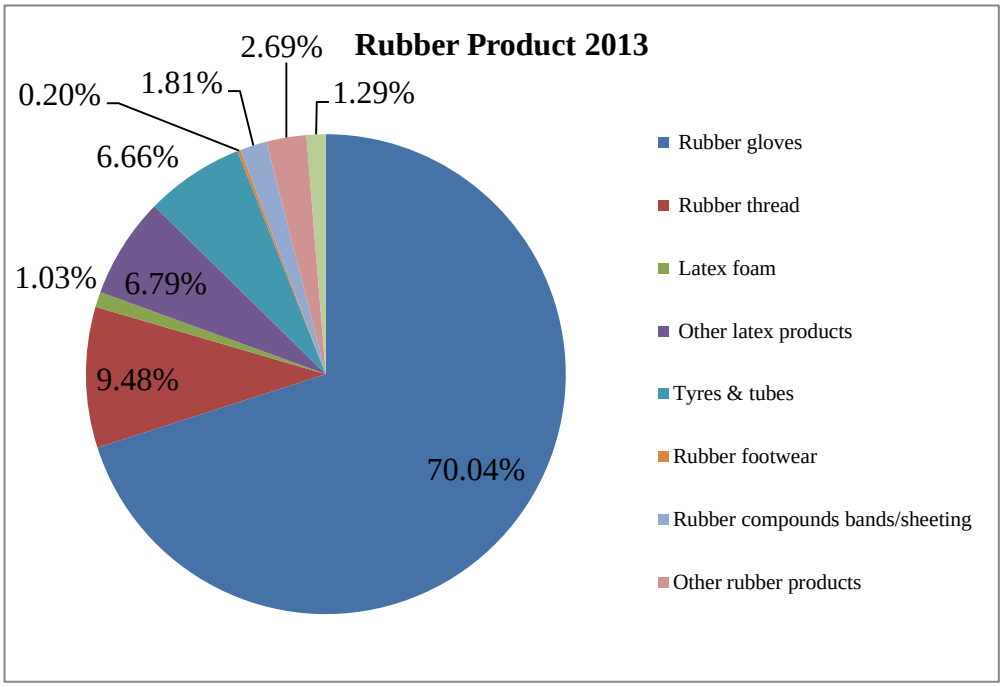

Figure 1.1: Malaysian domestic consumption of NR products in 2013 (MARGMA, 2014).

According to Mathew *et al*. (2001), the formation of a higher percentage of waste latex rubber (WLR) in latex factories is due to the unstable nature of the latex compound and the strict specifications in the quality of latex products. These latex rejects contain about 95% rubber hydrocarbon of very high quality, which is only lightly cross-linked. These rejects, if not properly used, can create serious ecological and environmental problems. Due to the pollution caused by latex, many attempts to