The characterization and properties of Recycled Natural Latex Gloves (rNL-G) filled Acrylonitrile Butadiene Rubber (NBR) compounds

by

OMAR SABBAR DAHHAM
(1431621162)

A dissertation submitted in the partial fulfillment requirements for the degree of Master of Science (Polymer Engineering)

School of Material Engineering
UNIVERSITI MALAYSIA PERLIS

2015

UNIVERSITI MALAYSIA PERLIS

DECLARATION OF THESIS

Author's full name : OMAR SABBAR DAHHAM
Date of birth : 24 04 1987

Title : The characterization and properties of Recycled Natural Latex Gloves (rNL-G) filled Acrylonitrile Butadiene Rubber (NBR) compounds

Academic Session : 2015

I hereby declare that the thesis becomes the property of Universiti Malaysia Perlis (UniMAP) and to be placed at the library of UniMAP. This thesis is classified as :

☐	**CONFIDENTIAL**	(Contains confidential information under the Official Secret Act 1972)*
☐	**RESTRICTED**	(Contains restricted information as specified by the organization where research was done)*
☐	**OPEN ACCESS**	I agree that my thesis is to be made immediately available as hard copy or on-line open access (full text)

I, the author, give permission to the UniMAP to reproduce this thesis in whole or in part for the purpose of research or academic exchange only (except during a period of_____years, if so requested above).

Certified by:

_____ _____

SIGNATURE **SIGNATURE OF SUPERVISOR**

(G2099186) DR. NIK NORIMAN BIN ZULKEPLI

Date : 23 /06 /2015 Date : 23 /6 / 2015

ACKNOWLEDGEMENTS

The favor, above all, before all, and after all, is entirely to Allah (SWT), to whom my never-ending thanks and praise are humbly due.

I would like to take this opportunity to convey my sincere thanks and deepest gratitude to my supervisor, Dr. Nik Noriman Bin Zulkepli for all the help and valuable guidance provided to me during throughout my period of research. I consider myself privileged to have had the opportunity to work under his guidance. I'm also grateful to my friends especially (Abdulkader Alakrach and Alhamza Alalousi) for their help and support.

I would like to express my appreciation to University Malaysia Perlis (UniMAP) for giving me the opportunity to have my master research. During this research I have received a lot of supervision and help from the following people whom guidance me and support me.

Moreover, I would like to thank those who are always in my heart; my father, mother, brothers and my sisters for their endless and continuous encouragement and constant support. Finally, my thanks with love to my wife Marwa to afford the difficulties life away from me.

Omar Sabbar Dahham

April 2015

LIST OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ACN	Acrylonitrile
ASTM	American Society for Testing and Materials
CaCO3	Calcium Carbonate
CB	Carbon Black
CBS	N-cyclohexyl-2-benzothiazole sulfonamide
CV	Conventional system
DOS	Department Of Statistic
EV	Efficient system
MDR	Monsanto moving die rheometer
MPa	Mega Pascal
NBR	Acrylonitrile Butadiene Rubber
NR	Natural Rubber
rNL-G	Recycled Natural Latex Gloves
Phr	Part per hundred rubber
SD	Sawdust short fiber
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric analysis
TOR	Trans Polyoctylene Rubber
ZnO	Zinc Oxide

LIST OF SYMBOLS

cm	Centimeter
Eb	Elongation at break
g	gram
M100	Modulus at 100% elongation
M_H	Maximum torque
M_L	Minimum torque
mm	Millimeter
μm	Micrometer
Q_m	Total swelling weight
t_2	Scorch time
t_{90}	Cure time
Ts	Tensile strength
V_r	Volume fraction of swollen rubber
V_s	Molar volume of solvent
ρ	Density

Sifat-sifat dan Pencirian Sarung Tangan Lateks Asli (rNL-G) Terisi Dalam Sebatian Akrilonitril Butadiena (NBR)

ABSTRAK

Penggunaan getah buangan daripada sarung tangan lateks asli yang dikitar semula (rNL-G) dengan pencampuran bersama getah sintetik seperti getah akrilonitril butadiena (NBR) boleh menghasilkan produk yang baru yang mempunyai sifat-sifat yang boleh diterima. Keputusan dalam siri pertama di mana sebatian NBR/ rNL-G terutamanya saiz halus hingga 20 bahagian per seratus getah (bsg) kandungan rNL-G menunjukkan peningkatan keseluruhan dalam sifat kematangan, sifat tensil, fizikal dan termal berbanding dengan saiz yang lebih besar dan kandungan rNL-G lain. Manakala dalam siri kedua, nilai kandungan rNL-G yang optimum yang diperoleh daripada siri pertama digunakan di mana penambahan habuk kayu bergentian pendek (SD) sebagai pengisi semulajadi pada kandungan yang berbeza telah dikaji. Keputusan telah menunjukkan bahawa penambahan SD pada kandungan 5 bsg telah meningkatkan kelekatan antara NBR dan dengan pengisi rNL-G, di mana membawa kepada penambahbaikan sifat kematangan seperti masa kematangan yang pendek dan meningkatkan kekakuan dan ketegaran seperti modulus dan kekerasan. Pada siri ketiga, penambahan 6 bsg getah trans-polietilena (TOR) sebagai agen pengkupel telah meningkatkan ketumpatan sambungsilang dan meningkatkan keserasian sebatian getah NBR/ rNL-G. Kebanyakan sifat kematangan, tensil, fizikal dan termal sebatian getah NBR/ rNL-G yang telah dicampurgaul dengan TOR, terutamanya pada kandungan TOR 6 bsg, menunjukkan ciri-ciri keseluruhan yang lebih baik berbanding sebatian getah NBR/ rNL-G yang tidak dimasukkan TOR. Gabungan semua bahan merujuk dari nisbah optimum sebatian siri 1 pada 20 bsg/ saiz halus, siri 2 pada 5 bsg dan siri 3 pada 6 bsg. Sebatian NBR / rNL-G / SD / TOR telah mempamerkan peningkatan sifat yang paling tinggi terutamanya kestabilan termal, ketegangan dan sifat fizikal. Permukaan patah tensil bagi kesemua siri telah disokong dengan pemerhatian oleh mikroskopi penskanan elektron (SEM) telah membuktikan kelakuan kekuatan optimum setiap sebatian masing-masing.

The Characterization and Properties of Recycled Natural Latex Gloves (rNL-G) Filled Acrylonitrile Butadiene Rubber (NBR) Compounds

ABSTRACT

The utilization of waste rubber from recycled natural latex gloves (rNL-G) by means of compounding together with synthetic rubber: acrylonitrile butadiene rubber (NBR) could represents a new product with an acceptable properties. Results in first series which NBR/ rNL-G compounds particularly fine size up to 20 phr loading of rNL-G, showed overall improvement in cure characteristic, tensile, physical and thermal properties compared to coarser size and other rNL-G loading. Meanwhile, in second series, the incorporation of sawdust short fiber (SD) as natural filler at different loading was studied with optimum rNL-G loading filled NBR from the first series. Results indicated that, the addition of SD loading at 5 phr increased the adhesion between NBR matrix, which led to improve the cure characteristics such as lower cure time and increase the stiffness and rigidity such as modulus and hardness. At third series, the addition of 6 phr of trans-polyoctylene rubber (TOR) as a compatibilizer has increased the crosslinking density and enhanced the incorporation of NBR/ rNL-G compounds, therefore improving the compatibility of NBR/ rNL-G compounds. Most of cure characteristics, tensile, physical and thermal properties of compatibilised NBR/ rNL-G compounds, particularly 6 phr TOR showed better overall properties than uncompatibilised NBR/ rNL-G compounds. The combination of all material referring from optimum loading of 1st series at 20 phr rNL-G/ fine size, 2nd series at 5 phr SD and 3rd series at 6 phr TOR. The NBR/ rNL-G /SD/TOR compound exhibited the most improvement properties particularly the thermal stability, tensile and physical properties. The tensile fracture surface of all series were supported by scanning electron microscopy (SEM) observation proved the behavior of optimum strength of each compound respectively.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Nowadays, rubber represents a significant material that used in industry and several researches were published to enhance rubber products quality. Malaysia is one of the largest suppliers of the rubber in the world, particularly the high quality of natural rubber products, such as gloves, condoms, catheters, etc. According to the department of statistic (DOS 2014) in Malaysia, natural rubber (NR) production has registered 52004 tonnes in December 2014. This value has been reduced by 32% compared to December in 2013 year. The main donor of (NR) production was from the smallholding sector at 91.2%, whereas the estate sector only contributed 8.8 %. Figure 1.1 displays the amount of (NR) production in Malaysia within 14 years.

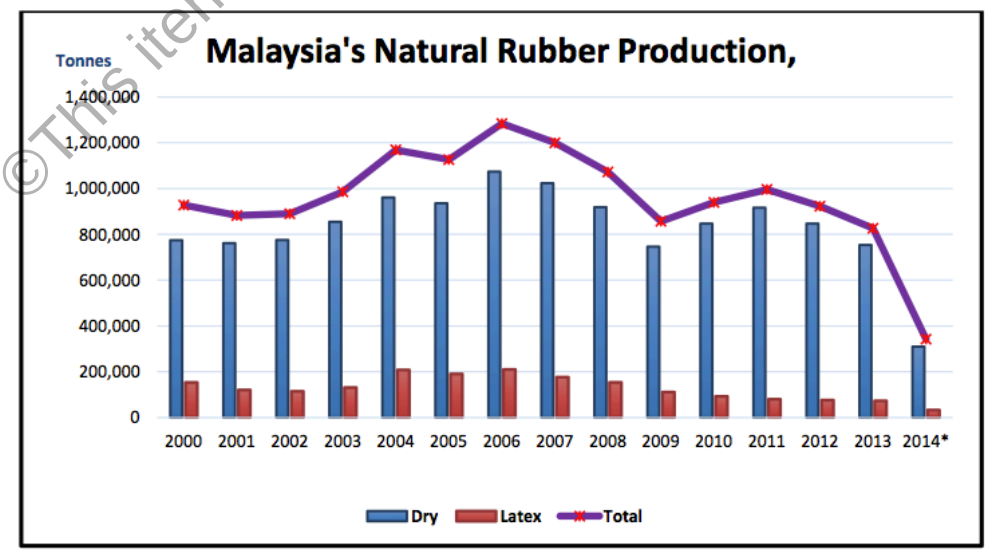

Figure 1.1: Statistics of (NR) production in Malaysia (Department Of Statistic, 2014).

The examination and surgical gloves production in Malaysia is the largest, producing about 65% of the rubber gloves in the world, included many companies such as TopGlove Corp. Bhd., SuperMax Glove Manufacturing Bhd., Hartalega Holdings, Kossan Rubber Industries Bhd, and others. The conventional glove market, which is dominated by Malaysian manufacturers, global consumption is about 140 billion pieces of gloves annually (Jusha, 2011). The major factor that led to increase the gloves consumption was the low cost of rubber gloves. Moreover, the societies became more awareness and anxiety about the health, particularly when the dangerous human virus detected and spread out rapidly such as H1N1 virus. The increasing of gloves consumption has enlarged the amount of waste gloves gradually. Furthermore, the strict specifications for the latex gloves led to about 15% of the products as rejected gloves. Most of defects faced in materials produced by latex dipping are pinholes and blisters, which were due to the air bubbles interrupted or the presence of impurities inside the latex products.

One of the major problems in 21st century is the waste disposal, which became a big concern to be serious with the industry development and the population growth. Several researches have worked on suitable solution toward the waste rubber increment and the waste rubber utilization (Guo et al., 2010). The waste rubber, particularly non-degradable rubber became a serious problem in recent years, which was due to the increasing of the wastes amounts. The massive amount of the waste rubber generated every year from disposal of post-consumer products and industries urged scientists to find an effective way to eliminate or at least to minimize the huge amount of waste rubber, which may consider as an environmental problem and caused a health risk.

In recent years, the reuse culture has spread widely and the recycling has been encouraged by increasing awareness in environmental matters and the subsequent desire to save resources (Perez et al., 2010). Recycling was one of the noteworthy methods that used to minimize the waste rubber in environment, which includes many processes to change the waste rubber to a reusable form (Wu and Zhou, 2009). The using of recycled rubber in the form of either ground waste vulcanizates or reclaimed rubber compounds could give an economic and processing advantages. In attempt to reduce the cost of rubber compounds, the use of cross-linked rubber particles has beneficial effects such as faster extrusion rate, reduced die swell and better molding characteristics (Srivanasan et al., 2008). Recycled latex became more interesting than other types of recycled rubber due to the lightly cross-linked and high quality nature of rubber hydrocarbon. Many attempts were made to improve the mechanical properties, durability, processability, performance, and to reach to an economic advantage when compounding recycled latex with virgin rubber (Abraham et al., 2011 and Anandhan et al., 2003). Through rubber recycling technology, the compounding of different type of polymer together, particularly elastomers with recycled rubber could be used in a wide range of applications such as road, roof surfaces, playground surfaces, rubber flooring, float, marine, sporting mats and much more. However, the dissimilarity of chemical structure and polarity of virgin and recycled rubber compound could effect negatively on processability, performance, durability and physical properties.

In this study, the non-polar recycled natural latex gloves (rNL-G) have a limited compatibility with polar acrylonitrile butadiene rubber (NBR) as virgin rubber, which effected on some properties. Nevertheless, the presence of certain additives such as cellulosic materials or compatibilizer could improve the properties of rubber compound. Therefore, the utilization of the waste gloves could be a great deal of interest in the

rubber industry to develop low cost and use an effective techniques to convert waste and used rubber into a processable form in future.

1.2 Problem statements

Usually, the direct recycling or reshaping of the vulcanized rubber is not easy because of the irreversible three-dimensional crosslinking; therefore the preprocessing for vulcanized rubber is important. Several attempts were made to eliminate or at least to reduce the waste rubber, such as burning method and discarding in landfills. These methods did not present an effective solution because they caused another problems, such as soil and air pollution. Other methods have been made to reuse waste, such as reclamation (Dubkov et al., 2012), devulcanization (Myhre et al., 2012), fuel recovery (Jasmin et al., 2007) and others. However, most of those processes need mechanical shear, heat, and energy input together with chemicals such as oils, accelerators, amines, or disulfides to reduce the concentration of sulfur crosslinks in the vulcanized rubber (Myhre et al., 2012).

Currently, grinding technique is used for waste rubber processing, which could be more suitable than other methods because it does not need additional energy, reactions, or chemical treatments (Fernández et al., 2012). The ground rubber that obtained from this method could be used in a wide range, such as fillers for rubber compounds, fillers for thermoplastic and also could use as modifiers for asphalt concrete.

From economic and environmental viewpoints, this study has used the grinding method of recycled natural latex gloves (rNL-G) to form a ground rubber as filler in virgin rubber.

1.3 Research objectives

The major aim of this research is to study the possibility of producing a new elastomeric material with acceptable properties from compounding the recycled natural latex gloves (rNL-G) with virgin acrylonitrile butadiene rubber (NBR). Therefore it can be outline as follows:

a) To investigate the effects of different sizes of recycled natural latex gloves (rNL-G) on properties of NBR/rNL-G compounds.

b) To study the effects of sawdust short fiber (SD) as natural filler on properties of NBR/rNL-G/SD compounds.

c) To determine the effects of trans-polyoctylene rubber (TOR) as a compatibilizer on properties of NBR/rNL-G/TOR compounds.

1.4 Scope of study

The first part of study was compounding two different sizes of recycled natural latex gloves (rNL-G) (300-700) μm for fine size and (2-4) cm for coarser size with virgin acrylonitrile butadiene rubber (NBR), the loading of different sizes were 0,10,20 and 30 phr, respectively. The second part of study was compounding of rNL-G at 20 phr / fine size as optimum loading of the first NBR/rNL-G compound with sawdust short fiber (SD) as natural filler that ranged from 300 to 600 μm size and the loading was 5,10,15 and 20 phr, while the third part of study was the compounding of rNL-G at 20 phr / fine size as optimum loading of first NBR/rNL-G compound with trans-polyoctylene-rubber (TOR) as a compatiblizer and the loading started from 2,4,6 and 8 phr. The last part of study was compounding of NBR with optimum loading of rNL-G, SD and TOR for 1st, 2nd and 3rd series respectively.

All the previous series have been compounded using two-roll mill and vulcanized using hydraulic hot compress machine according to ASTM D 412 for tensile testing. Curing characteristic of the compounding was studied before vulcanization process. Tensile properties (tensile strength, elongation at break and tensile modulus) were studied by tensile Instron machine. Shore A was used according to ASTM D-2240-81 to test the hardness of the vulcanized compound. Toluene solvent was used for the swelling test based on ASTM D471-79 to calculate crosslinking density of the vulcanized rubber compounds. Thermo gravimetric thermograms (TGA) test was studied as a thermal properties and the morphology of fractured surface of the vulcanized rubber samples after tensile testing was analyzed using scanning electron microscopy (SEM).

CHAPTER 2

LITERATURE REVIEW

2.1 Rubber recycling

The relatively high cost of crude rubber has encouraged the industry to develop the recycling processes of the vulcanized rubber. One of the earliest recycling method have been done by Charles Goodyear, which involved grinding the vulcanized rubber to fine size as filler and blend it with virgin rubber. This old method has faced many difficulties, such as the separation of impurities (fabric, steel and carbon black) forming after grind tires, in addition to the high-energy consumption of rubber grinding machines. Other method produced by Champan Miichell. involving boiling the rubber for several hours with strong formic acid or sulfuric solution to disassemble the fabric and then passing a high-pressure steam to wash and devulcanize the waste rubber. The disadvantage of this process was the incapability to process the waste rubber because of high sulfur level, which tends to form a further vulcanization process (Schidrowitz and Dawson, 1952).

Alkali digester process has been applied by Arthur Marks in 1899, which used a dilute caustic soda solution with ground rubber at high temperature and pressure about 20 hours to devulcanize the rubber scrap in one step. This process was used widely in that time to reclaim most of rubber scrap. A year later, in 1900, same inventor has found another patent on a development that comprised steam jacketing vessel and agitation of the mass. The relatively new method has used by most of rubber reclaimers for more than 50 years (Ball, 1947).

In recent years, the world became more interested to reuse and recycle the rubber and several techniques have been developed to improve the rubber recycling technology. De, (2005) stated various reasons that led to increase the reclaiming or recovering process for vulcanized rubber:

a) The lower cost of the reclaimed rubber, which could reach to half cost of virgin rubber.
b) Excellent method to dispose of the waste rubber, which was always problematic.
c) Some properties of reclaimed rubber could be better than virgin rubber.
d) The producing of reclaimed rubber needs less energy than virgin rubber.
e) Many useful products derived from reuse rubber.
f) Recycling activates created job opportunities in many countries.

One of the most common recycling methods that used lately is mixing of recycled rubber powder as filler with virgin rubber. The usual methods that used for rubber powdering were cryogenic grinding (Shi at al., 2013), ambient grinding (Adhikari et al., 2000), and wet grinding (Fernández et al., 2012). Lee et al., (2009) studied the influence of physical treatments of waste rubber powder on the mechanical properties of the revulcanizate and found the ozone/ultrasonic treatment was the most effective treatment to improve the mechanical properties of waste rubber powder revulcanizate. Kumar et al., (2007) showed a possible way that could study both recycled rubber-virgin rubber properties; either increasing the effective surface area by reducing the granulate size or by surface modification of granulates to improve the adhesion bonding between the matrix and granulates. Other researchers, such as Yun and Isayev, (2003) studied the superior mechanical properties of ultrasonically recycled

EPDM rubber. They found that the tensile properties of revulcanized EPDM is much better than original vulcanizates.

2.2 Recycled natural latex gloves (rNL-G)

In general, natural latex has wide vegetable sources. It is created by enzymatic processes in several plants, such as Euphorbiacea, Compositea, Moracea and/or Apocynacea family. However, it is formed largely from the tree called Hevea Brasiliensis, which belong to Euphorbiacea family. The chemical structure of Hevea Brasiliensis latex is poly-cis-1.4 isoprene containing more than 99.9 % of cis 1.4 structural units as shown in Figure 2.1, which gives high elastic properties (Tg ~ -70°C) and spontaneously crystallizes (maximum crystallization rate is approximately at - 25°C).

The waste rubber formed in natural latex based industries is around 10–15% of the rubber consumed. The formation of high natural latex amount as waste in industry is due to the unstable nature of this latex and the strict specifications in the quality of latex products (Riyajan et al., 2012). The rejected latex, particularly the rejected natural latex gloves contain about 95% of high quality rubber hydrocarbon, which is only lightly cross-linked. Mathew et al., (2001) studied the effects of recycled natural latex as powder on the properties of epoxidised natural rubber and found that the induction and cure time decreased with increasing concentration of latex waste filler. Additionally, most of physical properties of the rubber compounds were improved.