# Characterization and Properties of Recycled Acrylonitrile Butadiene Rubber (rNBR) Filled Epoxidized Natural Rubber (ENR 25) Compound



**By**

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## LIST OF ABBREVIATIONS

| | |
|---|---|
| ACN | Acrylonitrile |
| ASTM | American society for testing and materials |
| BD | Butadiene |
| CBS | N-cyclohexyl-2- benzothiazyl sulfenamide |
| CV | Conventional vulcanisation |
| DPG | Diphenyl guanidine |
| ENR 25 | Epoxidized natural rubber with 25 mol% epoxidation |
| EV | Efficient vulcanisation |
| FTIR | Fourier transforms infrared |
| IRSG | International Rubber Study Group |
| ISO | International organization for standardization |
| MBT | Mercaptobenzothiazole |
| MDR | Monsanto moving die rheometer |
| NBR | Acrylonitrile butadiene rubber |
| NR | Natural rubber |
| Phr | Part per hundred rubber |
| rNBR | Recycled acrylonitrile butadiene rubber |
| SEM | Scanning electron microscopy |
| SEV | Semi-efficient vulcanisation |
| TMTD | Tetramethylthiuramdisulfide |
| TOR | Trans Polyoctylene Rubber |
| UV | Ultraviolet |
| ZDBC | Zinc dibutyl dithiocarbamate |

## LIST OF SYMBOLS

| | |
|---|---|
| $t_2$ | scorch time |
| $t_{90}$ | cure time |
| Eb | elongation at break |
| $M_{100}$ | stress at 100% elongation |
| $M_L$ | minimum torque |
| $M_H$ | maximum torque |
| % | percentage |
| °C | degree celsius |
| $g/cm^3$ | gram per cubic centimetre |
| g | gram |
| h | hour |
| min | minute |
| mm | milimetre |
| µm | micrometre |
| nm | nanometre |
| MPa | mega pascal |
| ρ | density |
| $m^2/g$ | metre square per gram |

**Pencirian dan Sifat Getah Akrilonitril Butadiena Kitar Semula (rNBR) Diisi Ke Dalam Sebatian Getah Asli Epoksida (ENR 25)**

## ABSTRAK

Kegunaan getah kitar semula dalam sebatian getah menjadi satu kaedah alternatif untuk mengurangkan sisa getah di tapak pelupusan dan memberi peluang untuk menghasilkan produk baru. Dalam kajian ini, tumpuan mengenai sifat-sifat getah sarung tangan akrilonitril butadiena kitar semula (rNBR) yang diisi ke dalam getah asli epoksida (ENR 25) telah dijalankan. Proses sebatian telah dijalankan dengan menggunakan mesin penggiling bergulung dua pada suhu bilik dan sistem pemvulkanan semi-efisen (SEV) telah dipilih dalam kajian ini. Masa membakar (t2), masa awet (t90), tork maksimum (MH) dan tork minimum (ML) telah ditentukan dengan menggunakan reometer Monsanto. Penentuan sifat-sifat getah tervulkan merangkumi ujian tegangan, ujian kekerasan, ujian daya tahan, ujian pembengkakan, ketumpatan sambung silang dan SEM. Keputusan dalam siri pertama menunjukkan bahawa saiz halus, S1 rNBR yang diisi ke dalam sebatian ENR 25 menyumbang kepada sifat-sifat yang lebih baik seperti ciri awet, sifat tegangan, sifat-sifat fizikal dan morfologi berbanding dengan saiz kasar, S2 rNBR, terutamanya pada 15 phr kandungan rNBR . Walau bagaimanapun, saiz kasar rNBR mengalami kemerosotan pada semua sifat disebabkan oleh penggumpalan rNBR semasa proses pemvulkanan. Sifat optimum (mempunyai 15 phr rNBR yang diisi ke dalam ENR 25) telah dipilih untuk kajian lebih lanjut dalam siri kedua dengan kemasukan *Imperata Cylindrica* sebagai pengisi semula jadi. Keputusan menunjukkan susutan dalam sifat-sifat tegangan dengan peningkatan *Imperata Cylindrica*. Walau bagaimanapun, ciri-ciri awet, fizikal dan morfologi menunjukkan hasil yang lebih baik pada 5 phr serbuk *Imperata Cylindrica* terutamanya bagi saiz halus, C1. Pada siri ketiga, penambahan getah trans-polyoctylene (TOR) sebagai kompatibilizer ke dalam sifat optimum dalam siri 2 menunjukkan sifat tegangan tertinggi pada 6 phr TOR dan getah menjadi lebih lembut apabila kandungan kompatibilizer meningkat. Sifat-sifat lain seperti ciri-ciri awet, fizikal dan morfologi menunjukkan peningkatan dengan kehadiran TOR ke dalam sebatian getah.

**Characterization and Properties of Recycled Acrylonitrile Butadiene Rubber (rNBR) Filled Epoxidized Natural Rubber (ENR 25) Compound**

## ABSTRACT

The uses of recycled rubber in rubber compounding become an alternative method to reduce the landfill of rubber waste and gives opportunity to produce new product. In this research, the study on the properties of recycled acrylonitrile butadiene rubber (rNBR) gloves filled epoxidized natural rubber (ENR 25) has been done. The compounding process was conducted by using two roll mills at room temperature and semi-efficient vulcanization (SEV) system was selected in this study. The scorch time ($t_2$), cure time ($t_{90}$), maximum torque (MH) and minimum torque (ML) were determined by using a Monsanto rheometer. The determination of rubber vulcanizate's properties includes tensile test, hardness test, resilience test, swelling test, crosslink density, and SEM. Results in first series indicated that the fine size, S1 of rNBR filled ENR 25 compound contributed to the better properties such as cure characteristics, tensile properties, physical properties and morphology compare to coarser size, S2 of rNBR, mainly at 15 phr of rNBR content. However, the coarse size of rNBR particles size exhibited deterioration in all properties due to agglomeration of rNBR during vulcanization process. The optimum properties (having 15 phr of rNBR filled ENR 25) were selected for further study in second series with incorporation of *Imperata Cylindrica* as natural filler. Result shows a decrement in tensile properties with the increment of *Imperata Cylindrica* loading. However, cure characteristics, physical properties and morphological properties show better result at 5 phr loading of *Imperata Cylindrica* powder especially for fine size, C1 powder. At third series, the incorporation of trans-polyoctylene rubber (TOR) as compatibilizer into optimum properties in series 2 shows highest tensile properties at 6 phr of TOR and the rubber become softer as the compatibilizer content increased. Other properties such as cure characteristics, physical properties and morphological properties show an improvement with the presence of TOR into rubber compound.

# CHAPTER 1

# INTRODUCTION

## 1.1 Research Background

Rubber is a versatile material with multiple usages. It forms a part of mechanical devices in many products. It helps to exclude draughts and to insulate against noise. Sofas and chairs may be upholstered with foam meanwhile rubber cushions and beds may have natural rubber. Clothing and footwear may contain rubber such as elasticized threads in undergarments or shoe soles. Most sports equipment, virtually all balls, and many mechanical toys contain rubber in some or all of their parts (Eldho et al., 2011 and Rehan et al., 2008).

Rubber plantation began in Malaysia in 1877, only as ornamental plants. Commercialization of rubber in Malaysia started in the late 19$^{th}$ century. Until 1992, Malaysia was the world's top natural rubber producer. However, as Malaysia shifted its emphasis on oil palm plantations and other non-agricultural investments, the nation has lost its status as the top natural rubber produce. Currently, Malaysia slipping to 6$^{th}$ spot in the world's rubber production ranking, behind India, China, Vietnam, Indonesia and Thailand. Nevertheless, Malaysia still remains the world's number one producer of high-end rubber products including condoms, Foley catheters and NBR gloves (Muhammad Feisol, 2015).

According to the statistics of International Rubber Study Group (IRSG), the world natural rubber and synthetic rubber production in 2014 was 11.8 million tons and 16.7 million tons, respectively (Malaysian Rubber Board, 2014). The domestic consumption of natural rubber in Malaysia grew by 3.3 %, recording a total of 448,499 tons in 2014 compared to 434,192 tons in 2013 (Malaysian Rubber Board, 2014 & Monthly Rubber Statistics Malaysia, 2014). The Malaysian rubber products industry is made up of more than 500 manufacturers producing latex products; tyres and tyre-related products; and industrial and general rubber products (Muhammad Feisol, 2015). The rapid growth of the industry has enabled Malaysia to become the world's largest consumer of natural rubber latex.

Fig. 1.1 illustrates the summary of distributions of Malaysian rubber product companies by product sector in 2014 according to Department of Statistic Malaysia. The rubber products can be divided into general rubber goods, latex products, industrial rubber goods, footwear, inner tubes and tyres. Latex products show higher production after general rubber goods with 54 gloves, 6 catheters, 2 latex thread and 41 other. Rubber gloves shows a dominant productions with their production capacity in 2014 was 32 434 million pairs where it shows a decrease in production compared in 2013 (34 628. 16 million pairs) (Muhammad Feisol, 2015 and Malaysian Rubber Board, 2014).

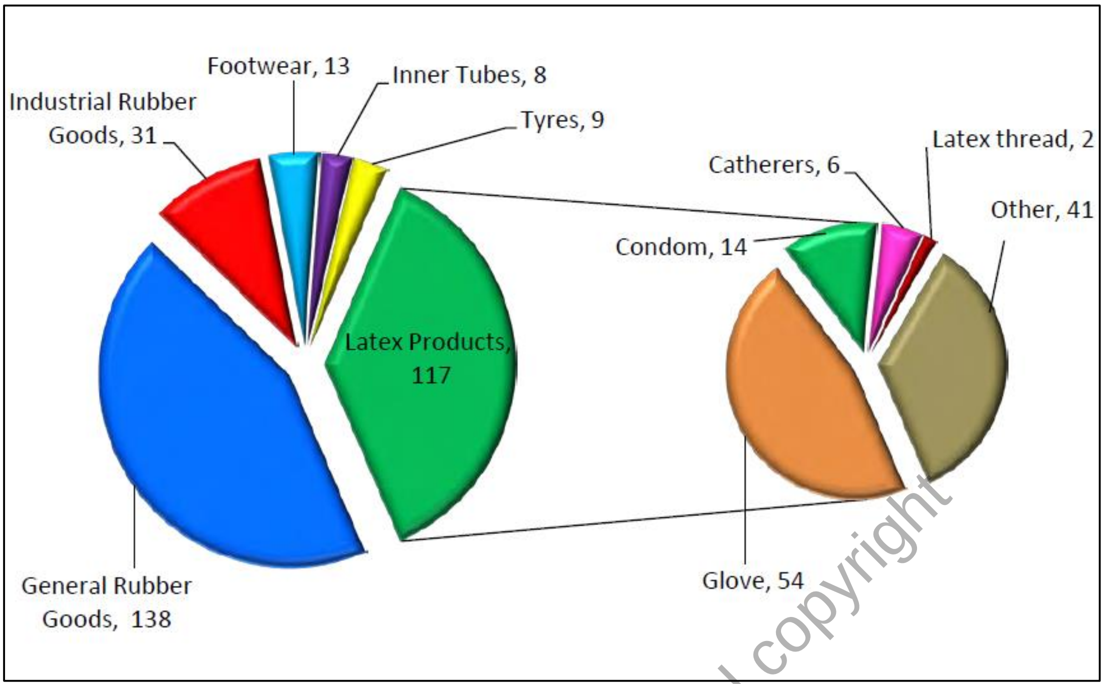


Figure 1.1: Malaysian rubber product companies by product sector in 2014 (Department of Statistic Malaysia, 2014).

Currently, Malaysia is the leading supplier of examination and surgical gloves, satisfying 45 % of the world's demand. Nitrile gloves are currently used in many areas such as the medical field, food, automotive, and research activities (Noriman and Ismail, 2011). Nitrile gloves are known for providing protection to various chemicals. In addition, nitrile gloves provide excellent barrier protection providing three times more puncture resistance than natural rubber latex gloves. Due to its durability, an excellent abrasion resistance and puncture resistance, nitrile glove is mostly used in industrial applications such as automotive and chemical industries. In addition, nitrile gloves have begun replacing natural rubber latex gloves in the recent past in the sanitary and cleaning applications because its surface is highly resistant to degradation unlike NR gloves (Galpayage, 2009).

The development of rubber industry produced a lot of rubber waste in the world every year. With the increase in demands, the manufacturing and use of rubber and the rubber products have increased tremendously both in the developed and less developed countries (Teresa, 2014). After some time, these polymeric materials are not serviceable and mostly discarded, hence generated a significant quantities of discarded rubber. The main source of waste rubber are discarded tires, rubber pipes, rubber belts, rubber shoes, edge scraps and waste products which are produced in rubber processes, and others. Considering the environmental and economic advantages, recycling is one of the best options. (Orathai et al., 2008)

Recently, the importance of recycling waste materials has been stressed out for all industries worldwide. The best way to recycle rubber products would be to devulcanize and reuse them in the rubber industry. Processes for devulcanization, including chemical, thermal, thermomechanical, and ultrasonic, have been worked out but they are costly and not suitable for commercial application. The other alternative to recycling rubber waste is to blend the crumb or ground rubber with a material having the ability to flow under heat and pressure so that it can be shaped into useful articles at a reasonable cost (Jinxia Li, 2008). Therefore, the use of recycled nitrile gloves that obtained from industrial production rejects become an effort to create something value that would otherwise be scrapped (Noriman and Ismail, 2011).

## 1.2 Problem Statement

Rubber is a highly useful material. The applications of rubber are expected to increase as more new products are developed to meet demands. The increased use and production of rubber in many applications results in a growing volume of rubber waste (Eldho, 2011). Rubber waste has become an important global issue that can address three major problems; wasting of valuable rubber, health and environmental pollution. The best solution to overcome this problem is by recycling the rubber waste.

However, direct material recycling is commonly known as difficult process because of the irreversible three-dimensional crosslinking of rubber molecules. This is because they cannot be re-melted or dissolved in organic solvents. The simplest method of rubber recycling is the grinding of rubber waste and utilization of powdered rubber. Powdered rubber has been used for various applications, such as fillers for rubber, thermoplastic compounds, and modifiers for asphalt concrete (Kim et al., 2007). The rubber waste is ground to powder and then devulcanized with the aid of oils and chemicals (a reversal of the process which hardens rubber latex with the addition of sulphur) to become soft reclaimed rubber, normally done under high heat in a chamber. However, most of these processes were either conducted at high temperature, which lead to a higher degradation of the rubber backbones, or used chemicals as devocalizing agents, which lead to a higher cost and environmental pollution.

The most important recycling process currently is to utilize waste rubber as a very finely ground powder, produced either by ambient grinding or by cryogenic grinding. In general, the powdered rubber is combined with virgin elastomer compounds to reduce the costs with the additional advantage of an improvement of the processing behaviours. However, some loss in physical properties and performance is observed (Rajan et al., 2007). This factor has motivated the search for cost effective in devulcanization of the scrap rubber to provide recycled material with superior properties. Thus, through this study, the usage of waste rubber as filler can overcome this problem by filling raw elastomers with recycled rubber during compounding.

## 1.3 Research Objectives

The aim of this study is to develop a new rubber material with the addition of recycled acrylonitrile butadiene rubber (rNBR) gloves as filler. Thus, it's become a solution of disposing the waste material generated from industries. It is also expected to improve the properties of rubber with the addition of recycled NBR gloves filler and natural filler.

The main objectives of this work are:

i. To characterize the recycled acrylonitrile butadiene rubber (rNBR) gloves and *Imperata Cylindrica* fibres using particle analyser, FTIR and SEM.
ii. To determine the effects of different size of recycled acrylonitrile butadiene rubber (rNBR) gloves and its compound ratio on the properties of epoxidized natural rubber (ENR 25) compound.
iii. To investigate the effect of different loading and sizes of natural filler, *Imperata Cylindrica* on properties of epoxidized natural rubber (ENR 25) compound filled with recycled acrylonitrile butadiene rubber (rNBR) gloves.
iv. To examine the effects of trans-polyoctylene rubber (TOR) as a compatibilizer on the properties of epoxidized natural rubber (ENR 25) compound filled with recycled acrylonitrile butadiene rubber (rNBR) gloves.

## 1.4 Scope of Study

This research is focused on the effect of recycled acrylonitrile butadiene rubber (rNBR) gloves with different loading and size used in rubber compounding and how this variable could influence the properties of epoxidized natural rubber (ENR 25). For series 1, five different loading of recycled NBR gloves filler which are 5, 15, 25, 35 and 45 phr was used into rubber compounding with the total compound of 250 grams. ENR 25 was compounded by using two-roll mills with two different sizes of recycled NBR gloves. The curing characteristics for the fine and coarse size of rNBR filled ENR 25 were studied before vulcanization process using hot press machine. The tensile test was carried out on the vulcanized ENR 25 compound. The optimum result obtained in series 1 was further used for series 2 by addition of natural filler which is *Imperata Cylindrica*. Five different loading of *Imperata Cylindrica* were used; 5, 15, 25, 35, and 45 phr with two different size. For series 3, the optimum result from the compounding in series 2 was further added with compatibilizer which is trans-polyoctylene rubber (TOR) at 5 different compositions; 2, 4, 6, 8, and 10 phr. Curing characteristics were studied before vulcanizations process and proceed to mechanical test (tensile test) and physical test such as hardness, resilience, swelling and crosslink density. Surface morphology of the fractured surface obtained from the Scanning Electron Microscopy (SEM).