THE PROPERTIES OF STYRENE BUTADIENE RUBBER/RECYCLED CHLOROPRENE RUBBER (SBR/CRr) BLENDS

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The Properties of Styrene Butadiene Rubber/Recycled Chloroprene Rubber (SBR/CRr) Blends

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SIFAT-SIFAT ADUNAN GETAH STIRENA BUTADIENA/GETAH KITAR SEMULA KLOROPRENA (SBR/CRr)

ABSTRAK

Kesan terhadap sifat-sifat pematangan, sifat-sifat fizikal dan mekanikal dan sifat-sifat morfologi adunan getah stirena butadiena/getah kitar semula kloroprena (SBR/CRr) telah dikaji. Adunan SBR/CRr dengan nisbah adunan iaitu 95/5, 85/15, 75/25, 65/35 dan 50/50 telah disediakan dengan menggunakan penggiling bergulung dua pada suhu bilik dan diikuti oleh pengacuan mampatan. Keputusan terhadap perbandingan adunan getah stirena butadiena/getah asli kloroprena (SBR/CRv) dengan SBR/CRr menunjukkan bahawa pada nisbah adunan yang sama, terutamanya sehingga 15 phr, adunan getah SBR/CRr menunjukkan peningkatan pada kekuatan tegasan manakala M100, kekerasan dan ketumpatan penyambungsilangan adunan getah SBR/CRr menunjukkan peningkatan dalam semua nisbah. Saiz CRr yang paling halus, S1 (346-486 µm) bagi adunan getah SBR/CRr menunjukkan sifat-sifat pematangan dan sifat-sifat mekanikal yang lebih baik berbanding dengan semua nisbah adunan bagi S2 (664-891 µm) dan S3 (0.3-0.7 mm). Tambahan pula, pemprosesan akan menjadi lebih efisien dan luas kawasan permukaan sentuhan akan meningkat di mana akan menyebabkan ikatan pelekatan-pelekatan yang lebih efisien. Keserasian bagi adunan getah SBR/CRr dengan 3 phr getah *trans- polyoctylene* (TOR) telah menambahbaik pelekatan antara-muka bagi CRr dan matrik SBR. Seterusnya, meningkatkan keserasian adunan getah SBR/CRr. Sifat-sifat pematangan adunan getah SBR/CRr yang dicampurgaul dengan TOR mempunyai masa skorj, t_2 dan masa pematangan, t_{90} yang lebih singkat berbanding adunan getah SBR/CRr yang tidak dicampurgaul dengan TOR. Adunan getah SBR/CRr yang dicampurgaul dengan TOR menunjukkan minimum tork, (M_L) yang lebih rendah berbanding adunan getah SBR/CRr yang tidak dicampurgaul dengan TOR pada semua nisbah adunan. Walau bagaimanapun, maksimum tork, (M_H) bagi adunan getah SBR/CRr yang dicampurgaul dengan TOR menunjukkan trend yang bertentangan berbanding dengan adunan getah SBR/CRr yang tidak dicampurgaul dengan TOR pada semua nisbah adunan. Kekuatan tegasan, M100, kekerasan dan ketumpatan penyambungsilangan adunan getah SBR/CRr yang dicampurgaul dengan TOR juga bertambah baik berbanding dengan adunan getah SBR/CRr yang tidak dicampurgaul dengan TOR. Masa pematangan, t_{90} bagi adunan getah SBR/CRr/CB dan adunan getah SBR/CRr/$CaCO_3$ menurun dengan peningkatan kandungan CRr dalam kedua-dua adunan. Walau bagaimanapun, masa skorj, t_2, meningkat dengan peningkatan kandungan CRr bagi kedua-dua adunan. Adunan getah SBR/CRr/CB menunjukkan minimum tork, (M_L) yang lebih tinggi berbanding adunan getah SBR/CRr/$CaCO_3$ pada semua nisbah adunan. Walau bagaimanapun, maksimum tork, (M_H) bagi adunan getah SBR/CRr/CB menunjukkan trend yang bertentangan berbanding dengan adunan getah SBR/CRr/$CaCO_3$. Adunan getah SBR/CRr/CB mempamerkan keputusan yang lebih baik dalam semua sifat-sifat mekanikal/fizikal berbanding dengan adunan getah SBR/CRr/$CaCO_3$ bagi semua nisbah adunan.

THE PROPERTIES OF STYRENE BUTADIENE RUBBER/RECYCLED CHLOROPRENE RUBBER (SBR/CRr) BLENDS

ABSTRACT

The effects of cure characteristics, physical and mechanical properties and morphological properties on styrene butadiene rubber/recycled chloroprene rubber (SBR/CRr) blends were investigated. SBR/CRr blends with blend ratios 95/5, 85/15, 75/25, 65/35 and 50/50 were prepared using two roll mill at room temperature and followed by compression moulding. The results on comparison of styrene butadiene rubber/virgin chloroprene rubber (SBR/CRv) blends with SBR/CRr blends showed that at similar blend ratios, particularly up to 15 phr, SBR/CRr blends exhibited improvement in tensile strength while the M100, hardness and crosslink density of SBR/CRr blends exhibited increment value in all blend ratios. The smallest size of CRr particles S1 (346-486 µm) in SBR/CRr blends showed a better cure characteristics and mechanical properties compared with all other blend ratios in S2 (664-891 µm) and S3 (0.3-0.7 mm). Futhermore, the processing become more efficient and the contact surface area increased which provided more efficient interfacial bonds. The compatibilization of SBR/CRr blends with 5 phr of *trans*-polyoctylene rubber (TOR) improved the adhesion between CRr and the SBR matrix, thus, improving the compatibility of SBR/CRr blends. Cure characteristics of compatibilised SBR/CRr blend have shorter scorch time, t_2 and cure time, t_{90} than uncompatibilised SBR/CRr blends. Compatibilised SBR/CRr blends showed lower minimum torque (M_L) compared to uncompatibilised SBR/CRr blends at all blend ratios. However, maximum torque (M_H) of compatibilised SBR/CRr blends exhibit the opposite trend compared with the uncompatibilised SBR/CRr blends. The tensile strength, M100, hardness and crosslink density of compatibilised SBR/CRr blends also improved compared with uncompatibilised SBR/CRr blends. The cure time, t_{90} of SBR/CRr/CB blends and SBR/CRr/$CaCO_3$ blends decreased with increasing CRr content in both blends. However, scorch time, $t_{2,}$ increased with increasing CRr content in both blends. SBR/CRr/CB blends showed higher minimum torque (M_L) compared to SBR/CRr/$CaCO_3$ blends at all blend ratios. However, maximum torque (M_H) of SBR/CRr/CB blends exhibit the opposite trend compared with the SBR/CRr/$CaCO_3$ blends. SBR/CRr/CB blends exhibited a better result in all mechanical and physical properties compared with SBR/CRr/$CaCO_3$ blends at all blend ratios.

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DECLARATION OF THESIS

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
ATR	Attenuated total reflection
BR	Polybutadiene rubber
$CaCO_3$	Calcium carbonate
CAFE	Corporate average fuel economy
CAGR	Compound Annual Growth Rate
CB	Carbon black
CBS	N-Cyclohexyl-2-benzothiazole sulfenamide
CR	Chloroprene rubber
CRr	Recycled chloroprene rubber
CRv	Virgin chloroprene rubber
CV	Conventional system
DCSBR	Dichlorocarbene modified styrene butadiene rubber
DPNR	Deproteinised Natural Rubber
ENR	Epoxidized Natural Rubber
EPDM	Ethylene Propylene Diene Monomer
ESBR	Emulsion styrene butadiene rubber
EV	Efficient system
FTIR	Fourier transform infrared spectroscopy
HAF	High abrasion furnace
IIR	Isobutylene isoprene rubber
LCB	Long chain branching
M100	Stress at 100% elongation

MDR	Monsanto moving die rheometer
MPa	Megapascal
MRB	Malaysian Rubber Board
MWD	Molecular weight distribution
NBR	Nitrile Butadiene Rubber
NR	Natural rubber
phr	Part per hundred of rubber
RM	Ringgit Malaysia
SBR	Styrene butadiene rubber
SEM	Scanning electron microscopy
SMR	Standard Malayisan Rubber
SSBR	Solutionstyrene butadiene rubber
TARRC	Tun Abdul Razak Research Centre
TMTD	Tetramethylthiuram disulfide
TOR	*Trans*-polyoctylene rubber
TPE	Thermoplastic elastomer
TPENR	Thermoplastic Epoxidized Natural Rubber
USD	United State Dollar
UTM	Universal Testing Machine
ZnO	Zinc oxide

LIST OF SYMBOLS

cm	Centimeter
E_b	Elongation at break
kg/m^3	Relative density
m^2/g	Unit for BET surface area
M_H	Maximum torque
M_L	Minimum torque
$M_{L(1+4)}$	Mooney viscometer
mm	Millimeter
nm	Nanometer
Q_m	Total swelling weight
t_2	Scorch time
t_{90}	Cure time
T_g	Glass transition temperature
V_r	Volume fraction of the swollen rubber
V_s	Molar volume of the solvent
θ_1	The initial angle (45°)
θ_2	The maximum rebound angle
µm	Mikrometer
ρ	Density of the rubbers
χ	Interaction parameter of the rubber

CHAPTER 1

INTRODUCTION

1.1 Recycling

The concept of recycling has been around for a long time and people have reused the materials and refashioned them into needed items. Recently, more efforts encouraged conservation and reuse of materials, and in the 1970s recycling got its official start when recycling centers were created. Nowadays, curbside recycling programs and recycling centers are common. In 2009, approximately 9,000 curbside recycling programs and 3,000 composting communities existed in the United States (Environmental Protection Agency's 2010).

Recycling is the process of recovering and reusing waste products from household use, manufacturing, agriculture, and business, therefore reducing their burden on the environment. Back to the World War I and World War II, shortages of essential materials led to collection drives for silk, rubber, and other commodities. In recent years the environmental benefits of recycling have become a major component of waste management programs (Palliser, 2011).

For many years direct recycled by producers of surplus and defective materials constituted the main form of recycling. However, indirect recycling, the collection of materials after used by consumers, became the focus of activity in the 1990s. For some time, most solid waste has been deposited in landfills or dumps and this led to environmental problems.

Industry has found that when it undertakes serious recycling programs, the savings can sometimes be considerable. In addition to reduce manufacturing and materials costs, such programs can insulate the companies from liability for environmental violations. For example in agriculture, which caused of much environmental degradation, used organic recycling, or the reuse of manure and crop residues (sometimes called "green manure").

A large part in recycling used by the individual consumer. Originally, household containers such as beverage cans and bottles were recycled as a matter of course, with a glass beer container or milk bottle being refilled as many as 30 times. In 1935, brewers began putting their products in nonrefillable, "one-way" cans for the convenience of customers, and soon glass containers were declared disposable as well. With the rise of environmentalism in the early 1970s, recycling regained favor. Several states instituted deposit laws for beverage containers; a 5- or 10-cent deposit was charged the consumer at the time of purchase for each can or bottle, then refunded when the container was returned to a store or recycling center. The newspapers also take up much volume in landfills, and some recycling programs seek to collect them (along with other sorted categories of waste, such as organic matter, bones, and plastic) (Roosevelt, 2011).

1.2 Uses of Recycled Materials

In 1996, the United States was recycled almost 27% of solid waste in large quantities including paper and paperboard, ferrous metals, aluminum and other nonferrous metals, glass, plastics, and yard wastes. Although many local communities have instituted comprehensive recycling programs, these remain expensive. The quality of recycled items is often inferior (often due to the mixture or age of the materials in the items being recycled) and not suitable for their original purpose, the price for many recycled materials remains low and makes recycling economically nonviable in some instances (Roosevelt, 2011).

In other ways to solve this problem, an alternative use have been created to recover waste material. Crushed glass, or called ‘glassphalt’, can be substituted for gravel or sand in road surfacing and other construction applications. Scientists and entrepreneurs are also working on ways to turn the world's growing piles of discarded automobile tires into new products or to use them to generate safe energy (http:// www.questia.com/library/science–and-technology/environmental–and-earthsciences/ recycling).

1.3 Waste Rubber Recycling

Most of waste rubber (non-degradable material) have created major environmental problems. The usual method of disposing of waste rubber, such as discarding in a landfill or burning, are not suitable since it caused severe environmental pollution and are uneconomical (Ismail et al., 2004 and 2005, Yehia, 2004 and Jana, 2007). Generally, the blending of two or more types of rubbers is a useful technique for the preparation and development of materials with properties superior to those of individual constituents. Waste rubber can also be blend with virgin materials to produce rubber blends with desired properties. The purpose of blending the recycled rubbers is to improve the physical and mechanical properties as well as modify processing characteristics and reduce the cost of the final product (Egodage et al., 2009 and Noriman et al., 2010).

Rubber recycling nowadays includes all processes where rubber scrap is transformed into a reusable form to produce new articles or services. Rubber recycling processes keep developing, aiming at the re-utilization of rubber as close as possible to its virgin form. This type of recycling method where rubber is reused like in its virgin form is called devulcanization (or reclaiming) (Adhikari et al., 2000 and Zulkepli et al., 2009). Rubber recovery can be a difficult process. However the rubber should be reclaimed or recovered;

a) Recovered rubber can cost half that of natural or synthetic rubber.
b) Recovered rubber has some properties that are better than those of virgin rubber.
c) Producing rubber from reclaim requires less energy in the total production process than does virgin material.

The waste rubber is generated from objects that are not practical and discharged. The post-industrial waste was generated during the processing and molding elastomers in the production line and in some situations the amount of waste can be equivalent with the production. Improving recycled methods is the most appropriate way to reduce the volume of polymeric waste and minimized the environmental impact. Currently, due to difficult on reprocessing techniques, the vulcanized rubbers are a big problem in the recycle field. One of the main forms of discharge rubber is to apply as fuel to generate electricity and steam, this process is still in use but creates a new problem of air pollution and is also a low value to recovery process of the waste rubber (Scagliusi et al., 2009).

1.4 Background of studies

A lot of waste rubber is produced all over the world every year i.e., 10 million tyres are discarded every year. Meanwhile, adhesives are used in almost every industrial workplace with an industry value of 40 billion Euros. This invention turns waste rubber into multifunctional adhesive. One of the problems facing mankind as we enters into the 21st century is the problem of waste disposal. Since polymeric materials do not decompose easily, disposal of waste polymers is a serious environmental problem.

Scrap rubbers are made up of rubber that do not meet processing and product specifications, leftover rubber from manufacturing activities and old and defective rubber products such as gloves, catheters, tubes, old tyres etc. Presently, the amount of discarded tyres reaches 10 million/year worldwide. In Malaysia, the output of waste rubber gloves in 2003 was 13.05 billion pairs, catheters 84.75 million units and inner tubes 13.05 million units. With the development of the rubber industry, a lot of waste rubber is produced not only in Malaysia but all over the world every year.

In fact, the majority of elastomers used today have been invented in the 1950s and 1960s, even for advanced applications such as in medical and space technologies. The focus now on the modification rather than on development of novel materials. If materials with required properties can produced by blending existing polymers with fillers, the costs as well as the development time can be reduced (prr.hec.gov.pk/Chapters/284S-1.pdf). Through rubber recycling technology (the blending of polymer, especially elastomers together with recycled waste) can meet the performance and processing requirements to manufacture a wide range of rubber based products such as road and playgorund surfaces, recycled rubber flooring, adhesive glues, sporting mats, floats, marine and automotive parts, and so muh more. Many elastomers that have dissimilar chemical structure are blended to improve processability, performance, durability, physical properties, and to achieve an economic advantage.

1.5 Problem statements

Generally, when chloroprene rubber is recycled to create new products, it is blended with other types of synthetic rubbers. The properties of this material, including its durability, insulation properties, and resistance to oil, make it an ideal substance for a number of uses. By blending recycled rubber products into new ones, waste is minimized and costs are lowered as well.

One of the medical application is external male catheters that has been use for the relief of male urinary incontinence. In medical application, a product with a bit of defect will consider rejected and has been thrown away without any consequence. At medical industry like Teleflex Medical Sdn. Bhd., has faced this situation and need a guide solution to overcome the waste. The amount rejected of chloroprene catheters from Teleflex medical Sdn. Bhd. from week 2 until week 25 is almost 1 million pieces. The quantities are very high and the reject was scrapped and wasted. In order to clean up the wasted the company has to bear more cost. This project will focus to solve this problem by optimization the process thru the studies of curing characteristics, properties of the blends, the effect of the particle size, the effect of compatibilizer and the effect of filler.

1.6 Objectives of study

The main objectives in this study is to gain a better understanding the possibility of producing a new elastomer materials from the blend of styrene butadiene rubber (SBR) and chloroprene rubber (CR). The activities of this work such as:

a) To characterize recycled chloroprene rubber.
b) To study the comparison of mechanical, physical and morphological properties of SBR/CRv blends and SBR/CRr blends.
c) To investigate the effects of different size of CRr and it's blend ratios on mechanical, physical and morphological properties of SBR/CRr blends.
d) To examine the effects of *trans*-polyoctylene rubber (TOR) as a compatibilizer on mechanical, physical and morphological properties of SBR/CRr blends.