

**VALUE ADDITION TO WASTE ACRYLONITRILE
BUTADIENE RUBBER BY COMPOUNDING WITH
CARBON BLACK**

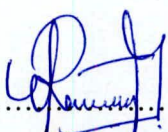
By

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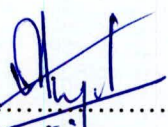
**Thesis submitted to the University of Sri Jayewardenepura for the
award of the Degree of Master of Science in Polymer Science and
Technology**

DECLARATION

I hereby declare that this research project was conducted by me, under the supervision of Dr. Upul N Ratnayake, Senior Research Officer, Department of Raw Rubber Processing Development and Chemical engineering, Rubber Research Institute, Rathmalana, Sri Lanka. I also certify that, this thesis has not been submitted in whole or in part to any University or any other institute for another Degree/Diploma.


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ABSTRACT

Acrylonitrile butadiene rubber (NBR) is a copolymer of acrylonitrile (ACN) and butadiene which has a remarkable resistance towards mineral oils, hydrocarbon fluids and aromatic solvents. In general NBR is compounded with conventional fillers such as carbon black (CB) to achieve the required reinforcement.

A waste NBR generated from one of the leading glove manufacturing companies was used in this research project. Waste NBR received was subjected to detailed characterization with rheometry, Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), FTIR-Attenuated Total Reflectance (ATR), total ash content test and total nitrogen content test. Characterization results revealed that waste NBR is a carboxyl terminated NBR with about 45 % of acrylonitrile content and it contains a significant quantity of sulfur, accelerator and filler.

This waste NBR was compounded with carbon black and other vulcanizing ingredients. Sulfur to accelerator ratio of the semi-efficient vulcanizing system was optimized to reduce the marching effect. Carbon black filled waste NBR vulcanisates showed good physio-mechanical properties such as, tensile strength, hardness, rebound resilience and oil resistance. Waste NBR vulcanisate containing 30 phr of carbon black showed the best processing capability whilst maintaining good physical properties compared to that of other carbon black filled vulcanisates.

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1. INTRODUCTION

1.1.General Background

Acrylonitrile-butadiene rubber (NBR/Nitrile rubber) is a co-polymer of butadiene and acrylonitrile (ACN) which is produced by emulsion polymerization. Acrylonitrile gives a highly polar structure to the NBR molecule due to its carbon nitrogen triple bond. The large dipole moment and the lone-pair electron effect created by the nitrogen atom give the ability to make very strong hydrogen bonds [1].

Unique properties inherited by NBR, such as oil resistance and chemical resistance are also a result of this nitrile pendant group. Hence nitrile rubber shows remarkable resistance towards aromatic solvents, petroleum based oils and hydrocarbon fluids. Therefore the above properties are directly proportional to the Acrylonitrile content of the rubber [2].

In glove industry NBR plays an important role. Properties such as oil resistance and chemical resistance are highly critical in industrial gloves where natural rubber latex gloves fail. For example, in automotive industry, natural rubber (NR) latex gloves simply dissolve when they make contacted with grease, oil, diesel fuel or gasoline. Therefore NBR gloves are more suitable over NR latex gloves. Besides above, NBR gloves are approximately three times puncture resistant than NR latex gloves. Puncture resistance of a glove is very important for the users who operate under infection-prone environments. Therefore the nitrile glove is an excellent candidate for dentists, ambulance operators, health clinics and paramedics. Since NBR doesn't carry any latex proteins, it doesn't make allergen reactions toward the people who are sensitive for protein allergies [3]. So 'NBR gloves' is a much better choice for dentists because of the reduced possibility of allergic reactions towards their patients.

In glove industry some amount of latex will be lost as a waste. This latex waste could occur in different steps in the industry depending on the manufacturing process. Most of the times a waste could be generated between the dipping and the coagulation steps.

NBR can be classified according to the acrylonitrile content [2]. Most of the time in glove industry high acrylonitrile content (40% ACN) and very high acrylonitrile content (45% ACN) NBR latices are used. NBR is usually expensive and the price increases with the ACN content [1]. Owing to this, High and very high ACN content nitrile rubber are fairly expensive. So it will be detrimental to lose a good amount of ACN rich latex as a waste. But if there is an acceptable method to reclaim this waste the loss could be minimized. However reclaimed rubber is not pure or better in properties as the starting raw material. But it may be fulfill the aspects as a raw material for another product/industry. For an example, studies show that slightly cross-linked latex rejected from industries such as glove industry and condom industry could be blend with Styrene-butadiene rubber (SBR) and acquire a blend which has superior mechanical properties and a better cure time than virgin SBR [4]. Therefore nowadays most of the synthetic glove manufacturers are looking forward to recycle their latex waste to minimize their loss. Although using reclaim rubber can reduce compound cost and can conserve raw materials and energy. So this would be also an advantage for manufacturers.

In this study, a waste NBR generated from a glove manufacturer was used as the raw material to achieve a compound with useful properties. Compounding with carbon black (CB) was done to enhance the properties of the vulcanisates. The waste, which is used in this study, was collected from a local NBR glove manufacturer, ATG Gloves Private Limited. The company has developed an effective method to collect and coagulate the waste latex. (Refer Figure 3.1. for the waste generating process). Then the coagulum was dried under low humidity and heat conditions in order to get a minimum moisture amount.

Most economical and applicable methods were used in mixing and compounding to achieve a cost effective composite.

1.2.Objectives

The main objective of the study is to prepare a value added elastomeric composite based on CB with good physical properties from the NBR waste generated from the dipping plant.

- To characterize the waste nitrile rubber.
- To prepare a vulcanizing recipe and compounding method.
- To prepare conventional composites with the optimized vulcanizing recipe.
- To prepare CB filled waste NBR compound with optimum physical properties and with good processability.

2. LITERATURE REVIEW

2.1. General background of Nitrile Butadiene Rubber (NBR)

2.1.1. Structure

Nitrile rubber is an amorphous, high molecular-weight co-polymer of acrylonitrile and 1,3-butadiene. NBR is synthesized by emulsion polymerization and most of the time it is carried as a batch process [5,6]. Synthesis of NBR is shown in Figure 2.1.

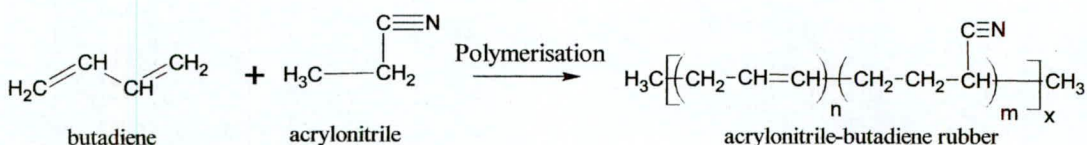


Figure: 2.1. The synthesis of NBR

Within the process, butadiene monomers give birth to three types of co-polymers with different structures trans-1,4, cis-1,4 and 1,2(vinyl). With the temperature of synthesis, proportions of the above forms can be slightly changed. However in typical NBR trans configuration (~90%) dominates. Cis (~8%) and vinyl (~2%) structures stay as minor structures. At higher nitrile contents (higher than 33%) cis configuration decreases with the ACN content and vice versa [2]. Due to its symmetry of molecular structure, butadiene is a very stable non-polar hydrocarbon. But in the other hand ACN behaves as a highly polar molecule due to its triple bonded nitrogen atom and the nitrogen lone pair effect. With this large dipole moment and the lone pair effect of the nitrogen atom, it has a very strong hydrogen bonding potential. Also the resistance towards oils, petroleum fuels and industrial chemicals are a direct result of this ACN group.

Specifications of commercially available NBR's done according to three major aspects:

- (1) ACN content
- (2) Polymerization temperature
- (3) Mooney viscosity [1,2]

Classification of nitrile rubber according to ACN content along with the approximate values of swelling resistance is given in Table 2.1.

Table: 2.1. Volume swell of nitrile rubber vulcanisates (standard recipe) in a light petroleum-benzene mixture (3:1) after 72 hours at 23 °C [1]

	Acrylonitrile content (%)	Volume Swell (%)
low	about 20	80-90
medium low	25	50-60
medium	30	40-50
medium high	35	33-40
high	40	25-33
very high	above 40	less than 25

2.1.2. Properties

When compared with NR, the most valuable property of NBR is its oil [2,7] and fuel resistance. With this property combined with other favorable physical properties such as tensile strength/hardness makes NBR an outstanding polymer.

As explained before, it is the acrylonitrile component which gives fuel and oil resistance to NBR. Also many other vulcanisate properties of NBR are directly related to the ACN content [5,8] as shown below in Figure 2.2.

Polarity of butadiene and acrylonitrile are totally different from each other. Since acrylonitrile component is far more polar than butadiene, polarity of the copolymer increases with the ACN content of the polymer. With the polarity, the solubility parameter also increases and changes the solubility of NBR in solvents with different polarities. For example: acetone is a good solvent for NBR with ACN content of 34% but not for NBR with 45% ACN.

Besides of NBR grade, swelling resistance is also depend on the compound components, filler loading, type and amount of plasticizer, immersion temperature, nature of the liquid and the degree of vulcanization [1]. However the swelling behavior of NBR isn't sensitive to the degree of vulcanization all the time. NBR with low ACN