

**Rheology, Cure Characteristics and Mechanical Properties of
Carbon Black filled Low Grade Natural Rubber Composites**

By

Wajirani Karunaratne Adhihetty

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

M.Sc

2008

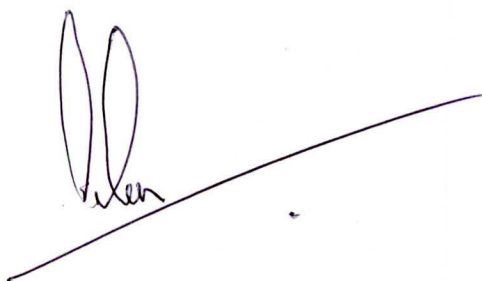
Declaration

The work described in this thesis was carried out by me under the supervision of Dr. Susantha Siriwardena, Head/Department of Raw Rubber Process Development and Chemical Engineering at Rubber Research Institute of Sri Lanka and a report on this has not been submitted in whole or in part to any university or any other institution for another Degree or Diploma.



Wajirani Karunaratne Adhihetty

16/10/2008



Dr Laleen Karunanayake
BSc (SJP), PhD (North London)
Senior Lecturer
Department of Chemistry
University of Sri Jayewardenepura

I certify that the above statement made by the candidate is true and that this thesis is suitable for submission to the University of Sri Jayawardenapura for the purpose of evaluation for the award of the M.Sc in Polymer Science and Technology.



Dr. Susantha Siriwardena

Head/Department of Raw Rubber Process Developmet and Chemical Engineering

Rubber Research Institute of Sri Lanka

List of Tables

Table No	Title	page
01.	Total NR Production by Types (MT).....	02
02.	Domestic Rubber Consumption (MT).....	03
03.	Income from Different Rubber Products Categories (Rs-Min).....	05
04.	Properties of Scrap Rubber	25
05.	Properties of Reclaimed Rubber	26
06.	Composition of NR/Low Grade Rubber/CB Composites.....	27
07	Formulation for the Vulcanization of the Samples.....	28
08.	Summary of Mechanical Properties Studied.....	30
09.	Cure Characteristic of NR/RR/CB Composites.....	31
10.	Cure Characteristics of NR/SR/CB Composites.....	31
11.	Mechanical Properties of NR/RR/CB omposites.....	38
12.	Mechanical Properties of NR/SR/CB Composites.....	39
13.	Mechanical Properties of Aged NR/RR/CB Composites.....	50
14.	Mechanical Properties of Aged NR/SR/CB Composites.....	50

List of Figures

No Figure	Title	Page
01.	Variation of Cure Rate α with Low grade Rubber Loading in Rubber Composites	32
02.	Variation of Scorch Time with Low grade Rubber Loading in Rubber Composites	34
03.	Variation of Maximum Torque with Low grade Rubber Loading in Rubber Composites	36
04.	Variation of Tensile Strength with Low grade Rubber Loading in Rubber Composites	40
05.	Variation of Elongation at Break with Low grade Rubber Loading in Rubber Composites	42
06.	Variation of Modulus at 100% Elongation with Low grade Rubber Loading in Rubber Composites	44
07.	Variation of Tear Strength with Low grade Rubber Loading in Rubber Composites	46
08.	Variation of Hardness with Low grade Rubber Loading in Rubber Composites	48
09.	Variation of Abrasion Resistance with Low grade Loading in Rubber Composites	49
10.	Variation of Tensile Strength with Low grade Rubber Loading in Aged Rubber Composites	51
11.	Variation of Elongation at Break with Low grade Rubber Loading in Aged Rubber Composites	51
12.	Variation of Compression Set with Low grade Rubber Loading in Rubber Composites (At Ambient condition and Aged condition)	53

List of Abbreviations

NR	Natural Rubber
RR	Reclaimed Rubber
CB	Carbon Black
SR	Scrap Rubber
SBR	Styrene Butadiene Rubber
RRI	Rubber Research Institute of Sri Lanka
TMTD	Tetra Methyl Thiuram Disulfide
MBT	Mercaptobenzthiazole
IPPD	N-isopropyl-N'-phenyl-p-phenylendiamine

Acknowledgement

I would like to extend my deepest gratitude to my supervisor Dr. Susantha Siriwardena, Rubber Research Institute of Sri Lanka, for identifying a research work according to my interest, supervision, stimulation, facilitation and widen the knowledge on the subject.

I would like to take the opportunity to extend my deepest gratitude to Dr. Sudantha Liyanage, former Course Coordinator, M.Sc in Polymer Science and Technology, University of Sri Jayawardenapura, , who enlightened my post graduate education through out by giving encouragement and all the support for fulfillment of the postgraduateship. At the same time I will extend my sincere gratitude to Dr. Lalin Karunanayaka, Course Coordinator, Polymer Science and Technology, University of Sri Jayawardenapura for the given opportunity by extending the time of fulfillment of the research project considering all the inconvenience occurred though out the research work.

I am grateful to Mrs. Dilhara Edirisinghe, Rubber Research Institute of Sri Lanka for encouragement, stimulation and the knowledge input and information in the field and research methodology, provided for fulfillment of the research work.

I wish to extend my sincere thanks with gratitude to the staff of the Rubber Technology Division, Library and Information Centre and to the staff of Rubber Specification Division, Rubber Research Institute of Sri Lanka, who helped me in all possible avenues to complete my project successfully.

Rheology, Cure Characteristics and Mechanical Properties of Carbon Black filled Low Grade Natural Rubber Composites

ABSTRACT

This research work aims to study and compare the performance of composites of Natural rubber (NR)/Reclaimed rubber (RR)/Carbon Black (CB) and Natural rubber (NR)/Scrap rubber (SR)/Carbon Black (CB) in the similar compounding conditions using semi efficient sulfur vulcanizing system. The properties studied were rheological properties, cure characteristics, and mechanical properties of the vulcanized composites. The mastication time was remaining constant for three mill passes.

The results under the test conditions suggested the cure rate and the scorch time were found to decrease with the reclaimed rubber loading, while the cure time is increased. With regards to the scrap rubber, the cure rate is decreased slightly with the scrap rubber percentage in the composite while scorch time is increased. Scorch time of NR/SR/CB composites are higher than the NR/RR/CB composites while the cure rate is slightly less than the NR/RR/CB composites. Maximum torque is decreased with the addition of SR in to composites and increased with loading of RR.

It was observed that the modulus at 100% elongation of the rubber compound increased with the RR loading. However in the case of tensile strength and elongation at break had shown opposite trends. The hardness and abrasion resistance of the vulcanizates increased with the reclaimed rubber loading where as the tear strength was again showed the same observations as for the tensile strength and modulus at 100% elongation. The compression set was increased with the reclaimed rubber loading. The variations of the mechanical properties of the vulcanizates involved the changes in

cross link density and the molecular mobility due to the presence of carbon black and Styrene Butadiene Rubber (SBR) in the reclaimed rubber.

The mechanical properties such as tensile strength, modulus at 100% elongation, elongation at break, hardness and abrasion resistance are decrease with the increasing of the percentage of scrap rubber loading in the rubber vulcanizates. Only the compression set is increased with the SR loading in the NR/SR/CB composites. Considering the ageing properties, the tensile strength and elongation at break is decreased with the RR or SR loading in to NR phase than the corresponding properties of composites in normal condition. These properties of NR/RR/CB composites are slightly higher than NR/SR/CB composites.

According to the results and observations, it could be suggested that processable compounds can be prepared by using both SR and RR, if in overall; NR/RR/CB composites show the better mechanical properties than NR/SR/CB composites.

However, there is a possibility of using NR/SR/CB composites with the requirement of composites having lower mechanical properties, in addition to use NR/RR/CB composites.

It is difficult to use either scrap rubber or reclaimed rubber alone to manufacture a value added product without blending with another quality grade of NR. According to this study, it could be suggested to use composites having 25% - 50% of RR or SR, to obtain better mechanical properties

1.0 INTRODUCTION

1.1 NR industry in Sri Lanka

Sri Lanka is one of the most important countries in the world as far as the NR industry is concerned. The history of Sri Lanka's rubber industry began way back in 1876 with the planting of rubber trees in Henarathgoda, in Gampaha district by Sir Henry Wickham. Since then Sri Lanka has built a reputation for producing high quality raw natural rubber in the world. The value added industries for raw natural rubber were started nearly 50 years ago and it has become the key factor of the development of Sri Lankan rubber industry today¹. The Sri Lanka Rubber industry consists of plantations sector, which grows rubber trees and harvests latex and converts this latex into processed raw rubbers of different types, and the rubber products manufacturing sector, which converts raw rubber into value added rubber goods. A third sector is emerging is the rubber wood furniture industry. Rubber plantations sector holds by both public and private estates which is having a total extent of 118,000 ha in the country². The private sector plantations could be either small level or medium level plantation holders. The majority of the rubber plantations is owned by small holders. The main types of rubber produced in Sri Lanka are RSS, latex crepe and centrifuged latex. Technically Specified Rubber (TSR) is not produce in significant quantities due to many reasons such as higher investment and non availability of raw rubber in large quantities to run the industry economically. There are approximately 110 NR processing factories in Sri Lanka² which belongs to public and private sector. However majority of sheet rubber (RSS) production is come from the small holders as a domestic industry and medium

scale sheet rubber manufacturers. Table no 1 illustrates the total NR production by types for last seven years.

Table 01: Total NR Production by Types (MT)

Year	Sheet RSS	Sole Crepe	Scrap Crepe	Latex Crepe	TSR	Latex & Other	Total
2000	34,003	4,512	1,788	28,110	3,879	15,344	87,636
2001	30,344	3,915	2,743	26,111	3,656	19,461	86,230
2002	42,770	2,988	2,184	20,831	1,231	20,514	90,518
2003	50,015	2,195	3,117	17131	1,193	18,359	92,010
2004	46,705	2,035	3,708	12,481	2,812	27,000	94,741
2005	50,170	2,739	2,883	12,914	5,880	29,766	104,352
2006	46,260	3,949	1,606	20,224	9,038	28,076	109,153

Source: Rubber Development Department- Statistics Hand book- 2007

The global position for Sri Lankan NR industry as the NR producer and exporter fluctuates according to the total NR production. The country's total rubber production in 2005 was 104,400 MT with a productivity of about 1000Kg/ha and in 2006 was 109,200 MT. According to the current statistics, 70% of the total rubber production is used for value added products while the rest is exported¹. Domestic rubber

consumption in last few years, is illustrated in Table -2. However, Sri Lanka is well recognized as the major supplier of high quality latex crepe to the world market.

Table-02: Domestic Rubber Consumption (MT)

Year	Dry Rubber	%	Latex	%	Total Con.
2001	35,215	65.2	18,790	34.8	54,005
2002	35,524	65.3	18,863	34.7	54,408
2003	39,368	69.3	17,414	30.7	56,782
2004	29,273	53.8	25,132	40.2	54,405
2005	41,835	57.5	30,914	42.5	72,749
2006	36,397	57.7	26,667	42.3	63,064

Source: Rubber Development department – Statistics Hand book - 2007

The Rubber product manufacturing industry in the country has developed during last 30 years significantly. This industry can be divided into three broad categories. They are Export oriented BOI enterprises, large scale traditional enterprises and Small and medium scale non-BOI and non-traditional enterprises. It is categorized based on the type of market whether local or foreign, regulatory framework whether BOI or non-BOI and on the scale of the operation³.

The rubber products manufacturing industry is also categorized as dry rubber based products industry and latex based products industry according to the NR form feed to the product manufacturing process.

The industry produces a wide array of products ranging in size, shape, and purpose. Half of the rubber consumption in domestic rubber products manufacturing industry is used to manufacture of solid and pneumatic tires and tubes, while majority of remaining balance is consumed by dipped products industry mainly in the production of gloves. Latex based products offer articles such as industrial, household, medical and surgical gloves, balloons, sport goods, mattresses, cushion and rubber thread. Solid and pneumatic tires, tubes, carpets, hot water bottles, autoparts, rubber bands, industrial components, footwear and footwear components, and many other products are manufactured using dry NR as the main raw material. The bulk of these value-added products are for the export market. The export performance of rubber products has shown a remarkable growth during the past few years. The export income from different products is shown in Table-3.

Table-3: Income from Different Rubber Products Categories (Rs. Mn)

Products	2000	2001	2002	2003	2004	2005	2006
Rubber thread	53.5	8.6	17.0	15.8	17.2	32.6	3.5
Unhardened rubber	398.6	477.1	543.3	709.8	849.0	903.7	1,010.3
Rubber horse	0.4	1.3	2.4	17.0	3.2	0.4	2.5
Rubber bells	0.3	0.1	0.4	1.8	1.0	0.3	1.1
Tires & Tubes	7,705.4	7,510	8,292.9	11,667.8	16,331.1	26,030.4	30,623.6
Apparel clothing	4,994.7	5,478.6	6,327.7	7,574.9	8,339.0	9,310.0	10,879.2
Articles of unhardened rubber	1,659.9	1,806.6	2,127.9	2,128.8	3,043.0	3,205.7	3,806.3
Foot wear	1,247.0	643.7	375.2	322.4	187.0	112.8	123.7
Rubber products- Unclassified	113.5	148.1	163.9	195.3	165.0	240.5	414.2
Total	16,173.4	16,074.5	17,850.8	22,633.6	28,935.4	39,836.3	46,864.4
Raw rubber Total	2,175.0	2,115.0	2,516.0	3,706.0	5,137.0	4,684.0	9,341.5
Total Raw rubber + Rubber products	18,348.4	18,189.5	20,366.8	26,339.6	34,072.4	44,520.3	56,205.9

Source: Export Development Board, Sri Lanka

The rubber industry generates direct employment in plantations and raw rubber processing plants as well as rubber products industry to people mainly from rural areas. Starting from tapping latex to manufacturing semi finished or semi processed rubber products and to value added products combining with trading and marketing create employments over 200,000². There are affiliated services like chemical suppliers, machinery suppliers and some service organizations like testing, research and development and quality improvement, banks and other financial supporting institutes adjoined to rubber industry in Sri Lanka for its development.

Sri Lankan companies have lead in capturing global markets and have shown creditable performance. Among them, Loadstar Limited, which markets 'Solideal' industrial tires and wheel systems; and Dipped Products Limited, which markets industrial and household latex gloves under its own brand name are the main contributors. Loadstar Ltd contributes 25% of the need of solid tires of the world market as the leading solid tires manufacture in the world. Dipped Products Limited is the 5th largest industrial glove manufacturer in the world³. Both companies have resorted to forward integration by acquiring global distribution networks.

As the local rubber product industry is expanding, Sri Lanka has forced to import natural rubber from India, Thailand and Vietnam to cater to the value added rubber industry in addition to the local supply, because there is scarcity of rubber alone with increasing the rubber prices. Use of non conventional rubber grades such as Scrap rubber and Recycled rubber, to replace the portion of raw rubber in products has gain a keen interest.