

**Reclaiming of Natural Rubber Latex
Product Waste by a
Mechanochemical Process for
Production of Solid Tire Treads**

By

Janadara Chaminda Jayawarna

MSC

2015

**Reclaiming of Natural Rubber Latex Product Waste by a
Mechanochemical Process for
Production of Solid Tire Treads**

By

Janadara Chaminda Jayawarna

Registration No: 5546 PS 2011012

**A Research submitted to the University of Sri
Jayewardenepura in partial fulfillment of the requirements
for the Degree of Master of Science in Polymer Science and
Technology on 30.04.2015**

Declaration

“The work described in this research was carried out by me under the supervision of Dr. Dilhara G. Edirisinghe and a report on this has not been submitted in whole or in part to any university or any other institution for another Degree/Diploma”



.....

Signature of the Student

.....

Date (30.04.2015)

“I certify that the above statement made by the candidate is true and that this project is suitable for submission to the university for the purpose of evaluation”

..........

Signature of the Supervisor

Dr. Dilhara G. Edirisinghe

**Head, Rubber technology and Development Department,
Rubber Research Institute of Sri Lanka, Ratmalana.**

.....*30.04.2015*.....

Date

Table of Contents

Table of contents	v
List of Tables	vii
List of Figures	viii
Acknowledgments	x
Abstract	xi

Contents

CHAPTER 1: GENERAL INTRODUCTION	1
1.0 Introduction	1
1.1 Problem	5
1.2 Objectives	6
1.3 Significance.....	7
1.4 Scope and coverage.....	7
1.5 Limitation.....	7
CHAPTER 2: LITERATURE REVIEW	8
2.0 Introduction.....	8
2.1 Definitions.....	8
2.2 Method of recycling, reclaiming and devulcanisation	10
2.3 Types of devulcanisation technologies	13
2.4 Reaction mechanisms during reclamation of vulcanized rubber	23
2.5 Different types of reclaiming processes.....	31
2.6 Natural rubber latex waste reclaiming	39
2.7 Uses of reclaimed rubber	42
2.8 Change of physical properties.....	49
2.9 Solid tyres	49
CHAPTER 3 : MATERIALS AND METHODS	53
3.0 Introduction.....	53
3.1 Experimental	53

3.2 Reclamation experiments.....	54
3.3 Characterization of novel reclaiming rubber	57
3.4 Preparation of natural rubber based solid tyre tread compound with novel reclaimed natural rubber latex product waste.....	59
3.5 Characterization of virgin NR/ novel reclaimed rubber blend compounds	60
CHAPTER 4: RESULTS & DISCUSION	64
4.0 Introduction.....	64
4.1 Characterization of reclaimed rubber.....	64
4.2 Selection of the best reclaiming agent and time for reclaiming of natural rubber latex product waste.....	68
4.3 Properties of tyre tread compounds with natural rubber novel reclaimed rubber blends.....	69
CHAPTER 5 : CONCLUSIONS AND FURTHER WORK	87
5.0 Conclusions.....	87
5.1 Suggestions for further work.....	88

List of table

Table 1.1 Rubber production in Sri Lanka by different types.....	2
Table 1.2 Export of rubber products.....	3
Table 1.3 Sri Lanka total NR production, centrifuge rubber production, export quantity and domestic usage of centrifuged latex (MT).....	4
Table 2.1: Reclaiming agents used in mechano- chemical methods	36
Table 2.2: Typical formulation for balloons	51
Table 2.3: Typical formulation for gloves	52
Table 3.1: Time intervals used for reclaiming of natural rubber latex product waste by a mechanical process without reclaiming agents.....	54
Table 3.2: Concentration of reclaiming agents used for reclaiming of natural rubber latex product waste by a mechanical process	55
Table 3.3: Different concentrations of selected reclaiming agent (IPPD) used to reclaim natural rubber latex product waste	56
Table 3.4: Solid tyre tread formulation -Natural rubber / novel reclaimed rubber based tread compound formulations.....	60
Table 4. 1 : Properties of Mooney viscosity, swelling value and volume fraction of rubber in the swollen gel of reclaimed rubber produced according to a mechanical process.....	64
Table 4.2 : Properties of reclaimed rubber produced with IPPD	65
Table 4.3 : Properties of reclaimed rubber produced with CBS	66
Table 4.4 Properties of reclaimed rubber produced with TMTD	67
Table 4.5 : Properties of reclaimed rubber latex produced with 1:1 CBS:TMTD	68
Table 4.6: Percentage retention of physico-mechanical properties after ageing	80
Table 4.7: Glass transition temperatures of virgin NR/ Reclaim rubber compounds..	84

List of figure

Fig 2.1: Oxidation mechanism for the PH-FeCl ₂ system	24
Fig 2.2: Bolland oxidation mechanism (RH = Rubber hydrocarbon).....	25
Fig 2.3: Decomposition of peroxide by iron metals (Redox mechanism)	25
Fig 2.4: Opening of sulphur crosslinks by triphenyl phosphine	26
Fig 2.5: Proposed reaction mechanism of crosslink and main chain scission with disulphides	27
Fig 2.6: Opening of sulphur crosslinks by oxidation (ROOH Organic hydroperoxide)	28
Fig 2.7: Opening of sulphur crosslink by heat or shear	29
Fig 2.8: Opening of sulphur crosslinks by nucleophilic reagents	29
Fig 2.9: Opening of sulphur crosslinks by rearrangement	30
Fig 2.10: Opening of sulphur crosslinks by substitution	30
Figure 2.11: Cross Section of Solid tyre	49
Fig 4.1 : Variation of Mooney viscosity of virgin NR / novel reclaimed rubber blend compounds.....	70
Fig 4.2 : Variation of minimum torque with novel reclaimed rubber content.....	71
Fig 4.3: Variation of the maximum torque with novel reclaimed rubber content	71
Fig 4.4: Variation of (maximum–minimum) torque with novel reclaimed rubber content	72
Fig 4.5: Variation of cure rate index with novel reclaimed rubber content	73
Fig 4.6 : Variation of scorch time with novel reclaimed rubber content	74
Fig 4.7 : Variation of cure time with novel reclaimed rubber content.....	74
Fig 4.8: Variation of tensile strength of virgin NR/ novel reclaimed rubber blend compounds with reclaimed rubber content.....	75
Fig 4.9 : Variation of modulus at 300% elongation of virgin NR/ novel reclaimed rubber blend compounds	76
Fig 4.10: Variation of elongation at break of NR/novel reclaimed rubber blend compounds with reclaimed rubber content.....	77
Fig : 4.11: Variation of tear strength of Virgin NR/ novel reclaimed rubber blend with reclaimed rubber content.....	78

Fig: 4.12: Variation of hardness values of virgin NR /novel reclaimed rubber blend compounds with reclaimed rubber content.....	79
Fig 4.13: Variation of abrasion volume loss of virgin NR/novel reclaimed rubber blend compounds with reclaimed rubber content.....	82
Fig 4.14 Variation of rebound resilience of virgin NR/novel reclaimed rubber blend compounds with reclaimed rubber content.....	83
Fig.4.15: Variation of Mod 300% / Mod 100% of virgin NR/ novel reclaimed rubber blend compounds with reclaimed rubber content.....	84
Fig 4.16 : Glass transition and flex temperatures of virgin NR/ novel reclaimed rubber blend compounds	86

ACKNOWLEDGEMENT

It gives me a great pleasure to extend my sincere gratitude for the help I received to complete this project.

My sincere thanks go to my supervisor Dr. Dilhara G. Edirisinghe for her unreserved assistance, suggestions and guidance.

I would like to express my thanks to Dr. M.A.B. Prashantha and Dr. R. Gunarathne for the valuable comments given as examiners.

Also, I express my special thanks to course coordinator Dr. Thilini Gunasekara and other lecturers who thought and guided us in the MSc. Programme, 2011. I admire their support and advice given to me.

Further, my thanks go to the management and staff of Laugfs Corporation (Rubber) Ltd. and Rubber Research Institute of Sri Lanka for providing assistance and testing facilities.

ABSTRACT

Use of reclaimed rubber in rubber compounds is a common practice to improve processability and reduce cost. The main aim of this research was to develop a novel mechanochemical reclaiming process for natural rubber latex product waste. Mechanochemical reclaiming was performed at low temperature with IPPD, an amine type antioxidant. Thereafter, virgin natural rubber (NR) was blended with the novel reclaimed rubber according to a solid tyre tread formulation. A series of virgin NR / novel reclaimed rubber composites was prepared by replacement of virgin NR with novel reclaimed rubber at 10 phr intervals; the maximum loading of the reclaimed rubber was 50 phr. Reclaimed rubber was characterised and Mooney viscosity, glass-transition temperature (T_g), cure characteristics, physico-mechanical properties and aging performance of the composites were evaluated.

Above characterisation techniques indicated that 2 phr and 5 min. was the optimum loading and milling time, respectively for reclaiming with IPPD. Minimum and maximum torques increased with the increase of novel reclaimed rubber content, whereas scorch and cure times showed a decreasing trend with rheometer results. However, the lowest Mooney viscosity and T_g was obtained by the composite with the highest reclaimed rubber loading. There was no significant decrease in tensile strength up to 40 phr loading. Moduli, elongation at break and resilience did not vary significantly with the increase of reclaimed rubber content from 10 to 40 phr. Hardness, tear strength and abrasion volume loss of the composites prepared with 10 to 30 phr loading of reclaimed rubber were at the acceptable level for tyre treads. As the reclaiming agent was an antioxidant, the aging performance of the composites

containing reclaimed rubber was superior to that of the 100% virgin NR composite. Results in overall indicated that the 70:30 virgin NR / novel reclaimed rubber composite would be suitable to manufacture solid tyre treads.

CHAPTER 1: INTRODUCTION

1.0 Introduction

Sri Lanka has the potential to be one of the world leading rubber product manufacturing countries due to its production of high quality raw materials, top quality grade of natural rubber (NR) with a very low level of proteins, high quality production of RSS and relatively low processing cost. A wide variety of rubber products is currently manufactured by the rubber manufacturing sector in Sri Lanka. Surgical, household, agricultural and examination gloves, balloons, hallowing masks and rubber toys are among the major products manufactured by the latex industries in Sri Lanka.

The Rubber industry in Sri Lanka has expanded significantly over the last decade and presently it produced around 152MT annually (Table 1.1). Centrifuge latex production has gone up in Year 2012 by 40%.

Table 1.1 Rubber production in Sri Lanka by different types (MT)

Year	Sheet	Sole Crepe	Latex crepe	Scrap crepe	TSR	Centrifuged latex and other	Total
2000	34,003	4512	28110	1788	3879	15344	87636
2001	30,344	3915	26112	2743	3657	19461	86236
2002	42,770	2987	20831	2185	1231	20514	90519
2003	50,015	2195	17131	3117	1193	18359	92010
2004	46,705	2035	12481	3708	2812	27000	94741
2005	50,170	2739	12914	2883	5880	29766	104352
2006	46,260	3949	20224	1606	9038	28076	109153
2007	48,875	4077	21756	1693	9564	31586	117551
2008	55,011	3937	21043	2711	10968	35573	129243
2009	54,550	5448	31670	3502	11775	29934	136880
2010	59,248	6711	52504	1842	8341	24341	152987
2011	60,699	3384	59933	1332	7981	24869	158198
2012	59,242	1,902	36,550	1,280	8,672	44,403	152,050
2013	62,800	2,379	15,373	2, 440	9,566	37,863	130,421

Source: Rubber Development Department

Sri Lanka has many leading rubber product manufacturers in the country whose products are very competitive in global markets. Some of them are Ansell Lanka (Pvt.), DSI Group, Camoplastsolideal (Pvt.) Ltd., Lalan Group, Dipped Products Ltd, Trelleborg (Pvt.) Ltd, Associated Motorways Ltd., Richard Peiris Group, etc.

In terms of export value, the rubber products industry (solid tyres, pneumatic tyres and tubes, plates, sheets and strips, surgical gloves and other gloves, floor coverings and mats, etc.) recorded a high growth from US \$ 539.91 million in the year 2008 to US \$ 889.40 million in the year 2014 (Table 1.2)

Sri Lanka can boast of international accepted products such as solideal branded industrial tyres manufactured here by Loadstar Ltd. Loadstar enjoys more than 20% of the international market. Trelleborg Lanka Ltd. also produces solid tyres to the global market. Sri Lanka in Southeast Asia which enjoys a large rubber output, developed rapidly in solid tyre manufacturing field in recent years by virtue of their advantages in resources.

USA is the largest importer of solid tyres from Sri Lanka. Belgium, Germany, Italy are the other major importers of solid tyre products. Solid industrial tyres are primarily used in material handling vehicles in areas such as airports, ports and transporting goods for storage. Sri Lanka has developed into a center for the production of solid industrial tyres. Sri Lankan solid tyre sector earned US \$ million 352 in year 2011 and US \$ million 331 in year 2012. However the quantity of solid tyre exports had come down by 15% in year 2012.

Table 1.2 Exports of Rubber Products Value in US\$ Mn

Product	2008	2009	2010	2011	2012	2013	2014
Pneumatic & Retreated Rubber Tyres & Tubes	337.97	214.27	337.78	571.4	541.22	554.6	567.59
Industrial & Surgical Gloves of Rubber	117.22	113.87	136.92	180.98	176.34	195.4	175.93
Gaskets, Washers, Seals etc. of Hard Rubber	71.89	41.47	62.84	89.53	76.71	79.87	95.56
Rubber Plates, Sheets Rods of Vulcanized or Unhardened Rubber	10.14	12.21	17.21	39.25	59.65	54.83	47.76
Other Rubber Products	2.69	2.5	2.06	2.99	2.76	2.72	2.57
Total	539.91	384.32	556.81	884.15	856.68	887.42	889.4

(Source: Sri Lanka Customs)