NANOSTRUCTURED MONTMORILLONITE CLAY ON RAW RUBBER PROPERTIES OF SKIM NATURAL RUBBER AND PHYSICO-MECHANICAL PROPERTIES OF NATURAL RUBBER / SKIM RUBBER BLEND

by

Liyanapathiranage Anuradhi Nayana Kumari

Thesis submitted to the University of Sri Jayewardenepura for the award of the Degree of Master of Science in Polymer Science and Technology October 2015.

The work described in this thesis was carried out by me under the supervision of Dr Upul N Ratnayake PhD (Loughborough,UK) Head, Raw Rubber Process Development & Chemical Engineering Rubber Research Institute of Sri Lanka (RRISL) and a report on this has not been submitted in whole or in part to any university or any other institution for anther Degree/Diploma".

)	•	•	•	•	٠	٠	•	٠	٠	٠	•	٠		٠	٠	٠	٠	٠		٠	•	٠	٠	•	٠	•	٠	٠	•

.....

Signature

Date

I have supervised and accepted this	s thesis for the award of the degree
Atry	03/12/2015-
Signature	Date

i

Upul N Ratnayake, Ph.D. (UK) Head-RRPD & CE Department Rubber Research Institute of Sri Lanka Telawala Road Ratmalana.

DEDICATION

To my loving mother To my loving husband To my loving sister

ACKNOWLEDGMENT

Frist and foremost I immensely acknowledge the forbearance and fullest support of my supervisor Dr.Upul N.Ratnayake for offering me this highly valued research project and his continuous support given throughout the study.

I would like to wish my greatest gratitude to Dr.Thilini Gunasekara and Dr.Dilru Ratnaweera, the course co-ordinators –M.Sc in Polymer Science and Technology, Department of Chemistry, University of Sri Jayewardenepura, for providing me guidance and necessary instruction to fulfil this research project.

I would like to acknowledge Dr.Gamini Seneviratne, Director, Rubber Research Institute of Sri Lanka for granting permission to conduct this research work in the institute premises.

I highly appreciate support of staff members of Raw Rubber Process Development & Chemical Engineering Department and all staff members of Rubber Research Institute, Ratmalana.

I acknowledge Lalan Rubbers Pvt.Ltd – Centrifuging Plantation. Bulathsighala, for technical support given and granting permission to proceed bulk trail at their factory premises.

Finally, my sincere thanks to all personnel for their assistance, for being kind and considerate towards me at all times.

ABSTRACT

Skim natural rubber (SNR), a process by-product of centrifuged latex manufacturing, consists of low molecular weight rubber and a higher percentage of non-rubber constituents, especially nitrogenous substances. SNR, known as low quality grade of rubber, limits the industrial applications because of inappropriate physico-mechanical properties. Effect of nanostructured MMT clay on SNR was investigated in view of preparing value added raw rubber and hence improved industrial applicability.

At 1st phase of the research, montmorillonite (MMT) clay filled SNR nanocomposites were prepared by incorporating aqueous dispersion of MMT clay into skim natural rubber latex followed by latex coagulation. Characterization of raw rubber properties have shown that clay loading has increased the thermo-oxidative stability of the skim rubber. Improved green strength of MMT clay filled SNR nanocomposite has revealed the presence of MMT nanostructures and its effect on strain-induced crystallization. However, processability, as measured with low shear strain rate viscoelastic behaviour, is affected by the added MMT clay. With this latex compounding methodology, a novel MMT clay filled SNR with improved physical properties has been developed as a value added raw rubber for different applications.

During the 2nd phase of the research, the effect of MMT clay structure on reinforcement of NR / SNR blends was examined. MMT filled SNR master batch being formulated from latex coagulating method was melt blended with NR using a laboratory scale internal mixer. Processability and reinforcement of the NR/SNR –MMT blend was studied in comparison to NR/SNR blend containing no MMT clay. Stress-strain properties of the nanocomposites vulcanizates measured under tensile deformation, especially tensile strength, modulus ,hardness and abrasion resistance, were manifest to

iv

prove notable reinforcing effect of MMT clay as shown up to 32 % - 67 % increase of tensile modulus at 300 % elongation. Higher degree of exfoliation of MMT and resulted higher reinforcement at lower volume fraction of MMT (2- 4 phr) in NR/SNR-MMT blend justifies the formation of nano scale MMT clay platelets within the composite matrix. This phenomena can be further explained though adsorption of non-rubber substances onto MMT and formation of interactions with nano scale clay platelets.

Key words: Skim natural rubber, montmorillonite clay, green strength, thermo-oxidative degradation, nanocomposite, Mooney Viscosity, reinforcement, exfoliation, NR/SNR blend

v

TABLE OF CONTENTS

1

Page

DE AC AB	DICATION KNOWLEDGMENT STRACT	II III IV
1.0	INTRODUCTION 1.1. Background 1.2. Motivation for the study 1.3. Project Objectives	13 13 15 16
2.0	LITERATURE SURVEY	17
	 2.1. Natural Rubber and Skim Rubber 2.1.1. Introduction 2.1.2. Natural rubber latex 2.1.3. Concentrating NR latex	17 .17 .17 .19 21 .23
	2.1.4.1. Recovery of skim natural rubber2.1.4.2. Properties of skim natural rubber.2.1.4.3. Application of skim natural rubber	26 27 28
	 2.2. Composites and blends 2.2.1. Composites 2.1.1.1. General classification of composites. 2.1.1.2. Composite types based on continuous phase. 	29 .29 29 30
	 2.1.1.3. Composite types based on discontinuous /dispersed phase. 2.2.2.Rubber nanocomposites. 2.2.2.1. Rubber composites 2.2.2.2. Rubber nanocomposites. 2.2.2.3. Skim natural rubber composites. 2.2.2.4. Characterization of nanomaterial 	30 .31 31 31 32 33
	 2.2.3. Montmorillonite nanoclay (MMT)	.34 34 .37 37
	2.2.4.2. Melt blending method2.2.4.3. Solution blending method	38 39
	2.2.4.4. In-situ formation or in-situ polymerization	40

	Page
2.2.5. Factors affect polymer composite properties. (Galimberti,	Clipoletti, &
Kumar, 2013)	41
2.2.6. Analytical method of characterization of Rubber nanocompo	osites41
3.0 MATERIALS AND METHODS	50
3.1. Materials	50
3.1.1. Montmorillonite clay	
3.1.2. Skim rubber latex	
3.1.3. Ribbed smoke sheet (RSS)	
3.1.4. Skim Natural Rubber (SNR)	
3.1.6 Chemicals used in melt blending method	
5.1.0. Chemicals used in men ofending method	
3.1. Methodology	53
3.1.1. Preparation of MMT filled SNR composites	53
3.1.1.1. Preparation of MMT aqueous solution	53
3.1.1.2. Preparation of MMT filled SNR composite	53
3.1.2. Characterization of raw rubber properties of MMT filled SN	R57
3.1.2.1. Initial plasticity (P ₀)	57
3.1.2.2. Plasticity Retention Index (PRI)	57
3.1.2.3. Nitrogen content	58
3.2.2.4. Volatile matter	58
3.2.3. Viscoelastic behaviour of MMT clay filled SNR composites	
3.2.3.1. Mooney viscosity	59
3.2.3.2. Mooney stress relaxation	60
3.2.3.3. Mooney peak analysis of MMT filled SNR series	61
3.2.3.4. Measuring Thixotropic behaviour of the MMT filled	SNR
composites	61
3.2.4. Green strength analysis	62
2.2.5 Malt blanding a CNID (CNID and a initial DO (T) along	(2)
3.2.4 Characterization and evaluation of melt blended NR/SNR	03 MMT blend
series	
3.2.4.1. Vulcanization / curing parameters of NR/SNR-MMT	blend series
n na	65
3.2.4.2. Structure properties relationship using X-ray diffract	ion. 68
3.2.4.3. Physico-mechanical properties of NR/SNR-MMT blo	end series
and NR/SNR blends	70

4.0 RESULTS AND DISCUSSION	.GE 76
4.1. Characterization of MMT filled SNR composite series	76
4.1.1. Key observations of preparing MMT clay filled SNR through la compounding	atex 76
4.1.2. Raw rubber properties of MMT filled SNR composite 4.1.2.1. Initial Plasticity and PRI	77 77
4.1.2.2. Nitrogen Content	80
4.1.2.3. Volatile matter content	82
 4.1.3.Low shear strain rate rheological properties: 4.1.3.1. Effect of clay on Mooney viscosity of SNR. 4.1.3.2. Effect of temperature on Mooney viscosity of MMT filled SNI 	83 83 R in
different	85
4.1.3.3. Stress relaxation of MMT filled SNR series	86
4.1.3.4. Mooney peak analysis of MMT filled SNR composite	89
4.1.3.5. Thixotropic behaviour of MMT filled SNR nanocomposites	90
4.1.4. Effect of MMT clay on green strength of SNR	92
4.1.5. Mechanism of MMT and non-rubbers in SRLX to deliver value ad properties	ded 96
4.1.5.1. SNR structure and non rubbers	96
4.1.5.2. Protein adsorption mechanism on MMT in aqueous solution.	97
4.1.5.3. Proteins ammine groups adsorption on MMT	100
4.1.5.4. Fatty acids -carboxlyic group adsroption on MMT	101
4.1.6. Identification of suitable MMT loading level for bulk trail	105
4.2. RESULT AND DISCUSSION 2: Preparation and characterization blence MMT filled SNR and NR	l of 106
4.2.1. Curing/vulcanization parameters of NR/SNR - MMT blend 4.2.1.1. Scorch time (t _{s1})	106 106
4.2.1.2. Cure rate	108
4.2.1.3. Thermoplacity	110
4.2.2. Structure properties relationship using X-ray diffraction (XRD)	112

Page

	4.2.3. Evaluation of physico-mechanical properties of NR/SNR –MM series	T blend
	4.2.4. Aging properties of NR/SNR-MMT	130
	4.2.5. Factors of MMT and rubber reinforcement	134
	4.2.6. Performance evaluation of NR/SNR blend series	138
5.0	CONCLUSION	139
	5.1. Characterization of MMT filled SNR composites	139
	5.2. Characterization of MMT filled SNR and RSS blends	140
	5.3. Industrial implementation	142
6.0	FUTURE WORK	143
7.0	PUBLICATIONS	144
	7.1. IRRDB, International Rubber Conference 2015	144
	7.2. IIUPST 2015, Abstract number 23, Advances in Polymer materials	155
8.0	REFERENCES	157

LIST OF FIGURES

Pa	age
Figure 2.1: Industrial centrifuging machine	22
Figure 2.2: Top most collection as concentrated latex	22
Figure 2.3: Specification for centrifuged or creamed ammonia preserved natural rubbe	er 22
Figure 2.4: Particle size distribution of concentrated and skim lattices (Sakdaninanich	87
Pointhai 2012)	25
Figure 2.5: Molecular weight distribution of the rubber from concentrated and skim	25
lattices (Sakdapinanich & Pointhai 2012)	25
Figure 2.6: Classification of Composites (Jose et al. 2012)	21
Figure 2.7: MMT clay T_O_T structure (Koo I H 2006)	36
Figure 2.8: Emulsion blanding process of MMT clay (Calimberti Bubber Clay	50
Nanocomposites 2012)	38
Figure 2.0: Melt blending process of organophilic clay	30
Figure 2.10: Solution blending process of rubber and clay	30
Figure 2.11: In-situ polymerization of rubber and layered clay minerals	10
Figure 2.12: Different nanocomposites arrangement can be obtained through the proce	40
(Camargo Satvanaravana & Fernando 2000)	12
Figure 2.12: Schematic of WAXD notterns of different morphologies of lowered	42
Silicates (Causin 2012)	11
Figure 2.14: Typical Bheograph of a rubber compound to: ML tase and MHE are	44
significant readings	17
Figure 2.15: Stress strain curve of a rubber compound	41
Figure 2.15. Suess strain curve of a rubber compound	40
Figure 3.1: Step 1-Preparation of MMT aqueous dispersion	55
Figure 3.2: Step 2 - Mixing MMT Coagulation	55
Figure 3.3: Step 3 - Recovery of filled composite	55
Figure 3.4: Step 4 - Milling and removing excess water	56
Figure 3.5: Step 5- Air drying and labelling	56
Figure 3.6: Typical Mooney and relaxation curve	59
Figure 3.7: Stress relaxation interpretation using logarithm	61
Figure 3.8: Time extended Mooney curve	62
Figure 3.9: General rheograph of a rubber compound (Dick, 2003)	66
Figure 3.10: Reversion Rheograh – indicate material degradation (Dick, 2003)	67
Figure 3.11: Marching Rheograh – indicate material further crosslinking (Dick, 2003)	67
Figure 3.12: Bragg's law interpretation of crystal sites	68
Figure 3. 13: X-ray diffractometer	70
Figure 3.14: Stress strain curve of a Rubber compound	71
Figure 3.15: Device for compression set	73
Figure 4.1: P ₀ and PRI of MMT filled SNR nanocomposites	77
Figure 4.2: MMT influence in O ₂ diffusion	79
Figure 4.3: Nitrogen content of SNR and MMT filled SNR series	80
Figure 4.4: Volatile matter content of SNR and MMT filled SNR series	82
Figure 45: Mooney viscosity and Mooney stress relaxation curve of MMT filled SNR	
series	83

	Page
Figure 4.6: Mooney viscosity of MMT filled SNR series at 100°C.	84
Figure 4.7: Mooney viscosity behaviour of MMT filled SNR series in different	
temperatures	85
Figure 4.8: Lamella and amorphous segments in rubber.	86
Figure 4.9: Stress relaxation behaviour of MMT filled SNR series	87
Figure 4.10: Shows the effect of MMT on Mooney peak value	89
Figure 4.11: Time Extended Mooney curve of SNR –MMT filled SNR	90
Figure 4.12: Thixotropic behaviour of SNR –MMT filled series	91
Figure 4.13: Tensile properties of MMT filled SNR series – Tensile strength	93
Figure 4 14: Green strength based on tensile properties – Tensile strength	94
Figure 4.15: Green strength based on tensile properties – Tensile modulus	94
Figure 4.16: Presumed structure for a and a terminal group for NR (Sakdaninanich	8
Rointhai 2012)	06
Figure 4.17: Condensed (non hydrated) MMT structure (Calimberti Pubber Clay	90
Nanocomposites 2012)	07
Figure 4.19. Hydroted structure of MMT is an acusaus solution (Colimberti Dubb	91
Figure 4.18. Hydrated, structure of MMT in an aqueous solution (Ganinberti, Rubb	07
Clay Nanocomposites, 2012)	. 97
Figure 4.19: Chemisorption between ammine compounds (proteins and amino acids)
and MMT structural active groups. (Yariv, 2002). H bond is represented as H	100
•••N	100
Figure 4.20: Possible reaction with long chain fatty acid oxygen sheet of TOT struc	ture.
(Yariv, 2002)	102
Figure 4.21: Linkage formation fatty acids with exchangeable cation through water	
bridge. (Yariv, 2002)	102
Figure 4.22: Direct linkage with exchangeable cation (Yariv, 2002)	103
Figure 4.23: Linkage between COO- group and an exchangeable cation through a w	ater
bridge. (Yariv, 2002)	103
Figure 4.24: Direct linkage between COO- group and an exchangeable cation. (Yan	iv,
2002)	103
Figure 4. 25: Total performance of MMT -SNR filled series	105
Figure 4.26: t _{s1} of the NR/SNR – MMT blend series and NR/SNR blend.	106
Figure 4.27: Heat dependency of sulphur transition.	107
Figure 4.28: Cure rates of NR/SNR-MMT blend series and NR/SNR blend series	108
Figure 4.29: Energy requirement of sulphur crosslinking.	109
Figure 4.30: Energy requirement of sulphur crosslinking with presence of MMT.	109
Figure 4.31: Thermoplasticity of NR/SNR -MMT series and NR/SNR series.	110
Figure 4.32: X-ray diffraction of MMT(Cloesite Na, 30A) (Galimberti, 2012)	112
Figure 4.33: X-ray diffraction of 80NR20SNR-2	113
Figure 4.34: X-ray diffraction of 60NR40SNR-4	114
Figure 4.35: X-ray diffraction of NR40SNR60-6	114
Figure 4.36: X-ray diffraction of NR20SNR80-8	115
Figure 4.37: X-ray diffraction of SNR-10	115
Figure 4.38: Stress strain curves of NR, SNR and NR/SNR -MMT blend series	117
Figure 4.39: Tensile Strength of NR/SNR -MMT blend series and NR/SNR blend s	eries
	118
Figure 4.40: Tensile modulus of NR/SNR –MMT blend series and NR/SNR series	119
Figure 4.41: Elongation at break NR/SNR-MMT series and NR/SNR blends series	119
	10000

	Page
Figure 4.42: Tear strength of NR/SNR-MMT blend series and NR/SNR series	120
Figure 4.43: Hardness of NR/SNR-MMT blend series and NR/SNR series	124
Figure 4.44: Compression set of NR/SNR- MMT blend series and NR/SNR series	125
Figure 4.45: Abrasion of NR/SNR-MMT Blend series and NR/SNR series	127
Figure 4.46: Rebound resilience of NR/SNR-MMT blend series and NR/SNR series	s 128
Figure 4.47: Percentage tensile strength retention of NR/SNR -MMT series in	
comparison to NR/SNR blend	131
Figure 4.48: Retention of tensile modulus of NR/SNR-MMT blend series and NR/S	SNR
series	131
Figure 4.49: Retention of elongation at break of NR/SNR-MMT blend series and	
NR/SNR series	132
Figure 4.50: Retention of tear strength of NR/SNR- MMT series and NR/SNR series	es132
Figure 4.51: Formation of primary and aggregations (Samsuri, 2014)	136

LIST OF TABLES

Page

Table 2.1: Chemical composition of fresh NR latex (Mathew, 2001)	18
Table 2.2: Chemical composition of SNR (Nithi-Uthai, et al., 1999); (Ho, 2014)	27
Table 2.3: Classification of clays based on surface electrical charge (Galimberti, 20)	12)
	34
Table 2.4: SNR- MMT nanocomposite main analytical methods and testing	43
Table 2.5: Significant features of XRD	45
Table 2.6: Tensile test parameter and indicating properties	49
Table 3.1: Properties of RSS rubber. (Seneviratne, 2003)	51
Table 3.2: Chemicals in dry and wet solution forms used in this process	52
Table 3.3: Chemicals involved in melt blending, which were used to	52
Table 3.4: Estimation of required SRLX and MMT aqueous solution volumes for 60)0 g
of the SNR.	54
Table 3.5: Rubber ratios of series 1 NR /SNR-MMT blend.	63
Table 3.6: Rubber ratios of series 2 NR/SNR blends.	64
Table 3.7: General formula being used	64
Table 3.8: Melt blending internal mixer (brabender) mixing circle. Chemicals are	
introduced as mentioned order.	64
Table 3.9: Melt blending two roll mill mixing introduced as in order of mentioned.	65
Table 3.10: Rheograh parameter and resembling properties.	66
Table 3.11: Tensile test parameter and indicating properties	71
Table 4. 1:1 +a Rate of relaxation -shows elasticity of rubber, K is viscosity of the	
compound after 1s of shear force removal.	88
Table 4.2: Cure characteristics of NR/SNR-MMT and NR/SNR series.	111
Table 4.3: X-ray diffraction test summery	116
Table 4.4: Performance of NR/SNR-MMT Blend series.	138

Table 4.4: Performance of NR/SNR-MMT Blend series.

1.0 INTRODUCTION

1.1. Background

From centuries, Sri Lanka has been recognised as one of the largest and finest natural rubber (NR) and Latex (LX) manufactures. However, LX based industries can be sighted, as one of the key consumers of total rubber production. Mostly, LX being used to manufacture thin wall items, rubber gloves, balloons and etc. These products indeed to acquire superior physical and mechanical film properties. Therefore, in this process, ammonia preserved field LX being centrifuged in order to enhance its Dry Rubber Content (DRC) and other molecular properties. This process, centrifuging yields concentrated latex as the major output and Skim rubber latex (SRLX) as its process biproduct.

SRLX is being separated by centrifuging machine, giving angular rotation, leading latex to separate as per density of the rubber particles. As a result, low density latex which contains higher DRC and larger rubber molecules separate as the upper layer. Shorter rubber chains and higher amount of non-rubber carrying high density SRLX collects as the bottom layer.

As an industrial practise, SRLX is being sold to the cottage or small scale manufactures in bulk. SRLX is then coagulated using 10 % w/w, sulphuric acid (H₂SO₄) to produce Skim natural Rubber (SNR). SNR is being inherited poor physio-mechanical properties as well as poor aging due to higher amount of non-rubber constituents. Henceforth, usage of SNR to manufacture of value added products is restricted. Even though, SNR is being used to produce low quality products or being mixed with NR to