

NANO ACTIVATORS FOR NATURAL LATEX

By

Wickramasinghage Ravindra Nalaka Alles

**Thesis submitted to the University of Sri Jayewardenepura for the
award of the Degree of Master of Science in Polymer Science and
Technology on September, 2009.**


University of Sri Jayewardenepura
Graduate Studies.

Declaration.

The work described in this thesis was carried out by me under the supervision of Dr. Nilwala Kottegoda 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.

Signed:.....Ravindra.....

Wickramasinghage Ravindra Nalaka Alles.
18/09/2009.


22/10/2009
Coordinator

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

University of Sri Jayewardenepura
Graduate Studies

I/We certify that the above statement made by the candidate is true and that this thesis is suitable for submission to the University for the purpose of evaluation.

Signed:



.....
Dr. (Mrs) Nilwala Kottegoda
Senior Lecturer
Department of Chemistry
University of Sri Jayewardenepura
Nugegoda,
.....
.....
.....

Date: 18/09/2009

TABLE OF CONTENTS

LISTS OF TABLES	IV
LISTS OF FIGURES	V
ACKNOWLEDGEMENTS	VI
ABSTRACT.	VII
CHAPTER 1. INTRODUCTION.	1
1.1 Background.	1
1.2 Aims of This Project.	2
CHAPTER 2. LITERATURE REVIEW.	3
2.1 Nanotechnology.	3
2.1.1 Introduction to nanotechnology.	3
2.1.2 Properties of the nanoscale.	3
(I) Surface area.	3
(II) Quantum effects.	3
2.1.3 Synthesis of nanomaterials.	3
(I) Top down manufacturing.	4
(II) Bottom up manufacturing.	4
2.2 Chemical Synthesis of Nanomaterials.	5
2.2.1 Synthesis of nanoparticles by coprecipitation.	5
(I) Coprecipitation mechanisms.	6
(II) Growth termination and nanoparticle stabilization.	6
(III) Different type of coprecipitation method.	7
2.2.2 Coprecipitation of oxides from aqueous solutions.	7
2.2.3 Coprecipitation of LDH and followed calcination.	8
(I) Structure of LDH.	8
(II) Coprecipitation of LDH.	9
(III) Calcinations of LDH.	10
2.3 Latex Technology.	12
2.3.1 Hevea Latex (Natural Rubber Latex).	12
2.3.2 Preservation & Concentration.	13
2.3.3 Storage of Preserved & Concentrated Latex.	14
2.3.4 Latex Compounding Ingredients.	15
(I) Surface-active agents.	16
(II) Vulcanizing ingredients.	16
2.3.5 Compounded latex maturation.	17
2.3.6 Processing.	18
(I) Latex Dipping.	18

2.3.7 Drying and vulcanising.	18
(I) Vulcanization chemistry.	18
(II) Vulcanizate network.	22
2.4 A Review of the Nano ZnO and Nano ZnAl₂O₄.	26
2.4.1 Nano ZnO.	26
2.4.2 Nano ZnAl ₂ O ₄ .	27
CHAPTER 3. MATERIALS AND METHODS.	28
3.1 Nano Materials Preparation.	28
3.1.1 Preparation of nano zinc oxide.	28
3.1.2 Preparation of nano ZnAl ₂ O ₄ spinel.	29
(I) Coprecipitation, and followed decomposition of “Zn/Al-CO ₃ LDH”.	29
(II) Synthesis of “Zn/Al-borate-LDH” and calcinations.	29
(III) Coprecipitation of nano ZnAl ₂ O ₄ .	30
3.2 Nano Materials Characterization.	30
3.3 Dispersion of Nano Materials.	30
3.4 Latex Compounding.	31
3.4.1 Formulation without any ZnO as activator.	31
3.4.2 Formulations with activator bulk ZnO (0.5 phr, 0.25 phr).	32
3.4.3 Formulations with nano particles (0.5, 0.25, 0.1 phr of ZnO or ZnAl ₂ O ₄).	32
3.5 Latex Dipping, Drying and Vulcanizing.	33
3.6 Measurements.	33
3.6.1. The tensile and tear experiment.	33
3.6.2. Swelling measurements.	33
3.6.3 Abrasion experiment.	34
3.6.4 Samples clarity.	34
CHAPTER 4. RESULTS & DISCUSSIONS.	35
4.1. Characterization of Nano Materials.	35
4.1.1. Nano ZnO.	35
4.1.2. Characterization of nano ZnAl ₂ O ₄ spinel using “Zn/Al-carbonate” LDH.	37
4.1.3 Nano ZnAl ₂ O ₄ spinel prepared in the presence of borate anions.	42
4.1.4 Nano ZnAl ₂ O ₄ by direct coprecipitation.	46
4.2 Preparation of Nanoparticle-Rubber Compound.	48
4.3 Bulk ZnO as Latex Activator.	48
4.4 Nano ZnO as Latex Activator.	54

4.5 Nano ZnAl₂O₄ as Latex Activator.	61
4.5.1 Nano ZnAl ₂ O ₄ -(A) as latex activator.	62
4.5.2 Nano ZnAl ₂ O ₄ -(B) as latex activator.	64
4.5.3 Nano ZnAl ₂ O ₄ -(C) as latex activator.	65
CHAPTER 5. CONCLUSIONS.	67
REFERENCES.	69
APPENDIX (A)-PHYSICAL MEASUREMENTS.	74
Appendix (A-1).	74
Appendix (A-2).	75
Appendix (A-3).	76
Appendix (A-4).	77
Appendix (A-5).	78
APPENDIX (B) - ASSIGNMENT OF INFARED BANDS.	79

LISTS OF TABLES

Table. 1 pH values of precipitation of some M^{II} and M^{III} hydroxides.	10
Table. 2 Preservation systems employed in the Sri Lankan latex industry.	14
Table. 3 Preservatives and chemicals used in the manufacture of centrifuged latex.	15
Table. 4 Influence of degree of crosslinking on physical properties of vulcanizates.	23
Table. 5 Influences of di- and polysulfide crosslinks on properties.	23
Table. 6 Composition of prepared nano dispersions.	30
Table. 7 Formulation absence of activator.	31
Table. 8 Formulation with bulk activator.	32
Table. 9 Formulation with nano particles (0.5 phr, 0.25 phr, 0.1 phr of ZnO or ZnAl ₂ O ₄).	32
Table. 10 Assignment of soluble starch bands according to literature.	37
Table. 11 Viscosity of latex compounds, as prepared and after maturation for one day.	48
Table. 12 Change of tear strength and abrasion resistance of nano activated samples Vs reference amples.	58
Table. 13 Change of tear strength and abrasion resistance of spinel (A) activated samples Vs reference samples.	63
Table. 14 Change of tear strength and abrasion resistance of spinel activated samples Vs reference samples.	65

LISTS OF FIGURES

Fig. 1 Manufacturing techniques in nanotechnology.	5
Fig. 2 Idealized structure of a layered double hydroxide with interlayer carbonate anions.	8
Fig. 3 Generally accepted LDH decomposition mechanism.	10
Fig. 4 Diagrammatic representation of probable structure of natural rubber particle.	12
Fig. 5 Zinc oxide thickening.	13
Fig. 6 Basic steps for accelerated sulfur vulcanization.	19
Fig. 7 Complexes with the zinc ion stabilized with ligands.	20
Fig. 8 Polythiocarbamate-zinc (II) complex that traditionally been thought to involve.	20
Fig. 9 Proposed dithiocarbamate vulcanization mechanism by Nieuwenhuizen.	21
Fig. 10 Graphical depiction of empirical relationship between degree of crosslink and physical properties.	24
Fig. 11 Change of properties of rubber compounds during vulcanization.	24
Fig. 12 General scheme of sulfur vulcanizate network.	25
Fig. 13- Stacking patterns of the ZnO spectra.	36
Fig. 14- FT-IR spectra of soluble starch.	37
Fig. 15- Powder X-ray characterization of ZnAl ₂ O ₄ spinel.	40
Fig. 16- FTIR characterization of ZnAl ₂ O ₄ spinel.	40
Fig. 17 FT-IR spectra of sulphonate dispersing agent.	41
Fig. 18 FTIR characterization of ZnAl ₂ O ₄ spinel in the presence of borate anions.	43
Fig. 19 XRD characterization of ZnAl ₂ O ₄ spinel in the presence of borate anions.	45
Fig. 20 XRD pattern of coprecipitated spinel.	46
Fig. 21 FTIR pattern of coprecipitated spinel.	47
Fig. 22 Change of modulus with bulk activator loading.	49
Fig. 23 Change of calculated degree of cross-linking Vs curing time.	52
Fig. 24 Change of tensile strength with bulk activator loading.	52
Fig. 25 Variation of tensile strength (series 1), EAB % (series 2) and calculated degree of cross-linking (series 3) within a compound.	54
Fig. 26 Modulus of nano modified samples Vs reference samples.	55
Fig. 27 Change of calculated degree of cross-linking of nano modified samples Vs reference samples.	57
Fig. 28 Change of tensile strength of nano modified samples Vs reference samples through curing.	57
Fig. 29 Variation of tensile strength (series 1), EAB % (series 2) and calculated degree of cross-linking (series 3) Vs curing time of compounds 4, 5, and 6 respectively .	60
Fig. 30 Variations of samples clarities.	60
Fig. 31 Modulus of nano ZnAl ₂ O ₄ -(A) introduce samples Vs reference samples.	62
Fig. 32 Over-vulcanization resistance with spinel-(A) activation.	64
Fig. 33 Modulus of nano spinel introduces samples Vs reference samples.	66

ACKNOWLEDGEMENTS

It gives me special pleasure to be able to place on record my deepest appreciation to at least some of the many people who have made the completion of this thesis possible.

Firstly, I would like to express my deepest gratefulness to my supervisor Dr. Nilwala Kottegoda, for her advice, guidance and even financial supports at her own expenses during the period of my education in the Department of Chemistry at the University of Sri Jayawardenepura.

I would like to state my special thanks to Mr. Chris Amey- Department of Chemistry, University of Cambridge. Dr. U. Ratnayaka, Mrs. Dilhara Edirisinghe and Mr. M. Asela-Rubber Research Institute of Sri Lanka.

This thesis could not have been completed without the help of Dr. Lakshman Nethsinghe and Mr. Rasika Liyanage-Dipped Products (PVT) LTD) is greatly acknowledged.

NANO ACTIVATORS FOR NATURAL LATEX

ABSTRACT

The first aim of this thesis is to study the effect of nano ZnO on the NR latex vulcanisation. In this study, bulk ZnO replaced by nano ZnO as the activating species at equivalent loadings.

Zinc oxide nanoparticles were prepared by coprecipitation from aqueous solution using zinc chloride and sodium hydroxide as precursors and soluble starch as the stabilizing agent. Prepared particles then were made in to 10 % dispersion and light scattering measurements revealed that, the sizes of the particles in the prepared 10 % dispersion were around 250 nm even after few days of storage.

Nano ZnO activated latex films possessed, minimum of two times higher degree of cross-linking compared to conventional activator at equivalent loadings, comparable or little higher tensile strength with the presence of said cross-linking density, which is difficult to achieve simultaneously. Further advanced over-vulcanization resistance, three fold high tear strength and two fold high abrasion resistances, good transparency and finally half amount the nano activator compared to bulk is enough to give same or increased modulus, along with comparable tensile strength but yet higher tear and abrasion resistance as with the bulk activator.

In the final vulcanized compound various forms of zinc ions can be present. A part can still be present as ZnO without underwent of accelerator regeneration. Nano ZnO claims to posses inherent antimicrobial, antifungal, UV filtering and self-cleaning properties. Further studies are being carried out to evaluate the said properties of the nano activated latex films.

The next aim is to study the possibility of nano zinc aluminate spinel ($ZnAl_2O_4$) as curing activator. To the best of our knowledge, no work has ever been published to understand the effect of $ZnAl_2O_4$ spinel on the rubber vulcanization; neither solid rubber nor latex. Three methods were followed to synthesize $ZnAl_2O_4$ spinel.

- (1) By calcinations of "Zn/Al-carbonate-LDH" at 800 ° C
- (2) By calcinations of "Zn/Al-chloride-LDH" at 800 ° C, in the presence of borate anion.
- (3) By direct coprecipitation of nano $ZnAl_2O_4$.

Detailed characterization confirmed the presence spinel materials in all three samples with different morphology, and purity. The level of crystallization (amount and quality of crystallites) of $ZnAl_2O_4$ synthesized by the second routs was the best. Probably this would be the first time to make a similar observation with this particular LDH system. This novel but simple synthesis method itself is a subject of further studies because $ZnAl_2O_4$ spinel is a

well-known wide bandgap semiconductor and it is also useful in many catalytic reactions, such as cracking, dehydration, hydrogenation and dehydrogenation.

According to the light scattering measurements, the sizes of the spinel particles in the respective 10 % dispersion were around 250 nm even after few days of storage.

Quite interestingly, the modulus values of the latex films which “activated” by the nano ZnAl_2O_4 spinel laid between the values of the bulk-ZnO activated and nano-ZnO activated samples. The abrasion resistance and tear strength values were high and comparable with the nano ZnO activated samples. However, tensile strength was poor. Another distinguish observation made with this spinel compounding was that, there is a small increment of modulus while increasing the spinel loading from 0.1 to 0.5 phr and such a small quantity, 0.1 phr, has introduced so higher modulus to the final vulcanisate. So it would be an interesting question to ask possibility of spinel to be used as a cross-linking booster. However, it cannot be inferred from these results and thorough investigation is necessary.

NANO ACTIVATORS FOR NATURAL LATEX

CHAPTER 1

INTRODUCTION

1.1 Background

Rubber and plastics together as the polymer products industry over the last decade exceeds 17 % growth rate and the industry export turn over in the year 2006 only has exceeded US\$ 650 million. Polymer was selected as one of the ten potential areas for investment in Sri Lanka.¹ The year 2003 the production of raw natural rubber in Sri Lanka was 92,000 metric tons. Typical annual consumption of latex by the latex industry in Sri Lanka is of the order of 18,000 to 20,000 metric tones. Of this 80-85 % is utilized by the glove industry. Almost the entire production of gloves is exported and consequently the industry contributes significantly to foreign exchange earnings.^{1,2}

Rubber is an important material with many practical applications and is characterized by long-range elasticity. Elasticity is the ability of a material to return to its original shape when load causing deformation is removed.³⁶ This property is obtained after the vulcanisation process, where a plastic polymer is transformed into an elastic material by formation of a three-dimensional network of cross-links that connect the polymeric chains.

Accelerated sulfur vulcanization is the key step in rubber industry that prepares a wide range of useful rubber products. The vulcanization process involves heating a mixture of sulphur, accelerator, activator and an unsaturated polymer material. This results in the formation of sulfur bridges or cross-links between polymer molecules, which account for the elasticity and durability of rubber.

The prime function of organic accelerators is to speed up the rate of vulcanization. By adding a few parts of an organic accelerator, the vulcanisation time can be reduced significantly. The properties of a vulcanized rubber are determined by the type of accelerator.^{1, 3, 4} Latex accelerators are usually the metallic and amine dialkyl dithiocarbamates.^{1, 3, 4} Dithiocarbamates were first used as accelerators in 1919; these were and are still the most active accelerators with respect to both cross linking rate and extent of cross link formation.³ Although a considerable range of dithiocarbamates are available, it is probably true to say that zinc diethyl dithiocarbamates (ZDEC, ZDC) is by far the most widely used of the dithiocarbamates, indeed of all latex accelerators.^{1,3}

Zinc oxide (ZnO) acts as an activator to boost the effect of accelerators. ZnO is known as the best activator for sulphur vulcanization and exact activator role of ZnO is highly dependent on the type of accelerator present in the vulcanization system.^{1,3,4,5}

Although many researches have proposed mechanisms of sulfur vulcanization, up to date, the basic steps for accelerated sulfur vulcanization proposed by Morrison and Porter in 1984, have been accepted.^{1, 4, 5, 6, 7} Based on this mechanism, the role of the

zinc oxide used in the latex vulcanization is thought to be to react with dithiocarbamic acid and with thiuram disulphides, which are by-products of the cross-linking steps, to regenerate accelerator. Zinc oxide thus prevents vulcanization coming to a premature halt due to depletion of accelerator.¹

The degree of dispersion, particle size and specific surface area are parameters of paramount importance for the activity of ZnO.^{5, 6, 4} In commonly used active zinc oxides the mean particle size is decreased to increase the specific surface area, which results in an easier and better dispersion and a higher reactivity. The higher activity is probably due to the increased accessibility of Zn²⁺ ions at the surface compared to the conventional particle sizes. One of the latest and probably most promising developments, however in this field is the use of nano ZnO. Wei⁵ investigated the effect of nano sized ZnO on the physical properties of NR/BR (natural rubber/butadiene rubber) blend compound. It was found that with nano ZnO the physical properties are significantly improved, particularly the abrasion resistance, and tear strength. Heideman⁵ claims that, with EPDM (terpolymer of ethylene, propylene and diene), and SBR (styrene-butadiene rubber), only one tenth of the amount of nano ZnO is necessary to achieve the same cure characteristics compared with conventional ZnO.⁵

1.2 Aims of This Project.

The first aim of this project is to study the effect of nano ZnO on the NR latex vulcanisation. In this study, bulk ZnO replaced by nano ZnO as the activating species at equivalent loadings and foreshows to achieve all/few or single of the followings.

- Significant improvements in the physical properties with nano ZnO at equivalent loadings to conventional ZnO.
- Effect of reduced loadings of nano ZnO in order to minimize the impact on the environment and to minimize the cost of production.
- In the final vulcanized compound various forms of zinc ions can be present. A part can still be present as ZnO without underwent of accelerator regeneration. Nano ZnO claims to possess inherent antimicrobial, antifungal, UV filtering and self-cleaning properties.¹⁰ Hence when nano ZnO is used as curing activator, it would introduce mentioned properties inherently.

The next aim is to study the possibility of nano zinc aluminate spinel (ZnAl₂O₄) as curing activator. To the best of our knowledge, no work has ever been published to understand the effect of ZnAl₂O₄ spinel on the rubber vulcanization; neither solid rubber nor latex. Some metal oxides behave synergistically with ZnO.⁵ Hence studies on spinel zinc aluminate as activator would be an interesting subject. To study this, probably a maiden aspect it was synthesized three samples of ZnAl₂O₄ with different morphology, and purity.

NANO ACTIVATORS FOR NATURAL LATEX

CHAPTER 2

LITERATURE REVIEW

2.1 Nanotechnology.

2.1.1 Introduction to nanotechnology.

The term 'nano' is used to mean one billionth. e.g. a nanometer is a billionth of a meter (10^{-9} m). For comparison, a red blood cell is approximately 7,000 nm wide and a water molecule is almost 0.3 nm across.

'Nanotechnologies are the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale (atomic, molecular, and macromolecular scale) that produces structures, devices, and systems with at least one novel/ superior characteristic or property'.¹¹

2.1.2 Properties of the nanoscale.

At nano scales the ordinary rules of physics and chemistry no longer apply. For instance, materials' characteristics, such as their colour, strength, conductivity and reactivity, can differ substantially from the macroscale, due to two reasons.^{11, 12, 13, 14}

(I) Surface area

Nanomaterials have a relatively larger surface area when compared to the same mass of materials produced in a larger scale. As the surface area of a material increase, the portion of its constituent's atoms at or near the surface increases exponentially, creating more sites for bonding, catalysis or reaction with surrounding materials. This can make materials more chemically reactive (in some cases materials that are inert in their larger scale are reactive when produced in their nanoscale scale), and affect their chemical and physical properties.

(II) Quantum effects

Quantum effects can begin to dominate the behavior of matter at the nanoscale-particularly at the lower end (1-100 nm) - affecting the optical, electrical and magnetic behavior of materials.

2.1.3 Synthesis of nanomaterials.

Materials can be produced that are nanoscale in one dimension (for example, very thin surface coatings) or in two dimensions (for example, nanowires and nanotubes) or in all three dimensions (for example, nanoparticles, and quantum dots) by two fundamentally different approaches, termed "top down and bottom up".^{11, 12, 13, 14}

(I) Top down manufacturing

Macro scale systems are converted into nanoscale ones by a series of sequential reduction operations to remove the unwanted portions away from the object that is wanted.

Through this manufacturing process spend (relatively much) energy, use (sometimes very toxic) chemicals, produce (often quite a bit of) waste, need a lot of patience (these processes are relatively slow) and often the results are quite unique and not easily replicable. Material removing is done by employing ultra-precision engineering techniques. This can be carried out by any one or more of the following processes: etching, milling, diamond cutting, electrical discharge machining, laser machining, ion beam machining, and various nanolithographic processes (optical, X-ray, ion and electron) and nanoimprinting for patterning of nanometer size features. The most common top down fabrication technique is nanolithography and is fundamental to silicon chip manufacturing.^{11, 12, 13, 14}

(II) Bottom up manufacturing

Building structures atom by atom or molecule by molecule. Bottom up manufacturing is based on atomic or molecular manipulation, offers a way forward to construct shapes, devices and nanomachines with molecular precision. A number of approaches can be taken to achieve bottom-up manufacturing. These include chemical synthesis, self-assembly and positional assembly.^{11, 12, 13, 14}

One bottom-up method is nature's way: self-assembly. Self-organizing processes are common throughout nature and involve components from the molecular (e.g. protein folding) to the planetary scale (e.g. weather systems) and even beyond (e.g. galaxies). The key to using self assembly as a controlled and directed fabrication process lies in designing the components that are required to self-assemble into desired patterns and functions.

Exploiting nature's self-assembly tricks - together with chemical synthesis is real science and it's happening in labs already. For an example, the self assembling properties of biological systems, such as DNA molecules, can be used to control the organization of species such as carbon nanotubes, which may ultimately lead to the ability to 'grow' parts of an integrated circuit, rather than having to rely upon expensive top down' techniques.¹³

Positional assembly is man's way, there use tools to move each atom or molecule individually. Although this positional assembly offers greater control over construction, it is currently very laborious and not suitable for industrial applications.