SYNTHESIS OF NANO-SILICA FROM NATURAL RESOURCES AND APPLICATIONS

LIBRARY UNIVERSITY OF MORATUWA, SRI LANKA MORATUWA

Wijenayaka Mudiyanselage Gayan Indika Priyadarshana

(108030F)



Department of Chemical and Process Engineering

University of Moratuwa

Sri Lanka

April 2013

106913

University of Moratuwa
106913

CD-ROM

DECLARATION OF THE CANDIDATE AND SUPERVISOR

I declare that this is my own work and this thesis does not incorporate without acknowledgement any material previously submitted for a degree or diploma in any university or other institute of higher learning and to the best of my knowledge and belief it does not contain any material previously published or written by another person except where the acknowledgement is made in the text.

Further I hereby grant the University of Moratuwa the right to archive and to make available my thesis or dissertation in whole or part in the university libraries in all forms of media, subject to the provisions of the current copyright act of Sri Lanka. I retain all property right to use in future works (Such as articles or books) all or part of this thesis or dissertation.

Signature	Date:
Signature	Date.

I have supervised and accepted this thesis for the award of the degree.

University of Moratuwa, SPanka. Electronic Theses & Dissertations

Dr. W. A. P. Jeewantha Premaratnet. ac.lk

Senior Lecturer,

Dept. Of Chemistry,

University of Kelaniya

Date:

Senior Lecturer,

Dept. Of Chemical and Process Engineering,

University of Moratuwa

ACKNOWLEDGEMENT

I acknowledge with gratitude the Sri Lanka Institute of Nanotechnology (SLINTEC) for giving me the opportunity to conduct this project with full financial support along with National Science Foundation while providing the access for its valuable high end equipment facilities.

I am grateful to Dr. W. A. P. Jeewantha Premaratne and Dr. (Mrs.) S. H. P. Gunawardena, my supervisors who very generously spent their precious time to provide necessary guidance and assistance to carry out this task.

I also extend my gratitude and thank to Dr. Asitha Siriwardena at SLINTEC, providing me with all necessary guidance in carrying out this project.

Further I wish to sincerely thank Mr. Dileepa Premathunga and Mr. Sunanda Gunasekara at SLINTEC who helped me in numerous ways to complete my project successfully.

I am also thankful to all my colledgues ad SEANTEC for encouragement.

Electronic Theses & Dissertations

www.lib.mrt.ac.lk

W. M. G. I. Priyadarshana

Abstract

A fast growing interest in applying nanomaterials in various fields has been observed in recent years. Nano-silica is one of the widely used nanomaterials in adhesives, fiber optic strands, sealants, surface coatings, defoamers, cosmetics, food additives, cement-based building materials and rubber composites. As an agricultural country, Sri Lanka produces tones of paddy husk annually. The benefit of using paddy husk has been identified in many applications. Paddy husk is burnt to generate energy resulting paddy husk ash (PHA). PHA is rich in silica (~60 %) and can be an economically viable raw material for the production of nano-silica through chemical method as a value added product. Also Sri Lanka has highly pure vein quartz (~98%) which can be converted in to nano-silica. In this research, nano-silica was prepared by precipitation method from both PHA and vein quartz and characterized by various analytical techniques. Scanning electron micrographs showed that nano-silica particles from both resources were in the agglomerated form (primary particle size 50-70 nm). The particle shape was found to be spherical. X-ray diffractograms showed a strong broad peak at 22 ° (20) indicating that the obtained products from both starting materials were amorphous and also the Infrared spectra data supports the presence of hydrogen bonded siling groups and silexane groups in silica. Silica nanoparticles were surface modified by office acid and characterized using TGA and www.lib.mrt.ac.lk FT-IR techniques.

Reinforcing ability of the synthesized nano-silica from PHA (NS) in natural rubber composites (NRNS) was investigated. Cure characteristics and mechanical properties of the NRNS nanocomposites were compared with that of commercial grade silica (PS) reinforced natural rubber composites (NRPS) and it was found that NS has lower reinforcing ability compared to that of PS.

Key Words: PHA, Vein quartz, nano-silica, surface modification, nanocomposites

TABLE OF CONTENT

DECLARATIONi
ACKNOWLEDGEMENT ii
Abstractiii
TABLE OF CONTENTiv
LIST OF FIGURESvii
LIST OF TABLESx
LIST OF ABBREVIATIONS AND SYMBOLSxi
CHAPTER 11
1. INTRODUCTION1
1.1 Introduction to silica
1.1.1 Crystalline silica
1.1.2 None crystalline (amorphous) silica
(a) Continuous randominetwork of depratuwa, Sri Lanka. 4 Electronic Theses & Dissertations (b) Microcrystalline modellib mrt. ac. lk. 4
1.2 Nano-silica
1.3 Methods for synthesis of nano-silica
1.3.1 Paddy husk ash as a renewable resource
1.3.2 Vein quartz as an earth resource
1.4 Applications of nano-silica
1.4.1 Application of nano-silica as reinforcing filler in rubber composites 13
1.5 Research objectives
CHAPTER 2
2 LITERATURE REVIEW

	2.1 Synthesis of nano-silica by various raw materials	17
	2.2 Surface modification	21
	2.3 Applications of nano-silica	22
2	HAPTER 3	24
3.	. EXPERIMENTAL	24
	3.1 Characterization Techniques	24
	3.1.1 Fourier Transform Infrared Spectroscopy (FT-IR)	24
	3.1.2 Powder X-ray Diffraction (PXRD)	25
	3.1.3 Thermo Gravimetric Analysis (TGA)	26
	3.1.4 Particle Size Analysis	26
	3.1.5 Scanning Electron Microscopy (SEM)	28
	3.1.6 Energy Dispersive X-ray Spectroscopy	29
	3.1.7 Cure Characterization of rubber composites	29
	3.1.8 Evaluation of mechanical properties of vulcanized rubber composites	30
	(a) Tensile properties iversity of Moratuwa, Sri Lanka.	
		30
	(a) Tensile properties (a) Tensile properties (a) Tensile properties (a) Electronic Theses & Dissertations	30
	(a) Tensile properties Electronic Theses & Dissertations (b) Hardness www.lib.mrt.ac.lk	30
	(a) Tensile properties Electronic Theses & Dissertations (b) Hardness www.lib.mrt.ac.lk 3.2 Methodologies	31
	(a) Tensile properties of Moratuwa, Sri Lanka. Electronic Theses & Dissertations (b) Hardness www.lib.mrt.ac.lk 3.2 Methodologies 3.2.1 Characterization of Paddy Husk	31
	(a) Tensile properties iversity of Moratuwa, Sri Lanka. Electronic Theses & Dissertations (b) Hardness www.lib.mrt.ac.lk 3.2 Methodologies 3.2.1 Characterization of Paddy Husk (a) Elemental and Thermal Analysis of Paddy Husk	3131313131
	(a) Tensile properties (b) Hardness (c) Hardness (d) Hardness (e) Hardness (e) Hardness (f) Hardness (g) Hardness (h) Ha	30 31 31 31 32
	(a) Tensile properties iversity of Moratuwa, Sri Lanka. Electronic Theses & Dissertations (b) Hardness www.lib.mrt.ac.lk 3.2 Methodologies 3.2.1 Characterization of Paddy Husk (a) Elemental and Thermal Analysis of Paddy Husk (b) Ash Analysis of Paddy Husk 3.2.2 Characterization of Paddy Husk Ash	31 31 31 32 32
	(a) Tensile properties versity of Moratuwa, Sri Lanka. Electronic Theses & Dissertations (b) Hardness 3.2 Methodologies 3.2.1 Characterization of Paddy Husk (a) Elemental and Thermal Analysis of Paddy Husk (b) Ash Analysis of Paddy Husk 3.2.2 Characterization of Paddy Husk Ash 3.2.3 Characterization of vein quartz	303131313232
	(a) Tensile properties ity of Moratuwa, Sri Lanka. Electronic Theses & Dissertations (b) Hardness	30313131323232

(a) Optimization of silane coupling agent for NRPS and NRNS composites	.34
(b) Cure characteristics and mechanical properties of NRPS and NRNS	
composites	
4. RESULTS AND DISCUSSION	39
4.1 Characterization of Paddy Husk	. 39
(a) Elemental and Thermal Characterization of Paddy Husk	. 39
(b) Ash Analysis of Paddy Husk	
4.2 Characterization of Paddy Husk Ash (PHA)	. 42
4.3 Characterization of vein quartz	45
4.4 Synthesis of nano-silica from PHA	48
4.5 Synthesis of nano-silica from vein quartz	54
4.6 Surface modification of nano-silica	57
4.7 Application of nano-silica in rubber composites as a reinforcing filler	63
4.7.1 Characterization of commercial grade precipitated silica (PS)	63
4.7.2 Optimization of the silane coupling agent for NRPS and NRNS compos	sites
Electronic Theses & Dissertations	
www.lib.mrt.ac.lk 4.7.3 Effects of silica loading on cure characteristics and mechanical properti	
of NRPS and NRNS composites	72
(a) Cure characteristics	72
(b) Mechanical properties	77
CHAPTER 5	82
5. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORKS	82
5.1 Conclusions	82
5.2 Recommendations for future works	83
REFERENCES:	. 84

LIST OF FIGURES

Figure 1. 1: Interrelationship between forms of silica	2
Figure 1. 2: Arrangement of Si and O atoms in crystalline silica	3
Figure 1. 3: Three-dimensional schematic diagram of crystalline silica structure	
Figure 1. 4: Arrangement of Si and O atoms in non-crystalline (amorphous)	
silica	5
Figure 1. 5: Types of silanol groups exist on the silica surface	6
Figure 1. 6: Surface modification and functionalization of silica nanoparticles	6
Figure 1. 7: The paddy producing regions in Sri Lanka	.10
Figure 1. 8: Vein quartz deposits of Sri Lanka	.12
Figure 3. 1: Bruker Vertex 80, Fourier Transform Infrared Spectrophotometer	25
Figure 3. 2: D8 Focus X-ray powder diffractometer at	25
Figure 3. 3: TA Instruments SDTQ600	26
Figure 3. 4: Malvern Zetasizer analyzer nano ZS (size range, 0.6 nm – 6 μm	27
Figure 3. 5: FRITSCH, ANALYSETTE 22 MicroTec plus laser particle size	
analyzer (size range, 0.08 μm to 2,000 μm)	27
Figure 3. 6: HITACHI SU6600 iScanning Electron MicroScope (SEM)	28
Figure 3. 7: Moving Dic Rheometer (MDR. Ekiron, Pictor)	29
Figure 3. 8: (a) Elastocon AB Specimen Cutting Press, EP 08 and (b) dumbbell	
shape specimen.	30
Figure 3. 9: (a) Bareiss digitest hardness meter and (b) Test specimen for	
measure the hardness	31
Figure 3. 10: Haake Rheomix 600, laboratory scale Internal Mixer	35
Figure 3. 11: (a) Two-roll mill and (b) Hot press	35
Figure 4. 1: Paddy Husk sample used in this study	39
Figure 4. 2: Spectral image of paddy husk	40
Figure 4. 3: TGA/ DTG thermogram of paddy husk.	41
Figure 4. 4: EDX Spectrometric data of PHA after burning at 700 °C	43
Figure 4. 5: SEM image of PHA after burning at 700 °C	44
Figure 4. 6: PXRD pattern of PHA after burning at 700 °C	44
Figure 4. 7: PXRD pattern for natural vein quartz (from GSMB, Sri Lanka)	45



Figure 4. 8: FT-IR Spectrum of vein quartz (from GSMB, Sri Lanka)	47
Figure 4. 9: PXRD patterns of (a) silica prior to HCl acid treatment, (b) silica	
after acid treatment followed by a washing cycle, (c) nano-silica	
(PHA) and (d) nano-silica (standard)	49
Figure 4. 10: FT-IR Spectra of (a) nano-silica (PHA) and (b) nano-silica	50
Figure 4. 11: TGA and DTG thermagrams of (a) silica prior to HCl acid	
treatment, (b) silica after acid treatment followed by a washing	
cycle, (c) nano-silica (PHA) and (d) nano-silica (standard)	52
Figure 4. 12: Scanning Electron Microscopic images of the nano-silica	
obtained from PHA	53
Figure 4. 13: Particle size distribution of nano-silica powder obtained from	
PHA	54
Figure 4. 14: FT-IR spectra of (a) vein quartz, (b) nano-silica (from vein	
quartz) and (c) nano-silica (standard)	55
Figure 4. 15: PXRD pattern of (a) vein quartz, (b) nano-silica prior to wash, (c)	
nano-silica (from vein quartz) and (d) nano-silica (standard)	56
Figure 4. 16: Scanning Electron Microscopic images of (a) ground vein quartz	
and (band c)mano-silica (from yein quartz)ri Lanka.	57
Figure 4. 17: FT-(Repectra of (a) offer a lacid and (b) is fer lacid modified nano-	
silica www.lib.mrt.ac.lk	58
Figure 4. 18: TGA and DTG thermograms of (a) nano-silica, (b) pure oleic acid	
and (c) nano-silica modified with oleic acid	60
Figure 4. 19: Particle size distribution of oleic acid modified nano-silica	
dispersion in different time intervals	61
Figure 4. 20: Transmission Electron Micrograph (TEM) of oleic acid modified	
silica nanoparticles	62
Figure 4. 21: Particle size distribution of commercial grade precipitated silica	63
Figure 4. 22: PXRD pattern of commercial grade precipitated silica	64
Figure 4. 23: FT-IR spectrum of commercial grade precipitated silica	64
Figure 4. 24: Variation of maximum torque and $(M_{H}-M_{L})$ in (a) NRPS and (b)	
NRNS composites against the addition of Si69	66

Figure 4. 25: Variation of scorch time and optimum cure time of (a) NRPS and	
(b) NRNS composites against the addition of Si69	.67
Figure 4. 26: Variation of minimum torque of (a) NRPS and (b) NRNS	
composites against the addition of Si69	.68
Figure 4. 27: Tensile modulus of (a) NRPS (b) NRNS composites as a function	
of Si69 content	.70
Figure 4. 28: Tensile strength and hardness of (a) NRPS (b) NRNS composites	
as a function of Si69 content	.71
Figure 4. 29: Vulcanization curves of NRPS and NRNS composites with	
different loadings of precipitated silica (PS) and nano-silica	
(NS)	.74
Figure 4. 30: Comparison of minimum torque of NRPS and NRNS composites	.75
Figure 4. 31: Comparison of scorch time of NRPS and NRNS composites	.76
Figure 4. 32: Comparison of optimum cure time of NRPS and NRNS	
composites	.77
Figure 4. 33: Comparison of (a) 100 %, (b) 300 % and (c) 500 % modulus of	
NRPS and NRNS composites	.78
Figure 4. 34: Comparison of tensile strength of NRPS and NRNS composites	.79
Figure 4. 35: Comparison of hardness of TRPS and NRNS tomposites	.80

LIST OF TABLES

Table 1. 1: Chemical composition of paddy husk ash	9
Table 3. 1: Compositions in parts per hundred rubbers (phr) of NRPS	
vulcanizate containing different concentrations of Si69	36
Table 3. 2: Compositions in parts per hundred rubbers (phr) of NRNS	
nanocomposite vulcanizate containing different concentrations of	
Si69	36
Table 3. 3: Compositions in phr of NRPS vulcanizate containing different	
loading of PS	37
Table 3. 4: Compositions in phr of NRNS nanocomposite vulcanizate	
containing different loading of NS	.38
Table 4. 1: Elemental compositions of the paddy husk	40
Table 4. 2: Ash analysis data of Paddy Husk	.42
Table 4. 3: Elemental composition of the PHA after burning at 700 °C	.43
Table 4. 4: PXRD peaks obtained for vein quartz	.46
Table 4. 5: EDX analysis data of vein quartz	.46
Table 4. 6: Elemental analysis of the samples at different steps of the process	.48
Table 4. 7: Elemental analysis of weini quartz and mano-silica (from Vein quartz)	.55
Table 4. 8: Cure characteristics of NRPS composites with different loadings of	
Si69 www.lib.mrt.ac.lk	.65
Table 4. 9: Cure characteristics of NRNS composites with different percentages	
of Si69	.65
Table 4. 10: Cure characteristics of NRPS composites with different loadings of	
PS	.72
Table 4. 11: Cure characteristics of NRNS composites with different loadings of	
NC	72



LIST OF ABBREVIATIONS AND SYMBOLS

% Percentage

°C Degree Celsius

A Angstron

ASTM American Society for Testing and Materials

cm Centimeter

CTAB Cetyltrimethylammonium bromide

DI Deionized

DTG Derivative Thermogravimetric Analysis

EDX Energy Dispersive X-ray analysis

FT-IR Fourier Transform Infrared Spectroscopy

g Gram

GSMB Geological Survey and Mines Bureau

Hz Hertz

ICDD International Centre for Diffraction Data

IPPD N-isopropyl-N'-phenyl-p-phenylenediamine

kV

M

Ukilo Moltsy of Moratuwa, Sri Lanka.

Kleatrapic Theses & Dissertations

M₁₀₀ www.lib.mrt ac lk Modulus at 100% elongation

M₃₀₀ Modulus at 300% elongation
 M₅₀₀ Modulus at 300% elongation
 MBTS Mercaptobenzthiazole disulfide

MDR Moving Die Rheometer

mg Milligram

 M_H Maximum Torque $M_{H^+}M_L$ Torque difference

ml Milliliter
mm Millimeter
Mt Metric Tons
nm Nanometer

NR Natural Rubber

NRNS Natural Rubber/ Nano-Silica (from PHA)

NRPS Natural Rubber/ Commercial grade precipitated Silica

NS Nano-Silica

PDF Portable Document Format

PEG Polyethyleneglycol
PHA Paddy Husk Ash

phr Parts per Hundred Rubber

PS Precipitated Silica

PU Polyurethane

PXRD Powder X-ray Diffraction rpm Revolutions per minute

RSA Rice Straw Ash

RSS Ribbed smoked sheet
SDS Sodium dodecyl sulfate

SEM Scanning Electron Microscope

SiO₂ Silica

SLINTEC

Tc90

TEM

Stinkarks Institute of Nanotechnologyka.

Electronic Theses & Dissertations

www.lib.mrt.ac.lk

Transmission Electron Microscope

TEOS Tetraethylorthosilicate

TGA Thermo Gravimetric Analysis/ Analyzer

T_{s2} Scorch time

USA United State of America

wt% Weight percentage

 $\lambda \hspace{1cm} Wavelength$

μm Micrometer