EFFECT OF HIGH PURITY RICE HUSK SILICA SYNTHESISED USING SOLVENT-THERMAL TREATMENT METHOD ON THE PROPERTIES OF NATURAL RUBBER COMPOUNDS

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FACULTY OF SCIENCE UNIVERSITI MALAYA KUALA LUMPUR

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EFFECT OF HIGH PURITY RICE HUSK SILICA SYNTHESISED USING SOLVENT-THERMAL TREATMENT METHOD ON THE PROPERTIES OF NATURAL RUBBER COMPOUNDS

ABSTRACT

In recent years, research on bio-based materials, such as rice husk is steadily gaining momentum. Despite their huge developmental potential, rice husks are often left unutilised following the harvesting season, wasting a natural wealth that could be explored. Their high silica content makes them potential fillers to replace commercial precipitated silica (PS) in the rubber industry. For first series, highly pure silica with small particle size and high surface area was extracted from rice husks via solvent-thermal treatment, followed by leaching with different concentrations of hydrochloric acid (HCl). This treatment method was modified from TAPPI T204 (2007) and TAPPI T264 (1997) standards, which are used for wood extraction in the pulp and papermaking industry. For second series, characterisation on treated rice husk silica (RHS) was conducted. RHS that was leached with 1.0 M HCl recorded the highest particle purity with 99.99% of SiO₂ content and the highest BET surface area of 234.25 m²/g compared with RHS leached with 0.01 M, 0.1 M, 2.0 M, and 3.0 M HCl. All RHS samples were in the amorphous state following incineration at 700°C for 4 hours. For third series, RHS sample with the highest purity was incorporated in NR compounds at 2, 4, 6, 8, and 10 parts per hundred rubber (phr). Even without surface modification, the RHS-filled NR compounds showed improvements in strength-related properties at the optimum loading of 4 phr. The thermal stability of the NR compounds had also improved with RHS addition. The properties of the RHS-filled NR compounds were further enhanced following RHS surface modification with silane coupling agents. Surface modification is vital to improve the compatibility between the hydrophilic RHS and the hydrophobic NR by making RHS hydrophobic, which reduced the filler-filler interaction. This transformation had also

increased the cure rate of the rubber compounds because the silane-modified RHS stopped reacting with cure activators and accelerators, consequently increasing the cure efficiency. In fourth series, three types of silane coupling agents with different functional groups, which are namely; bis[3-(triethoxysilyl)propyl]tetrasulfide (TESPT), (3mercaptopropyl)trimethoxysilane (MPS), and (3-aminopropyl)triethoxysilane (APTES) were used to modify RHS surface. The modified RHS samples were incorporated in NR at the optimum loading of 4 phr. The increased reinforcing efficiency due to the strong rubber-filler interaction greatly improved the mechanical, thermal, and dynamic mechanical properties of all silane-modified RHS-filled NR compounds. However, TESPT led to the most outstanding performance of the RHS-filled NR compound compared with the other two alkoxy-based silanes, in terms of cure characteristics, overall strength-related properties and thermal stabilities. In fifth series, the effectiveness of RHS as a filler was compared to PS. Both types of silica were modified with TESPT and incorporated in NR at 4 phr loading. The performance of RHS as a filler was equivalent to PS in most properties. This shows that RHS synthesised using the solvent-thermal treatment method is suitable to be used as NR filler.

Keywords: Solvent-thermal treatment method, rice husk silica, curing characteristics, mechanical properties, thermal properties.

KESAN SILIKA SEKAM PADI BERKETULENAN TINGGI YANG DISISTESISKAN MELALUI KAEDAH PENGOLAHAN PELARUT-TERMA TERHADAP SIFAT-SIFAT SEBATIAN GETAH ASLI

ABSTRAK

Beberapa tahun kebelakangan ini, penyelidikan mengenai bahan berasaskan bio, seperti sekam padi semakin berkembang. Walaupun ia berpotensi untuk dimajukan, sekam padi sering dibiarkan selepas musim menuai, lalu membazirkan kekayaan semula jadi yang boleh diterokai. Kandungan silika yang tinggi di dalam sekam padi menjadikannya berpotensi sebagai pengisi untuk menggantikan mendakan silika komersial (precipitated silica, PS) di dalam industri getah. Untuk Siri 1, silika yang sangat tulen dengan saiz zarah kecil dan luas permukaan yang tinggi diekstrak daripada sekam padi melalui pengekstrakan pelarut-terma, diikuti dengan proses larut-lesap dengan kepekatan asid hidroklorik (HCl) yang berbeza. Kaedah pengolahan ini diubahsuai daripada piawaian TAPPI T204 (2007) dan TAPPI T264 (1997) yang digunakan dalam pengekstrakan kayu di dalam industri pembuatan pulpa dan kertas. Untuk Siri ke-2, pencirian terhadap silika sekam padi (rice husk silica, RHS) terawat dijalankan. RHS yang dilarut-lesap dengan 1.0 M HCl mencatatkan ketulenan zarah tertinggi dengan 99.99% SiO₂ dan luas permukaan BET tertinggi pada 234.25 m²/g, berbanding dengan RHS yang dilarut-lesap dengan 0.01 M, 0.1 M, 2.0 M, dan 3.0 M HCl. Kesemua sampel RHS berada dalam keadaan amorfus selepas pembakaran pada 700°C selama 4 jam. Untuk Siri ke-3, sampel RHS dengan ketulenan tertinggi digabungkan dengan sebatian NR pada 2, 4, 6, 8, dan 10 bahagian per seratus getah (per hundred rubber, phr). Walaupun tanpa pengubahsuaian permukaan, sebatian NR yang digabung dengan RHS menunjukkan peningkatan sifatsifat yang berkaitan dengan kekuatan pada pemuatan optimum iaitu 4 phr. Kestabilan terma sebatian NR juga meningkat dengan penambahan RHS. Sifat-sifat sebatian NR yang digabungkan dengan RHS dipertingkatkan lagi selepas pengubahsuaian permukaan

RHS menggunakan agen pengganding silana (silane coupling agent). Pengubahsuaian permukaan adalah penting untuk meningkatkan kesesuaian antara RHS yang hidrofilik dengan NR yang hidrofobik dengan menjadikan RHS hidrofobik, yang kemudiannya mengurangkan interaksi pengisi-pengisi. Transformasi ini juga meningkatkan kadar pematangan sebatian getah kerana RHS yang diubahsuai dengan silana berhenti bertindak balas dengan pengaktif dan pencepat pematangan, seterusnya meningkatkan kecekapan pematangan. Dalam Siri ke-4, tiga jenis agen pengganding silana dengan kumpulan berfungsi yang berbeza, iaitu bis[3-(triethoxysilyl)propyl]tetrasulfide (TESPT), (3mercaptopropyl)trimethoxysilane (MPS), dan (3-aminopropyl)triethoxysilane (APTES) digunakan untuk mengubahsuai permukaan RHS. Sampel RHS yang diubahsuai digabungkan dengan NR pada pemuatan optimum 4 phr. Peningkatan kecekapan pengukuhan yang disebabkan oleh interaksi pengisi-getah yang kuat meningkatkan sifat mekanikal, terma, dan sifat mekanik dinamik kesemua sebatian NR yang digabungkan dengan RHS terubahsuai dengan silana. Bagaimanapun, TESPT menghasilkan prestasi yang paling cemerlang dalam sebatian NR yang digabungkan dengan RHS berbanding dengan dua lagi silana berasaskan alkoksi daripada segi ciri-ciri pematangan, keseluruhan sifat berkaitan kekuatan, dan kestabilan terma. Dalam Siri ke- 5, keberkesanan RHS sebagai pengisi dibandingkan dengan PS. Kedua-dua jenis silika ini diubahsuai dengan TESPT dan digabungkan dengan NR pada pemuatan 4 phr. Prestasi RHS sebagai pengisi menyamai PS dalam kebanyakan sifat. Ini menunjukkan bahawa RHS yang disintesiskan menggunakan kaedah pengolahan pelarut-terma adalah sesuai digunakan sebagai pengisi NR.

Kata kunci: Kaedah pengolahan pelarut-terma, silika sekam padi, ciri pematangan, sifat mekanikal, sifat terma.

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LIST OF SYMBOLS AND ABBREVIATIONS

%	:	Percent
θ	:	Theta
<i>a*</i>	:	Red/green coordinate (in colour analysis)
<i>b</i> *	:	Yellow/blue coordinate (in colour analysis)
°C	:	Degree Celsius
E'	:	Storage modulus
E_b	:	Elongation at break
ΔE^*	:	Total colour difference
L^*	:	Lightness symbol (in colour analysis)
<i>t</i> 90	:	Optimum cure time
ts ₂	:	Scorch time
tan <i>δ</i>	:	Tangent delta
T_g	:	Glass transition temperature
Al ₂ O ₃	:	Aluminium oxide
APTES	:	(3-Aminopropyl)triethoxysilane
BaO	:	Barium oxide
BET	:	Brunauer Emmett Teller
$C_6H_8O_7$:	Citric acid
Ca	:	Calcium
CaO	:	Calcium oxide
CB	:	Carbon black
CBS	:	N-Cyclohexyl-2-benzothiozole sulfenamide
Cl	:	Chlorine
cm ⁻¹	:	Reciprocal centimeter
cm ³ /g	:	Cubic centimeter per gram

CO ₂	:	Carbon dioxide
CPPD	:	n-cyclohexyl-n'-phenyl-4-phenylenediamine
Cr_2O_3	:	Chromium (III) oxide
CuO	:	Copper (II) oxide
DMA	:	Dynamic mechanical analysis
dNm	:	Deci Newton meter
DTG	:	Derivatives thermogravimetric
ENR	:	Epoxidized natural rubber
Fe	:	Iron
Fe ₂ O ₃	:	Iron (III) oxide
FESEM	:	Field Emission Scanning Electron Microscopy
FTIR	:	Fourier-transform infrared spectroscopy
g/ml	:	Gram per mililiter
h	:	hour
H_2SO_4	:	Sulphuric acid
HC1	:	Hydrochloric acid
HDPE	:	High density polyethylene
HNO ₃	÷	Nitric acid
Hz	•	Hertz
IRHD	:	International Rubber Hardness Degrees
ISO	:	International Organisation for Standardisation
K	:	Potassium
K ₂ O	:	Potassium oxide
KBr	:	Potassium bromide
kV	:	Kilovolt
М	:	Molar

m^2/g	:	Meter square per gram
MDR	:	Moving die rheometer
M_{H}	:	Maximum torque
μm	:	Micrometer
min.	:	Minute
M_L	:	Minimum torque
mm	:	Milimeter
Mn	:	Manganese
MnO	:	Manganese oxide
MPa	:	Megapascal
MPS	:	(3-Mercaptopropyl)trimethoxysilane
Mt.	:	Montmorillonite
N_2	:	Dinitrogen
Na	:	Sodium
Na ₂ SO ₄	:	Sodium sulphate
NaOH	:	Sodium hydroxide
NH ₂	:	Amide
NiO	:	Nickel (II) oxide
nm	•	Nanometer
NR	:	Natural rubber
-OH	:	Hydroxide
phr	:	Per hundred rubber
PS	:	Precipitated silica
RH	:	Rice husk
RHA	:	Rice husk ash
RHS	:	Rice husk silica

SBR	:	Styrene butadiene rubber
Si-69	:	Bis[3-(triethoxysilyl)propyl]tetrasulfide
SiO ₂	:	Silicon dioxide
SMR	:	Standard Malaysian Rubber
T _{25%}	:	Decomposition temperature at 25% weight loss
T5%	:	Decomposition temperature at 5% weight loss
T50%	:	Decomposition temperature at 50% weight loss
T _{75%}	:	Decomposition temperature at 75% weight loss
TAPPI	:	Technical Association of the Pulp and Paper Industry
TEA	:	Toluene, ethanol and acetone solvents mixture
TEM	:	Transmission Electron Microscopy
TESPT	:	Bis[3-(triethoxysilyl)propyl]tetrasulfide
TG	:	Thermogravimetric
TGA	:	Thermal gravimetric analyser
TiO ₂	:	Titanium dioxide
T _{max}	:	Maximum thermal decomposition temperatures
wt.%	:	Weight percent
XRD	:	X-ray diffraction
XRF	÷	X-ray fluorescence
ZnO	:	Zinc oxide

CHAPTER 1: INTRODUCTION

1.1 Research Background

Raw rubber, as received from rubber fields or plantations, has limited uses due to its poor overall performance. The strength-related properties of the unvulcanised state of natural rubber are completely insufficient to meet the requirements of typical applications of rubber, such as rubber hoses, tubes, cables, tire treads, and automotive parts. Abrasion resistance, tensile strength, rebound resilience, and hardness are properties that can be developed by mixing raw rubbers with various compounding ingredients prior to vulcanisation.

Vulcanised rubber that contains the necessary ingredients for the vulcanisation process is known as unfilled, or gum vulcanisate. Gum rubber compounds generally show poor mechanical and physical characteristics, as well as poor processability. Thus, the addition of fillers is necessary to overcome these shortcomings. The role of fillers as the compounding ingredients in rubber compounds is threefold; to lower the cost of the end products, to modify the processing performance, and for reinforcing purpose. Two general classes of fillers that are used in rubber industry are carbon black and mineral fillers, which include calcium carbonate, clay, and silica (Samsuri, 2013).

Amorphous silica has been used as a filler in the rubber industry for decades. A variety of silica sources has been explored including sodium silicate from quartz, or sand, and from tetraethoxysilane and tetramethoxysilane (Hassan et al., 2014; Jang et al., 2009). However, the production of pure silica by smelting quartz and sand at 1300°C is energy intensive (Faizul et al., 2013; Liou & Yang, 2011), while tetraethoxysilane and tetramethoxysilane to have high toxicity (Baccile et al., 2009; Hassan et

al., 2014). Therefore, researchers are seeking alternatives for silica from other natural sources including biomass wastes. Rice husk is one of the agricultural wastes that has inevitably attracted researchers due to its abundance and low in cost (Dominic et al., 2013).

The process of milling paddy would yield 70% rice as the main component, with byproducts of 20% rice husk, 8% rice bran, and 2% rice germ (Nagendra et al., 2011). Based on statistics, Malaysia produces approximately 2.6 million metric tonnes of paddy per year (Department of Agriculture, 2014). Considering that 20% of paddy production is husks, a total of 0.5 million metric tonnes of this biomass waste can be obtained. Due to the abundance of rice husks from paddy production, the current disposal methods of field dumping and open burning have led to environmental issues and serious health problems (Alshatwi et al., 2015). Thus, researchers are searching for productive ways to utilise rice husks in industrial applications, such as for ceramic products, additives for concrete and other building materials, and additives in rubber compounds. The utilisation of rice husks in the rubber industry is quite promising because rice husk ash was reported to have high silica content (Dominic et al., 2013; Noushad et al., 2012). Approximately 20% of rice husk ash can be obtained upon combustion of rice husks. Rice husk ash contains 80% to 95% of silica, with trace amounts of metallic impurities (Soltani et al., 2015).

Many studies have been conducted to synthesise silica from rice husks, considering that rice husk silica shows tremendous strength-related properties when incorporated in polymer composites (Ginting et al., 2014; Chen et al., 2021). To date, various processing methods have been developed to synthesise silica from rice husk, including precipitation method (Khorsand & Masoomparast, 2012; Liou & Yang, 2011; Noushad et al., 2012; Selvakumar et al., 2014; Thuadaij & Nuntiya, 2008), sol-gel method (Dominic et al., 2013; Hassan et al., 2014; Le et al., 2013), and calcination (Gu et al., 2015a; Gu et al.,

2015b). However, each method had different limitations that restricted it from further development.

In this study, high purity silica was synthesised from rice husks using a solvent-thermal treatment method with different concentrations of acid for leaching. This method was adopted from Technical Association of the Pulp and Paper Industry (TAPPI) standard (T204 and T264), with some significant modifications. Hydrochloric acid (HCl) was used in the leaching process because HCl treatment could effectively remove metallic impurities in rice husks better than other acid treatments, such as nitric and sulphuric acids (Soltani et al., 2015). The produced ultrafine silica was characterised and incorporated in the matrix of natural rubber as filler. The optimum loading of rice husk silica (RHS) in natural rubber (NR) was determined. The influence of silane coupling agents on the interaction between RHS and the NR matrix was also analysed. Comparisons, in terms of cure characteristics, mechanical properties, and thermal behaviour between RHS and commercial precipitated silica (PS) as fillers in NR, were also conducted.

1.2 Problem Statement

Most silicas are manufactured from quartz, or sand using the extraction process. However, this manufacturing process leads to high energy consumption (Faizul et al., 2013). Silica can also be produced from tetraethoxysilane and tetramethoxysilane through hydrolysis reaction, but the required reagents have high toxicity (Hassan et al., 2014; Liou & Yang, 2011). Therefore, the production of silica from natural sources like biomass wastes is required as an alternative to commercial silica. At present, rice husks are discarded in land fields, or burned in the open, leading to air pollution and serious health issues. Consequently, researchers are attempting to optimise the value of the residues. Due to high silica content (approximately 15-20%), rice husks have become the ultimate alternative of silica source that can be used as fillers in rubber products manufacturing (Marin et al., 2015).

Rice husk contains several metallic impurities, such as Fe, Na, Mn, K, and Ca. These impurities can reduce the purity and surface area of the resulting silica. Several treatment methods are available for synthesising pure rice husk silica by removing these notorious metallic impurities, namely, chemical precipitation, thermal pyrolysis, sol-gel method, and calcination (Dominic et al., 2013). Among these methods, precipitation with acid and the dissolution of sodium silicate from rice husks is the preferred way to produce silica. Although high purity silica can be achieved using this method, the complicated process and large chemical consumption prevent this method from undergoing further development (Gu et al., 2013). Silica obtained from sol-gel methods was also reported to have high purity and homogeneity. However, the synthesis process based on the low-temperature hydrolysis was time-consuming (Gu et al., 2015a).

In contrast, the calcination process is more cost-effective due to its stable performance. By taking into account all of the restrictions from previous researches, Gu et al. (2015b) introduced a novel technique by combining pyrolysis and calcination method to produce silica from rice husks. Through this two-stage thermal synthesis method, with controllable surface areas and pore volumes, different levels of purity can be achieved. However, the complex procedures of preparing the rice husks and the various stages of pyrolysis prior to calcination make this method the least popular. In addition, this method is impractical for high volume production of silica as it takes longer and requires high energy consumption.

Therefore, a simple and practical method for producing high purity silica, with high surface area from rice husks, is vital since silica is on demand for many industrial applications, such as fillers to produce various rubber products. The main interest of this research was to synthesise high purity silica from rice husks using a simple solvent-thermal treatment, which was modified from a treatment method for wood in pulp and paper making industries. The limited knowledge and understanding of this method makes it a novel approach to explore.

Although several attempts have been made to synthesise silica from rice husks, the effect of RHS fillers on rubber compounds has not been extensively studied. Knowledge on the properties of silica as a filler in a rubber matrix is very important to prove the usefulness of the RHS in rubber industries. A major issue with silica-reinforced natural rubber is the incompatibility between the hydrophilic silica, due to the presence of surface silanol groups, and the hydrophobic natural rubber, causing the formation of a strong silica-silica network due to the low rubber-filler and high filler-filler interaction. This is detrimental to the reinforcing capability of the silica particles on the rubber matrix. Silica particles also tend to agglomerate and re-agglomerate, which are caused by the –OH groups on the silica surface. This condition creates rubber compounds with inferior properties (Dominic et al., 2013). An established method for improving the reinforcement effect in rubber compounds is to treat the silica surface with silane coupling agents to promote interactions between silica particles and rubber chains (Chen et al., 2013). Thus, an extensive study on the effect of silane coupling agent on the RHS and on the rubber compounds is required to ensure better results are obtained.

1.3 Research Objectives

The main objectives of this research are:

- to synthesise high purity silica from rice husks using a solvent-thermal treatment (modified from TAPPI standard: T204 and T264), with different concentrations of acid leaching;
- 2. to characterise the structural behaviour, surface morphology, size, surface area, and composition of the RHS particles using XRD, FESEM, BET, TEM, FTIR, and XRF;
- 3. to determine the optimum value of RHS filler in NR compounds;
- to analyse the influence of different functional groups of silane coupling agents used in modified RHS-filled NR compounds; and
- 5. to compare the properties of RHS-filled NR with commercial PS-filled NR.

Cure characteristics (minimum torque, maximum torque, scorch time, and optimum cure time), mechanical tests (tensile, hardness, resilience, abrasion, and swelling test), thermal tests (DMA and TGA), and morphology tests (FESEM) were conducted to justify the third, fourth, and fifth objectives.

1.4 Research Significance

Silica (SiO₂) is an outstanding non-black filler used specifically to produce coloured rubber products. Its ability to give low heat built-up and lower rolling resistance make it suitable to be used in the production of green tire thread (Rattanasom et al., 2007). However, the production of commercial pure silica requires intensive energy and the silica source was reported to have high toxicity (Faizul et al., 2013; Hassan et al., 2014). Due to these restrictions, local silica sources from biomass residues found in rice husks would be the best alternative.

Rice husk ash contains about 90-98% of silica (Hassan et al., 2014). By processing rice husks into synthesised silica, the greenhouse effect and pollutions due to out-dated disposal methods of field dumping and openly burning rice husks can be reduced (Dominic et al., 2013). Because of its greater availability, low cost, and non-toxicity, RHS is an appropriate alternative to replace commercial synthetic silica, to be used in a wide range of applications, such as medical additives, constructions, adsorption materials, and fillers in polymer materials. Its amorphous state and high surface area (Hassan et al., 2014) makes it even more attractive as the reinforcing filler in rubber compounds.

There is no detailed study on the process of treating rice husks using the solventthermal treatment method, which in this study, was modified from the treatment used for wood in pulp and paper making industries. This solvent-thermal treatment method is safer and requires simpler equipment because it is operated at atmospheric pressure in an open system, and at a temperature of no higher than the boiling point of the solvents. According to TAPPI standards T204 and T264, a combination of polar and non-polar solvents (e.g., toluene, ethanol, acetone, or benzene) can remove the extractive compounds that comprise of fats, waxes, fatty acids, and other phenolic compounds, which are known to have negative impact on the strength properties of paper (Sefara & Birkett, 2004). This method would also be beneficial for eliminating approximately 2-5% of extractive compounds in rice husks during the first stage of the pre-treatment process. Acid leaching process, on the other hand, is crucial in the process of synthesising silica from rice husks, to remove the notorious metallic impurities that will affect the surface area and purity of the resulting silica.

1.5 Thesis Outline

This thesis consists of eight (8) chapters and the contents are summarised as follows;

Chapter 1 comprises of the research background, the problem statement, the research objectives, and the significance of this research. A brief description on the research method is also summarised in this chapter.

Chapter 2 delivers a brief description of the different classes of rubber and filler, and the important steps in rubber processing, including the mixing and curing process. The compounding additives and their function are also briefly described. The main focus of this chapter is to review the various methods to synthesise rice husk silica (RHS) conducted by previous researchers, the characteristics of the resulting RHS, and the role of coupling agents in the surface modification of the RHS. The application of RHS as filler in polymer composites is also reviewed in this chapter.

Chapter 3 describes the materials, research equipment, and research activities involved. It covers the synthesis and modification techniques to obtain RHS with different functional groups of silanes, the mixing and compounding of the NR compounds, as well as all testing standards and procedures.

Chapter 4 describes the characteristics and physical properties of the obtained RHS by using the solvent-thermal treatment method.

Chapter 5 discusses the effect of adding purified RHS in NR compounds as fillers, in terms of the cure characteristics, and the mechanical, physical, and thermal properties.

Chapter 6 discusses the influence of different functional groups of silane coupling agents in modified RHS-filled NR compounds, in terms of the dispersion and reinforcing

efficiency of the RHS. The influence of the coupling agents on other properties, such as mechanical and thermal properties are also covered.

Chapter 7 discusses the comparative study between RHS-filled NR compounds and commercial precipitated silica (PS)-filled NR compounds. The discussion focuses mainly on the cure characteristics, mechanical, and thermal properties of each compound.

Chapter 8 summarises the findings of the research work. The conclusions are based on the findings and several recommendations for future work and development are suggested in this chapter.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction to Rubber

Rubbers are non-conductive polymeric materials, which are waterproof, elastic and flexible. When force is applied on the rubber molecules, the rubber chains will tend to stretch out in the direction of the force and spontaneously return to its original state once the force is released (Hernández et al., 2015). Rubber is a significant material in everyday life, particularly in engineering applications such as tire and automotive manufacturing, and for the production of latex-dipped products. Rubber can be classified into two categories; natural rubber and synthetic rubber.

2.1.1 Natural Rubber

Natural rubber (NR) is obtained from *Hevea brasiliensis* tree that was first found in the Amazon rainforest in 1830. NR is harvested in the form of sticky, milky white liquid called latex in a process called tapping. It is mainly poly-cis-isoprene containing rubber hydrocarbon and traces of impurities like protein, organic and inorganic metal ions in the phase of serum. Table 2.1 displays the composition of field NR latex.

Constituent	Content (%)
Rubber hydrocarbon	30–40
Water	55–65
Proteins	1.9–2.5
Fat and related compounds	0.9–1.0
Sugars (carbohydrates)	1.0–1.5
Ash	0.4–0.6

 Table 2.1: Composition of field NR latex (Source from Ghosh, 2011)

NR can be purchased either in latex form or dry rubber form. After tapping, the latex is then preserved and transported to the factories to produce latex-dipped goods such as surgical and examination gloves, balloons and condoms. Concentrated latex can also be coagulated and processed into bale by the addition of chemical ingredients under strictly controlled procedures to produce Standard Malaysian Rubber (SMR) latex grade such as SMR L for the production of surgical and pharmaceutical products and SMR CV for automotive components, bridge bearings and mechanical mountings, especially for engines and machinery. Field grade rubbers (i.e., SMR 5, SMR 10, SMR 20) are produced from field coagulum such as cup lump, tree laces, bark scrap, and ground scrap, mainly for the production of tires, inner tubes, footwear and moulded products (Akay, 2012; Blackley, 1997; Samsuri, 2009).

Rubbery behaviour is shown by many polymeric materials. NR holds a unique place in rubber technology due to its outstanding tack and strength in the unvulcanised state and high tensile strength, abrasion resistance and crack growth resistance exhibited by its vulcanisates.

2.1.2 Synthetic Rubber

Synthetic rubber is an artificial elastomer synthesised from petroleum, coal, oil, natural gas, and acetylene. Synthetic polyisoprene can be manufactured with most of the properties comparable to those of natural rubber with a purity of 98–99%. However, the stress stability, process ability and other properties like tackiness and adhesiveness of synthetic polyisoprene are still less satisfying than those of natural rubber (Ali Shah et al., 2013). The various types of synthetic rubbers available in market now are styrene-butadiene rubber (SBR), acrylonitrile-butadiene copolymers or nitrile rubber (NBR),

butyl rubber (IIR), ethylene-propylene (EPDM), and polychloroprenes (neoprene/CR). The structures of the commonly used rubbers are shown in Figure 2.1.



Figure 2.1: Structures of common elastomers (Source from Ciullo, 1996)

2.2 Rubber Processing

In rubber processing, compounding and mixing are two different terms. Compounding refers to the decision making on the types of elastomers, together with the types and quantities of the compounding ingredients to be used to achieve the requirements of the products. The requirements involve the properties of the compound during subsequent processes of shaping or curing, and the mechanical, physical and chemical properties of the final products. Mixing, on the other hand, focuses on the type of machinery, equipment and instrumentation to be used according to the formulation given. It also comprises all parameter settings such as temperature, speed, time, pressure, and cycle,
together with the methods to produce a well-mixed compound. In summary, compounding is deciding on what to mix, while mixing is determining on how to mix it (Ghosh, 2011).

2.2.1 Rubber Mixing and Curing Process

Rubber mixing involves high-intensity kneading, and shearing of rubber and ingredients in a closed mixing chamber, which is also known as the internal mixer or on an open mill. The main objective of this process is to ensure the ingredients and additives are all dispersed and distributed well within the rubber compounds at minimal cost, time and energy usage, so that the rubber compounds will be cured efficiently in the next process and possess significant properties for the final product application. There are four mechanisms of the mixing process, which are the incorporation, dispersion, distribution, and plasticisation:

- 1. Incorporation, or also known as wetting, is the first step in mixing, where the compounding ingredients are added in sequence in the mixer or mill to the masticated rubber to form a coherent mass.
- 2. Dispersion is the stage where filler agglomerates are fractured and reduced to smaller sizes.
- 3. Distribution is a homogenisation stage, where all compounding ingredients that have been added are randomly distributed all over the mass of the mix.
- 4. Plasticisation is where the viscosity of the mix is reduced as the plasticisers efficiently lubricate the mix.

During storage, natural rubber will experience further increment of viscosity and molecular weight due to cross-links that form between the polymer chains and nonpolymeric constituents. To achieve optimum homogenisation, it is required to reduce the viscosity of the rubber before mixing process. The reduction of rubber viscosity can be done by the combination of shear and heat that effectively forms chemical and physical changes of the rubber (Johnson, 2001). The breakdown process of the molecular chains by exposing the rubber to high mechanical shearing action is known as mastication. Masticated rubber has low viscosity; it is softer and flows more easily than the unmasticated rubber (Ghosh, 2002). Mastication can be conducted effectively at temperatures below 55°C in an open mill or above 130°C in an internal mixer by thermal-mechanical shearing action (Johnson, 2001).

Due to the high viscosity and elastic nature of rubber, strong, durable and sturdy machinery like internal mixers and open mills is required to attain optimum homogenisation of rubber and the compounding ingredients. An internal mixer consists of two horizontal rotors, which are placed in a casing in a closed chamber, as in Figure 2.2. During mixing, rubber and compounding ingredients are added through the hopper at the top, and the hydraulic ram will press the ingredients through the rotors. The mixing happens between the rotors and the body of the casing. Unlike in an open mill, the mastication and mixing occur only in the nip area between the two rolls. The front and the back rolls of the two-roll mill rotate at different speed, known as the friction ratio. Usually, the back roll rotates faster to force the compound to stay on the front roll and allow shearing action to take place at the nip of the rollers. According to Ontsuka & Toh (2015), rubber mixes and makes contact with the compounding ingredients at the bank on top of the nip and the rubber is milled when it passes through the nip, as in Figure 2.3.



Figure 2.2: Features of an internal mixer



Figure 2.3: Features of a two-roll open mill

In general, the internal mixer is more powerful and can perform mixing at higher speed with shorter time compared to the two-roll open mill. However, to prevent scorching effects, the main vulcanising agents like sulphur and accelerator are usually added at a later time in a two-roll mill. Even though mixing is done using an internal mixer, the discharge of irregular lumps of the rubber compound still need to pass through a two-roll mill to obtain a thinner sheet form of compound to ease further processing (Ghosh, 2011). To ensure optimum dispersion and distribution of the mix, homogenisation step is essential during the mixing process. Based on the ISO standards, SMR homogenisation methods consist of passing the sheet of rubber compound 10 and 6 times, respectively, through the nip, in which they are set to 1.3 mm and 1.6 mm, respectively, between the rolls of a two-roll mil. As emphasised by Kim et al. (2007), the homogenisation step is an important parameter to determine the rubber compound quality, especially between different batches.

After mixing, rubber compounds exhibit viscoelastic behaviour. Viscoelastic properties of an uncured rubber largely depend on the properties of the base polymer and types and amounts of additives used. The uncured rubber compounds have poor physical properties; mostly are soluble in suitable solvents and easily deformed due to the separate rubber chains that are distinct from one another. Therefore, vulcanisation process or curing is needed to link the inter-mingled rubber chains by chemical bonds to produce an elastic three-dimensional network, which is not easily deformed.

Curing or cross-linking process is a chemical and irreversible process for rubber. Sulphur curing systems are the most widely used in rubber industry due to their ability to generate cross-links with the diene rubbers. Sulphur curing systems are usually assisted by other chemical additives, namely, accelerators, activators and retarders. Accelerators and activators are added to increase the rate of cross-linking reaction and boost the reaction, respectively, while retarders are able to delay the initiation of the cross-linking reaction to reduce premature vulcanisation. Balancing the combination of these multicomponent curing systems to give the ideal cure characteristics for the process and the required properties is crucial and apparently a complicated phase. The compounder must ensure that the cross-linking does not happen during the mixing and milling process and at temperatures below which no curing should occur. Conversely, rapid and complete curing should take place above that certain temperature, depending on the behaviour of the rubber compound. Failing to do so will not only complicate the further processing, but will also affect the physical properties and surface appearance of the final product. Therefore, it is necessary to determine the effect of temperature on the scorch and cure rates, especially for a newly developed compound. The information can be gained from the two most common tests, namely, Mooney viscometer, and rheometer or also known as the curemeter, to determine just how scorchy a compound really is. ASTM D1646 requires a temperature of 120°C for Mooney, while ASTM D2084 specifies a test temperature of 160°C for rheometers. Rheometer test measures is resistant to deformation during complete curing cycle, thus higher test temperature is used to cure the compound fairly rapidly (Johnson, 2001).

2.2.2 Rubber Formulation and Compounding Ingredients

Developing a rubber formulation with the correct type of elastomers and compounding ingredients or additives is very critical to meet certain qualities in terms of performance and durability of the end products. With a wide range of natural and synthetic elastomers together with abundant types of additives with different functions and roles, there is no specific standard of formulations that can fully guarantee the precise qualities of the product.

Rubber product manufacturers all over the world are not restricted to create their own formulations, they can compete with each other to market their own products with certain values. To develop a formulation, numerous trial batches need to be compounded for various in-lab testing. The best formulation will further proceed for a factory evaluation, meaning that a prototype will be produced based on the formulation and will be tested according to the exact production scale. Poorly designed formulation with either wrong choice of elastomers and additives or incorrect manufacturing practices will contribute to the product failure that lead to the significant cost and loss. Therefore, selection of right elastomers and compounding ingredients together with correct manufacturing procedures are very crucial.

Theoretically, a rubber compound consists of an elastomer, either natural or synthetic rubber, and a cross-linking agent. However, practically, a rubber compound may be comprised of five or more ingredients and additives, depending on the purpose of the final products, applications and their service performance. Each ingredient has a specific function that may affect the processability, properties and cost. Table 2.2 shows some basic compounding ingredients with their function(s). A rubber formulator or compounder is facing a critical challenge to develop a high quality rubber product at the lowest cost possible. Knowledge on the function and effectiveness of each compounding ingredient together with the hands-on compounding experience are indispensable to achieve this objective (Samsuri, 2009).

Ingredients	Main Function(s)	Amount (pphr)
Elastomer / Rubber	Impart flexibility and rubbery properties	100
Zinc oxide	Activator, cross-linking agent	3–5
Stearic acid	Activator, processing additive	1–3
Filler	Reinforce and modify physical properties, impart certain processing properties, or reduce cost	Varies
Antidegradant	Protection against heat and oxidative ageing	1–3
Antiozonant	Protection against ozone cracking and flex cracking	1–3
Accelerator	Speed up vulcanisation reaction	0.1–3
Sulphur, peroxide, metallic oxide, amines and resins	Cross-linking agent	0.1–5
Oil (aromatic, napththenic, parafinnic)	Softener, processing additive	5–50

 Table 2.2: Basic rubber compounding ingredients (Source from Samsuri, 2009)

For most types of services, relatively large amounts of materials known to increase hardness, stiffness, strength, and abrasion must be present in any given formulation. These include materials like carbon blacks, calcium silicates, precipitated calcium carbonates and clays; these materials are commonly known as fillers. Fillers are used to overcome the shortcomings of poor process ability while improving and modifying both the mechanical strength and physical properties of the vulcanised rubber. Apart from these two roles, fillers are incorporated into rubbers for cost reduction. Among these fillers, carbon black is second only to rubber as the most critical and widely used raw material in the rubber industry. When fine particles of carbon black are incorporated into the rubber, the physical properties and resistance to mechanical failure are greatly improved.

2.3 Filler

The subject of fillers reinforcement in vulcanised rubber is very wide and complex among rubber technologists and researchers. Unfilled rubber, also known as gum vulcanisate, is vulcanised rubber that contains ingredients necessary for vulcanisation or curing process. The use of fillers as compounding ingredient in rubber mixes is threefold. Firstly, they are added to the mix for the cheapening of the compound, that is to lower the cost of the final products. The cost of fillers used in the rubber industry is usually below than that of the polymers. Secondly, fillers are added to the rubber during mixing to modify the processing performance since fillers have a major influence on most aspects of the processing behaviour of the rubbers. Apparently, gum mix rubber compounds show poor processing characteristics such as giving high extrudate swell and high calender shrinkage. Thirdly, there are those fillers that are added to the compound for reinforcing purposes (Rothon, 1995; Samsuri, 2013). The term reinforcement has been extensively used by rubber technologists to denote the enhancement of strength and strength-related properties such as abrasion resistance, hardness and modulus (Rattanasom & Prasertsri, 2009; Samsuri, 2013). Particulate fillers that enhance mechanical strengths like tensile strength, tear strength and abrasion resistance are termed as reinforcing fillers. Those particulate fillers that do not enhance mechanical strengths but reduce the compounding cost are classified as diluents or nonreinforcing fillers, while semi-reinforcing fillers are used to control hardness and modify other physical properties of the rubber compounds for applications where very high tensile and abrasion resistance are not critical (Carli et al., 2011; Praveen et al., 2009; Zhao et al., 2012).

2.3.1 Classification and Characterisation of Fillers

The classification of fillers for rubbers (Figure 2.4) varies considerably according to the nature of the product. Users of fillers must be quite clear of the fact that no two fillers are the same. All fillers increase the hardness, modulus and stiffness of vulcanised rubber, whether or not they are reinforcing or non-reinforcing ones (Ali Shah et al., 2013).



Figure 2.4: Classification of fillers (Source from Samsuri, 2013)

The main characteristics of fillers that will influence the properties of the vulcanised rubber are particle size, particle surface area, particle shape, and its surface activity. The reinforcing effect of filler in rubber compound would be better if the particle size of the filler is small. The sizes of filler particle can be categorised as follows:

1.	>10,000 nm (10 µm)	: Degradants
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- 2. 1000–10,000 nm $(1-10 \ \mu m)$: Diluents
- 3. 100–1000 nm (0.1–1 μm) : Semi-reinforcing
- 4. 10–100 nm (0.01–0.1 μm) : Reinforcing

The specific surface area of the materials is practically determined by Brunauer– Emmett–Teller (BET) method (Kreyling et al., 2010). Filler particles sized between 10– 100 nm is categorised as reinforcing fillers, where they possess high surface area with more contact area available to interact with the rubber matrix. The strong rubber-filler interaction offers tremendous improvements in stiffness and strength with a minimal loss in impact and crack resistance in rubber compounds. Presumably, the surface area of the filler particles is higher if the particle size is smaller. This situation can improve the interactions between the rubber and filler particles. If the size of the filler particles is bigger than the distance of the inter-chain in polymer, an area of localised stress would be formed, leading to the elastomer chain rupture on stretching and flexing. A filler must make an intimate contact with the rubber chains if it is going to reinforce the rubber-filler compound. Fillers with a larger surface area have more contact area available, and consequently, they have a higher potential to reinforce the rubber chains (Mujkanovi et al., 2009; Samsuri, 2013).

The particle shape also plays a significant role in its ability to divert stress applied to the elastomer. The basic particle shapes of mineral fillers are shown in Figure 2.5, along with their typical aspect ratios (the measure of their anisometry).



Figure 2.5: Basic particle shapes of fillers (Photo sourced from Mujkanovi et al., 2009)

For needle- and fibre-shaped fillers, the aspect ratio is the ratio of length to diameter, while for other platy fillers, it is the ratio of the diameter of a circle with the same as the face of the plate to the thickness of the plate. In general, anisometric particles (those having a significant difference in length versus width) are more effective as reinforcement than isometric particles (those similar in length and width). Particles with a planar shape have more surface area available for contact with the rubber matrix than isotropic particles do with an equivalent particle diameter (Mujkanovi et al., 2009; Samsuri, 2013).

A filler can have high aspect ratio, high surface area and small particle size, but still provide poor reinforcement if it has low specific surface activity. Surface activity denotes the ability of the surface filler to bond with the rubber matrix. Non-polar fillers are best suited to non-polar elastomers, while polar fillers work best in polar elastomers. Beyond this general chemical compatibility is the potential for reaction between the elastomer and active sites on the surface filler. Among the various fillers available, carbon black promotes an intimate contact with elastomers due to the presence of carboxyl and other functional groups in its particles. The non-black fillers generally offer less affinity and less surface activity toward the common elastomers. This can be compensated to a greater or lesser extent by certain surface treatments (Ciullo, 1996).

2.3.2 Conventional Fillers for Rubber Compounds

2.3.2.1 Carbon Black

Carbon black (CB) is the most extensively used, also the oldest reinforcing filler served for improving strength-related properties such as tensile and tear strength, modulus, hardness, abrasion, and wear characteristics. It has been discovered since the early 1900s and has been used virtually in all sorts of rubber products (Noordermeer and Dierkes, 2009). Approximately 90% of the CB production worldwide is used in tire industry (Praveen et al., 2009; Zhao et al., 2012).

CB is essentially elemental carbon in the form of fine amorphous particles, manufactured by various processing methods including furnace, thermal, channel, and lampblack. For CB-filled vulcanised rubber compounds, the reinforcement is mostly influenced by the nanoscale particle size, larger surface area and high specific surface activity that promote the extensive rubber-CB interactions (Zhao et al., 2012).

The addition of CB in the rubber compound imparts the monotonous black colour to the finished products (Chan et al., 2013). As the source of CB is petroleum, the preparation and processing of CB is quite hazardous (Praveen et al., 2009). Therefore, considerable research efforts are being carried out to discover any alternative fillers that are capable of reinforcing any specific elastomers as well as CB can.

2.3.2.2 Clay

Clay minerals from natural sources are widely used in numerous industrial applications, mostly as cheapening fillers. However, several decades ago, researchers discovered that a small amount of clay added as filler had resulted in additional benefits for the polymeric matrices, including the rubber ones. Layered silicate clays, such as montmorillonite (Mt), hectorite, halloysite and muscovite have been used to improve properties of the polymers due to their potentially high aspect ratios. In fact, their small sizes (typically <1 mm) combined with large specific surface areas allow the clay minerals, also known as nanoclay, to be in close contact with the rubber matrices for better rubber-filler interaction (Bergaya et al., 2013).

In that infinite family of layered silicates, Mt is a very well-known reinforcing filler for rubber nanocomposites due to its availability, environmentally friendly nature, and relatively low cost (Ansarifar et al., 2013). However, surface treatment and modification of clay silicates are necessary in order to improve the compatibility between the hydrophilic surface of the clay and the hydrophobic rubber matrix (Praveen et al., 2009). In addition, most researchers believe that the interlayer structure of the clay needs to be separated into individual platelets to achieve an intercalated structure in rubber compounds. The intercalation of polymer chains promotes clay exfoliation to ensure ultimate clay dispersion, which favours improvement in the properties of the polymers, as shown in Figure 2.6 (Galimberti et al., 2013).



Figure 2.6: Structures of polymer clay nanocomposites; a) Conventional composites, b) Intercalated nanocomposites, and c) Exfoliated nanocomposites (Photo sourced from Sengupta et al., 2007)

2.3.2.3 Silica

Precipitated silicas and silicates emerged in the early 1950s as fillers to white and coloured rubber products such as shoe soles and heels. In 1970s, silica gained commercial importance in mechanical rubber goods and heavy truck tires because of its ability to resist abrasion and enhance the adhesion of steel cord reinforcement with the rubber. These white reinforcing fillers not only provide an improved resistance to wear and tear for soles of athletic footwear, but are also able to decrease self-heating of technical rubber goods like seals and rubber hoses (Noordermeer & Dierkes, 2009). Until now, silica is widely used in ceramics, cosmetics, electronics, and polymer material industries. Because

of its superfine particle diameter, silica powders are also used as thickening and flattening agents, thermal insulators and composite fillers (Carmona et al., 2013). Table 2.3 summarises the approximate volume usage of amorphous silica in various industries.

Application	% of Silica (Tonnage)
Elastomers	50.1
Food and personal care	7.2
Agricultural products	5.5
Coatings	5.0
Adsorbents	4.9
Batteries	3.5
Plastics	3.2
Sealants	2.5
Anti-foams	1.9
Catalysts	1.8
Resins	1.8
Other miscellaneous	12.6

Table 2.3: Usage of amorphous silica in various applications (Source from Lázaro,2014)

Over the last decade, the largest breakthrough of precipitated silica, particularly in passenger car tires, has been discovered. The addition of easy dispersion silica as replacement of CB, combined with the suitable rubber types with proper coupling agent have provided a significant reduction in rolling resistance of tires and consequently, the reduction in fuel consumption of the vehicles. This new discovery of silica technology not only benefits the environment, but can also overcome the higher production cost of the tires due to complicated processing behaviour and high cost of raw materials (Noordermeer & Dierkes, 2009).

Silica is obtainable in both amorphous and crystalline forms and can be of natural origin or synthetically produced. Jal et al. (2004) mentioned that silica is a polymer of

silicic acid that consists of interlinked SiO₄ units in tetrahedral configuration with a general formula of SiO₂. Natural occurring silica from minerals such as quartz, cristobalite and tridymite are mostly available in crystalline phase, while silica that is extracted from plant like rice and bamboo is in the amorphous state (Liou & Wang, 2020). The different types of silica are summarised in Figure 2.7. Apart from these varieties, precipitated silica and fumed (pyrogenic) silica are being used for elastomer reinforcement (Wilson & Thomas, 2013).



Figure 2.7: Different types of silica (Source from Ciullo, 1996)

Funed silica is produced by flame hydrolysis of silicon tetrachloride. The chemical reaction (2.1) shows that almost all water formed is used for the hydrolysis, consequently, producing silica with relatively low bound water:

$$SiCl_4 + 2 H_2O \rightarrow SiO_2 + 4 HCl$$
(2.1)

Generally, fumed silica has less than 1.5 wt.% of adsorbed water (Noordermeer & Dierkes, 2009). Therefore, it comes with a fluffy powder form with a very low bulk density. Even though fumed silica provides smaller particle size that could give more reinforcement, they are occasionally used as fillers in rubber products. Not only are they more expensive than precipitated silica, but because of its light weight, the direct addition

to dry rubbers such as natural rubber and styrene butadiene rubber would be very challenging, as most of it would float in the air and cause significant loss of silica in the rubber compound (Prasertsri & Rattanasom, 2012). However, there were studies conducted to use fumed silica in the form of suspension to reduce such mixing problems. At present, the use of fumed silica is nearly exclusively limited to silicone rubber compounds.

Hydrated amorphous precipitated silica is produced by wet process, using alkaline silicate solutions, preferably water-soluble sodium silicate (water glass), as a starting material. Silica is precipitated from this solution by the addition of a mineral acid, such as sulphuric acid or hydrochloric acid. The chemical reaction involved in the process is described below:

$$Na_2SiO_3 + H_2SO_4 \rightarrow SiO_2 + Na_2SO_4 + H_2O$$

$$(2.2)$$

A by-product of this reaction is the sodium salt that needs to be washed out. The silica is then filtered and dried before it is ground into the required particle size. The process diagram of precipitated silica is shown in Figure 2.8.



Figure 2.8: Process diagram of precipitated silica (Photo sourced from Hewitt, 2007)

At the initial stage of precipitation process, small isolated particles called primary particles are formed. The size of the primary particles is only a few nanometres. The amount and size of these particles increase with time and start to form aggregates with a particle size of a few hundred nanometres, in which they are characterised by the Si-O-Si bonds between the primary particles; these bonds are irreversible. The aggregates then continue to grow and start to condense in an even larger size, presumably a few hundred micrometres, and are called as agglomerates. These agglomerates are held together by weak van der Waals forces and hydrogen bonds that are reversible, which can be broken down by mechanical treatment into the size of aggregates. According to Fruijtier-Pölloth (2012), these synthetic amorphous silicas can be categorised under the definition of nanostructured materials because of its having internal or surface structure at the nanoscale. The formations of primary particles, aggregates and agglomerates occur not only during the precipitation process, but also in pyrogenic process of fumed silica, as shown in Figure 2.9.





Silica can be characterised in terms of their particle dimensions, surface morphology and surface activity, while for elastomer reinforcing purposes, their bonding ability with coupling agents is considered. CB and silica have different surface chemistry, which affects the reinforcing efficiency of the rubber compound. The surface of CB is saturated with hydrocarbon functional groups that react with sulphur during curing and vulcanisation. The sulphur bonds not only link the rubber chains, but also tie the CB with the rubber. In contrast with CB, silica does not react with sulphur. The presence of silanol groups on silica surface promotes strong silica-silica networking, which induces particle aggregation following the agglomeration process. Besides silica particle agglomeration, its polar surface and hydrophilic character results in low compatibility with hydrocarbon rubber such as natural rubber and styrene butadiene rubber, which leads to poor dispersion and process ability (Sae-Oui et al., 2006; Surya et al., 2014). Therefore, coupling agents is used to modify the silica surface and improve the silica-rubber interaction.

2.3.2.4 Natural Fibres and Biomass Fillers

The search for non-petroleum-based fillers that are environmentally friendly, cheap, abundant, and renewable has steered the research into natural fibres and bio-based fillers from biomass. In recent years, natural fibres like jute fibre, kenaf fibre, bamboo fibre, cellulose fibre, coir fibre, sisal fibre, et cetera have been broadly used in NR compounds. However, natural fibres possess some disadvantages, such as quality variations, moisture absorbing and poor compatibility with the hydrophobic polymer matrix that limits their usage (Chen et al., 2013). Meanwhile, in some cases, bio-based composites show unique advantages over traditional inorganic particles. Commonly used bio-based fillers in NR are cellulose whiskers, chitosan, nanocrystals of starch, and extracted silica from rice husk and bamboo fibres. These natural sources of silica have recently attracted considerable attention as an alternative to the synthetic silica (Chan et al., 2013; Chen et al., 2013; Ch

The studies on these fillers are aimed at competitive production cost and equivalent properties as compared to other petroleum-based fillers. In addition, the biocompatibility and biodegradability of bio-based fillers are hoped to be retained after dispersion in the NR matrix (Chan et al., 2013).

2.4 Rice Husk Silica (RHS)

Rice is a staple food for the world population. Globally, over 700 million tonnes of rice are generated every year. Approximately 100 million tonnes of the amount is rice husk (Ugheoke & Mamat, 2012). Rice husk is a biomass residue from rice milling industry. It is the protective coat covering the outer layer of rice. Rice husks are essentially made up of organic and inorganic compounds, which comprise carbon-based plant polymers such as cellulose, hemicellulose and lignin, termed as lignocellulosic and silica. Rice plants naturally deposit amorphous silica in husks. Besides lignocellulosic materials and silica, rice husks also contain a small amount of soluble extractives and metallic oxides that are also known as alkali oxides. The percentage of the lignocellulosic components, silica, metal oxides, and other extractives are different according to the types and parts of the plants. Figure 2.10 showed the possible composition of each component in rice husk.



Figure 2.10: Composition of rice husk (Source from Dominic et al., 2013; Noushad et al., 2012)

Cellulose is a linear polymeric molecule with 7,000–15,000 glucose molecules per polymer. The cellulose microfibrils are formed by ordered linear polymer chains that are closely packed together, forming the crystalline region It is stable in room temperature due to the hydrogen bonds that exist between the molecules inside, as shown in Figure 2.11. Cellulose is hydrophilic and insoluble in water and most organic solvents. However, cellulose can react with water under a certain condition, where the oxygen bonds of water molecules break, causing the breakage of the long-chain cellulose into short-chain cellulose. When all oxygen bonds rupture, the cellulose transforms into glucose. The cellulose can be broken down into its glucose units by treating it with either acidic or alkaline solution. The reaction took place in three steps. At first, the water molecules may cause swelling to the cellulose. Then, the acidic or alkaline solution used may be infused in the crystalline region of the cellulose (Li, 2014).



Figure 2.11: Structure of lignocellulosic components in rice husk (Photo sourced from Li, 2014)

Hemicellulose is a low molecular weight, branched polymer with a series of polysaccharides. It contains shorter chains of 500–3,000 sugar monomers that include galactose, xylose, rhamnose, mannose, and arabinose. It is an amorphous matrix material that binds the stiff cellulose fibrils in place. Hemicellulose is more prone to hydrolysation than cellulose (mostly in acidic condition) due to its non-crystalline nature.

Lignin is a very irregular, amorphous cross-linked polymer derived from the phenylpropanoid compound. Compared to cellulose and hemicellulose, lignin is the toughest component that is insoluble in most solvents due to its high molecular weight and crystalline structure. Lignin is chemically bounded to cellulose and hemicellulose to provide rigidity and protection to the plant cell. The structure of lignin consists of aromatic "ring chains" that are randomly connected by ether and C-C linkages, which leads to extremely complex extraction and characterisation. The extraction of lignin from lignocellulosic components is conducted by breaking down the long polymer chains of lignin to low molecular weight by hydrolysing its ether bonds. Most of the delignification processes are conducted in either base-catalysed or acid-catalysed conditions.

The term plant extractive describes a group of low molecular weight organic compounds that are extractable from plants by means of combining the polar and non-polar solvents. The compounds consist of fat, fatty acids, terpenoids, waxes, sterols, steryl esters, and other phenolic compounds. The composition of extractives in plants differs, depending on the species. In rice husks, the composition of extractives is approximately 2-5%, as reported by most researchers.

The silica and metallic impurities are intermingled within the lignocellulosic components in the husk, which provide a solid protective barrier for the seed embryo within, as reported by Shen (2017) in Figure 2.12. Rice plants naturally absorb silica from

the soil and water. The extracted amorphous silica is then placed at the outer covering layer of rice seeds, which is known as rice husks. The silica provides protection to the germ or embryo within. In the rice milling process, the rice husks are removed, creating a waste disposal problem.



Figure 2.12: Silica in lignocellulosic component of rice husk (Photo sourced from Shen, 2017)

Based on the statistics from Malaysian Ministry of Agriculture, each year, about 0.4 million tonnes from the total amount of 2.6 million tonnes of rice production in Malaysia is rice husk (Department of Agriculture Peninsular Malaysia, 2014), resulting in a serious issue in waste management. Due to its unfavourable properties like low in nutrition, occupying large spaces and resistance to degradation, rice husks are left unutilised after harvesting, causing wastage of natural wealth that needs exploring. Rice husk is frequently dumped or burnt in landfills, causing serious air and soil pollutions that can potentially lead to serious health problems (Moraes et al., 2014). Rice husk ash was reported to have 90–98% silica content (Hassan et al., 2014). This discovery has attracted researchers to develop various techniques in obtaining high purity ultrafine silica

synthesised from rice husk. The resulted ultrafine silica can be utilised in numerous industrial applications such as thermal insulators, building materials, medical and laboratory devices, and composite fillers (Noushad et al., 2012).

The intensive energy used in the production of silica from sodium silicate hampers the large-scale production of silica for future use (Setyawan & Balgis, 2012). The current knowledge on the synthesised silica from rice husk as a substitute for commercial silica has recently attracted wide attention, motivated by the fact that these materials are cheap, less hazardous and abundantly available, thus making it preferable than the sodium silicate compounds.

2.4.1 Synthesis of RHS

The conventional manufacturing method of silica at industrial scale requires high intensity of mechanical, chemical and thermal operations, which significantly produce large amounts of effluent and pollutions (Faizul et al., 2013; Fernandes et al., 2017). Ma et al. (2012) have emphasised on the fact that the production of pure silica is from the reaction between quartz or sand with sodium carbonate at high temperatures, mostly at 1300°C to form sodium silicate. Sodium silicate, the precursor of silica, is then reacted with sulphuric acid to form silica. This method not only requires a large amount of energy, but also needs further purification, which finally contributes to environmental pollution (Ghorbani et al., 2015). Realising the importance of environmental sustainability, an intense research worldwide is currently being commenced to develop a not only environmentally-benign process, but also economically feasible method of obtaining silica from plant biomass such as the rice husk.

Numerous approaches of producing silica from rice husk that have been reported in literature were mostly sol-gel via the acid precipitation method and thermal pyrolysis. The term rice husk ash (RHA) was used by most researchers to define the ashes produced after the non-controllable incineration of untreated rice husk. RHA usually contains incomplete combustion of organic residues and a mixture of amorphous and crystalline silica, whereas rice husk silica (RHS) is used to define the products from the controllable incineration of treated rice husk. RHS generally contains low level of impurities compared to that of RHA (Chen, 2013). Different methods of producing RHS will give variables in the surface morphology, structure, size, and purity. Table 2.4 shows a list of previous studies on the synthesis method of obtaining silica from rice husk. In most synthesis methods, parameters such as incineration temperature, types and concentration of acid used for leaching, and the process flow significantly affect the properties of silica, especially in view of its purity, crystallinity, size, surface area, shape, and colour (Ugheoke & Mamat, 2012).

Authors, Year	Objective	Summary of method	Main findings on produced RH silica
Khoshnood Motlagh et al., 2020	To compare silica extracted from rice husk and rice straw	 Carbonized at 700°C for 1 h Treated with 1 M HCl at 80°C for 2 h Treated with 4 M K₂CO₃ aqueous solution Combusted at 1000°C for 1 h Treated with 1 M HCl at 80 °C Gel separation, washing, and aging for 3 h at room temperature, and oven drying 	 Amorphous silica nanosize particles (< 50 nm) were obtained

Table 2.4: Studies on methods used to synthesise silica from rice husk

Authors, Year	Objective	Summary of method	Main findings on produced RH silica
Kamari & Ghorbani, 2020	To extract highly pure silica from rice husk to be applied in the production of magnetic mesoporous silica	 Treated in 1-N solutions of HCl, HNO₃, H₂SO₄, and H₃PO₄ at 100°C for 1 h Combusted at 600°C for 6 h 	• Highest purity of silica obtained after leached with HCl with 95.48% silica content
Dhaneswara et al., 2020	To synthesise amorphous silica from rice husk ash by alkaline extraction followed by acidification	 Combustion at 700°C for 5 h Refluxed using 5% NaOH and 10% NaOH Acidification using 1 M HCl and 1 M CH₃COOH to produce silica gel Heated to 120°C for 12 h to produce silica 	 Higher concentration of NaOH with HCl acidification led to higher purity of RHA with 99.9% silica content
Suryana et al., 2018	To produce and characterise the crystalline silica from rice ash.	 Combustion at 300°C for 1 h Sintering at various temperatures: i) 900°C for 2 h ii) 1200°C, 1400°C and 1600°C at 6 h 	 Crystalline silica was formed at temperature above 1000°C with 95.11% silica content.
Halim et al., 2018	To obtain and characterise the amorphous precipitated silica and silica aerogel from RH as filler for the unsaturated polyester composite.	 Precipitated silica (PS): Incineration at 700°C until the white ash was obtained. Dissolved in NaOH at 90°C for 8–12 h to produce sodium silicate solution. Acid precipitation Hydrogels were crushed, washed and dried at 80°C for 24 h. Silica aerogel (SA): Incineration at 700°C until the white ash was obtained. 	• PS and SA were amorphous with BET surface area 130 m ² /g and 773 m ² /g, respectively.

Table 2.4, continued

Authors, Year	Objective	Summary of method	Main findings on produced RH silica
		 Dissolved in NaOH at 90°C for 8–12 h to produce sodium silicate solution. Acid precipitation Hydrogels were aged in water at 60°C for 1–2 days. Extraction with ethanol. Dried in sealed autoclave at 245°C with pressure 6.2 MPa. 	S
Moosa & Saddam, 2017	To prepare and characterise the silica nanoparticles from RH ash to be used as nanofiller in epoxy/SiO ₂ nanocomposites.	 Combustion at 400°C for 3 h. Leaching with 2 N HCl for 1 h. Incineration at 650°C and 750°C for 3 h. Refluxed with acid for 3 h. Extraction with NaOH to form sodium silicate at various mixing time: 10, 12, 14, and 16 h. H₂SO₄ added drop by drop until pH 8 and forming nanosilica gel. Washed until pH 7 and dried at 50°C for 48 h. 	 High purity silica (96%) with amorphous structure was obtained at 650°C At 750°C, the amorphous silica was transformed to alpha quartz, the stable state of crystalline silica. The best average particle size of the nanosilica was achieved at 14 h mixing time with NaOH, which is 53 nm.
Mahmud et al., 2016	To evaluate the effectiveness of two different acids, HCl and citric acid, in the process of producing high purity silica from RH	 Leaching with two different acids, 10% HCl and 10% w/v citric acid for 2 h. Incineration at 700°C for 2 h. 	 Both acid treatments (HCl and citric acid) produced the highest purity of silica at 99.76%. RH silica leached with HCl has a larger surface area (234.6 m²/g) compared to RH silica leached with citric acid (215.8 m²/g)

Table 2.4, continued

Authors, Year	Objective	Summary of method	Main findings on produced RH silica
Bakar et al., 2016	To determine the ideal acids and incineration temperatures in producing high purity amorphous silica form RH.	 Leaching with two different acids, 0.5 M HCl and 0.5 M H₂SO₄ at ~60°C for 30 min. Incineration at various temperatures: 500, 600, 700, 800, and 900°C for 2 h. 	 Completely amorphous silica was obtained at temperature below 900°C At 900°C, crystalline silica started to develop. Average particle size varied from 0.5 μm to 0.7 μm HCl-leached silica gave higher purity silica (99.58%) than H₂SO₄- leached silica (99.08%) at 600°C.
Sankar et al., 2016	To synthesise silica nanoparticles from three different types of rice husk ashes: sticky, red and brown.	 Combustion of RH in an open atmosphere. Leaching with 10% HCl for 2 h. Incineration at 700°C for 2 h. 	 Completely spherical and amorphous silica with high specific surface area was obtained.
Taku et al., 2016	To investigate the effect of the calcination temperature of rice to the resulting RH ash.	 Combustion at 400°C for 2 h. Leaching with 2 M nitric acid for 2 h. Incineration at various temperatures: 400, 500, 600, 700, and 800°C for 3 h. 	 The silica content increases as the incineration temperature increases. Metallic impurities were reduced and eliminated during calcination.

Authors, Year	Objective	Summary of method	Main findings on produced RH silica
Ismail et al., 2014	To study the phase transformation of RH silica produced at different firing temperatures.	 Incineration from room temperature to 700°C until 1200°C with a heating rate of 10°C /min. 	 Amorphous RH silica was formed at 700°C and 800°C. Crystalline RH silica formation occurred at 1100°C. Crystobalite, tridymite and quartz were the major phases present in the RH silica.
Ghorbani et al., 2015	To optimise the silica extraction procedure from RH and improve its purity by an environmental- friendly technique.	 Leaching with three different acid solutions of 1 N: HCl, HNO₃ and H₂SO₄. Incineration at 700°C for 6 h. Dissolved in 0.5 M NaOH at 100°C for 4 h to form sodium silicate solution. Acid precipitation with H₂SO₄. The gel was fragmented, filtered, washed, and freeze-dried overnight. 	 Completely amorphous, white and spherical silica nanoparticles with an average particle size of 200 nm were produced. Leaching with HCl followed by incineration produced highest purity amorphous silica (95.55%), compared to HNO₃ and H₂SO₄.
Hassan et al., 2014		 Incineration at 700°C for 4 h. Refluxed with 1.5 M HCl for 3 h at 120°C, filtered, washed and dried. Refluxed with 2.5 M NaOH for 4 h, filtered and washed. HCl added until pH is 2. 	 Amorphous and high purity silica (95.41%) produced Nanosilica produced with surface area 653 m²/g and size around 20–25 nm

Table 2.4, continued

Authors, Year	Objective	Summary of method	Main findings on produced RH silica
		 NH4OH added until pH is 8.7. Dried at 120°C. Ignited at 700°C for 3 h. 	 Nanosilica that were dried at 120°C before ignition showed separated particles, while after ignition, they were aggregated.

Table 2.4, continued

Most studies applied the sol-gel method with alkaline extraction, which produces sodium silicates, followed by acid precipitation to form nanosilica from rice husk. To produce high purity and completely amorphous silica, the rice husk needs to be leached with acid before subjecting to incineration at a temperature not more than 700°C for at least 3 hours. Higher incineration temperature, which is more than 700°C, is not advisable as crystalline phase silica will start to develop. According to the studies conducted by Moosa and Saddam (2017), XRD pattern of RHS that was incinerated at 650°C for 3 hours showed a broad peak at $2\theta = 22^\circ$, which confirms the amorphous phase of RHS, while a sharp peak of XRD pattern of RHS that was incinerated at 750°C reveals the presence of alpha quartz, the only stable state of crystalline silica that was found at that temperature. This is in agreement with the results obtained by Suryana et al. (2018), Bakar et al. (2016) and Ismail et al. (2014). They mostly traced the formation of crystalline silica at temperatures above 800°C. Crystalline silica is less preferred because it has limited applications due to its low reactivity (Chen, 2013; Feng, 2002).

Even though the amount of the metallic impurities is just approximately 1-3% of the total composition of rice husks, the presence of those metallic elements would tend to create microscopic 'hot spots', resulting in the overheating of the silica, making it capable

of transforming the amorphous silica to undesirable crystalline silica during incineration. The situation is worsening when the high molecular weight lignin becomes difficult to be completely burnt, leaving the traces of carbon behind. The incomplete combustion of carbon would produce black or grey rice husk ashes after incineration (Vasamsetti et al., 2018).

Acid leaching treatment is crucial to remove as much metallic impurities as possible from the rice husk that would effectively improve the purity of silica and increase the surface area of the silica particles. Sulphuric acid (H_2SO_4), nitric acid (HNO_3), citric acid ($C_6H_8O_7$), and hydrochloric acid (HCl) solutions are traditionally used in leaching treatment. Among all of the acids listed, HCl is more favourable as it can eliminate the highest amount of impurities in rice husk compared to other types of acids. According to Ghorbani et al. (2015), the result of XRF analyses reveals the effectiveness of HCl treatment in producing the highest purity silica, which was 95.55% silica content compared to H_2SO_4 and HNO_3 with 92.89% and 94.79% silica content, respectively. The acid treatment substantially reduced the amount of metallic oxides, especially potassium, calcium and phosphate oxides in the rice husk, and produced completely white coloured silica, whereas the combustion of raw rice husk produced grey colour of RHA, indicating the presence of unburnt carbon with only 85.15% silica content. The carbon residue greatly influences the colour of the produced silica.

The effectiveness of HCl in leaching treatment was also proven in a research conducted by Bakar et al. (2016). In their study, HCl-treated rice husk produced higher silica content of about 99.58% after incineration compared to H₂SO₄ treated rice husk and unleached rice husk that produced 99.08% and 95.77% silica content, respectively. Kurama et al. (2003) have conducted a research on the effect of HCl acid concentration on the purity of RHS. Three different HCl concentrations were used: 1 M, 2 M and 3 M.

The authors found out that the silica content of rice husk did not show any linear relationship with the molarities of acid used during the leaching treatment. However, the silica content of the untreated rice husk had increased from 88.02% to 99.50% after it was treated with 2 M HCl concentration. It was the highest purity achieved compared to 1 M HCl and 3 M HCl with 97.63% and 97.95% silica content, respectively. Similar result was reported by Feng et al. (2002), where the highest purity silica was obtained at 1 M HCl and there was no increment of silica content at concentration of 3 M. Treatment with 1 M HCl acid not only gave the highest purity, but also produced silica particles with the highest surface area. High purity silica with small particle size and large surface area finds its use in numerous applications, such as in building construction, electronics and engineering sectors as thermal insulators and polymer composite fillers (Mahmud et al., 2016).

Rafiee et al. (2012) have proved that through the acid treatment of rice husk followed by thermal combustion under controlled conditions (precipitation of extracted silica), 22.50% ash of which 90.469% is silica can be produced. Based on their findings, highly purified silica with high surface area, high reactivity and 99.9% of amorphous form can be obtained at optimised conditions. This claim can also be supported by a similar research that was done by Gu et al. (2013). The authors have successfully figured the optimised parameters in producing nanosilica from rice husk with its silica content reaching a record of 99.92%. The optimum condition required were 250–420 µm particle size of the cleaned rice husk feedstock with the pyrolysis temperature and hydrolysis temperature of 610°C and 120°C, respectively. The acid ratio to rice husk is 10:1 (g/ml) and the hydrolysis time required was 4 hours. By applying these parameters, especially with the determined particle size of the rice husk feedstocks, the resulted properties of nanosilica was superior to the commercial fumed silica in terms of its uniformity, homogeneity and photosensitivity.

Gu et al. (2015b) had placed more emphasis on calcination due to its economical and effectiveness in the preparation of amorphous silica by influencing both the removal of metallic impurities and further decomposition of organic compounds in the rice husk ash. The authors have introduced a novel two-staged thermal synthesis method by combining pre-pyrolysis with calcination method in generating nanosilica from rice husk. Nanosilica with different levels of purity and textural properties were successfully synthesised by using CO_2/N_2 as pyrolysis gases at its designated pyrolysis temperatures (300–800°C). The pyrolysed rice husk was then calcined at 610°C for 2–3 h to remove the organic compounds when producing the nanosilica powder. The resulted nanosilica with purity of 95.85–99.62%, a specific surface area of 204.3–352.6 m²/g, and total pore volume of 0.3513-0.5228 cm³/g were achieved. The particle size of the nanosilica produced were all less than 20 nm, except for that of particles prepared under the N₂ atmosphere, which gained 50 nm in size. Even though this novel two-stage thermal treatment method is said to be effective in controlling the textural characteristics of the produced nanosilica that may be suitable to be used in various technological fields, the multiple stages and stringent procedures that particularly involve the control of the flow of the pyrolysis gases have prevented this method from further development.

There were also a few methodologies introduced in extracting lignin from rice husk and one of the recent developments in delignification was known as organosolv. This method uses organic solvents and catalysts, and the delignification process is conducted at a designated pressure at high temperatures. Rosa et al. (2017) had tested the organoslov technique by using low cost organic solvent, which was ethanol and sulphuric acid as the catalyst. The delignification process was conducted at atmospheric pressure and the reflux took place for 24 hours to extract lignin from the rice husk. In this current study, the main concept of the organosolv delignification was practiced, but with some significant modifications to it. A simpler yet more efficient procedure using basic lab instrumentation is required in optimising the synthesis of rice husk into functional silica. This could indirectly add some values to the biomass residues that can benefit many manufacturing industries.

2.4.2 Characterisation of RHS

Numerous characterisation techniques are available in determining the overall properties of silica generated from rice husk. X-ray powder diffraction (XRD) is a rapid analytical technique commonly used in materials characterisation for phase identification of a crystalline material that also provides information on the unit cell dimensions. Most researchers have observed the presence of wide peak at $2\theta = 22^{\circ}$ in their resulted RHS. Those broad diffraction peaks indicated the characteristic of amorphous state of the RHS sample tested (Hassan et al., 2014; Khorsand & Masoomparast, 2012; Nittaya & Apinon, 2008). To obtain amorphous silica, the incineration temperature shall not exceed 700°C, as the phase transition to the crystalline structure would soon take place (Ugheoke & Mamat, 2012).

The specific surface area and pore volume of the RHS powder sample can be measured via the Brunauer-Emmett-Teller (BET) instrument by determining the physical adsorption of a gas on the surface of the solid at the temperature of liquid nitrogen. Before the test is carried out, it is necessary to eliminate the gases and vapours on the sample surface to prevent any discrepancies on the result obtained. The specific surface area of RHS obtained from various treatment methods as discussed earlier were all more than 200 m²/g, which were higher than that of commercial silica (178 m²/g) (Dominic et al., 2013). Through surfactant-free sol-gel method, Hassan et al. (2014) had successfully generated RHS with the highest specific surface area of 653 m²/g, three times higher than the value from the template-free sol-gel method reported in literature. The higher the

surface area, the lower the particle size, and the reinforcing efficiency of the filler will be higher (Dominic et al., 2013).

Electron microscopes are scientific instrument that use electron beam to analyse objects on a very fine scale. To get a clear image of the surface topography of the RHS, scanning electron microscope (SEM) can be an appropriate instrument. Prior to the observation, the RHS sample surfaces need to be sputter-coated with a gold layer to minimise sample charging effects due to the electron beam. From the three-dimensional micrograph obtained from SEM, the particle shape distribution as well as the size of the agglomerated powder of RHS can be predicted. Transmission electron microscope (TEM) has higher resolution than SEM and provides the information on the internal composition of the RHS. TEM delivers a two-dimensional picture on the details of the inside and beyond the surface of RHS. The combination of SEM and TEM provides different means of the sample analysis and the information gathered can be correlated to achieve an overall picture of the sample properties. Most researchers reported a uniform and homogeneous spherical particle shape of their RHS samples with a wide distribution of sizes in the nanoscale, which were less than 100 nm (Ugheoke & Mamat, 2012).

The purity and chemical composition of the RHS can be measured by using X-ray fluorescence (XRF) analyser. The silica content would vary by method of treatment used (Rahim et al., 2015). The higher purity of silica with lower traces of other metallic impurities proved the efficiencies and effectiveness of the treatment methods used. By using the pyrolysis method, Gu et al. (2013) have claimed to achieved the highest purity silica, which was 99.92%. By soaking pretreatment (using deionised water), most of the alkali metal impurities were removed to make the subsequent hydrolysis process more efficient, thus improving the purity of the nanosilica.

Fourier transform infrared spectroscopy (FTIR) provides information on the chemical structures and functional groups of the RHS. Tables 2.5 and 2.6 summarise the peak identification of FTIR spectra of raw RH and treated RHA, respectively. The information was gathered from the previous analysis done by other researchers.

Table 2.5: PeakidentificationofFTIRspectraofrawRH(Source from Daffalla et al., 2010; Turmanova et al., 2012)

Wavenumber (cm ⁻¹)	Functional group
3700 - 2800	O-H stretching
(broad band)	Adsorbed water
2920 - 2900	Aliphatic C-H groups
1740 - 1660	C=O stretching vibrations of ketones, aldehydes,
	lactones or carboxyl groups
1500 - 1460	C-H deformation vibration
1090 - 1080	Stretching vibration Si-O
800 - 780	Stretching vibration Si-O
485 - 450	Bending vibration O-Si-O

Table 2.6: Peak identification of FTIR spectra of treated RH ash(Source from Bakar et al., 2016; Dominic et al., 2013; Ghorbani et al., 2015; Hassanet al., 2014; Rafiee et al., 2012)

Wavenumber (cm ⁻¹)	Functional group
3750–2850	O-H stretching
(wide and highly intense peak)	Adsorbed water
1640–1600	O-H bending
1150–1050	Asymmetric stretching Si-O
815-780	Symmetric stretching of Si-O
485–430	Bending vibration O-Si-O

From Table 2.6, there was no peak detected between 2800 and 2850 cm⁻¹ of the RHA samples. It means that there was no original organic compounds in the silica after the controlled combustion and extraction process (Rafiee et al., 2012).

There are many other characterisation techniques that may be useful to describe the produced RHS in detail. However, the abovementioned instruments provide the most appropriate data that can later be related to the overall performance of the filled rubber compounds. The most important information from the characterisation analysis include the composition of the RHS, the surface area and estimation of the particle size, the morphological behaviour, and the functional groups of the RHS.

2.4.3 Surface Modification of RHS by Coupling Agents

The hydrophilic nature of RHS may lead to low compatibility that is associated with the hydrophobic properties of most polymers. However, by some chemical modifications made in the compounding formulations, for instance, by the addition of some amounts of silane coupling agents, these restrictions can be reduced and they may not affect the final properties of the polymer composites as much (Dominic et al., 2013; Ginting et al., 2014).

The surface chemistry of RHS is completely different from that of carbon black due to the existence of silanol groups. Therefore, the interaction between RHS and rubber matrix must be taken into serious consideration to gain the maximum efficiency of the reinforcement. The RHS surface is polar and naturally hydrophilic due to the presence of silanol groups, which results in a strong filler-filler interaction via the hydrogen bonds. This condition leads to poor dispersion of filler in the rubber matrix. Furthermore, the silanol groups on the RHS surface can react with both the cure activator (ZnO) and accelerators, thus influencing the cure efficiency of the rubber compounds and resulting in slow curing rate and low cross-link density of the sulphur-cured rubber compound (Siriwong et al., 2014). In order to enhance the interaction between the filler and the rubber matrix, surface modification of the RHS filler needs to be done by the addition of coupling agents. The most efficient and preferable coupling agent is silanes (Coleman,
2011). Silane coupling agents are mostly developed as a bifunctional compound; firstly, they are able to react chemically with silanol groups on the silica surface and transform it into hydrophobic silica; secondly, they can provide chemically active silica surface that is relatively non-polar, in which they can participate in sulphur vulcanisation to form chemical linkage with rubbers. In other words, the silane coupling agents could act as a bridge, connecting silica and rubber, therefore, improving the silica-rubber interaction. As a result, significant reinforcing efficiency in silica-filled rubber compounds could be achieved (Sae-Oui et al., 2006). There are various types of silane coupling agents that are commercially available in the market. Tetrasulfide and mercapto are groups of organosilane (Figure 2.13) that are extensively used with non-black fillers, especially silica and clay in the rubber industry.



Figure 2.13: Tetrasulfide and mercapto silanes structure (Source from Pongdong et al., 2015)

(3-Mercaptopropyl)trimethoxysilane was one of the earliest coupling agents for rubber application. The addition of mercapto silane to silica-SBR (styrene butadiene rubber) and silica-NR compounds had increased its tensile strength, tear resistance and modulus, decreased the permanent set, and lowered the hysteresis. However, there are some limitations of mercapto silane that limits its use. During mixing, mercapto silane produced strong and unpleasant odour, especially at elevated temperatures. Besides that, the reactivity of the methoxy-silyl bonds towards silica was considered too high to allow for sufficient mixing prior to the reaction. The evolution of methanol, a highly toxic substance, during the silanisation had worsen the condition. Due to the said boundaries, the use of mercapto silane is restricted (Ciullo & Hewitt, 1999; Noordermeer & Dierkes, 2009).

Bis[3-(triethoxysilyl)propyl]tetrasulfide (known as TESPT or Si-69), is the most preferable polysulfide silanes compared to others. The existence of sulphur atoms in TESPT is advantageous, especially to the rubber compound cured by sulphur vulcanisation. It is mainly due to the co-vulcanisation phenomenon, where TESPT may act as sulphur donors to a certain extent in the system (Siriwong et al., 2014). The use of this silane coupling agent showed remarkable improvements not only in the cure characteristics of the rubber compounds, but also in mechanical properties such as tensile strength, modulus, tear strength, and abrasion resistance (Hosseini & Razzaghi-Kashani, 2014; Luginsland et al., 2002; Siriwong et al., 2014; Tangudom et al., 2014).

The silane coupling bond is represented in Figure 2.14. The chemical interaction would be similar, either the high surface area silica was pre-treated with the silane before mixing, or the silane was added during the mixing; this is called as in-situ mixing. During in-situ mixing, extra care must be taken when adding the silane coupling agents, especially when using tetrasulfide. The recommended method is by mixing the rubber, silica and silane coupling agent for at least 1 to 2 minutes before adding other ingredients that could interfere with the reaction between the silica and the silane. The temperature control during the mixing is also important, as too high temperatures (more than 150°C) would break the tetrasulfide group prematurely, consequently reducing its ability to bond with the rubber during vulcanisation (Ciullo & Hewitt, 1999). To prevent these possible circumstances in in-situ mixing, most researchers will choose to modify the silica surface with silane coupling agent prior to mixing.



Figure 2.14: Silane coupling bond (Photo sourced from Ciullo & Hewitt, 1999) 2.4.3.1 Silanisation and Possible Reaction of Silane-Modified RHS with Rubber

The reaction mechanism between silane coupling agent and silica surface is known as silanisation. Silanisation is postulated to occur in three stages. First, the alkoxy groups of the silane coupling agent are hydrolysed by the water in the solution to form silanol groups. In the second stage, the hydrolysed silanes (silanol groups) would react with the hydroxyl groups on the silica surface through hydrogen bond formation. The addition of acid during this primary silanisation stage can accelerate this reaction. Condensation reaction, which is also known as secondary silanisation, occurs in the third stage where the siloxane (Si-O-Si) linkage is formed between the adjacent functional groups on the silica surface, with the elimination of water. The secondary silanisation stage is accelerated by the presence of water and increasing temperature (Sato, 2018).

The effectiveness of TESPT as a silane coupling agent in silica-filled rubber composites is partly due to the following chemical reactions: i) the silanisation of the silica; and ii) the coupling of the silanised silica with the rubbers that form chemical bridges connecting silica surfaces and rubber molecules (Hayichelaeh et al., 2018). Silanisation can be divided into primary and secondary reactions, as shown in Figure 2.15 (a) and Figure 2.15 (b), respectively. As previously mentioned, in the primary stage, reactions can occur in two possible ways: either by direct condensation between the silanol groups of the RHS surface and one end of the triethoxysilyl group of TESPT; or by hydrolysis of the alkoxy groups of TESPT to form reactive hydroxyl groups before condensation reaction takes place. Both ways release ethanol as the by-product. The secondary silanisation stage involves the reaction between the neighbouring TESPT molecules on the RHS surface. To implement the reinforcing effect of RHS, the sulphur part of the TESPT, which is already attached to the RHS, has to react with the rubber. During mixing and curing, the tetrasulphide groups on the other side of the TESPT-modified RHS would then react with NR to form rubber-filler bonds, as illustrated in Figure 2.16.

a) Primary silanisation reaction between RHS and TESPT



Figure 2.15: Possible reaction mechanism between TESPT and RHS surface; a) Primary silanisation reaction; and b) Secondary silanisation reaction (Source from Hayichelaeh et al., 2018, Sengloyluan et al., 2016, and Sarkawi et al., 2015) b) Secondary silanisation reaction between RHS and TESPT



TESPT modified RHS

Figure 2.15, continued



Reaction of TESPT modified RHS with NR

Figure 2.16: Possible reaction between TESPT-modified RHS and NR (Source from Sarkawi et al., 2015)

The same mechanism applies with the other two most common silane coupling agents used in rubber; (3-mercaptopropyl)trimethoxysilane (MPS) and (3-aminopropyl) triethoxysilane (APTES), where the hydrolysed alkoxy groups at one end would interact

with the silanol groups on the RHS surface. The possible mechanisms that could occur during the silanisation reaction of MPS and APTES are illustrated in Figure 2.17 and Figure 2.18, respectively.

a) Hydrolysis of MPS



MPS modified RHS

Figure 2.17: Possible reaction mechanism between MPS and RHS surface (Source from Wu et al., 2014)



b) Condensation reaction with RHS surface



APTES modified RHS

Figure 2.18: Possible reaction mechanism between APTES and RHS surface (Source from Siriwong et al., 2014)

The hydrophobic functional groups of mercapto and amino (-SH and -NH₂) on the other end of the MPS- and APTES-modified RHS would interact with NR chains, as

illustrated in Figure 2.19 and Figure 2.20, respectively. These reactions would occur during the mixing and curing process. The chemical linkages between RHS fillers and NR matrices would enhance the adhesion and compatibility, which strengthens the rubber-filler interaction. An increase in the degree of dispersion of the RHS fillers in the rubber could possibly enhance the overall properties of the rubber compounds (Kapgate et al., 2015).



Reaction of MPS modified RHS with NR

Figure 2.19: Possible reaction between MPS-modified RHS and NR (Source from Kapgate et al., 2015)



Reaction of APTES modified RHS with NR

Figure 2.20: Possible reaction between APTES-modified RHS and NR (Source from Ismail et al., 2012)

2.5 Applications of RHS Fillers in Polymer Composites

The use of high purity silica generated from rice husk as an alternative for commercial silica has recently attracted wide attention among researchers. Motivated by the fact that these materials are cheap, non-hazardous and abundantly available, a number of studies have been conducted to optimise the use of these local silica sources, especially as fillers in various polymer composites (Turmanova et al., 2012).

Based on the study conducted by Midhun et al. (2014), the incorporation of RHS in high density polyethylene (HDPE) showed significant improvement in the overall strength-related properties of the polymer composites. In their study, RHS with low particle size, which was found to be 20 nm, and high surface area (150 m²/g) was generated by the calcination of acid treated rice husk in a cost-effective way. The enhancements in tensile strength and Young's modulus properties at 1.5 wt.% of RHS filler loading were due to the high surface area, low particle size, high purity, and uniform distribution of the filler in the HDPE matrix. Under applied stress, the dispersed RHS has helped in the distribution of localised stress, thus delaying the failure of the HDPE composites, even without any surface modification of the RHS.

Dominic et al. (2013) had proved that RHS filler gave better properties than commercial silica (CS) filler when incorporated into the natural rubber matrix. The comparison was made by the addition of 2 phr filler in the natural rubber compound. The RHS-NR compound gave a higher differential torque than the CS-NR compound did, which indicated higher cross-link density and stiffness of the RHS-NR compound. The presence of silica-rubber cross-link delayed the deformation of the RHS-NR compound, thus resulting in higher tensile strength and tear strength values than that in an CS-NR compound. Besides, the smaller particle size of RHS filler (252 m²/g) compared to CS filler (178 m²/g) gave higher surface area that contributed to better rubber-RHS filler interaction. This assisted the deviation of tear crack in prevention of the propagation, thus resulting in higher tear resistance. The RHS-NR compound also showed a significantly lower value of abrasion loss compared to CS-NR compound, again, indicating better reinforcing efficiency of the NR filled with RHS filler. The higher purity of RHS, as opposed to CS, might be one of the important key performance indicators to the superior overall mechanical properties of the RHS-NR compound. The effectiveness of silica from rice husk as filler in rubber was also reported by a similar research done by Lemessa & Fanta (2017). The rice husk ash silica (RHAS) used in their study was synthesised by a simple alkaline extraction followed by acid precipitation. RHAS with 83.7% silica with other mineral oxides were obtained. BET surface area of RHAS was 25.78 m²/g, while BET surface area of CS used was 37.57 m²/g. The mixing of 12 phr of RHAS and CS in NR (SMR 20) with other compounding ingredients was conducted separately on a two-roll laboratory size mill. Table 2.7 summarises the curing characteristics and mechanical properties of the NR compounds.

Table 2.7: Curing characteristics and mechanical properties of RHAS, CS and unfilled natural rubber compound (Source from Lemessa & Fanta, 2017)

Curing characteristics	RHAS-NR	CS-NR	Unfilled NR
Scorch time, t _{s2} (min.)	1.20	1.22	1.14
Optimum cure time, t ₉₀ (min.)	3.36	3.27	2.85
Mechanical properties	RHAS-NR	CS-NR	Unfilled NR
Tensile strength (MPa)	17.98	18.62	15.30
Modulus, 300% (MPa)	9.46	9.18	9.10

CS-NR compound was reported to have the longest scorch time, followed by the RHAS-NR compound as compared to unfilled NR. The addition of both silicas, CS and RHAS, had delayed the curing reaction of the compounds. Silica would react with the activator, zinc oxide (ZnO) in conjunction to its polarity to form silica-zinc bond; this would indirectly deactivate the function of accelerators. This claim can be reinforced through a similar allegation by Maghami et al. (2016). The acidic nature of the silanol groups on the surface of silica made it prone to react with the alkali nature of ZnO, as illustrated in Figure 2.21. The formation of this premature cross-link network would prolong the start of the curing reaction.



Figure 2.21: Possible reaction between silica and zinc oxide (Source from Maghami et al., 2016)

The curing time was also affected by the possible interaction between the silica and accelerators. Lemessa & Fanta (2017) reported that the presence of silica in the system had slowed down the curing process due to the ability of the silica to absorb accelerators into its porous structure, thus leading to the highest optimum cure time of RHAS-NR, followed by the CS-NR. The authors also suggested that the surface area of the filler is one of the vital roles in indicating the tensile strength of the composites, whereas the surface activity that involved the interaction between the rubber matrix and filler controlled the modulus of the composites. This explained the higher modulus of RHAS-NR rompound caused by the stronger mobility restriction of the polymer chain, which then complicated the movement of the polymer molecules. Smaller particle size with higher surface area of CS as compared to RHAS contributed to a uniform dispersion of CS in the rubber matrix, leading to better tensile properties of CS-NR than RHAS-NR compounds, as in Table 2.7. The authors agreed that the presence of other mineral oxides in RHAS with different physical and chemical properties might reduce the reinforcing effect of the silica in the rubber composite (Lemessa & Fanta, 2017).

Surya et al. (2014) reported the increment of cure characteristics of silica-filled SMR L compound with the addition of organosilane, (3-aminopropyl)triethoxysilane (APTES). The cure retardation caused by the silica, as previously mentioned, was prevented by the addition of APTES. APTES was said to have acted as a co-curing agent, since the polar parts of this additive had reacted with the silanol groups of silica to convert the hydrophilic nature of silica to hydrophobic, thus making its reaction with ZnO relatively less. Thus, this condition had optimised the function of ZnO in activating the accelerator.

This assertion can also be supported via a study conducted by Pongdong et al. (2015). In their study, RHAS and CS were compounded in epoxidised natural rubber (ENR-25) at various ratios (10, 20 and 30 phr). Comparison was made at 30 phr loading of RHAS and CS between the unmodified and surface modified with silane coupling agent, TESPT, as in Table 2.8. It was found that both RHAS and CS silane modified compounds had displayed shorter cure time (t₉₀) and scorch time (t_{s2}), and higher torque differences as compared with the unmodified compounds for both types. The presence of sulphur atoms in the TESPT had increased the amount of sulphur in the rubber compounds, which led to the cross-linking reactions, hence, shortening the scorch and cure times. At equal loading (30 phr), RHAS showed shorter scorch and cure times than the CS. As reported by Pongdong et al. (2015), the surface area of RHAS was lower than that of the CS, which was 0.91 m²/g for the former and 173 m²/g for the latter. This would be the probable factor contributing to the faster cure rate of RHAS. Low specific surface area would have less hydroxyl groups on the RHAS surface, thus reducing the risk of cure retardation by the adsorption of the curatives.

Table 2.8: Curing characteristics, mechanical and dynamic properties of unfilled ENR-25, RHAS-ENR25, and CS-ENR25 compounds (Source from Pongdong et al., 2015)

Curing characteristics	Scorch time, t _{s2} (min.)	Cure time, t90 (min.)	Delta torque (dNm)
Unfilled ENR25	3.84	8.16	4.46
RHAS-ENR25	2.40	4.59	5.89
*RHAS-ENR25	1.03	2.73	6.81
CS-ENR25	3.67	19.54	9.32
*CS-ENR25	2.68	9.28	12.11
Mechanical properties	Tensile strength (MPa)	Young's Modulus (MPa)	Elongation at break (%)
Unfilled ENR25	11.00	0.75	815
RHAS-ENR25	15.00	1.10	770
*RHAS-ENR25	16.25	1.85	630
CS-ENR25	12.20	1.60	485
*CS-ENR25	17.50	2.75	515
Dynamic properties	Storage modulus G' (MPa)	Loss modulus G" (x10 ⁵) (MPa)	Max. damping factor (tan δ _{max})
Unfilled ENR25	746.96	2.87	2.77
RHAS-ENR25	841.64	3.22	2.69
*RHAS-ENR25	1428.10	3.91	1.96
CS-ENR25	2927.50	3.25	1.34
*CS-ENR25	3017.50	3.58	1.41

* denotes surface modified with TESPT

Pongdong et al. (2015) also reported the increment in mechanical properties such as Young's modulus and tensile strength of the ENR-25 compound filled with RHAS. The addition of RHAS particles has restricted the mobility of the molecular chains and consequently increased the stiffness of the compound. This result was in line with the raise of the delta torque as compared to the unfilled ENR-25, as in Table 2.8. The reduction in mobility of the rubber chains have also caused the decrease of elongation at break values for all silica-filled compounds as compared to the unfilled compounds.

High tensile strength and Young's modulus of RHAS-ENR25 was due to the chemical interaction between the silanol groups on the silica surface and epoxide groups in ENR-

25 matrix, as displayed in Figure 2.22 (a). The silanisation of RHAS and CS had also further reinforced the ENR-25 compounds. It was believed that the new linkages of silica-TESPT-ENR had increased the cross-link density of the compounds, as schematically proposed in Figure 2.22 (b). As previously mentioned, the silane coupling agents are typically bifunctional compounds, in which they do not only react with silanol groups on the silica surface to transform naturally hydrophilic silica to hydrophobic silica, but also tend to provide chemically active surface of silica to react with sulphur during vulcanisation in forming molecular bridges with the rubber matrix. This phenomenon has improved the adhesion between the rubber and filler, enhanced the reinforcing efficiency, and consequently boosted up the mechanical properties of the rubber compounds.



Figure 2.22: The proposed reaction models for RHAS and CS dispersed in ENR-25 matrix: (a) Without silanisation, (b) With silane coupling agent, TESPT (Source from Pongdong et al., 2015)

It is known that the storage modulus of the filled rubber compounds is influenced by the effectiveness of the interfacial interaction between the particulate filler and the rubber matrix. Theoretically, a stronger interfacial interaction between the filler and the rubber matrix would result in a superior storage modulus of the rubber composites. Figure 2.23 (a) clearly indicated that the incorporation of silica filler, either RHAS or CS, had increased the modulus of the rubber compounds as compared to the unfilled or gum ENR-25 compound. The compounds with TESPT has higher modulus than the compound without TESPT. It proved that the restriction of the molecular chain mobility was due to the strong rubber-filler interaction. According to Figure 2.23 (b), unfilled ENR-25 has the lowest loss modulus, while the other filled compounds with and without TESPT, showed a broader peak than the unfilled compound. Pongdong et al. (2015) claimed that besides an increase in energy absorption caused by the fillers, the molecular chain mobility restriction of the filled compounds was the main reason that contributed to this finding.

This result was in line with the tan δ values, as in Figure 2.23 (c). Unfilled compounds have recorded the lowest storage and loss modulus, but it has the highest tan δ values in the glass transition region. Tan δ value is associated with the damping properties of materials, which is relatively dependent on the nature of the matrix, filler, and also its interface. The damping peak commonly happens in the glass transition phase and is correlated to the movement of the low molecular weight units or side groups within the rubber molecules. Therefore, the maximum damping peak (tan δ_{max}) indicated high molecular movement, as shown in unfilled ENR in Figure 2.23 (c). The highest tan δ_{max} of unfilled ENR-25, as seen in Table 2.8, clearly indicated good damping characteristics and mobility. Once filler is added into the system, the restriction of segmental motion of the rubber molecules had occurred and the presence of silane coupling agent (TESPT) had strengthened the rubber-filler interaction of the rubber compounds. This condition had decreased the damping properties of the filled rubber compounds and resulted in broad and low damping peaks, as shown in Figure 2.23 (c). It is also noted that the tan δ peaks of the filled ENR-25 compounds, with and without silane, have obviously shifted to higher temperatures than the unfilled compound. The temperature at which the tan δ peak appeared was referring to the glass transition temperature (T_g) of the rubber compound. The slight increase in T_g of the filled ENR-25 compounds was due to the

presence of filler (RHAS and CS) that was well dispersed within the ENR-25 matrix that had strongly interacted with the ENR-25 molecular chain.



Figure 2.23: (a) Storage modulus, (b) Loss modulus, and (c) Tan δ as a function of temperature of gum ENR-25 (unfilled) and filled compounds with 30 phr of RHAS and CS, with and without silane coupling agent, TESPT (Source from Pongdong et al., 2015)

The assertions made by Pongdong et al. (2015) can also be supported by a research done by Ojinmah et al. (2017). In their study, semi-nano rice husk (RH) filler was added in ENR-50 and the properties were compared to ENR-50 filled with CB at various ratios (10–50 phr). The addition of both types of fillers had increased the strength-related properties of the rubber compound compared to unfilled rubber. However, despite having lower tensile strength and modulus compared to CB-ENR50 compounds, RH-ENR50

compounds showed higher compression set and rebound resilience values than CB-ENR50. Compression set is important to predict the service life and performance of the rubber articles, while resilience is related to the flexibility of the molecular chains of the rubber compounds. These properties are crucial in dynamic seals and semi-nano RH filler would perform better in such applications.

Fillers are added into the rubber matrix to serve specific objectives of the final products. Even though, the incorporation of rice husk silica filler in the rubber matrix may not achieve higher or the same level of strength as other conventional fillers like commercial silica and carbon black; this fact does not affect the potential use of rice husk as filler since it is a waste product, whereby it can become attractive when cost considerations are well thought-out. Therefore, it is important to develop a simple, yet efficient method of synthesising high purity silica from rice husk with the purpose of providing alternative to the current silica source that could indirectly reduce the environmental pollution associated with the poor disposal management of this agrowaste.

CHAPTER 3: METHODOLOGY

3.1 Materials

Rice husks were obtained from a local mill in Kuala Selangor, Malaysia (Figure 3.1). Hydrochloric acid (37%) for leaching process and solvents for extraction, namely, toluene, ethanol, and acetone were purchased from Merck (M) Sdn. Bhd., Petaling Jaya, Selangor, Malaysia.



Figure 3.1: Rice husks

The solvents were used as received from the suppliers. The physical and chemical properties of these solvents are summarised in Table 3.1.

Solvent	Formula	Chemical structure	Purity (%)	Polarity index (P')	Boiling point (°C)	Toxicity information *TWA (ppm v/v)
Toluene	C7H8	СНз	99.5	2.4	110	100
Ethanol	C ₂ H ₆ O	H H H—C—C—OH H H	99.9	4.3	78	1,000
Acetone	C ₃ H ₆ O	О Ш Н3С СН3	99.5	5.1	56	750

Table 3.1: Physical and chemical properties of solvents

*TWA: time weighted average is a measure of the permissible exposure levels (Sefara & Birkett, 2004)

Natural rubber (NR) grade SMR L with density 0.92 g/cm³ was supplied by Malaysian Rubber Board (MRB), Sungai Buloh, Selangor, Malaysia and was used as a matrix. Other compounding ingredients, such as zinc oxide, stearic acid, sulphur, antioxidant (CPPD), and N-cyclohexyl-2-benzothiazolesulfenamide (CBS) were purchased from Bayer Co. (M) Sdn. Bhd., Petaling Jaya, Selangor, Malaysia and were used as received. The commercial precipitated silica, with product grade Tokusil 255G, which was used in the comparison study with the produced RHS, was obtained from OSC Siam Silica Co. Ltd., Bangkok, Thailand. The chemical structures of each compounding ingredient used in this study are listed in Table 3.2.

Name	Purity (%)	Chemical structure
Zinc oxide (ZnO)	> 99.5	Zn=O
Stearic acid (SA)	> 35	
		$CH_3(CH_2)_{15}CH_2$ OH
N-cyclohexyl-N'- phenyl-4- phenylenediamine (CPPD)	> 96	NH NH
N-cyclohexyl-2- benzothiazole sulfonamide (CBS)	> 96	$s \rightarrow s \rightarrow h$
Sulphur	> 99.5	S ₈
Precipitated silica (PS)	>93	O = Si = O

Table 3.2: Chemical structures of compounding ingredients

Silane coupling agents; bis[3-(triethoxysilyl)propyl]tetrasulfide (TESPT), grade SCA-S69X and (3-mercaptopropyl)trimethoxysilane (MPS), grade SCA-S89M were supplied by Nanjing Capatue Chemical Co. Ltd., China while (3-aminopropyl) triethoxysilane (APTES), grade KBE903 was supplied by Shin-Etsu Chemical Co., Ltd., Tokyo, Japan. The characteristics of the silane coupling agents are given in Table 3.3.

Table 3.3:	Characteristics	of silane	coupling	agents
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Bis[3-(triethoxysilyl)propyl]tetrasulfide			
Formula	$S_4[C_3H_6Si(OC_2H_5)_3]_2$		
Specific gravity (g/cm ³)	1.069		
Appearance	Yellowy, transparent liquid		



3.2 Methods

To accomplish the research objectives mentioned in the previous section, this study was divided into five different series:

- Series 1 Synthesising RHS using the solvent-thermal treatment, with different concentrations of acid leaching.
- Series 2 Characterising the structural behaviour, surface morphology, size, surface area, and composition of RHS.
- Series 3 Determining the optimum value of the RHS filler in NR compounds.

- Series 4 Analysing the influence of different functional groups of silane coupling agents used in modified RHS-filled NR compounds.
- Series 5 Comparing the RHS-filled NR compounds with commercial precipitated silica (PS)-filled NR compounds.

3.2.1 Synthesis of RHS

The main intention of this synthesis is to extract all extractives and metallic oxides impurities from the rice husk to gain only the silica. The extractives, metal impurities and silica are intermingling in between the lignocellulosic components. Therefore, the first step that needs to be taken is to hydrolyse the high molecular weight of lignocellulosic components and transform them into low molecular weight components, as shown in Figure 3.2. The low molecular weight components would dissolve or at least swell easily during the solvent-thermal treatment. Once the low molecular weight lignocellulosic components dissolve or swell, the extractives and metallic oxides impurities are exposed to the solvent mixture and released in it. The second step required is acid leaching. Acid acts as the catalyst to the hydrolysis process. Any residual impurities that may not dissolve during the solvent-thermal treatment would dissolve during the acid treatment. There are certain impurities that are insoluble in solvents but will dissolve in acidic solution. Different acid concentrations would influence the final composition of the silica. The more the impurities extracted from the rice husk, the higher purity silica obtained. Finally, the treated rice silica would be incinerated to obtain only the silica ashes. The incineration would burn all the residual carbon-based materials from the rice husk, especially the hydrolysed lignocellulosic components. Based on the study conducted by Brebu & Vasile (2010), lignin decomposes slower over a wider range of temperature (200-500°C) than cellulose and the hemicellulose components, which mostly decomposes at 350°C and 250°C, respectively. Lignin consists of many components with different decomposition pathways, making the thermal degradation more complex. In this study, the incineration temperature was set at 700°C to diminish all carbon-based materials that would affect the crystallinity of the silica, since temperatures that are higher than 700°C tend to produce crystalline silica that no longer has the required properties.



Figure 3.2: Hydrolysis of lignocellulosic components (Photo source from Li, 2014)

The solvent-thermal treatment method in this study was adapted from TAPPI T204 (2007) and TAPPI T264 (1997) standards with some modifications. These standards are normally used to extract the extractives from wood in the pulp and papermaking industries. The same mechanism was applied to rice husks to obtain high purity silica with the finest particle size. A combination of solvents consisting of benzene and ethanol at a ratio of 2:1 v/v is commonly recognised as a standard method to remove most extractives from wood (Sefara & Birkett, 2004; Tappi, 1997; Tappi, 2007). Benzene is a

colourless organic solvent. It is a highly hazardous solvent, in which exposure to it in both high and low concentrations may cause dizziness and inconsistent of heartbeat, which can lead to death (Nasser & Al-Mefarrej, 2009). Since benzene is a known carcinogen, numerous researches have been conducted to find the alternative solvents to replace it.

Sefara & Birkett (2004) had confirmed that a combination of toluene and ethanol at 75% and 25%, respectively, could remove almost the same amount of wood extractives as the benzene-ethanol mixture would. Besides, Nasser & Al-Mefarrej (2009) had concluded that mixtures of acetone and ethanol can be considered as the best alternative to benzene-ethanol in ASTM method in determining extractives content in wood. Therefore, a mixture of these three low toxicity and different polarity solvents: toluene, ethanol and acetone (3:2:1 v/v) were used in this study to replace benzene to extract extractives in the rice husks prior to acid leaching.

Leaching rice husk with acidic solution such as hydrochloric (HCl), sulfuric acid (H₂SO₄), acetic acid (CH₃COOH), or nitric acid (HNO₃) before subjecting to thermal treatment is very effective in accelerating the hydrolysis of lignocellulose components in rice husks and removing most of the metallic impurities (Shen, 2017). In this study, HCl was used in the leaching process, as many researchers have shown that the HCl treatment could effectively remove metallic impurities in rice husks better than other acid treatments such as HNO₃ and H₂SO₄ can (Soltani et al., 2015). The solvent treated rice husks were leached with five different molarities of HCl separately, before subjected to incineration at 700°C for 4 hours. The characteristics of the produced RHS such as the composition, BET surface area, morphological behaviour, crystallinity, and the thermal behaviour were analysed.

3.2.1.1 Solvent-Thermal Treatment Method

Rice husks were washed with distilled water to remove any dirt and any soluble particles. Then, the rice husks were dried in an oven at 110°C for 24 hours before being subjected to the solvent-thermal treatment method.

The solvent mixture, which consisted of toluene, ethanol, and acetone (named as TEA solvents) with ratio of 3:2:1, with a total volume of 1,800 mL, was prepared in a beaker. The TEA solvent mixture was then poured into a 2 L glass reaction flask containing 180 g of cleaned rice husks. The extraction process was conducted for 45 minutes at 110°C. The extracted rice husks were then washed with distilled water before being subjected to the acid leaching process. The extraction set-up as in Figure 3.3.



Figure 3.3: Extraction set-up

Different concentrations of acid were used for leaching; 0.01, 0.1, 1.0, 2.0, and 3.0 M HCl. The rice husks were soaked in the acid solution for 24 hours. Then, the treated rice husks were washed thoroughly with distilled water to remove the remaining acid and then dried in an oven at 110°C for 24 hours. The dried rice husks were incinerated in a furnace

at 700°C for 4 hours to obtain white ash silica. Finally, the rice husk ash was ground with an agate mortar until super fine white silica powder was obtained. Around 10-15% of RHS from the total weight of rice husk can be obtained in each cycle. Figure 3.4 shows the process flow diagram of the solvent-thermal treatment method with acid leaching to obtain RHS.



Figure 3.4: Process flow diagram showing the solvent-thermal treatment method with acid leaching of RHS

3.2.2 Characterisation of RHS

3.2.2.1 Colour Analysis

The colour of the untreated RHA and treated RHS powder were evaluated using chroma meter (model Konica Minolta CR-400; NJ, USA). Around 10 to 15 g of samples of untreated RHA and treated RHS were placed in different transparent zipper bags prior to measurement. The measuring head of the chroma meter was first calibrated with a

white calibration plate. Three readings were obtained for each sample. The colour of the commercial precipitated silica (PS) was evaluated as a standard. The colour difference can be identified as the numerical comparison of a sample's colour to a standard by using Commission Internationale de l'Eclairage (CIE) L*a*b* coordinates, where L* indicates lightness, a* is the red/green coordinate, and b* is the yellow/blue coordinate. The total difference, delta E (Δ E*), was calculated according to the colour difference equation (Hirschler, 2012) in equation 3.1. The subscripts 1 and 2 represent the standard and the sample, respectively.

$$\Delta E^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2}$$
(3.1)

Whiteness can also be measured using whiteness index (WI) which was originally proposed by Hunter (Hirschler, 2012), as in equation 3.2:

$$WI_{HUNTER} = L^* - 3b^* \tag{3.2}$$

3.2.2.2 XRF Elemental Analysis

The elemental composition and purity of the RHS powder were measured using an Xray fluorescence (XRF) spectrometer (model WDXRF; Shimadzu, Kyoto, Japan). Around 10 to 15 g of sample was placed into a plastic sample cup with a plastic support film. A flat surface of the support film to the X-ray analyser is important to ensure the sample was supported over the X-ray beam during analysis.

3.2.2.3 Morphological Study and Surface Analysis

The morphology and surface characterisations of RHS samples were conducted using a scanning electron microscope (SEM) (SUPRA 40VP; Carl Zeiss AG, Oberkochen, Germany) with a constant applied voltage of 10 kV. The powder samples were subjected to gold sputtering in a sputter coater (Type SCD 005; Bal-Tec Inc., Balzers, Switzerland) prior to the electron microscopy to prevent any electrostatic charges during the analysis.

A high-resolution transmission electron microscope (HRTEM) (model TECNAI G2 20 S-TWIN; FEI Company, Hillsboro, USA) was used to further investigate the structure and the average particle size of the synthesised RHS. The RHS sample (10 mg) was sonicated in acetone for 3 minutes to break the agglomerates. A little drop of the RHS suspension was taken using a micro-pipette and spread on the carbon coated copper grid and allowed to dry in room temperature. The copper grid was inserted into the HRTEM instrument and the sample was scanned along the path of the electron beam at the acceleration voltage of 200 kV.

To obtain the specific surface areas and average pore volumes of the RHS particles, the Brunauer-Emmett-Teller (BET) method was used. Surface area analysis was conducted using a micropore surface area analyser (model MIC271002 REV B; Micromeritics, Norcross, USA). After the powder samples have undergone the degassing procedure for 5 to 6 hours, measurements were taken under nitrogen adsorption at liquid nitrogen temperature. The average size of the RHS particles was measured using a Zetasizer Nanoseries (Malvern Instruments Ltd, Malvern, United Kingdom). The RHS powder was dispersed in water and then sonicated for 30 minutes prior to analysis.

3.2.2.4 XRD Analysis

The X-ray powder diffraction (XRD) data of the RHS samples were obtained from the XRD instrument (model Xpert Pro; Pan Analytical, Netherlands). It is a versatile, nondestructive technique that reveals detailed information about the chemical composition and crystallographic structure of the material. The RHS powder was pressed onto the metal holder to obtain a flat upper surface before being subjected to the analysis.

3.2.2.5 FTIR Analysis

Fourier transform infrared spectroscopy (FTIR) (model Spectrum One, PerkinElmer, Boston, USA) was used to determine the functional groups and chemical characteristics of the RHS through molecular absorption and transmission. The thin and translucent KBr pellets that were mixed with RHS samples were prepared prior to the analysis. The FTIR spectrometer was operated at a scanning range of 4,000 to 450 cm⁻¹.

3.2.3 Determining the Optimum Value of the RHS Filler in NR Compounds

To determine the optimum value of RHS filler in NR compounds, mixing was done by incorporating only the highest purity RHS filler powder, with the highest surface area, obtained during Series 1 and Series 2. The mixing was conducted on a two-roll laboratory size mixing mill according to ISO 1658, as formulated in Table 3.4.

Ingredients	Amount (pphr)					
	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6
Natural rubber (SMR L)	100	100	100	100	100	100
Zinc oxide (ZnO)	3	3	3	3	3	3
Stearic acid (SA)	2	2	2	2	2	2
CPPD	1	1	1	1	1	1
RHS	0	2	4	6	8	10
CBS	1.4	1.4	1.4	1.4	1.4	1.4
Sulphur	2	2	2	2	2	2

Table 3.4: Experimental formulation for Series 3

The total mixing time for all compounds was approximately 20 min. The mixing sequence is simplified in Table 3.5.

Mixing sequence	Time (min)
NR mastication	2
Addition of RHS	4
Addition of ZnO	2
Addition of SA	2
Addition of CPPD	2
Addition of CBS	2
Addition of sulphur	2
Homogenisation step	4
Total	20

Table 3.5: Mixing sequence of NR compound

3.2.4 Analysing the Influence of Different Functional Groups of Silane Coupling Agents Used in Modified RHS-Filled NR Compounds

The RHS surface modification method using three different functional groups from different silane coupling agents, as listed in Table 3.3 was adapted from the study conducted by Sun et al. (2005). Arkles (2014) affirmed that at least 1.5 wt.% of silane coupling agent relative to silica content is required to get a minimum monolayer coverage

of silica with average particle of size less than 1 μ m. In this study, 2 wt.% of silane coupling agent was used based on the optimum loading of RHS from the previous series.

Firstly, a mixture of 5 g of deionised water, 95 g of ethanol, and 10 g of RHS were sonicated for 30 min. Then, a specific amount of coupling agent, as indicated in Table 3.6, was added into the mixture. The pH value of the mixture was adjusted to pH 4 using formic acid. The mixture was then refluxed at 90°C for 4 hours. After cooling down, the RHS mixture was filtered. The modified RHS was then dried in an oven at 80°C for 24 hours (Sun et al., 2005). The powdered RHS was modified separately with each coupling agent prior to mixing.

The optimum amount of RHS, as determined during Series 3, was used in the mixing formulation for Series 4. The modified RHS with NR was mixed with other compounding ingredients on a two-roll laboratory size mixing mill according to ISO 1658, as formulated in Table 3.6.

Inquadianta	A mount (nnhr)			
Ingredients	Amount (ppnr)			
	Mix 1	Mix 2	Mix 3	Mix 4
Natural rubber (SMR L)	100	100	100	100
Zinc oxide (ZnO)	3	3	3	3
Stearic acid (SA)	2	2	2	2
CPPD	1	1	1	1
RHS	Ор	timum va	lue (Serie	es 3)
*Bis[3-(triethoxysilyl)propyl]tetrasulfide (TESPT)	-	2	-	-
*(3-Mercaptopropyl)trimethoxysilane (MPS)	-	-	2	-
*(3-Aminopropyl)triethoxysilane (APTES)	-	-	-	2
CBS	1.4	1.4	1.4	1.4
Sulphur	2	2	2	2

Table 3.6: Experimental formulation for Series 4

*Amount of coupling agent used is in wt.% and based on the optimum value of RHS

The total mixing time for all compounds was approximately 20 min. The mixing sequence was the same as in Series 3 and as shown in Table 3.5.

3.2.5 Comparing the Modified RHS-Filled NR Compounds with Commercial Precipitated Silica-Filled NR Compounds

The silane coupling agent that gave the best overall properties in Series 4 was used to modify RHS and commercial precipitated silica (PS) in Series 5. The mixing was conducted on a two-roll laboratory size mixing mill according to ISO 1658, as formulated in Table 3.7.

Ingredients	Amount (pphr)					
	Neat NR	NR-RHS	NR-RHS*	NR-PS	NR-PS*	
Natural rubber (SMR L)	100	100	100	100	100	
Zinc oxide (ZnO)	3	3	3	3	3	
Stearic acid (SA)	2	2	2	2	2	
CPPD	1	1	1	1	1	
RHS/PS	-	0	ptimum valu	e (Series	3)	
Silane coupling agent (from Series 4)	-	-	2	-	2	
CBS	1.4	1.4	1.4	1.4	1.4	
Sulphur	2	2	2	2	2	

Table 3.7: Experimental formulation for Series 5

*Surface modified RHS/PS with 2 wt.% of silane coupling agent from Series 4

The total mixing time for all compounds was approximately 20 min. The mixing sequence was the same as in Series 3 and Series 4, and as shown in Table 3.5.

3.2.6 Testing and Measurement of RHS-NR Compounds

Testing and measurements were conducted on all NR compounds obtained during Series 3, Series 4, and Series 5.

3.2.6.1 Curing Characteristics

The cure characteristics of the rubber compounds were measured using a moving die rheometer (model MDR UR-2010: U-CAN Dynatex INC., Taiwan) at a testing temperature of 160°C. The scorch time (ts₂), the optimum cure time (t₉₀), the minimum torque (M_L) and the maximum torque (M_H) values were obtained from this test.

3.2.6.2 Mechanical Properties

Tensile properties were measured using a tensile tester (model Instron 5569; Norwood, USA) equipped with a 2 kN load cell. The specimens were cut into dumb-bell shape (Type 2) using a Wallace die cutter having a dimension of 75 x 12.5 x 2 mm, with a test length of 20 mm. The tests were carried out at 24°C, with cross head speed of 500 mm/min according to the ISO 37 methods. Five specimens for each compound were tested. The average values of tensile strength, elongation at break, modulus at 100% elongation (M100) and modulus at 300% elongation (M300) were recorded.

Wallace Akron abrasion tester (Elektron Technology Series, Cambridge, United Kingdom) was used to test the abrasion resistance of the rubber compounds in accordance with the BS903: Part A9 methods. The mean values of the volume loss after five test runs were recorded for each specimen.

The hardness of the rubber compounds was measured in a Wallace IRHD Dead Load Hardness Tester (Wallace Instruments, Surrey, England, United Kingdom) at 24°C
according to ISO 48 methods. The average readings from three different locations on each rubber specimen were recorded.

Resilience tests were conducted according to ISO 4662 methods using the Wallace Dunlop Tripsometer (Wallace Instruments, Surrey, England, United Kingdom). The rebound resilience was calculated according to the following equation 3.3:

% Resilience =
$$\frac{(1 - \cos \theta_2)}{(1 - \cos \theta_1)} \times 100$$
 (3.3)

where θ_1 is the initial angle of displacement (45°) and θ_2 is the maximum rebound angle. The average percentages of resilient readings of five repeated impacts for each specimen were recorded.

3.2.6.3 Morphological Study

The tensile fracture surface of the rubber compounds was examined using a scanning electron microscope (SEM) (model SUPRA 40VP; Carl Zeiss AG, Oberkochen, Germany) with a constant voltage of 10 kV. The surface of the rubber compounds was gold-coated prior to the SEM analyses to prevent any electrostatic charging. The dispersion of fillers and the crack propagation of the rubber compounds were observed at various magnifications (100×, 200×, and 500×).

3.2.6.4 Measurement of Cross-link Density

The cross-link density is very important in measuring the equilibrium swelling as it affects the mechanical properties of the rubber compounds. The relationships of swelling measurement with cross-link density, [X]_{phy} were quantitatively expressed in the Flory Rehner equilibrium swelling as in equation 3.4 (Kapgate et al., 2015). In this equation,

 v_r is the volume fraction of the swollen rubber, χ is the natural rubber-toluene interaction parameter (0.39), ρ is the density of rubber (natural rubber = 0.92 g/cm³) and V_o is the molar volume of the toluene (106.3 ml/mol).

$$[X]_{phy} = \frac{-\ln(1-v_r) - v_r - \chi v_r^2}{2\rho V_0(v_r^{\frac{1}{3}})}$$
(3.4)

The v_r was calculated based on equation 3.5 which the W_s is swollen weight, W_d is the dried weight, ρ_r is the density of rubber, and ρ_s is the density of solvent (toluene = 0.8669 g/cm³).

$$v_r = \frac{\left(\frac{w_d}{\rho_r}\right)}{\frac{(W_d)}{\rho_r} + \left(\frac{w_s - w_d}{\rho_s}\right)}$$
(3.5)

3.2.6.5 Measurement of Rubber-Filler Interaction

The interaction between rubber and filler was measured by swelling the cured rubber compounds in toluene, according to ISO 1817. The samples, measuring $30 \times 5 \times 2$ mm, were prepared from the cured moulded sheets of each rubber compound. The initial weights were recorded prior to immersion. The samples were then immersed in toluene at room temperature, for 72 hours in a dark environment. After the immersion period, the samples were taken out of the toluene bath and the weights of the swollen samples were recorded. The swollen samples were then dried in an oven at 70°C until constant weights were obtained. The rubber-filler interaction was calculated using the Lorenz and Park's equation, as shown by equation 3.6 (Lorenz & Parks, 1961; Muniandy et al., 2012):

$$\frac{Q_f}{Q_g} = ae^{-z} + b \tag{3.6}$$

where the subscripts f and g in equation 3.6 represent filled NR and gum vulcanisates, respectively. Z is the ratio by weight of filler to hydrocarbon rubber in the vulcanisate, while a and b are constant values. The higher the Q_f/Q_g value, the weaker the rubber-filler interaction would be. In this study, the weight of toluene uptake per gram of hydrocarbon rubber (Q) was measured according to equation 3.7 (Surya et al., 2014). The formula weight is the total weight of the compounding ingredients used as in the experimental formulation.

$$Q = \frac{\text{Swollen weight - Dried weight}}{\text{Initial weight } \times 100/(\text{Formula weight})}$$
(3.7)

The reinforcing efficiency (RE) of the rubber compounds which indicates the degree of reinforcement by the filler loading was calculated based on the equation 3.8 (Surya et al., 2014):

$$RE = \frac{(M_{\rm H} - M_{\rm L})_{\rm f} - (M_{\rm H} - M_{\rm L})_{\rm g}}{(M_{\rm H} - M_{\rm L})_{\rm g}}$$
(3.8)

 $(M_H - M_L)_f$ is the difference in torque values of filled compound, while $(M_H - M_L)_g$ is the difference in torque values of gum vulcanisate. High rubber-filler interaction will contribute to high RE. This is the result of the degree of filler dispersion. The higher the degree of filler dispersion, the greater the surface area for rubber-filler interactions.

3.2.6.6 Thermal Analysis

The thermal gravimetric analyser (TGA) (model TG 209 F3 Tarsus; Netzsch, Germany) was used to obtain information about the decomposition of the NR-RHS

compounds. The sample was weighed around 5 to 10 mg in alumina crucible and heated under nitrogen atmosphere from room temperature to 1,000°C, with the heating rate of 20°C/min. The weight loss of the compound as a function of temperature was recorded.

The dynamic mechanical analysis (DMA) was conducted using rectangular shaped specimens, measuring $25 \times 10 \times 2$ mm, on a DMA machine (model DMA 8000; Perkin Elmer, Boston, USA). The set mode for the DMA was auto-tension, with a fixed frequency of 10.0 Hz, while the temperature range was varied from -80 to 100°C. Using the DMA, the storage modulus (*E*'), the tangent of loss angle (tan δ) and the interaction between the rubber matrix and the RHS filler could be studied.

CHAPTER 4: CHARACTERISATION OF UNTREATED RHA AND TREATED RHS PRODUCED BY SOLVENT-THERMAL TREATMENT METHOD

4.1 Introduction

The objective of this study is to determine the effectiveness of the solvent-thermal treatment method with acid leaching in synthesising high purity silica from rice husk. This method is modified from TAPPI standards (T204 and T264), which are practically used for wood extraction in pulp and papermaking industries. The solvent-treated rice husks were leached with different concentrations of acid solution prior to incineration. The highest purity with the largest surface area of rice husk silica is chosen to be incorporated in NR for the next series.

In this study, the term rice husk ash (RHA) is used to describe the ashes produced after the incineration of untreated rice husk, while the term rice husk silica (RHS) is used to define the products from the controllable incineration of solvent-thermal treated rice husk. The properties of treated RHS were compared to the untreated RHA to verify the effectiveness of the treatment method used.

4.2 Colour Analysis

The colour of the rice husk ashes obtained after incineration could be the first indicator of the traces of carbon and metallic impurities in the rice husk. Figure 4.1 shows the appearance of the RHA and RHS after incineration at 700°C. The RHA from untreated rice husks was grey in colour, as shown in Figure 4.1 (a), which indicated the presence of metallic impurities and unburnt carbon from the lignocellulosic components. However, the solvent-thermal-treated rice husks that were leached in 1.0 M HCl showed an incredible result, whereby the ash was completely white in colour after incineration, as shown in Figure 4.1 (b).



Figure 4.1: Appearance of RHA and RHS samples: (a) RHA extracted from untreated rice husks incinerated at 700°C; and (b) RHS extracted from solvent-thermal treated and leached rice husks in 1.0 M HCl, followed by incineration at 700°C

Colour analysis was conducted to determine the whiteness index (*WT*) and the total colour difference (ΔE^*) of the untreated RHA and treated RHS with the standard (white commercial silica). As indicated in Table 4.1, RHS leached with 1.0 M HCl recorded the highest *WI* compared to untreated RHA, unleached RHS and RHS leached with lower concentration of HCl. The highest ΔE^* value recorded by untreated RHA. The colour changed drastically whiter after solvent-treatment and acid leaching process. The higher the concentration of HCl, the whiter the RHS became.

Sample	Whiteness index <i>(WI)</i>	Colour difference index (⊿E*)		
Untreated RHA	73.94	21.97		
Unleached RHS (Solvent treated)	81.38	9.15		
RHS leached with 0.10 M HCl	83.26	3.73		
RHS leached with 1.0 M HCl	89.94	2.58		

Table 4.1: Colour analysis of RHA and RHS

As reported by Della et al. (2002), the changes in colour of the treated rice husks were due to the complete combustion process, which can be associated with the structural conversion of the silica in the rice ash. RHA usually contains incomplete combustion of organic residues and a mixture of amorphous and crystalline silica, whereas RHS generally contains low level of impurities compared to that of RHA (Chen, 2013).

The colour of ashes also depends on the temperature setting for the incineration. Ugheoke & Mamat (2012) had summarised that the transformation of grey raw rice husks to white is also critically dependent on the incineration temperature. Temperatures between 300°C to 450°C would produce dark grey carbonised ash, while at higher temperatures of approximately 500°C to 650°C, the rice ash would become light grey and white ash. The disappearance of the grey colour in RHS indicated the effectiveness of the solvent-thermal treatment method in extracting undesirable organic extractives and heavy metal impurities that were interwoven within the lignocellulosic components. In addition, leaching the solvent-treated rice husk with 1.0 M HCl acid had effectively hydrolysed the lignocellulosic components contained in the rice husks, indirectly removing other traces of metal oxides residues that still existed. In consequence, high purity RHS was successfully obtained via this synthesis method, as reported further in XRF analysis.

4.3 XRF Elemental Analysis

The XRF elemental analysis was conducted to determine the percentage composition of the resulting RHS. As indicated in Table 4.2, the untreated RHA contained 91.63% of SiO₂ and other metallic impurities, namely, K₂O, TiO₂, CaO, BaO, MnO, Fe₂O₃, and NiO. The content of the residual metallic impurities of the solvent-treated RHS showed a significant drop of K₂O and NiO, while TiO₂ and BaO were completely removed from the rice husk in comparison with the untreated RHA. After leaching with low concentration acid (0.01 M HCl), K₂O and MnO were totally removed, while CaO content showed a huge drop and had totally diminished after being leached with higher concentration of HCl (0.1 M). The highest content of SiO₂ was recorded at 99.99% after the solvent-treated rice husk was leached with 1.0 M HCl. All traces of metallic oxides residues were totally removed, except for a very small amount of Fe₂O₃. Leaching with HCl at higher concentrations of more than 1.0 M (2.0 M and 3.0 M) showed no linear relationship on the content of the SiO₂, however, the percentage of SiO₂ still recorded more than 99% for both. This finding is in conjunction with other claims made by other researchers. Most of the researchers reported that 1.0 M HCl is the ideal concentration molarity of the acid used for leaching, as molarity of more than 2.0 M HCl showed no significance improvement in the purities of the RHS produced (Feng et al., 2002; Kurama et al., 2003).

Constituents (wt.%)	SiO ₂	K ₂ O	TiO ₂	CaO	BaO	MnO	Fe ₂ O ₃	NiO
Untreated RHA	91.63	5.80	0.79	1.16	0.26	0.14	0.12	0.09
Unleached RHS (Solvent treated)	97.30	1.44	-	1.01	-	0.13	0.11	0.02
RHS leached with 0.01 M HCl	99.55	-	-	0.36	-	-	0.08	0.01
RHS leached with 0.10 M HCl	99.76	-	-	-	-	-	0.24	-
RHS leached with 1.0 M HCl	99.99	-	-	-	-	-	0.01	-
RHS leached with 2.0 M HCl	99.90	0.03	-	0.03	-	-	0.03	-
RHS leached with 3.0 M HCl	99.87	0.03	-	0.03	-	-	0.06	-

Table 4.2: XRF elemental analysis of RHA and RHS

According to Chen et al. (2017), acid treatment for rice husks usually reacts in two distinct ways. Firstly, it speeds up the hydrolysis of the lignocellulose to monosaccharides by removing extractives and hydrogen bonds. Soon after the polysaccharides are converted to monosaccharides, metal impurities that are bound in the lignocellulosic matters would be exposed and have the chelate reaction with acids, then would directly release to the acid leaching solutions. Metal impurities in rice husks can be categorised in three different forms; solvent and water-soluble form, the acid leachable form, and the residual. Based on Table 4.2, the composition of K₂O and NiO was dropped significantly after the solvent treatment, while BaO was fully removed. On the other hand, the percentage of CaO, MnO and Fe₂O₃ were not much affected during the solvent treatment, but gradually decreased after the acid leaching treatment. It shows that K₂O, NiO and BaO are mostly dissolved in the mixture of TEA solvents, while most of CaO, MnO and Fe₂O₃ are leached by the acid. This explains the difference in the solubility reactions and the distribution of those metal oxides in the rice husks. It can be deduced that K₂O, NiO and BaO were distributed at the edge of the lignocellulosic compounds or present in unbound state, while CaO, MnO and Fe₂O₃ were possibly bound inside the organic compounds, which might complicate the hydrolysis process. The addition of hydrogen ions accelerated the hydrolysis and the chelate reaction of the lignocellulosic components,

especially lignin and hemicellulose, which are more unstable than cellulose (Chen et al., 2017).

It is known that TiO_2 is insoluble in organic solvents. However, Taku et al., (2016) have reported that Cl, TiO_2 , Cr_2O_3 , MnO, CuO, ZnO, BaO, and Fe₂O₃ (traced in untreated rice husks) were reduced and eliminated during the incineration process. Even though elements like TiO_2 may not be affected by the solvents and HCl during leaching, the thermal treatment after the solvent extraction has, however, managed to improve the pozzolanic properties of RHS. The results showed that the purification through the solvent-thermal treatment method and leaching with 1.0 M HCl had successfully eliminated almost all the metallic impurities, except for Fe₂O₃ (0.01%). Therefore, the percentage of SiO₂ in the treated and leached RHS had increased to 99.99%.

4.4 Morphological Study and Surface Analysis

The SEM images of the untreated RHA and treated RHS samples are shown in Figure 4.2. Figure 4.2 (a) shows untreated RHA with no clear boundaries between the particles. The irregularity in the shape of the untreated RHA was due to the presence of lignocellulosic components that is comprised of cellulose, hemicellulose and lignin. These carbon-based components bound not only the silica, but also other impurity particles together. The solvent-thermal treatment that was used in the synthesis of rice husk had modified the morphology of the RHS as in Figure 4.2 (b). The spherical shape of RHS after solvent-thermal treatment was due to the decomposition of the lignocellulosic components. The lignocellulosic components of the rice husk tend to swell during the solvent extraction process, indirectly transforming the lignin from high to low molecular weight (Li, 2014). When the decomposition of the lignocellulosic components

exposed. The extractives and soluble impurities would dissolve in the TEA solvent mixture during the extraction process. This is aligned with the previous XRF result that clearly showed the decrement on the percentage of the metal impurities of the RHS after the solvent-thermal treatment as compared to the untreated RHA. The low molecular weight cellulose and lignin were then completely decomposed during incineration at 700°C.

The solvent-thermal treated RHS with acid leaching also shows a spherical shape, but smaller than unleached RHS in size, as in Figures 4.2 (c) and (d). Other residual impurities that were insoluble in the solvent mixture would have the chelate reaction with HCl acid, then, released to the acid leaching solution. In terms of the morphological properties of the RHS, the concentrations of HCl acid at 0.01 M and 0.1 M for leaching did not show any major difference, except for the early formation of aggregates. After leaching with higher concentration of acid of 1.0 M HCl, the RHS particles became smaller because almost all metallic impurities have been removed, as previously reported in the XRF analysis. This finding is in agreement with Faizul et al., (2013). Smaller particle size of RHS that at first was forming aggregates, had transform into agglomerates, as in Figure 4.2 (e). The fast agglomeration was due to the large amount of bound water on the surface of the RHS, which resulted in strong interactions among the RHS particles. The presence of these hydroxyl groups will be discussed further based on the FTIR results.



Figure 4.2: SEM images of RHA and RHS at 30.0k x magnification: (a) Untreated RHA; (b) Unleached RHS; (c) RHS leached with 0.01 M HCl; (d) RHS leached with 0.1 M HCl; and (e) RHS leached with 1.0 M HCl



Figure 4.2, continued

Due to the fast agglomeration of RHS, the measurement of the exact primary particle size is complicated. From the Zetasizer analysis and SEM images, the size of the primary particles of solvent-thermal treated RHS before acid leaching was estimated around 80 to 100 nm (Figure 4.2 b), while the size of solvent-thermal treated RHS leached with 1.0 M HCl acid was getting smaller, which was at approximately 50 nm. When compared to the particle size of the RHS leached with lower concentration of acid (0.01 M and 0.1 M), the particle size of the RHS leached with 1.0 M HCl acid was the smallest with a uniform narrow size distribution. This claim can also be supported by research conducted by Permatasari et al. (2016) and Xu et al. (2018).

The tendency of the treated RHS to form aggregates and agglomerates can be observed using TEM, as in Figure 4.3. Low and high magnification of TEM images of solventthermal treated RHS were captured. Figures 4.3 (a) and (b) of RHS leached with 0.01 M HCl acid showed wide size distribution of the primary particles with an irregular geometry, causing difficulty in measuring the exact size. However, the TEM image of RHS leached with 0.1 M HCl acid shows a clearer picture of spherical shape of the primary particles. The average diameter of the RHS primary particles was observed at 80 nm, as in Figures 4.3 (c) and (d). Aggregation had largely occurred to RHS leached with 1.0 M HCl. The primary particles were overlapping and adhering to one other, making it aggregated into clusters, as in Figure 4.3 (e). At high magnification, agglomeration of the aggregates was clearly observed (Figure 4.3 f). Agglomerates are clusters of loosely bound particles of aggregates, held together by weak van der Waals forces (Fruijtier-Pölloth, 2012). Smaller primary particle size of RHS leached with 1.0 M HCl acid provides larger surface area to adsorb more water molecules from the surrounding moisture, causing interconnection between the particles.



Figure 4.3: TEM images of solvent-thermal treated RHS at low magnification (200 nm) and high magnification (100 nm): (a–b) RHS leached with 0.01 M HCl; (c–d) RHS leached with 0.1 M HCl; and (e–f) RHS leached with 1.0 M HCl

The analysis of the surface area was done by using BET instrument. The BET surface area and pore volume of the produced RHA and RHS leached in different concentrations of HCl acid are given in Table 4.3. From the table, the untreated RHA had a surface area of 11.41 m²/g, while the unleached RHS was 93.76 m²/g. The surface area of RHS had then gradually increased, as the concentration of the HCl acid for leaching also increased. The higher the concentration of the HCl acid used, the larger the surface area of the RHS. However, there was no significant difference on the surface area of the RHS leached with HCl at concentration higher than 1.0 M. RHS leached with 1.0 M HCl acid has recorded the highest BET surface area, which was at 234.25 m²/g. It proved that 1.0 M is the most ideal concentration of HCl acid, which it had effectively purified the RHS by removing most of the undesired impurities, resulting in the highest surface area of the RHS. This result is consistent with SEM images analysis, as previously reported. Theoretically, a smaller particle size would result in a higher surface area that would perhaps yield a higher reinforcing effect on the rubber matrix (Dominic et al., 2013; Sankar et al., 2016).

Sample	BET Surface Area (m²/g)	Pore Volume (cm ³ /g)
Untreated RHA	11.41	0.0786
Unleached RHS	93.76	0.1983
RHS leached with 0.01 M HCl	176.25	0.2605
RHS leached with 0.10 M HCl	227.93	0.3000
RHS leached with 1.0 M HCl	234.25	0.2957
RHS leached with 2.0 M HCl	229.57	0.3110
RHS leached with 3.0 M HCl	208.17	0.2743

Table 4.3: BET surface area and pore volume of RHA and RHS

As previously mentioned, smaller particles and fine particle size tend to form agglomeration due to the van der Waals attraction and hydrogen bonding. The formation of aggregates and agglomerates of the primary particles leads to the increment of pore volume, as indicated in Table 4.3. RHS leached with 0.1 M, 1.0 M, and 2.0 M HCl acid

recorded the largest pore volume, which were 0.3000, 0.2957 and 0.3110 cm³/g, respectively. The pore volume of the untreated RHA and unleached RHS were 0.0786 and 0.1983 cm³/g, respectively, smaller than RHS leached with acid. Coarser particles of RHA and unleached RHS was due to the presence of metal impurities that were still attached to the particles. The decrement of pore volume of the untreated RHA and unleached RHS might be due to the high proportion of metal oxides and other residues that were blocking the pores. Although scarce, this claim can be supported by a similar research done by Liou & Yang (2011).

4.5 XRD and FTIR Analysis

Incineration temperature and time are the two important factors to determine whether the silica particles remain amorphous or have transformed into crystalline phase. Crystallisation is avoided in most cases, as silica is inactive in crystalline form. Several studies have indicated that amorphous silica is formed at temperature below 700°C and higher temperature would induce the formation of crystalline silica such as quartz, cristobalite and tridymite (Fernandes et al., 2017; Ghorbani et al., 2015). However, crystallisation may occur below 700°C due to eutectic reaction of silica with other alkali metals that is present in the rice husk. The efficient treatment and leaching process of rice husk is crucial to eliminate most of the metal impurities to prevent this eutectic phenomenon that may lead to crystallisation formation at lower temperature (Bakar et al., 2016; Umeda & Kondoh, 2010). To verify the amorphous phase of the silica produced after incineration at 700°C, XRD patterns of the untreated RHA and treated RHS are presented in Figure 4.4. The broad diffused peaks were displayed at $2\theta = 22°$ for RHA and RHS, indicating the amorphous nature of silica. There is no sharp peak observed due to the absence of an ordered crystalline structure. It implies that the produced RHS is amorphous in nature and the eutectic phenomenon did not occur. (Fernandes et al., 2017).



Figure 4.4: X-ray diffraction diagram of RHA and RHS: (a) Untreated RHA; (b) Unleached RHS; (c) RHS leached with 0.01 M HCl; (d) RHS leached with 0.1 M HCl; and (e) RHS leached with 1.0 M HCl

FTIR measurements were conducted to identify the functional groups present on the surface of the RHA and RHS. FTIR transmittance spectra were taken in the range of 4000 to 400 cm⁻¹ and several peaks were detected, as in Figure 4.5. The broad band in the range of 3750 to 3250 cm⁻¹ was detected in all of the treated RHS samples (Figure 4.5 b– g), except for untreated RHA (Figure 4.5 a). This broad peak is mainly corresponding to the O-H stretching vibration of surface hydroxyl (-OH) groups.



Figure 4.5: FTIR spectrum of RHA and RHS: (a) Untreated RHA; (b) Unleached RHS; (c) RHS leached with 0.01 M HCl; (d) RHS leached with 0.1 M HCl; (e) RHS leached with 1.0 M HCl; (f) RHS leached with 2.0 M HCl; and (g) RHS leached with 3.0 M HCl

According to Premaratne et al. (2014), the broadening of the -OH peak was due to the physically and chemically adsorbed water molecules on the silica surface. The medium peak had also appeared at 1640 cm⁻¹ for all RHS samples due to the bending vibration of the O-H bonds from the adsorbed water molecule. No peak had appeared in the untreated RHA at these two points, 3750 to 3250 cm⁻¹ and 1640 cm⁻¹, as in Figure 4.5 (a), while only small bands were detected in the unleached RHS sample at these two points, as in Figure 4.5 (b). These two O-H peaks became more intense as the concentration of acid used for leaching is higher. The higher the concentration of acid used for leaching, the deeper the slope of both peaks will be.

This result shows that lignin is still present in the untreated rice husk ash and is strongly attached to the silica. The presence of lignin in the rice husk not only prevents the fungal decomposition, but also resist water adsorption and penetration (Rosa et al., 2017). Therefore, there is no trace of O-H bond from the water molecules in the untreated RHA. After solvent-thermal treatment and leaching, the lignin in the rice husk was probably transformed to low molecular weight polymer and decomposed. Consequently, the silica particles were no longer protected by lignin, thus water molecules from surrounding may easily be adsorbed on the surface of the silica particles. This indirectly proved that the solvent-thermal treatment with acid leaching to be efficient in producing high purity RHS. The bands located at 1090 cm⁻¹ and 800 cm⁻¹ are related to the asymmetric stretching vibration and symmetric stretching vibration of the Si-O-Si bond, respectively. The small peak detected at 475 cm⁻¹ is corresponding to the bending vibration of the Si-O elements (Dominic et al., 2013; Premaratne et al., 2014; Sankar et al., 2016). There is no significant difference of Si-O element peaks that had appeared in all of the RHA and RHS samples, as shown in Figure 4.5.

In summary, the solvent-thermal treatment method with HCl leaching at 1.0 M concentration is the novel technique that effectively produced the highest purity of RHS with 99.9% of silica content and the largest BET surface area in amorphous state. These characteristics make RHS the right alternative for commercial precipitated silica used as filler in the rubber composites.

CHAPTER 5: OPTIMUM VALUE OF RHS FILLER IN NR COMPOUNDS

5.1 Introduction

In this chapter, the cure characteristics, and the mechanical, physical, and thermal properties of RHS-filled NR compounds are discussed. A comparison between RHA-filled NR and RHS-filled NR, in terms of curing behaviour, mechanical properties, and thermal stability were also conducted to verify the effectiveness of the solvent-thermal treatment method in producing RHS fillers for NR. The optimum loading of RHS in NR compounds produced efficient filler reinforcement to the NR compounds.

Primary particle size, surface area, and surface activity are the main characteristics of a rubber filler (Cardona-Uribe et al., 2018). These characteristics are dependent on one another in enhancing the properties of the rubber compounds. The primary particle size of fillers, as indicated by the measurement of the surface area, is the most significant factor to predict reinforcement. It is well-known among rubber technologists that the term reinforcement refers to the high values of tensile strength, modulus, tear strength, and abrasion resistance of rubber compounds. Practically, small-sized filler particles with a high surface area would give superior reinforcement. Surface activity that denotes the presence of surface functional groups is important in providing an extensive interaction between the fillers and the rubber (Ciullo & Hewitt, 1999; Hewitt, 2007). Efficient reinforcement of the rubber compounds can be achieved by considering all three characteristics previously mentioned. Therefore, the highest purity RHS with the largest surface area that was successfully extracted in this study and discussed previously was chosen to be incorporated in the NR at various ratios.

5.2 Cure Characteristics of the RHA/RHS-Filled NR Compounds

Curing behaviour; scorch time (t_{s_2}), optimum cure time (t_{s_0}), minimum torque (M_L) that indicates rubber viscosity, and maximum torque (M_H) that can be related to the stiffness of the rubber compounds, were analysed at 160°C using a U-CAN moving die rheometer (MDR). According to Figure 5.1, the addition of RHA in the rubber compound had initially increased the ts₂ value, before it started to decline and increased again at higher loadings of RHA. The fluctuating trend of the RHA-filled NR compounds can also be observed at t_{90} in Figure 5.2. The addition of RHA had accelerated the cure time of the rubber compounds. Theoretically, fillers that have a low surface area with high metal oxides content would lead to a faster cure of the rubber compounds. The increment in cure rate is possibly due to the presence of different types of components (carbon and silica), which have various characteristics with different surface activities (Costa et al., 2001). The effect of silica in the rubber compounds was barely detected due to the existence of other elements that could have distracted the real functions of the silica. This finding is in agreement with the results obtained by Sae-Oui et al. (2002). They found that both ts₂ and t₉₀ values were reduced with increasing RHA loading. They concluded that the presence of metal oxides could have accelerated the curing process. At present, the possible mechanism of this phenomenon is incomprehensible. However, both the ts₂ and t₉₀ values of the RHS-filled NR compounds had gradually increased with increasing RHS loading. It is well established that the incorporation of silica fillers into the NR compound causes cure retardation.



Figure 5.1: Scorch time (ts₂) of RHA/RHS-filled NR compounds at different filler loadings



Figure 5.2: Optimum cure time (t90) of RHA/RHS-filled NR compounds at different filler loadings

Apart from the dispersibility of silica in the rubber compounds, the characteristics of silica surface also play a significant role on the adsorption effect. Silica is an inorganic material with a highly polarised surface, which is saturated with silanol (SiOH) groups, as illustrated in Figure 5.3. These silanol groups are responsible for the hydrophilic nature of silica. Meanwhile, the hydroxyl groups are acidic and have the tendency to cause a

delay in scorch time, and impede the cure rate of the rubber compounds (Choi et al., 2003; Ciullo, 1996).



Figure 5.3: Hydrophilic silica surface (Photo sourced from Hewitt, 2007)

During compounding, silica surface is exposed to other compounding ingredients, and tend to react with polar compounds that contain oxygen and nitrogen, such as water, amines antioxidants, zinc compounds, and accelerators, as well as rubbers (Kaewasakul, 2013). Fatty acids in NR will lead to a certain amount of soluble zinc. The reaction between silica surface silanol groups with soluble zinc was the main factor that contributed to the low cure rates of the RHS-filled NR compounds. This reaction may have occurred in two steps, as shown in Figure 5.4. First, zinc oxide, which acted as an activator in the rubber formulation, reacted with fatty acid from NR and produced soluble zinc ions. Then, the zinc ions became strongly bound to silanol groups on the silica surface. Zinc attachment to the silanols shifted parts of the adsorbed water and consequently, produced a heterogeneous surface with various zinc-to-water ratios. These ratios increased either when zinc oxide was added early in the mixing sequence or when the adsorbed water evaporated during high mixing temperatures. High zinc-to-water ratios contribute to the loss of soluble zinc from its original function as a cure activator (Hewitt, 2007; Surya et al., 2014). These phenomena could have occurred during compounding, whereby zinc activity was reduced once it reacted with the RHS surface. RHS-zinc bond was unable to activate the accelerator, and this had obviously led to longer curing time, as shown in Figure 5.4.



Figure 5.4: Soluble zinc reaction with silica (Source from Ciullo & Hewitt, 1999)

The silanols on the surface of RHS would produce hydrophilic adsorption with the surrounding water. The strong adsorptive interaction between silica surface and polar compounds, like water, occurs through hydrogen bonding. The network of hydrogen bonded silanols causes the primary particles of silica to form clusters. Silica clusters may lead to a higher viscosity of the rubber compound during processing, and may also be responsible for higher stiffness and hardness after curing. Higher loading of RHS would form more clusters and restricts the molecular movement of the rubber chains. This condition was observed through the slight increment in both M_L and M_H values, which indicated the rise in viscosity and stiffness respectively, as presented in Table 5.1.

Moreover, RHS-filled NR showed a higher torque difference than the unfilled NR (control). These values gradually increased when the RHS loading was increased. The torque differences can be linked to the stiffness in the rubber compound (Lemessa & Fanta, 2017). The increasing torque difference with the increasing RHS content was expected since the rubber phase was replaced with the RHS filler that has a higher rigidity.

A similar increasing trend was obtained with the addition of RHA. This result is in agreement with the work by Kanking et al. (2012).

Filler loading	M _L (dN m)		M _H (dN m)		Delta torque (M _H - M _L)		
(phr)	RHA	RHS	RHA	RHS	RHA	RHS	
0	0.24	0.24	2.83	2.83	2.59	2.59	
2	0.28	0.30	3.5	3.30	3.22	3.00	
4	0.31	0.35	3.58	3.12	3.27	2.77	
6	0.35	0.34	3.57	3.51	3.22	3.17	
8	0.26	0.39	3.42	3.84	3.16	3.45	
10	0.27	0.41	3.49	3.84	3.22	3.43	

Table 5.1: Torque values of RHA/RHS-filled NR compounds at different filler loadings

5.3 Mechanical Properties of the RHA/RHS-Filled NR Compounds

5.3.1 Tensile Properties

The results of the tensile strength of the RHA/RHS-filled NR compounds with different filler loadings is presented in Figure 5.5. The tensile strength of the treated RHS-filled NR was higher than for the RHA-filled NR. The addition of RHA had steadily reduced the tensile strength of the NR compound. The highest tensile strength value was recorded with the addition of 4 phr of RHS, before it dropped steadily with further increase in RHS loading. As expected, the higher surface area of the treated RHS compared to the lower surface area of the untreated RHA contributed to the improvements of tensile strength and other properties, such as modulus and abrasion resistance of the rubber compounds. The high surface areas improved the interaction between the rubber matrix and the RHS fillers. Fillers with high surface areas would have more contact areas available to the rubber matrix, which would reinforce the rubber chains. Meanwhile, the presence of metallic impurities in the untreated RHA, as previously discussed in the XRF

analysis, had decreased the purity and surface area of the RHA. This would weaken the interaction between the rubber matrix and the RHA fillers, which consequently would reduce the strength-related properties.



Figure 5.5: Tensile strength of RHA/RHS-filled NR compounds at different filler loadings

The earlier increment in tensile values was due to the evenly distributed smaller-sized RHS in the rubber matrix, as indicated by Fig. 5.6 (a). The smaller RHS particles led to larger surface areas being exposed to the rubber matrix. This condition had encouraged a good interaction between the RHS and the rubber matrix, even with no surface modification of the RHS. At 4 phr loading of RHS, the rough surface and the matrix tearing line of the tensile fractured sample can be observed in Fig. 5.6 (b). A good dispersion of RHS particles had altered the crack track of the sample, which then resisted the spread of the crack when the sample was stretched. High resistance to crack propagation indicated a good reinforcement by the RHS, and consequently caused an increase in tensile properties. The SEM images of the tensile fractured surfaces are in good agreement with the results obtained by Idrus et al. (2011) and Surya et al. (2013). They used precipitated silica with a minimum BET surface area of 180 m²/g. In their

studies, they claimed that the surface roughness and the matrix tearing line were caused by the high energy used to break the samples, providing a strong evidence for good reinforcement of the compound.

When the RHS filler loading was increased from 6 to 10 phr, the ultrafine fillers became agglomerated and the higher population of the filler particles volume would activate the hydrogen bonds of the silanol groups on the RHS surface, which induced filler-filler interactions. They formed bigger-sized RHS with smaller surface areas, as shown in Figures 5.6 (c) and 5.6 (d). The surface areas were insufficiently wetted by the rubber matrix, which weakened the interaction between the RHS fillers and the rubber matrix. Subsequently, this condition caused the reduction in tensile strength values at 6 phr loading and onwards, as shown in Figure 5.5. A similar claim on the interaction between NR and silica at high loadings was also proposed by Jarnthong et al. (2017).



Figure 5.6: SEM images of the tensile fracture surface of RHS-filled NR compounds at various loadings: (a) 2 phr of RHS at 500×; (b) 4 phr of RHS at 100×; (c) 10 phr of RHS at 100×; and (d) 10 phr of RHS at 500× magnification

Figure 5.7 shows that the elongation at break (E_b) values had decreased for both RHAand RHS-filled NR compounds when filler loading was increased. Theoretically, the E_b value is related to the elastic properties of the rubber compounds. A rubber compound with a higher elasticity value would produce a higher E_b value. This finding showed that both the RHA and RHS-filled rubber compounds became less elastic at higher filler loadings, which led to noticeably decreased E_b values. Both fillers even showed a similar trend, whereby the E_b values for the RHS-filled NR compound were lower than the E_b values for the RHA-filled NR compound. The rigidity of the RHS that was due to the high silica content in the ash had increased the stiffness and reduced the elasticity of the rubber compound. Meanwhile, the RHA that contained some impurities was not rigid. Thereby, the more incorporation of RHS in the NR restricted the movement of the rubber chains and consequently, reduced the E_b value (Tiwari et al., 2015; Lemessa & Fanta, 2017).



Figure 5.7: Elongation at break (E_b) of RHA/RHS-filled NR compounds at different filler loadings

The modulus at 100% (M100) and 300% elongation (M300) of the RHA and RHSfilled NR are shown in Figures 5.8. The incorporation of RHA and RHS in the NR compounds had increased the M100 and M300 values. As expected, RHS-filled NR compounds recorded higher modulus values than RHA-filled NR compounds. The stiffness of the NR compounds had noticeably increased when the filler loading was increased. The mobility of the rubber chains was restricted by the presence of the rigid filler, which resulted in a higher modulus value for the RHS-filled compounds. The increased modulus values had affected the reinforcing efficiency of the RHS in the rubber matrix due to improved rubber-filler interaction (Ismail & Ramli, 2008; Ismail et al., 1999).



Figure 5.8: Modulus (M100 and M300) of RHA/RHS-filled NR compounds at different filler loadings

5.3.2 Rubber-filler Interaction

As previously mentioned, the results of the tensile strength analysis were closely related to the interaction between the rubber matrix and the filler itself, which depended on the degree of filler dispersion in the rubber phase. Fillers that are well dispersed will result in strong rubber-filler interactions. Based on the equation proposed by Lorenz & Parks (1961), the rubber-filler interaction within the RHS-filled NR compounds can be

predicted, as shown in Figure 5.9. The swelling ratio between filled NR and gum vulcanisates (Q_f/Q_g) had initially decreased with increasing RHS loading of up to 4 phr. Then, this value was increased when the filler loading was further increased. The initial decreasing Q_f/Q_g values showed that the interaction between NR and RHS became stronger with the addition of RHS up to 4 phr. However, with higher RHS loading, the filler particles started to form aggregates and became bigger in size, which reduced their interaction with the rubber matrix. The rubber-filler interaction results are in agreement with the tensile strength results that were previously discussed.



Figure 5.9: Q_f/Q_g values of RHS-filled NR compounds at different RHS loadings

5.3.3 Abrasion Resistance

Abrasion resistance, in terms of volume loss of the rubber compounds, is presented in Figure 5.10. During the abrasion process, a small pit initially formed on the rubber surface. After continuous rubbing according to the test standard, more bits of rubber were abraded away. A smaller number of volume loss indicated better abrasion resistance, while higher volume loss resulted in inferior abrasion resistance (Arayapranee, 2012; Rattanasom et al., 2007).



Figure 5.10: Volume loss of RHA/RHS-filled NR compounds at different filler loadings

The abrasion resistance of both the RHA and the RHS-filled NR compounds had markedly decreased with increased filler loading. Nonetheless, the addition of RHS filler produced better abrasion resistance to the rubber compounds compared to RHA filler. Incorporation of RHS at 2 and 4 phr had improved the abrasion resistance of the NR compound. The smaller particle size with the larger surface area of RHS, compared to RHA as indicated in the previous chapter, could explain the obtained results. RHS with fine particle size offered a higher surface area to interact with the rubber matrix, thus providing a better abrasion resistance than the coarse particles of the RHA. However, at higher loadings, RHS particles started to agglomerate and created a larger particle, as indicated by the SEM image in Figure 5.6 (d). This rigid particle would effectively form a 'damage zone' to the surrounding particles, where debonding and micro-cavitation would occur during the abrasion test. The agglomeration of RHS particles at higher loadings could have initiated a strong filler-filler interaction, which is proposed to be the main cause for the increased volume loss. Similar outcomes were also reported by Sae-Oui et al. (2002) and Arayapranee et al. (2005).

5.3.4 Resilience and Hardness

The effect of various RHA and RHS loadings on the resilience of the NR compounds is presented in Figure 5.11. It shows that the resilience of RHA and RHS-filled NR compounds had steadily decreased when the filler loadings were increased. However, at 2 to 8 phr of RHA loadings, the resilience of the filled rubber compound was higher than the resilience of the unfilled compound. The presence of different impurities in RHA could have contributed to the high resilience of the rubber compounds filled with RHA. On the other hand, the addition of RHS had recorded a gradual reduction of resilience values, which were lower compared to the values of the unfilled compound.



Figure 5.11: Resilience of RHA/RHS-filled NR compounds at different filler loadings

Resilience is a measure of rubber elasticity. Theoretically, unfilled NR compounds should have higher resilience since there is nothing to obstruct the extension and contraction of the rubber chain. The incorporation of fillers would create such an obstacle and consequently, influence the strength of the compound. Therefore, resilience values are always contrary to filler loading and reinforcement values (Ciullo & Hewitt, 1999). The addition of fillers could prevent the rubber chains from returning to their original sizes and shapes after stress is removed. This explains the decreasing resilience values when the RHS filler loading was increased, which was the opposite of the hardness values, as indicated in Figure 5.12. Harder and stiffer rubber composites are less resilient, as reported by Ismail et al. (2013). The gum rubber with no RHS filler added was more elastic, which resulted in the highest resilience value due to the absence of obstacles between the rubber chains during deformation.



Figure 5.12: Hardness of RHA/RHS-filled NR compounds at different filler loadings

5.4 Thermal Properties of RHS-Filled NR Compounds

The thermogravimetric (TG) and derivatives thermogravimetric (DTG) curves of the unfilled NR (control) and the RHS-filled NR compounds are shown in Figures 5.13 and 5.14, respectively. A summary of the important characteristic temperatures obtained in

TG and DTG curves is listed in Table 5.2. It lists a clear comparison between the TGA results on the decomposition temperature at various weight loss percentages ($T_{5\%}$, $T_{25\%}$, $T_{50\%}$, and $T_{75\%}$), the maximum (T_{max}) thermal decomposition temperatures, and the remaining char residues at 900°C. The characteristic temperatures within this degradation region demonstrated the effect of RHS particles on the thermal stability of the NR matrix. The temperature at the maximum weight loss (T_{max}) was indicated by the lowest peak in the DTG curve.



Figure 5.13: Thermogravimetric curves of RHS-filled NR compounds at different RHS loadings

All compounds started their initial weight loss at lower than 200°C due to the evaporation of absorbed water from the compounds. However, due to the small weight loss rate, no peaks were indicated in both the TG and DTG curves. The thermal decomposition trends for the unfilled NR compound (control) and the RHS-filled NR compounds were comparable. Only one bend was apparent in the TG curves (Figure 5.13), and one peak was indicated in the DTG curves (Figure 5.14). The one-step thermal

decomposition corresponded to the thermal scissions of C-C chain bonds of the rubber cross-links into low molecular weight segments (Chen et al., 2008).



Figure 5.14: Derivative thermogravimetric curves of RHS-filled NR compounds at different RHS loadings

The incorporation of RHS had delayed the decomposition process of the rubber composites. The addition of 2 phr of RHS had significantly increased the initial degradation temperature ($T_{5\%}$) of the unfilled NR compound from 292°C to 318°C, which had further increased to 330°C with the addition of 4 phr of RHS. Increments were also detected for the thermal decomposition properties of $T_{25\%}$, $T_{50\%}$, and $T_{75\%}$. The decomposition temperature was delayed in the range of 2°C to 5°C with every addition of 2 phr of RHS loading, which became stable at 6 phr loading onwards. No significant difference was recorded between the decomposition temperatures at 8 and 10 phr of RHS loadings. A similar trend was also detected at T_{max} . The shift to higher degradation temperatures after the incorporation of RHS in the rubber matrix, even at low loadings, indicated the strong interaction between RHS and NR molecular chains through several
factors, such as particle size, surface area, and surface structure. These results have been proven by the mechanical properties of the compounds, as discussed in section 5.3 earlier. According to Halim et al. (2018), the strong interaction between the RHS fillers and the rubber matrix created a barrier that hindered the diffusion of volatiles to the surface. The increasing decomposition temperatures suggested that the thermal aging resistance of the RHS-filled NR compounds was improved. Thermal stability analysis is important to determine how far the RHS fillers could withstand the vulcanisation temperature during the curing process of rubber compounds (Lemessa & Fanta, 2017).

 Table 5.2: Thermal decomposition properties and residues of RHS-filled NR compounds at different RHS loadings

RHS loading (phr)	T5% (°C)	T25% (°C)	T50% (°C)	T75% (°C)	T _{max} (°C)	Residue (%)
0	292	370	387	415	382	0.1
2	318	373	389	414	383	1.0
4	330	373	391	419	385	5.2
6	329	374	394	422	389	7.1
8	329	374	394	424	389	7.6
10	330	375	395	425	390	10.5

The percentage of char residues was also obtained from the TGA curve. The residue percentages of all compounds at the end of the decomposition process are summarised in Table 5.2. It shows that the unfilled rubber (control) compound was mostly decomposed, leaving only 0.1% of residue behind. The lowest percentage of char residue was obtained by NR filled with 2 phr of RHS, while the highest percentage of residual content was obtained by NR filled with 10 phr of RHS. The residual contents of the RHS-filled NR compounds were proportional to the phr loadings, where higher phr loadings gave higher residues. The residual contents were close to the actual weight fraction of the RHS in the rubber matrix. Therefore, it was concluded that RHS was thermally stable and will not decompose at temperatures lower than 900°C.

In a study conducted by Srisuwan et al. (2018), the DTG curve of untreated RHAfilled NR compound showed peaks at 353°C, 303°C, and 536°C. These peaks can be respectively attributed to the decomposition of cellulose, hemicellulose, and lignin. However, no peak was detected within this temperature range for all RHS-filled NR compounds, as shown in the DTG curve in Figure 5.14. The absence of cellulose, hemicellulose, and lignin decomposition peaks strongly proved the effectiveness of the solvent-thermal treatment with acid leaching in removing all lignocellulosic components in the RHS.

To demonstrate the efficiency of the solvent-thermal treatment method in producing high purity RHS with high thermal stability, a comparison was made between the thermal properties of untreated RHA-filled NR and of RHS-filled NR at 10 phr loading, as shown in Figure 5.15. Figure 5.15 (a) shows that the main difference between these two compounds is the residual contents at the end of the decomposition stage. As listed in Table 5.2, 10.5% of residues were left by the RHS-filled NR compound, while only 4% of residues were obtained by the RHA-filled NR compound. As previously discussed, RHS consists solely of silica, which proved to be thermally stable and unaffected under a decomposition temperature of 900°C. Therefore, it produced higher residues, which were the equivalent to the weight fraction of the RHS loading. On the other hand, RHA consists mostly carbonaceous materials and impurities other than silica. Thus, it would decompose at high temperatures, which explained why the RHA-filled compound has lower residual content compared to the RHS-filled NR compound (Figure 5.15 (a)). The 4% of residues left consisted mainly of non-combustible silica, which was thermally more stable at higher temperatures.



Figure 5.15: Thermal properties of RHA/RHS-filled NR compounds at 10 phr loading; (a) TGA curves, and (b) DTG curves

Figure 5.15 (b) shows a comparison between the DTG curves of RHA and RHS-filled NR compounds at 10 phr loadings. Both compounds showed a similar trend, except for one significant difference. One additional peak appeared at 380°C of the RHA-filled NR curve. This peak may correspond to the decomposition of lignin, a thermally more stable aromatic polymer that could endure gradual decomposition between 370°C to 600°C, as

reported by Bakar et al. (2016). At higher temperatures, the two DTG curves began to converge forming a plateau, leaving the thermally stable silica residues.

5.5 Dynamic Mechanical Properties of RHS-Filled NR Compounds

Dynamic mechanical analyses of the unfilled NR (control) and RHS-filled NR compounds with different loadings were performed. Figures 5.16 and 5.17 depict the temperature dependence of storage modulus (E') and the tangent of loss angle (tan δ), respectively, under a scanning frequency of 10 Hz, which usually used in testing of natural rubber-based tire compound (Sengloyluan et al., 2016). Storage modulus measures the energy stored in a deformed sample that denotes the elastic response of that material. Initially, at low temperatures, the unfilled NR was in the glassy state and its storage modulus remained constant approximately at 4.60 GPa, since at this stage, molecular movements were mostly restricted to small rotational motions and vibrations. The incorporation of 2 and 4 phr of RHS had enhanced the glassy modulus to 4.94 and 5.30 GPa, respectively. The modulus was gradually improved with the addition of more RHS fillers. The highest modulus was obtained by the NR compound containing 10 phr of RHS, which was at 6.13 GPa. The improved storage modulus, even at lower than the glass transition temperature (T_g) , was a good sign of the reinforcing potential of the RHS in the rubber matrix. In addition, all samples experienced a sharp fall in storage modulus in the range of -60° C to -45° C, before reaching a plateau in the rubbery state, as shown in Figure 5.16.



Figure 5.16: Storage modulus of RHS-filled NR compounds at different RHS loadings

The sharp decrease in modulus was due to the main energy dissipation close to the T_g , which involved the obliging motions of the macromolecular long chain. This was related to the peak in the loss tangent (tan δ) that can be observed in Figure 5.17. Theoretically, storage modulus at higher than the T_g is known as the rubbery modulus. It relies on the formation of cross-links within the rubber matrix and filler network, which would increase the stiffness of the rubber compounds (Zhang et al., 2014). In this case, it can be suggested that RHS fillers had strongly interacted with the NR molecular chains. Consequently, the stiffness of the NR compounds was increased, which substantially improved the storage modulus. This observation is supported by a similar study by Srisuwan et al. (2018).

The tangents of the loss angle (tan δ), as a function of temperature for the unfilled NR and the RHS-filled NR compounds at different RHS loadings, are presented in Figure 5.17. The highest peak in the tan δ graph indicates the glass transition temperature (T_g) of the rubber compound. The T_g of the unfilled NR compound was at -46° C, while the T_g of the RHS-filled NR compounds recorded similar values, except for the RHS-filled NR with 10 phr loading, where the T_g had slightly shifted to the higher temperature of -44° C. The slight increase in T_g , which had only affected the RHS-filled NR compound at higher filler loading, can be attributed to the limited movement of the NR molecular chains. This was due to the presence of the rigid RHS fillers, which was physically well dispersed within the NR compound and formed a stiffer compound.



Figure 5.17: Tan δ of RHS-filled NR compounds at different RHS loadings

CHAPTER 6: INFLUENCE OF DIFFERENT FUNCTIONAL GROUPS OF SILANE COUPLING AGENTS USED IN MODIFIED RHS-FILLED NR COMPOUNDS

6.1 Introduction

The presence of numerous silanol groups on the surface of silica particles make them highly polar and hydrophilic in nature, hence, incompatible with hydrophobic elastomers, such as natural rubber and styrene butadiene rubber (Hewitt, 2007). The acidic surface of silica reacts relatively easy with either basic or polar materials, such as activators and accelerators during the compounding process, which would consequently delay the cure rate, as extensively discussed in the previous chapter. Furthermore, silica particles have a strong tendency to interact with each other through strong hydrogen-bonds resulting in the formation of silica aggregates and agglomerates, and causing poor dispersion of silica fillers in the rubber compound. This strong filler-filler interaction will lower the reinforcing efficiency and give poor overall strength-related properties of the rubber compound. In addition, high loading of silica fillers would significantly increase the viscosity of the rubber compound and causing processing difficulties (Kaewasakul, 2013; Surva et al., 2014). Therefore, coupling agents, which are able to react chemically with both silica surface and rubber molecules during mixing and curing stages, are used to overcome such deficiencies. When a coupling agent is utilised, it forms a hydrophobic shell around the silica particle, thus improving the compatibility between silica particle and rubber molecules.

Silane coupling agent is a bifunctional compound, which is composed of two functionally active end-groups, bonded to the silicon atom in a molecule. One of the active end-groups (alkoxy groups, such as methoxy, ethoxy, and propoxy groups) is able to form a chemical bond with the surface of inorganic materials, such as silica, glass, clay or metal. Meanwhile, the other end of the active group (functional groups, such as amino, mercapto, epoxy, and vinyl groups) is able to form a chemical bond with various types of organic materials, such as polymers. It was found that silanes are capable of forming chemical bonds between inorganic and organic materials (Sato, 2018).

Silane coupling agents were used to chemically react with both silica and rubber, which were mostly vulcanised by sulphur, containing carbon-to-carbon double bonds. The readily hydrolysable alkoxy group will react with silanols on the silica surface to form stable siloxane linkages. Meanwhile, the other end-group, known as the organo-functional group, takes part in sulphur vulcanisation, forming a chemical linkage with the rubber (Sae-oui et al., 2005). The silane-modified silica is capable of improving the compatibility between silica and hydrocarbon rubber, enhances the processability and vulcanisation properties, and substantially improve the reinforcing efficiency of the compounds (Noordermeer & Dierkes, 2009).

In this study, three types of organosilanes with different functionalities were tested as coupling agents; bis[3-(triethoxysilyl)propyl]tetrasulfide (TESPT), (3-mercaptopropyl)trimethoxysilane (MPS), and (3-aminopropyl)triethoxysilane (APTES). These three organosilanes consist of different alkoxy groups with different reactivity. TESPT is a well-known coupling agent that can improve the mechanical properties of the filled rubber compounds by donating free sulphur to form cross-linking with the rubber matrix during vulcanisation. The high reactivity of thiol-group in MPS and amine-group in APTES may accelerate the curing process and increase the cure rate of the rubber compounds (Roy & Potiyaraj, 2019). Due to the difference of functionalities and reactivity, the influence of these silane coupling agents on the cure characteristics, and the mechanical, thermal, and dynamic mechanical behaviours of the NR compounds were

studied. The surface modification of RHS was conducted and the modified RHS was characterised using FTIR prior to compounding and mixing. The loading of 4 phr of RHS was chosen as it appeared to give the optimum enhancement in overall strength-related properties, as thoroughly discussed in the previous chapter. The best coupling agent was then used to modify commercial precipitated silica (PS). A comparative study between the modified RHS-filled NR compound and the modified PS-filled NR compound was performed and discussed in the following chapter.

6.2 FTIR Analysis of Modified RHS

The functional groups of unmodified and modified RHS were characterised using FTIR. The spectra with wavenumber ranging between 4000 and 450 cm⁻¹ of unmodified RHS and modified RHS, with three different types of silane coupling agents with different functional groups, are shown in Figure 6.1.



Figure 6.1: FTIR spectra: (a) Unmodified RHS; (b) TESPT-modified RHS; (c) MPS-modified RHS; and (d) APTES-modified RHS

Following the silanisation step, the FTIR spectra of silane-modified RHS show the additional absorption bands compared with that of unmodified RHS, as shown in Figure 6.1 (a). As for the TESPT-modified RHS shown in Figure 6.1 (b), the bands that appear

at 3000–2800 cm⁻¹ and in the 1500–1300 cm⁻¹ regions can be attributed to the C – H stretching and deformation bands, respectively. As reported by Marrone et al. (2004), the C – S and the S – S stretching modes could be detected at 900 cm⁻¹ or less. The results in this study showed that one additional peak was detected at 900 cm⁻¹, which could either be C – S or S – S stretching modes. Both C – H and S – S peaks were strong evidence of the presence of TESPT in RHS.

Figure 6.1 (c) shows the FTIR spectrum of MPS-modified RHS. Compared to the unmodified RHS, additional peaks were observed in the 3000–2800 cm⁻¹ region. The peaks at 2948 cm⁻¹ and 2841 cm⁻¹ are characteristic bands of MPS, corresponding to the symmetric and asymmetric stretching of $-CH_2$ group, respectively, which were also observed in the TESPT/RHS spectrum. Further observation of this spectrum revealed the emergence of a very weak band at 2560 cm⁻¹ that corresponds to the S – H group of MPS. The presence of these additional characteristic peaks in the spectrum of MPS-modified RHS proved that the functional groups of MPS were successfully grafted onto the RHS surface. S – H and other peaks attributed to MPS molecules were not clearly observed in the spectrum of the modified RHS due to the strong vibration of RHS, which overlapped with the vibration of the MPS functional groups. This claim can be supported by similar study conducted by Wu et al. (2014).

Figure 6.1 (d) shows the FTIR spectrum of APTES-modified RHS. A medium peak at 1640 cm⁻¹ was detected, which can be attributed to the bending vibration of N – H of APTES-modified RHS. A small peak was observed at 2875 cm⁻¹, which represents the stretching model of C – H. Similar to TESPT- and MPS-modified RHS, the peaks that correspond to the stretching of alkyl (CH₂ and CH₃) were detected within the range of 3000-2800 cm⁻¹.

Compared to the spectrum of the unmodified RHS in Figure 6.1 (a), the O – H bands in the 3750–3000 cm⁻¹ region of all modified RHS, as shown in Figure 6.1 (b-d), have evidently been disturbed. The peaks in this region have become broader, which proved that all silane coupling agents have reacted with the silanol groups on the RHS surface. Other absorption bands that appeared at 1090 cm⁻¹ and 800 cm⁻¹ could be related to the asymmetric and the symmetric stretching vibrations of the Si – O – Si bonds, respectively. The emergence of these two absorptions peaks, which became sharper in the presence of silane coupling agents, implied that the siloxane groups of the coupling agents have reacted with the hydroxyl groups on RHS surface through physical or chemical bonding, as suggested by Srisuwan et al. (2018). The FTIR analyses confirmed that the functional groups of each type of silane coupling agents used in this study were successfully introduced onto the RHS surface.

6.3 Cure Characteristics and Cross-link Density of Silane-Modified RHS-Filled NR Compounds

The scorch time (ts₂) and the optimum cure time (t₉₀) of silane-modified RHS-filled NR compounds are shown in Figures 6.2 and 6.3, respectively. Initially, the addition of RHS to the rubber compound had clearly retarded the cure rate. The function of the activator and the accelerator system were deactivated due to the reaction with the active silanols groups on silica surface. However, the silane-modified RHS surface has been transformed from hydrophilic to hydrophobic. The alkoxy groups of silanes were hydrolysed to form a hydroxyl group, which were subjected to condensation reaction with silanol groups on the RHS surface (Katueangngan et al., 2016). The hydrophobic RHS interacted relatively less with the zinc oxide, thus, zinc oxide can function optimally in activating the accelerator system to increase the cure rate of the rubber compounds.

Consequently, the scorch time and cure time of the silane-modified RHS-filled NR compounds were decreased.

According to Figure 6.2, TESPT/RHS-filled NR compounds produce better scorch safety compared to MPS/RHS-filled NR and APTES/RHS-filled NR compounds. Sulphur-containing silane coupling agents like TESPT have more impact on the properties of silica-filled rubber compared to sulphur-free silane coupling agents. TESPT, which contains four sulphur atoms in its molecule, is able to donate additional sulphur atoms to the rubber compound during vulcanisation, hence, increasing the cure rate (Saeoui et al., 2005; Sengloyluan et al., 2016) and produced lower scorch time and optimum cure time compared to the RHS-filled NR compound without silane.

With MPS, the decreasing scorch time was due to the highly reactive methoxy-silyl bond towards silica, leading to insufficient mixing prior to the reaction. The ethoxy-silyl groups in TESPT are less reactive towards silica compared to the methoxy-silyl groups in MPS (Noordermeer & Dierkes, 2009). Ten Brinke (2002) reported that silane coupling activity could also be influenced by the types of alkoxy groups, namely, methoxy, ethoxy, and propoxy derivatives. He mentioned that the rate of the silanisation or hydrophobation reaction decreases in the following order; $CH_3O - > C_2H_5O - > C_3H_7O - > C_4H_9O$. Coupling agents with propoxy groups are not preferred as their reaction rates are too slow. Even though the methoxy group is capable of producing a fast reaction rate, for toxicological reason, its uses are limited since it may evolve into methanol, which is harmful to human. Therefore, the ethoxy group is preferable as it reacts fast enough, and the toxicological rate is harmless to human and to the environment.

In addition, the reactivity of the mercapto group, or also known as the thiol end-group (S - H) in MPS, is considered too high, which would result in premature scorching during

vulcanisation. At lower temperatures (less than 120°C) at the very beginning of the curing process, the thermal energy is insufficient to overcome the activation energy of the vulcanisation due to the catalytic effect of the thiol group on the accelerated sulphurvulcanisation system of the rubber, thus, speeding up the curing process and reducing the scorch time (Sengloyluan et al., 2016). Poh & Ng (1998) affirmed that the effect of the thiol groups on the vulcanisation was significant at amount of 2 to 8 wt.% at a temperature not exceeding 120°C. In this case, 2 wt.% of silane coupling agent was used in RHS, which strengthened the effect of the thiol group in accelerating the cure rate and consequently, reducing the scorch time of the rubber compound containing MPS. However, at higher vulcanisation. Towards the end of the curing process, the thermal energy has influenced the vulcanisation rate more than the acceleration effect of the thiol group in MPS. Consequently, MPS/RHS-filled NR compound gave a higher optimum cure time than TESPT/RHS-filled NR compound.

Similarly, the modification of RHS by APTES has also accelerated the cure rate of the compound and recorded a lower t₉₀ compared to unmodified RHS-filled NR compound. APTES consists of amine groups within its molecules. Amine is an alkaline substance that functions as the accelerator activator in the rubber during vulcanisation (Surya et al., 2014). The addition of APTES could speed up the cure rate and solve the cure retardation problems in silica-filled rubber compounds. However, compared to TESPT and MPS, APTES produces the highest cure time, as shown in Figure 6.3. In this case, the stearic hindrance caused by the bulky triethoxy-silane end-groups of APTES may have affected the cross-linking, hence, slowing down the curing process and increasing the cure time of the compound.



Types of silane coupling agent

Figure 6.2: Scorch time (ts2) of silane-modified RHS-filled NR compounds



Types of silane coupling agent

Figure 6.3: Optimum cure time (t90) of silane-modified RHS-filled NR compounds

The minimum torque (M_L) is a measure of the relative viscosity of the rubber compound and it characterises the filler-filler inter agglomeration. A lower M_L value indicates a weaker interaction between the fillers and produces lower viscosity of the rubber compound (Surya et al., 2014). As shown in Table 6.1, the silane-modified RHS surface has lower M_L values compared to NR compounds containing unmodified RHS. The values of M_L for all compounds with different types of coupling agents were comparable. The lower values of M_L represent the reduced filler-filler interaction, resulting in a lower viscosity. These results showed that the modification of RHS with TESPT, MPS, and APTES would reduce the viscosity, which would improve the processability of the RHS-filled NR compounds.

NR compounds	ML (dN.m)	Мн (dN.m)	Delta torque (M _H - M _L)
Unfilled NR	0.24	2.83	2.59
Without silane	0.35	3.12	2.77
TESPT	0.14	3.19	3.05
MPS	0.13	3.01	2.88
APTES	0.14	3.08	2.94

Table 6.1: Torque values of silane-modified RHS-filled NR compounds

Maximum torque (M_H) represents the stiffness of the rubber compound at the end of the vulcanisation process. Table 6.1 shows a significant rise in the M_H value of the TESPT/RHS-filled NR compound compared to other silane-modified compounds. This marked increment can be linked to its sulphur donating effect. The high sulphur rank with a weak bonding energy of S - S in TESPT could lead to a high reactivity of TESPT towards bonding with rubber during the vulcanisation process (Sengloyluan et al., 2016). As previously mentioned, TESPT tends to donate some of its sulphur atoms to the rubber compound to increase the concentration of free sulphur atoms, leading to the formation of extra cross-linking. Thus, the mobility and the molecular motion of the rubber chains would be restricted. This strong rubber-filler interaction would lead to the increase in stiffness of the rubber compound, resulting in the raised M_H value of the TESPT/RHSfilled NR compound. This phenomenon was not observed with the other two compounds containing MPS and APTES. The raised M_H value can be linked to the highest torque difference, which was also dominated by the TESPT/RHS-filled NR compound. Theoretically, torque difference or delta torque, as indicated in Table 6.1, can be a good indication of the cross-link density of the rubber compound. The higher the compound stiffness, the larger the M_H value and the greater the cross-link density will be (Sae-Oui et al., 2006).



Figure 6.4: Cross-link density of silane-modified RHS-filled NR compounds

The type and the degree of the cross-link density determine the mechanical and physical properties of the cured rubber. For instance, high cross-link density would result in greater tensile and tear strength, modulus, hardness, and abrasion resistance, but lower in elongation at break, rebound resilience, and heat build-up (Choi, 2006). As shown in Figure 6.4, the highest cross-link density is obtained by the TESPT/RHS-filled NR compound, followed by MPS/RHS- and APTES/RHS-filled compounds. The cross-link density essentially consists of both sulphide cross-links and physical cross-links. The hydrophobic surface of silane-modified RHS allows the zinc oxide to function effectively in activating the accelerator, in this case CBS, to accelerate the sulphur reaction and raise the sulphide cross-link. As reported by Surya et al. (2014), the compatibility between the

NR and silica can be determined by the hydropobicity of the silica surface. Thus, the more hydrophobic the surface of silica becomes, the more compatible it will be with the NR. The presence of silane coupling agents in the compound would reduce the filler-filler interaction, and improve the rubber-filler interaction. This would encourage the formation of more cross-links between the silanes and both RHS and NR, which would contribute to the total cross-links of the RHS-filled NR compounds.

6.4 Effect of Silane Coupling Agents on Rubber-Filler Interactions

Based on the Lorenz & Park's equation, the rubber-filler interaction of the silanemodified RHS-filled NR compounds can be predicted through the swelling ratio between filled NR and gum vulcanisates (Q_f/Q_g) (Lorenz and Parks, 1961). The Q_f/Q_g value is crucial to the mechanical performance of the rubber compounds, while offering an overall idea of the reinforcing mechanism and efficiency of the filled rubbers. Figure 6.5 shows the Q_f/Q_g index of the RHS-filled NR compounds, with and without the surface modification of silane coupling agents. In general, the rubber-filler interaction can be linked to the dispersion of the fillers in the rubber matrix. The lower the Q_f/Q_g index, the stronger the rubber-filler interaction and the better the filler dispersion would be. As shown in Figure 6.5, all silane-filled NR compounds record lower Q_f/Q_g index compared to the unmodified compound; whereby TESPT/RHS-filled NR compound has the lowest Q_f/Q_g index, followed by APTES/RHS- and MPS/RHS-filled NR compounds. TESPT is proven to be the most efficient coupling agent to chemically modify the surface of the RHS and makes it easily dispersed within the rubber matrix. The high compatibility of the TESPT/RHS-filled NR compound has enhanced the interaction between the rubber and the filler.



Figure 6.5: Q_f/Q_g index of silane-modified RHS-filled NR compounds

The reinforcing efficiency (RE) of the rubber compounds can be predicted using the Q_f/Q_g index, where the higher RE value corresponds to the stronger rubber-filler interaction, which is influenced by the degree of filler dispersion (Surya et al., 2014). The RE results, as presented in Figure 6.6, are in agreement with the Q_f/Q_g index in Figure 6.5. The TESPT/RHS-filled NR compound, which has the strongest rubber-filler interaction and better filler dispersion as proven by the Q_f/Q_g result, has recorded the highest RE, followed by APTES/RHS- and MPS/RHS-filled compounds. This observation can be associated with the effectiveness of TESPT as a bi-functional coupling agent with sulphur moiety, which is capable of modifying the RHS surface and simultaneously improving its compatibility with the NR matrix. The alkoxy-based silanes without sulphur moiety (APTES and MPS) showed considerably lower reinforcement efficiencies than TESPT. The RE value reflects the overall strength-related properties of the compound, whereby the greater the value of RE, the better the overall mechanical and physical performances of the compound would be.



Figure 6.6: Reinforcing efficiency (RE) of silane-modified RHS-filled NR compounds

6.5 Mechanical Properties of Silane-Modified RHS-Filled NR Compounds

6.5.1 Tensile Properties

The tensile strength and elongation at break (E_b), and the modulus at 100% and 300% elongation (M100 and M300) of RHS-filled NR compounds, with and without the addition of silane coupling agents, are presented in Figure 6.7 and Figure 6.8, respectively. Obvious raises in both tensile strength and modulus values were observed in compounds containing silane coupling agents. This could be due to the improved rubber-filler interaction during mixing, which could have also contributed to the improved RHS dispersion. Among the three silanes, TESPT recorded the highest tensile strength, followed by MPS and APTES. This was in line with the highest cross-link density and reinforcing efficiency values of TESPT/RHS-filled compounds, as previously discussed.



Figure 6.7: Tensile strength and elongation at break (E_b) of silane-modified RHS-filled NR compounds



Figure 6.8: Modulus (M100 and M300) of silane-modified RHS-filled NR compounds

The results of the tensile strength and modulus (M100 and M300) were supported by the Q_f/Q_g index, cross-link density, and reinforcing efficiency, as previously discussed. All three alkoxy-based organosilanes had successfully reduced the filler-filler interaction in the RHS-filled NR compounds. Thus, these results have verified their ability to transform the hydrophilic surface of RHS to hydrophobic, leading to improved compatibility between RHS fillers and the rubber matrix. However, different types of alkoxy-silanes would produce different levels of efficiency due to the differences in functionalities on the other side of their molecules.

TESPT, with its sulphur functionalities, is able to form cross-links during mixing and influence the viscosity of the compound, RHS dispersion, and the RHS-RHS interaction in the compound. This observation was supported by the lower M_L value of TESPT/RHS-filled NR compound, which indicated a weaker RHS-RHS interaction, leading to lower viscosity of the compound during mixing. The other two alkoxy-based silanes (MPS and APTES) showed less reactivity compared to the alkoxy-polysulphide-based silane, TESPT. Kaewsakul et al. (2014) reported that the free sulphur atoms released from TESPT are able to lightly cross-link with rubber, even after the mixing process. These cross-linking networks provided better stability to the dispersed RHS aggregates through the chemical linkages formed between the modified RHS and the rubber matrix. Consequently, the RHS mobility in the rubber matrix was restricted, which prevented the re-agglomeration of RHS. This showed that sulphur moiety in silane could offer additional advantages for the enhancement of RHS dispersion stability in RHS-filled NR systems.



Figure 6.9: Possible reactions of silanes with different key functionalities: a) alkoxy-based silane; and b) alkoxy-polysulphide-based silane (Source from Kaewsakul et al., 2014)

According to Kaewsakul et al. (2014), when alkoxy-polysulphide-based silanes are used, three possible mechanisms could occur during mixing or after mixing; 1) the reaction between silane and silica (hydrophobation), or also known as silanisation; 2) the reaction between silane and rubber or coupling reaction; and 3) cross-link reaction between rubber and rubber, from the active sulphur donated by polysulphide-based silanes. The reaction mechanisms of alkoxy-polysulphide-based silane and alkoxy-based silane-modified silica with rubber are shown in Figure 6.9.

The network structures of silica-silane-rubber and rubber-rubber cross-links primarily contribute to the increase in cross-link density and better RHS dispersion within the rubber matrix with lower RHS-RHS interaction. Silanes with alkoxy groups, in this case APTES and MPS, have been proven to improve the rubber-filler interaction, cross-link density, and strength related properties, such as tensile strength and modulus, of rubber compounds. However, TESPT, the bifunctional coupling agent containing high sulphur rank, has better overall properties compared to APTES and MPS. As in Table 6.2, TESPT has an average sulphur rank of 3.7, whereas MPS has only 1 sulphur atom per molecule,

while APTES has no sulphur atom. Thus, the total sulphur atom in the compounds that could affect the network formation would therefore be different. The results of the overall strength related properties have proven that rubber compound mixed with high ranked sulphur-containing coupling agents would more likely influence the silica-rubber coupling than silanes containing less sulphur or no sulphur atoms at all.

 Table 6.2: Silane coupling agents with their corresponding sulphur ranks

 (Source from Sengloyluan et al., 2016)

Silane coupling agent	Sulphur rank		
Bis[3-(triethoxysilyl)propyl]tetrasulfide	2 7		
$C_{18}H_{42}O_6S_4Si_2$	5.7		
(3-Mercaptopropyl)trimethoxysilane	1.0		
HS(CH ₂) ₃ Si(OCH ₃) ₃	1.0		
(3-Aminopropyl)triethoxysilane	0		
C ₉ H ₂₃ NO ₃ Si	U		

Cross-link density is the main indicator to the reinforcement efficiency of the rubber compound, and it also has a strong relation with elongation at break (E_b) (Siriwong et al., 2014; Surya et al., 2014). In this study, TESPT has the highest cross-link density, followed by MPS and APTES. Meanwhile, an opposing trend can be seen in Figure 6.7, where the APTES/RHS-filled compound shows the highest E_b value, followed by MPS/RHS- and TESPT/RHS-filled compounds. This trend showed that higher cross-link density would lead to lower E_b .

For the compound containing unmodified RHS with low cross-link density where it still soluble in solvent, a minimum stress was required to break the rubber when stretched. For silane-modified RHS-filled NR compounds, the cross-link density increased and the rubber molecules eventually became insoluble in solvent, thus higher stress was significantly needed to break the rubbers. Necessity for this is that the chemical bonds in the rubber compounds have to be ruptured to break the rubbers when stretched. Theoretically, when vulcanised rubber is being stretched, the input energy is converted into heat and rubber elasticity through molecular motion, which both help to prevent the breaking of the rubber molecules. However, when the crosslink density is increased, the rubber chains mobility is restricted and unable to dissipate the heat generated by deformation through molecular motion, causing in rupture of the rubbers at low elongation. For this reason, the compound containing TESPT with the highest cross-link density experienced the lowest E_b compared to the other compounds.

6.5.2 Resilience and Hardness

Figure 6.10 shows the rebound resilience and hardness values of silane-modified RHSfilled NR compounds, in comparison with the unmodified RHS-filled compound. The presence of silane coupling agents has reduced the resilience of the rubber compounds, whereby the TESPT/RHS-filled compound showed the lowest resilience, followed by MPS/RHS- and APTES/RHS-filled compounds. Resilience is known as the measure of elasticity of the rubber compound. The surface modification of RHS by a coupling agent has increased the compatibility and adhesion between the RHS filler and the rubber matrix, as well as increased the rubber-filler interaction. The cross-link networks produced from this strong interaction has restricted the mobility of the RHS filler in the rubber matrix. This condition prevented the compound from returning to its original size and shape once the stress is removed due to reduced elasticity. This would explain why resilience would normally have opposing values to reinforcing efficiency and hardness. Figure 6.10 shows that the TESPT/RHS-filled compound has lower resilience, which indicates higher reinforcement and hardness. Meanwhile, APTES/RHS- and MPS/RHSfilled compounds showed higher resilience, with lower reinforcing efficiency compared to TESPT/RHS-filled compound.



Figure 6.10: Resilience and hardness of silane-modified RHS-filled NR compounds

6.5.3 Abrasion Resistance

According to Park et al. (2018), abrasion resistance is commonly affected by various factors, such as rubber-filler interaction and cross-link density. Abrasion resistance describes the ability of the rubber compounds to resist tearing-off small pieces of rubber from its surface caused by the continuous rubbing on the rough counter surface. Abrasion resistance is expressed in volume loss and represents the strength of the rubber-filler interaction. The stronger the rubber-filler interaction, the more difficult it is to tear-off small pieces out of the rubber compound, which would result in low volume loss and high abrasion resistance.



Figure 6.11: Volume loss of silane-modified RHS-filled NR compounds

Figure 6.11 shows the abrasion resistance in terms of the volume loss of silanemodified RHS-filled NR compounds, in comparison with the unmodified NR compound. The figure shows that the silane coupling agents in the compounds are able to improve the abrasion resistance by strengthening the rubber-RHS filler interaction compared to the compound without silane. The TESPT/RHS-filled compound showed the highest abrasion resistance, with the lowest volume loss, followed by MPS/RHS- and APTES/RHS-filled compounds. It was clear that compounds with sulphur-containing coupling agents were more susceptible to show the effects of rubber-silica coupling than sulphur-free coupling agents. A higher concentration of TESPT sulphur to the RHS surface could cause a gradient of cross-link density as also reported by Kaewsakul et al. (2014). Consequently, the RHS particles would be more immobilised in the rubber matrix and their extraction by sharp asperities would be prevented (Zhong et al., 2015). Even though sulphur is also present in the MPS structure, the number of sulphur atoms might not have effectively promote cross-link density. However, the sulphur end-group might still be able to co-cure with rubber, and therefore, slightly increase the cross-link efficiency compared to APTES (Nakamura et al., 2009).

6.6 Thermal Properties of Silane-Modified RHS-Filled NR Compounds

The thermogravimetric (TG) and derivatives thermogravimetric (DTG) curves of the silane-modified RHS-filled NR compounds, in comparison with unmodified RHS-filled NR (control), are shown in Figure 6.12 and Figure 6.13, respectively. A clear comparison in the TGA results is displayed in Table 6.3. The table shows various weight loss percentages ($T_{10\%}$, $T_{50\%}$, and $T_{75\%}$), the maximum thermal decomposition temperatures (T_{max}), and the remaining char residues at 900°C. The characteristic temperatures within this degradation region demonstrated the effect of the surface modification of RHS with silane coupling agents on the thermal stability of the NR matrix. The temperature at the maximum weight loss (T_{max}) was indicated by the lowest peak in the DTG curve.

From Figure 6.12, the initial weight loss of all compounds starts below 200°C due to the evaporation of adsorbed water. At this point, the NR compound containing unmodified RHS has recorded a higher weight loss caused by higher adsorbed water than the compounds with modified RHS. This indicated that silane modification had reduced moisture adsorption on the surface of RHS (Srisuwan et al., 2018). Similar thermal degradation trends are recorded for all compounds, where only one bend can be seen in the TG curves in Figure 6.12, and one peak was indicated in the DTG curves in Figure 6.13. The steep weight loss recorded at the temperature range of 350°C to 450°C could be due to decomposition corresponding to the thermal scissions of C – C chain bonds of the NR cross-links into the low molecular weight segments (Chen et al., 2008). It was observed that there was no significant weight loss recorded beyond 450°C.



Figure 6.12: Thermogravimetric (TG) analysis curves of silane-modified RHS-filled NR compounds



Figure 6.13: Derivative thermogravimetric (DTG) curves of silane-modified RHS-filled NR compounds

The surface modification of RHS by silane coupling agents has delayed the decomposition process of the rubber compounds. The difference in decomposition temperatures between the unmodified RHS and the modified RHS began at $T_{10\%}$, where the decomposition temperature of NR compounds recorded a small increase in the presence of silanes. The increasing decomposition temperature becomes more obvious at 50% and 75% of weight loss, especially in the TESPT/RHS- and MPS/RHS-filled compounds, while the APTES/RHS-filled compound only show a slight increase, as listed in Table 6.3. The decomposition temperatures of compounds containing silanes were higher than the compound with unmodified RHS, in the range of 2° C to 7° C at $T_{50\%}$ and 1°C to 11°C at T_{75%}. A similar trend is detected at T_{max}, where the temperature of the maximum weight loss of the NR compound has shifted to the higher temperature in the presence of silanes, as indicated by the lowest peak in DTG curves in Figure 6.13. The increasing thermal degradation temperature of the compounds with silane-modified RHS indicated the strong interaction between RHS and NR molecular chains, as proven by its mechanical and physical properties. The strong interaction between the modified RHS and rubber delayed the diffusion of the decomposed products to the surface. The modified RHS-NR char acted as a heating barrier to protect the NR within. Similar observations were made by Halim et al. (2018) and Chen et al. (2008), where SiO_2 /polymer chars had significantly improved the thermal resistance of the host polymers. This observation showed that the surface modification of RHS by silane coupling agents has improved the strength-related properties of the NR compounds, as well as improved its thermal stability.

The amount of char residues can also be obtained from the TGA. The values of the residues left for all compounds at the end of the decomposition process are summarised in Table 6.3. The residual amount of NR compounds with silane-modified RHS was greater than the residual amount of unmodified RHS-filled NR compound, even at similar

RHS filler loading of 4 phr. It has been shown that the silane surface modification of RHS could lead to a lower degradation of the cross-linked NR compounds at higher temperature than of the unmodified compound. This condition was again due to the improved interaction between RHS and rubber, due to the surface modification of RHS by silane coupling agents.

Parameter	T _{10%} (°C)	T _{50%} (°C)	T75% (°C)	T _{max} (°C)	Residue (%)
Without silane	351	391	419	385	5.2
TESPT	353	395	423	388	5.9
MPS	353	398	430	388	6.0
APTES	352	393	420	388	5.6

 Table 6.3: Thermal decomposition properties and residues of silane-modified RHS-filled NR compounds

6.7 Dynamic Mechanical Properties of Silane-Modified RHS-Filled NR Compounds

It is well known that the storage modulus of a filled polymer compound can be influenced by the effective interfacial interaction between the inorganic filler particles and the polymer matrix. Theoretically, a higher storage modulus of a polymer composite can be achieved by a stronger interfacial interaction between the filler and the polymer host (Pongdong et al., 2015). Dynamic mechanical analyses were performed to characterise the modified RHS-filled NR compounds.

Figure 6.14 and Figure 6.15 display the temperature dependence of storage modulus (*E*') and the tangent of loss angle (tan δ), respectively, under a scanning frequency of 10 Hz. At a low temperature in the glassy region, TESPT/RHS-filled compound recorded the highest storage modulus of 7.23 GPa, followed by MPS/RHS-filled compound with

6.14 GPa and APTES/RHS-filled compound with 5.64 GPa. Meanwhile, the storage modulus of the compound containing unmodified RHS was at 5.30 GPa. At this stage, only small molecular vibrations and movements would occur. For the filled rubbers, the modulus was influenced mostly by the amount of filler added, cross-link density, filler-filler and rubber-filler interactions. These factors could affect the segmental motions of the rubber chains. In most cases, the modulus increases with increasing amount of fillers, and with the degree of rubber-filler interaction (Sengloyluan et al., 2017). The enhancement of the storage modulus in the presence of silane coupling agents, even below the glass transition temperature (T_g), would be a sign of the rubber-filler interaction, causing more restricted molecular mobility and consequently, improves the storage modulus in the glassy region. In this study, the highest storage modulus was obtained by TESPT/RHS-filled NR compound, indicating a good rubber-filler interaction, and the highest cross-link density, which was due to the sulphur from TESPT molecules.

On the other hand, the increasing temperature had caused a decrease in the storage modulus of all compounds before the transition, forming plateaus in the rubbery region. The large decrease in modulus in the range of -60° C to -45° C, as seen in Figure 6.14, indicates the temperature of the glass to rubber softening transition. At this point, the main energy dissipation would have occurred, which would involve the obliging motions of the macromolecular long rubber chain. The peak appears in the loss tangent (tan δ) curve, shown in Figure 6.15, to represent T_g .



Figure 6.14: Storage modulus of silane-modified RHS-filled NR compounds

Tan δ provides information on the overall flexibility and the interaction between the filler and the polymer host of a composite material. The height and the area under the tan δ curves indicate the total amount of energy that can be absorbed by a material during dynamic deformation. A large area under tan δ curve denotes a high degree of molecular mobility, showing the ability of the material to absorb and dissipate energy. As shown in Figure 6.15, the silane-modified RHS-filled compounds produce higher tan δ peak intensities compared to the rubber compound filled with unmodified RHS. However, the silane-containing compounds produced lower tan δ values compared to NR compound without silane at higher temperature in the rubbery region, where the rubber chains are in motion. All compounds with silanes, even with different functional groups, showed comparable values of tan δ . This proved that the modification of RHS surface with silane coupling agents has efficiently improved the rubber-filler interactions and reduced the filler-filler interactions. The strong interactions between the rubber and silane-modified RHS had reduced the tan δ values because the modified RHS had imposed restrictions

against the molecular motion of the rubber chains, thus, less energy was dissipated. The values of T_g taken from the tan δ peaks and the values of tan δ at different temperatures in the rubbery region are summarised in Table 6.4.



Figure 6.15: Tan δ of silane-modified RHS-filled NR compounds

With regards to the dynamic mechanical behaviour of the filled rubber compounds in the transition region, the mobility of the rubber chains was restricted by the rubber-rubber cross-link network and the rubber-filler interactions. Thus, higher energy was required to move the rubber chains. Therefore, in most cases, T_g of the silane-containing compounds were shifted to a higher temperature compared to the one without silane. Even though there is no significant difference on T_g recorded in Table 6.4, the lower tan δ values of the silane-containing compounds at low temperature (5°C) and high temperature (60°C) in the rubbery region prove that improved rubber-filler interactions would lead to lower energy losses. These losses corresponded to the efficient coupling or bridging between rubber and RHS, which restricted the mobility and movement of the rubber chains (Saramolee et al., 2016).

Types of silane	$T_g(^{\circ}\mathrm{C})$		Tan ð	
Types of shalle	at tan δ peak	at peak	at 5°C	at 60°C
TESPT	-46.5	2.505	0.034	0.015
MPS	-46.1	2.492	0.033	0.017
APTES	-46.6	2.435	0.033	0.017
Without silane	-46.0	2.231	0.072	0.021

Table 6.4: T_g and tan δ values of silane-modified RHS-filled NR compounds

The tan δ peaks have shown that there was a shoulder on the low temperature side and a broad sub- T_g relaxation. During curing, the rubber will undergo phase separation, leading to a two-phase system. DMA provides a convenient probe to macroscopically examine phase separation. A rubbery material will have segmental mobility in the separated phase, thus, the broad sub- T_g relaxation peak on the tan δ curve would suggest this condition (Akay, 2012).

Tan δ can provide information on the overall flexibility and the interactions between the components of a composite material. The height and area under the tan δ curve offer an indication of the total amount of energy that can be absorbed by a material. A large area under the tan δ curve indicates a great degree of molecular mobility, which translates into better damping properties. This means that the material can absorb and dissipate energy better. Therefore, to design a material that can absorb impact better, the area under the tan δ curve must be increased (Sengupta et al., 2007).

CHAPTER 7: A COMPARATIVE STUDY BETWEEN RHS-FILLED NR COMPOUNDS AND COMMERCIAL PRECIPITATED SILICA (PS)-FILLED NR COMPOUNDS

7.1 Introduction

A comparative study between RHS-filled NR compound and commercial precipitated silica (PS)-filled NR compounds was conducted. Comparisons in terms of curing behaviour, and mechanical and thermal properties were conducted to determine whether RHS is suitable as the alternative to PS or not.

In this study, TESPT was chosen as the ideal silane coupling agent to modify the surface characteristics of both RHS and PS prior to compounding, as the compound that contained TESPT produced the highest cross-link density, the strongest rubber-filler interaction, and the greatest reinforcing efficiency compared with MPS and APTES. These factors have indirectly improved the overall mechanical and physical performances of the compound containing TESPT.

Table 7.1 lists the composition and the physical characteristics of both PS and RHS. These types of information are very important in this comparison because any possible differences in conjunction with the curing, and mechanical and thermal behaviours might be due to the dissimilarities between PS and RHS, as listed.
Types of silica	PS	RHS
1. Chemical Composition (%)		
SiO ₂ (min.)	93.0	99.0
Al_2O_3 (max.)	1.0	-
Salt (Na ₂ SO ₄) (max.)	2.0	-
Other metallic oxides (max.)	-	1.0
2. Physical Data		
Surface Area, BET (m ² /g)	180	234
Average Particle Size (nm)	50-120	50-100

Table 7.1: Chemical composition and physical data of PS and RHS

7.2 Cure Characteristics of RHS-Filled NR Compounds and Commercial Precipitated Silica-Filled NR Compounds

Table 7.2 presents the curing behaviour of RHS-filled NR compound and PS-filled NR compound compared with the unfilled NR. The scorch time of the unfilled NR compound was the lowest compared with RHS- and PS-filled compounds. The addition of RHS and PS at 4 phr have retarded the cure time of the NR compounds. These results showed that the unfilled compound has a tendency to scorch early and form premature cross-link network before reaching all the edges of the mould cavities. The added silica fillers have delayed the scorch time due to their ability to absorb the activator (zinc oxide) in the compound. Silica reacts with zinc oxide to form silica-zinc bond due to its polarity, which consequently would deactivate the function of the accelerator.

Both TESPT-modified RHS and PS have shortened the cure time of the NR composites compared with the unmodified silica and unfilled NR compounds. The polar groups of silane acted as curing agents and reacted with the silanol groups of RHS and PS. This reaction transformed the hydrophilic silica to hydrophobic, which interacted less with zinc oxide. Thus, the function of zinc oxide was optimised in activating the accelerator to speed up the curing process, as discussed in the previous chapters.

Table 7.2 also shows that the RHS-filled NR compound has a higher scorch time and optimum cure time compared with the PS-filled compound. These results showed similar trends following silane modification to the surface of the RHS and PS fillers. The presence of metal oxide (Al₂O₃) in PS has accelerated the curing process of the rubber compound. According to Pongdong et al. (2015), metal oxide would enhance the cross-linking reactions and increase the cure rate of the rubber compounds. A comparison in terms of the surface area and the average particle size between both fillers showed that RHS has larger surface area and smaller average particle size than PS, as seen in Table 7.1. The low surface area of PS, as indicated in Table 7.1, allowed less hydroxyl groups to be on its surface, which reduced cure retardation by the adsorption of curatives. Furthermore, zinc oxide can become more efficient in activating the accelerator system to speed up the curing process when it has less interaction with the hydroxyl groups on the PS surface.

Differences in torque (delta torque) would indicate the stiffness and cross-link density of the rubber compound. In this case, rubber compounds containing both types of silica showed higher differential torques than the unfilled NR compound. The presence of silica could increase rubber cross-links that restrict the molecular movement of the rubber chains (Lemessa & Fanta, 2017). However, the delta torque of RHS-filled NR compound was slightly higher than the delta torque of the PS-filled compound. Silane modification on the high surface area of RHS has decreased the interaction between the fillers, while increasing the interaction between the fillers and the rubber matrices. Thus, the mobility of the rubber chains was hampered by RHS, which increased the stiffness of the compound.

NR compounds	Scorch time, ts2 (min.)	Cure time, t90 (min.)	ML (dN.m)	M _H (dN.m)	Delta torque (MH - ML)
Unfilled NR	2.24	4.13	0.24	2.83	2.59
NR-RHS	2.47	4.36	0.35	3.12	2.77
NR-PS	2.42	4.31	0.33	3.05	2.72
NR-modified RHS	2.38	3.29	0.14	3.19	3.05
NR-modified PS	2.35	3.22	0.18	3.15	2.97

Table 7.2: Cure characteristics of RHS-filled NR and PS-filled NR compounds

7.3 Mechanical Properties of RHS-filled NR Compounds and Commercial Precipitated Silica-filled NR Compounds

Figure 7.1 shows the tensile strength of RHS- and PS-filled NR compounds, with and without the addition of silane coupling agent, compared with the unfilled NR compound. Adding RHS and PS at 4 phr has improved the strength of the filled NR compounds compared with the unfilled NR compound. The filler-matrix interfacial bonding was also significantly improved with the addition of TESPT. This coupling agent imparted better wetting and dispersion due to the larger amount of functional groups that could react with the silanol groups on the silica surface, which weakened the silica-silica interactions (Katueangngan et al., 2016). This has resulted in a better interfacial adhesion between the RHS and PS fillers with the NR matrix.



Figure 7.1: Tensile strength of RHS- and PS-filled NR compounds, with and without the addition of TESPT

The matrix tearing line and surface roughness of the tensile fractured samples, as observed in Figures 7.2 (a) and (b), indicate good reinforcement by the RHS- and PS-modified TESPT, respectively. The reinforced NR compounds showed higher resistance to crack propagation, which consequently enhanced their tensile properties. Without surface modification, weak interfacial adhesion between RHS and the NR matrix is formed, resulting in failure to withstand the applied stress, which leads to a very smooth and flat fractured surface of unmodified RHS-NR compound, as shown in Figure 7.2 (c). Obvious filler detachment from the NR matrix, as shown in Figure 7.2 (d), occurs due to the poor rubber-filler interaction in the unmodified PS-NR compound.



Figure 7.2: SEM images of tensile fractured surfaces at 200× magnification: (a) NR-modified RHS; (b) NR-modified PS; (c) NR-RHS; and (d) NR-PS

Without surface modification, the tensile strength of the RHS-filled NR compound was lower than that of the PS-filled NR compound. Agglomeration of the unmodified RHS within the rubber compound was responsible for the reduced tensile strength. A similar observation was made by Lemessa & Fanta (2017). However, the results became comparable after the silica fillers underwent surface modification by TESPT. The significant improvement observed for the modified RHS-filled NR was due to the large RHS surface area, as indicated by the BET surface area data in Table 7.1. Although surface modification by 2 wt.% of TESPT may not have completely modified the surface of each primary RHS particle, larger surface areas became available to the silane coupling agent during surface modification. Furthermore, the regular shape of the modified RHS particles, as shown in Figure 7.3 (a), has led to a good interaction between RHS and the NR matrix. The primary particles of the modified RHS are spherical and regular in shape, as opposed to the irregular shape of the modified PS, as shown in Figure 7.3 (b). The structure or the degree of irregularity of the filler unit is one of the key factors that could affect NR reinforcement (Da Costa et al., 2000).



Figure 7.3: SEM images of modified silica at 30.0k × magnification: (a) modified RHS filler; and (b) modified PS filler

The rubber-filler interaction can also be measured through the reinforcing efficiency of the filled rubber compounds. A high reinforcing efficiency would indicate a high rubber-filler interaction, which can be affected by the degree of filler dispersion. Good filler dispersion provides a higher surface area for interaction with the rubber matrix (Surya et al., 2014). As shown in Figure 7.4, the reinforcing efficiency of the NR compounds filled with either RHS or PS is greatly increased following surface modification by TESPT. This result can be associated with the function of the silane coupling agent as a surface modifier for the silica. Once the compatibility of the silica fillers with the NR matrix has improved, the dispersion and the rubber-filler interaction would also be enhanced. As indicated in Figure 7.4, the modified RHS-filled NR compound has a higher reinforcing efficiency than the modified PS-filled NR compound. This result is in line with the improved tensile strength shown by the modified RHS-filled NR compound, as previously discussed.



Figure 7.4: Reinforcing efficiency (RE) of RHS- and PS-filled NR compounds, with and without the addition of TESPT

As for the stiffness properties, a slight difference was identified in modulus at 100% elongation (M100) and hardness value. The RHS-filled NR compounds show higher M100 and hardness values compared with the PS-filled NR compounds, both with and without the presence of TESPT, as shown in Figure 7.5 and Figure 7.6, respectively. The higher purity of the RHS fillers, as indicated in Table 7.1, could have contributed to their superior mechanical properties, in conjunction with the stiffness of the compounds. Although the same amount of fillers was added, RHS fillers contained more silica than the commercial PS, thus, improving the stiffness of the RHS-filled NR compounds. These results are in good agreement with the elongation at break (E_b) values shown in Figure 7.7, where the E_b value of the RHS-filled compound was lower than the E_b value of the PS-filled compound. It has been proven that a stiffer compound would offer less elasticity, which would consequently reduce the value of E_b .



Figure 7.5: Modulus at 100% elongation (M100) of RHS- and PS-filled NR compounds, with and without the addition of TESPT



Figure 7.6: Hardness of RHS- and PS-filled NR compounds, with and without the addition of TESPT



Figure 7.7: Elongation at break (E_b) of RHS- and PS-filled NR compounds, with and without the addition of TESPT

The volume loss for the RHS-filled NR compound was higher than for the PS-filled NR compound, as indicated in Figure 7.8. The larger particle surface area of the RHS has led to the formation of aggregates of the primary particles. Surface modification by TESPT was unable to eliminate all hydroxyl groups on the RHS surface, as shown in the FTIR spectra of the unmodified RHS and the TESPT-modified RHS samples in Figures 6.4 (a) and (b), respectively. The hydroxyl groups, which were still present on the surface of the modified RHS, could form strong intermolecular hydrogen bonds with other hydroxyl groups on the adjacent RHS particle. These inter-particle bonds would form tight aggregates, which could lead to a poor RHS dispersion in the NR matrix. Silane modification may not be able to disintegrate them further due to their strong bonds. These rigid aggregates could have effectively weakened the rubber-filler interaction area surrounding the particles, where detachment was observed during the abrasion test. These aggregates of the RHS particles could also initiate a strong filler-filler interaction that was thought to be the main reason for the higher volume loss in the RHS-filled NR compound compared with the PS-filled NR compound. Similar observations were reported by Cardona-Uribe et al. (2018).



Figure 7.8: Volume loss in RHS- and PS-filled NR compounds, with and without the addition of TESPT

7.4 Thermal Properties of RHS-filled NR Compounds and Commercial Precipitated Silica-filled NR Compounds

The effects of adding RHS and PS on the thermal degradation behaviour of the rubber matrix were investigated. The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves are shown in Figures 7.9 and 7.10, respectively. A summary of the important characteristic temperatures obtained from the TGA curve and the remaining char residues are listed in Table 7.3. The decomposition temperatures within the degradation phase directly represented the effects of the added RHS and PS fillers on the thermal stability of the NR matrix.

Generally, two main degradation stages would occur in silica-filled NR compounds (Halim et al., 2018). In this study, the first stage involved the initial weight loss that occurred at a temperature lower than 200°C. This process can be associated with the elimination of volatile components, such as water. Due to the small weight loss from absorbed water, no bend or peak appeared in both TG and DTG curves. The second stage

occurred between 350 to 450°C. During this stage, all compounds experience maximum decomposition with a large weight loss, as seen in Figure 7.9. The temperature at the maximum weight loss (T_{max}) is indicated by the lowest peak of the DTG curve in Figure 7.10. The maximum weight losses could be attributed to the primary chain scission of the NR cross-links into low molecular weight segments. However, the DTG curve of the modified PS-filled NR compound showed an additional shoulder close to the maximum DTG peak at 380 to 390°C. In addition to silica, PS also contains other inorganic elements, such as aluminium oxide (Al₂O₃) and sodium sulphate (Na₂SO₄), as indicated in Table 7.1. The additional stage of small weight loss prior to the major degradation of NR compound could be due to the reaction between the inorganic elements in PS and TESPT. The shifting of the degradation temperature of the modified PS-filled NR compounds could be due to the barrier effect created by the PS particles to hamper diffusion of volatiles to the surface. This rare observation is reinforced by similar reports by Halim et al. (2018).



Figure 7.9: Thermogravimetric (TG) analysis curves of RHS- and PS-filled NR compounds, with and without the addition of TESPT



Figure 7.10: Derivative thermogravimetric (DTG) curves of RHS- and PS-filled NR compounds, with and without the addition of TESPT

The delay in the degradation process following the addition of RHS and PS fillers to the NR compounds can be clearly understood based on Table 7.3. The decomposition temperature at $T_{10\%}$ of the NR compound was delayed by 11°C with the addition of unmodified RHS and only 1°C with the addition of unmodified PS. However, the degradation temperatures were increased with the addition of silane coupling agents to both types of fillers, especially to the PS-filled NR compounds. Significant increases were also detected at thermal decomposition properties of $T_{50\%}$ and $T_{75\%}$, where both silanemodified RHS- and PS-filled NR compounds recorded higher decomposition temperatures compared with unmodified silica-filled NR compounds. These results showed that the surface modification of the fillers has strengthened the interaction between the filler particles and the rubber matrix. Consequently, the degradation of the cross-linked rubber was decreased at higher temperatures and improved the thermal stability of the compounds. The amount of the remaining char residues can also be measured by TGA. Based on Table 7.3, the unfilled compound was mostly decomposed into volatiles, leaving only 0.1% of residues behind. The amount of char residues of the modified RHS-filled NR compound was slightly higher than for the unmodified RHS-filled compound. These values were close to the actual weight fraction of the RHS in the NR matrix. A similar trend was recorded for the PS-filled NR compound, where the amount of char residues of the modified PS-filled compound was higher than for the unmodified PS-filled compound. However, the char residues of the modified PS-filled compound showed an excess from the weight fraction of the PS in the NR matrix. According to Fu et al. (2013), Al₂O₃ played an important reinforcing effect, not only on the mechanical and physical properties, but also on the thermal stability of the NR compounds. In this study, silane modification of PS could have indirectly reacted with Al₂O₃ and Na₂SO₄ in PS. Therefore, any possible reactions between silane and other elements in PS during the degradation stages at high temperatures could possibly delay the decomposition process, thus increasing the char yield of the compound.

Table 7.3: Thermal decomposition properties an	nd residues	of RHS-	and	PS-filled
NR compounds, with and without the addition of	f TESPT			
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Parameter	T10% (°C)	T50% (°C)	T75% (°C)	T _{max} (°C)	Residue (%)
Unfilled NR	342	387	415	382	0.1
NR-RHS	351	391	419	385	5.2
NR-modified RHS	353	395	423	388	5.9
NR-PS	343	391	417	383	3.1
NR-modified PS	355	396	425	393	7.2

CHAPTER 8: CONCLUSIONS AND RECOMMENDATIONS

8.1 Introduction

Conclusions on the findings for all series are summarised in this chapter. Recommendations for future work on synthesising RHS and the process parameters for the filled-rubber are also included.

8.2 Conclusions

The following conclusions were drawn based on the experiments that have been conducted:

- 1. Highly pure white silica was effectively extracted from rice husks using the solvent-thermal treatment method, followed by HCl leaching with different concentrations.
- 2. RHS leached with 1.0 M HCl, which was approximately 50 nm in size, as seen in the SEM and TEM images, recorded the highest purity with 99.99% of silica content and the highest BET surface area of 234.25 m²/g. The XRD results showed that following incineration at 700°C, all RHS samples remained in the amorphous state. Thus, 1.0 M was chosen as the optimum molar concentration for HCl, to be used in leaching the treated RHS for further study since higher acid concentrations had shown no significant modification to the overall properties of RHS.
- 3. The strength-related properties of the treated RHS-filled NR compounds had shown higher improvements compared to the properties of untreated RHA-filled NR compounds. The presence of metallic impurities in the untreated RHA had reduced its purity and surface area, thus weakening the interaction between the

rubber matrix and the RHA particles. NR compounds filled with 4 phr of RHS displayed remarkable enhancements in overall properties as at higher filler loading, the fillers became agglomerated and formed bigger-sized RHS as shown in SEM images. This caused the reduction in overall strength-related values. Thus, the amount of 4 phr was chosen as the optimum loading of RHS for further study in Series 4. The thermal stability of RHS-filled NR compounds was also improved compared with the unfilled NR compounds.

- 4. This study has shown that all three types of silane coupling agents, namely, TESPT, MPS, and APTES used in the surface modification of RHS, were capable of significantly improving the overall properties of RHS-filled NR compounds. The combined enhancements in the cross-link density, rubber-filler interaction, and reinforcing efficiency of the silane-modified RHS-filled NR compounds were responsible for the improved mechanical and thermal properties. Based on these results, it can be summarised that the NR compound with sulphur-containing coupling agent was more prone to show the effects of rubber-RHS coupling than the sulphurless coupling agents. TESPT had shown the most practical and technical benefits for the RHS-filled NR compound compared with MPS and APTES.
- 5. Comparisons were made between RHS and commercial PS as fillers in NR compound. The performance of RHS as fillers for NR was equivalent to PS. Thus, RHS synthesised by solvent-thermal treatment method is suitable to be further developed as a reinforcing-filler for NR.

Further research on the effectiveness of RHS as filler in rubber would help to develop a sustainable alternative to the silica source in rubber industry. The following suggestions can be implemented to feed the purpose:

- The effectiveness of RHS filler in rubber synthesised by other treatment methods that were previously developed can be compared with the RHS synthesised by solvent-thermal treatment method.
- 2. The organic acids such as acetic acid, oxalic acid, and citric acid can be utilised as an alternative for strong acids like HCl to treat rice husks due to their low cost.
- 3. Higher loadings of RHS fillers could be incorporated into the rubber blend using an internal mixer. The internal mixer is a robust mixing mill, which is able to reduce the viscosity of the rubber blend and could also disperse the higher loadings of filler aggregates and agglomerates better than a two-roll mill.
- 4. Early addition of RHS to the internal mixer is recommended, while the addition of zinc oxide is withheld until the second stage of the mixing procedure to prevent undesirable reactions between silica and zinc oxide.
- 5. Hybrid fillers that consist of carbon black and silica from rice husks can be studied as the combination of both may offer superior properties to the rubber compound. The synergistic effect and compatibility of the hybrid fillers in various types of rubber matrices and rubber blends can be analysed. A comparison with other conventional fillers shall be conducted, in terms of curing characteristics, crosslink density, reinforcing efficiency, and mechanical properties. The findings from these studies might be useful for developing a new formulation of hybrid fillers with RHS to be utilised in various commercial applications, such as tire treads hoses and engine mounts.

- 6. Future work on examining the effect of particle size distribution (PSD) of the RHS on the properties of the rubber composites can be conducted, especially for filler with nanoscales. Nano-filler with high BET surface area would give good interaction with the polymer matrix.
- 7. The determination of silanol concentration or the number of silanol per square nanometer of surface area of silane-modified RHS should be analysed, thus the interface of RHS fillers with the rubber matrix could be studied in detail.
- The repeatability of TGA analysis of silane-modified RHS-filled NR compounds is required to confirm the results obtained, since the differences in the values are too close to each other.

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