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Silica Extraction from Aluminum Sulfate Byproduct and its Application as Rubber Filler in the Tire Industry

by

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Confirmation Page

The thesis by Tujuba Tamiru, titled " ***Silica Extraction from Aluminum Sulfate Byproduct and its Application as Rubber Filler in the Tire Industry***" for the master of science in materials engineering degree, has been certified to meet university regulations and standards for originality and quality.

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Declaration

I confirm that this thesis is my own work and has not been previously submitted for a degree at any university. I have properly cited all sources used in the thesis.

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The thesis has been submitted for examination with my approval as university advisor

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List of acronyms

AAS	Atomic absorption spectrophotometer
AMCF	Awash Melkasa Chemical Factory
ASTM	American standards for testing and measuring
COS	Commercial silica
FCS	Filter cake silica
FTIR	Fourier Transform Infrared Spectroscopy
LOI	Loss on ignition
MBTS	Mercaptobenzothiazole disulfide
IPPD	N-isopropyl-N'-phenyl-p-phenylenediamine
PHR	per hundred resins
SEM	Scanning Electron Microscope
XRD	X-Ray Diffraction
XRF	X-ray Fluorescence

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Abstract

Valorization of byproducts from chemical manufacturing is critical for reducing environmental impact advocating circular economy. High silica filter cake from Awash Melkasa Chemical Factory (AMCF) is disposed in landfills after producing aluminum sulfate. This study aimed to produce amorphous precipitated silica from byproduct of Awash Melkasa Chemical Factory and explore its potential as rubber filler in tire industry. Filter cake byproduct from Awash Melkassa Chemical factory was calcinated at a controlled temperature of 550 ℃ for 3 hours, followed by the extraction of amorphous silica using sol-gel technique. To characterize phase composition, chemical structure, morphology, and surface area of the as prepared silica filler, XRD, FTIR, SEM, BET, AAS, and XRF were employed. Silica with purity of 92.50% was obtained and tested as reinforcing rubber filler in tire industry. Curing characteristics of natural rubber compound filled with filter cake silica and commercial silica were examined with Rheo-line moving die and Mooney viscometer. Compound reinforced with filter cake silica has shorter curing time than compound filled with commercial silica due to finer particle size and high surface area revealed by SEM and BET respectively. Filter cake silica filled rubber compound showed better mechanical properties, compared to commercial silica reinforced rubber compounds. The lower Mooney viscosity of filter cake reinforced rubber compound makes filter cake reinforced rubber compound easier to process compared to commercial silica reinforced compounds. Morphology analysis of filter cake silica shows it is fine, and better filler for rubber applications in tire industries. Commercial silica has lower specific gravity and has less reinforcing ability in rubber compound, while filter cake silica filler has higher specific gravity that makes better reinforcing filler in rubber compounds. Therefore, amorphous silica from filter cake is potential filler in tire industry and the use of filter cake silica filler is a potential solid waste management in Awash Melkasa Chemical Factory and related industries.

Key words:filter cake silica,sol-gel technique,rubber filler, rubber curing characteristics, Mooney viscosity

CHAPTER ONE

1. Introduction

1.1 Background

Tire industry heavily relies on the incorporation of fillers to enhance the properties and performance of rubber compounds utilized in tire applications [1]. Fillers are essential for enhancing the mechanical properties and curing characteristics of rubber compounds and its choice significantly impact the final properties of the rubber compounds. The type, size, and loading level of fillers play a crucial role in shaping the final properties of the rubber compound, making filler selection a critical consideration in rubber formulation. Amorphous and large surface area fillers enhance the properties of natural rubber and improve the curing and mechanical properties of rubber compounds [2].

Carbon black derived from petroleum has long been a cornerstone in the rubber industry for its exceptional reinforcement properties. It is widely utilized to enhance the tensile strength, abrasion resistance, and durability of rubber compounds, making it a popular choice in tire manufacturing and various rubber compounds [3]. High hysteresis, non-renewability, and environmental concerns associated with carbon black production and usage have prompted researchers and industry stakeholders to explore alternative filler materials that offer comparable performance benefits while addressing sustainability and environmental impact considerations [4]. The quest for sustainable and eco-friendly filler alternatives has become a focal point in the rubber industry, driving innovation and research towards developing novel solutions that balance performance with environmental responsibility.

Commercially available precipitated silica is also widely used filler in tire industry for rubber filler, where it plays a crucial role in improving wet grip, reducing rolling resistance, and enhancing overall durability [5]. Silica fillers offer several advantages over carbon black like improved fuel efficiency, better traction, and enhanced wear resistance [6]. However, conventional precipitated silica presents challenges related to dispersion and processing due to its surface characteristics, which can impact the overall performance of rubber compound.

Precipitated Silica is traditionally produced by melting quartz sand with sodium carbonate at a high temperature of 1300 °C, which consumes a lot of energy [7]. Traditional technique involves reacting sodium carbonate powder and quartz sand to generate intermediate sodium silicate solution, which is then precipitated with hydrochloric acid solution [8]. Researchers are looking into alternative sources of silica from industrial byproducts as a sustainable and environmentally friendly option for rubber filler materials in the tire industry. This is due to the limitations associated with conventional silica fillers and the significant threat they pose to human health and the environment [9].

Ethiopia is facing challenges in importing commercial silica for its manufacturing industries due to revaluation of foreign exchange rates and increasing demand from silica-consuming industries. However, there is potential to use locally sourced industrial byproduct silica as an alternative to traditional silica fillers in the rubber industry. Valorization of industrial byproduct in the production has become a feasible substitute material to reduce resource scarcity and save natural resources for future generations [10]. Utilization of industrial byproducts for industrial raw materials is the main focus of current study due to its economic significance, environmental safety, cost competitiveness, and local availabilities. During aluminium sulfate extraction process 58% to 68% silica with additional trace oxides are dumping into landfills [10, 11].

By extracting silica from industrial byproducts, tire industries can address environmental issues, reduce waste, and promote sustainability in rubber manufacturing [12]. Also, silica from byproducts offers a range of advantages, including improved dispersion, enhanced processing efficiency, and cost-effectiveness compared to conventional silica fillers [13]. Additionally, utilizing industrial byproducts as fillers aligns with circular economy principles by valorizing waste materials into valuable resources for the rubber industry [10]. Using silica derived from industrial byproducts in tire industry as rubber filler provides performance advantages while promoting environmental responsibility and resource efficiency [14]. This highlights the significance of sustainable practices and innovation within the rubber sector.

1.2. Statement of the problem

The rubber industry is confronted with a critical challenge concerning the selection and utilization of fillers in rubber compounds, as fillers play a pivotal role in shaping the properties and performance of rubber compounds [15]. Carbon black is traditional filler that has been instrumental in providing reinforcement benefits to rubber compounds and accompanied by significant problems like high hysteresis, non-renewability, and environmental concerns [16, 17].

Commercially available precipitated silica fillers are known for their ability to enhance wet grip, reduce rolling resistance, and improve overall durability of rubber compounds in tire industry. Conventional method of extracting precipitated silica for rubber filler from quartz consume huge amount of energy, resource-intensive and environmentally hazardous [3]. Rubber filler is made by energy-intensive and wastage releasing ore-based silica production process. To prepare commercial amorphous silica, quartz sand and sodium carbonate powder are reacted at a high-temperature to produce intermediate sodium silicate solution, which is then titrated with hydrochloric acid to precipitate silica [8]. Negative side of conventional silica preparation method was its high energy consumption, heavy environmental pollution, and huge CO_2 production these are against the sustainable development goals. In order to prepare ton of precipitated silica from sulfuric acid and sodium carbonate, carbon dioxide (CO_2), sodium sulfate, and huge amount of wastewater are released into the environment this showing the conventional method is environmentally hazardous and unfriendly [18]. Drawbacks of carbon black and commercial silica necessitate a shift towards more sustainable and eco-friendly options that can maintain or enhance the performance of rubber compounds while minimizing environmental impact [19].

Using FCS as rubber filler in the tire industry offers advantages of enhancing energy efficiency, lowering carbon emissions, and preserving natural resources for future use. Minimal energy needed for extraction, the high silica content, the affordability of raw materials, health considerations for nearby communities, and the extensive area occupied by waste disposal from the aluminum sulfate extraction process are driving factors for extracting amorphous precipitated silica from filter cake byproduct.This study focuses on developing innovative rubber fillers that improve rubber properties, reduce environmental impact, and promote sustainability in tire manufacturing. Additionally, the

study seeks to find a solution for the issue of filter cake from Awash Melkassa chemical factory, which is impacting local residents and posing challenges for the factory in disposing of its byproducts. By valorizing silica from aluminum sulfate byproduct as rubber filler in the tire industry, the research aims to benefit both the nearby communities and the factory itself, while also enhancing corporate social responsibility efforts.

Therefore, Valorization of filter cake silica in tire industry as rubber filler saves foreign currency for the country and aligns with sustainable development goals by promoting eco-friendly practices in the industry [20, 21].

1.3. Research questions

- What are the effect of leaching time and acid concentration on silica yield?
- How does the surface area and specific gravity of FCS impact the reinforcement and overall properties of rubber compounds compared to conventional silica filler?
- How does utilization of filter cake silica as rubber filler in tire industry affect the mechanical properties and curing characteristics compared to conventional silica?

1.4 Objectives

1.4.1 General objective

The general objective of this study is to extract silica from aluminum sulfate byproduct and study its application as rubber filler in the tire industry

1.4.2 Specific objectives

- To enhance silica purity by using appropriate solvent and operating parameter
- To investigate the effect of leaching time and acid concentration on the silica yield
- To study the effect of filter cake silica on curing characteristics and mechanical properties of rubber compounds

1.5 Significance of the study

Managing solid waste effectively, reduction of environmental impact and lowering carbon dioxide emissions during silica production for rubber filler are some benefits of valorizing filter cake byproduct as rubber filler in tire industry. Using FCS as rubber filler has environmental advantages, revenue opportunities, and cost savings for filter cake byproduct producer. Quality improvement, cost reduction and competitiveness are advantage of using FCS as rubber filler in tire industry. Additionally, the significance of incorporating FCS in tire manufacturing as rubber filler extends beyond material substitution; it represents a shift towards more sustainable, cost-effective, and innovative practices within the industry.

1.6. Scope of the study

The study covers amorphous precipitated silica extraction, characterization, studying the effect of rubber fillers,FCS and COS, on curing characteristics and mechanical properties of rubber compounds.

CHAPTER TWO

2. Literature review

2.1. Silicon dioxide

Silicon dioxide is a natural mineral compound composed of silicon and oxygen, which are abundant elements in the earth's crust. It is commonly found in nature and in various living organisms. Silicon dioxide occurs naturally in both crystalline and amorphous forms. Silica is a mineral found in volcanic rock and gemstones. One of the most prevalent oxide and silicon compounds in the Earth's crust. Silica is a low-cost and versatile inorganic filler used in building, automotive, consumer goods, and polymer applications [21]. Silicon dioxide, also known as silica, occurs naturally as sand and serves as a raw material for several valuable compounds, including silicone and silicates [2].

2.1.1. Physical properties of silicon dioxide

Silica, also known as silicon dioxide, is a versatile material with various physical properties that make it valuable in different industries. It is a hard, transparent crystalline solid with a high melting point, making it suitable for high-temperature applications like refractories and ceramics. Silica is also known for its thermal stability, resistance to thermal shock, and poor electrical conductivity, making it useful in insulating coatings, electronics, and semiconductor industries. Its high hardness contributes to abrasion resistance, while low thermal expansion is beneficial for precision optics and semiconductor manufacturing [22]. Additionally, silica is chemically inert, non-toxic, and biocompatible, making it safe for use in pharmaceuticals, food processing, cosmetics, and as a binder or filler in composite materials. Its diverse properties make it a versatile material with applications in construction, manufacturing, healthcare, and environmental protection. Silicon dioxide has a high melting point because of its unique tetrahedral structure [23]. To break the strong silicon-oxygen covalent bonds, high temperatures of around 1700 ℃ are required. Another result of the strong covalent link between silicon and oxygen is silicon dioxide, which is exceedingly hard and rigid. Silicon dioxide is an insulator and poor electrical conductor due to its chemical structure, which lacks free electrons. Water and other organic solvents are unable to dissolve silicon dioxide. However, it is soluble in both alkalis and hydrofluoric acid [22].

2.1.2. Chemical properties of silicon dioxide

Silica is known for its inertness at low temperatures and resistance to chemical interactions. It remains stable even at high temperatures, making fused quartz a popular choice for chemical equipment where blocking metal cation catalytic processes are important. This lack of reactivity is attributed to silica's macromolecular structure and the strong Si-O bond it possesses.

Alkaline compounds, such as KOH, can also damage SiO_2. The size of the crystal and the change influence how rapidly the reaction occurs. In hot, watery, alkaline liquids, crystalline quartz dissolves slowly, but amorphous SiO_2 dissolves quickly at room temperature [23, 24].

$$SiO_2 + 2KOH \rightarrow K_2SiO_3 + H_2O \quad \text{……..…2.1}$$

Silica reacts with strong bases, including NaOH and KOH, HF at room temperature, Na_2CO_3 and K_2CO_3, $CaCO_3$ at high temperatures, carbon at extremely high temperatures, and water. Under high temperatures and pressures, water hydrolyzes silica to form silicon hydroxide, which is extremely unstable [24, 25].

2.1.3. Amorphous silicon dioxide

Amorphous silica particles with a large surface area are commonly used in various products such as defoamers, adhesives, plastics, sealants, coatings, inks, toners, and cosmetics. They are also important in catalysis and have potential applications in advanced composite materials and controlled drug release printing on cotton fabric [15]. The final colloidal particles' binding strength determines whether amorphous silica is in the form of a gel or powder. Silica gels have a structured three-dimensional network of continuous particles, while silica powders consist of loosely connected aggregates of submicron particles or small silica gel granules [26, 27].

Amorphous silica is a natural material made up of tiny particles or small silica gel granules. It is composed of silicon and oxygen atoms in a disordered, non-crystalline arrangement [18]. Amorphous silica is a versatile material that can be produced using different techniques like sol-gel processing, silane hydrolysis, and precipitation. It possesses special characteristics like a large surface area, stability at high temperatures, and strong mechanical properties. These qualities make amorphous

silica valuable for a wide range of uses, such as drug delivery, catalysis, water treatment, and enhancing polymers [24].

Amorphous silica is made up of interconnected SiO_4 tetrahedral, with each silicon atom bonded to four oxygen atoms. The oxygen atoms can form bonds within the network (Si-O-Si) or outside the network (Si-O), depending on how it is made. The surface of amorphous silica is usually covered with silanol groups (Si-OH), which can be stabilized by hydrogen bonding or siloxane bridges (Si-O-Si). These surface characteristics are important for how amorphous silica interacts with other substances and its various uses [2].

The structure of amorphous silica can be modified by changing the way it is made, resulting in materials with different pore sizes, shapes, and capacities. This flexibility makes amorphous silica suitable for a range of uses, including adsorption in processes like ion exchange, water purification, and drug release.

2.2. Preparation of silica from industrial byproducts

The preparation of silica from industrial byproducts represents a significant advancement in sustainable materials science and resource utilization [19]. By harnessing waste materials which is abundant in silica content, researchers and industries can extract valuable silica for various applications. This innovative approach not only addresses the challenge of waste management but also contributes to the circular economy by transforming byproducts into functional materials [25]. The process of preparing silica from industrial byproducts involves sophisticated extraction, purification, and processing techniques to ensure the quality and performance of the final product. Through careful optimization of these methods, silica with tailored properties can be obtained to meet the specific requirements of different industries, such as rubber manufacturing for tire treads [26].

The utilization of silica from industrial byproducts offers a sustainable alternative to traditional silica sources, reducing the reliance on finite natural resources and minimizing the environmental footprint of industrial processes [27]. Recycling of waste materials for silica production also aligns with the principles of green chemistry and sustainable development, promoting resource efficiency and waste reduction. The incorporation of silica derived from industrial byproducts in rubber compounds can

lead to enhanced mechanical properties, improved performance, and potential cost savings in tire manufacturing [6].

2.3. Silica production by commercial method

Silica is commonly made from sodium silicate, which is created by heating quartz sand with sodium carbonate at high temperatures. This process is expensive and energy-intensive, leading to significant wastewater and greenhouse gas emissions. However, sodium silicate can also be produced at lower temperatures using industrial byproducts, offering a more cost-effective and environmentally friendly method for extracting silica.

2.4. Parameters affecting silica production

The production of silica from byproducts like rice husk ash involves key parameters that impact efficiency and quality. Optimizing impregnation ratio, extraction reagent concentration, reaction time, and reusing reagents are crucial for maximizing yield and sustainability. Purification methods like filtration and washing are essential for obtaining high-purity silica powders.

2.4.1. Burning temperature

The temperature at which byproducts like rice husk ash are burned is crucial for extracting silica efficiently. A higher burning temperature can enhance the decomposition of organic components in the byproduct, leading to a higher silica concentration in the ash [10]. This increased silica content aids in the extraction process by providing a better starting material yield. However, excessively high temperatures can cause issues like thermal degradation of silica or the formation of unwanted impurities, impacting the quality of the extracted silica. Therefore, it is important to optimize the burning temperature to balance organic matter decomposition, silica preservation, and overall yield. By carefully managing the burning temperature, researchers and industry professionals can improve the efficiency and quality of silica extraction from byproducts in a sustainable and cost-effective manner.

Filter cake ash, which is abundant in silica, can be transformed into pure silica by carefully controlling the burning process. By adjusting factors such as temperature and duration of incineration, it is possible to produce high-quality amorphous silica from filter cake ash.

2.4.2. Effect of reaction temperature

The study explores how changing the reaction temperature affects the yield of silicon dioxide. By adjusting the temperature at different stages of the reaction, it is possible to control the nucleation and growth rates, ultimately influencing the final performance of the silica. making temperature constant throughout the silica preparation process is important to analyze its impact on silica preparation [28].

2.4.3. Effects of caustic soda concentration

The effect of reaction time on silica extraction and yields is crucial in the production process. By varying the reaction time, the efficiency of silica extraction can be optimized. It has been observed that the yield of silica increases with the extension of the reaction time up to a certain point. However, beyond this optimal reaction time, there may not be a significant increase in silica yield [29]. Therefore, determining the appropriate reaction time is essential to achieve the maximum extraction of silica from the raw material, such as rice husk ash. The effectiveness of the silica formed during precipitation is greatly influenced by the concentration of the base solution. In optimal conditions, a white precipitate is produced. To create silica with a high specific surface area, a low concentration of the base solution is often used, causing the nucleation rate of the reaction to exceed its growth rate [25].

2.4.4. Effect of reaction temperature

Because reaction temperature has a direct impact on chemical reaction rate, raising it will result in faster nucleation and growth. More reaction time helps to complete the caustic soda and silica procedures. As a result, we may adjust the temperature of the reaction at different stages to control the rate of silica nucleation and growth before determining its final performance [26, 27].

2.4.5. Aging time

The aging process is crucial for defining the quality and quantity of prepared silica. Gel synthesis without ageing resulted in the lowest concentration and extraction yield of SiO_2, indicating that ageing time is required for optimal gel formation. The early aging stage may contribute in the formation of silica precipitates. Increasing the ageing duration did not always result in a higher concentration and extraction yield of SiO_2. The optimal time to develop and produce silica gel should be determined [27, 28].

2.4.6. Effect of leaching on silica yield

Leaching is a great method for extracting silica. The metallic components, notably potassium, have a substantial impact on the quality of FCS by causing surface melting and accelerating amorphous silica crystallization. Furthermore, a strong contact arises between the metallic ions and the silica, resulting in a significant reduction in surface area. Filter cake is a significant industrial byproduct. Filter cake has a high level of inorganic oxides. Silica makes up a major part of industrial waste, with the balance being Al_2O_3, K_2O, CaO, MgO, and P_2O_5, which reduces silicon dioxide concentrations [29]. As a result, leaching methods that reduce or remove metallic impurities are necessary to improve the properties of the produced filter cake ash and increase the chances of obtaining silica with a high yield, purity, and surface area.

2.5. Forms of silica extraction

Kaolin, quartz, silica sand, and feldspar are industrial minerals polluted by harmful impurities such as aluminum, iron, titanium, magnesium, calcium, and potassium oxides. Silica can be extracted in a variety of ways, including fumed silica, precipitated silica, silica gel, and colloidal silicon.

2.5.1. Silica gel

Silica gel is a porous solid form of hydrous silicon dioxide with the chemical formula $SiO_2.xH_20$. It consists of an irregular tridimensional framework of silicon and oxygen atoms with nanometer-sized spaces and pores. Silica gel is made up of polymerized silicate particles and is commonly produced using the sol-gel process [30, 31]. Silica gels have a wide range of applications including gas

adsorption, chromatography, optics, cosmetics, personal care products, medication administration, and chemical reaction catalysis. Silica gel is used as a support material for catalysts in a variety of chemical reactions because of its high surface area and ability to immobilize catalytic species. Its high porosity and surface area allow components to be effectively separated based on how similar they are to the silica surface, and its biocompatibility and adjustable pore.

Silica gel is a popular desiccant because of its ability to adsorb water molecules. It is also used as a texturizer and absorbent in cosmetics and personal hygiene products, such as powders and creams, as well as in advanced electronic and optical devices such as micro resonators, waveguides, and photonic crystals. It is also used to protect electronics from corrosion, keep paperwork safe, and storing sensitive information.

2.5.2. Colloidal silica

Colloidal silica is silica that exists as a colloidal dispersion in a liquid medium, typically water. Silica sol and silica nanoparticles are other names for the same thing. Under a microscope, the particles in this non-crystalline, amorphous kind of silicon dioxide (SiO_2) appear translucent. Colloidal silica particles range in size from nanometers to micrometers, depending on how the material is manufactured and purified. Because of the small size of these particles, colloidal silica has unique properties such as great dispersion stability, large surface area, and excellent adsorption [39]. Colloidal silica is used as a paint ingredient to improve the overall performance of the paint, including leveling, sedimentation stability, and anti-sagging properties [32].

Colloidal silica is used as a binder, dispersion, and viscosity modifier in the production of ceramics and glass, allowing for more control over the density, porosity, and other properties of the finished product. To enhance the casting process, colloidal silica is added to the melt to suppress the formation of air bubbles, increase the fluidity of the melt, and fine-tune the cast microstructure. Colloidal silica is added to cement-based products to improve performance, such as greater compressive and flexural strength, reduced water permeability, and increased durability. Colloidal silica is employed as a selective adsorbent or catalyst in many treatment processes to remove organic pollutants, heavy metals, and other contaminants from water, soil, and air. Because of its high surface area, inertness,

and capacity to regulate the release of active substances, colloidal silica is used as an excipient in a variety of formulations [40].

2.5.3. Precipitated silica

Precipitated silica is a type of silicon dioxide created by mixing sodium silicate with acids. It is valued for its characteristics like a high surface area, porous structure, and strong bonding with rubber, making it a popular choice for enhancing rubber and tire performance [33]. Precipitated silica is a white, powdery amorphous form of silica. Precipitated silica is obtained by precipitating silicate salts from a solution. Amorphous silica is divided into three types: pyrogenic, precipitated, and silica gel. Precipitated silica, also known as amorphous silica, is created by acidifying sodium silicate solutions.

Fused quartz is created by melting pure quartz crystals at temperatures of around 2000 ℃ using specialized furnaces powered by electricity or gas and oxygen [6]. Precipitated silica possesses a significant surface area of 100 to 500 m^2/g, allowing for enhanced interactions with rubber chains. This leads to improved mechanical properties in materials, including modulus, tensile strength, and abrasion resistance [39]. The porous nature of precipitated silica enhances its interaction with the rubber matrix, leading to stronger reinforcement effects. Additionally, the porous structure helps improve the dispersion of silica particles within the rubber, ultimately enhancing the overall performance of the material [41].

Hydrophilic means that precipitated silica has a strong attraction for water. Depending on the intended purpose, this trait may be advantageous as well as disadvantageous. The hydrophilicity of precipitated silica in tyre applications can improve wet traction performance. Precipitated silica's hydrophilicity, on the other hand, may be undesirable in applications where water resistance is critical, such as adhesives, coatings, or some types of rubber. The surface chemistry of precipitated silica can be modified by adding organic moieties to the silica surface using a process known as silanization. These surface modifications can have a significant impact on the interaction between the silica and the rubber matrix, resulting in improved mechanical properties and compatibility with other composite materials.

In instances where the material will be exposed to high temperatures, precipitated silica often exhibits good thermal stability. Furthermore, because precipitated silica can change the glass transition temperature of a composite material, its thermal stability can have an impact on its reinforcing properties.

2.6. Natural rubber

Polyisoprene is a pure version of natural rubber (NR), an elastomeric substance. Organic impurities, such as proteins and phospholipids, include trace amounts of natural rubber (NR), a biopolymer generated from rubber trees. It is made up of isoprene units (C_5H_8) that are connected to create long polymer chains, also known as cis-1,4-polyisoprene. The general structure of the resulting polymer, polyisoprene, is [-CH2-CH=(CH3)-CH2-]n where n indicates the number of isoprene units polymerized to form the long polymer chains.

The glass transition temperature (T_g) for NR is around -70 °C. Rubber bands, condoms, gloves, threads, and other materials are just a few of the many applications for NR, which has exceptional strength, flexibility, and resilience to a wide range of corrosive substances. However, because isoprene units include many double bonds, NR is easily broken down by heat, oxygen, and ozone.

The mechanical and elastic properties of NR are not high enough for practical use without crosslinking. During the manufacturing process, rubber is treated with a variety of additives, including fillers, sulfur, activators, and accelerators, to enhance or enable sulphur vulcanization [24]. Fillers are frequently added to rubbers to increase their mechanical strength, processability, and cost-effectiveness [25].

2.6.1. Chemistry of rubber compounding

Compounding uses a variety of chemicals, such as elastomers, accelerators, antidegradants, processing aids, and fillers. Elastomers have elastic, flexible, robust, and water and air impermeable properties [39]. They can fast return to their original shape and have double bonds in the backbone that can be vulcanized to provide elastic characteristics. Chemical reactions and cross-linking of elastomer molecules are caused by vulcanization agents like sulphur. Activators, like as MBTS, accelerate the vulcanization process and shorten its duration. Antidegradants like zinc oxide and

stearic acid are added to rubber compounds to prevent degradation from various factors like oxygen, ozone, heat, light, metal catalysis, and mechanical stress. Additionally, processing aids such as fatty acids, fatty acid metal salts, low molecular weight polymers, hydrocarbon oils, and peptizer are used to treat rubber compounds for easier processing. Fillers are often added to rubber, the main polymer in tires, to enhance its properties [10]. Fillers, such as carbon black and silica, are used to improve physical properties, impart processing features, or reduce costs. Overall, compounding is the act of combining multiple chemicals to create a long-lasting product.

2.7. Precipitated silica in rubber compounds

Rubber composites incorporating silica have emerged as an intriguing alternative to standard carbon black fillers due to their higher reinforcing capabilities and improved performance in a wide range of applications. Silica-based rubber compounds offer improved mechanical properties, reduced rolling resistance, and enhanced wet grip, making them ideal for use in tire treads. Silica has been utilized in rubber compounds since the early 1970s, when it was developed to replace carbon black. Advances in silica processing and formulation have led to the development of precipitated silica, which has higher reinforcing properties than typical silica fillers.

Silica-based rubber compounds' performance is greatly affected by the molecular interactions between silica particles and rubber molecules. Silane coupling agents enhance these interactions by forming covalent bonds between the silica surface and the rubber matrix, leading to improved overall performance [21]. As a result, silica particles are distributed more evenly throughout the rubber matrix, resulting in improved adhesion and mechanical properties.
To achieve optimal performance, silica-based rubber compounds must be appropriately designed, taking into account factors such as filler loading, rubber type, and processing circumstances. The choice of rubber polymer has a significant impact on silica particle dispersion and adhesion, with natural rubbers frequently being more friendly with silica than synthetic rubbers. Furthermore, due to their high compound viscosity, silica-based rubber compounds can be difficult to process, necessitating changes to the compounding and processing properties [22].

2.8. Description of reinforcing fillers

Filler reinforcement involves incorporating additional materials into a compound to enhance its mechanical properties, including stiffness, strength, toughness, and durability against wear and environmental factors. Fillers are widely utilized in rubber compounds and have a significant influence on both compound and vulcanizate properties. Fillers used to modify rubber properties often have an essential capacity that allows them to connect to the rubber matrix, hence enhancing processability and ultimate product performance. Active fillers or reinforcing fillers, are categorized based on factors such as particle surface activity, size, surface area, and structure.

2.8.1. Factors influencing filler reinforcement

2.8.1.1. Particle surface activity

Active fillers, unlike inert fillers, can form a strong bond with the rubber matrix because of their ability to interact with and react with rubber. The specific type and form of functionality present on the filler's surface play a crucial role in determining the chemical interaction between the filler and rubber. In some cases, fillers need to be customized to match the surface chemistry of a particular type of rubber [35].

2.8.1.2. Filler size and distribution

Distribution and size of filler particles in a composite material are important factors that influence how effectively they strengthen the material. Smaller filler particles often provide better reinforcement due to their increased surface area and ability to form stronger interactions with the matrix material. To produce the best mechanical properties, filler particles must be equally dispersed. Silica and carbon black are small reinforcing fillers with primary particle sizes between 10 and 100 nm, while semi-reinforcing and non-reinforcing fillers have larger particle sizes ranging from 100 to 1,000 nm. When the particle size exceeds 10,000 nm, the filler forms a zone of localized tension.

2.8.1.3. Particle surface area and filler loading

Reinforcing fillers have a greater potential to reinforce filler-rubber contacts in rubber compounds due to their wide surface area, which creates more active contact points. The size of primary particles

directly influences the specific surface area. The amount of filler added to the composite material has a direct influence on its mechanical properties [30]. Higher filler loading usually results in greater reinforcing, to some extent. Excessive filler content can cause clumping, reducing performance and potentially harming the composite's mechanical properties. The ideal amount of filler depends on the filler type, matrix combination, and desired composite properties [31].

2.8.1.4. Matrix compatibility

To ensure effective reinforcement, it is essential for the filler and matrix materials to be compatible. Incompatibility between these components can lead to issues such as poor adhesion, phase separation, or filler particle aggregation, which can negatively impact the mechanical properties of the composite material. By carefully optimizing these parameters, the mechanical properties of the composite material can be enhanced [32].

2.9. Summary of related works and gap identification

The mechanical properties of vulcanized hybrid rubber compounds containing COS and industrial byproducts silica were studied and improved the mechanical properties while maintaining good processability [20, 33]. Also, silica powder from byproduct was developed to be used as as tire tread filler and recommended the use of industrial byproducts as a more affordable option compared to traditional precipitated silica for reinforcing natural rubber in tires was investigated [34].

Silica was extracted from Awash Melkasa Chemical Factory Filter Cake ,characterized and next work was suggested as silica should be extracted from filter cake for different industrial raw materials to solve challenges related to cost, sustainability, and environmental impact in conventional silica [11].

The use of filter cake industry byproduct as a substitute for traditional Portland cement in concrete production was examined and revealed that integrating these byproducts can lower the expenses associated with making concrete, decrease the environmental footprint of the byproducts, and enhance the strength and longevity of the concrete [10]. This study will develop innovative rubber filler from AMCF filter cake that improve rubber properties, reduce environmental impact, and promote sustainability in tire manufacturing.

CHAPTER THREE

3. Materials and Methods

3.1. Silica extraction and rubber compounding raw materials

Filter cake byproduct (Awash Melkasa Chemical Factory, Ethiopia), Natural rubber (Matrix , FGV Rubber Industries, Malaysia), FCS , COS (Jinsha Precipitated Silica Manufacturing Co.,Ltd , China), zinc oxide (98%, Singhal Commodities, India), MBTS (Mercaptobenzothiazole Disulfide, Acmechem, India), stearic acid (Godrej Industries Limited, India) as activators, 4010 NA (IPPD,Sennics Co. Ltd., China) as antioxidant, and ground sulfur (Standard Chemical, India ,Cross linking agent) were used for rubber compound formulation. Except filter cake byproduct and FCS all raw materials were commercial grade.

3.2. Chemicals

Sodium hydroxide pellets (NaOH,98%, Analytical grade, from Alpha Chemicals), Hydrochloric acid (HCl,37%, Analytical grade, from Alpha Chemicals) and Distilled water were used during silica extraction.

3.3. Instruments and Apparatus

X-ray Diffractometer shimadzu corporation (Kyoto, Japan), SEM ((JCM-6000PLUS BENCHTOP SEM, JOEL, Japan),Horriba surface area analyzer (SA9603,USA), FTIR (IS50 FTIR ABX, Germany), Mooney viscometer (Prescott Instrument Technology, UK), Reo-line, moving die instrument (Prescott instrument technology), AAS (Spectry-20 plus, Japan), Muffle Furnace(SX-5-12II,INDIA),XRF (NitoXL2 , China), specific gravity tester (Elatest Brabender Technology, Germany), Analytical balance(Model:E42S-B,Gibertini,Germany), pH meter (PHS-3C, Hanna instruments U.S.A), Filter paper (What man Filter paper (Grade 40 Ashless,150mm), Hot plate magnetic stirrer(CDL,JISLCO), Dryer (oven dryer DHG-9055,China) Sieve, beaker, crucible, flask, pycnometer,Material handling (plastic bag) and Grinder machine were used for silica extraction and characterization.

3.4. Methods

3.4.1. Sampling methods

During sample collection from Awash Melkassa Chemical Factory, a meticulous sampling method was implemented. The sample collection procedure involved gathering samples in 8 batches, each weighing 5 kg, resulting in a total sample size of 40 kg. To ensure the homogeneity of the collected samples, thorough mixing was carried out before dividing the sample into four parts using the quartering method. Subsequently, each quarter was further subdivided into quarters, and two opposite quarters for further analysis. These selected samples were then carefully placed in polypropylene bags, with one sample designated for the determination of oxide composition percentages and acid leaching, while the other sample was reserved for subsequent analysis.

3.5. Characterization of raw filter cake byproduct

3.5.1. Moisture content

Mass of raw filter cake was measured and put into crucible. The mass of crucible was measured and crucible with filter cake oven dried at 105 ℃ for 4 hours. The sample was taken out from the oven, cooled, and measured until constant mass obtained. Finally, average mass of the sample was calculated and moisture content was obtained using equation 3.1 where A is mass of original filter cake and B is mass of dried filter cake.

$$moisture = \frac{A-B}{A} * 100 \quad \text{..... 3.1}$$

3.5.2. Loss on ignition

Mass of Crucible was measured with and without filter cake sample. The muffle furnace heated at 15 ℃ per minutes until it reaches 950 ℃.To determine the loss on ignition the sample was heated at 950 ℃ for 4 hours in a furnace. Heated sample was put in desiccators for 1 hour for cooling and then weighed for weight loss. Loss on ignition in the sample was calculated from mass of sample before heating and after heating using equation 3.2 where A is mass of sample plus mass of crucible, B is mass of sample after calcination, and C is mass of original sample.

$$LOI = \frac{A-B}{C} * 100 \quad \text{.....} \quad 3.2$$

3.6. Preparation of silica from filter cake

Preliminary study was performed to select silica extraction solvent via leaching. Two 10 gram filter cake ashes were leached with 1M of HCl (37%) and 1M sulfuric acid (98%) for one hour. The as-prepared samples were filtered, washed with distilled water, oven dried and characterized by AAS and XRF. Silica yield using HCl was 61% while silica yield using sulfuric acid was 56.8% as confirmed by AAS and XRF analysis. Thus, HCl was selected as a leaching solvent for silica extraction.

3.6.1 Acid leaching

Filter cake byproduct was collected from AMCF. The filter cake was grinded, sieved and oven dried at 105 °C until constant mass obtained. Then, oven dried and calcinated by controlling the temperature at a heating rate of 30 °C/minutes in electric furnace at 550 °C and held at this temperature for 3 hours to reduce carbonaceous substances and other impurities to enhance the yield of silica [35]. Effect of acid concentration and leaching time was investigated by making temperature constant at 90 °C as shown in Table 3.1. The samples were coded based on acid concentration and reaction time. For example, sample S190 represents silica extracted using a 1M HCl and 90 minutes reaction time. Oxide composition was characterized by XRF to understand the effect of leaching parameters on silica yield. S290 was selected for further silica extraction.

In a typical experiment, 60 g of calcinated filter cake was leached with 2M HCl at 90 ^{0}C for 90 minutes to remove metallic impurities [36]. The solution was cooled at room temperature, filtered, washed repeatedly by distilled water to remove the acid from the samples and oven dried at 105 ^{o}C for 24 hours.

Table 3.1 Effect of leaching parameters on silica yield

Run	Acid concentration (mol/L)	Reaction time (minutes)	Sample Code	Silica yield (%)
1	1	90	S190	
		60	S160	
		45	S145	
2	2	90	S290	
		60	S260	
		45	S245	
3	3	90	S390	
		60	S360	
		45	S345	

3.6.2 Sol-gel extraction

To further purify the silica content, 50g of sample S290 was reacted with 2.5M NaOH solution for 2.5 hours at 100 °C with continuous stirring on oil bath to form golden color sodium silicate solution as intermediate product [37] (equation 3.3). Non-reactive contaminants and impurities during digestion were removed through filtration with Whatman filter paper. Clear sodium silicate was formed by multiple filtrations [38]. 1M HCl solution was added in drop wise to clear sodium silicate solution with continuous stirring to form precipitated silica gel until the solution become neutral and precipitation stops (equation 3.4). At pH 7, white colored solution which contains silica gel was formed [39]. The gel is aged with the mother liquor for 18 hours at room temperature as indicated in Figure 3.1. Aged solution was filtered by vacuum filtration and repeatedly washed with distilled water to remove dissolved salts and NaCl generated by acid-base side reactions. Finally, the sample was oven dried at 80 ^{0}C for 24 hours to give FCS. FCS was characterized and used for rubber filler application in tire industry. The silica preparation experiment was done at Addis Ababa, institute of technology, reaction laboratory.

SiO_2 (Filter cake ash) + 2NaOH $\rightarrow Na_2SiO_3 + H_2O$……...…….…….……3.3 [37]

$Na_2SiO_3 + 2HCl \rightarrow SiO_2 + 2NaCl + H_2O$……..…….……..... 3.4 [40]

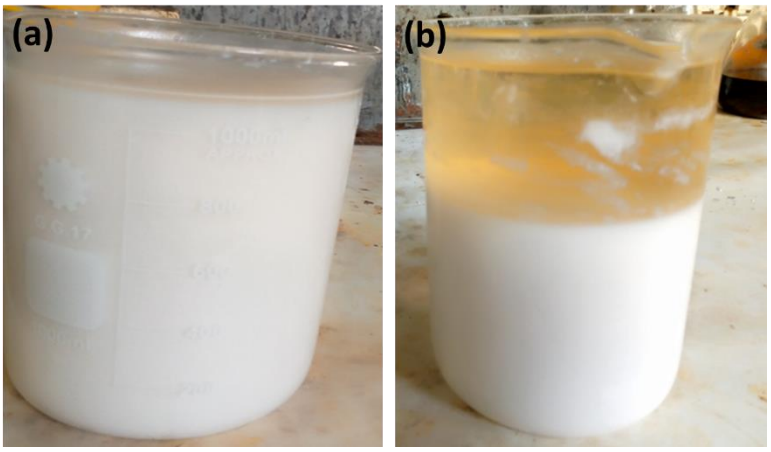


Figure 3.1 Precipitated silica gel (a) before aging and (b) after aging

3.7. Characterization of silica fillers

3.7.1 Chemical composition analysis

In this study, AAS was used to characterize the chemical constituents (Major and Minor oxides) of filter cake as well as the extracted silica. $LiBO_2$ FUSION, HF attack, gravimetric, colorimetric and AAS analytical method was used in order to assess its chemical composition. The AAS chemical composition analysis was done at geochemical laboratories.

3.7.2. Morphology analysis

The silica obtained from the aluminum sulfate industry byproduct was characterized with Scanning electron microscope and compared with the rubber industry requirement. SEM analysis was employed to observe dispersion capability of the fillers in a rubber compounds. Sample morphology analysis was done by using SEM ((JCM-6000PLUS BENCHTOP SEM, JOEL, Japan) on carbon tape and at distance of 44mm. The SEM was run at 3000 times magnification with an operating energy of 15 kV [37].Morphology analysis was done at Adama science and technology university.

3.7.3. Functional group analysis

Functional groups present in the extracted silica were identified and observed by FTIR. The infrared spectrum was recorded by passing a beam of infrared light through extremely fine powder sample.

The characterization was performed at AASTU by FTIR (IS50 FTIR ABX, Germany). All the spectra were recorded and processed using FTIR software.

3.7.4. Phase composition analysis

X-ray diffraction is versatile non-destructive analytical techniques used to analysis phase composition, and crystal structure of the materials. Phase composition of FCS and COS was investigated at Adama Science and Technology University, materials engineering department.

Phase nature of extracted silica and commercially available COS was studied by X-ray Diffractometer shimadzu corporation (Kyoto, Japan). Cu radiation with scanning rate of 3^{o} per minutes ,10-90 degree scanning range, acceleration voltage of 40 kilo volt, and 30 mili ampere current were used during phase composition of FCS and COS.

3.7.5. Surface area analysis

The study involved finely grinding precipitated silica for homogeneity, followed by degassing under vacuum at 150 ℃ to remove gases and contaminants. Brunauer-Emmett-Teller (BET) analysis was then conducted using nitrogen as the adsorbate, with adsorption data recorded at various pressures. The instrument was calibrated by zeroing detector baselines and injecting a known volume of nitrogen. The sample cell was surrounded by a liquid nitrogen bath to maintain temperature, and nitrogen gas was passed through the sample cell for adsorption onto the silica surface. The amount of desorbed nitrogen after reaching adsorption equilibrium was measured for further analysis. Surface area analysis was performed using a SA-9600 surface area analyzer at Addis Ababa Science and Technology University.

3.7.6. Specific gravity determination

Specific gravity is a critical parameter in tire industries, ensuring consistency and purity of precipitated silica products. It predicts dispersion capabilities of silica in natural rubber compounds and measured by pycnometer. Specific gravity determination was conducted at Horizon Addis Tyre factory. Clean and dry pycnometer with empty weight (W_1) was obtained, Filled with a known mass (M) of the dry precipitated silica sample and total weight was recorded as of the pycnometer filled

with the sample (W_2). The pycnometer was filled with hexane solution by Ensuring the liquid completely covers the sample and there are no air bubbles and Record the total weight of the pycnometer filled with the liquid and the sample (W_3). Finally, specific gravity calculated by the following equations:

Mass of the sample (M) using: $M = W_2 - W_1$…….…….…….……....3.5

Mass of the liquid displaced by the sample using: $= W_3 - W_1$….....3.6

$$\text{Specific gravity} = \frac{W2-W1}{(W2-W1)-(W3-W1)} * \text{density of hexane solution} \quad \text{……....3.7}$$

3.8. Rubber compounding

Compound without silica filler, with COS filler and with FCS filler were prepared. Compound without silica filler was used as a reference and the properties of COS reinforced compound and FCS reinforced compounds were compared with unreinforced compound. Curing characteristics and Mechanical properties of rubber compounds were characterized in Horizon Addis Tire factory. Mixing rubber with its ingredients and fillers were done as per ASTM D-3185 (2006) on calendaring [34].Table 3.2 show formulations of unfilled, FCS filled and COS filled compounds. Temperature and speed of rotor of the calendar was set at 80 ℃ and 40 rates per minutes respectively. The natural rubber was masticated for 12 minutes, followed by addition of activators, accelerators, antioxidant, cross linkers, fillers and rubber was compounded by average time for 6 minutes per addition of each additives. To ensure reliable test results, stability, consistency, optimal curing, and dimensional accuracy, compounded materials were allowed to maintain at room temperature for 24 hours before testing.

Table 3.2 Formulation of rubber compounds

Ingredients	Function	Unfilled compound		COS filled compound		FCS filled compound	
		PHR	Gram	PHR	Gram	PHR	Gram
Natural rubber	Matrix	100	456	100	417.89	100	417.89
FCS	Reinforcing filler	**0**	**0**	0	0	**10**	**41.79**
Zinc oxide (98%)	Activators	5	22.8	5	20.89	5	20.89
MBTS	Accelerators	0.1	0.46	0.1	0.42	0.1	0.42
Stearic acid	Activators	1.05	4.79	1.05	4.39	1.05	4.39
4010 NA(IPPD)	Antioxidant	1	4.56	1	4.18	1	4.18
COS	Reinforcing filler	**0**	**0**	**10**	**41.79**	0	0
Ground Sulfur	Cross linking agent	2.5	11.4	2.5	10.45	2.5	10.45
TOTAL		109.65	500	119.65	500	119.65	500

PHR: parts per hundred of rubber, MBTS: Mercaptobenzothiazole Disulfide
4010 NA(IPPD): N-isopropyl-N'-phenyl-p-phenylenediamine

3.8.1. Characterization of rubber compounds

3.8.1.1. Mooney viscosities

Previous to curing, FCS filled, COS filled and unfilled Rubber undergo testing, as per ASTM D1646 (2004). At 100 ℃, natural rubber strips with a thickness of approximately 1 cm and a diameter of 4.5 cm were cut into samples for the Mooney viscosity test using a large-rotor Mooney viscometer made by Prescott Instrument Technology. In order to determine the Mooney viscosity for each of the three samples independently, preheat time of one minute and test time of four minutes were applied. Mooney viscosity of rubber compounds were measured after the rubber compounds sheared for one minute and then allowed to relax for four minutes at a temperature of 100 °C.

3.8.1.2. Curing and Molding

The test samples were vulcanized in a hydraulic press with 150mm*150mm platen at 150 ℃ and 200 kg/cm^2 pressure for 30 minutes. The cure characteristics of the mixes were analyzed using an oscillating Reo-line, moving die instrument (Prescott instrument technology) following ASTM D3182 (2007) standards.

3.8.1.3. Specific gravity determination for rubber compounds

Specific gravity of a rubber compound can affect various aspects of the manufacturing process and the properties of the final rubber compounds. Prior to vulcanization, the compounded rubber's specific gravity for unfilled, FCS filled, and COS filled rubber was determined using a specific gravity tester (Elatest Brabender Technology, Germany).

3.8.1.4. Curing characteristics

The curing characteristics of a rubber compounds were studied using reo-line to determine the cross-linking density of the rubber matrix with fillers. A 5g sample of compounded rubber was subjected to small deformations at 50 cycles per minute and 175 °C. The torque transducer measured forces transmitted through the rubber, providing data such as minimum torque (M_L), maximum torque (M_H), final torque (M_F), scorch time (T10), and optimum cure time (T'90) from the torque-time curve.

3.8.1.5. Stress-strain properties

Stress-strain tests were conducted according to ASTM D412-06 standards using dumbbell specimens on a Tensometeric machine. The tests measured the modulus, tensile strength, load at break, and elongation at break, with the results recorded in Mpa.

3.8.1.6. Hardness

The testing was conducted according to ASTM D 2240-05 using a shore A type Durometer. Readings were taken 15 seconds after the indentation when firm contact was made with the specimens, and the results were recorded in shore A units.

3.8.1.7. Abrasion resistances

The study focused on testing the resistance of vulcanized rubber compounds to abrasion using a rotating cylindrical drum device known as a DIN Abrader, following ASTM-D 5963 standards. The abrasion loss was calculated using equation 3.8 to determine the material's durability against abrasive forces.

$$\textbf{Abrasion loss} = \frac{\textbf{weight loss}}{\textbf{initial weight}} \times \textbf{100} \quad \text{…..……...……} \quad 3.8$$

Three runs for each sample was tested and the results were expressed as the mean value.

3.8.1.8. Tear strength

The tear strength of unfilled, FCS filled and COS filled compounds were tested according to ASTM D 624-00 guidelines using a Tensometer instrument. The test involved applying a tearing strain to samples at a 90-degree angle and measuring the force in kilogram-force (Kgf).

3.9 Data analysis

Triplicate measurements (n=3) were conducted to characterize the silica fillers used in the rubber compounds and reinforcing effect of FCS and COS were compared to unfilled rubber compound. The data from three individual experiments were analyzed using Excel to calculate the mean and standard deviation. Origin 9.5 software was utilized for FTIR spectra, XRD pattern, and draw bar graphs. For the rubber compound tests, five unique tests (n=5) were conducted for tensile, tear, elongation, hardness, and elastic modulus of rubber compounds. The results were recorded in an Excel sheet after each test for mean calculation of the results.

CHAPTER FOUR

4. Results and Discussion

4.1 Characterization of raw filter cake byproduct

4.1.1 Moisture Content

The moisture in the filter cake byproduct (raw filter cake) was measured as soon as it arrived and calculated using Equation 3.1. The experiment was repeated three times, and the findings are presented in Table 4.1. The raw filter cake had an average moisture content of 6.05%. Higher moisture content significantly impact the silica yield from industrial byproducts by affecting extraction process [25]. The raw filter cake contains a little amount of moisture, which has insignificant impact on silica extraction.

Table 4.1 Moisture content of raw filter cake

Run	Mass before drying (g)	Mass after drying (g)	Moisture content (%)
1	6	5.65	5.83
2	6	5.67	5.50
3	6	5.59	6.83
Mean		5.64	6.05 ± 0.69

4.1.2 Loss on ignition

Ash present in silica affects qualities of silica and rubber reinforcement capabilities. The presence of impurities and organic matter in raw filter cake can significantly impact the loss on ignition (LOI), silica yield, and rubber reinforcement capability.The filter cake from aluminum sulfate extraction may contain organic residues, unburned carbon, and other volatile components that contribute to a high LOI. During the silica extraction process from this byproduct, the high LOI can result in a lower silica yield due to the loss of volatile materials and incomplete combustion of organic matter. Proper calcination and purification steps are essential to reduce the LOI and maximize the silica yield from the filter cake.

The presence of organic impurities and residues in the silica samples derived from filter cake with high LOI can affect their surface properties and interaction with rubber matrices. High LOI values can lead to poor dispersion of silica fillers in rubber compounds, hindering their reinforcement capability. The organic content in the silica samples may interfere with the filler-rubber bonding, resulting in reduced mechanical properties and compromised reinforcement effects in the rubber compound. Loss on ignition was calculated using Equation 3.2.The experiment was carried out three times, and the findings are presented in the Table 4.2.

Table 4.2 Loss on ignition (LOI) for raw filter cake

Run	Mass of sample and crucible in gram (A)	Mass after calcination in gram (B)	Mass of original sample in gram(C)	LOI (%)
1.	18.98	18.86		9.45
2.	18.98	18.89	1.27	7.08
3.	18.98	18.87		8.66
Mean		18.84		8.4 ± 1.2

4.2. Effect of leaching treatment on silica yield

Leaching treatment is a technique used to improve the yield and quality of silica final products by eliminating contaminants. Leaching agent, pH of the solution, treatment temperature, and duration of the treatment affect silica yield and qualities. HCl is commonly used in leaching treatment to increase purity and yield of FCS. It was discovered that acid leaching causes greater silica concentration in filter cake byproduct by reducing the amount of oxide contaminants present in filter cake. Insolubility of silica in acid solutions is an advantege of acid leaching process and metal oxides are removed from filter cake ash via acid leaching, which employs the chemical process of proton attack. From Equation 4.1, we can observe that the H^+ ion displaces the cation from the ash particle matrix, causing metal dissolution. The H^+ ions react with the aluminium, iron, and other metals that are gradually exposed on the surface and within the pores of the ash particles as the leaching process progresses.

4.2.1. Deciding level of time during leaching time

Vaporization of an acid solution during the extraction of silica from filter cake byproduct lead to several effects on the yield. The loss of the acidic medium, which is crucial for the leaching process, can result in incomplete extraction and lower silica yields. Incomplete leaching occurs when the acid solution evaporates before sufficient interaction with the biomass material, compromising the extraction process. Acid concentration gradients can also form, affecting the uniformity of the leaching process and the overall silica yield. The loss of acid through evaporation can also affect the extraction process's effectiveness. Proper process control and optimization are essential to maximize silica yield and improve the extraction process efficiency. Extended leaching time results in vaporization of acid solution. Hence, leaching time is fixed to 45 minutes, 60 minutes and 90 minutes to study effect of leaching time on silica yield. To study effect of extended leaching time on silica yield it is important to use closed vessels to prevent solution loss by evaporation during leaching time.

4.2.2. Effect of acid concentration on silica yield

The concentration of acid plays a crucial role in determining the silica yield during the leaching process. It is an important factor to consider when extracting silica from byproducts to enhance the removal of impurities and improve the overall silica yields. The chemical composition of filter cake silica after leaching is presented in the Table 4.3. Using a high concentration of HCl resulted in a faster leaching rate and the highest silica percentage. S390 gave the maximum silica yield (84.02%) while S290 gave a comparable silica yield (82.28%) as S390 as shown in Table 4.3.S390 and S290 represents silica extracted using a 3M HCl and 90 minute reaction time and ,2M HCl and 90 minutes reaction time for S390 and S290 respectively. The optimal acid concentration should be determined based on the silica types and pollutants, as greater amounts of acid concentration might cause silica to break down because of the solution's high saturation level [51]. It is important to carefully choose the right acid concentration in order to achieve the highest silica yield and effectively dissolve impurities. In addition, using a highly concentrated acid raises the production cost of precipitated silica. Therefore, the optimal HCl concentration in this study was taken as 2M HCl where large percentage

of contaminants were removed from the filter cake ash and the silica yield was very close to S390 .S390 silica extracted

Table 4.3 Effect of acid concentration and reaction time on silica yield

Sample	Chemical composition (%)										
	SiO_2	Al_2O_3	K_2O	MgO	Fe_2O_3	MnO	P_2O_5	CaO	Na_2O	SO_3	Others
Untreated FC	53.20	19.04	0.84	0.04	0.42	<0.01	0.09	0.12	0.14	1.08	25.03
S145	56.36	17.79	0.3	1.09	<0.01	0.001	0.0012	0.13	0.92	6.47	16.94
S160	60.71	17.42	0.29	1.11	<0.01	0.012	0.02	0.25	1.14	2.14	16.91
S190	71.69	2.53	0.04	1	<0.01	0.01	0.031	0.19	0.45	0.29	23.769
S245	61.35	17.67	0.28	1.15	<0.01	0.011	0.025	0.82	1.10	1.02	16.57
S260	65.02	14.42	0.19	1.01	<0.01	0.012	0.02	0.25	1.14	2.14	15.8
S290	82.28	8.82	0.14	0.16	0.1	0.02	0.02	0.76	0.5	0.89	6.31
S345	72	9.41	<0.01	<0.01	0.21	<0.01	0.02	0.8	0.52	1.03	16.01
S360	77.84	4.27	<0.01	<0.01	0.38	<0.01	0.01	0.20	0.92	2.15	14.23
S390	84.02	2.92	<0.01	0.02	0.21	0.01	0.02	0.3	0.15	0.19	12.16

S=silica, 1, 2, 3 represent Molarity of acid and 45, 60, 90 represent time in minutes

4.2.3. Effect of leaching time on silica yield

Careful control of the leaching time is essential for efficient silica extraction and achieving the desired yield in the final product. The filter cake byproduct was leached with HCl at different times to study the influence of leaching time on silica yield. The samples were leached for 45, 60 and 90 minutes and the corresponding silica yield is shown in Table 4.3. Silica yield and impurity dissolving

rates are affected by the length of the leaching time. The length of the treatment time has an impact on dissolving contaminants in the leaching time. Extended treatment durations result in a more effective silica extraction process. They may also raise the possibility of silica dissolution and the loss of important components. As it can be seen from Table 4.3, increasing leaching time resulted in the removal of more soluble impurities from the sample irrespective of the HCl concentration. The purity of silica was found to be high for S290 (silica extracted at 2M HCl and 90 minutes reaction time) and S390 (silica extracted at 3M HCl and 90 minutes reaction time) samples. Therefore, 90 minute leaching time was chosen for silica extraction.

4.3. Characterization of fillers

4.3.1. Chemical composition of filter cake silica and commercial silica

The raw filter cake was initially leached with 2M HCl for 90 minutes and 82.28 % silica was found. To further purify the silica content, sol-gel method was utilized as mentioned in section 3.6.2. Chemical composition of purified silica from leached filter cake and commercially available silica is presented in Table 4.4. Table 4.4 shows that the silica concentration of FCS and COS is comparable.

Table 4.4 Chemical composition of FCS and COS

	Chemical composition (%)										
Sample Type	SiO_2	Al_2O_3	K_2O	MgO	Fe_2O_3	MnO	P_2O_5	CaO	Na_2O	SO_3	Others
FCS	92.50	0.99	0.02	0.04	0.01	<0.01	0.03	0.03	0.05	0.01	6.32
COS	94.26	0.63	0.05	0.00	0.04	0.00	0.07	0.05	0.46	1.04	3.40

4.3.2. FTIR spectra of filter cake silica and commercial silica

FTIR spectra of FCS and COS is shown in figure 4.1. The major functional groups present in FCS and COS show presence of silanols (Si-O-H) and siloxane (Si-O-Si) groups with absence of impurity bands for FCS while COS has an impurity band at 2360.61 cm^{-1} [9]. Impurity band at 2360 cm^{-1} is carbon dioxide band that may be due to production techniques of commercial silica. Symmetric stretching of Si-O-Si bonds were observed at 798.08 and 795.16 cm^{-1}, while Si-O bending bands were at 447.31 and 445.68 cm^{-1} for COS and FCS, respectively [9, 41]. O-H stretching for hydroxyl groups was detected at 964.15 and 953.51 cm^{-1} for COS and FCS, and Si-O stretching peaks were at 432.30 and 431.57 cm^{-1} for COS and FCS, respectively [31, 42].

The bands observed at 1632.78 cm^{-1} and 1635.38 cm^{-1} represent bending vibrations of the water molecule in the Si-OH group for COS and FCS. Additionally, the broad bands at 3396.41 cm^{-1} and 3405.37 cm^{-1} for COS and FCS are attributed to the stretching vibration of the O-H group [9]. The band observed at 3396.41 and 3405.37 cm^{-1} is associated with the vibration of silanols groups and the hydrogen bonding interaction between water molecules and nearby silanols [43]. The strong bands observed at 1068.12 and 1058.45 cm^{-1} in the spectra indicate the asymmetric stretching vibration of Si-O-Si in both the synthesized FCS and COS. The similarities between the two spectra suggest that the properties of the synthesized silica (FCS) are comparable to those of the COS.

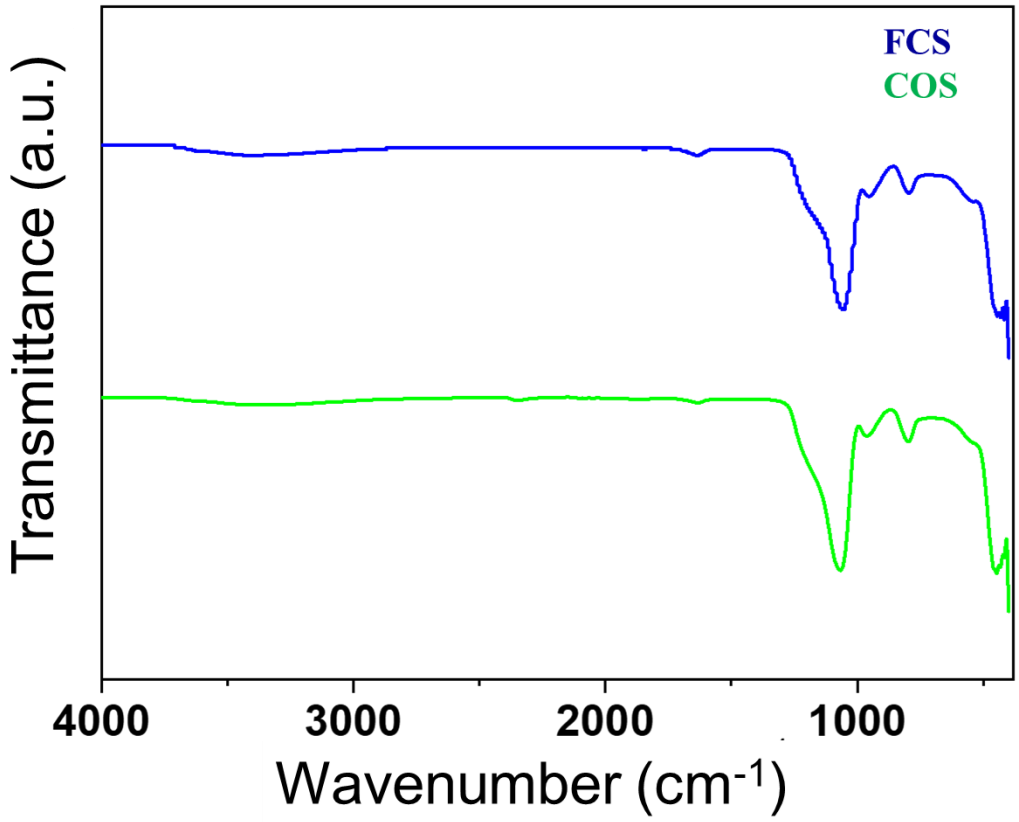


Figure 4.1 FTIR spectra for FCS and COS

4.3.3. Phase composition of silica fillers

The XRD pattern of FCS and COS is shown in Figure 4.2. The XRD pattern for COS and FCS shows an amorphous pattern with no sharp peaks, it indicates that the materials are predominantly non-crystalline. There are no sharp peaks observed in the scanning angles between 10° and 90°, indicating the absence of any organized crystalline arrangement in the samples .Lack of sharp diffraction peaks suggests that the silica samples do not have a well-defined crystalline structure and exhibit characteristic of an amorphous or disordered material. Both silica samples showed a broad peak at a 2Θ angle of 22 degree, indicating their amorphous and non-crystalline nature. Amorphous substances have a random or very short-range atomic arrangement.. Amorphous silica materials have higher surface areas, which can enhance their adsorption capacity, reactivity, and performance in applications like fillers. They are generally more thermally stable than crystalline forms due to their

absence of well-defined crystal structures, which can undergo phase transformations at high temperatures.

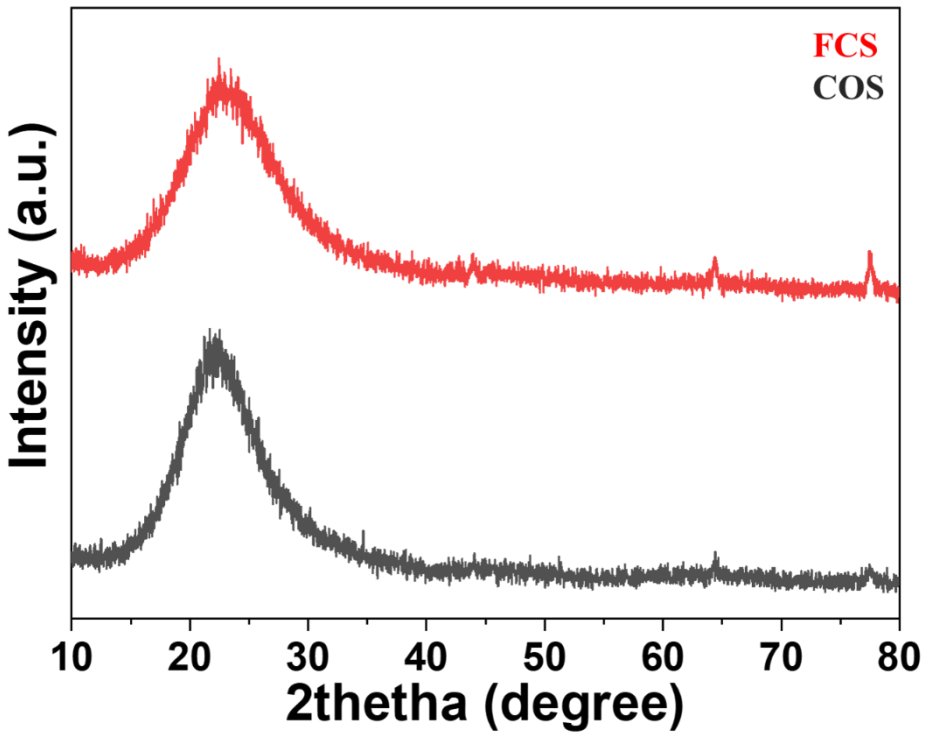


Figure 4.2 X-ray diffraction patterns of FCS and COS

4.3.4. Morphology analysis for silica fillers

Figure 4.3 shows SEM image of the FCS and COS. Acid leaching alters the morphology of silica particles by dissolving certain parts of the silica structure, resulting in more porous and irregularly shaped particles The extent of these changes depends on the specific conditions of the leaching process [44]. The acid leaching process generally reduces particle size and causes the formation of new and smaller particles due to the dissolution and precipitation of silica. In the case of COS, the silica is more pure due to sample preparation and processing techniques, while in FCS, the particles are less pure since the silica is extracted from industrial byproducts. In the case of COS, the particles were more agglomerated and separated by clear boundaries. However, in FCS, the particles are less agglomerated and not separated by clear boundaries. The SEM results are consistent with the BET surface areas since FCS displayed larger BET surface area compared to COS due to the finer particles

of FCS (see section 4.3.5). The difference observed in Figures 4.3 a and 4.3 b is due to the production process and the quality of the raw materials.

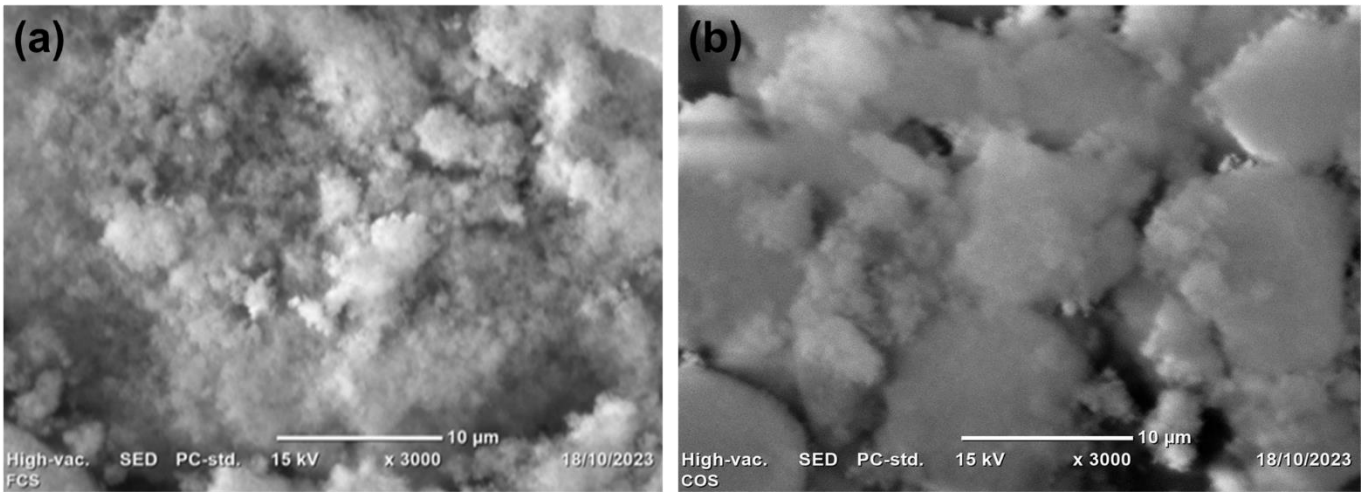


Figure 4.3 SEM images of (a) FCS and (b) COS

4.3.5. Surface area for silica fillers

The specific surface area of the silica fillers were measured at 26 °C using nitrogen adsorption desorption with a Horriba surface area analyzer. Prior to analysis, the samples were degassed at 150 °C for one hour. BET surface area of FCS was 419.704 m^2 g^{-1} and it was almost twice the surface area of COS, 231.104 m^2 g^{-1}. A higher surface area typically leads to more active sites accessible for interaction with the rubber matrix, enhancing the reinforcing capacity. This higher surface area of FCS makes it a more effective reinforcing filler in rubber compounds due to its increased reinforcing efficiency [15]. Increasing number of silanol functional groups enhances interaction and dispersion of rubber filler, leading to improved reinforcing capabilities [45].

4.3.6. Specific gravity of silica fillers

Specific gravity is the ratio of equal volume of hexane solution displaced by the precipitated silica. High specific gravity of silica increases natural rubber's reinforcing capability due to good interaction with the rubber matrix and increased surface area for dispersion [31]. FCS displayed a specific gravity of 2.35 while COS has a specific gravity of 2.24. The reduced mechanical properties

reinforced with COS is attributed to the lower specific gravity of COS, resulting in limited surface area for effective interaction with the rubber matrix. As a result, the silica particles may not be evenly distributed within the rubber matrix or may not have sufficient surface area to form strong bonds with the rubber [28]. Therefore, rubber compound filled with COS will show inferior mechanical properties than FCS filled natural rubber.

4.4. Characterization of rubber compounds

4.4.1. Effect of silica fillers on specific gravity of rubber compounds

The specific gravity of a material is determined by its density relative to the density of a reference substance. High surface area silica fillers in rubber compounds can increase the specific gravity by factors like particle size and packing density, surface area-to-volume ratio, surface functionalities, filler loading, and dispersion. Table 4.5 shows the specific gravity of unfilled, COS filled, and FCS filled rubber compounds. Both FCS and COS filled rubber compounds displayed better specific gravity than the unfilled one due to the fillers higher surface area.

Table 4.5 Specific gravity of rubber compounds

Compound type	Specific gravity
COS filled	1.010 ± 0.05
FCS filled	1.012 ± 0.01
Unfilled	0.963 ± 0.02

Particle size and packing density allow for more particles to be packed closely together, increasing the compound's density and specific gravity [20]. The increased surface area-to-volume ratio allows for greater interaction between filler particles and the rubber matrix due to the higher amount of exposed surface area per unit volume of filler. Surface functionalities enhance the compatibility of the filler with the rubber matrix, promoting better dispersion and bonding within the compound. Filler loading also impacts the specific gravity of the composite material. Increasing the amount of filler in

a compound leads to a higher density and specific gravity due to the greater proportion of filler particles present.

4.4.2. Curing characteristics of rubber compounds

The rubber compounds were tested for their curing properties at a temperature of 150 °C for 30 minutes. The key parameters measured included minimum torque (M_L), maximum torque (M_H), optimal curing time (tc_{90}), scorch time (ts_2), final torque, and torque difference [46].

It can be seen from Table 4.6 that natural rubber filled with FCS exhibits lower minimum torque, scorch time, and optimal cure time compared to COS fillers. This is attributed to the improved dispersion of the filter cake filler. The torque difference is considered as a measure of crosslinking density and stiffness in rubber composites. The presence of silica rubber crosslinks in the FCS-filled natural rubber restricts deformation, leading to a higher torque difference. This suggests that the crosslinking density of rubber compounds increases when natural rubber is filled with FCS compared to COS while unfilled compounds show lower crosslinking density compared to both fillers

Table 4.6 Effect of silica fillers on curing characteristics of rubber compounds

Curing characteristics at 150 °C	Unfilled Compound	COS filled compound	FCS filled Compound
Minimum torque (Nm)	0:56	1:39	1.29
Maximum torque (Nm)	2:42	3:94	4.27
Final torque (Nm)	2:36	3:94	4:26
Torque difference (Nm)	1:86	2:55	2:98
$TS_{2\ (}$minute)	3:32	2:23	1:38
T10 (scorch time, Minute)	0:38	0:38	0:32
T50 (scorch time, Minute)	1:17	1:28	1:16
T’90 (optimum cure time, Minute)	2:46	4:06	3:49

The minimum torque (M_L) is an indicator of the initial viscosity of natural rubber composites and their processability. An increase in minimum torque is associated with higher viscosity of rubber when precipitated silica is present. Enhancement of minimum torque with fillers is attributed to cross-linking of rubber by precipitated silica, which limits the mobility of rubber chains. Surface area of fillers also impacts torque in natural rubber. For FCS, minimum torque was 1.29 Nm, which was lower than that of COS-filled compound [34, 47].

Maximum torque achieved during curing test, is a measure of the stiffness of a compound and is influenced by the modulus molecular rigidity. Higher M_H values in reinforced rubber indicates stronger interactions between silica particles and rubber matrix, indicating a greater crosslinking density in rubber compound [21, 46]. Low COS rubber filler interaction with natural rubber lowers maximum torque for COS filled natural rubber (3:94 Nm) compared to FCS reinforced natural rubber (4:27 Nm) [46].

Final torque is a crucial parameter in rubber compound characterization, representing the torque value when the compound is fully mixed and stable. It reflects the consistency, filler dispersion, and processability of the compound. As rubber and filler particles combine during mixing, the torque value increases until reaching a stable state, indicating complete mixing. This occurs after vulcanization agents react with the rubber, leading to the desired cross-linking level. A higher final torque suggests better filler dispersion. Final torque of rubber compound reinforced with FCS is 4:26 Nm and has better filler dispersion capability of FCS filler inside the rubber compared to COS reinforced compound (3:94Nm) which shows lower capability of COS filler dispersion.

The torque difference in rubber compound characterization measures the dispersion of fillers, additives, and components in the rubber matrix. It is calculated as the difference between the maximum and minimum torque during mixing. A higher torque difference indicates better dispersion and distribution of fillers and additives, leading to improved mechanical properties. Monitoring torque difference helps manufacturers optimize mixing processes for better dispersion and overall product performance. Rubber compound filled with FCS has maximum torque difference (2.98Nm) than COS filled rubber compound (2.55Nm).

.TS_2 measures how quickly a material begins to vulcanize. Rubber compounds vulcanized rapidly when fillers were present, with vulcanization time of 3:32 for unfilled, 2:23 for COS filled, and 1:38 for FCS filled rubber compounds. For unfilled rubber compound crosslinking process is slower and less effective, requiring a longer vulcanization time to achieve the desired level of crosslink density and mechanical properties compared to FCS and COS filled compounds. Thus, fillers enhanced crosslinking efficiency of rubber compounds by providing nucleation sites for crosslink formation.

Scorch time of rubber compound is the time it takes for rubber to start vulcanization during rubber processing while shorter scorch time is desired for faster rubber processing. Silica fillers decrease scorch time of rubber compounds due to increased reactivity, enhanced dispersion, and changes in rubber compound viscosity. Surface silanol groups in silica fillers interact with accelerators and activators, accelerating the vulcanization process and reducing scorch time. Scorch time of FCS reinforced compound is reduced compared to COS because FCS forms strong interactions with rubber matrix, due to its high surface area and lower particle size [15]. For unfilled rubber compound vulcanization was slower due to absence of fillers that interact with activators and accelerators to reduce scorch time. On the other hand, COS has lower silanols group to interact with the activators and accelerators due to its coarse particle size and lower surface area as witnessed from SEM image and BET analysis, respectively, thereby its scorch time became higher than FCS reinforced rubber compound.

The T'90 value indicates the time needed for a material to reach 90% of its maximum torque while curing. A higher optimum curing time value indicates a slower curing rate, which means it requires a longer time to reach its optimal state of vulcanization or crosslinking. From table 4.6, we can observe that optimum cure time for FCS reinforced compound (3:49 minutes) is lower than COS reinforced compound (4:06 minutes). The delay in curing time for COS reinforced rubber compound is caused by inadequate dispersion of the filler in the compounds. Longer curing time in COS reinforced compound results in increased energy consumption and affects production efficiency of rubber compounds. Therefore, using FCS as filler enhances mechanical properties, reduce energy consumption, and enhance production efficiency making vulcanization economically feasible. On the other hand, unfilled rubber compound has shorter optimum cure time compared to FCS and COS reinforced rubber compounds. This is due to the addition of COS and FCS fillers that increase the

viscosity of the rubber compounds, making it difficult for vulcanizing agents to penetrate and react with the rubber molecules.

4.4.3. Effect of silica filers on Mooney viscosity of rubber compounds

Mooney viscosity of rubber compounds is a key factor that reflects their processing characteristics. It is affected by factors such as the particle size and surface area of fillers used in the compound. Mobility of rubber's macromolecular chains is restricted by fillers and Mooney viscosity was found to be higher in reinforced compounds than in unreinforced compound. High viscosity for COS filled natural rubber compound suggest that macromolecules' molecular motion is highly restricted, as a result of the larger filler size restricted molecular motion and shows lower compound processability and less sensitive to scorch time [46, 48]. FCS filled rubber compound has a lower Mooney viscosity than COS as a result of finer particle size and higher surface area of FCS which lowers the resistance of the rubber compound against rotor rotation making rubber processing easier [49, 50].

Table 4.7 Effect of silica fillers on Mooney viscosity

Sample name	Mooney viscosity (M.U)
Unfilled	37.325 ± 0.36
FCS	58.15 ± 0.59
COS	68 ± 1.03

4.5. Effect of silica filler on mechanical properties of rubber compounds

Mechanical property of unfilled rubber compounds and rubber compounds reinforced with COS and FCS were examined. The compound reinforced with FCS exhibited superior mechanical properties compared to COS reinforced compound. This was attributed to high surface area, improved dispersion, and strong interfacial adhesion of FCS with the rubber matrix. Therefore, the interaction between fillers and rubber matrix was enhanced, resulting in better stress transmission and improved mechanical properties compared to COS.

Table 4.8 Effect of silica fillers on tensile strength, tear strength, elongation at break, abrasion loss, and hardness of rubber compounds

Filler Types	Tensile strength (Mpa)	Tear strength (Kgf)	Elongation at break(%)	Abrasion loss (%)	Hardness (Shore A)
Unfilled	16.3 ± 0.25	5.46 ± 0.15	1012.1± 159.79	7.5 ± 0.73	32 ± 0.03
COS filled	17.94 ± 3.16	3.94 ± 0.72	905.52 ± 92.29	7.26± 0.54	34.5 ± 0.05
FCS filled	19.52 ± 2.12	5.48 ± 0.60	876.49 ± 44.93	6.3± 0.62	33.04 ± 0.06

4.5.1. Effect of silica fillers on tensile strength of rubber compounds

Tensile strength is a property that indicates the maximum force a material can endure before it breaks. A particle size, surface area and uniform dispersion of fillers affects tensile strength of rubber compounds since it determines if the filers disperse easily inside the rubber matrix or not. Effect of filler types on tensile strength of rubber compounds is demonstrated in Table 4.8. Rubber compound reinforced with FCS shows higher tensile strength (19.52 ± 2.12 MPa) compared to COS (17.94 ± 3.16 MPa) and unreinforced (16.3 ± 0.25 MPa) rubber compounds. This is because the FCS has a larger surface area as witnessed from BET analysis, allowing for strong interaction between the silica particles and the rubber matrix [51, 52]. Strength of FCS reinforced products improved because the silica was finely dispersed in the rubber matrix, leading to enhanced adhesion between the silica and rubber [53, 54]. Improved tensile strength is also attributed to the uniform distribution of applied stress, restricted molecular mobility due to fillers, and increased cross-linking density in the rubber compound. In general, smaller particle size, high surface area, and uniform dispersion of FCS contributed to the enhanced tensile strength of the rubber compound [15, 34]. In compound reinforced with FCS stress is more transferred between filler and rubber matrix.Therefore,tensile strength is enhanced more than unfilled and COS filled rubber compounds.

4.5.2. Effect of silica fillers on tear strength of rubber compounds

The impact of fillers on the tear strength of rubber compounds is illustrated in Table 4.8. Tear strength is a way to measure how well rubber can resist tearing or cracking. Tear strength of rubber

compound is affected by surface area and particle size of fillers [20]. When fillers are evenly distributed in rubber, they create a barrier that restricts molecular movement, resulting in a less brittle material. COS reinforced rubber compound has lower tear strength (3.94 ± 0.72 kgf) than FCS reinforced compound (5.48 ± 0.60 kgf) due to lower surface area of COS and filler-filler interaction that might lead to agglomeration in the case of COS [38]. Dispersion of silica particles with higher surface area, in the case of FCS, are responsible for the improved crosslinking and better adherence in the rubber matrix [34, 40]. Hence, FCS can improve tear resistance by effectively blocking or dispersing tear fractures.

4.5.3. Effect of silica fillers on elongation at break of rubber compounds

Elongation at break is a measure of how much a material can bend and shape before breaking, calculated as the ratio of the length after breakage to the initial length [20]. Elongation is also related with flexibility and elasticity of rubber materials. Adding high surface area fillers to rubber compounds can decrease the elongation at break by enhancing interfacial adhesion, reducing molecular mobility, ensuring uniform distribution of silica particles, increasing crosslinking density, and creating stress concentration. As a result, the material becomes stiffer, more brittle, and less elastic, ultimately leading to a decrease in elongation of the compound [55].

The unreinforced rubber compound showed the highest elongation at break (1012.1 ± 159.79 %) compared to COS (905.52 ± 92.29 %) and FCS (876.49 ± 44.93 %) [56]. The increase in elongation at break for unfilled natural rubber compound was attributed to the lack of fillers, which typically reduce elasticity by limiting molecular movement. As indicated in Table 4.8, addition of fillers caused for reduction of elongation at break is due to filler particles adhesion to the rubber matrix, which causes stiffness of the rubber compound and decreases stretching capability of the material [56].

4.5.4. Effect of silica fillers on the abrasion loss of rubber compounds

Durability of rubber compounds, particularly in tire manufacturing, is determined by their resistance to abrasion. This property, measured by the volume loss in abrasion tests, reflects the wear resistance of the material and plays a crucial role in determining the lifespan of tires [5, 33]. The impact of

different filler types on rubber compound abrasion loss was illustrated in Table 4.8. The FCS showed superior abrasion resistance (abrasion loss of 6.3 ± 0.62 %) in rubber due to better dispersion in the matrix, reduced interaction between fillers, and its high surface area. In contrary, lower abrasion resistance for COS reinforced natural rubber compound (abrasion loss of 7.26 ± 0.54 %) is due to poor silica dispersion inside the rubber matrix and higher silica –silica interaction [20]. Hence, FCS is suitable filler for rubber applications where abrasion loss is a crucial factor, such as in the tire industry. Abrasion loss is lowered in natural rubber compound reinforced with FCS because of interfacial connection of high surface area filler with rubber matrix [33, 52].. Enhanced maximum torque for FCS reinforced rubber compound results in increased crosslink and stiffness of the material in addition to lower abrasion loss, and increasing the compound durability [57].

4.5.5. Effect of silica fillers on hardness of rubber compounds

The hardness of a material reflects how resistant it is to indentation or deformation. Adding fillers typically increases hardness as shown in Table 4.8, particularly when the fillers have large particles. Larger filler particles restrict the movement of the rubber matrix, resulting in stiffer compounds when the material is indented and ultimately leading to increased hardness [34, 56, 58]. Improving the dispersion of silica in rubber compounds leads to increased crosslink density, resulting in higher hardness values. This can also be attributed to greater crosslinking of rubber materials with silica. FCS, when used to reinforce natural rubber, results in a lower hardness compared to COS. This is attributed to the smaller particle size of FCS and its ability to disperse easily in the rubber matrix. Furthermore, the high specific gravity of FCS and differential torque makes FCS reinforced rubber compound more harder than the unfilled one [13, 34, 58].

4.5.6. Effect of silica fillers on modulus of rubber compounds

Modulus of rubber compounds reinforced with higher surface area fillers increases due to the enhanced interaction between the filler particles and the rubber matrix. FCS filler has higher surface area which has more reactive sites to interact with the rubber molecules, leading to improved stress transfer within the compound [31]. This results in a higher modulus, as the compound becomes more resistant to deformation under applied stress. Fillers with higher surface areas tend to have a lower tendency to aggregate, form stronger chemical bonds with the rubber molecules, and suppress

particle-particle interactions which causes for individual particles to be evenly dispersed within the rubber matrix, improved adhesion between the filler particles and the rubber matrix, and reduction in particle-particle interactions which helps to improve the modulus of the rubber compound [59]. COS reinforced rubber compound has lower elastic modulus due to lower surface area of fillers which is not accessible to interact with rubber matrix and large particle size which makes difficult for filler to be dispersed for in rubber matrix.

Influence of FCS and COS fillers on modulus of elasticity of rubber compounds for 100%, 200%, and 300% is illustrated in Table 4.9. FCS reinforced rubber compound exhibited higher modulus of elasticity for a different stress of 100%, 200%, and 300% than COS and unfilled natural rubber compounds [60, 34]. Rubber compound containing FCS exhibit a higher modulus compared to COS. This is because rubber forms stronger bonds with FCS than with COS due to surface area and finer size of FCS witnessed from BET analysis and SEM image respectively [43].

Table 4.9 Effects of silica fillers on modulus of rubber compounds

	Modulus (Mpa)		
Stress	Unfilled silica	COS filled	FCS filled
Stress at 100%	0.33 ± 0.03	0.40 ± 0.07	0.42 ± 0.05
Stress at 200%	0.47 ± 0.02	0.57 ± 0.09	0.60 ± 0.05
Stress at 300%	0.62 ± 0.02	0.79 ± 0.13	0.86 ± 0.07

The aforementioned results in this study indicated that FCS has a higher tensile strength compared to COS which indicates better resistance to deformation under tension. The results also showed that FCS possess a slightly higher tear strength compared to COS. Thus, FCS requires a minimum torque of 1:29 and a maximum torque of 4:27, indicating its processability and vulcanization characteristics. Lower minimum torque values suggest easier mixing and processing, while higher maximum torque values indicate better reinforcement and cross-linking efficiency. A higher final torque and torque difference can indicate better reinforcement and mechanical properties in the cured rubber compound. In addition, FCS has a lower Mooney viscosity compared to COS, suggesting easier processing and

improved mixing efficiency in rubber compound formulation. Lower TS_1 and TS_2 values indicate faster curing and potentially better processing characteristics. FCS demonstrated shorter scorch times (T10 and T50) compared to COS, leading to faster processing and curing cycles. Moreover, FCS shows a lower abrasion loss (6.30 %) compared to 7.26% for COS, suggesting better durability and wear resistance. Furthermore, FCS has a slightly lower hardness (33.04 Shore A) compared to COS, suggesting a slightly softer or more flexible for the FCS reinforced rubber compound. Modulus of rubber compound reinforced with higher surface area FCS increased due to the enhanced interaction between the filler particles and the rubber matrix when compared to COS reinforced compound.

CHAPTER FIVE

5. Conclusions and Recommendation

5.1. Conclusions

Amorphous filter cake silica filler with high surface area was extracted from filter cake byproduct and its application for reinforcement of natural rubber compound in tire industry was investigated. Morphology analysis revealed that FCS is finer in size, indicating its suitability for rubber applications.

Lower specific gravity of COS results in lower silica concentration, which reduces its reinforcing abilities in natural rubber but higher specific gravity of FCS resulted in higher silica concentration and therefore highly reinforce the rubber compounds. FTIR results show the presence of silanol groups that increase surface activity and reactivity, resulting in stronger interactions with rubber fillers and boosting reinforcing properties of COS and FCS.

Rubber compound reinforced with FCS showed superior performance characteristics compared to COS by higher maximum torque, higher modulus, higher torque difference, lower Mooney viscosity, lower scorch time, and lower cure time.

Curing characteristics and mechanical properties of FCS reinforced rubber compounds were affected by specific gravity of fillers, particle size of fillers, and functional silanol groups.

Reduced optimum cure time for FCS reinforced rubber compound can reduce production time, energy consumption and resources needed to produce natural rubber compounds in tire industries. Therefore, FCS has great potential for rubber filler application in tire industry.

5.2. Recommendation

The focus of this study was extraction of amorphous precipitated silica from filter cake by product and its application as rubber filler in tire industry. Precipitated silica and its properties are affected by different parameters that affect the silica yield and techniques of its extraction. Ageing time, reaction time of NaOH with FCS, effect of sodium silicate concentration, and pH are all critical parameters during silica extraction by sol-gel technique that were not included in this study and require additional exploration. This broader investigation will provide a more comprehensive understanding of the optimum parameters at which quality silica can be extracted with appropriate properties.

Future research should prioritize the discovery of eco-friendly leaching agents to align with sustainable development objectives. Additionally, interaction effects of leaching parameters that affect silica yield can be investigated.

Detailed morphology analysis, cross linking density, and Payne effect/filler interaction of rubber compounds should be characterized. This will enable to know the dispersion of filler inside the rubber compounds.

Because of limited resources, rising raw material costs, growing awareness of sustainable development, and environmental concerns, valorization of industrial byproduct is gaining attention of many researchers worldwide. Therefore, further studies should be conducted for improving the quality and quantity of FCS.

Additional research is required to properly understand the costs associated with using filter cake byproduct as rubber filler in the tire industries. It is critical to analyze the economic feasibility to determine whether the FCS can be implemented successfully on a larger scale.

Future research should also focus on an extensive study to reduce the import burden of precipitated silica by using filter cake byproduct for various industrial purposes and making FCS more appealing for sectors that require high purity silica at a reasonable price.

References

[1] N. Singh, B. Shanker, and A. Saha , “Rice husk silica as a sustainable filler in the tire industry,” *Arab. J. Chem.*, vol. 15 , p. 104086, 2022.

[2] P. E. Imoisili, K. O. Ukoba, and T. C. Jen , “Synthesis and characterization of amorphous mesoporous silica from palm kernel shell ash,” *Bol. la Soc. Esp. Ceram. y Vidr.*, vol. 59 , pp. 159–164, 2020.

[3] Peterson, S.C. Carbon Black Replacement in Natural Rubber Composites Using Dry-Milled Calcium Carbonate, Soy Protein, and Biochar .Vol. 10, P,123-125, 2022, https://doi.org/10.3390/pr10010123

[4] Y. Fan, G. D. Fowler, and M. Zhao , The past, present and future of carbon black as a rubber reinforcing filler – A review, vol. 247. Elsevier B.V., 2020.

[5] V. Dall, A. Veiga, T. M. Rossignol, S. Crespo, and L. N. Carli , “Tire tread compounds with reduced rolling resistance and improved wet grip,” vol. 45334, pp. 1–9, 2017.

[6] Akhayere, E.; Kavaz, D.; Vaseashta, A. Efficacy Studies of Silica Nanoparticles Synthesized Using Agricultural Waste for Mitigating Waterborne Contaminants. Appl. Sci. 2022, 12, 9279. https:// doi.org/10.3390/app12189279.

[7] R. V. Santos, L. Avila, C. Rocha, C. Alberto, M. Moraes, and C. Bom, “Replacement of Commercial Silica by Rice Husk Ash in Epoxy Composites : A Comparative Analysis,” Materials Research. 2018; 21(3): e20160562 DOI: http://dx.doi.org/10.1590/1980-5373-MR-2016-0562

[8] M. Laad, “Extraction and Characterization of S ilica from A gro- W aste for E nergy A pplications,” *2017 Int. Conf. Energy, Commun. Data Anal. Soft Comput.*, pp. 1946–1952, 2017.

[9] P. P. Nayak and A. K. Datta, “Synthesis of SiO_2-Nanoparticles from Rice Husk Ash and its Comparison with Commercial Amorphous Silica through Material Characterization,” *Silicon*,

vol. 13, pp. 1209–1214, 2021.

[10] Y. B. Bereda, B. B. Tesfamariam, T. D. Desissa, G. Habtamu, B. Singh, and P. J. Ramulu, “Utilization of silica-enriched filter cake industry by-products as partial ordinary portland cement replacement,” Mater. Res. Express, vol. 10, no. 2, 2023.

[11] R. Mehari, F. Teklemariam, H. Aweke, H. Gebregwergis, and A. Info, “Synthesis and Characterization of Silica from Awash Melkaasa Chemical Factory Waste,” vol. 9, no. 2, 2022.

[12] A. Ajinsamajan, A. Rungvichaniwat, and A. Saetung, “Utilization of silicon dioxide powder from industrial wastes as novel filler in rubber isolator application,” vol. 32, no. 1, pp. 93–100, 2022.

[13] G. Sudhakaran and S. A. Avirah, “The application of nano silica as a potential , cost-ef fi cient green fi ller in acrylonitrile butadiene rubber vulcanizates containing carboxy-terminated liquid natural rubber,” vol. 54 , pp. 815–827, 2022.

[14] A. B. Wassie and V. C. Srivastava, “Synthesis and Characterization of Nano-Silica from Teff Straw,” vol. 46, pp. 64–72, 2017.

[15] I. J. Fernandes *et al.*, “Comparison between Rice Husk Ash and Commercial Silica as Filler in Polymeric Composites,” vol. 869, pp. 209–214, 2016.

[16] Fabian Grunert , André Wehmeier and Anke Blume , “New Insights into the Morphology of Silica and Carbon Black Based on Their Different Dispersion Behavior,” 2020.

[17] Johannes W. van Hoek , Geert Heideman , Jacques W. M. Noordermeer , Wilma K. Dierkes , and Anke Blume , “Implications of the Use of Silica as Active Filler in Passenger Car Tire Compounds on Their Recycling Options,” pp. 1–19, 2019. https://doi:10.3390/ma12050725

[18] R. H. Alves, T. Vitória, S. Rovani, and D. A. Fungaro, “Green Synthesis and Characterization of Biosilica Produced from Sugarcane Waste Ash,” vol. 2017, 2017.

[19] J. A. Adebisi and J. O. Agunsoye, “Extraction of Silica from Sugarcane Bagasse , Cassava Periderm and Maize Stalk : Proximate Analysis and Physico-Chemical Properties of Wastes,” Waste and Biomass Valorization, vol. 5, p. 1-2, 2017. DOI 10.1007/s12649-017-0089-5

[20] V. C. Sethuramalingam, S. Prabagaran, and K. Ganesan, “Studies on influence of silica filler and rice husk ash on the mechanical properties of vulcanized hybrid rubber composite,” Mater. Today Proc., vol. 37, pp. 2207–2213, 2020.

[21] A. You, M. A. Y. Be, and I. In, “Evaluation of rice husk ash as filler in tread compounds,” vol. 512 , pp. 1–5, 2018.

[22] N. Cardona Uribe, C. Arenas Echeverry, M. Betancur Velez, L. Jaramillo, and J. Martinez, “Possibilities of rice husk ash to be used as reinforcing filler in polymer sector -a review,” *Rev. UIS Ing.*, vol. 17, pp. 127–142, 2018.

[23] N. Suzuki, F. Yatsuyanagi, M. Ito, and H. Kaidou, “Effects of surface chemistry of silica particles on secondary structure and tensile properties of silica-filled rubber systems,” *J. Appl. Polym. Sci.*, vol. 86, pp. 1622–1629, 2002.

[24] Q. Lei *et al.*, “Sol–Gel-Based Advanced Porous Silica Materials for Biomedical Applications,” *Adv. Funct. Mater.*, vol. 30 , pp. 1–28, 2020.

[25] N. Setyawan, Hoerudin, and A. Wulanawati, “Simple extraction of silica nanoparticles from rice husk using technical grade solvent: Effect of volume and concentration,” *IOP Conf. Ser. Earth Environ. Sci.*, vol. 309 , 2019.

[26] T. A. Amibo, S. M. Beyan, and T. M. Damite, “Production and Optimization of Bio-Based Silica Nanoparticle from Teff Straw (Eragrostis tef) Using RSM-Based Modeling , Characterization Aspects , and Adsorption Efficacy of Methyl Orange Dye,” Hindawi Journal of Chemistry ,vol. 2022, 2022. https://doi.org/10.1155/2022/9770520

[27] J. G. Croissant, K. S. Butler, J. I. Zink, and C. J. Brinker, “Synthetic amorphous silica nanoparticles: toxicity, biomedical and environmental implications,” *Nat. Rev. Mater.*, vol. 5, pp. 886–909, 2020.

[28] Q. Liu, W. Xu, Y. Lv, and J. Li, "Study on factors affecting properties of silica," *Adv. Mater. Advanced Materials Research Vols. 233-235 (2011) pp 332-336 .doi:10.4028/www.scientific.net/AMR.233-235.332*.

[29] Y. L. Ni'mah, S. Suprapto, A. P. K. Subandi, N. E. Yuningsih, and A. C. Pertiwi, "The optimization of silica gel synthesis from chemical bottle waste using response surface methodology," Arab. J. Chem., vol. 15, p. 104-329, 2022.

[30] Rahmaniar and Tri Susanto, "Impacts of rice husk ash filler loading on curing, morphological characteristics and tensile properties of natural rubber/ethylene propylene rubber blends", IOP Conf. Ser.: Mater. Sci. Eng. 509 012116 ,2019.

[31] A. Boonmee and K. Jarukumjorn, "Preparation and characterization of silica nanoparticles from sugarcane bagasse ash for using as a filler in natural rubber composites," *Polym. Bull.*, vol. 77, pp. 3457–3472, 2020.

[32] Choophun, N.; Chaiammart, N.; Sukthavon, K.; Veranitisagul, C.; Laobuthee, A.; Watthanaphanit, A.; Panomsuwan, G. Natural Rubber Composites Reinforced with Green Silica from Rice Husk: Effect of Filler Loading on Mechanical Properties. J. Compos. Sci. 2022, 6, 369. https://doi.org/ 10.3390/jcs6120369

[33] E. Sayed and A. Khalaf, "A comparative study for the main properties of silica and carbon black Filled bagasse-styrene butadiene rubber composites," Polymers and Polymer Composites Volume 31: pp.1–14 , 2023.

[34] Addis Lemessa Jembere, Solomon Workneh Fanta. Studies on the Synthesis of Silica Powder from Rice Husk Ash as Reinforcement Filler in Rubber Tire Tread Part: Replacement of Commercial Precipitated Silica. International Journal of Materials Science and Applications. Vol. 6, No. 1, 2017, pp. 37-44. doi: 10.11648/j.ijmsa.20170601.16

[35] N. S. M. Zarib, S. A. Abdullah, and N. H. Jamil, "Extraction Of Silica From Rice Husk Via Acid Leaching Treatment," ISSN: 2357-1330, pp. 175–183, 2019. https://doi.org/10.15405/epsbs.2019.05.02.16

[36] I. I. Ahmed *et al.*, “Optimisation of acid pre-treatment parameters in silica extraction process from cassava periderm,” *Mater. Today Proc.*, vol. 38 , pp. 749–755, 2021.

[37] Mengistu Tadesse, Enyew Amare, H. C. Ananda Murthy,and Eshetu Bekele , “Extraction and Characterization of Bio-Silica from Sugar Cane Bagasse Ash of Wonji Sugar Industry , Ethiopia,” IJRAR ,volume 6, P- ISSN 2349-5138,2016 .

[38] Seroka, N.S., Taziwa, R.T. and Khotseng, L. Extraction and Synthesis of Silicon Nanoparticles (SiNPs) from Sugarcane Bagasse Ash: A Mini-Review. Appl. Sci.vol.12,pp.2310, 2022. https://doi.org/10.3390/ app12052310

[39] J. A. Adebisi *et al.*, “Extraction of silica from cassava periderm using modified sol-gel method,” *Niger. J. Technol. Dev.*, vol. 15 , p. 57, 2018.

[40] Feven Hagereselam ,“Synthesis, Extraction and Optimization of Silica Production from Teff straw (Eragrostis tef) ,” Msc thesis, 2019.

[41] A. Kasinathan, R. Rama, and G. Sivakumar, “Extraction , Synthesis and Characterization of Nanosilica from Rice Husk Ash,” International Journal of Nanotechnology and Applications ISSN 0973-631, Volume 4 , pp. 61-66,2016

[42] A. Boonmee, P. Sabsiriroht, and K. Jarukumjorn, “ Preparation and characterization of rice husk ash for using as a filler in natural rubber,” vol. 17, pp. 2097–2103, 2019.

[43] P. Sae-Oui, C. Rakdee, and P. Thanmathorn, “Use of rice husk ash as filler in natural rubber vulcanizates: In comparison with other commercial fillers,” *J. Appl. Polym. Sci.*, vol. 83 , pp. 2485–2493, 2002.

[44] N. P. Bhengu, “Understanding Effect of Process Variables on Extraction of Silica (SiO2) from Coal Fly Ash (CFA) and Pulp Waste Ash,” Msc thesis, 2020.

[45] N. S. Chundawat *et al.*, “Rice husk silica as a sustainable filler in the tire industry,” *Arab. J. Chem.*, vol. 15 , p. 104086, 2022.

[46] L. Honorato, M. L. Dias, C. Azuma, R. Célia, and R. Nunes, “Rheological properties and curing

features of natural rubber compositions filled with fluoromica ME 100," vol. 26 , pp. 249–253, 2016.

[47] M. Linec and B. Mušič, "The effects of silica-based fillers on the properties of epoxy molding compounds," *Materials (Basel).*, vol. 12 , pp. 1–11, 2019.

[48] D. Zheleva, "an attempt for correlation between mooney viscosity and rheological properties of filled rubber compounds," vol. 48, pp. 241–246, 2013.

[49] N. Dortaj, A. Mohebbi, H. Bagheri, M. Aman-Alikhani, and M. R. Yazdi, "Effects of Hydrophilic Silica Nanoparticles on Morphology and Mechanical Properties of a Typical Tyre Compound," *Chem. Chem. Technol.*, vol. 16 , pp. 150–158, 2022.

[50] W. Arayapranee, N. Naranong, and G. L. Rempel, "Application of rice husk ash as fillers in the natural rubber industry," *J. Appl. Polym. Sci.*, vol. 98 , pp. 34–41, 2005.

[51] N. Bukit, E. M. Ginting, E. Sidebang, E. Frida, and B. F. Bukit, "Mechanical Properties of Natural Rubber Compounds with Oil palm boiler ash and Carbon Black as a Filler," *J. Phys. Conf. Ser.*, vol. 1428 , 2020.

[52] M. C. D. Dominic, P. M. S. Begum, R. Joseph, D. Joseph, P. Kumar, and E. P. Ayswarya, "Synthesis, characterization and application of rice husk nanosilica in natural rubber," *Int. J. Sci. Environ. Technol.*, vol. 2 , pp. 1027-1035., 2013.

[53] H. Zhang *et al.*, "Influence of silane coupling agents on vulcanised natural rubber : dynamic properties and heat buildup In fl uence of silane coupling agents on vulcanised natural rubber : dynamic properties and heat buildup," vol. 8011, pp. 8–15, 2016.

[54] C. A. Bao, S. Kamaruddin, T. K. Yeow, K. Ing, B. T. Jay Han, and C. S. Ying, "The effect of oil palm fiber/eggshell powder loading on the mechanical properties of natural rubber composites," *ARPN J. Eng. Appl. Sci.*, vol. 11 , pp. 128–134, 2016.

[55] Chen L, Jia Z, Tang Y, Wu L, Luo Y, Jia D, Novel functional silica nanoparticles for rubber vulcanization and reinforcement, Composites Science and Technology (2016), doi:

10.1016/j.compscitech.2016.11.005.

[56] S. H. O. OSABOHIEN, E; EGBOH, “Cure Characteristics and Physico-Mechanical Properties of Natural Rubber Filled with seeds chell of cherry.pdf,” *J. Appl. Sci. Environ. Manag.*, vol. 11, pp. 43–48, 2007.

[57] P. Nuinu, C. Sirisinha, K. Suchiva, P. Daniel, and P. Phinyocheep, “Improvement of mechanical and dynamic properties of high silica filled epoxide functionalized natural rubber,” *J. Mater. Res. Technol.*, vol. 24, pp. 2155–2168, 2023.

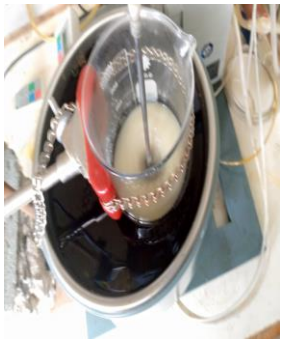
[58] S. Chuayjuljit and S. Eiumnoh, “Using Silica from Rice Husk as a Reinforcing Filler in Natural Rubber,” J. Sci. Res. Chula. Univ., Vol. 26, No. 2 (2001).

[59] B. B. Mukharjee and S. V. Barai, “Influence of Incorporation of Colloidal Nano-Silica on Behaviour of Concrete,” *Iran. J. Sci. Technol. - Trans. Civ. Eng.*, vol. 44, pp. 657–668, 2020.

[60] N. Thi, T. Anh, N. Hayati, and S. Kawahara, “Controlling the size of silica nanoparticles in filler nanomatrix structure of natural rubber,” *Polymer (Guildf).*, vol. 195, p. 122444, 2020.

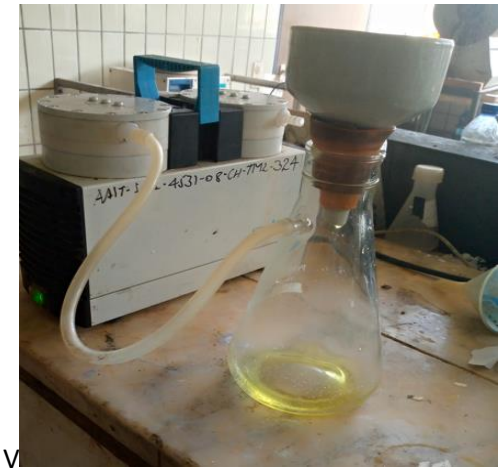
Appendix

Figure 1: Silica development process

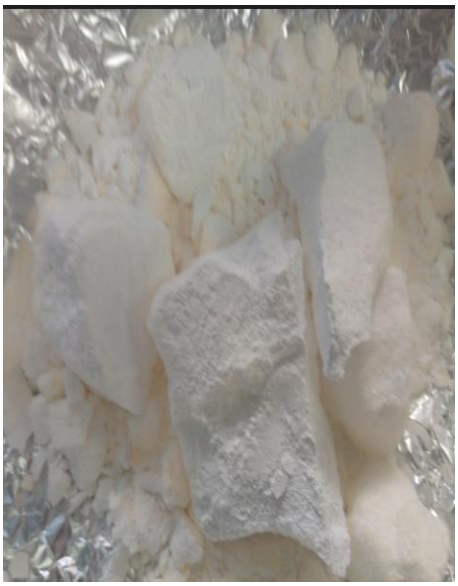


1A. Grinding **1 B**. Leaching **1C.** Calcination **1D**. Calcinated filter cake

1E. Sodium silicate solution **1F**. Precipitated sodium silicate solution



1G. Aged solution **1 H**. Vacuum filtration of precipitated silica **1I.** Filtered silica



1J. Oven dried silica powder 1K. Silica powder in plastic bag

Figure 2: FTIR result for COS and FCS

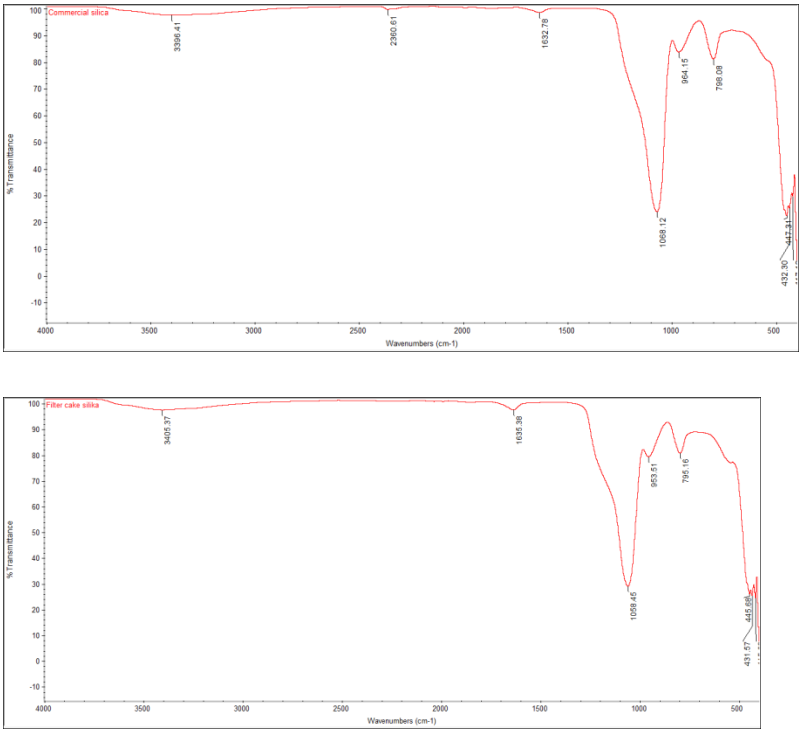
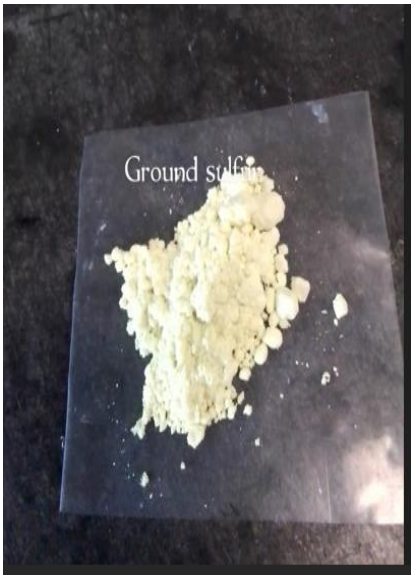
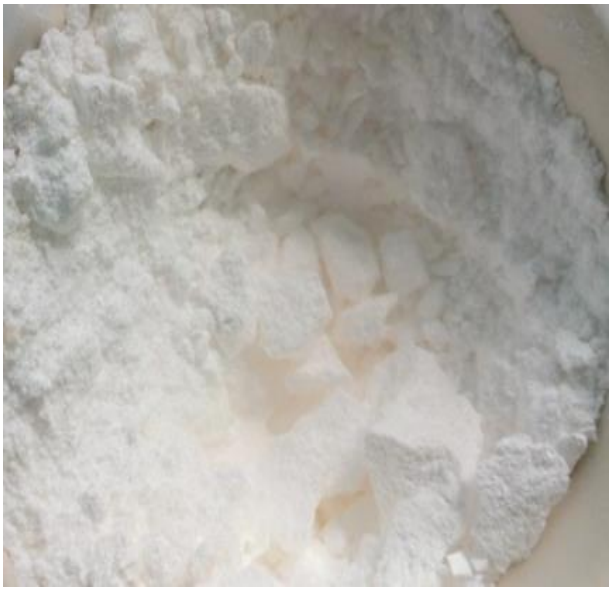


Figure 3 Rubber compound making ingredients

2A. Stearic acid 2B. 4010 (IPPD) 2C. Imported sio_2

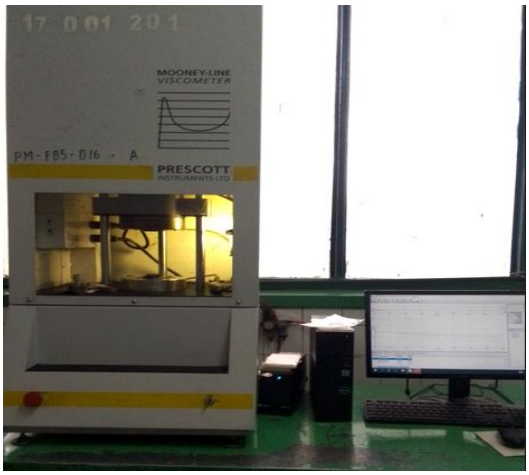


B4: Ground sulfur **B5**:MBTS **B6**:Natural rubber



2D. Zinc oxide **2E**. FCS

Figure 4 Laboratory equipment and sample photo



3A.Abrasion tester machine

3B.Mooney line visometer

3C. Vulcanizing machine

3D. Rheo line moving die

Figure 5 Researcher photo