FABRICATION OF SHOE SOLE USING NATURAL RUBBER REINFORCED WITH PYROLYSED WASTE TYRE RESIDUE

BY

UMAR IBRAHIM SHUAIB

DEPARTMENT OF PLOYMER AND TEXTILE ENGINEERING,

FACULTY OF ENGINEERING,

AHMADU BELLO UNIVERSITY

ZARIA, NIGERIA

APRIL, 2025

FABRICATION OF SHOE SOLE USING NATURAL RUBBER REINFORCED WITH PYROLYSED WASTE TYRE RESIDUE

BY

UMAR Ibrahim Shuaib
B.Sc. (TEXTILE SCIENCE AND TECHNOLOGY, ABU,2013)
P19EGPT8004

A THESIS SUBMITED TO THE POSTGRAUDUATE COLLEGE, AHMADU BELLO UNIVERSITY, ZARIA
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD
OF MASTER OF SCIENCE DEGREE IN TEXTILE SCIENCE AND TECHNOLOGY

DEPARTMENT OF POLYMER AND TEXTILE ENGINEERING,
FACULTY OF ENGINEERING,
AHMADU BELLO UNIVERSITY,
ZARIA, NIGERIA

APRIL, 2025

Declaration

I declare that the work in this Dissertation entitled *DEVELOPMENT OF SHOE SOLE USING NATURAL RUBBER REINFORCED WITH PYROLYSED WASTE TYRE RESIDUE*has been performed by me in the Department of Polymer and Textile Engineering. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma at this or any other institution.

UMAR IBRAHIM SHUAIB ---------- ----------

Student **Signature** **Date**

Certification

This Dissertation entitled *DEVELOPMENT OF SHOE SOLE USING NATURAL RUBBER REINFORCED WITH PYROLYSED WASTE TYRE RESIDUE by UMAR IBRAHIM SHUAIB*, meets the regulations governing the award of the degree of Master of Science in Textile Science and Technology of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

Prof. M. M. Bukhari _____ _____
(Chairman, Supervisory Committee) Signature Date

Prof. M.K Yakubu _____ _____
(Member, Supervisory Committee) Signature Date

Prof. H. R. Saliu _____ _____
(Head of Department) Signature Date

Prof. Muhammad Nasir Shuaibu _____ _____
(Provost, Postgraduate College) Signature Date

Dedication

This work is dedicated to almighty Allah for His grace, mercy and favour upon me all through this master's programme.

Acknowledgments

My sincerest gratitude goes to Almighty Allah for His grace, mercy and favour upon me all through the period of this work.

I wish to express my profound gratitude to my supervisors, Prof. M. M. Bukhari and Prof. M.K Yakubu, for their guidance, encouragements and intellectual contributions towards the success of this work.

To my beloved parents, Alhaji Shuaibu Umar and Hajiya Safiya Mahmud,also to my wife Saudatu Salis and children, Abdallah, Safiyya, Ahmad and Aisha, all my siblings and office colleagues,I wish them Allah's blessing and favours here and hereafter.

Lastly, my gratitude goes to all my good friends, especially Mr. Wasiu Salami, staff and students of the Department of Polymer and Textile Engineering. May the blessings of Allahbe with them.

Abstract

This study investigates the development of shoe sole composed of natural rubber (NR) reinforced with pyrolysed waste tire residue (PWTR). Ten samples of NR reinforced with PWTR were prepared using a two-roll mill at 65°C, with PWTR filler loadings ranging from 10 to 150 parts per hundred rubber (phr). The physicochemical properties of PWTR, including pH (6.3), moisture content (2.1%), and X-ray fluorescence (XRF) spectroscopy, were analyzed, revealing significant silicon oxide (40.054%), aluminium oxide (13.351%), and iron (III) oxide (7.1753%) content. Vulcanisation was performed at 130°C and 2.5 MPa for 30 minutes. Mechanical tests assessed tensile strength, modulus, elongation, hardness, wear rate, and coefficient of friction, while adhesive bond strength was evaluated using polyurethane and neoprene adhesives. Results indicated that 20 phr PWTR loading yielded optimal mechanical properties, with a tensile strength of 10.696 MPa and modulus of 872.0 MPa. Hardness increased with filler content, whereas elongation decreased. Wear rate rose from 0.12 $mm^3/N•m$ (20 phr) to 0.81 $mm^3/N•m$ (80 phr). The presence of silicon and aluminium oxides enhanced filler-rubber interaction, improving dispersion and durability. Beyond 20 phr, agglomeration reduced performance. The coefficient of friction initially increased with PWTR due to surface roughness but declined at higher loadings due to reduced contact area. Neoprene adhesive exhibited superior bonding strength (0.833 MPa) compared to polyurethane (0.5 MPa). The study concludes that 20 phr PWTR loading is optimal for shoe sole production, offering a sustainable approach to waste tyre valorisation. This research contributes to circular economy principles by transforming waste into high-value products, promoting environmental sustainability and efficient resource utilisation.

Key words: pyrolysis, waste tyre, shoe sole, natural rubber, recycling, reinforcement, XRF, tribology.

TABLE OF CONTENTS

Title page - - - - - - - - - - i

Declaration - - - - - - - - - - iv

Certification - - - - - - - - - - v

Dedication - - - - - - - - - - vi

Acknowledgements - - - - - - - - - vii

Abstract - - - - - - - - - - viii

Table of contents - - - - - - - - - ix

List of Tables - - - - - - - - - - xiii

List of Figures - - - - - - - - - - xiv

List of Plates - - - - - - - - - - xv

List of Appendices - - - - - - - - - xvi

List of Abbreviations and Symbols - - - - - - - xvii

1.0 INTRODUCTION - - - - - - - - 1

1.1 Background of the Study - - - - - - - 1

1.2 Statement of Research Problem - - - - - - 2

1.3 Justification - - - - - - - - - 3

1.4 Aim and Objective - - - - - - - - 3

1.4.1 Aim - - - - - - - - - - 3

1.4.2 Objectives - - - - - - - - - 3

1.5 Scope and Limitation - - - - - - - 4

2.0 LITERATURE REVIEW - - - - - - - 5

2.1 Some Components of Shoe - - - - - - - 5

2.1.1 Shoe Sole - - - - - - - - - 5

2.1.2 Insole - - - - - - - - - 5

2.1.3 Midsole - - - - - - - - - 5

2.1.4 Outsole - - - - - - - - - 6

2.2.0 Shoe Sole Mould - - - - - - - - 6

2.2.1 Types of soles and manufacturing process - - - - - 6

2.3.0 Natural Rubber - - - - - - - - 7

2.3.1 Vulcanisation of Rubber - - - - - - - 9

2.3.2 Physical Properties of Rubber - - - - - - 9

2.3.3 Harvesting of Rubber - - - - - - - 9

2.3.4 Applicationsof Rubber - - - - - - - 10

2.3.5 Challenges and Sustainabilityof Rubber - - - - - 11

2.3.6 Natural Rubber (NR) Latex - - - - - - - 11

2.3.7 Composition of Fresh NR Latex - - - - - - 12

2.4.0 Waste or Used Tyres - - - - - - - 12

2.4.1 Global TyreProduction - - - - - - - 12

2.4.2 Characterisation of Tyres

2.4.3 Average composition of New Passenger and Truck Tyres - - - 14

2.4.4 Control of Waste Tyres by Means of Recycling - - - - 14

2.5.0 Pyrolysis - - - - - - - - - 15

2.6.0 Carbon Black (CB) - - - - - - - - 16

2.6.1 Recycled Carbon Black (Waste Tyre Pyrolysis Residue) - - - 17

2.7.0 Related Works - - - - - - - - 17

3.0 MATERIALS AND METHODS - - - - - - 23

3.1 Materials - - - - - - - - - 23

3.1.1 Materials and Equipment - - - - - - - 24

3.1.2 Equipment - - - - - - - - - 24

3.2 Methodology - - - - - - - - 25

3.2.1 Collection and Preparation of Waste Tyre Pyrolysis Residue - - 25

3.3 Physiochemical Characterisation of the Waste Tyre Pyrolysis Residue Fillers - - - - - - - - - 25

3.3.1 Determination of pH - - - - - - - - 25

3.3.3 Determination of Pyrolysed Waste Tyre Residue Moisture Regain -- - 26

3.4.0 Formulation and Compounding of the Natural Rubber Composites - 27

3.5.0 Mechanical Test of the Blend (Natural Rubber/Pyrolysed Waste Tyre Residue) - - - 28

3.5.1 Tensile Strength, Modulus and Elongation - - - - - 28

3.5.2 Hardness Test - - - - - - - - - 28

3.5.3 Wear rate and Coefficient of Friction - - - - - - 29

3.6.0 Adhesive Bonding Strength Test - - - - - 29

3.6.1 Production of the Sole - - - - - - - 30

4.0 RESULTS AND DISCUSSION

4.1 Characterisation of Pyrolized Tyre Carbon Black - - - 31

4.1.1 X-ray Fluorescence (XRF) - - - - - - - 33

4.2 Physical Characterisation - - - - - - - 33

4.2 Mechanical Properties - - - - - - - 34

4.2.1 Tensile Strength - - - - - - - - 34

4.2.2 Tensile Modulus on natural rubber vulcanisate at 100% - - - 36

4.2.3 Percentage Elongation at Break - - - - - - 37

4.3 Physical Properties - - - - - - - - 39

4.3.1 Hardness - - - - - - - - - 39

4.4 Tribological Studies - - - - - - - - 41

4.4.1 Coefficient of Friction (CF) - - - - - - - 41

4.4.2 Wear Rate - - - - - - - - - 42

4.5 Adhesive Bonding Strength - - - - - - 44

5.0 SUMMARY, CONCLUSION AND RECOMMENDATIONS - - 46

5.1 Summary - - - - - - - - - 46

5.2 Conclusion - - - - - - - - - 46

5.3 Recommendations - - - - - - - - 48

REFERENCES - - - - - - - 49

APPENDICES - - - - - - - - 54

List of Tables

Table 2.1:Composition of NR latex in percentage - - - - - - 12

Table 2.2: Average Composition of New Passenger and Truck Tyres - - -14

Table 3.1: Materials, Chemicals and Glass-wares - - - - - - 23

Table 3.2: Equipment used - - - - - - - - - 24

Table 3.3: Typical Formulation for Compounding Natural Rubber and Pyrolysed Waste Tyre Residue Blends - - - - - - - - - - 27

Table 4.1: X-ray fluorescence (XRF) of waste tyre residue obtained from the pyrolysis - 31

Table 4.2: Comparison of the Physicochemical Properties of the Pyrolysed Waste

Tyre Residue - - - - - - - - - - - 33

List of Figures

Figure 1: Reaction of Isopentenyl pyrophosphate with dimethylallyl pyrophosphate to produce rubber poly (*cis-1,4isoprene*) - - - - - - - - - 8

Figure 4.1: Effect of Pyrolysed Waste Tyre Residue (PWTR) loading on the tensile strength of natural rubber vulcanisate - - - - - - - - - 34

Figure 4.2: Effect of Pyrolysed Waste Tyre Residue (PWTR) Loading on the tensile modulus of natural rubber vulcanisate at 100% - - - - - - - -36

Figure 4.3: Effect of Pyrolysed Waste Tyre Residue Loading on the percentage elongation at break of natural rubber vulcanisate - - - - - - - - 38

Figure 4.4: Effect of pyrolysed waste Tyre residue (PWTR) Loading on the Hardness of natural rubber vulcanisate - - - - - - - - - 39

Figure 4.5: Effect of Pyrolysed Waste Tyre Residue (PWTR) on the Coefficient of Friction of Natural Rubber Vulcanisates - - - - - - - - 41

Figure 4.6: Effect of Pyrolysed Waste Tyre Residue Loading on the wear rate of natural rubber vulcanisates - - - - - - - - - - 42

Figure 4.7: Effect of Adhesive Type on the Bonding Strength of Produced Sole and Footwear Materials - - - - - - - - - - - 44

List of Plates

Plate I: Stainless-steel mould size 40 - - - - - - - 7

Plate II: Stainless-steel mould size 27 and 29 - - - - - - 7

Plate III: Milky latex collection from rubber tree - - - - - - 10

Plate IV: Transversal cut of a radial tyre - - - - - - - 13

Plate V: Pyrolysis plant Reactor - - - - - - - - 16

Plate VI: Continuous pyrolysis plant by-product - - - - - - 16

Plate VII: Outer Part of the Produced Shoe Soles - - - - - - 45

Plate VIII:Inner Part of the Produced Shoe Soles - - - - - - 45

List of Appendices

Table 1: X-ray fluorescence (XRF) - - - - - - - 54

Table 2: Tensile Strength, Elongation and Modulus of NR and CB blend - - 56

Table 3: Bond Strength of Polyurethane Adhesive of Natural Rubber - - 56

Table 4: Bond Strength of Neoprene Adhesive of Natural Rubber - - - 57

Table 5: Coefficient of Fraction and Wear Rate - - - - - 57

Figure 1: Tribological Test Results of Sample with 0phr Loading - - - 59

Figure 2: Tribological Test Results of Sample with 10phr Loading - - - 59

Figure 3: Tribological Test Results of Sample with 20phr Loading - - - 60

Figure 4: Tribological Test Results of Sample with 30phr Loading - - - 60

Figure 5: Tribological Test Results of Sample with 40phr Loading - - - 61

Figure 6: Tribological Test Results of Sample with 50phr Loading - - - 61

Figure 7: Tribological Test Results of Sample with 60phr Loading - - - 62

Figure 8: Tribological Test Results of Sample with 80phr Loading - - - 62

Figure 9: Tribological Test Results of Sample with 100phr Loading- - - 63

Figure 10: Tribological Test Results of Sample with 150phr Loading - - 63

List of Abbreviations and Symbols

NA	Natural rubber
PWTR	Pyrolysed waste tyre residue
Phr	Part per hundred of rubber
CB	Carbon black
ABU	Ahmadu Bello University, Zaria
NILEST	Nigerian Institute of Leather and Science Technology, Zaria
XRF	X-ray fluorescence
XRD	X-Ray Diffraction
Symbols	**Full meaning**
<	Less than
>	Greater than
%	Percentage
-	Absent
+	Present
dL	Decilitre
eV	Electron volt
G	Gravity
g/dL	Gram per decilitre
g/L	Gram per litre

mg/L	Milligram per litre
g/Mol	Gram per mole
hr	Hour
hrs	Hours
Kg	Kilogram
M	Metre
M	Mole concentration
Mg	Milligram
Mg/kg	Milligram per kilogram
mg/ml	Milligram per millilitre
min	Minute
mm	Millimetre
mm^2	Millimetre square
mm^3	Millimetre cube
MW	Molar weight
ng	Nano-gram
nm	Nanometre
nmol/mg	Nanomole per milligram
rpm	Revolution per minute
v/v	Volume per volume

µg/ml	Microgram per millilitre
µL	Microlitre
µM	Micro molar
µm	Micrometre

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of the Study

Shoe is as old as the beginning of time which man has been using to protect the feet. The earlier fabrication of footwear has been from bark, twine and other natural man-made materials, while leather shoes have been in existence over 5000 years ago were made from a single piece of cow hide, fastened with a leather cord. In recent times, man has been using shoes for purposes other than feet protection such as decoration and fashion (Jessica *et al.*, 2020).

Sole is the bottom of a shoe which is in contact with the ground. It protects the feet against harm e.g. harsh weather conditions, sharp objects, etc. Soles can be made from a variety of materials which include rubber, wood, leather (Nenrit *et al.,* 2013).

Natural rubbers (NR) contain vegetable which is created by enzymatic processes in many plants, belonging mainly to families of *Euphorbiacea*, *Compositea, Moracea* and *Apocynacea*. It is industrially achieved mainly from the tree called *Hevea brasiliensis* belonging to *Euphorbiacea* family (Matador, 2007). It is grown as plant (average monthly temperature 25 – 28 °C) and humid (humidity around 80%) climate of South-Eastern Asia (Malaysia, India, (Matador, 2007) China, Sri Lanka, Vietnam), in Western Africa (Nigeria) and in North part of South America (Matador, 2007).

Latex is obtained through tapping from rubber trees that aged at least six years on the average, the tapping is mostly done at night or morning hours in order to avoid coagulation and sealing of the cut (Bello and Aliyu, 2018).

Carbon black (CB) stands as a very important product within the chemical industry, playing a fundamental role across various sectors of the material industry. CB is defined as micro or nano sized carbon powder, predominantly sourced from natural gas through combustion under oxygen-deficient conditions or derived from natural oil, such as through the process of cracking (Jebur, 2018).

Pyrolysed waste tyre residue (PWTR) consists of solid, liquid, and gaseous products generated during the thermal decomposition of waste tyre. The solid residue, often referred to as carbon black or char, can be utilized as a carbonaceous adsorbent or further processed for various applications. The pyrolysis process typically yields about 43% solid residues, alongside 41% liquid and 16% gas. The solid residues can be activated to enhance their surface area, making them suitable for applications in adsorption and catalysis (Staf *et al.*, 2022). Additionally, the liquid products can be fractionated into gasoline-like components, although these often contain high levels of unsaturated and aromatic compounds, limiting their direct use as fuels (Pyshyev *et al.,* 2024). The gaseous products, primarily methane and hydrogen, can be used for energy generation (Staf *et al.*, 2022). Overall, the pyrolysis of waste tyre presents a promising method for waste management and resource recovery, with potential applications in energy production and material science (Staf *et al.*, 2022).

Pyrolysis waste tyre residue (PWTR) has much potentials as it enhances the properties of the natural rubber such as low hysteresis, high durability, excellent toughness, increases hardness, tear resistance, abrasion resistance and high breaking stress on the produced shoe sole (Jebur, 2018). As such, the blend of natural rubber with PWTR will result into a good product that can be used as rubber shoe sole.

1.2 Statement of Research Problem

2.1 billion tyres were produced in 2023 and estimated to increase production of up to 2.9 billion by 2027. This rapid increase in tyre production and its use brings about accumulation of waste tyre which has become a significant environmental and public health concern (Analytica, 2024). With large volume of waste tyre generated annually, their non-biodegradable nature, coupled with limited recycling options, presents a growing challenge. These waste tyre often end up in landfills, illegal dumping sites or incinerated, contributing to soil and air pollution, thus, posing serious health challenges due to the hazardous gas emitted.

1.3 Justification

Petroleum based carbon black has been the major conventional reinforcement for natural rubber products. Hence, uses of pyrolysed waste tyre residue have a promising application in rubber reinforcement. Shoe sole produced from pyrolysed waste tyre residue will be cheap due to easy access to raw materials. Also, production of shoe sole from pyrolysed waste tyre residue usually disposed by littering or open burning will serve as means of environmental remediation and pollution control. Furthermore, this will also serve as means of job opening to many youths as there is a very large footwear global market.

1.4 Aim and Objectives

1.4.1 Aim

The aim of the research is to fabricate shoe soles using natural rubber reinforced with pyrolysed waste tyre residue.

1.4.2 Objectives

The objectives of the research are to:

a) Obtain pyrolysed waste tyre residue from tyre pyrolysis plant and analyse the physiochemical properties of the pyrolysed waste tyre residue (fillers) i.e. pH and moisture content and X-ray fluorescence (XRF) spectroscopy.
b) Compound the pyrolysed waste tyre residue with natural rubber in various proportion (10 – 150 phr).
c) Vulcanise the various natural rubber/pyrolysed waste tyre residue compounds produced and characterise the produced natural rubber/pyrolysed waste tyre residue vulcanisate (tensile strength, hardness, wear rate and coefficient of friction).
d) Produce shoe sole with the best performing sample and analyse its adhesive bond strength to different footwear materials using neoprene and polyurethane adhesives.

1.5 Scope and Limitation

This study focused on developing the outsole by sourcing pyrolysed waste tyre residue and reinforced with natural rubber at various proportions. The study utilised dry natural Rubber locally sourced from HAFSON Chemicals and Scientific Equipment, Olodi Apapa, Lagos State. The pyrolysed waste tyre residue used was sourced from pyrolysed waste tyre plant in Zaria while the adhesive bonding strength test will be limited to only two commonly used adhesives.

CHAPTER TWO

2.0 LITERARURE REVIEW

2.1 Some Components of Shoe

2.1.1 Shoe Sole

Sole is the bottom of a shoe which is in contact with the ground. It protects the foot against harm e.g. harsh weather conditions, sharp objects, etc. Soles can be made from a variety of materials which include; Rubber, wood, leather, etc (Nenrit *et al.*, 2013).

In recent years, soles are made from natural rubber, polyurethane or polyvinyl chloride (PVC) compounds. Soles can be simple (a single layer) or they can be complex (multiple structures or layers). When various layers are used, soles may consist of an insole, midsole and an outsole. (Karak, 2009).

2.1.2 Insole

Insole is the interior bottom of a shoe which sits directly beneath the foot under the footbed (also known as sock liner). The purpose of an insole is to attach to the lasting margin of the upper, which wrapped around the last during the closing of the shoe during lasting operation. Insoles are usually made of cellulose paper board or synthetic non-woven insole board. Many shoes have removable and replaceable footbeds. Extra cushioning is often added for comfort or health reasons (Nenrit *et al.*, 2013).

2.1.3 Midsole

Midsole is the layer in between the outsole and the insole that is typically there for shock absorption. Some types of shoes like running shoes have another material for shock absorption, usually beneath the heel of the foot where one puts the most pressure down. Different materials are used for midsole. Some shoes may not have a midsole at all (Nenrit *et al.*, 2013).

2.1.4 Outsole

Outsole is the layer in direct contact with the ground. This may comprise a single piece, or may be an assembly of separate pieces of different materials. Often, the heel of the sole has a rubber plate for durability and traction, while the front is leather for style. Dress shoes often have leather or resin rubber outsoles; casual or work oriented shoes have outsoles made of natural rubber or a synthetic material like polyurethane(John, 2011)**.**

2.2.0 Shoe Sole Mould

Shoe sole moulds are essential in the footwear industry for creating various designs. Shoe sole moulds are mainly fabricated from many different numbers of quality raw materials such as; PVC plastic moulds, cement product moulds, iron moulds, 3D computer aided design mould etc (Karak, 2009).

2.2.1 Types of soles and manufacturing process

1. Leather sole by means of assembling the components
2. Polyvinyl chloride (PVC) soles by injection process
3. Leather inserted PVC by injection process
4. Rubber by direct vulcanising process (Compression moulding)
5. Thermoplastic rubber (TPR) by injection process (TPR Granules)
6. Polyurethane by injection process and also by pouring process.

7. Blown PVC by injection process (Mag, 2020)



Plate I:Stainless-steel mould size 40.Plate II:Stainless-steel mould size 27 and 29 (NILEST Polymer Laboratory)(NILEST Polymer Laboratory)

Plate I and II above shows the stainless-still mould used in NILEST, Samaru, for production of different shoe sizes.

2.3.0 Natural Rubber

Natural rubber (NR), primarily derived from the latex of the rubber tree (*Hevea brasiliensis*), is a crucial material in for application in various industries due to its unique properties and versatility. Natural rubber is an elastic polymer, built on isoprene as its monomer. Natural rubber has elastomeric properties which are nearly non-compressible; it does not allow itself to be compressed only displaced. NR is stable is stable in solvents with the exception of alcohol and air.

It has low media compatibility with nonpolar media such as petroleum-based oils, synthetic lubricants, brake fluids based on glycol, overheated moisture, and aromatic hydrocarbons (gasoline) (Puskas *et al*., 2024).

The chemical name for natural rubber is polyisoprene. The monomer (meaning "one-part") from which it is built is isoprene. It is worth mentioning here that, although natural rubber is built of repeating isoprene units, isoprene is not the starting monomer for the natural product. Natural rubber is the result of a series of biochemical reactions which start with isopentenyl pyrophosphate within the tree(Miller, 2024).

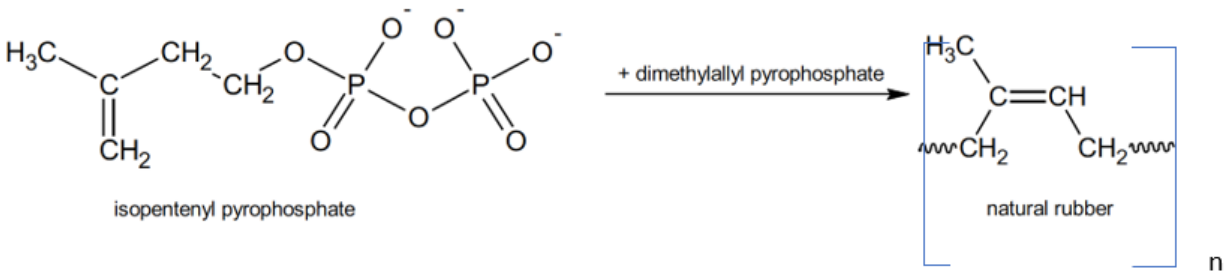


Figure 1: Reaction of Isopentenyl pyrophosphate with dimethylallyl pyrophosphate to produce rubber poly(cis-1,4isoprene).

NR exhibits high elasticity as well as good cold and damping behaviour at above room temperature ranging 60 to 80 °C. Natural rubber displays little resistance to high temperatures in combination with oxygen. The reactive double bonds still remaining after vu react easily with oxygen and break down the natural rubber (Puskas *et al*., 2024). To make it usable technically, the long polyisoprene chains of natural rubber are cross-linked with one another through the process of vulcanisation.

2.3.1 Vulcanisation of Rubber

This is a chemical process where sulphur is added to natural rubber under heat and pressure. This creates cross-links between the polymer chains, improving elasticity and durability while making it more resistant to environmental factors. In the process, sulphur atoms insert themselves between the double bonds of adjacent chain molecules to produce a three-dimensional molecule network whose parts can only shift against one another within certain limits. The material's properties can be controlled by changing the number of sulphur atoms within a bridge. Highly dynamic components generally have longer Sulphur bridges; while setting, behaviour and heat stability improves with shorter sulphur bridges. Natural rubber is the rubber with the longest molecular, which gives it very good dynamic qualities (Puskas *et al*., 2024).

2.3.2 Physical Properties of Rubber

It exhibits excellent mechanical resistance, electrical insulation, and permeability. Additionally, natural rubber maintains good performance at above room temperature ranging from 60 to 80 °C. However, it has limitations, such as susceptibility to degradation when exposed to high temperatures and oxygen (Puskas *et al*., 2024).

2.3.3 Harvesting of Rubber

Natural rubber is harvested through a process known as rubber tapping. This involves making incisions in the bark of the rubber tree to collect the milky latex that flows out. The latex is then processed into solid rubber through washing, homogenization, and drying.



Plate III: Milky latex collection from rubber tree (Puskas *et al*., 2024)

2.3.4 Applicationsof Rubber

Natural rubber is integral to numerous products across various sectors:

I. Automotive: It is predominantly used in tyre manufacturing due to its excellent wear resistance and elasticity. Approximately 75% of natural rubber produced globally is utilised for tyres.

II. Medical: Items such as surgical gloves and various medical devices are made from natural rubber due to its hypoallergenic properties and flexibility.

III. Consumer goods: Everyday products like footwear, balloons, and toys also rely on natural rubber for its unique characteristics.

2.3.5 Challenges and Sustainabilityof Rubber

Despite its advantages, natural rubber faces several challenges:

i. Environmental impact: The cultivation of rubber trees can lead to deforestation and biodiversity loss if not managed sustainably. However, responsible farming practices can contribute positively by acting as carbon sinks.

ii. Supply risks: Currently, about 99% of natural rubber comes from *Hevea brasiliensis*, making the industry vulnerable to diseases affecting these trees or climatic changes impacting their growth regions.

iii. Sustainability: Efforts are underway to explore alternative sources of natural rubber from other plants and improve existing cultivation methods to ensure a sustainable supply chain for this essential material (Puskas *et al*., 2024).

2.3.6 Natural Rubber (NR) Latex

NR latex in *Hevea brasiliensis* is located in latex vessels to be founded in various parts of the tree. The lowest occurring is in the wood and the highest in the secondary phloem. Natural rubber latex is a colloid system having the rubber particles dispersed in water. Latex particle sizeis varying approximately from 0.05 to 3μm. Fresh latex has mainly spherical shapes, that is under their aggregation gradually changed to pear shape. Besides these also small amounts of proteins, resinous matters (including lipids), hydrocarbons and mineral substances are present in NR latex. Part of these non-rubbery matters, mainly proteins and lipids, is surrounded by a surface of rubbery particles and gives them negative charge, which assures the latex stability.

Specific weight of fresh NR latex is 0.96 – 0.98g cm^{-3} and its pH ranges between 6.5 – 7.0. It coagulates through oxidation-reduction reaction to become stable.

Some rubber products (e.g. foam rubber, gloves, condoms, glues) are produced directly from latex. The latex is modified for these reasons to have higher dry rubber content (DRC) values (minimum 60 – 65 % of rubber). It is performed by means of its concentrations, the most often by centrifugation and sedimentation, but also water evaporation thickening and

electro-decantation is used. During these operations also eventual dirtiness and non-rubbery additives are removed from rubber besides increase of the dry rubber content in latex (Matador, 2007)

2.3.7 Composition of Fresh NR Latex

Table 2.1: Composition of NR latex in percentage(Matador, 2007)

S/N	Constituent	Content (%)
1.	Rubber	30 – 40
2.	Proteins	1.0 – 1.5
3.	Resins	1.5 – 3.0
4.	Minerals	0.7 – 0.9
5.	Carbohydrates	0.8 – 0.1
6.	Water	55 – 60

2.4.0 Waste or Used Tyres

2.4.1 Global TyreProduction

Approximately 2.1 billion tyres were produced in 2023. About 300 million tyres were estimated to be replaced annually due to the aging vehicle fleet. New Vehicle Sales Impact in 2023 was around 85 million carssold globally, necessitating approximately 425 million new tyres (five tyres per vehicle including spares) for these vehicles. The Global tyres market is estimated to increase production of up to 2.9 billion by 2027 (Analytica, 2024).

Tyres are built to be tough and durable, the properties that ensure a safe ride and long service life, but as well make scrap tyre disposal a difficult task. Waste tyres are defiant to natural degradation because the vulcanised rubber consists of long chain polymers (poly-isoprene, poly-butadiene, and

styrene-butadiene copolymers) that are cross-linked with sulphur bonds and are further protected by antioxidants and antiozonants that resist degradation (Francesco & Alessandro, 2022).

2.4.2 Characterisation of Tyres

Tyres consist of four key parts (as shown in Figure1) namely; tread (in contact with the ground), plies (portion of the tyre on which tread is vulcanised), sidewall (absorbs shock from the terrain) and heels (fit casing to the rim) (Torretta *et al.*, 2015).

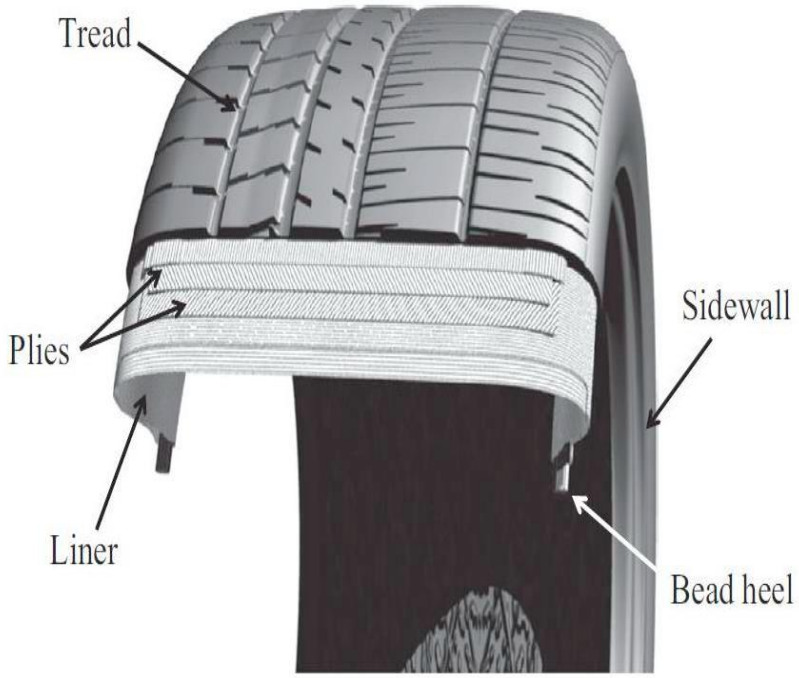


Plate IV:Transversal cut of a radial tyre (Hita *et al.*, 2016)

2.4.3 Average composition of New Passenger and Truck Tyres

Table 2.2: Average composition of New Passenger and Truck Tyres(Francesco & Alessandro, 2022)

S/N	Component	Passenger tyre (wt%)	Truck tyre (wt%)

1.	Natural Rubber	21.2	37.1
2.	Synthetic Rubber	24.5	10.0
3.	Carbon black	18.9	22.3
4.	Metals (e.g. steel)	10.8	21.1
5.	Textile (e.g. nylon)	3.7	0.2
6.	Process oil	4.4	0.8
7.	Silica	7.7	1.3
8.	Antioxidants, antiozonants, Sulphur	8.7	7.2

2.4.4 Control of Waste Tyres by Means of Recycling

Waste tyres have some properties (such as elasticity, durability, toughness, resistance to wear, stability in air atmosphere and high level of humidity etc.,) that make them have a number of alternative applications like;

i. In the Industry: retreading of the old tyres

ii. Shoemaking: soles, heels and straps of sandals can be made from tyre materials.

iii. In agriculture: as weights for silage cover sheets.

iv. In landscaping: as erosion protection for dam walls and slopes and drainages

v. In shore protection: as breakwaters.

vi. In harbors and docks: as dock bumpers and ship fenders.

vii. In the fishing industry: as artificial reefs for fish breeding.

viii. In household and communities: as bumpers in garages, playground equipment.

ix. Shoemaking: soles, heels and straps of sandals can be made from tyre materials.

x. Road construction: tyres are mixed with asphalt cement to form asphalt rubber. Asphalt rubber filler costs 40 % more than conventional material.

xi. Pyrolysis: Obtain carbon, fuels and gas.

2.5.0 Pyrolysis

Pyrolysis, a thermochemical process, involves the decomposition of complex macro molecular organic compounds in the absence of external oxygen, resulting in different products, such as oil, gas, water phase, and char. This transformation occurs within a temperature range of 400–800 ^{0}C. Pyrolysis methods vary based on operating parameters and can be categorized as atmospheric, vacuum, catalytic, fast, ultrafast (flash), and slow. Chemical transformations initiate at temperatures exceeding 150^{0}C. The rubber degradation process occurs between 250 and 500^{0}C, yielding the majority of pyrolysis oil and gas. The peak release of volatiles occurs in the 450–500^{0}C range. Beyond 550^{0}C, the release of volatiles from char diminishes, and tyre rubber undergoes near-complete decomposition. The secondary cracking of larger primary pyrolysis products into smaller molecules occurs in the 600–850^{0}C range (Rikmann *et al.*, 2024).

The entyre process then yields;

1. Non-condensable gas consisting of non-combustible e.g. carbon dioxide and combustible gases e.g. methane
2. Liquid fraction known as pyrolytic oil
3. A solid fraction consisting of metals wires, ash, aggregates and residual carbon (Torretta *et al.*, 2015)





Plate V:Pyrolysis plant Reactor Plate VI:Continuous pyrolysis plant by-product

(Han *et al.,* 2023)(Han *et al.,* 2023)

2.6.0 Carbon Black (CB)

Carbon black (CB), shows amajor role in enhancingrubber materials in terms of mechanicalandelectricalproperties (Jebur, 2018).

Rikmann *et al.*, (2024) reported that total manufactured CB was around 8,100,000 metric tons, after that the amount of CB consumption estimated globally in 2015 was more than 13.3 million tons and priced at $13.9billion, and it was predicted to reach 14 million tons at $14.6 billion in 2016. Advance prediction was to preserve 5.8% between 2016 and 2022 to reach 19.4 million tons, which is equivalent to $20.6 billion in 2022.

The general use for CB now a days is about 70% where majority of the usage is as reinforcing phase and pigment in automobile tyres. Likewise, the behaviour of heat away from the tread and

belt area of the tyre by the CB supports increases tyre-life by reducing thermal damage (Jebur, 2018) (Borchard, et al., 2014).

2.6.1 Recycled Carbon Black (Waste Tyre Pyrolysis Residue)

Pyrolysed waste tyre residue derived from waste tyres holds significant potential as a raw material for various valuable products. To unlock this potential, it is imperative to devise straightforward, economically viable, and environmentally sustainable technologies that are capable of eliminating undesirable contaminants from the recycled Pyrolysed waste tyre residue powder. The composition of pyrolysed waste tyre residue differs from that of virgin carbon black due to the substantial presence of additives used in rubber production. The high impurity content in Pyrolysed waste tyre residue precludes its direct reuse in the rubber industry, as these impurities significantly diminish the specific surface area of carbon black. Key additives include Sulphur (for vulcanisation), and ZnO, SiO_2, and TiO_2 (for enhancing rubber's mechanical properties). For instance, the addition of TiO_2, even in small concentrations, enhances the resistance of tyre mixtures to solar UV radiation, O_3, and other oxidizers. During the pyrolysis process, metal oxides react with sulphur, forming sulphides. Similarly, steel wire in tyres reacts with Sulphur, resulting in FeS (Rikmann *et al.*, 2024).

2.7.0 Related Works

Boukfessa and Bezzazi (2021) develop a formulation for the production of shoe sole. In their work, they investigated the effect of the amount of carbon black on curing and mechanical properties such as tensile strength, elongation at break, hardness and abrasion resistance of the natural rubber (NR)/ acrylonitrile-butadiene rubber (NBR) blend. Their blend composed of 65% NR and 35% NBR filled with different content of carbon black N330. A mixture of 65% natural

rubber type ribbed smoked sheet (RSS3) and 35% Acrylonitrile-Butadiene rubber (NBR with acrylonitrile content of 33%.) was prepared, using a laboratory two roll mixing mill at 23 °C . After forming a smooth band of rubbers, additives such as activators (ZnO and stearic acid), antidegradation (IPPD and TMQ), plasticizer (paraffinic oil) and filler (carbon black N330) were added slowly into the mixer. Then, accelerators (CBS and TMTM) and curing agent (sulphur) were introduced into the mixture. The rubber compounding ratios are summarized and the samples were produced in 0phr, 10phr, 30phr, 50phr, 70phr, 90phr and 110phr where 'phr' stands for (weight) parts per hundred concerning with rubber. After the mixing process, the vulcanisation was carried out at 160 °C for the predetermined optimum curing time in an electrically heated press under a pressure of about 14 MPa to get a vulcanised rubber sheet. The blending together of natural rubber (NR) and nitrile rubber (NBR) allows producing a vulcanisate with best properties from each component. In natural rubber (NR)/nitrile rubber (NBR) blends, results indicate that the carbon black particles diffuse and fill in the NBR network.

Robertson and Hardman (2021) reviewed and studied the nature of carbon black reinforcement of rubber: perspective on the original polymer nanocomposite. They reviewed key experimental observations of rubber reinforced with CB, including the finding that heat treatment of CB can greatly reduce the filler reinforcement effect in rubber. They further investigated the details of the particle morphology and surface chemistry described to give insights into the nature of the CB–elastomer interfaces. They also discussed rubber processing effects, the influence of CB on crosslinking, and various chemical modification approaches that have been employed to improve polymer–filler interactions and reinforcement. Finally, they contrast various models that have been proposed for rationalizing the CB reinforcement of elastomers. They reported another important aspect of the influence of CB filler on mechanical behaviour as the observation that

reinforcement index—steepness of the stress–strain curve—typically increases for longer mixing times. They also reported that the rubber mixing process also affects the morphology of the carbon black aggregates. Carbon black is composed of primary particles that are fused into larger-scale, complex shaped aggregates during the CB manufacturing process. Once the CB pellets/granules and then agglomerates are sequentially broken down and dispersed in the internal mixer, the aggregates are then exposed to the shearing forces and can fracture. More so, they reported that when CB is introduced into rubber, the overall Sulphur cure chemistry speeds up and this is an important aspect that must be considered in any attempt to rationalize carbon black reinforcement effects. Depending on the oil feedstock characteristics, commercial grades of CB used in the tyre and rubber industry have Sulphur contents that typically range from 0.2 to 2 wt.%. They further reported that, carbon black from the furnace process is at least 92% carbon. The current pyrolysis fuel oil feedstock in North America, the Sulphur content ranges from 0.6 to 1.5% depending on the specific feedstock and the grade of carbon black. The other main elements are oxygen, nitrogen, and hydrogen. On chemical modification effect of CB and NR they reported that Mechanical reinforcement of rubber by carbon black is closely linked to the nature of the polymer–filler interface. There have accordingly been significant efforts across several decades aimed at improving the interactions between elastomer chains and carbon black by adding polymer–particle coupling agents to the rubber formulation, using functionalised elastomers, and modifying the CB surfaces. Regarding possible polymer–filler interaction they reported a reaction scenario for a cross-linked elastomer reinforced with particles and stated that, If the CB type is a high surface area grade such as N110, N115, or N134, and the crosslink density is in a normal range for industrial rubber compounds, then approximate dimensions of 15nm × 15nm can be assign. The presence of CB in a rubber formulation accelerates the Sulphur vulcanisation kinetics

compared to unfilled elastomers. Consequently, it is a reasonable proposal that the crosslink density near the filler surfaces is elevated compared to the bulk rubber. They conclude that Carbon black is highly engineered nano-structured filler, and the mechanical performance of CB-filled rubber is a complex research area that is still being studied and debated today despite nearly 100 years of prior study. Heat treatment of CB at approximately 1000°C removes surface functional groups without significantly affecting the surface area, aggregate shape, or graphitic structure, and this greatly reduces the bound rubber and mechanical reinforcement. Considering the research literature in total, we believe that the most realistic scenario for polymer–CB interfaces is predominantly physical adsorption with some covalent chemical bonds also present.

Satta *et al*. (2020), reported a work in an article titled"optimizationoftherubberFormulationforfootwearapplicationsfromtheresponsesurfacemethod (RSF).

The work was targeted toinvestigatetheeffectoffiller/plasticizerfractions onshock attenuationofnatural rubber soles. The statisticalresponsesurface method (RSM)was usedtooptimizetheloadingof naturalrubber (NR),fillerscarbonblack (CB) andchinaclay (CC)andaplasticizer(paraffinicoil). Compoundmixingwasperformedintwostages. First, theNRwas masticatedinakneading machine(YFMDispersionmixers3L, YongFongMachineryCo., Ltd.,Samutsakorn,Thailand)at 90°C,ataroller speedof30rpm. Subsequently,theplasticizer andfillers wereaddedaccordinglywithinamixingtimeof30min. Second, themodifiedNRwasmixedwith theremainingZnO,stearicacidandWingstayLonatwo-rollmill (YFM400B,YongFong MachineryCo., Ltd.,Samutsakorn,Thailand).After the compound wascooled toambient temperature,itwas mixed withMBT andsulphur andheldatthattemperaturefor24htoallow

stressrelaxationtoproceed beforevulcanisation.Theoptimal curingtimewaschosenonthebasisofprior reports, an in-house NRexperience. Eachtestpiecewasmoulded atthesameconditionsof150°Cand150kg/cm^2 for10–15minandsubsequentlycooledatambient temperature for24hrprior totesting.

Coefficient of friction describes the resistance an object will be under as it tries to slide across a surface. It is the ratio of the force required to slide it along a flat surface to the normal force on the object. For most everyday objects and materials, the coefficient is a number between 0 and 1. The coefficient of friction for rubber shoe sole can vary depending on several factors, including the specific type of rubber, the surface in contact with and nature of the filler if blend (Mahmoud, 2016).

Studies indicate that, on average, the coefficient of friction for rubber shoe sole ranges between 0.6 to 1.0 which was observed between 0.701 and 0.978. The values obtained are within the required range because shoe soles are expected to have high friction for optimum slip resistance (Sotter *et al.*, 2005)

American Society for Testing and Materials test method ASTM C 1028-96 recommends 0.60 and higher CF for shoe soles while The Access Board of the United States Department of Justice on the Americans with Disabilities Act (ADA) suggested a minimum coefficient of friction of 0.80. This standard is supported by organizations such as the Ceramic Tiles Institute of America (Sotter *et al.*, 2005).

The CF in a shoe sole is affected by key factors such as, shoe outsole's tread surface area, heel shape, material hardness as well as the type of flooring. Understanding these parameters can help in selecting appropriate footwear for various activities and environments (Sotter *et al.*, 2005).

Ginting *et al*. (2017) reported their work on mechanicalpropertiesandmorphology of naturalrubberblendwithbentonite and carbon black. The projectwasto determinethemechanicalpropertiesandmorphologyof compositenaturalrubberandnatural bentonite with additionofNa-bentonitefillerandcarbon blackto naturalrubber.Themethodiscarried out with materialmixedwithfillercompositionvariations (0,10,20,30)phrusingopen millfor6 min. NaturalrubberSIR20,bentonite,carbonblack,ZnOofPTBrataco,sulphur,stearicacid from PT brataco, wax fromChina, butyl hydroxytoluene(BHT), diethyl zincdittocarbamate (ZDEC), distilled, saturated NaCl. The tools used in the characterization andmanufacturing testsamples is open mill,Scanning Electron Microscopy (SEM)Zeissmodels, tensiometerMosantoT-10Durometertype-A, X-RayFluorescence(XRF),XRD(6100 Shimadzu).

Result of the open mill were vulcanisedat170^{O}C.The resultsshowedthat theadditionofNa-bentonitefillerandcarbonblack influenceonthe mechanicalpropertiesoftensilestrength,elongation atbreak,modulusofelasticity,hardness,and strong tear.

Morphologicalresultsshowedcavitiesintherubbercompound andtheoccurrence agglomeration,therebyreducingthetensilestrength and elongationatbreak.

Yasir *et al*. (2015) studied the effect of carbon black types on curing behavior of natural rubber by insertion of various types of carbon black. The average of nitrogen surface area (34 for N660, 76 for N330, 77 for N326, and 91 for N375) m $^{2}/_{g}$ and range of particles size (26-63)nm high abrasive furnace. The curing kinetics was determined using the rheometer with an oscillating disk, in which the network formation process in registered by the torque variation during time. The vulcanisation was obtained in a hydraulic press at 185 ^{0}C. OSD rheometer results clearly indicate that optimum cure time, scorch time and cure rate (100/t90-ts2) are exponentially decreases with increasing in particles surface area. However, increase in max., min. torque of OSD rheometer,

reversion period time of cure characteristics and Mooney viscosity ML (1+4) at 100^0C with increasing the surface area.

Nenrit *et al*. (2013) produced a shoe sole from natural rubber reinforced with leather crumb. After compounding on a two-roll mill, the products (sheeted batches) obtained were moulded into a shoe sole using the hydraulic press. This was done by placing the sheeted batches in the shoe sole mould which was later placed between platens. The lower platen was then elevated to press the mould for ten minutes after which the moulded sole was removed and trimmed. Hardness, tensile strength and flexural test were all carried out on the different samples.

From the result obtained by Nenrit *et al*. (2013) for the hardness test, it was observed that sample A (NR vulcanisate containing 80g of leather crumb) has higher value than sample B (NR vulcanisate containing 60g of leather crumb).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

3.1.1 Materials and equipment

Table 3.1**:** Materials, Chemicals and Glass-wares

Material/Chemical	**Glass-ware**
Dry Natural Rubber (NR)	Round bottom flask
Waste Tyre	Stirring Devices
Mecapto Benzoyl Thiosulphite (MBTS)	Spatula
Dimethylformamide (DMF)	Filter paper
Stearic acid	Beakers
Sodium Hydroxide (NaOH)	Conical flasks
Hydrochloric Acid (HCl)	Gloves and mask
2,2,4-Trimethyl-1,2-dihydroquionoline (TMQ)	Desiccator
Zinc oxide	Stirring rod
Processing oil (Parafin)	Test tubes
Acetone	Measuring cylinder

The dry Natural Rubber and other chemicals were supplied by HAFSON Chemicals and Scientific Equipment, Olodi Apapa, Lagos State. All chemicals supplied are of analytical grade.

The PWTR was obtained as Industrial waste product from pyrolysis plant section of El-Hayat Fertilizer Plant, KM 15, Mararrabar Gwanda, Sabon Gari, Zaria, Kaduna State.

3.1.2 Equipment

Table 3.2:Equipment used

S/N	Name	Model	Manufacturer	Location
1.	Universal Testing Machine	(VDV 100KN-190536)	Thermocool, England	ABU
2.	Digital weighing balance	AB 204 (0 -180g)	Metter Teledo, Switzerland	NILEST
3.	Anton Paar Tribometer	(8054 Gras)	China	ABU
4.	Cole parmer hot air oven	Thermally Protected (60648)	Gallenkamp, England	NILEST
5.	Carver inc. hydraulic hot press	(3851-0)	Nebertherm, GmbH, Germany	NILEST
6.	Fortuna-wepke Abrasion tester	(158/2FBM)	Edward, England	NILEST
7.	Durometer Hardness tester	(model no. 5019)	PANalytical, Netherland	NILEST
8.	Allen-Bradley Laboratory	(802T –WS1P)	England	NILEST
9.	Anton Paar and Ball Milling machine	**(**8054, N-150**)**		NILEST
10.	Stainless-still Mould		China	NILEST

Key: NILEST = Nigerian Institute of Leather and Science Technology, Zaria, Kaduna State
ABU = Ahmadu Bello University, Zaria.

3.2 Methodology

3.2.1 Collection and Preparation of Waste Tyre Pyrolysis Residue

The obtained pyrolysed waste tyre residue was sorted to remove any form of contaminants and dried to a constant weight to reduce moisture. It was ball milled into fine particle size using ball milling machine at the Department of Chemical Engineering, ABU, Zaria.

Ten (10) different Samples were compounded using a laboratory scale two-roll mill (Allen-Bradley, 802T-WS1P) at of 65°C for 5 minutes before sheeting out. The order was in accordance with Table 3.2 with natural rubber first and then sulphur being introduced last. The control sample was denoted A while other samples were denoted B, C, D, E, F, G, H, I and J at 10, 20, 30, 40, 50, 60, 80, 100 and 150 parts per hundred of rubber (phr).

After compounding, the samples were vulcanised using hydraulic hot press machine. This was achieved by putting sizeable quantities of the compounded rubber into a metal mold of 100mm x 100 mm x 3 mm and placed in the machine at e130^{O}C and pressure of 2.5MPa for 30minutes for curing. The rubber/pyrolysed waste tyre residue vulcanisates produced were subjected to mechanical test i.e., tensile strength test, hardness test, water absorption test, wear rate and coefficient of friction.

3.3 Physiochemical Characterization of the Waste Tyre Pyrolysis Residue Fillers

3.3.1 Determination of pH (ASTM D1512)

Boiling slurry method was employed according ASTM D1512 method. To determine the pH of PWTR. The pH test method is crucial for assessing the acidity or alkalinity of the PWTR particularly in rubber application because it can influence vulcanisation process.

The PWTR was pulverized and mixed with boiling water in a ratio 1:10 (PWTR to water). Few drops of acetone were added to enhance wetting. The mixture was boiled for 15 minutes, making

sure it doesn't evaporate completely. After cooling, a pH meter was immersed to measure the pH of the slurry.

3.3.3 Determination of Pyrolysed Waste Tyre Residue Moisture Regain (ASTM D1509-18)

The moisture content of PWTR was carried out in accordance with ASTM D1509 by measuring the heat loss at 125^{o}C. 5g of PWTR was weighed in an evaporating disc and exposed to atmospheric conditions for 24 hours. It was placed in the hot air oven at 125^{O}C for 1 hour. The procedure was repeated until a constant weight was obtained. The moisture content was calculated using equation 3.5.

% Moisture Content = $\frac{Wo - Wi}{Wi} x\ 100$ ………………………………………………………. (3.5)

Where:

Wo = wet weight of the filler

Wi = dry weight of the filler

3.3.5 X-ray fluorescence (XRF) analysis of waste tyre pyrolysis residue (ASTM D1619).

XRF analysis of pyrolysed waste tyre residue was carried out according to ASTM D1619 standard. The PWTR was dried in an oven at 125^{0}C, it was cool in a desiccator at room temperature (23^{0}C) to avoid moisture interference, the sample was placed into a suitable container and placed unto the calibrated XRF Analyser. The elements, concentration and peaks of silicon oxide (SiO_2), aluminium oxide (Al_2O_3), sulphur oxide (SO_3) and other compounds present in the sample were illustrated in Appendix A.

3.4.0 Formulation and Compounding of the Natural Rubber Composites

The rubber was mixed with other ingredient according to ASTM (D15-72) standard under careful control of temperature, nip gap and sequence of ingredients addition.

Table 3.3:Formulation of Natural Rubber, pyrolysed waste tyre residue and other ingredient.

S/N	**Ingredient**	**Sample loading (parts per hundred of rubber) (prh)**									
		A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**
1	NR	100	100	100	100	100	100	100	100	100	100
2	Zinc Oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
3	Steric Acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
4	MBTS	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
5	TMQ	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
6	PWTR	0	10	20	30	40	50	60	80	100	150
7	Processing oil	5	5	5	5	5	5	5	5	5	5
8	Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

The samples were compounded using a two-roll mill laboratory scale (Allen-Bradley, 802T-WS1P) at a temperature of 65°C for 5 minutes before sheeting out. The order of introduction of the ingredients for compounding was in accordance with table 4 with natural rubber first and then sulphur being introduced last. The control sample was denoted A, while other samples were

denoted B, C, D, E, F, G, H, I and J at 10, 20, 30, 40, 50, 60, 80, 100 and 150 phr loading respectively.

After compounding, samples were vulcanised using hydraulic hot press machine. This will be achieved by putting the compounded rubber into a metal mould of 100 mm x 100 mm x 3 mm and placed in the machine at 130^{O}C and pressure of 2.5MPa for 30 minutes for curing.

3.5.0 Mechanical test of the blend (Natural rubber/pyrolysed waste tyre residue)

3.5.1 Tensile strength, modulus and elongation (ASTM D412)

The tensile test was carried out using the Universal Testing Machine at the Department Polymer and Textile Engineering, A.B.U, Zaria. Dumbbell shaped samples were subjected to a tensile force. The result of the tensile strength, elongation and modulus were calculated using the equation (3.7 to 3.9)

$$\text{Tensile Strength} = \frac{F}{bd}(\text{N/mm}^2) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.7)$$

$$\% \text{ elongation} = \frac{Extension}{Original\ \ Lengt\,h} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.8)$$

$$\text{Modulus} = \frac{Stress}{Strain} \ (\text{N/mm}^2) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.9)$$

Where:

F = Maximum tensile load

b = Sample thickness

d = Sample width

3.5.2 Hardness Test (ASTM D2240)

The hardness tests were carried out using the Durometer Hardness tester (model no. 5019) on shore A scale. The samples was placed on the mounting stage and the dial gauge adjusted to zero (0), the hand lever was used to raise the stage such that the sample come in contact with the dial

point and exact pressure/force on the sample and the reading was taken. This was repeated three (3) times at different positions on the sample, average hardness value was taken and recorded.

3.5.3 Wear rate and coefficient of friction

The wear rate analysis was carried out in accordance with ASTM D-3702 using Anton Paar Tribometer (8054 Gras). A prepared sample disc of 30 mm diameter was mounted on a rotating stage below a loading ball of radius 5mm, a force of 5.0 N was applied on the loading ball, in contact with sample's surface to create the wear and the test was run for 10 minutes at room temperature and atmospheric relative humidity.

The wear rate and the coefficient of friction of the sample was calculated and recorded by the machine automatically.

3.6.0 Adhesive Bonding Strength Test (ASTM D2558-69)

Polyurethane adhesive and neoprene adhesive were examined on leather, fibre and microcellular footwear material. This test method covers the determination of the peel strength of the adhesive bond on the NR/PWTR sole. The neoprene and polyurethane adhesives were applied by hand brush on the rubber sole, leather, fibre and microcellular footwear materials separately, the sole was bond to neoprene and polyurethane consecutively by applying a pressure of 60psi (4.2 kgf/cm^2) for 15 seconds, the bonded samples were conditioned at 30°C for 4hrs before testing. Tensile testing machine was used to peel the bonded samples at a peel angle of 180° maintaining a constant peeling rate. The load, thickness, area and bond strength for polyurethane and neoprene are shown in Table 3 and 4 respectively.

3.6.1 Production of the Sole

Three batches resulting to 300g weight of PWTR/NR blend was compounded on a two-roll mill. The blend was equally divided into two (150g) each using weighing balance. Each 150g portion was loaded in each of two mould cavity which has been rubbed with oil for easy removal to produce a pair of the shoe sole. The mould was closed and placed on the compression moulding machine platen which has already been preheated at 130^0C. Pressure was applied at 3MPa and allowed to stand for 30minutes for vulcanisation to take place. After 30 minutes of heating under pressure, the pressure was released and the mould was offloaded and opened, it was allowed to cool and the shoe sole were ejected in pairs.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Characterization of pyrolysed tyre Carbon Black

4.1.1 X-ray fluorescence (XRF)

In this work, XRF technique was used for analysis of the PWTR filler.

Table 4.1: X-ray fluorescence (XRF) of waste tyre residue obtained from the pyrolysis**.**

S/N	Element	Concentration (%)	Peak(CPS/Ma)
1.	Fe_2O_3	7.1753	26323
2.	SiO_2	40.054	3116
3.	Al_2O_3	13.351	201
4.	MgO	1.74	3
5.	P_2O_5	0.2533	60
6.	SO_3	0.1802	204
7.	TiO_2	0.8216	3201
8.	MnO	0.1526	691
9.	CaO	1.4248	2462
10.	K_2O	1.3224	1400
11.	CuO	0.00259	18
12.	ZnO	0.2154	104
13.	Cr_2O_3	0.01159	73
14.	V_2O_5	0.0120	102
15.	Rb_2O	0.00381	18
16.	Ga_2O_3	0.00227	37
17.	NiO	0.00378	18
18.	Cl	0.1629	89
19.	ZrO_2	0.1502	337
20.	WO_3	0.01705	39
21.	Y_2O_3	0.00271	10

22.	Ag_2O	0.00031	1
23.	Bi_2O_3	0.02533	1
24.	Sb_2O_3	0.028	2
25.	SnO_2	1.242	7

Table 4.1, presents the X-ray fluorescence (XRF) result for the PWTR obtained from tyre pyrolysis. The results indicated the elemental oxides that are contained in the sample. From the results obtained, it could be observed that the pyrolysed waste tyre residue is rich in silicon oxide (SiO_2), aluminum oxide (Al_2O_3) and iron (III) oxide (Fe_2O_3)with percentage concentration of 40.054, 13.351 and 7.1753 respectively. Sulphur oxide with 0.1802 percentage concentration among others was observed to be minimal in the sample.

The presence of silicon oxide SiO_2 and Aluminum oxide $Al_2\ O_3$ in the PWTR improves the filler-rubber interaction, which is crucial for achieving better mechanical properties, this interaction helps in dispersing the fillers more uniformly within the rubber matrix, leading to enhanced strength and durabilityin natural rubber (NR) vulcanisates produced (Alkhazraji, 2018; Wang *et al.*, 2021).

Cifriadi, *et al.*, (2022) indicated that varying Sulphur content significantly affects the mechanical properties of NR compounds, the sulphur form bridges between the polymer chains, thereby enhancing network structure of the rubber. Moreover, increasing sulphur can enhance hardness and improve thermal and surface properties. However, excess Sulphur can lead to over-crosslinking i.e creating a highly crosslinked network which limit the material's ability to stretch and make the rubber more brittle, while insufficient amount may result to inadequate cross-linking and inferior mechanical performance. Consequently, the balance of sulphur content is vital for

achieving optimal performance in rubber products. This result guides in the choice of the amount of sulphur content used for this research.

Table 4.2:Comparison of the Physicochemical Properties of the Pyrolysed Waste Tyre Residue

S/N	Characterization	Obtained value	Literature values
1	pH	6.3	5-7
2	Moisture Content	2.1 %	0.4 - 5.96%

The pH of the pyrolysed waste tyre residue was determined using ASTM D1512. An average pH value of 6.3 was obtained which is within the required range for rubber vulcanisation as evidence by El-Maadawy *et al.*, (2024), they further indicated that pH of pyrolysed waste tyre residue can affect its performance in rubber compounds. Generally, pyrolysed waste tyre residue is produced by incomplete combustion of hydrocarbons. Some studies reported to have obtained a pH between 5 to 7. pyrolysed waste tyre residue with low pH leads to premature vulcanisation due to incomplete reaction. The pH of pyrolysed waste tyre residue varies depending on its type and production process.

ASTM D1509 was adopted in determining the moisture content of the pyrolysed waste tyre residue. From the result obtained the average moisture content was found to be 2.1%. However, previous studies indicate that moisture content can be low, often ranges between 0.4 to 0.2% for different preparation methods. Whereas, other references indicated that moisture content can be higher in certain types of pyrolysed waste tyre residue with values ranging from approximately 3.54 to 5.96% depending on the specific characteristics of the samples (Rikmann *et al.*, 2024).

4.2 Mechanical properties

4.2.1 Tensile Strength

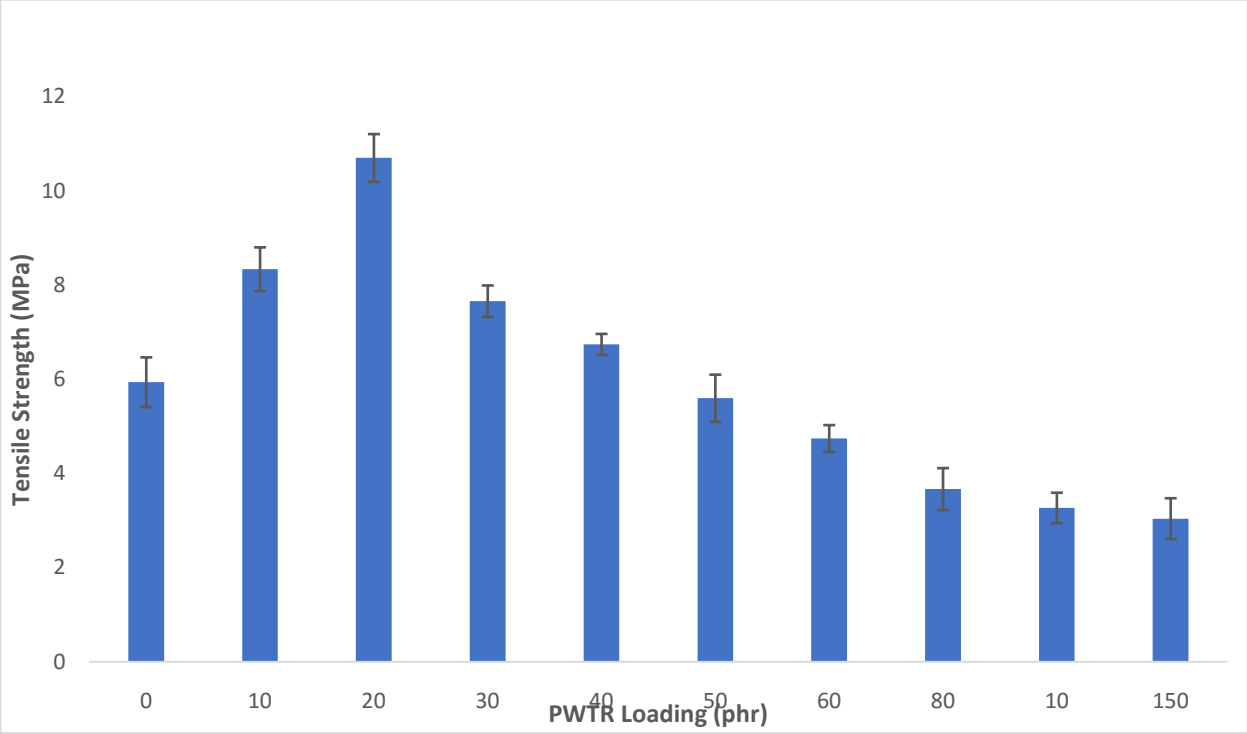


Figure 4.1: Effect of Pyrolysed Waste Tyre Residue (PWTR) loading on the tensile strength of natural rubber vulcanisate

Figure 4.1, shows that tensile strength of the produced samples initially increases with increasing pyrolysed waste tyre residue (PWTR) used as reinforcement, reaching a peak at 20phr with tensile strength value of 10.696MPa and then decreases for higher pyrolysed waste tyre residue (PWTR) loading to a value of 3.038MPa at 150 phr PWTR loading.

Robertson and Hardman, (2021) indicate that uniform distribution of Pyrolysed Waste Tyre Residue (PWTR) in a rubber matrix significantly influences the mechanical strength of the rubber compound.

This result corresponds with the findings of Tenebe *et al*. (2013), which established that the tensile strength of polymers is often influenced by the degree of cross-linking and the presence of

fillers, which can alter mechanical properties. Their work shows increase in tensile strength of the samples with highest peak at 20phr loading before a steady decrease was observed due to the formation of agglomerations by the filler particles.

Also, Christopher *et al*. (2020) in their work titled "Characterizing Distributions of Tensile Strength and Crack Precursor Size to Evaluate Filler Dispersion Effects and Reliability of Rubber" chose 20phr as the reference compound (Control) to demonstrate tensile strength data from 50 specimens to characterise the failure distribution behaviour of pyrolysed waste tyre residue (PWTR) reinforced styrene-butadiene rubber (SBR) compounds.

Furthermore, a value of 20 to 50phr is within a good region according to the work of Boukfessa and Bezzazi (2021) in which they investigated the effect of carbon black on the curing and mechanical properties of natural rubber/ acrylonitrile- butadiene rubber composites for shoe sole production, they found out that tensile strength increases with the addition of PWTR up to 50phr after which there is significant decrease in the strength from 70, 90 and 110phr of pyrolysed waste tyre residue (PWTR). However, formation of possible agglomerations of the filler in the matrix at higher filler loading results to the decrease in the tensile strength.

4.2.2 Tensile Modulus of natural rubber vulcanisate at 100%

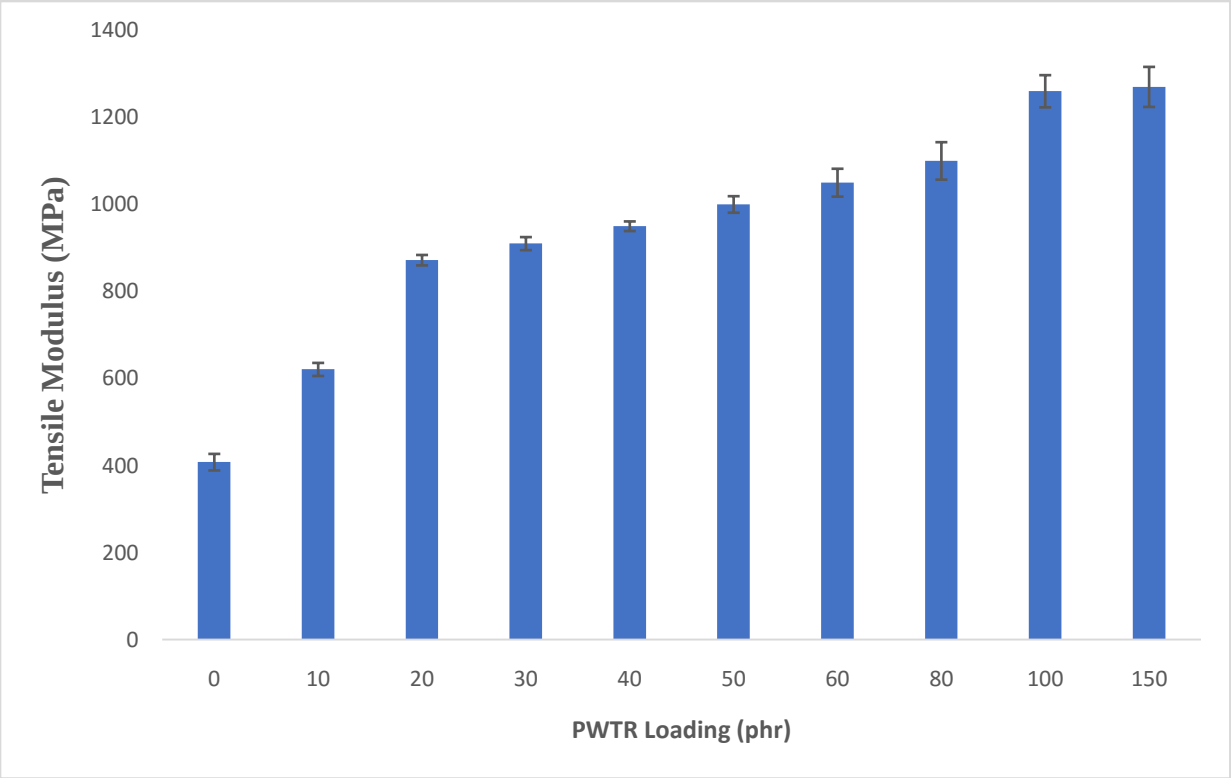


Figure 4.2:Effect of Pyrolysed Waste Tyre Residue (PWTR) Loading on the tensile modulus of natural rubber vulcanisate at 100%.

The tensile modulus results in Figure 4.2 shows increase in stiffness with increasing filler loading from 10-20phr which correspond to 621.0MPa and 872.0MPa, respectively. The result showcase almost uniform stiffness thereafter up to 80phr which correspond to 815.0MPa but an utmost uniform increase in stiffness was observed at 100-150phr corresponding to 1260 and 1270 MPa respectively. This behavior might be attributed to the presence of silicon oxide and aluminum oxide in the material. Both silicon oxide and aluminum oxide play crucial roles in enhancing the tensile modulus of pyrolysed waste tyre residue and rubber blends by improving filler-rubber interactions and overall mechanical performance. The silicon improves tensile strength and hardness due to better interaction between the silicon containing specie and siloxane (Si-O-Si)

groups in the silicone polymer. Aluminum oxide also contribute to the reinforcement of rubber compounds, the aluminum oxide in the pyrolysed waste tyre residue enhances the interfacial adhesion between the filler and rubber matrix, leading to improved mechanical properties. This allows better stress transfer and increased tensile modulus in the matrix (El-Sabbagh *et al.,* 2006).

Husnan *et al.*, (2018) explained that the presence of filler content in the rubber matrix restricts the free chain mobility associating with rubber vulcanisates, this bring about increment in crosslink density of the rubber blend and in turns caused increased in modulus and hardness. When more carbon black was incorporated into the rubber blend, the flexibility and elasticity of the rubber chain reduced which caused an increase in hardness and more rigid rubber vulcanisates. Furthermore, attributed the effect of CB loading on curing characteristics and mechanical properties of virgin acrylonitrile butadiene rubber (NBRV)/recycled acrylonitrile butadiene rubber (NBRR) blends, carbon black was used as the only reinforcing filler with different loading ranging from 30 up to 70 phr, the addition of fillers to polymeric materials leads to improve in mechanical properties of the polymer matrix.

4.2.3 Percentage Elongation at Break

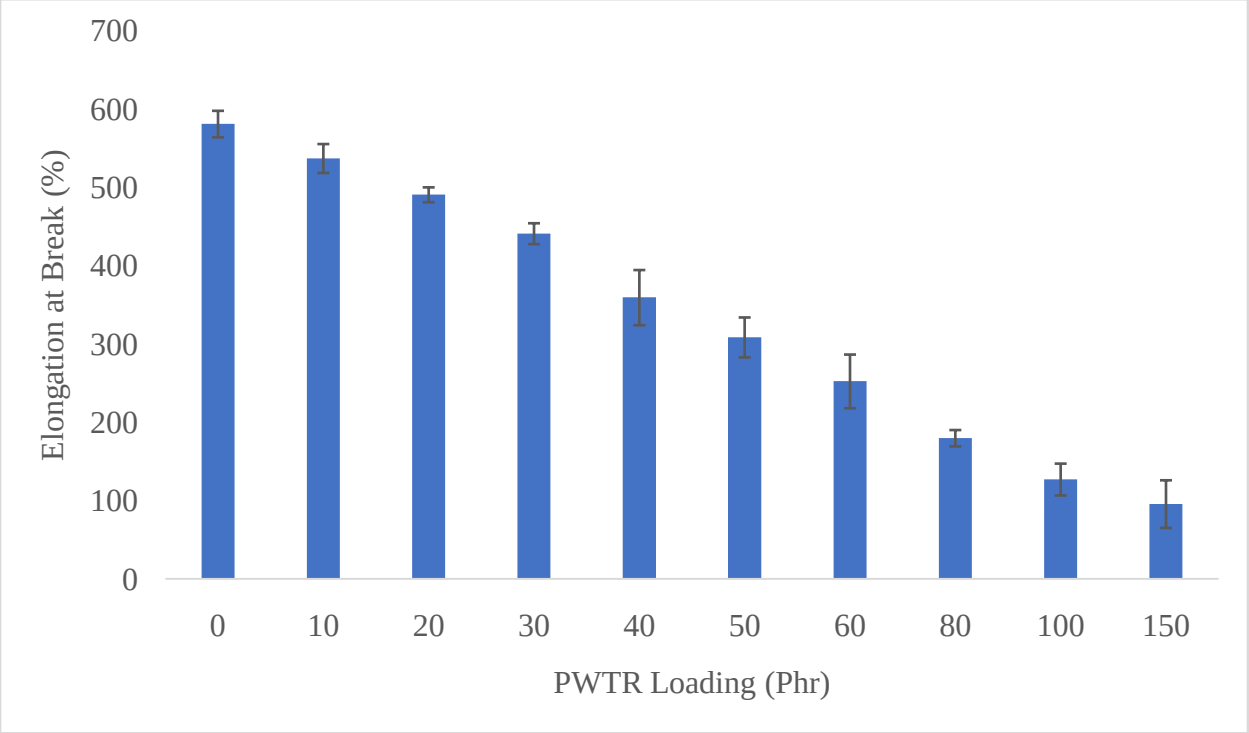


Figure 4.3:Effect of Pyrolysed Waste Tyre Residue Loading on the percentage elongation at break of natural rubber vulcanisate

From the result shown in Figure 4.3, the natural rubber vulcanisate has its maximum elongation at 10 phr correspond to 537 % apart from the control sample of filler loading of about 600%, from the result; it was observed that the percentage elongation decreased from 537% to 96%. This trend could be due to the fact that the matrix is a rubber material which has excellent elastic property but as PWTR is added to it, the elongation at break tends to decrease. This is because the PWTR particles increase the stiffness of the polymer chain and hence, limiting their ability to stretch (Sayan, 2018) (Boukfessa and Bezzazi, 2021).

The findings also correspond to the work of Alshangiti (2021) who studied a series of natural rubber/butyl rubber NR/IIR blend loaded with N660 CB and triethoxy vinyl silane treated clay

nano particles (TCNP) prepared using gamma irradiation in the presence of polyfunctional monomer, trimethylolpropane triacrylate (TMPTA).

Susanto and Marlina (2019) in their work on the effect of CB composition in styrene butadiene rubber and natural rubber blending towards its ageing and organic solvent resistance properties, attributed the decrease in elongation to stiffening effect modified by the interface between NR-SBR-CB, Silica also restrict the mobility of the rubber and rubber filler network so results in decreasing elongation at break.

4.3 Physical properties

4.3.1 Hardness

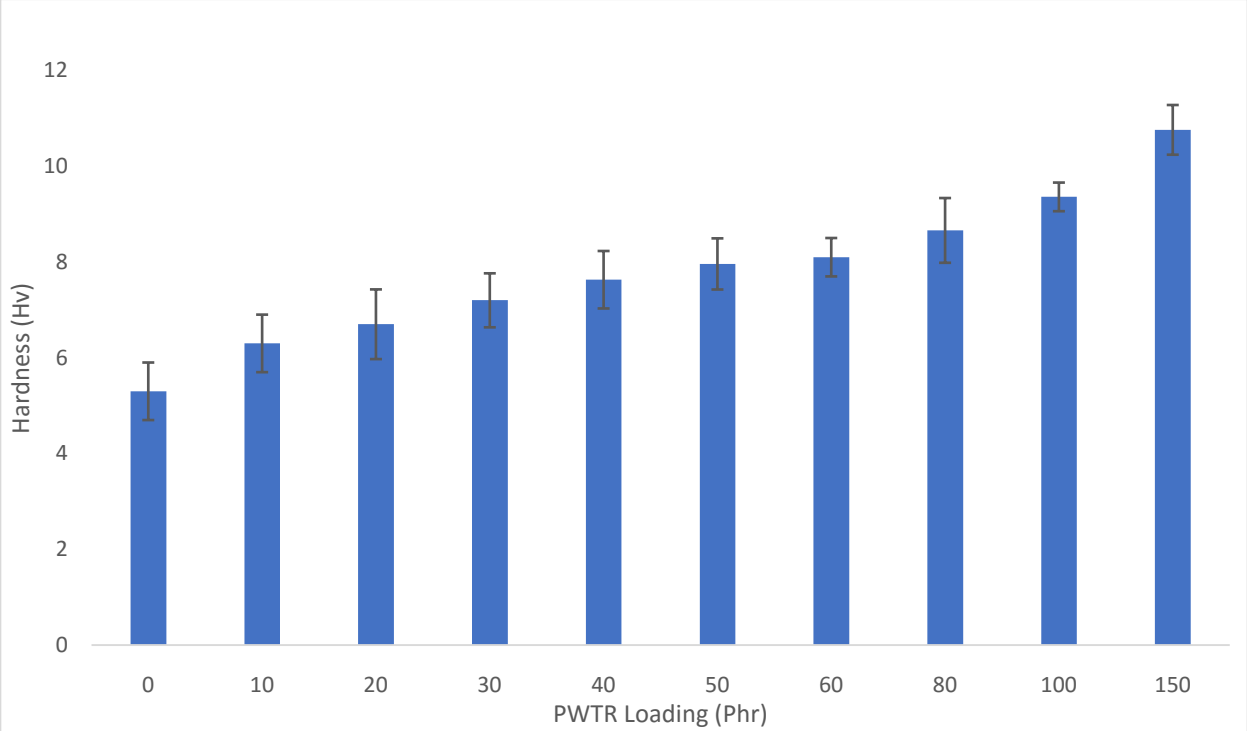


Figure 4.4:Effect of pyrolysed waste tyre residue (PWTR) Loading on the Hardness of natural rubber vulcanisate.

The result in Figure 4.4 showed a steady increase in the hardness values as the filler loading increases with 150 phr as the highest and 10 phr as the lowest corresponding to 10.8Hv and

6.1Hv. The pyrolysed waste tyre residue is widely used as reinforcing filler in rubber compounds due to its ability to enhance mechanical properties such as hardness, tensile strength and abrasion resistance. Saputra *et al.*, (2021) and Boukfessa and Bezzazi (2021) discussed the reinforcement of the pyrolysed waste tyre residue affected by the loading of the hardness in the rubber blend. Also, pyrolysed waste tyre residue particles act as stiffening agent in the rubber matrix significantly enhancing its hardness. Higher loading levels of PWTR result in a denser and more rigid network of filler particles within the rubber, thereby increasing the overall hardness of the blend.

Robertson & Hardman (2021) and Saputra *et al.*, (2021) attributed the increase in hardness to coating by carbon black on the surface or cavity of the vulcanised natural rubber and presence of silica.

4.4 Tribological Studies

4.4.1 Coefficient of friction (CF)



Figure 4.5:Effect of Pyrolysed Waste Tyre Residue (PWTR) on the Coefficient of Friction of Natural Rubber Vulcanisates**.**

Figure 4.5 presents the variation of the coefficient of friction as a function of PWTR (pyrolysed waste tyre residue) loading in phr (parts per hundred rubber). The trend suggests an initial decrease in the coefficient of friction with increasing PWTR loading up to 30 phr, followed by an increase that peaks around 50–60 phr, and then a subsequent decline at higher loadings.

This behavior can be explained by considering the effects of PWTR incorporation on the composite's surface properties and mechanical interactions. At lower PWTR loadings, the decrease in friction could be due to a lubricating effect or improved dispersion of the filler, which smoothens the contact surface. Myshkin *et al*., (2005) explained that, as the loading increases, the roughness and rigidity of the composite surface increased, leading to a higher coefficient of friction. However, beyond a critical threshold (≥80 phr), excessive filler content may result in particle agglomeration, reducing the effective contact area and, consequently, the coefficient of friction.

4.4.2 Wear Rate

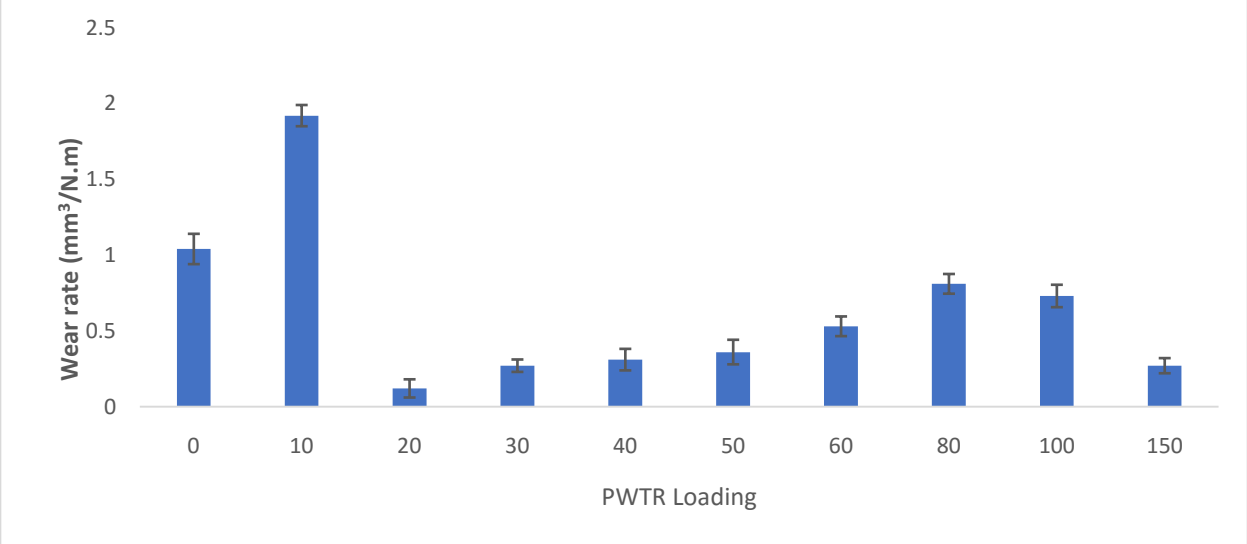


Figure 4.6:Effect of Pyrolysed Waste Tyre Residue Loading on the wear rate of natural rubber vulcanisates.

Figure 4.6 represent the wear rate test results for the produced vulcanisates. The results show a steady increase in the wear property of the vulcanisates from 20phr to 80phr which correspond to 0.12 to 0.81 mm^3/N.m filler loading before a declined trend was observed from 100phr to 150phr. The minimum wear rate of 0.12 was obtained from sample filled with 20phr CB and the maximum was obtained from sample filled 10phr CB. Literature confirmed that wear rate for shoe sole range from 1.0 and 20.0 mm^3 /Nm depending on the type and the end use of the shoes.

The finding correspond to the work of Baoukfessa and Bezzazi, (2021) which they investigated the effect of carbon black on the curing and mechanical properties of natural rubber/ acrylonitrile-butadiene rubber composites, on wear rate, they found out that When carbon black is added to rubbers blend, the loss of volume increases up to 50phr of filler. They indicated it as a good interaction between the filler and the polymer. They observed a feature decrease at 70, 90 and 110phr of carbon black. They also attributed to the agglomeration of carbon black particles due to the insufficient amount of rubber to contain the filler.

4.5 Adhesive Bonding Strength

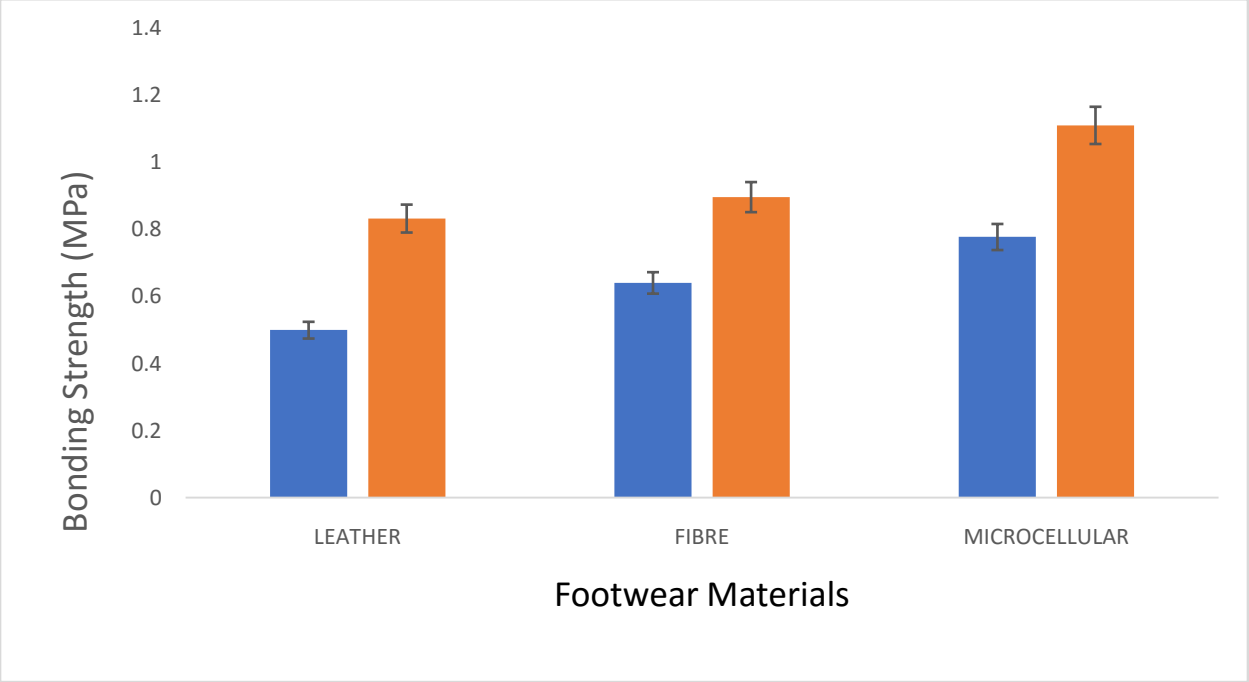


Figure 4.7:Effect of adhesive type on the bonding strength of produced sole and footwear materials.

From the findings on the use of polyurethane and neoprene adhesive on leather, neoprene perform best at 0.833MPa against polyurethane with 0.5MPa as illustrated in Figure 4.7 It was also observed that neoprene adhesive performs better on both Fibre and microcellular footwear materials bonding to the produced shoe sole as illustrated in Figure 8.This shows that neoprene adhesive is better adhesive of choice on the produced rubber shoe sole compared to polyurethane adhesive. This could be attributed to the fact that both the neoprene and the shoe sole are rubber base material that may tend to interact better than polyurethane. Neoprene adhesive outperforms polyurethane adhesive for rubber sole due to its superior bonding strength and flexibility. This is because neoprene creates a robust, water proof bond suitable for various materials including rubber and leather making it ideal for extensive shoe making and repairs.



Plate VII: Outer part of the produced Shoe soles



Plate VIII:Inner Part of the Produced Shoe Soles

CHAPTER FIVE

6.0 SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 Summary

This work studied the development of shoe sole using natural rubber blend with pyrolysed waste tyre residue. This was achieved through pH, moisture content, X-ray fluorescence (XRF) spectroscopy characterization of the pyrolysed waste tyre residue (PWTR) used as reinforcement, compounding of the PWTR with NR in various proportion ranging from 10 to 150 phr loading. The various rubber compounds produced were vulcanised and analysed for tensile strength, hardness, wear rate and coefficient of friction. The sample loaded with 20phr pyrolysed waste tyre residue (PWTR) was observed to perform better among others and was therefore adopted for production of shoe sole. Adhesive bond strength test of the produced sole to different footwear materials using neoprene and polyurethane adhesive were carried out using polyurethane and neoprene adhesive. At 20phr, the reinforced sole has the highest tensile strength of 10.69MPa and lowest wear rate of 0.12mm^2/Nm which made it suitable for rubber shoe sole formation.

5.2 Conclusion

From the findings, it has been noticed that there is an excellent interaction between pyrolysed waste tyre residue (PWTR) and natural rubber (NR) as far as composite is concerned. The result showed that the pyrolysed waste tyre residue (PWTR) obtained from pyrolysis plant is a low-grade affected by the pyrolysis activities.

The mechanical properties registered an improvement with increasing pyrolysed waste tyre residue (PWTR) loading. This indicates that pyrolysed waste tyre residue (PWTR) had a reinforcing effect in rubber matrix. The XRF test carried out confirm the composition and

presence of sulphur oxide SO_3, silicon oxide SiO_2, aluminum oxide Al_2O_3 and others. The sulphur enhances vulcanisation process, increase hardness and improved thermal and surface properties. The silicon oxide improves tensile strength and modulus by improving filler-rubber interactions. The aluminum oxide enhances the interfacial adhesion between the filler and rubber matrix.

The study indicates that 20phr sample have the best performance compared to the remaining samples (10phr, 30phr, 40phr, 50phr, 60phr, 80phr, 100phr and 150phr) in terms of mechanical performance, as such it will have more quality and durability in shoe sole production.

The sample with 20phr was observed to be the best sample in terms of tensile strength, modulus, wear rate, water absorption and hardness, followed by 30phr and then 100 and 150phr samples were observed to have the poorest performance.

Adhesive bonding test was carried out after the sole was produced. Polyurethane and neoprene adhesives were applied on leather, fibre and microcellular footwear material. From the findings on the use of polyurethane and neoprene adhesive on the leather, neoprene performed best with 0.833MPa against polyurethane with 0.5MPa, it also performed best on both fibre and microcellular footwear materials i.e. neoprene adhesive is best used on rubber shoe sole compared to polyurethane adhesive.

5.3 Recommendations

The following are recommended for further studies

i. The purification and treatment of pyrolysed waste tyre residue (PWTR) for industrial and commercial purposes be carried out to enhance its reinforcement performance in rubber matrix;

ii. Alternative rubber or plastic should be used as matrix for other suitable applications of pyrolysed waste tyre residue (PWTR) particles for conversion of waste to wealth, and

iii. Quality of the pyrolysed waste tyre residue (PWTR) should be improved via simple air oxidation to yield hollow carbon nanosphere which have applications in energy storage devices, including battery electrodes and supercapacitors.

iv. Optimization and degradation studies should be look into.

5.4 Contributions to knowledge

The study makes several key contributions to materials science and sustainable manufacturing:

1. Optimal PWTR Loading Identification
Establishes 20 parts per hundred rubber (phr) as the ideal filler loading for shoe soles, balancing tensile strength (10.696 MPa) and modulus (872.0 MPa) while minimizing agglomeration.

2. Mechanical Property Trends
Demonstrates that hardness and wear resistance increase with PWTR content, while elongation at break declines-quantifying trade-offs between durability and flexibility.

3. Filler-Rubber Interaction Mechanism
Reveals that silicon oxide (40.054%) and aluminium oxide (13.351%) in PWTR enhance interfacial bonding, improving dispersion and composite durability.

4. Tribological Behavior
Documents a non-linear relationship between PWTR loading and coefficient of friction: initial

improvement (roughness-induced grip) followed by reduction at >20 phr due to decreased contact area.

5. Adhesive Performance

Identifies neoprene as superior to polyurethane for bonding PWTR composites, with 0.833 MPa vs. 0.5 MPa bond strength-critical for manufacturing processes.

6. Waste Valorization Pathway

Validates a circular economy approach by repurposing 20 phr PWTR (from tire pyrolysis) without compromising mechanical standards, reducing reliance on virgin carbon black.

7. Agglomeration Threshold

Defines the 20 phr limit beyond which filler clustering degrades performance, providing a processing guideline for rubber composites.

REFERENCES

Alkhazraji, A. N. (2018). Enhancement of mechanical properties and handling characteristic of tyre rubber using different percentage of nano aluminum oxide and carbon black. *International Journal of Nanoelectronics and Materials,* 11(3), 263-270.

Alshangiti, D. M. (2021). The impact of a nanomixture of carbon black and clay on the mechanical properties of A series of irradiated natural rubber/ butyl rubber blend. *e-Polymers,* 21(1), 77-89.

Analytica, A. (2024). *Global automotive tyre market report, dynamics and forecast to 2032,* Chicago Illinos: Astutteanalytica inc. Retrieved from:Automotive Tire Market Size, Competitors & Forecast to 2032 (researchandmarkets.com)

Bello, K. and Aliyu, A. (2018). Data envelopment analysis of rubber smallholders: BCC and CCR models and bootstrapping techniques. *International Journal of Research- Granthaalayah,* 6, 346 -368.

Borchard, N., Ladd, B., Eschemann, S., Hegenberg, D., Moseler, M. B. and Amelung, W. (2014). Black carbon and soil properties at historical charcoal production sites in Germany. *Science of the Total Enviroment Journal, 232,* 236–242. https://doi.org/10.1016/j.scitotenv.2014.04.059

Boukfessa, H. and Bezzazi, B. (2021). The effect of carbon black on the curing and mechanical properties of natural rubber/ acrylonitrile- butadiene rubber composites. *Journal of Applied Research and Technology,* 19(3), 194-201.

Christopher, G. R. Lewis, B., Maciag, L., Buman, M. A., Miller, K., Herd, R. C.and Mars, V. W. (2020). Characterizing Distributions of Tensile Strength and Crack Precursor Size to Evaluate Filler Dispersion Effects and Reliability of Rubber. *Polymers,* 12(1),203. https://doi.org/10.3390/polym12010203

Cifriadi, A., Purwantiningsih, S., Tetty, K. and Siti, N. (2022). Influence of Sulphur Ratio to Accelerator on the Crosslink Density, Mechanical, Dynamic, and Damping Properties of Unfilled Natural Rubber Vulcanisate. *Journal of Hunan University (Natural Sciences,* 49(4), 111-143.

DuBay, S. G. and Carl, C. F. (2017). Bird Specimens Track 135 Years of Atmospheric Black Carbon and Environmental Policy. *Proceedings of the National Academy of Sciences,* 9(43), 114.

El-Maadawy, M. M. Elzoghby, A. A., Masoud, A. M., El-Deeb, M. Z., El-Naggar, M. A.A. and Taha, H. M. (2024). Conversion of carbon black recovered from waste tyre into activated carbon via chemical/microwave Methods for efficient removal of heavy metal ions from wastewater. *Royal Society of Chemistry,* 14(9), 6324-6338.doi: 10.1039/d4ra00172a

El-Sabbagh, S. H., Nivin, M. A. and Mohamed, S. M. (2006). Preparation and characterisation of high performance rubber vulcanisates loaded with modified aluminium oxide. *Pigment and Resin Technology*, 35, 119-131.

Francesco, V. and Alessandro, P. (2022). End-of-life options of tyres. A review. *Advanced Industrial and Engineering Polymer Research Journal*, 5(2), 203-213.

Ginting, E., Bukit, N., Muliani, B. and Frida, E. (2017). Mechanical properties and morphology of natural rubber blend with bentonite and carbon black. Mechanical properties and morphology,*IOP Conference Series: Materials Science and Engineering*, 223, 012003.

Gonzalez-Gonzalez, R. B. Gonzalez, L.T., Iglesias-Gonzalez, S., Gonzalez-Gonzalez, E., Martinez-Chapa, O. S., Madou, M., Alverez, M. and Mendoza, A. (2020). Characterization of Chemically Activated Pyrolytic Carbon Black Derived from Waste Tyres as a Candidate for Nanomaterial Precursor. *Nanomaterials*, *10*(11), 2213. https://doi.org/10.3390/nano10112213

Han, D., Chen, Y., Pan, Y., Wang, C., & Zhang, D. (2022). Research on Friction and Wear Properties of Rubber Composites by Adding Glass Fiber during Mixing. *Polymers*, *14*(14), 2849. https://doi.org/10.3390/polym14142849

Hen, W., H., Deshang and Hongbo, C. (2023). Pyrolysis of Waste Tires. A Review. *Polymers*, *15*(7), 1604. https://doi.org/10.3390/polym15071604

Hita, I., Arabiourrutia, M., Olazar, M., Bilbao, J., Arandes, J. M., & Castaño Sánchez, P. (2016). Opportunities and barriers for producing high quality fuels from the pyrolysis of scrap tires. *Renewable and Sustainable Energy Reviews*, *56*, 745-759. https://doi.org/10.1016/j.rser.2015.11.081

Husnan, M. A., Ismail, H. and Shuib, R. K. (2018). The effect of carbon black (CB) loading on curing characteristics and mechanical properties of virgin acrylonitrile butadiene rubber (Nbrv)/recycled acrylonitrile butadiene rubber (Nbrr) blends. *IOP Conference Series: Materials Science and Engineering*, 309: 012028. doi:10.1088/1757-899X/309/1/012028

Ishaiku, U. S., Yang, X.Y. and Leong,Y. W. (2007). Effect of fibre contents and alkali treatment on the mechanical and porphological properties of poly(lactic acid)/ poly(caprolactone) blend jute fibre-filled biodgradble composit. *Journal of Materials and Bioenergy*, 1, 78-86.

Jebur, S. K. (2018). Carbon black production, analyzing and characterization. Master's thesis,Missouri University of Science and Technology. Available at: https://scholarsmine.mst.edu/masters_theses/7869/

Jessica, H. G., Smith, M.B. A., Sciarratta, M. L., Sytdam, S., Shim, K. J. and Miller, H. R. (2020). Standardized lab shoes do not decrease loarding rate variability in recreational runners. *Journal of Applied Biomechanics*, 36 (5), 340-344.

John, V. (2001). Fixing Your Feet : Prevention and Treatments for Athletes. 2nd ed. Footwork Publications. Retrieved from:https://search.worldcat.org/en/title/237106025

Karak, N. (2009).*Fundamentals of Polymers: Raw Materials to Finish Products.* PHI Learning Pvt. Limited, New Delhi.

Mahmoud, M. M. (2016). Friction coefficient of recycled rubber soles. *Journal of the Egyptian Society of Tribology,* 13(4), 1-12.

Manaila, E., Craciun, G. and Ighigeanu, D. (2020). Water Absorption Kinetics in Natural Rubber Composites Reinforced with Natural Fibers Processed by Electron Beam Irradiation. MDPI *Polymers*, *12*(11), 2437. https://doi.org/10.3390/polym12112437

Matador, R., (2007). *Rubber Chemistry*. Matador Rubber s.r.o. publication of Tyre producing company, Púchov, Slovakia. Retrieved from:https://www.studocu.com/row/u/66614023?sid=01744063125

Miller, D. J. (2024).Natural Rubber: Structure and Function – Beyond the Cis-1,4 Structure – Some Reasons Why Synthetic Rubber May Never Replace Natural Rubber. Halcyon AgriCorporation limited, Raffle City Tower, Singapore, 2017 Annual report. Retrieved from: Natural Rubber: Structure and Function - Halcyon | The world's leading rubber franchise (halcyonagri.com)

Myshkin, N. K., Petrokovets, M. I. and Kovalev, A. V. (2005). Tribology of polymers: Adhesion, friction, wear, and mass-transfer. *Tribology International Journal,* 38(11), 910-921.

Nenrit, L. S., Ibrahim, U. I. and Umar, U., (2013). Production of shoe sole using natural rubber reinforced with rubber crumb. *HND final year project. Department of polymer Science at Nigerian Institute of Leather and ScienceTechnology, Zaria,Nigeria.*

Okoye, C. O., Zhang, Z. and Dongke, Z. (2024). Carbon black preparation by partial oxidation of spent tyre pyrolysis oil – Influence of temperature, residence time and oxygen to feed ratio. *Waste Management Journal*,174, 273-281. https://doi.org/10.1016/j.wasman.2023.11.040

Puskas, J. E., Cornish, K., Kenzhe-Karim, B., Mutalkhanov, M., Kaszas, G. and Molnar, K. (2024). Natural rubber - Increasing diversity of an irreplaceable renewable resource. *Heliyon*, *10*(3), e25123. https://doi.org/10.1016/j.heliyon.2024.e25123

Pyshyev, S. veses, J.D., Martinez, A., Sanchis, J.M. and Lopez. T. (2024). Study on the composition of gasoline fractions obtained as a result of waste tyres pyrolysis and production bitumen modifiers from it. *Journal of The Energy Institute,* 4 (2), 10-45.

Rikmann, E., Maeorg, U. and Liiv, J. (2024). Recycling of Low-Quality Carbon Black Produced by Tyre Pyrolysis. *Applied Science Journal*, *14*(5), 2192. https://doi.org/10.3390/app14052192

Robertson, C. and Hardman, N. J. (2021). Nature of Carbon Black Reinforcement of Rubber: Perspective on the Original Polymer Nanocomposite. *Polymers,* 13(4), 538-596. doi: 10.3390/polym13040538

Saputra, A. H., Sari, T. I., Maspanger, D. R. and Bismo, S. (2021). Loading Silica for Supporting Carbon Black Filler to Prevent Degradation Natural Rubber Caused DME. *MATEC Web of Conference,* 333, 13001 https://doi.org/10.1051/matecconf/202133313001

Satta, S., Charoenyutr, D. and Surap, M. (2020). Optimization of the Rubber Formulation for Footwear Applications from the Response Surface Method. *Polymer,* 12(9), 2032. doi: 10.3390/polym12092032

Sayan, B. (2018). A Comparative Study between the Physical properties of Natural Rubber/Carbon Black blend and Natural Rubber/non Carbon Black blend. *International Journal for Research in Engineering Application & Management (IJREAM),* 04(02), 34-58.

Sotter, G., Steven, S. and Michael, J. M. (2005). Analysis of floor-shoe static friction needed to control a wheelchair, gurney, or pallet jack on a ramp manually, International Society for Occupational Ergonomics and Safety (ISOES) manucript. Reyrieved from:Microsoft Word - ISOES manuscript 3/18/05 (safetydirectamerica.com)

Staf, M., Bela, O. and Vit, S. (2022). Activation of solid residues from batch pyrolysis of waste tyre. *International Journal of Rubber Chemistry,* (14), 105-116.

Susanto, T. and Marlina, P. (2019). The Effect of Carbon Black Composition In Styrene Butadiene Rubber And Natural Rubber Blending Towards Its Ageing And Organic Solvent Resistance Properties. *Jurnal Dinamika Penelitian Industri,* 30(2), 93-100.

Tenebe, O. G., Ayo, M. D., Ichetaonye, S. I., Igbonazobi, L. C. and Eguare, K. O. (2013). Effect of Filler Loading on the Mechanical Properties of Natural Rubber Filled with Guinea Corn Husk *(Holcus sorghum), International Journal of Life Sciences,* 2(4), 156-161.

Torretta, V., Rada, C. E., Ragazzi, M., Trulli, E., Istrate, A. I. and Cioca, I. L (2015). Treatment and disposal of tyres: Two EU approaches. A review, *Waste Management (New York)*, 45, 152-160.https://doi.org/10.1016/j.wasman.2015.04.018

Wang, X., Wu, L., Yu, H., Xiao, T., Li, H. and Yang, J. (2021). Analysis of Effect of Modification of Silica and Carbon Black Co-filled Rubber Composite on Mechanical Properties. *e-Polymers,* 21(1), 279-288. https://doi.org/10.1515/epoly-2021-0034

Yasir, H. A., Al Maamori, M. H., and Ali, H. M. (2015). Effect of carbon black types on curing behaviour of natural rubber. *European Journal of Advances in Engineering and Technology, 2*(5), 77–80.

APPENDICES

APPENDIX A

Table 1: X-ray fluorescence (XRF)

Sample List: Standard Method EDXRF Analyzer :Ahmad **Analyzed:** Wed Jan. 04 12:14:18 2023

Analysis Technique: Linear
Method File: C:\...\XXXX\@Geological Calibration Oxide in air updated.mth

Last Calibrated: Wed Jan 04 11:51:38 2022
Software version: 10.3.0.159

Comments:

Conditions

Mid Zb

Voltage	20 kV	Current	Auto
Livetime	60 seconds	Counts Limit	0
Filter	Pd Medium	Atmosphere	Air
Maximum Energy	40 keV	Count Rate	Medium
Warmup time	0 seconds		

Low Za

Voltage	4 kV	Current	Auto
Livetime	60 seconds	Counts Limit	0
Filter	No Filter	Atmosphere	Air
Maximum Energy	40 keV	Count Rate	Medium
Warmup time	0 seconds		

Low Zc

Voltage	12 kV	Current	Auto
Livetime	60 seconds	Counts Limit	0
Filter	Al	Atmosphere	Air
Maximum Energy	40 keV	Count Rate	Medium
Warmup time	0 seconds		

High Za

Voltage	40 kV	Current	Auto
Livetime	60 seconds	Counts Limit	0
Filter	Cu Thin	Atmosphere	Air
Maximum Energy	40 keV	Count Rate	Medium
Warmup time	0 seconds		

High Zb

Voltage	50 kV	Current	Auto
Livetime	100 seconds	Counts Limit	0
Filter	Cu Thick	Atmosphere	Air
Maximum Energy	40 keV	Count Rate	Medium
Warmup time	0 seconds		

Results

Element	Concentration	Peak(cps/mA)
EDXRF Analyzer AHMAD - IBRAHIM HUNKUYI		
Fe2O3	7.1753 %	26323
SiO2	40.054 %	3116
Al2O3	13.351 %	201
MgO	1.74 %	3
P2O5	0.2533 %	60

SO3	0.1802 %	204
TiO2	0.8216 %	3201
MnO	0.1526 %	691
CaO	1.4248 %	2462
K2O	1.3224 %	1400
CuO	0.00259 %	18
ZnO	0.2154 %	104
Cr2O3	0.01159 %	73
V2O5	0.0120 %	102
As2O3	[0.0029] %	0
PbO	0.0633 %	0
Rb2O	0.00381 %	18
Ga2O3	0.00227 %	37
NiO	0.00378 %	18
Cl	0.1629 %	89
ZrO2	0.1502 %	337
Ta2O5	0 %	0
WO3	0.01705 %	39
Br	0.00058 %	2
ThO2	0 %	0
Y2O3	0.00271 %	10
I	0.000679 %	7
Ag2O	[0.00031] %	1
Bi2O3	0.02533 %	1
Cs2O	0 .00042%	0
Sb2O3	[0.028] %	2
CdO	0 %	1
Lu2O3	[0.000013] %	2
Co3O4	0 %	0
SnO2	1.242 %	7

APPENDIX B

Table 2: Tensile Strength, Elongation and Modulus of NR and CB blend.

Sample	Tensile Strength (MPa)	Elongation (%)	Strain	Tensile Modulus (MPa)
0	5.935	581.043	1452.584	408.00
10	8.332	537.096	1342.7403	621.00
20	10.696	490.768	1226.920	872.00
30	7.654	441.095	1103.232	910.00
40	6.737	359.470	898.593	950.00
50	5.594	308.648	771.599	1000.0
60	4.738	252.484	631.210	1050.0
80	3.666	179.957	449.892	1100.0
100	3.265	127.206	318.016	1260.0
150	3.038	95.813	239.534	1270.0

Table 3: Bond Strength of Polyurethane Adhesive of Natural Rubber

S/N	Material	Load (MPa)	Thickness (mm)	Area (mm^2)	Bond Strength (MPa)
1	LEATHER	1.50	1mm	3.0	0.500
2	FIBER	2.50	1.3mm	3.9	0.641
3	MICROCELLULAR	3.50	1.5mm	4.5	0.778

Length of Test Specimen = 50 mm

Width of Test Specimen = 3 mm

APPENDIX C: Neoprene adhesive bonding test results

Table 4:Bond Strength of Neoprene Adhesive of Natural Rubber

S/N	Material	Load (MPa)	Thickness (mm)	Area (mm^2)	Bond Strength (MPa)
	LEATHER	2.50	1mm	3.0	0.833
1					
2	FIBER	3.50	1.3mm	3.9	0.897
3	MICROCELLULAR	5.0	1.5mm	4.5	1.111

Length of Test Specimen = 50 mm

Width of Test Specimen = 3 mm

Table 5: Coefficient of Fraction and Wear Rate

Sample	Coefficient of Friction	Wear rate(m^3/Nm)
0	1.002	1.04
10	0.897	1.92
20	0.872	0.12
30	0.883	0.27
40	0.978	0.31
50	1.05	0.36
60	1.026	0.53
80	0.884	0.81
100	0.904	0.73
150	0.701	0.27

APPENDIX D

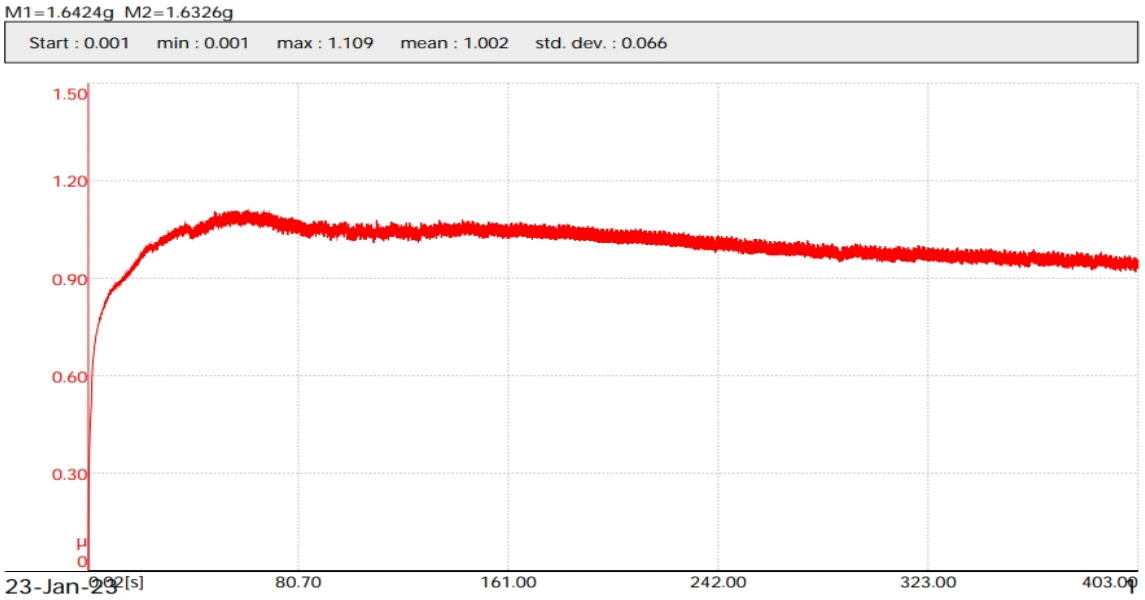


Figure 1:Effect of PWTR on the coefficient of friction and wear rate of natural rubber at 0phr loading.

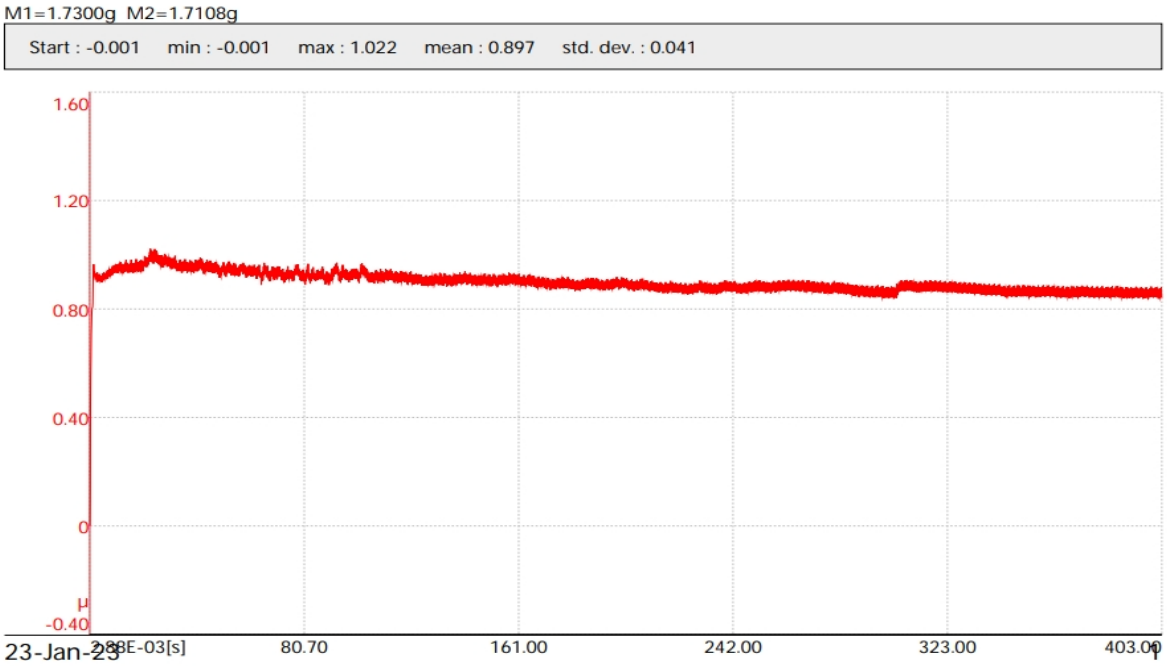


Figure 2: Effect of PWTR on the coefficient of friction and wear rate of natural rubber at10phr loading.

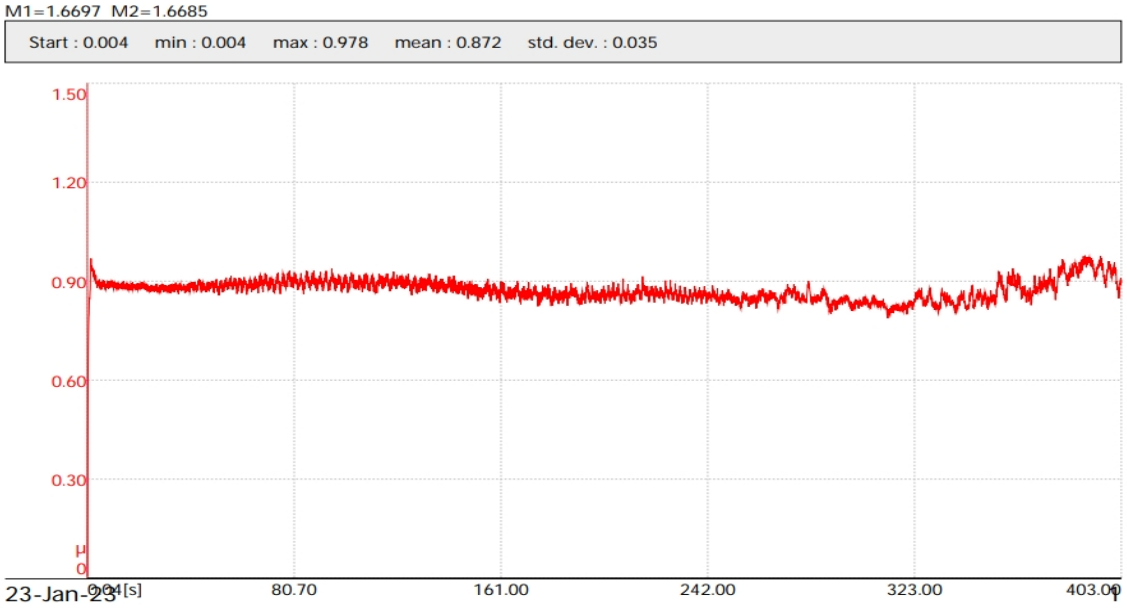


Figure 3:Effect of PWTR on the coefficient of friction and wear rate of natural rubber at 20phr loading.

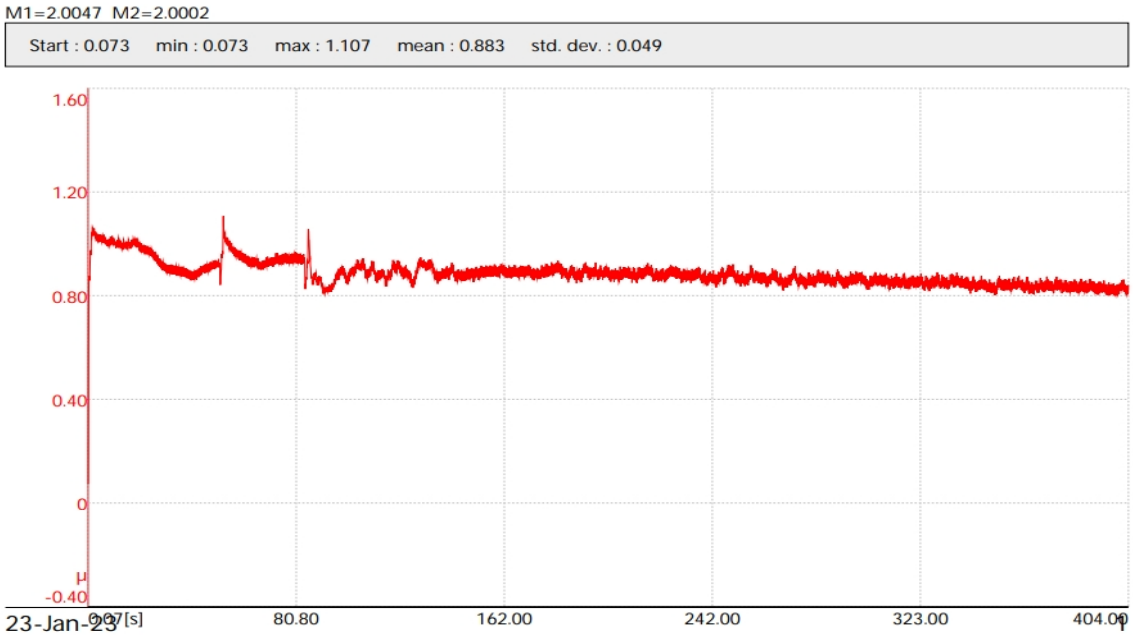


Figure 4:Effect of PWTR on the coefficient of friction and wear rate of natural rubber at 30phr loading

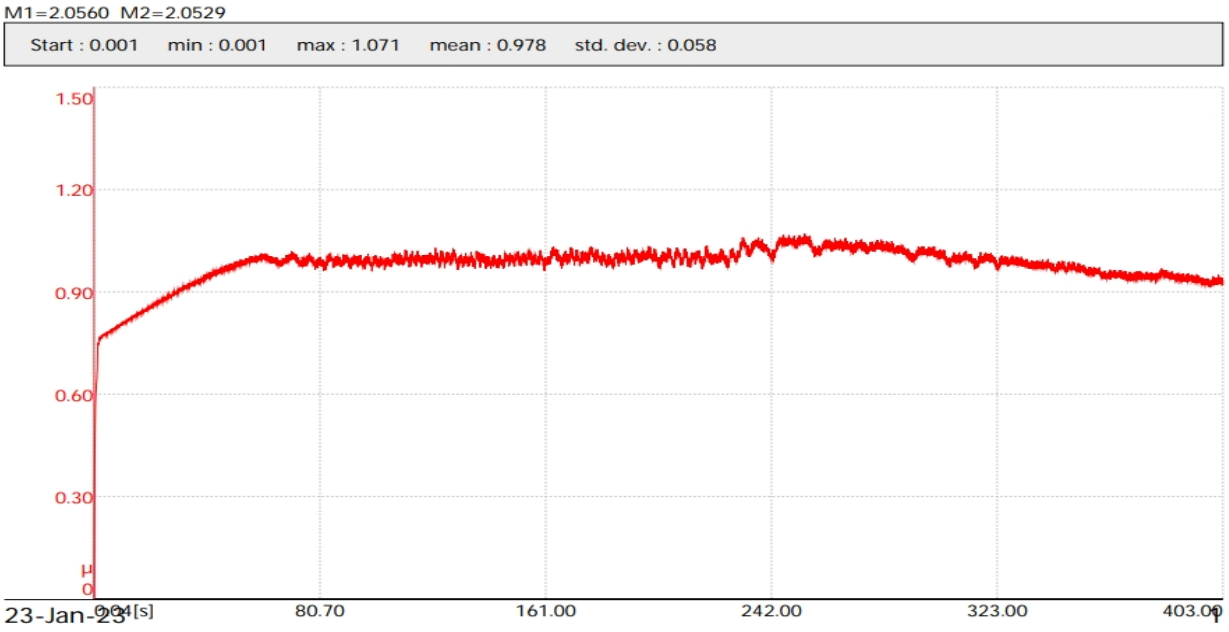


Figure 5:Effect of PWTR on the coefficient of friction and wear rate of natural rubber at 40phr loading.

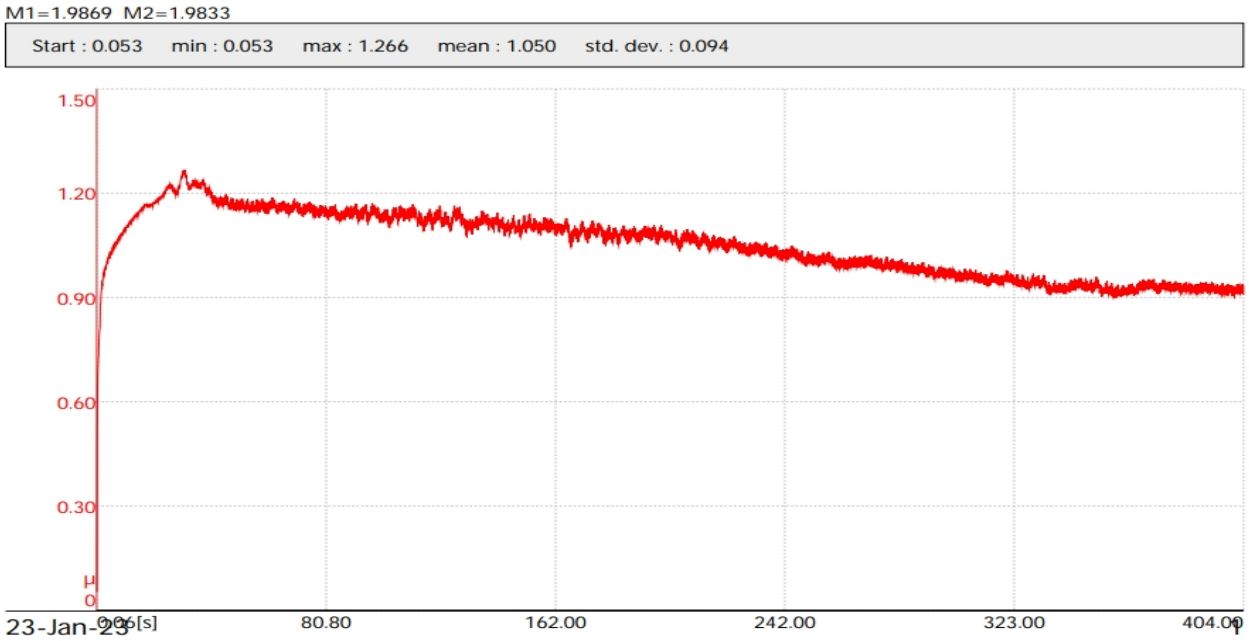


Figure 6:Effect of PWTR on the coefficient of friction and wear rate of natural rubber at 50phr loading.

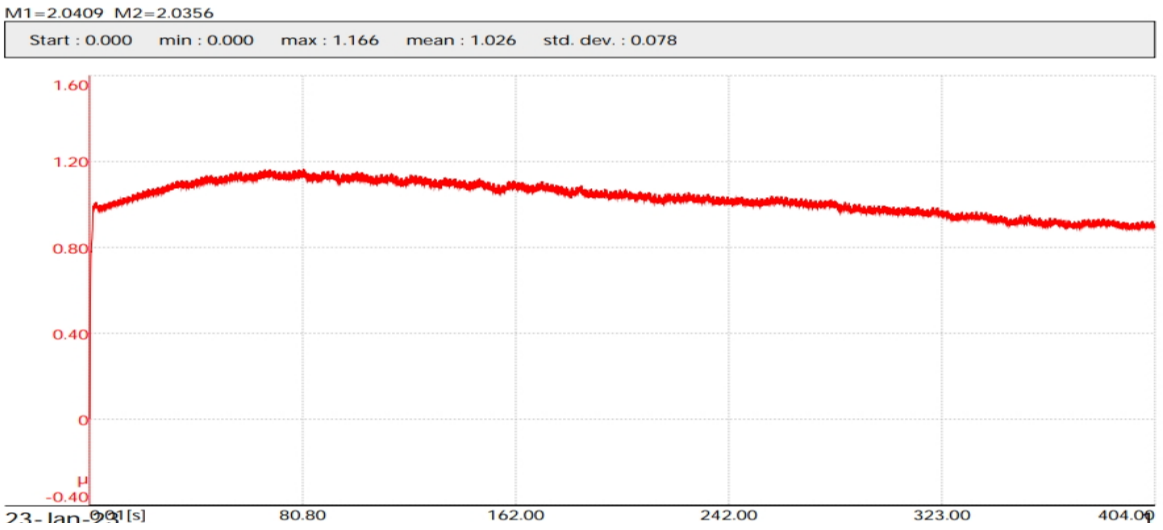


Figure 7:Effect of PWTR on the coefficient of friction and wear rate of natural rubber at 60phr loading.

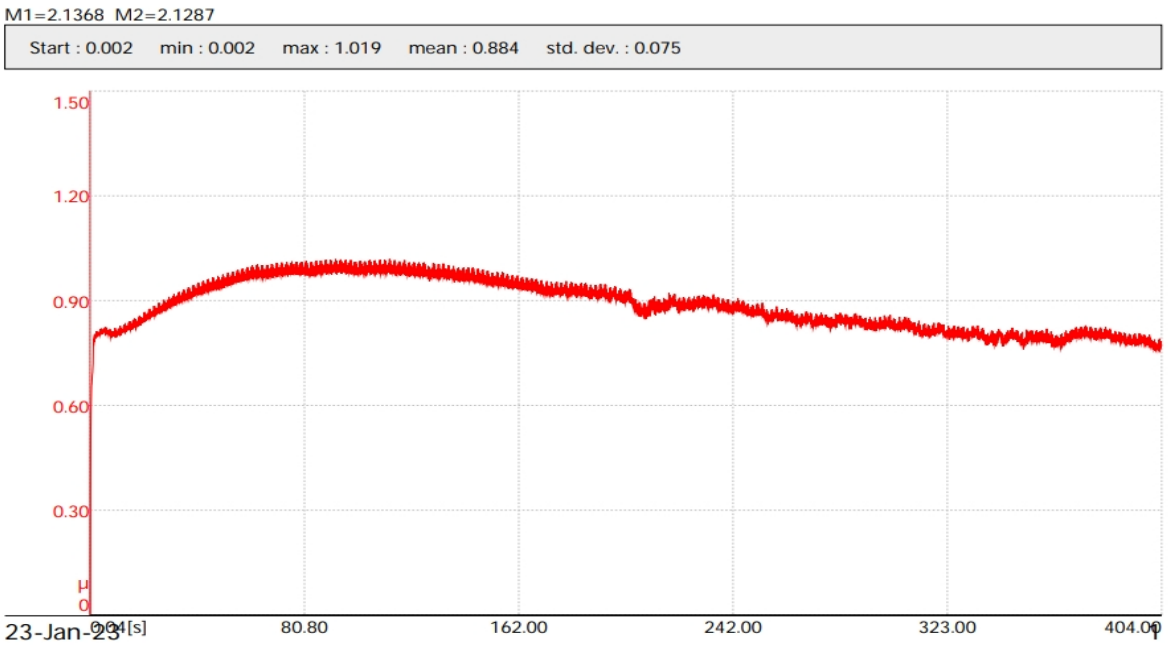


Figure 8: Effect of PWTR on the coefficient of friction and wear rate of natural rubber at 80phr loading.

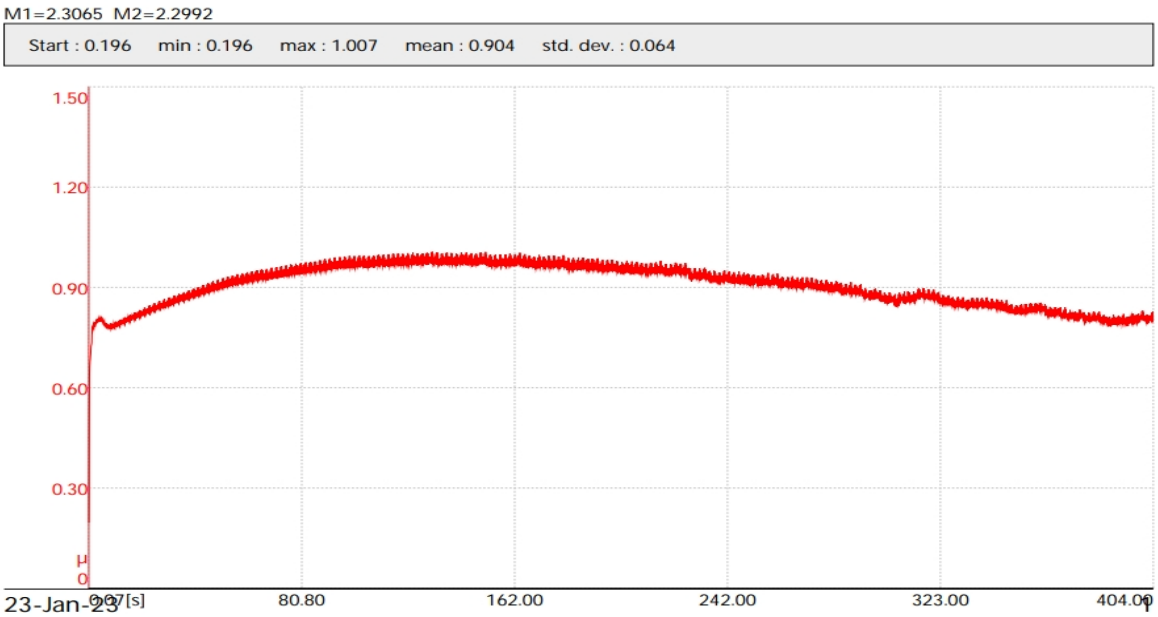


Figure 9: Effect of PWTR on the coefficient of friction and wear rate of natural rubber at 100phr loading.

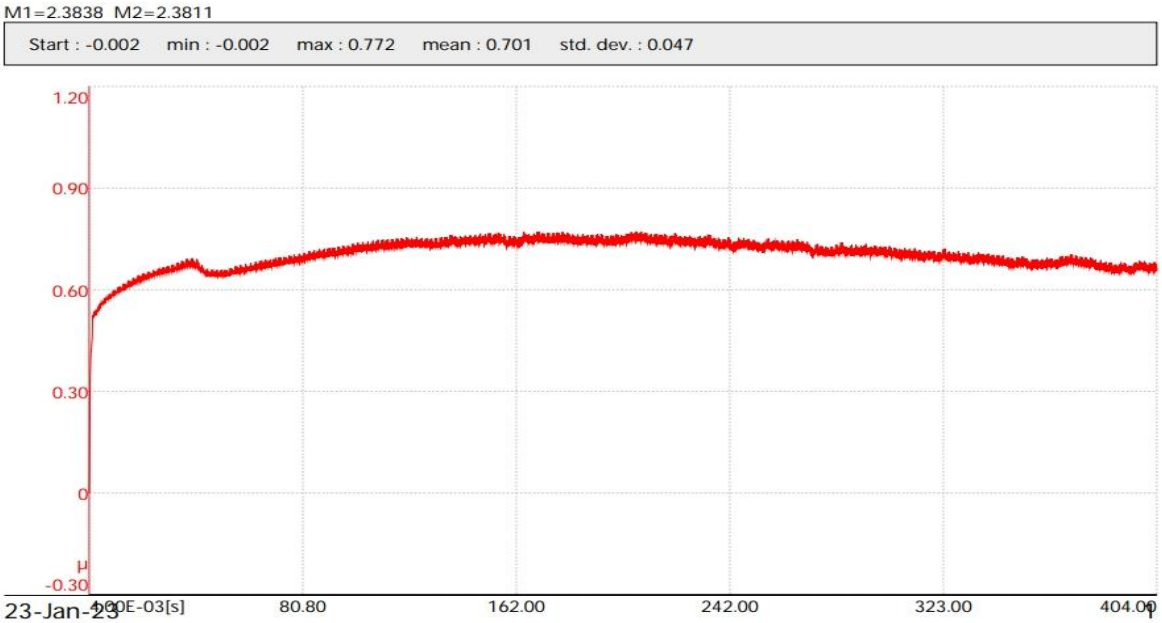


Figure 10:Effect of PWTR on the coefficient of friction and wear rate of natural rubber at 150phr loading.