PHYSICO-MECHANICAL PROPERTIES OF NATURAL RUBBER FILLED WITH CARBONIZED CHERRYAND RUBBER SEED SHELLS

BY

CORDELIA ONEGBEDAN (B.Eng.)
REG. NO: 20104845408

A THESIS SUBMITTED TO THE POSTGRADUATE SCHOOL FEDERAL UNIVERSITY OF TECHNOLOGY, OWERRI, IMO STATE

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF SCIENCE (M.Sc.) IN POLYMER SCIENCE AND ENGINEERING

APRIL 2016

CERTIFICATION

I hereby certify that this project work titled; Physico-mechanical Properties of Natural Rubber Filled with Carbonized Cherry and Rubber Seed Shells was written and submitted by ONEGBEDAN, CORDELIA (20104845408), in partial fulfillment of the requirements for the award of Degree of Master of Science (M.Sc.) in Polymer Science and Engineering in the Department of Polymer and Textile Engineering, Federal University of Technology, Owerri, Imo State.

.....
Engr. Prof. UC. Madufor
(Supervisor)

20/7/16
.....
Date

.....
Engr. Dr. M.U. Obidiegwu
(Head of Department)

20/07/16
.....
Date

.....
Engr. Prof. G.I. Nwandikom
(Dean, SEET)

.....
Date

.....
Prof. Mrs. N.N .Oti
(Dean, Postgraduate School)

.....
Date

.....
Prof . S.H.O. Egboh
(External Examiner)

20/07/16
.....
Date

DEDICATION

This thesis work is dedicated to my Husband Engr. Oseghale, Francis and my Children.

ACKNOWLEDGEMENT

This research work wouldn't have been possible without the conscientious supervision and understanding of my supervisor Engr. Dr. 1. C. Madufor. Special thanks go to my Postgraduate Lecturers; Prof 0. Ogbobe, Prof. A. E. Iheonye, Prof. C. B. C. Ohanuzue, Prof. I. 0. lgwe and Dr. G. N. Onyeagoro for the priceless knowledge given to me.

Thanks go to my lovely husband Engr. Oseghale, Francis and the entire family for their care, financial, material and spiritual support which had been a source of inspiration to me. I am indebted to my Mother, Mrs. E. N. Obiekea for her advice and encouragement when the need arises.

Appreciations go to my colleagues in the postgraduate studies, Engr. O. T. Tenebe and other for their encouragement, care and concern showii towards the realization of this research work. Appreciations go to the management and staff of Rubber Research Institute, Iyanomoh, Benin City and the Department of Polymer Technology, Auchi Polytechnic, Auchi for giving me the privilege to explore their research facilities. Above all, God Almighty, Jehovah El-shadai for making this research work and my study a possibility.

TABLE OF CONTENTS

CHAPTER THREE: MATERIALS AND METHODS

CHAPTER FOUR: RESULTS AND DISCUSSION

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

CV: Constant Viscosity

SMR: Standard Malaysia Rubber

RSS: Rubber seed shell

CSS: Cherry Seed Shell

CCSS: Carbonized Cherry Seed Shell

SAR: Standard Africa Rubber

NRS: Nigeria Standard Rubber

PRI: Plasticity Retention Index

SMRV: Standard Malaysia Rubber Viscosity

ASTM: American Standard for Testing Machines

GPR: General Purpose Rubber

LV: Low Viscosity

TMQ: Trimfd, Mlethylquinoline

TMTD: Tetramethyl thiuram disulphide

BDH: British Drug House

MBT: 2-Mercaptobenzothiazole

CBS: N-Cyclohexylbenzole

MBTS: Mercaptobenzothiazole sulphenamide

MRPRA: Malaysia Rubber Producers Research Association

CCI4: Carbon Tetrachioride

IRHD: International Rubber Hardness Degrees

PPD: Paraphenyldiamine

TG: Glass Transition Temperature

EVS: Efficient Visosity System

S_X: Polysulphide Cross-links

NR: Natural Rubber

SIR: Standard Indonesia Rubber

P_c: Density Composite

P_c: Density of the Matrix

P_c: Density of the fibre

V_m: Volume fractions of the Matrix

V_f: Volume fractions of the fibre

ABSTRACT

Physico-mechanical properties natural rubber filled with carbonized cherry and rubber seed shell as fillers were studied. Samples of cherry and rubber seed shells were carbonized at varying temperatures (100, 200, 300, 400, 500, 600 and 700^{o}C for three hours each and sieved through a 100μm mesh. The physical properties of fillers such as the swelling behavior, loss on ignition, iodine absorption number, moisture content, the pH and the bulk density results evaluated show that pH, iodine adsorption number and loss on ignition increase with carbonization temperature, moisture content decreases while bulk density varies with increase in carbonization temperature. The percentage swelling behaviour results show that carbonized cherry seed shell filled vulcanizates are more resistant to solvents used than carbonized rubber seed shell filled vulcanizates, The mechanical properties of the vulcanizate which include enlongation at break, compression set and flex fatigue decreases with increase in filler carbonization temperature. some mechanical properties Such as tensile strength, mochulus, Hardness and abrasion resistance increase with increase in filler carbonization temperature. The mesh size of 100μm were used as to obtain a fine particles size. Any mesh size above 100μm will be lesser. Thus for high quality vulcanizates carbonization should be done at 600^{o}C.

Key words: Carbonization, Vulcanizate, Cherry, Rubber, Characterization.

CHAPTER ONE

INTRODUCTION

1.1 Background Information

Fillers as one of the major additives used in natural rubber compounds are either used raw or modified. These fillers function to modify the physical and to some extent, the chemical properties of the vulcanizates. The search for means and methods of improving the properties and processing of rubber products dates back to over a century ago. One way of achieving these extensions of service life of these rubber products is the incorporation of additives into the polymer matrix. The use of agricultural by-products as fillers for renewable polymer additives tried by several authors is drastically taken its position in the polymer industry (Kalia et al, 2009). Many people have tried to use various agricultural by-products as fillers in compounding. These fillers are either used raw or modified agro-base resources that contain celluloses and lignin. Lignocelluloses include wood, agricultural residues, water plants, grasses and other plant substances. In recent years, the interest in using natural fibres in bio- composites have grown because they are light weight, combustible, non-toxic, low cost and easy to recycle (Jorts et al, 2005). Emergence of polymer in the beginning of the 19^{th} century ushered a new ear of research with a new option of using the natural fibers in more diversified fields. This renewed in interest in the natural fibers has resulted in a large number of modifications to bring it a far and even superior to synthetic fillers. Because of such tremendous changes in the quality of natural

fibers, they are fast emerging as a reinforcing material in composites (Laka and chernyavskay S. 2007).

1.2 Problem Statement

In recent years, the interest in using natural fibers in bio- composites has grown because they are light weight, combustible, non-toxic, low cost and easy to recycle. On the other hand, lack of good interfacial adhesion and poor resistance to moisture absorption make the use of natural fibres reinforced composite less attractive, as a result of the fact that cellulosic fibre are hygroscopic in natural. Moisture absorption can result in the swelling of the fibres which may lead to micro-cracking of the composite and degradation of mechanical properties (Kamel, 2007). Carbonization of the fibre can stop the moisture absorption process, clean the fibres surface and modify the surface or increase the surface roughness, by decreasing the hydroxyl groups which may be involved in the hydrogen bonding within the cellulose molecules (Ray et al, 1989).

1.3 Objective of the Study

The main objective of the study is to evaluate the physico-mechanical properties of natural rubber filled with carbonized cherry rubber seed shells

The specific objectives of the study are to:

i. Characterize the effect of carbonization temperature on the filler.

ii. Compound and investigate the mechanical properties of the rubber vulcanizates.

iii. Determine the swelling behavior of the rubber vulcanizates in Carbon tetrachloride CCL_4, xylene and cyclohexane solvents

iv. Compare the reinforcing potentials of the fillers.

1.4 Justification of the Study

The success of this research work will help to reduce the price of rubber products adequately curb the menace posed by waste generated from agricultural by-product and solve the problem of inadequate waste disposal. It will also provide income to farmers since they will be involved in the search of these agricultural by-products for rubber products.

The use of agricultural by-product as fillers will help to cheapen the price of rubber products, improve the quality of the rubber products and could as well lead to ban on importation of fillers and could even lead to exportation thereby improving balance of trade.

1.5 Scope of the Study

This research work is limited to production of natural rubber composite material using carbonized cherry and rubber seed shells and evaluating the physico-mechanical properties of natural rubber filled with carbonized cherry and rubber seed shells; characterizing the effect of carbonization temperature on the filler; investigating the mechanical properties of the rubber vulcanizates; determining swelling behaviour of the vulcanizates and comparing the reinforcing potentials of the fillers.

CHAPTER TWO

LITERATURE REVIEW

2.1 History of Fillers

The use of filler in rubber is almost as old as the use of rubber itself. As soon as rubber mixing machinery was developing, filler such as ground whiting, barites or clay were added to cheapen the product to achieve low cost or high volume rubber product. Zinc oxide, originally used for whiteness was the first "active" filler. The concept of reinforcing relates basically to textile enhancement. Reinforcing has been defined as the incorporation into rubber of small particle. Substances gives to the vulcanizations high abrasion resistance, high tear and tensile strength and some increases in stiffness (Rowel, 1990). In general, when a reinforcing agent is added to a base pure gum recipe, that agent imparts greater stiffness and higher ultimate tensile strength that would be obtained by using an equal volume of a recognized filler e.g. co-course particle size whiting. The most characteristics require of reinforcement is small particle size, associated with this toughening of the rubber and also a decrease in solubility of the compound in solvent (Scandola et al, 2000). In the production of raw polymer in a convenient commercial form which may be subjected to elected temperature during fabrication with mechanical stress and thermal oxidation. Obviously this polymer may be exposed to high load, mixture, and ozone and atmosphere pollutant. With this introduction of filler, the high load resistance and creep of most polymers is enhanced. Also, external work has been done on the

use of filler in cost reduction and comparing the tensile properties (Chum and Parker 1985).

In 1939, the first reinforcing silicon filler was introduced. The development over the next 10 years, led to the emergence of two types of percolated silica containing about 85-90% (SiO_2) with ignition losses of 10-14%, the phylogenic silica which contain 99.8% silica. Because its much higher price, it is mainly fused as filler for high cost compound such as silicon rubber (Allcock and Lampe 1990).

In 1947, lignin, a bye product firm paper manufacture, was introduced as reinforcing filler. This material has to be added to natural or synthetic rubber in the form of aqueous solution to observe the reinforcing effect in the form of aqueous solution to observe the reinforcing effect in the dried and vulcanized final product. Leo Beckland's in 1907 produced the first phenolic molded product which contained wood flour as for thermosetting resins. Also, Emile Hemming used asbestos slate, limestone and diatomaceous earth as filler for pitch and asphalt (Allcock and Lampe 1990).

Was Percha discovered the reinforcing effect of carbon black. He reported the tensile strength value of 29.3MPa which was a very high value for the existing processing technique. This practice becomes a common one in compounding.

Ellis and Foster introduced the first glass fiber filler (reinforced) polyester resin in 1938. Also, the silica filler calcium silicate ($CaSiO_3$) was introduce in

1938. Van Aphan in 1954 reported the use of amino plastics such as aniline ($C_6N_5NH_2CH_2O$) melamine ($C_3H_6N_6$) formaldehyde product found in stabilized acidified latex and epoxy-resin in 1958, William Sitla of General Electrical Company produced sapphire whiskers for reinforcing composite, that same year. Graphite fibre produced by pyrolysis of polyacrylonitrile fiber was produced in England in 1960 which was later produced in pitch in the early 80's. Microfibre such as slay fibre (processed mineral fibre) calcium sulphate and sodium aluminum hydroxyl carbonite fiber was introduced in the '70s'Akpa,2005 a

2.1.1 Fillers

Fillers are generally classified as either black or non black filler. Under these categories, it is further classified as reinforcing and non-reinforcing. Reinforcement is meant to enhance the properties such as tensile strength, tear and abrasion resistance. Fillers are materials in particular form which ranges form every fine powder to microscopically sized granules. The number of materials used as filler is large and include silicates, carbonate, carbon polymeric material and derivative of naturally occurring material like wood, petroleum oil especially the reinforcing filler (Ahmedna et al, 1997).

2.1.2 Types of Filler

These are three main groups of fillers, these include:

i. Particulate filler

ii. Resineous filler

iii. Fibrous filler

2.1.2.1 Particulate Filler

Particulate filler are divided into reinforcing filler and inert fillers. The inert filler may affect the physical properties when in corporate into a polymer e.g. the addition of inert filler into plasticized PVC compound will reduce die swell on extension, increase modulus and hardness, improve electrical insulation properties and reduce tackiness. Inert fillers will also usually reduce the cost of a compound to greater extent. Among the filler used such filler should be insoluble in any liquid with which the polymer compound is liable in contact. Chemical type of filler is available in a number of grades and differs in the following ways (Ahmedna et al, 1997):

i. Particle shape and porosity.

ii. Average particle size and size distribution.

iii. Chemical nature of the surface.

iv. Impurities.

It has been observed that when employed in the elastomeric system the finer the particles size, the higher the value of such properties as tensile strength

modulus, and hardness. They can function in a number of ways in a polymer matrix such as (Eichom et al, 2001):

i. Improve wear and abrasion characteristics of the matrix
ii. Increase the heat deformation temperature of the matrix
iii. Reduce solvent and gas permeability in the matrix
iv. Increasing lubrication properties of the matrix
v. Electrical insulation properties (reduces)
vi. Viscosity increase
vii. Specific gravity increase.
viii. Transparency (decreased)

2.1.2.2 Resineous Filler

When particulate fillers are added to rubber, there is a considerable increase in the viscosity and the filler properties become extremely poor. In order to facilitate processing by improving flow, plasticizers are added but the level of plasticizer is required to be kept low. It is because of this, resinous filler are used in rubber. The resinous filler have a further advantage as testing of the rubber compound is little affected. There is equally little or no heart build up the case with the particle filler as loading in increased (Imanah Okieimen 2003).

The resinous filler commonly used are:

i. Styrene-butadiene (50/50 resin)

ii. Phenolic phenol + formaldehyde resin

2.1.2.3 Fibrous Filler

There are generally fibers of cotton rayon, wood, carbon asbestos etc. The fiber used have a higher modulus than resin in which they are embedded so that when the composite of resin + fiber is stained in the place of fibrous layer, the bulk of the stress is taken up by the fibre (Kalia et al, 2009).

2.1.2.4 Reinforcing Filler

Generally, reinforcing fillers are those additions which increase the tensile strength, tear strength, modulus, hardness and abrasion resistance of rubber compound vulcanization in which they are incorporated (Kalia et al, 2009).

2.1.2.5 Non-Black Reinforcing Filler

However for light colour product meeting specification was very tasking as the non black filler up to 1945 were non reinforcing, Hence, it becomes imperative than non black filler used for light colored goods give more reinforcing properties in order to be used in non-self reinforcing elastomers such SBR, NBR, EPDM. The experience has resulted in the development of non black filler for the production of rubber article with improved physical properties such as increasing hardness, tensile strength; tear strength and abrasion resistance (Kamel, 2007). The following constitute some of the non black reinforcing filler presently in use in the rubber industry are silica, zinc oxide, natural silica,

hydrated precipitated silica, hydrated aluminum hydroxide etc (Laka and Sherny avskay 2007).

2.1.2.6 Non-Black Non-Reinforcing Filler

These are inner material (dilutes) mainly used reduce compounding cost and cheapen or extend the material. Examples include (Allcock and Lampe 1990):

i. Barites:

An inner material used to reduce cost and it is an attractive candidate for chemical resistance compounds for tank lining.

ii. Talcum (Talc French Chalk):

Mica powder naturally washed and grounded to about 200-300 mesh. Due to its lamellar structure can substantially reduce gas permeation and also impact good resistance to heat. This consist mainly silicate of magnesium and aluminum used as inert filler in heat resistance compound for gasket battery cases and auto clawing joints. Talc is now mostly used as a dusting agent to prevent uncured stock form sticking to themselves and other surfaces (Hepworth et al, 2000).

2.2 Characteristics of Filler

The interaction of particulate filler with an elastomeric is depended on a number of factors that can classify as extensity geometrical and intensity factor (Ishak and Baker 1995).

i. Extensity Factor

The extensity factor is the total amount of surface escape cubic centimeter of compound in contact with the elastomer.

ii. Intensity Factor

Is the specific activity of the fluid surface per square centimeter of interface termination by the physical and chemical nature of the filler surface and to some extent of the elastomeric.

iii. Geometric Factor

The geometric characteristic deals with or can be determined by the surface of the filler that is determined by under standardized packing condition and porosity of the filler.

iv. Porosity

The porosity of the filler is usually a minor factor which can be varied over a wide range with carbon black because weight of the individual spongy particles is lower than that of solid particles. The number of particles per cubic centimeters

(cm^3) and the umber of such porous particles of one gram will be 15% higher than solid particles. Porosity also has great influences on properties which depends on volume coating and inter particle distance. Therefore porous black gives higher electrical conductivity than sold black. Since porosity can be black, is obtained by oxidation the black often contains many oxygen group on the surface this would counteract easy passage of electrons and increases the resistance easy passage of electrons and increases the resistance of the rubber compound made with such black. Therefore, one cannot state the porous carbon black will give highly conducting compound. All the same the effect of porosity on reinforcement is a secondary one (Jorts et al, 2005).

2.2.1 Effect of Filler Characteristics

The main effect of the filler characteristics are as follows (Kamel, 2007):

i. **Particle Size**

An increase in the surface activity (physical absorption) result in higher modulus at higher strain (300% upward), higher abrasion resistance, higher absorptive properties, higher bound rubber and lower hysteresis.

ii. **Porosity**

Porosity results in higher viscosity and higher electrical conductivity as in the case of carbon black.

iii. Structure

The structure of filler has considerable on the properties of rubber vulcanized. These effects are (Nakagaito et al, 2005):

i. The low structure fillers produce rubber products of high tear and tensile strength abrasion resistance products. High structure filler on the hand give higher abrasion resistant product.

ii. The level of die swells and shrinkage fall considerable with high level for structure.

iii. Stiffness increase with the structure of the filler and so does modulus.

iv. Dispersion in more difficult at high level of structure. Taking all the characteristics of filler together, it is the effect of particle size that predominates. Other factors only modify complement this effect. This is so, because the particle size of a filler also affects the extent of filler inter-particle and hence, the level of the structure. The small the particles size, the greater, the interaction and the higher the level of structure.

2.2.2 Uses of Filler

Filler plays a vital role in the processing of polymer. it is added to enhance various described properties. There must be adhesion (bond) between the filler polymer interface in order for (filler) to perform favourable in the following application. Filler are used in polymer for variety reasons (Asore, 2000).

i. Cost Production

Filler (non black i.e. non reinforcing filler) such as calcium carbonate helps to extend (increase) the volume of product therefore reducing he cost.

ii. Aid Processability

Processing problem such as nerve, higher viscous, material sticky to rocks are reduced by incorporation of filler such as thermal black.

iii. Flame Retardancy

Fillers like antimony trioxide are capable of giving a maximum flame resistance product. Others are calcium carbon etc.

iv. Reinforcement

Fillers are used to improve on the strength property, abrasion and tear resistance of natural rubber. Some resins could also impact high strength under certain condition e.g. high styrene can produce strength increase in NBR.

v. **Pigmentation**

Most polymers will not need additional colour and after using fillers. This is because filler like carbon black would give the product a black would give the product a black colour e.g. for tyre.

vi. **Tack and Britleness**

Fillers are used to reduce the tackiness of highly plasticized compounds. An example is china clay. The incorporation of filler such as glass fibre and wood flour in high impact, polystyrene can also help to reduce brittleness on compound.

2.2.3 Factors Guiding the Choice of Filler

Certain factors are to be taken into consideration before choosing particular filler to be used, for rubber compounding in the production of polymer articles. This is quit important because other kind of filler used will be determined by the properties article filler such will be determined by the properties article filler such will be determined by the properties required of the end product, during service application the following factors are (Chukwu, 2002):

i. Processability

Before any reinforcing filler is chosen, the ease of processing operation must be taken into consideration. Processing operation is referred as mixing ability, extraction and calendaring etc. the rubber compounds may run into undue difficulties during processing if this factor is ignore, and for this reason semi reinforcing clay is required during extrusion because it provides smoothness and reduce mould shrinkage during processing.

ii. Product Requirements

Any rubber compounded, the product is expected to meet service application properties required of it. Specification of properties required of the end product is per-required for formula in choosing typical filler for compounding to meet such and product requirement. Meeting the end product requirements is mostly important because it is the sole determinant of low efficiency e.g. the compounder must know whether he is formulating for a product that should have good abrasion properties.

iii. **Colour**

The colour of any given product must be considered before choosing filler. For example; it is not advisable to use carbon black product as reinforce filler where the end product colour is expected to be white, yellow or green. Carbon black is best used in products like tyres or any product where flamboyant colour is not necessary (Asore, 2000).

iv. **Cost**

The ultimate aim of any producer is to make profit. Therefore, before any particulate filler is chosen, the price should be commensurate with the cost of production. Thus, this is why non-reinforcing filler (cheaper) are used to boost the rubber product to reduce cost of the ultimate product. Reinforcing filler of

finest particles size are proven to have the greatest reinforcement compared to those of coarse particle size. But for the fact that they are more difficult to incorporate into the polymer matrix during mixing, it requires more time and energy to achieve this aim. This certainly increases the cost of production. It is important to control the cost of production since this will determine the cost of the end products, if the selling price if too high it may remain on the shelf for a long time and too long on shelf may upset its service performance (Chukwu, 2002).

v. **End Use Requirement**

The product specification plays a vital role in these aspects, such that the over all strength requirements will be determined by the service condition which the production be subjected to. Therefore, the product will have to possess certain properties such as the tensile strength, tear strength, hardness, abrasion resistance etc. while some other product do not require these properties. Thus, the choice of filler is governed by the end use requirement of such products (Asore, 2000).

2.2.4 Source of Filler

Filler are sourced in many ways. This includes carbon black which is gotten from petroleum or coal. Carbon black can be processed in many ways but it's merely conversion of either liquid or gaseous hydrocarbon to elemental carbon and hydrogen by partial combusting. Filler can also be source from

agricultural by product such as cherry and rubber seed shell pericap which form the basis of this Study. They are sourced locally, dried during using sunlight grinded into fine powder and finally sieve to achieve a finer particle sizes (Iannace et al, 2001).

Other sources include filler from mineral sources fibrous materials and organic materials (Chukwu, 2002).

2.2.4.1 Fillers from Mineral Deposit

Example of filler gotten from material deposit is barites which are gotten from coarse ground natural day. Also, is china clay derived from natural deposit example including soft clay and hard clay (Mizahur et al, 2007).

2.2.4.2 Fillers from Fibrious Material

An example of fillers of sourced from fibrous material is wood flour from hard wood which are firmly grounded to give fine grades of fillers. Others include wood flour, asbestos which are naturally occurring siliceous fibres both the shorter fibres and the ground material as filler for flame (heat resistance materials) like gasket and shoe (Mizahur et al, 2007).

2.2.4.3 Fillers from Organic Material

Examples of filler source from organic materials are phenolics resins, dikanut shell, rice husk, cherry seed shell, rubber seed shells etc. The cherry and rubber seed shells are dried and grounded to a fine powder, sieve to particle size.

2.3 Natural Fibres

Agro-based resources also referred to as lignocelluloses are resources that contain cellulose, hemicelluloses and lignin. Lignocelluloses include wood, agricultural residues, grasses and other plant substances (Komolafe et al, 1980). When considering lignocellulosics as possible engineering materials, there are several very basic concepts that must be considered.

Firstly, lignocellulosics are hydroscopic resources that were designed to perform in nature in a wet environment (Lawrence, 1974). Secondly, nature is programmed to recycle lignocellulosics in a timely way through biological, thermal, aqueous, photochemical, chemical and mechanical degradations (Mohanty et al, 2001).

2.3.1 Classification of Fibres

Natural fibres can be classified according to their origin as follows (Ayo et al, 2010):

i. Animal fibres

ii. Mineral fibres

iv. Plant fbres

i. **Animal Fibres:** These are fibres taken from hairly animals e.g. sheep's wool, goat hair (cashmer, mohair), alpaca hair horse hair etc, fibre

collection from desired salawa of bugs or insect during the preparation of cocoons e.g. silk worms or fibres from birds e.g. feathers.

ii. **Mineral Fibres:** These are naturally occurring fibres or slightly modified form mineral. They are categorized into the following:

Asbestos: This is the only naturally occurring mineral fibre. The various classes of asbestos fibres are serpentine, amphiloles and anthophyllite.

Ceramic Fibres: Example are glass fibres, silicon, carbide and boron carbide.

Metal Fibres: Aluminm fibres

Plant Fibres: Plant fibres are generally made up of cellulose. Example include: cotton, flax namie, jute and hemp. Plant fibres can be grouped into seed fibres, leaf fibres, skin fibres and fruit fibres.

2.3.2 Cherry and Rubber Seed Shell Fillers

Locally sourced agricultural by-products have been discovered as potential fillers over the years as a result of investigation. Cherry and rubber seed shells have been waste products in the past years and the need to investigate their potentiality as filler become a major concern in the present day rubber industry.

This study investigated if CCSS and RSS can serve as fillers or not and to check whether reinforcing, semi reinforcing or non-reinforcing. Their potentiality as fillers will help to cheapen the price of rubber products, improve their quality and could as well lead to ban on importation of fillers and could even lead to exportation thereby improving balance of trade (Ekebafe et al, 2010).

Table 2.1: Showing types of Degradations and their agents(Imanah and Okiemen 2004)

S/NO	DEGRADATIN TYPE	AGENTS
1	Biological degradation enzymatic reactions chemical reaction mechanical	Fungi, bacteria, insects, termites, oxidation, hydrolysis, reduction, oxidation, hydrolysis, reduction chewing.
2	Fine degradation Paralysis'	Lightening, sun, degradation hydrolysis, oxidation.
3	Water Degradation, Water interactions	Rain, Sea, Ice Aid rain, Dew Swelling, Shrinking, Freezing, Cracking.
4	Whether Degradation, Chemical Creation Mechanical	Acids, bases, salts oxidation, reduction, Dehydrating, hydrolysis
5	Chemical degradation, Chemical Reaction	Acids, bases, salts oxidation, reduction, Dehydrating, hydrolysis
6	Mechanical degradation mechanical	Dust, wind hail, snow, sand, stress, cracks, fracture, abrasion

Wood and other lignocellulosics material have been used as engineering material because they are economical low in processing energy, renewable and strong however; they have several undesirable properties such as dimensional instability caused by moisture absorption with varying moisture content, biodegradability, flammability and degradability by ultra violet light, acid and basis. Because of the undesirable of lignocellulosic materials, most composite made from them have a limited service life (Imanah and Okieimen 2004).

2.4 Natural Rubber

Natural rubber is a gummy substance isolated from the white fluid of rubber tree, commonly the Havea Brasiliensis found in South America. However, there are over 200 different species of plant sources of which Hevea brasiliensis is of commercial significant. Natural rubber is a hydrocarbon polymer of 2-methyl-1, 3 – butadiene (isoprene) and contains one double bond per repeat unit. It consist of over 85% of linear cis 1,4-polyisoprene and the remaining being trans isomers (Asore, 2000).

Table2.2: Detailed Representative Sample of Natural Rubber (Komolafe *et al* 1980)

Components	**Percentage %**
Ash	0.5
Acetone	2.7
Protein	2.8
Hydrocarbon	93.6
Total	100.0

2.4.1 Grades of Natural Rubber

Natural rubber may be available in many grades related to its 'dirt' content and precise method of production. Popular grades are ribbed smoked sheet (RSS) and technically specified rubber such as standard Malaysia rubber (SMR); standard Indonesia rubber (SIR), standard African Rubber (SAR) and Nigeria

standard Rubber (NSR). The sub grades are RSS5, SMR5, 10, 20 and 50 and NSR5, 10, 20 and 50. They are grades based on dirt content, ash content, volatile matter and plasticity retention index (PRI). Another grade of natural rubber is the SMR CV. This grade has 0.15% hydroxylamine salt added to prevent a cross-linking phenomenon known as storage hardening, which causes an increasing viscosity during storage.

Table 2.2 Standard Malaysia Rubber Specification

Parameter	**SMR CV**	**SMR LV**	**SMR 5**	**SMR GP**	**SMR 10**	**SMR 20**	**SMR 50**
Dirt content	0.03	0.03	0.05	0.10	0.10	0.20	0.50
Ash content	0.50	0.50	0.60	0.75	0.75	1.00	1.50
Nitrogen content	0.60	0.60	0.60	0.60	0.60	0.60	0.60
Volatile matter	0.80	0.80	0.80	0.80	0.80	0.80	0.80
Mallace rapid	-	-	30	-	30	30	30
Plasticity retention index	60	60	60	50	50	40	30

The NSR5, 10, 20 and 50 are similar to the SMR

2.4.2 Properties of Natural Rubber

i. Natural rubber has excellent green strength which is attributed to its ability to undergo strain-induced crystallization when stretched or strain at low temperature due to its high regular structure (Asore, 2000).

ii. Natural rubber has excellent resistance to tearing, particularly at high temperatures. The formation of crystallites during crystallization impedes tearing, particularly at points of high stress (Chukwu, 2002).

iii. Natural rubber has a unique combination of low hysteresis and therefore high resilience at low strains.

iv. The abrasion and wear resistance of natural rubber are fairly good. The abrasion resistance decreases rapidly with rise in temperature.

v. Natural rubber has a very good resistance to flex cracking at low strains. Under dynamic deformations the growth of cracks is very low, particularly where the cycle has a finite minimum to ensure that the crystallized rubber at the cracks tips does not melt.

vi. Natural rubber has a fairly good resistance to heat when heated with the total exclusion of air or oil. It has very poor resistance to petroleum oils, vegetable oils and swells readily in organic solvents.

vii. The presence of unsaturation in natural rubber makes it highly susceptible to oxidation and ozone attack. The unprocessed, unvulcanized raw rubber is very readily attacked by oxygen either directly or in the presence of an oxidizing agent such as metals and metal oxides.

viii. Natural rubber has a very good resistance to electricity.

ix. Natural rubber has very good tack and it is usually not necessary to add tackifying agents to its compounding (Asore, 2000).

2.4.3 Application of Natural Rubber

Natural rubber is used in application requiring high strength, high resilience, excellent damping properties and moderately high thermal stability. Natural rubber is used mainly in tyre manufacture, especially truck tyres and in bridge bearings, engine mountings and conveyor belt etc (Asore, 2000). Natural rubber also has important application in the production of latex dip products such as balloons, surge gloves or sanitary rubber product due to its strain induced crystallization and self-reinforcing properties. Natural rubber can be used for making adhesive tapes, rubber solutions or art gum (Katchy, 2000).

2.5 Rubber Compounding Ingredients

The manufacture of rubber product required the addition of many different types of additives to the rubber. These additives are often added to facilitate processing, improve the properties of the rubber and also to reduce cost. The rubber in its raw state is not suitable in any given application. Rubber is visco-elastic in nature. This tendency gives rise to its many engineering and other application. They exhibit thermoplastic behavior within a limited range of temperature and are soluble in wide range of organic solvent. These factors impose several limitations on the usefulness of the rubber material (Chukwu, 2002).

i. Base Polymer

This is the base material in compounding. Raw rubber, whether it is natural or synthetic in the dry form or latex is usually compounded with various ingredients to change it from a soft plastic material to a strong, non-plastic and even hard substance. A blend of two rubbers may also be used in the rubber compound formulation (Asore, 2000).

ii. Vulcanizing Agent

These are ingredients added to the base polymer to help effect cross linking of the polymer chain. The most important vulcanizing agent or curing is still sulphur (Sharma, 2006). The other vulcanizing agent are sulphur monochloride, selenium, tellurium, thiuram peroxide, etc.

iii. Accelerators

Accelerators are ingredients used in compounding to accelerate the rate of vulcanization. Organic compounds having nitrogen or sulphur or both are used to increase the rate of vulcanization of rubber from several hours to few minutes. In addition less sulphur is required and more uniform product is obtained. The addition of accelerators has also been found to decrease vulcanization temperature (Sharma, 2006).

iv. **Activators**

Activators are used to increase the effect of accelerators. Example of activators are zinc oxide, stearic acid, litharge, magnesium oxide, amine soap, etc. (Sharma, 2006). Full activation of vulcanization is obtained with about 3-5 ph of zinc.

v. Antidegradant

Antidegradants are ingredient used to retard deterioration of rubber compound initiated by oxygen, ozone, light, heat, metal impurities and mechanical flexing. In compounding, antidegradants are divided into antiozonant and antioxidants. Antiozonants are chemical which diffuse to the surface and react with the ozone, there by protecting the rubber from attack. Commonly used antiozonants are paraphenylediamine (PPD) and micro crystalline waxes. Antioxidants are chemical which extend the life of rubber products by first reacting with polymeric free radicals and stopping propagation of polymer oxidation. Commercially available antioxidants fall in three (3) groups. Secondary amine, phosphates and phenolics. Examples are N- phenyl 1-2-naphthyamine, P,P-diaminediphenyl methane, etc (Chukwu, 2002).

vi. Processing Aids

Processing aids are the ingredients added to rubber compound to facilitate processing operation, such as mixing, calendering, extrusion and moulding.

Examples of processing aids are fatty acids, metal salts of fatty acid, low molecular weight polymers, hydrocarbon oil and peptizer (Katchy, 2000).

vii. Fillers

Fillers are ingredient used to reinforce physical properties or to reduce cost. Fillers are classified as reinforcing, semi reinforcing and non-reinforcing filler.

2.6 Polymer Composites

One of the very factors which make composites attractive for engineering applications is the possibilities of property enhancement through fibre reinforcement. These materials have useful combination of properties as a result of a combined effort of two or more different constituents. One component may be light and strong but too brittle to be used alone, another constituent may be tough and ductile but without sufficient strength, hence, effective combination is needed to enable this composites display excellent service performance properties. Composite materials may be selected to give an unusual combination of stiffness, strength, weight, high temperature performance, conductivity, hardness, corrosion resistance etc. Composite drew attention to how different materials can combine to produce effect greater than the sum of their separate efforts.

2.6.1 Definition of Composite

According to Beghezan, a composite is a compound material which differs from alloys such that the individual components retain their characteristics but are so incorporated into the material so as to take advantage of their attributes and not their short "coming" in order to obtain an improved material.

Jantiz also defined composite as a multifunctional system that provide characteristics not obtainable from any discrete material. They are cohesive structures made by physically combining two or more compatible materials which are different in composition and characteristics and sometimes in form.

2.6.2 Classification of Composites.

2.6.2.1 Laminar Composites

Laminar composites are built up of layers of different materials. These layers may be sheet of different metals with one metal providing strength and the other providing hardness or corrosion resistance. The layers may include sheets of fibre – reinforced material bonded to metal or polymer sheets or fibre-reinforced sheets having different fibre orientation. These composites are always anisotropic. Example is plywood having alternating layers of wood veneer (Crawford, 1998).

2.6.2.2 Particulate Composites

They are designed to produce unusual combinations of properties rather than to improve strength. They contain large amount of coarse particles that do

not block slip effectively. The rule of mixture can be used to predict properties of these composites. For instance, the density of a particulate composite is given as:

$$\rho_c = v_m\rho_m + V_f\ \rho_f \qquad 2.1$$

Where ρ_c is the density of the composite

ρ_m and ρ_f are the densities of the matrix and fibre

V_m and V_f are the volume fractions of the matrix and fibre respectively.

Example of this composite is concrete mixture of cement and gravel.

2.6.2.3 Fibre – Reinforced Composites

These composites provides improved strength, fatigue resistance, young modulus, strength to weight ratio by incorporating strong, stiff but brittle fibres into a softer more ductile matrix. The matrix provides protection for the fibre surface and minimized diffusion of species such as oxygen or moisture that can degrade the mechanical properties of the fibres. The strength of the composite may be high at both room and elevated temperatures. The role of mixture can be used to predict the density of these fibres (Crawford, 1998).

$$\rho_c = \rho_m f_m + \rho_f f_f \qquad 2.2$$

Where; m and f refers to the matrix and fibre respectively.

The modulus of elasticity of the fibre-reinforced composite is given as:

$$E_c = E_m f_m + E_f F_f \qquad 2.3$$

While the modulus perpendicular to the fibre is give as:

$$\frac{1}{Ec} = \frac{Fm}{Em} + \frac{Ff}{Ef} \qquad 2.4$$

Example of this composite is fibre glass embedded in a polymer.

2.6.3 Methods of Making Composites

There are several methods of making composites (Asore, 2000).

i. **Spray up:** The fibres and the resins are sprayed onto the mould. The layers are densified with rollers. As for hand lay-up, gel coat are used for good surface finish. Polyester or epoxy thermosetting resins are commonly used.

ii. **Mixing:** The particulate filler-reinforced composites are usually prepared by homogenous mixing of the filler, polymer and other additives in a mixing machine (Bambury mixer, two roll mills or an extruder). The composite is vulcanized after complete mixing cycle.

iii. **Puttrusion:** The fibres are impregnated with resins and pulled through a mould shaped to produce the desired cross-section in the product. The mould is then heated to promote setting after impregnating the fibres. It is used for very strong aligned composites.

iv. **Filament Winding:** The filaments are in bundles and usually consist of thousands of individual fibres and are referred to as roving or tow. It consists of winding continuous filament over a suitable shaped mandrel.

v. **Hand lay-up:** The fibres are laid unto a mould by hand and the resins is painted on and allowed to cure. The method is simple, versatile, and cheap but labour intensive.

2.6.4 Application of Composites

Composites are used in a wide range of applications where high strength to weight ratios is required. Areas of applications include; automobile, marine and construction industries. Others areas requiring high performance are in the aerospace industries. Composites fibre glass was employed to reinforce plastics which were used in the nose radar domes to protect aircraft antennas in the early 1940s. In 1950, reinforced plastics were also employed as aircraft propeller blades saving both weight and cost (Crawford, 1998).

CHAPTER THREE

MATERIALS AND METHOD

3.1 Materials

The materials used in this research work are natural rubber, cherry and rubber seed shells and compounding ingredients.

3.1.1 Materials and their Sources

i. The natural rubbers was obtained from Rubber Research Institute, Benin, Edo State, Nigeria.

ii. The cherry and rubber seed shells were procured from Ogwashiku, Azugwu, Delta State.

Tetramethyl thiuram disulphide (TMTD), Mercarptobenzothiazole sulphenamide (MBTS), Stearic acid, Sulphur, Trimethylquinoline (TMQ), Zinc Oxide, Paraffin Wax were produced by British Drug House (BDH), England

3.1.2 Equipment

The equipment used include

i. Monsanto Tensile Tester Model 1/m, Manufactured by British Company Limited, England ± 0.35

ii. Wallace Hardness Tester Model c8007/25, Elektron Technology Series, UK. ± 0.40

iii. Wallace Akron Abrasion Tester, Elektron Technology Series, UK. ± 0.75%

iv. DuPont Machine, Manufactured by British Company Limited, England ± 1.15

iv. Muffle Furnace METTm-525, Elektron Technology Series, UK.

v. Two Roll Mill, Manufactured by British Company Limited, England

vi. Hydraulic press, Elektron Technology Series, UK.

3.2 Method

3.2.1 Filler Carbonization and Characterization

Carbonization is a process of converting an organic compound to high carbon content by heating it in the absence of oxygen (inert). Carbonization of fillers used in this research work was carried out using a laboratory muffle furnace set at varying temperatures from 100, 200, 300, 400, 500, 600 and 700^{o}C by creating an inert environment via the passage of nitrogen gas for three hours each (Ayo et al, 2010). The cherry and rubber seed shells were washed in water and dried in air to remove sand particles and moisture respectively. After drying, one portion of the cherry and rubber seed shells were milled to fine powder as well as the carbonized portion, and sieved through a mesh size of 100µm. The fine particles that passed through were collected and used for compounding.

Filler characterization

3.2.2 Determination of Iodine Value

0.1molar solution sodium thiosulphate was titrated against 20.0ml of the various cherry and rubber seed shell powder free aliquot solution (prepared by centrifuging 0.5g of the powdered carbonized and uncarbonized cherry and rubber seed shell powder separately in 25.0ml of 0.488ml iodine solution) using 5.0ml of freshly prepared starch solution as indicator. Similarly, the quantity of thiosulphate needed to titrate the blank solution was determined and procedure carried out in triplicate and the average of the values obtained in each case were calculated and recorded. The volume of sodium thiosulphate employed in aliquot solution is recorded as volume "S" while that of the blank solution is recorded as B.

$$\text{Iodine Value} = \frac{B - S}{B} \times 300.14 \qquad 3.1$$

Iodine adsorption number is equal to the inverse of iodine value. (Ayo *et al* 2010)

3.2.3 Determination of Moisture Content

The moisture content of each filler sample was determined by adopting the method described in ASTMD 1509 at 125^{o}C. This method is used to determine the percentage of water in a sample by drying the sample to a constant weight. The moist sample was weighed and recorded as initial weight of sample; the wet sample was dried to a constant weight at a temperature of 125^{o}C in an oven. The

sample was allowed to cool, reweighed and recorded as the final weight of the sample.

$$\text{Moisture Content (\%)} = \frac{\text{Initial Weight} - \text{Final Weight}}{\text{Initial Weight}} \times 100 \quad \text{(Ekebafe } et\ al \text{ 2010)} \qquad 3.2$$

3.2.4 Determination of Loss on Ignition

Loss on ignition refers to the mass loss of a combustion residue whenever it is heated in an air or oxygen atmosphere to high temperatures. The loss on ignition of the various samples was determined gravimetrically, in accordance to the procedure described in ASTMD 7348. 10g of the sample was place in a tarred, pre-ignited crucible and placed in a furnace for some time (about 2hours). It was removed from the oven, cool and weighed. It was then put in the oven and heated until the weight is constant. (Ekebafe *et al* 2010)

3.2.5 Determination of Bulk Density

Bulk density of the various samples was determined by the tapping procedure (Ahmedna, et al, 1997). Accurately weighed samples were poured into a uniform cylinder of cross sectional area and were then tapped several times until there was no change in the volume occupied. This volume was then recorded and the bulk density calculated.

3.2.6 Determination of pH

The pH of the carbonized and uncarbonized cherry and rubber seed shell powder samples were determined using ASTMD 1512 method by immersing

1.0g samples in 20.0ml of deionized water in a 250ml beaker. The mixture was stirred for 15minutes and the pH meter was then inserted into the solution to obtain reading directly. (Okiemen and Akinlab 2002)

3.3 Processing of the Composites

This involves the compounding of natural rubber with carbonized cherry seed and rubber seed shell fillers. The formulation used for the compounding of the natural rubber (NSR 10) with the cherry and rubber seed shell fillers (carbonized and uncarbonized) is given in Table 3.2

Table 3.2: Formulation for Compounding Natural Rubber.

Ingredient	**Parts per hundred rubber**
Natural rubber	100
Fillers (CCSS/CRSS)	40
Zinc Oxide	5.0
Stearic acid	2.5
Sulphur	1.5
MBTS	1.5
TMTD	3.5
Processing Oil	5.0

A batch factor of six (6) was used.

3.3.1 Mixing Procedure

The rubber mixes were prepared on a laboratory size two roll mill according to the mixing cycle shown in Table 3.3. It was maintained at 70^{o}C to

avoid cross-linking during mixing after which the rubber composite was stretched out. Mixing follows ASTMD 3184–80 Standard.

Table 3.3: Mixing Steps and Mixing Time

Mixing steps	**Time (minutes)**
Natural rubber mastication	5
Addition of Stearic acid	1
Addition of Zinc Oxide	1
Addition of filler (CCSS/CRSS)	12
Addition of MBTS	1
Addition of TMTD	1
Processing Oil	1
Addition of Sulphur	2
Total	**24**

3.3.2 Curing

Curing of the vulcanizates was carried out at 122^{o}C for 15 minutes.

3.4 Mechanical Properties of the Vulcanizates

The mechanical properties of the vulcanizates were determined using standard test procedures.

3.4.1 Tensile Property Tests

Tensile properties were determined on a Monsanto tensile tester model 1/m at a cross speed of 500mm/min using dumbbell test pieces of dimension (45 × 5× 2mm) as contained in ASTMD 412-87 method. The test samples were tested in

the machine giving straight tensile pull, without any bending or twisting. The machine measures both the tensile stress and the tensile strain. The tensile stress is the strength of pull in the area between the notch marks and it is based on original cross sectional area. The tensile strain is a measure of how the test sample has been stretched by the pull.

3.4.2 Hardness Test

Hardness of the sample was determined by adopting the standard dead load method. The standard dead method of measurement covers rubber in the range of 30 to 85 International Rubbers Hardness Degrees (IRHD). The test was carried out using the Wallace Hardness Tester model C 8007/25 in accordance with BS903 Part A26.

3.4.3 Compression Set Test

Wallace Compression Set machine was used based on ASTM 385. Compression set evaluate the extent by which the specimen fails to return to its original thickness when subjected to standard compression load for a given period of time at a given temperature (Yemi, 1986). The test samples were cut to standard dimension and compressed between parallel steel plates under stress of $2.8MP_a$. It was then conditioned for a selected time of 24 hours at 70^oc after which the sample was removed and allowed to recover at room temperature for 30minutes. The compression set is the difference between the original thickness

of the sample and the thickness after the test expressed as a percentage of the original thickness.

$$\text{Compression Set (\%)} = \frac{t_o - t_r}{t_o} \times 100 \quad \text{(Yemi, 1986)} \qquad 3.3$$

Where t_o be the initial thickness of the sample and t_r is the recovered thickness of the sample.

3.4.4 Flex Fatigue Test

Flex fatigue was carried out in accordance to the procedure described in ASTMD 430 using the DuPont machine, which function by inducing surface cracking of the rubber vulcanizates sample.

3.4.5 Abrasion Resistance

The abrasion was carried out for per 1000 revolutions and the material loss for each run was noted. Wallace Akron abrasion tester was used. The angle between the test sample and the wheel was adjusted to an angle of 15^o. The specimen was re-reweighed between each test run. The mean of the four revolutions of the abrasive wheel was calculated.

$$\text{Abrasion Resistance} = \frac{\text{Weight Loss of the Standard}}{\text{Weight Loss of the Sample}} \times 100 \qquad 3.4$$

3.5 Swelling Behaviour of the Vulcanizates.

The swelling behaviour of the natural rubber vulcanizates in cyclohexane, CCL_4 and xylene were determined by using the method described in ASTM-D3010. Three samples each from the different cured samples were cut from the

1mm thickness mould, weighed and immersed in the various solvents in air tight containers at ambient temperature for 24hrs. The samples were then removed from the container, dried and reweighed. The change in weight of the sample was expressed as percentage absorption. The absorption behaviour which is a measure of the swelling resistance of the rubber compound is calculated using the equation:

$$\text{Swelling Index (\%)} = \frac{A_S}{W} \times 100 \qquad 3.5$$

Where A_S = Amount of solvent absorbed by the sample

W = Initial weight of the sample before swelling.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Results

The results are shown in Table 4.1- 4.3.

Table 4.1: Characteristics of the Carbonized Fillers

Carbonization temperature (^{o}C)	**Loss on Ignition (%)**	**Bulk Density (glml)**	**Iodine Adsorption number (mg/g)**	**Moisture content (%)**	**pH of slurry at 28(^{o}C)**
100	(5.95) [7.10]	(0.69) [0.75]	(49.04) [20.12]	(2.07) [1.90]	(5.87) [4.79]
200	(27.64) [29.00]	(0.72) [0.65]	(51.01) [36.50]	(1.09) [1.00]	(5.91) [5.20]
300	(56.78) [60.00]	(0.80) [0.78]	(52.37) [47.20]	(0.76) [0.58]	(6.46) [5.30]
400	(64.53) [73.80]	(0.71) [0.68]	(54.43) [50.44]	(0.72) [0.40]	(6.82) [5.75]
500	(73.97) [77.00]	(0.67) [0.63]	(69.77) [61.20]	(0.63) [0.28]	(6.88) [6.10]
600	(76.32) [77.80]	(0.73) [0.70]	(70.65) [66.70]	(0.21) [0.14]	(7.14) [6.20]
700	(82.04) [81.82]	(0.71) [0.66]	(79.81) [66.84]	(0.15) [0.11]	(8.99) [7.70]
Uncarbonized filler	(5.76) [7.00]	(0.78) [0.91]	(17.76) [20.00]	(2.25) [2.07]	(5.03) [4.10]
N330 carbon	91.83	0.56	81.07	0.85	6.03

Key: Carbonized Cherry Seed Shell (CCSS)
Carbonized Rubber Seed Shell [CRSS]

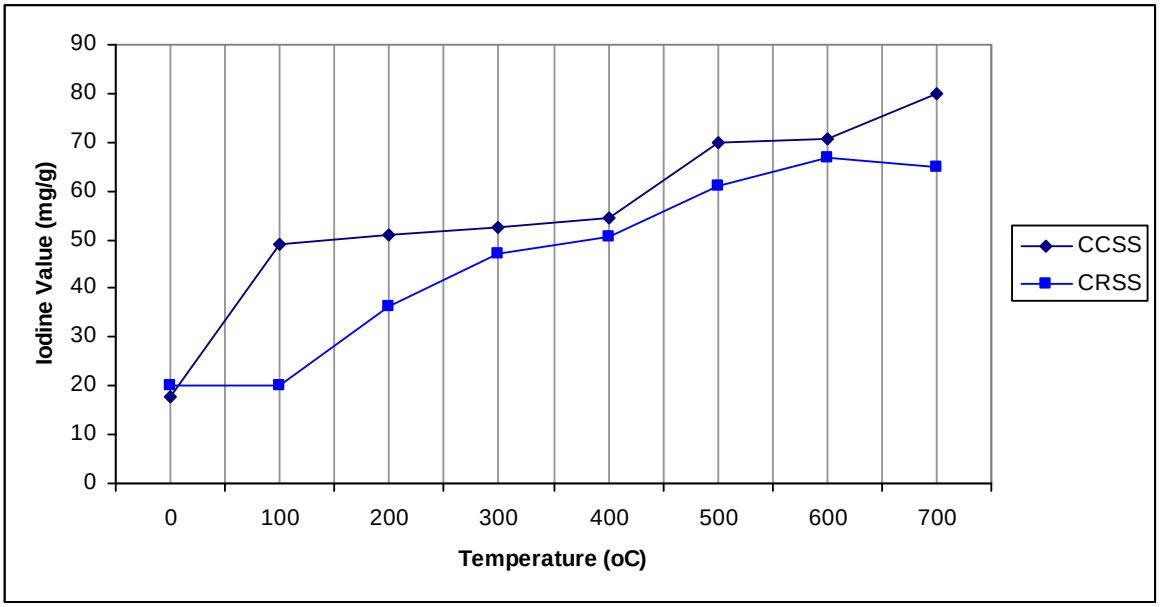

Figure 4.1: Effect of Carbonization Temperature on Iodine Value

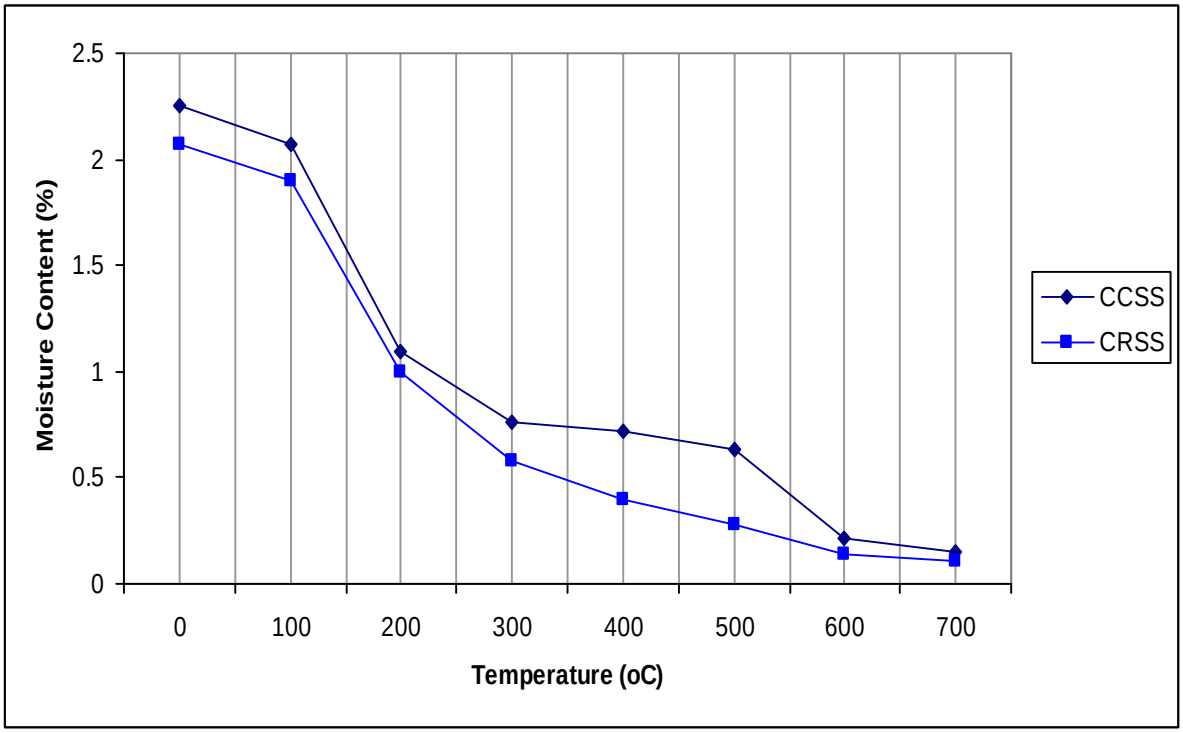

Figure 4.2: Effect of Carbonization Temperature on Moisture Content

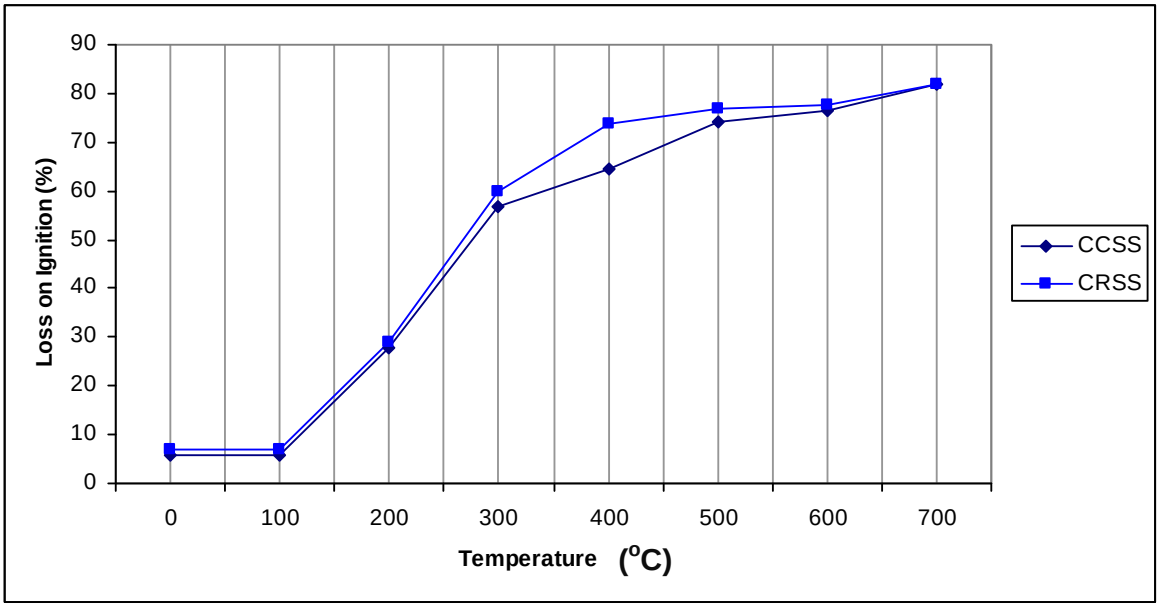

Figure 4.3: Effect of Carbonization Temperature on Loss on Ignition

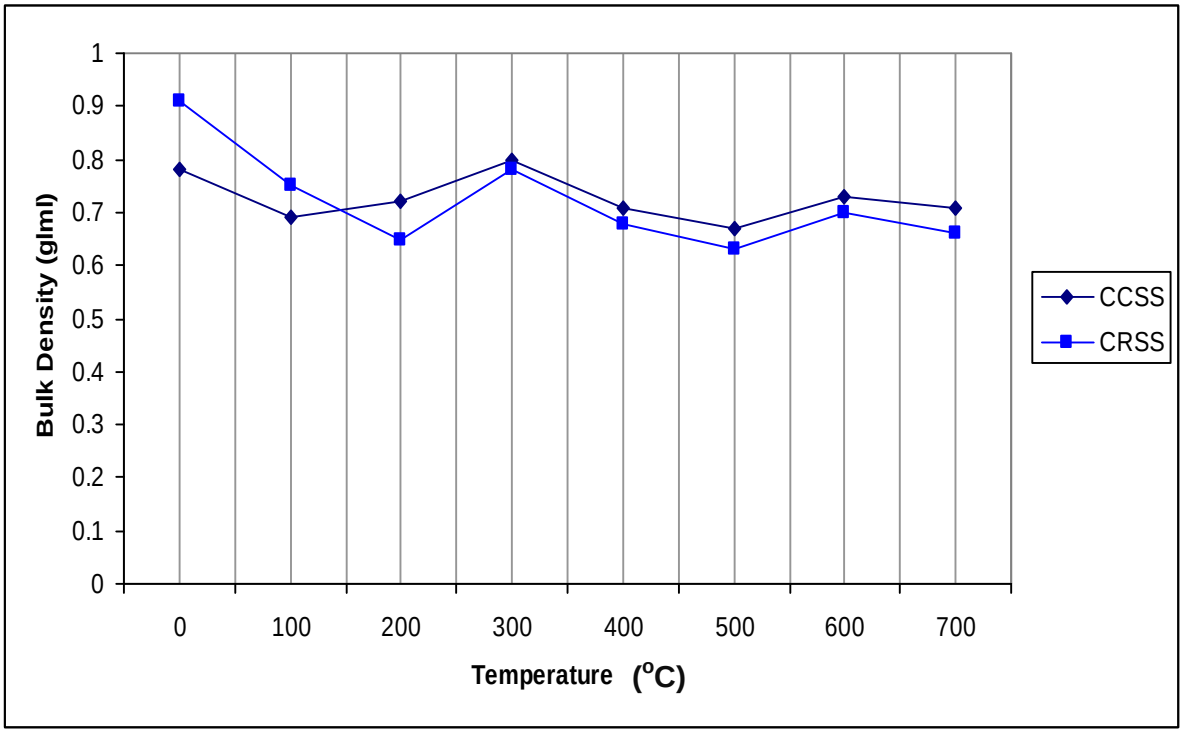

Figure 4.4: Effect of Carbonization Temperature on Bulk Density

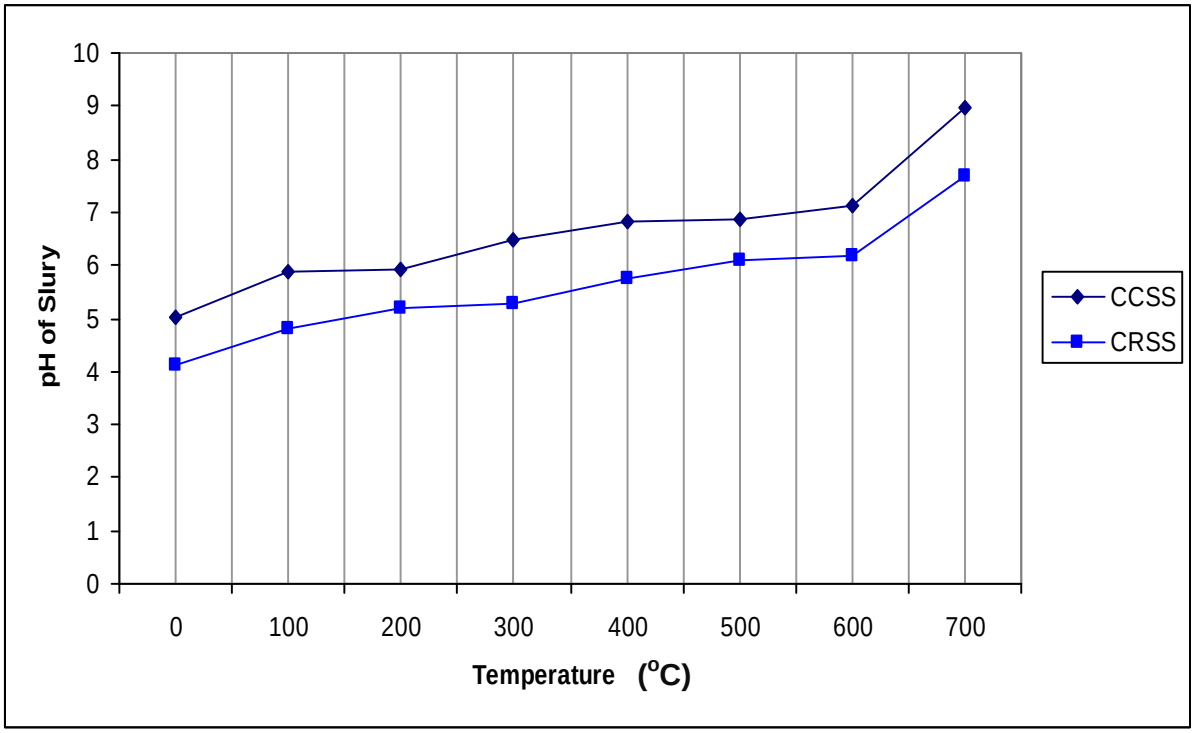

Figure 4.5: Effect of Carbonization Temperature on pH

Table 4.2: Mechanical Properties of the Vulcanizates

Properties	N330 carbon Black	Uncarbonized filler	Carbonization Temperature (^{o}C) at 40phr Filler Loading						
			100	200	300	400	500	600	700
Tensile strength (MPa)	28.86	(7.09) [6.08]	(7.87) [6.98]	(8.06) [7.28]	(9.24) [7.85]	(10.58) [8.93]	(11.40) [9.80]	(15.25) [12.50]	(14.09) [11.80]
Modulus (MPa)	5.80	(1.45) [1.30]	(1.98) [1.85]	(2.45) [2.35]	(2.53) [2.53]	(2.68) [2.72]	(2.78) [2.90]	(3.72) [3.80]	(3.47) [3.45]
Elongation at break (%)	322.09	(580.04) [550.00]	(569.07) [508.16]	(522.15) [493.25]	(501.00) [450.28]	(488.40) [412.24]	(487.11) [400.15]	(320.12) [335.10]	(367.08) [380.53]
Flex fatigue (kc x 10^{3})	5.01	(9.12) [10.02]	(8.88) [9.20]	(8.25) [8.92]	(8.01) [8.51]	(7.42) [7.40]	(7.23) [6.43]	(6.43) [5.76]	(6.85) [6.38]
Hardness (IRHD)	57.89	(40.15) [45.00]	(43.54) [47.24]	(44.23) [48.53]	(46.24) [50.88]	(49.43) [50.93]	(53.21) [54.63]	(55.24) [58.15]	(54.11) [57.08]
Abrasion Resistance (%)	41.67	(19.07) [20.10]	(19.21) [20.89]	(19.89) [20.95]	(20.63) [23.93]	(20.89) [26.75]	(21.24) [30.05]	(26.00) [38.24]	(25.07) [36.41]
Compression set (%)	7,99	(21.32) [19.02]	(20.70) [18.78]	(20.01) [16.43]	(18.44) [15.01]	(18.02) [14.00]	(18.06) [11.24]	(14.25) [9.70]	(13.00) [10.09]
Rebound Resilience (%)	85.75	(85.70) [92.67]	(80.12) [88.43]	(78.34) [80.25]	(76.55) [75.65]	(75.00) [70.09]	(75.89) [67.98]	(73.80) [63.56]	(74.56) [70.08]

Carbonized Cherry Seed shell –Filled vulcanizates ( )
Carbonized Rubber Seed Shell –Filled vulcanizates[ ]

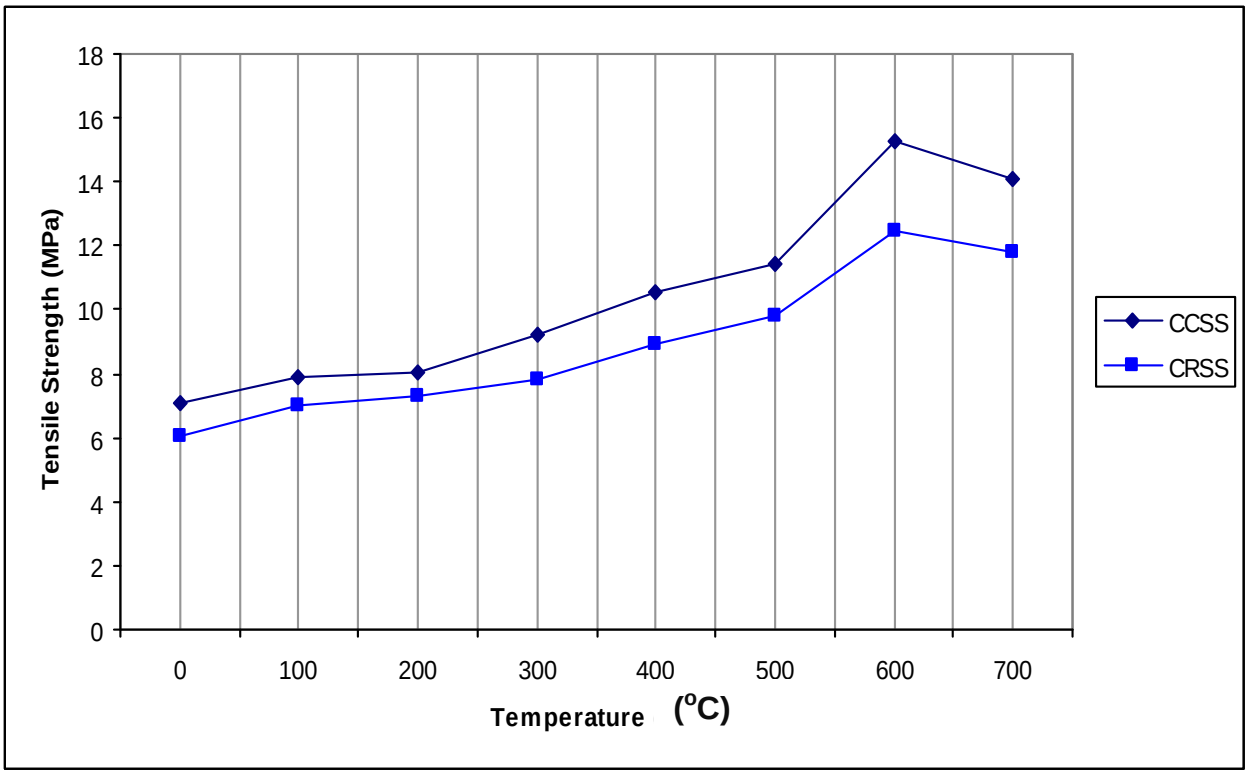

Figure 4.6: Effect of Carbonization Temperature on Tensile Strength of CCSS-filled and CRSS-filled Vulcanizates

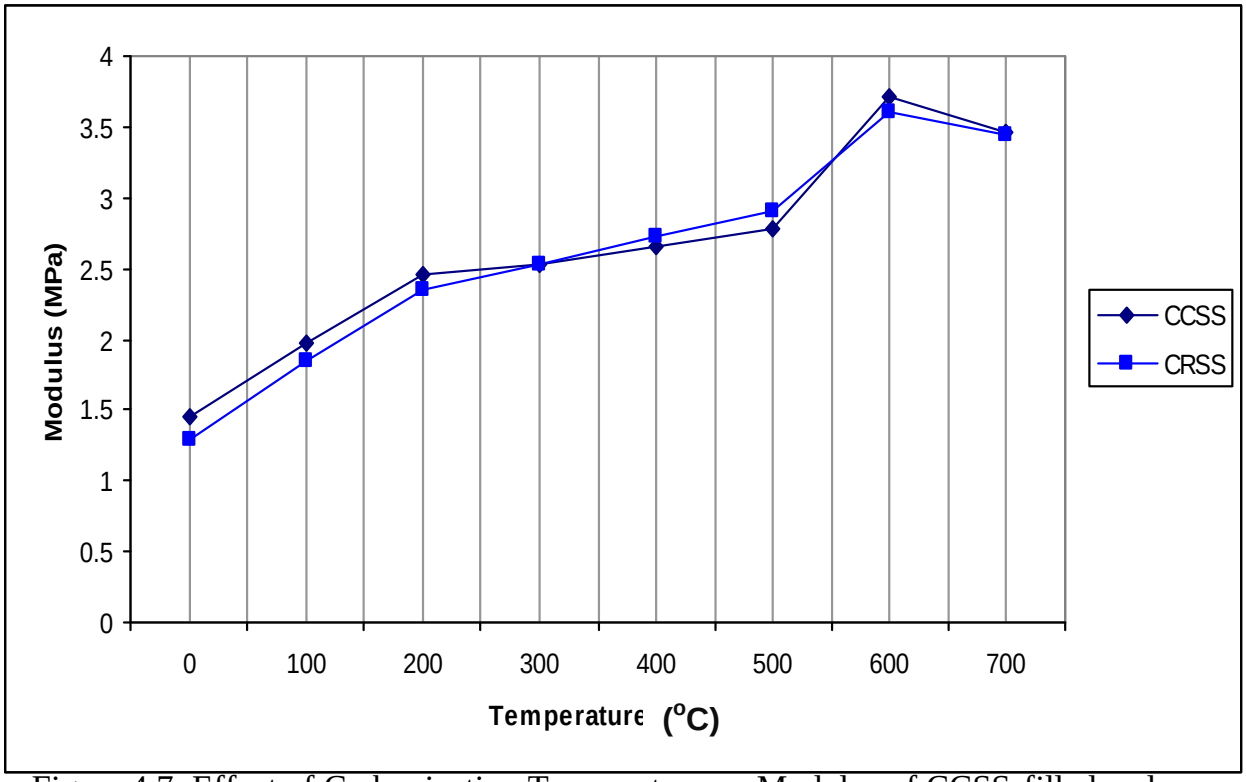

Figure 4.7: Effect of Carbonization Temperature on Modulus of CCSS-filled and CRSS-filled Vulcanizates

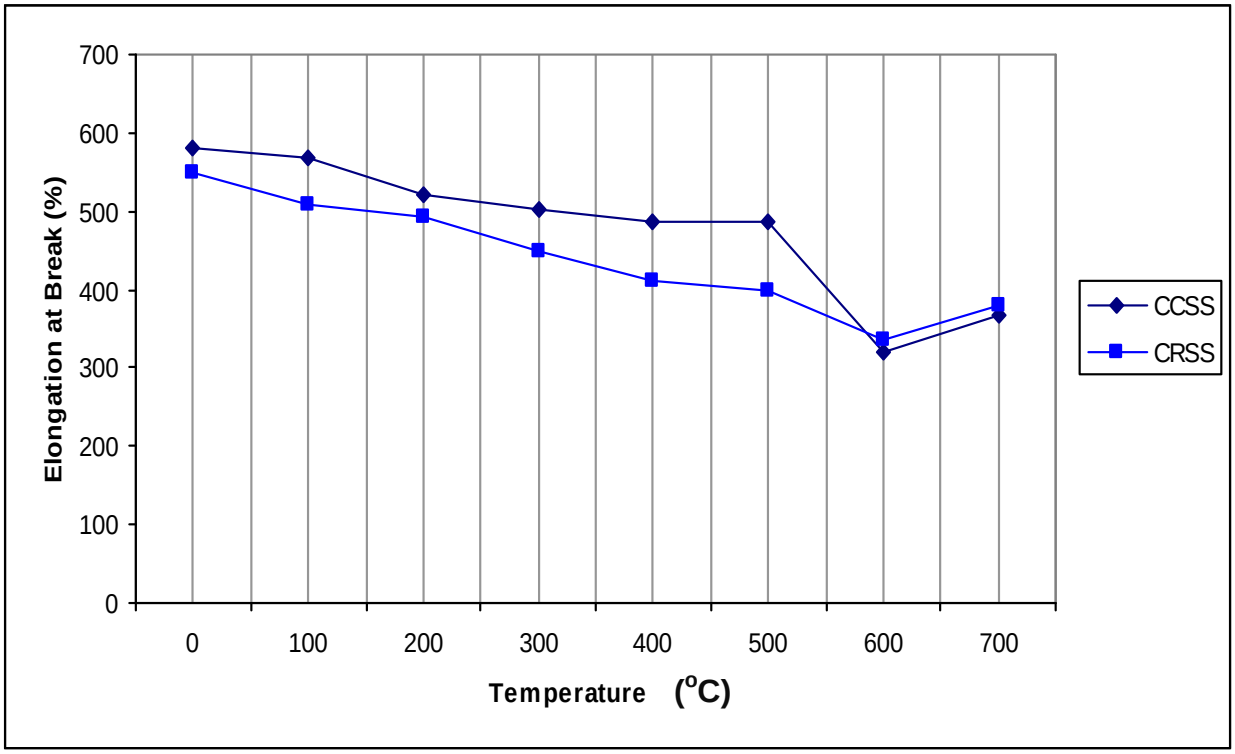

Figure 4.8: Effect of Carbonization Temperature on Elongation at break of CCSS-filled and CRSS-filled Vulcanizates

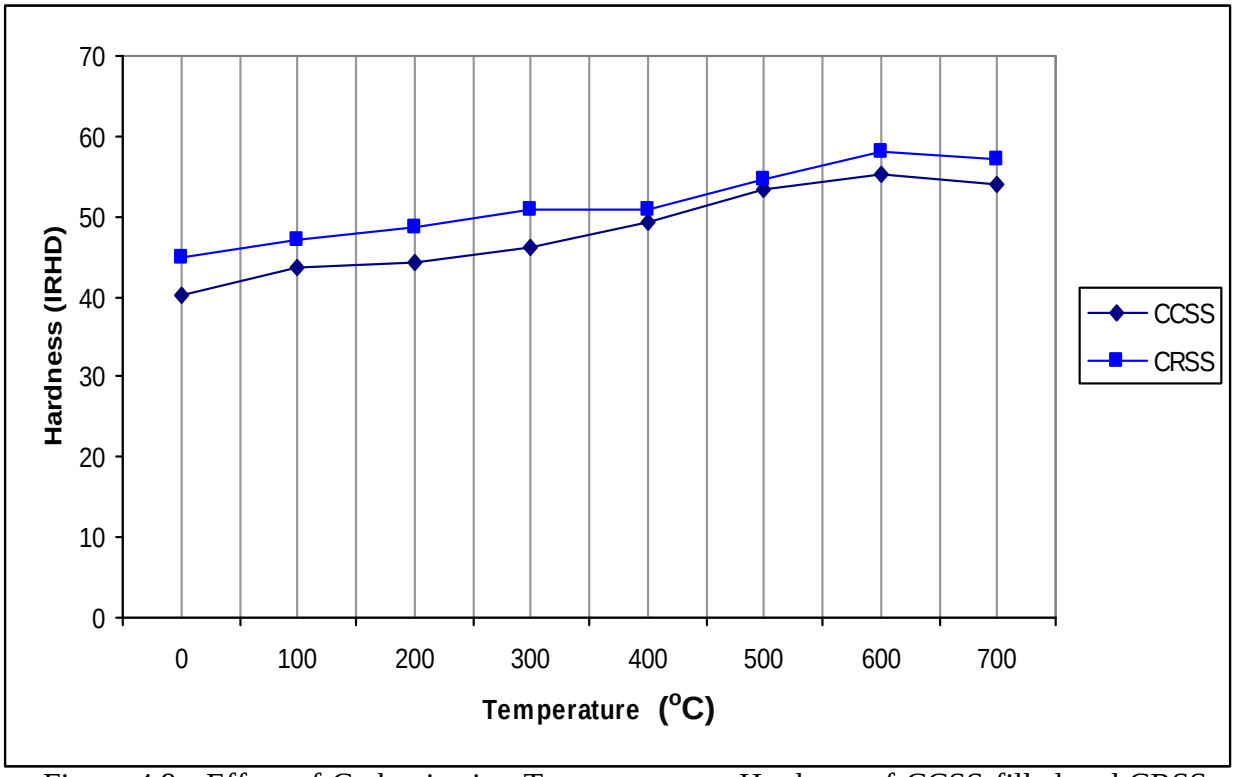

Figure 4.9: Effect of Carbonization Temperature on Hardness of CCSS-filled and CRSS-filled Vulcanizates

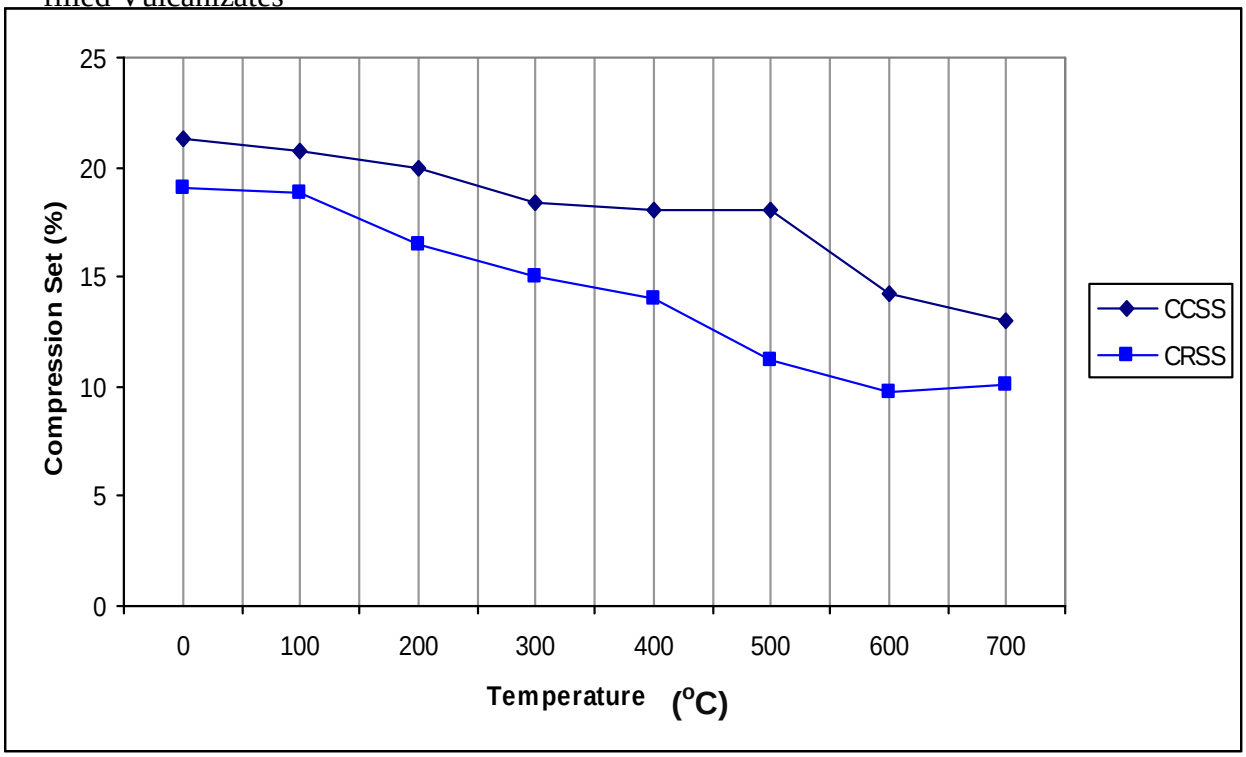

Figure 4.10: Effect of Carbonization Temperature on Compression Set of CCSS-filled and CRSS-filled Vulcanizates

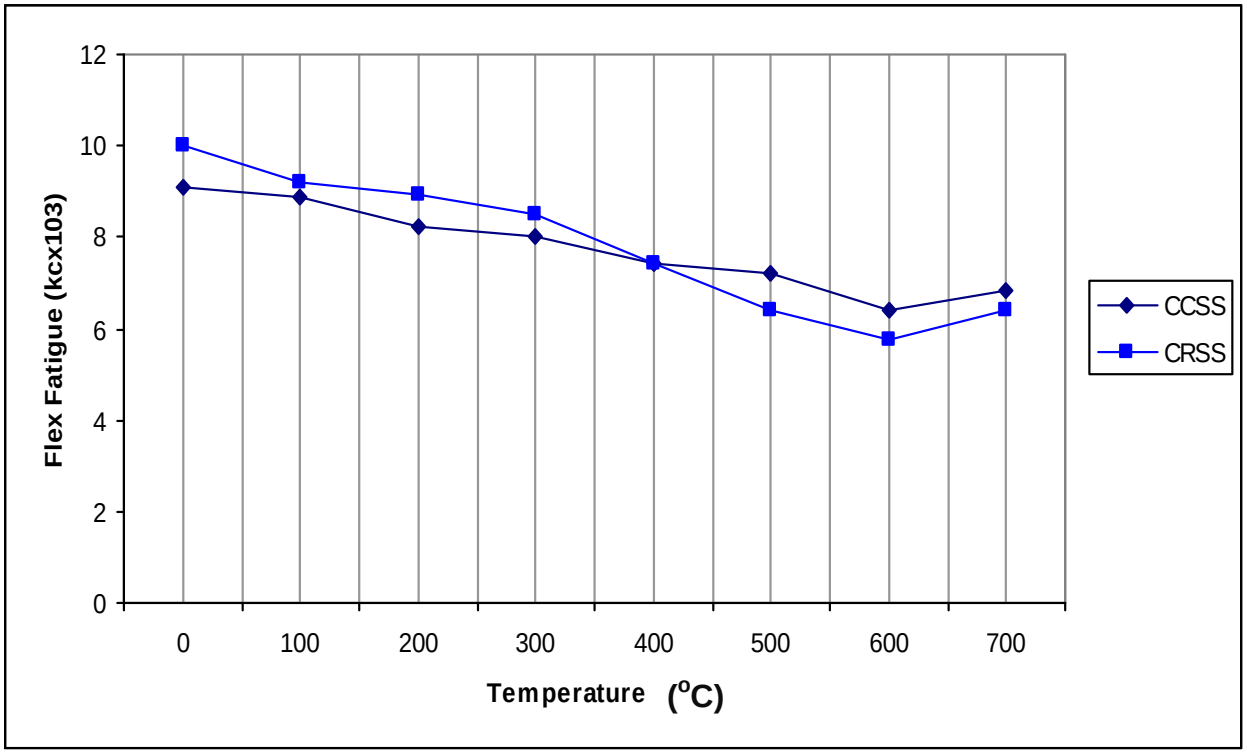

Figure 4.11: Effect of Carbonization Temperature on Flex Fatigue of CCSS-filled and CRSS-filled Vulcanizates

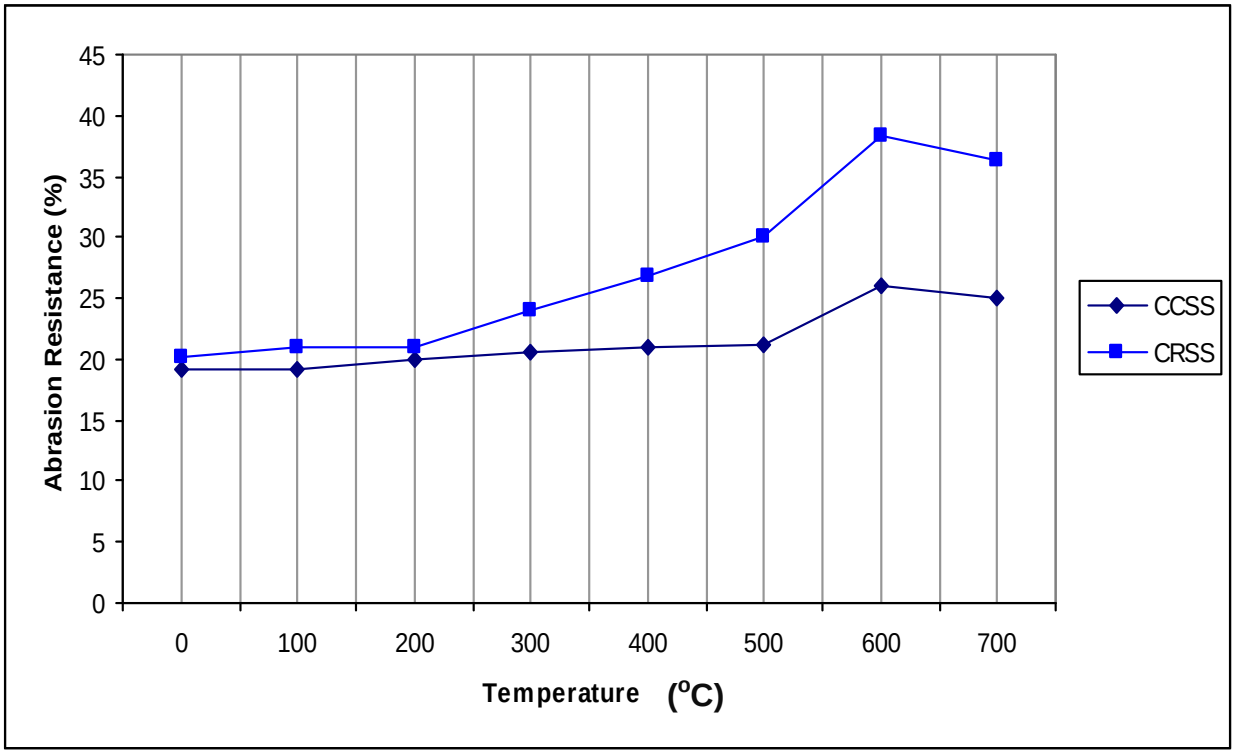

Figure 4.12: Effect of Carbonization Temperature on Abrasion Resistance of CCSS-filled and CRSS-filled Vulcanizates

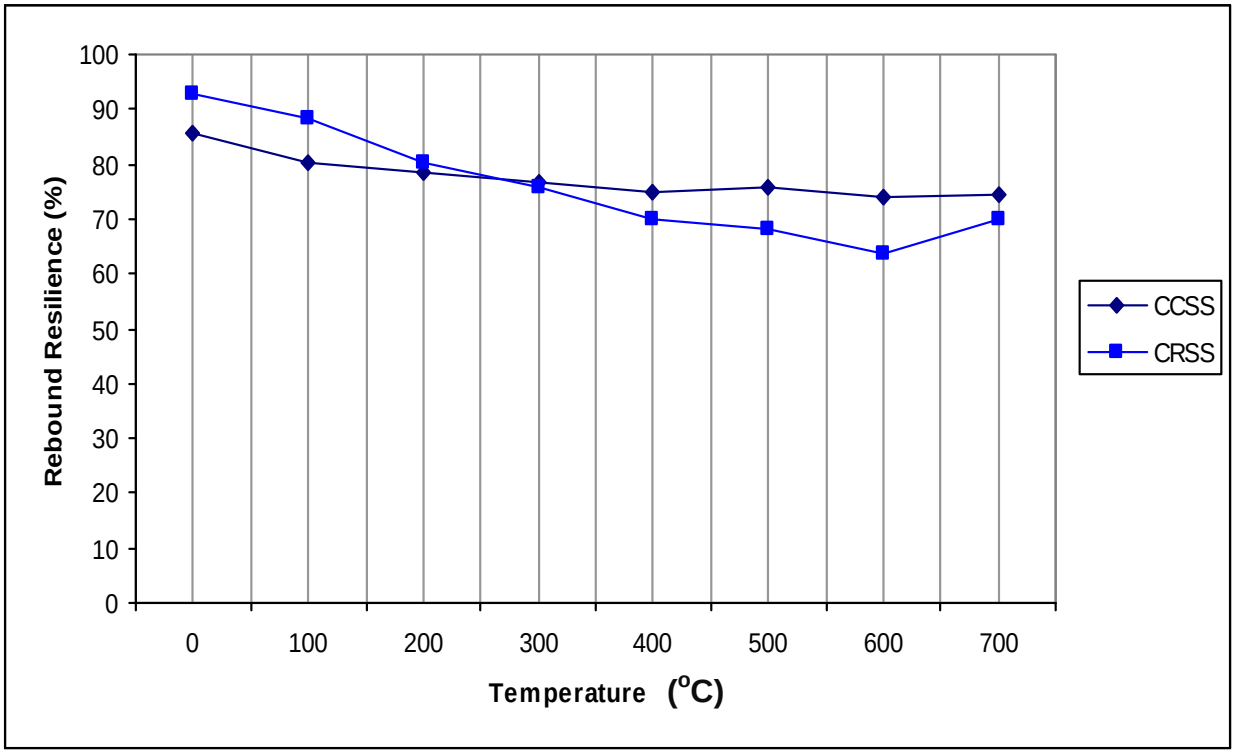

Figure 4.13: Effect of Carbonization Temperature on Rebound Resilience of CCSS-filled and CRSS-filled Vulcanizates

Table 4.3: Swelling Behaviour of the Vulcanizates

Carbonization temperature (°C)	**Cyclohexane (%)**	**Xylene (%)**	**CCl4 (%)**
100	(420) [445]	(321) [357]	(401) [421]
200	(411) [434]	(319) [332]	(397) [412]
300	(403) [427]	(314) [328]	(395) [407]
400	(401) [422]	(311) [323]	(391) [401]
500	(396) [408]	(309) [312]	(387) [389]
600	(391) [400]	(304) [308]	(368) [379]
700	(385) [392]	(293) [300]	(364) [371]
Uncarbonized filler	(473) [486]	(405) [416]	(427) [435]

Key: CCSS-filled vulcanizates ( )
CRSS-filled vulcanizates [ ]

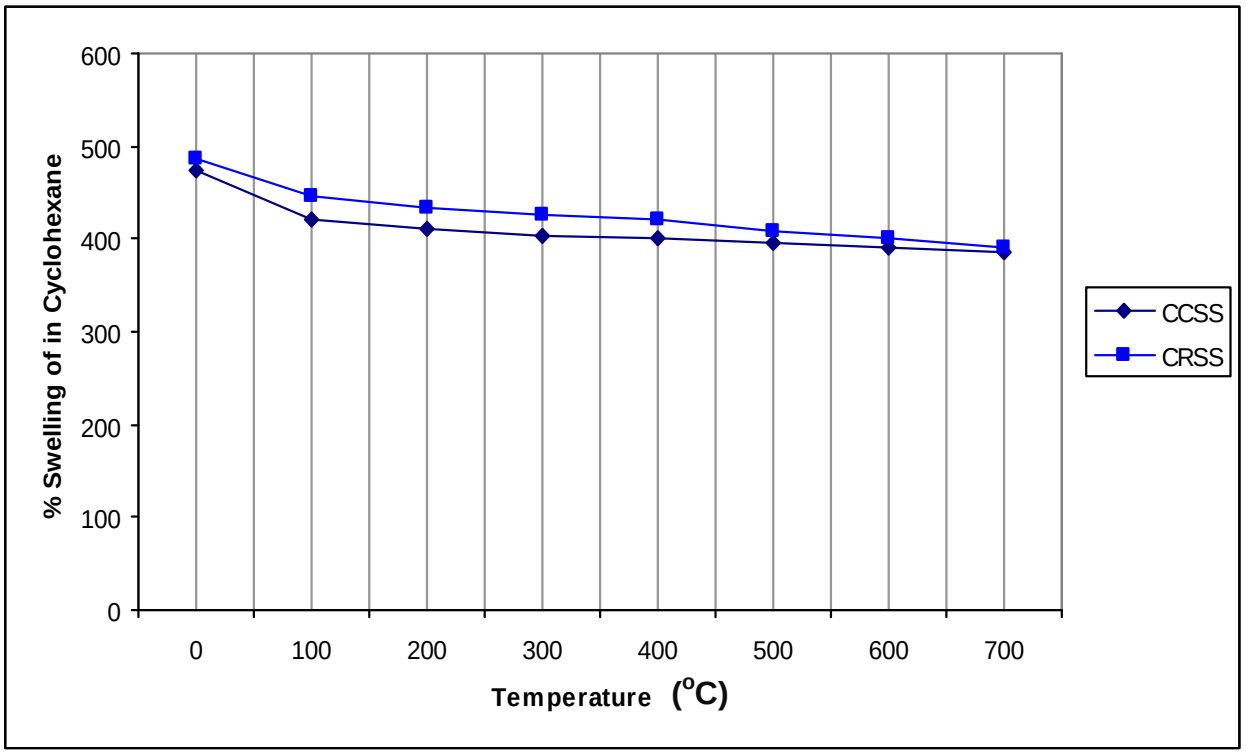

Figure 4.14: Effect of Carbonization Temperature on % Swelling of CCSS-filled and CRSS-filled Vulcanizates in Cyclohexane

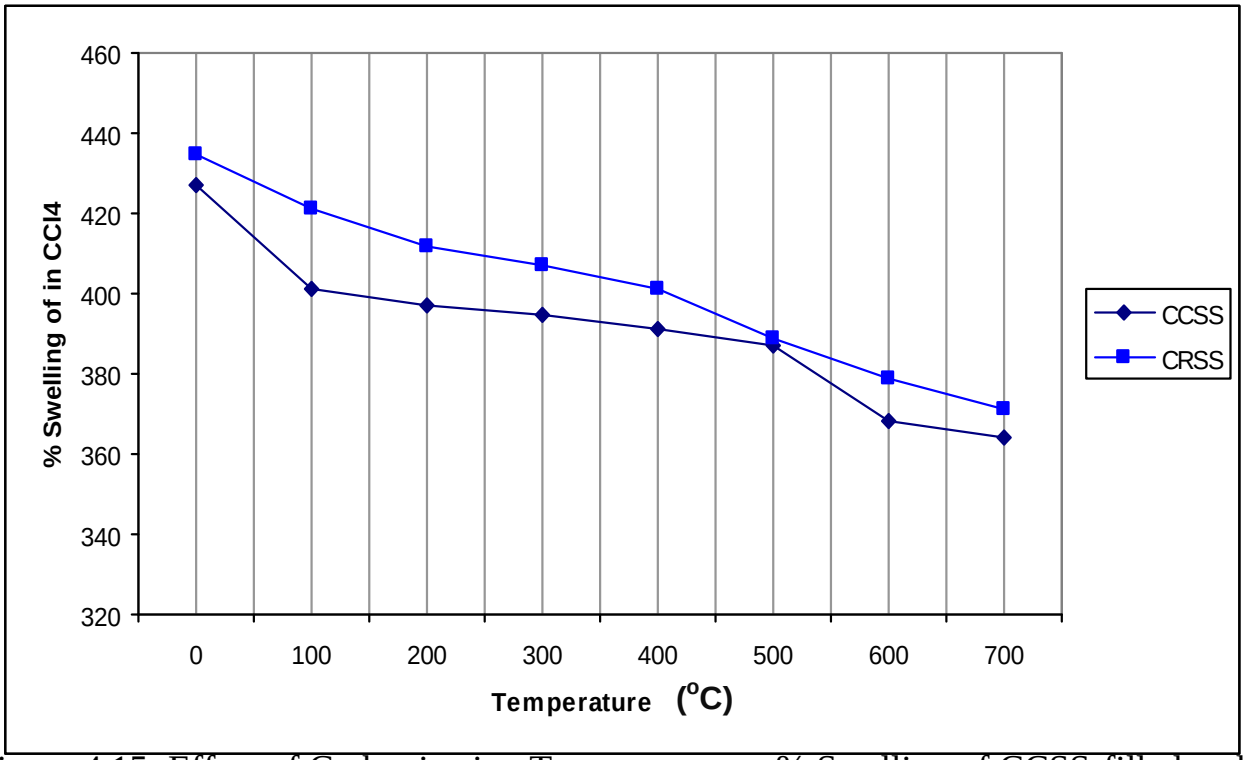

Figure 4.15: Effect of Carbonization Temperature on % Swelling of CCSS-filled and CRSS-filled Vulcanizates in CCl4

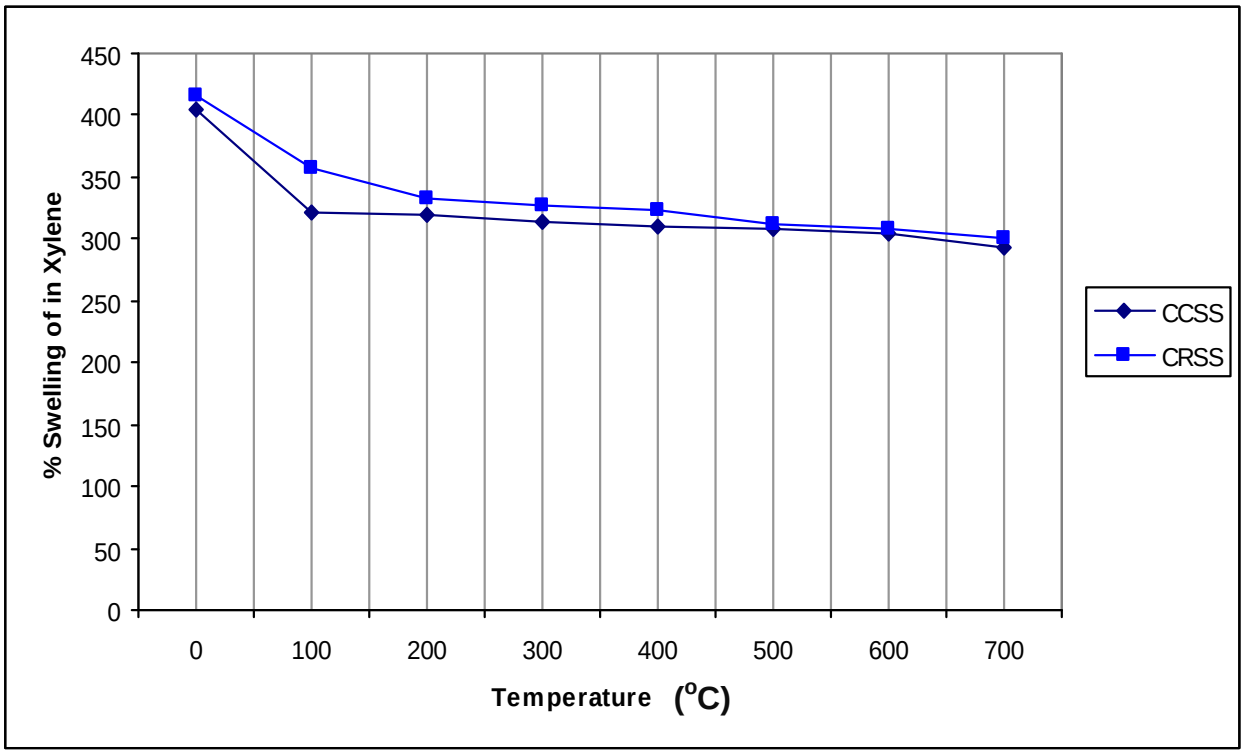

Figure 4.16: Effect of Carbonization Temperature on % Swelling of CCSS-filled and CRSS-filled Vulcanizates in Xylene

4.2 Discussion

4.2.1 Characterization of the Carbonized Fillers

The iodine value presented in Table 4.1 show the amount of iodine adsorbed per 100gram of the materials with increase in carbonization temperature. An increase in the surface activities results in higher modulus at higher strain, higher abrasion resistance and lower hysteresis (Jorts et al, 2005). The maximum iodine adsorption number 66.84mg/100g for CRSS and 79.81mg/100g for CCSS represent the adsorbed iodine which is formed when the carbonization temperature reaches 700^{o}C; eliciting the fact that the maximum surface area occurs at this temperature. At high temperature, the porosity reduces, thus, some cavities have been burnt and the corresponding surface area reduced. The iodine value is a measure of the unabsorbed iodine molecules on the carbon particles when iodine is mixed with the sample (Laka and Sheryavskay, 2007). The surface area value is much smaller when carbonizing at low temperature (100^{o}C) due to the low porosity resulting from incomplete carbonization.

The relationship between moisture contents of the fillers as a function of the carbonization temperatures is presented in Table 4.1 and Figure 4.2. The moisture content decreases from 1.90 - 0.11% for CRSS and 2.07 - 0.15% for CCSS. However, the amount of water present in a sample decreases as carbonization temperature increases since water boils at 100^{o}C. The moisture content of the filler is

often used to predict the degree of defects arising from shrinkage during curing particularly for products processed at elevated temperatures (Kamel, 2007).

Table 4.1 shows that the loss on ignition increases from 7.10 - 81.82% for CRSS and 5.95 – 82.04% for CCSS with increase in carbonization temperature. However, the loss on ignition for CCSS is higher than that of CRSS suggesting a high amount of carbon present and hence better reinforcement of natural rubber. The loss on ignition percentage increased rapidly with increasing temperature up to 700^{o}C caused by almost complete vulcanization of the volatile matter at high temperatures.

The bulk density of CRSSC and CCSS samples shown in Table 4.1 varied between 0.75- 0.66g/ml and 0.69 - 0.78g/ml respectively. Bulk density is principally influenced by the particle size and structure of the fibre and the lower the particle size, the lower the bulk density and therefore better the interaction between the polymer matrix and the reinforcing fibre which will thus enhance the vulcanizate processing and improve quality of the final product as desirable properties for fibre include excellent tensile strength and modulus, high durability, low bulk density, good moldability and recyclability (Ahmedna, et al, 1997).

The pH of the powdered fillers as a function of carbonization temperature presented in Table 4.1 varied over a range of 4.79 - 7.70 for CRSS and 5.87 – 8.99 for CCSS. The results show a progressive increase in pH from acidic to alkalinity with increase in carbonization temperature. This is possible because residuals

materials are being lost on combustion, leading to the alkalinity (Ray et al, 1989). However, pH at acidity level tends to slow cure rate and hence reduce the cross-links density (Scandola et al, 2000).

4.2.2 Results of Mechanical Properties

The results in Table 4.2 showed an increase in tensile strength with carbonization temperature of the filler up to 600^{o}C. It clearly indicates that as the temperature increases, there is a noticeable increase in tensile strength both CRSS-filled and CCSS-filled vulcanizates. The increases in tensile strength is as a result of high surface area of CCSS compared to CRSS, suggest better polymer filler interaction and hence enhanced better tensile properties for the CCSS-filled Vulcanizate than the CRSS-filled.

The modulus data in Table 4.2 showed increase with filler carbonization temperature for CCSS and CRSS up to 600^{o}C before showing a marked decrease with temperature above 600^{o}C. The fact that CCSS has a higher modulus, than CRSS suggest that fillers are more reinforcing when properly adhered into the polymer matrix.

The results in Table 4.2 shows that elongation at break (EAB) decrease with increasing carbonization temperature of the mixes for all the fillers below 600^{o}C, above which there was a gradual rise in the value of EAB. The decrease in EAB is as a result of adherence of the filler to the polymer phase leading to the stiffening of the

polymer chain and hence resistance to stretch when the strain is applied (Imanah et al, 2003).

The hardness value presented in Table 4.2 of CCSS-filled and CRSS-filled vulcanizates increased with increasing carbonization temperature. This result is expected because as more filler particles get into the rubber, the elasticity of the rubber chain is reduced, resulting in more rigid vulcanizates. The hardness results of CRSS-filled vulcanizates are higher than those of CCSS-filled.

The results of compression set in Table 4.2 show that as filler carbonization temperature increases, the compression of filled vulcanizates decreases for both CCSS-filled and CRSS-filled vulcanizates up to 600^{o}C before it start rising again. This observation is connected with the degree of filler dispersion and its particle size which may have enhanced the CCSS-filled vulcanizates (Nemour, 1986).

The values of flex fatigue presented in Table 4.2 showed decrease with increasing carbonization temperature of the mixes for all the fillers below 600^{o}C before it starts rising again which is caused by filler compactility in the polymer matrix (Conrad, 2008).

The trend of abrasion resistance with carbonization temperature of filler presented in Table 4.2 show a regular pattern of increase with increasing the filler carbonization temperature for both CCSS-filled and CRSS-filled vulcanizates. This indicates that filler carbonization temperature is a function of the measured parameter attributed to the degree of dispersion of the fillers. However the abrasion

resistance of the vulcanizates decreases above 600^{o}c, hence CCSS-filled has better abrasion resistance when compared with CRSS-filled vulcanizates.

The results of the vulcanizates presented in Table 4.2 show that CCSS-filled vulcanizates has excellent rebound resilience when stretched considerably than the CRSS-filled which has been explained in terms of filler adherence to the rubber matrix.

4.2.3 Swelling Behaviour

During immersion of the various vulcanizates in the relevant solvents, they absorbed the solvent and there were noticeable dimensional changes of the samples. A good estimate of this increase is obtained from weight increase calculations may be due to solvent pick-up by additives of volume of the vulcanizates (Ayo et, al, 2010). The results shown in Table 4.3 presents highest percentage swelling for cyclohexane for both CCSS-filled and CRSS-filled vulcanizates. This is expected because the solubility parameter of cyclohexane to natural rubber is closer than other solvents used. The solubility parameter of the relevant solvents used are; CCl_4 (8.6 $(cal/cm^3)^{0.5}$), xylene (8.8 $(cal/cm^3)^{0.5}$), cyclohexane (8.2 $(cal/cm^3)^{0.5}$) while that of natural rubber is 8.3$(cal/cm^3)^{0.5}$). However, the CCSS-filled vulcanizate show high resistance to swelling when compared with CRSS-filled vulcanizates in the relevant solvents. This may be explained in terms of adherence of the filler to the polymer phase leading to the stiffening of the polymer chain and hence resistance to solvent when immersed.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This study has revealed the effect of filler carbonization temperature of the cherry and rubber seed shells on its characteristics properties and hence the mechanical properties of natural rubber vulcanizates. The fact that CCSS has a higher modulus, better abrasion resistance and excellent rebound resilience, higher resistance to swelling when compared to CRSS filled vulcanizates. The result showed that CCSS filler is more reinforcing for natural rubber compound than CRSS filler. The results indicate that mechanical and swelling behaviour of the vulcanizates are greatly influenced by filler carbonization temperature and are therefore significant factor in determining the application in rubber compounding. The vulcanizates exhibit high quality characteristics at filler carbonization temperature (600^{o}C).this indicate that for high quality vulcanizates using both cherry and rubber seed shell as reinforcing fillers, carbonization should be done at 600°C for 3 hours

5.2 Contribution to knowledge

In the study has been well established that;

i The underutilized agricultural by- product CSS and RSS can be used as reinforcing filler in the rubber industry.

ii the filler carbonization temperature has actually improved the potential of CSS and RSS as filler in compounding natural rubber

iii The physical properties (loss on ignition, bulk density, iodine adsorption number, moisture content) and mechanical properties(tensile strength, abrasion resistance, compression set, flex fatigue, modulus) are greatly influenced by filler carbonization temperature

5.3 Recommendation

In order to modify and establish these research findings, the following recommendations have been suggested:

i. The future researcher should carry out the chemical treatment of CSS and RSS filler to investigate their reinforcing potential.

ii. The rheological behavior of the material should be investigated by carrying out the cure characteristics.

iii. From my evaluation optimum properties was obtained at carbonization temperature of 600^0C, therefore I want to recommend that future researcher should carry out carbonization temperature of CSS and RSS at 600^0C and then vary the filler loading of the composite to see the effect of the composite.

iv. The future researcher should carry out thermal properties of the vulcanizates to investigate the effect on the thermal degradation.

REFERENCES

Ahmedna, M., Johnson, M., Clarke, S.J., Marshal, W.E. and Rao, R.M. (1997):

Akpa, F.A.O. (2005) A: Polymers in Engineering Applications, 1st Edition, Jireh Publisher, Benin City, Nigeria, 14-20.

Akpa, F.A.O. (2005) B: The Synthesis and Conversion Processes of Polymers, 1st Edition, Jireh Publishers, Benin City, Nigeria, 41-62.

Allcock, H.R. and Lampe, F.W. (1990): Contemporary Polymer Chemistry, 2nd Edition, Prentice Hall Inc., New Jersey, 68-79.

Asore, E.J. (2000): An Introduction to Rubber Technology, 1st Edition, Joseg Book Limited, Benin City, Nigeria, 45-56.

Asore, E.J., Imanah, J.E. and Idiaghe, J.A. (2010): Principle and Techniques of Polymer Blends and Composites, Ribway Printers and Publishers Limited, Benin City, Nigeria, Vol 1, 23 - 30.

ASTM-D 1509: Standard Test Method for Moisture Content (1983)

ASTM-D 1512: Standard Test Method for PH (1983).

ASTM-D 3010: Standard Test Method for Swelling Behaviour of Composites (1983).

ASTM-D 3184- 80: Standard Test Method for Compounding Rubber (1983).

ASTM-D 385: Standard Test Method for Compression Set (1983)

ASTM-D 412 - 87: Standard Test Method for Tensile Strength (1983)

ASTM-D 430: Standard Test Method for Flex Fatigue of Compounded Rubber (1983).

ASTM-D 7348: Standard Test Method for Loss on Ignition (1983)

Ayo M. D, Madufor I. C, Ekebafe L. O, Chukwu M. N (2010): Effects of Carbonization Temperature on The Mechanical and Swollen behaviour of Natural Rubber Filled Groundnut shell, Researcher, Vol 3, No 11, 212-214.

Ayo M.D, Ekebafer L.O, Chukhu M.N and Madufor I.C (2011): Effect of Carbonzation Temperatures of the Filler Properties of Groundnut Shell Powder. International Journal of Chemistry Vol. 21 No 3, 55-58.

Blow, C.M. and Hepburn, C. (1971): Rubber Technology and Manufacture, 3rd Edition, Butterworth and Company Limited, London, 215-219, 355.

Breathy, J.R. (1986): Rubber Chemistry Technology, 3rd Edition, Butterworth and Company Limited, London, 25.

BS903 Part A26: Standard Test Method for Hardness Test (1983).

Chukwu, M.N. (2002): An Introduction to Rubber Technology, Formulation and compounding, 1st Edition, Anibik Press Publication, Benin City, Nigeria, 5-38.

Chum H.L and S.K Parker, (1985): The Economics Contribution of Lignins To Ethanol Production From Biomass, Solar Energy Research Institution, 231-2488.

Crawford, R.J. (1998): Plastic Engineering, 3rd Edition, Butterworth Heinmann, Library Cataloguing in Publication Data, Britain, 168 -188.

Eichhom, S. J., Baillie, C. A., Zafeiropoulos, N., Mwaikambo, L.Y., Ansell, M. P. and Dufresne, A. (2001): Current International Research into Cellulosic Fibres and Composites, Journal of Material Science, Vol. 36, No. 9, 2107-3144.

Ekebafe L.O, Ekebafe M.O and Akpa F.A.O (2011); Effect of Chemically Modified Powdered Rubber Seed Shell as Filler on the Rheological, Tensile and Equilibrium Swelling Properties of Natural Rubber Compounds, Journal of Chemical Society of Nigeria, Vol. 36, 70-77.

Ekebafe L.O., Ayo M.D. Eguare, K.O.and Ugbesia S.O. (2010): Effect of Chemical Modification of Powdered Rubber Seed Shell as Filler on the Tensile Properties of Natural Rubber Compounds. Journal of Polymer Science and Technology, 1113-1119.

Fried, J.R. (2005): Polymer Science and Technology. 2nd Edition, Prentice Hall Incorporation, New Delhi, 102-107.

Hepworth, D.G., Hobson, R.N., Bruce, D.M. and Farrel, J.W. (2000): The use of Unretted Hemp Fibre in Composite Manufacture. Composite Part A, Vol. 31, 1279 - 1283.

Iannace, S., Ali, R.and Nicolaise, L.E. (2001): Processing Conditions on Dimensions of Sisal Bers in Thermoplastic Biodegradable Composites. Journal of Applied Polymer Science 7 C Page 6.

Imanah J.E, and Okeimen F.E. (2004): Studies in the Mechanical Properties of Natural Rubber Reinforced with Agricultural by–Products, Proceedings of the 27th International Conference of the Chemical Society of Nigeria, 317-322.

Imanah, J.E. and Okieimen, F.E. (2003); Physico-Mechanical Properties of Natural Rubber Composite, Journal of Applied Science, Vol. 9, 3718-3722.

Ishak, Z. A. M. and Baker, A. A. (1995): Natural Rubber Blends abd Properties, European Polymer Journal, Vol. 31, No. 3, 259 – 269.

Jorts, J.W, Shay, J. Imam, S.H Glem, G.M. Guttmenn M.E. Rovel J.F, (2005), Application of Cellulose Microfibrills in polymer Nanocomposites. Journal of polymers and the Environment Vol. 13, No 4, 301-306.

Kalia S. Kaith B.S and Kar. I (2009): Pre-Treatment of National Fibres and their Applications as Reinforcing materials in polymer Composties: A Review. Polymer Engineering and Science Volume 313-323.

Kamel J. (2007): Nanotechnology and its application in lingocellulosic composites, A Mini review, Express Polymer letters, Vol. 1, No. 9, 546-550.

Komolafe, N.F., Adebola, A. A., Are, L. A. and Ashaye, T.I. (1980): Agricultural Science for West African Schools and Colleges, 2nd Edition, Oxford University Press, Ibadan, 55-63, 114.

Laka J.M. and Shernyavskay S. (2007), Obtaining Crystalline Cellulose from Softwood and Hard Wood Pulp, Bio Resources, Vol. 2, No 3, 583-589.

Lawrence, E.N (1974): Mechanical properties of Polymers and Composites, Marcel Dekker Intl, New York, Vol. 2, 76.

Mizahur, M., Mubarak, A. and Khan, B. (2007): Surface Treatment of Coin (Locos Nucifera) Fibres and Its Influence on the Fibre Physico-Mechanical Properties, Vol. 5, Page 117.

Mohanty, A. K., Misra, M., Aizal, L.T. and Kellys (2001): Surface Modification of Natural Fibres and Performance of the Resulting Biocomposites, An Overview of Composite Interfaces, Vol. 8, Page 5.

Nakagaito A.N, Iwamoto, S and Yano S. (2005), Bacterial Cellulose the Ultimate Nano-Scalar Cellulose Morphology for the Production of High – Strength Composites Applied Physics A, vol. 80. No 1, 93.97.

Nemour. E. I. (1986): Polymer Products Technology, Department of Languages of Rubber, 1st Edition, 120, Washington.

Okieimen, F. E. and Akinlabi, A.K. (2002): Processing Characteristics and Physic
Mechanical Properties of Natural Rubber and Liquid Natural Rubber Blends, Journal of Applied Polymer Science, Vol. 85, 1070-1076.

Ray R.G, Kokta, B.K, Maldas D and Daneault C (1989): Use of Wood fibres in Thermoplastic; the effect of coupling agents in Polyethylene Wood Polymer Science 37:1189-1193.

Rowel R.M (1990): Chemical Modification of Wood: its Application to Composite Products, Proceedings, Composite Products Symposium, Rotorua, New Zealand, 432-435.

Scandola M. Frisoni G and Bariando M. (2000): Chemically Modified cellulosic reinforcement. 219th AC5 national Meetings, san Francisco, 26-30.

Sharma, B.K. (2006): Industrial Chemistry, 1st Edition, Goel Publishing House, Darya Ganj, New Delhi, 18.

Silva, L.G. and AI-Qurasshi, H.A. (1999): Mechanics of Wetting System of Natural Fibres with Polymeric Resin, Journal of Material Process Technology, Vol. 12, Page 89.

Ski, K. B. (1990): Engineering Materials Proportion and Selection, Reston publishing company, 40.

Sukru, Y.O., Zlem, C, and Ahmet, C. (2008): The Effects of Fibre Contents on the Mechanical Properties of Adobes, Construction and Building Materials, Vol. 6, Page 22.

Whelan, A. and Lecks (1997): Developments in Rubber Technology, Applied Science Publishers, 1st Edition, London, 36.

Yemi, S. C. (1986): Encyclopedia of Polymer Science and Technology, Inter-Science, New York, Vol. 4, 102.