PHYSICO-MECHANICAL PROPERTIES OF NATURAL RUBBER FILLED WITH TREATED GROUNDNUT SHELL POWDER FOR SHOE SOLE PRODUCTION

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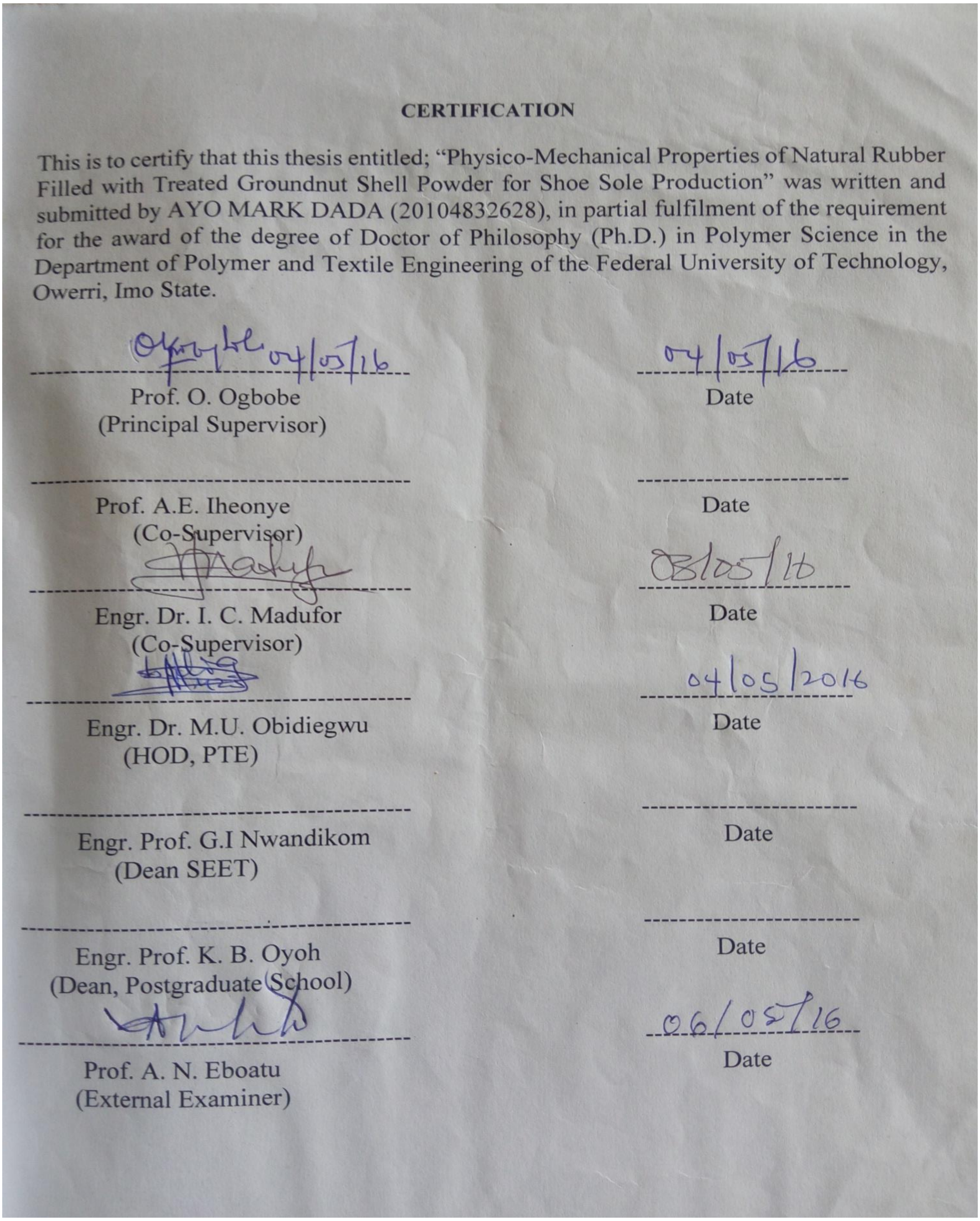

CERTIFICATION

This is to certify that this thesis entitled; "Physico-Mechanical Properties of Natural Rubber Filled with Treated Groundnut Shell Powder for Shoe Sole Production" was written and submitted by AYO MARK DADA (20104832628), in partial fulfilment of the requirement for the award of the degree of Doctor of Philosophy (Ph.D.) in Polymer Science in the Department of Polymer and Textile Engineering of the Federal University of Technology, Owerri, Imo State.

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DEDICATION

Dedicated to God Almighty for His infinite mercies and grace upon me and my family.

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CR: Crepe Rubber	11
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TSR: Technically Specified Rubber	12
SMR: Standard Malaysian Rubber	13
SIR: Standard Indonesia Rubber	13
SAR: Standard African Rubber	13
NSR: Nigerian Standard Rubber	13
PRI: Plasticity Retention Index	13
SMR CV: Standard Malaysian Rubber Constant Viscosity	13
RHC: Rubber Hydrocarbon	14
Phr: Parts per Hundred Rubber	18
UV: Ultra Violent	18
Bc: Before Christ	27
Ad: After Christ Died	27
PMCS: Polymer Matrix Composites	30
MMCS: Metal Matrix Composites	30
CMCS: Ceramic Matrix Composites	31
CCS: Carbon- Carbon Composites	31
V_m: Volume fractions of the Matrix	32
V_f: Volume fractions of the Fibre	32
$\Sigma_{c:}$ Density of the Composite	32

Σ_{m}: Density of the Matrix	32
Σ_{f}: Density of the Fibre	32
E_c: Modulus of Composite	33
E_m: Modulus of Matrix	33
E_f: Modulus of Fibre	33
MBT: 2-Mercaptobenzothiazole	38
CBS: N- cyclohexylbenzole-2- sulphenamide	39
TMTD: Tetramethyl thiuram disulphide	39
ZDMC: Zinc dimethyl dithio carbamate	39
PPD: Paraphenylediamine	41
$BaSO_4$: Barium Sulphate	43
$CaCO_3$: Calcium Carbonate	43
S_x: Polysulphidic Cross-links	47
S_1: Mono Sulphidic Network	48
S_2: Disulphidic Network	48
ENM: Extra Network Materials	48
MRPRA: Malaysia Rubber Producer Research Association	51
MgO: Magnesium Oxide	53
PbO: Lead Oxide	53
T_g: Glass Transition Temperature	53
TMQ: Trimethylquinoline	56
BDH: British Drug House	56

NaOH: Sodium Hydroxide	57
ASTMD: American Standard for Testing Material Department	60
GNS: Groundnut Shell	65
IRHD: International Rubber Hardness Degrees	67
MPa: Megga Pascal	67
ANOVA:Analysis of Variance	70
SST: Sum of Squares Total	70
SSTr: Sum of Squares Treatment	70
SSE: Sum of Squares Error	70
MSS: Mean Sum of Squares	70
LSD: Least Significant Difference	72
DMR: Duncan Multiple Range	72
SPSS: Statistical Package for the Social Sciences	73
UT: Untreated	85
FTIR: Fourier Transport Infra-red	169
C=C: Carbon-Carbon Bond	169
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ABSTRACT

Physico-Mechanical properties of natural rubber filled with chemically modified groundnut shells were studied. Natural rubber composites were prepared using modified fillers at varying concentrations of sodium hydroxide (NaOH) Solution and acetylating solutions respectively. The processing conditions, mechanical properties and sorption characteristics of these composites were analyzed. The cure characteristics of the compounded rubber were determined using Mosanto Rheometer (model MDR - 2000). The maximum torque and crosslinking density increases with increase in concentration of the mercerizing and acetylating agent. The fibre reinforcing efficiency of the chemically treated composites were compared with that of the untreated composite. Composites containing chemically treated fillers were found to posses improved tensile properties(from 18.30 to 31.50MPa for acetylated composites and 18.30 -28.00MPa for mercerized fillers), hardness (48 to 65 IRHD for acetylated filler and 48 to 58 for mercerized fillers) and abrasion resistance (from 31.55 t0 42.50% for acetylated filler and 31.5 to 39.30 for mercerized filler). These properties increases with increase in mercerizing and acetylating agent up to 20% concentration and starts decreasing. At higher concentration, the fibre is destroyed hence reduction in properties. These results were in agreement with empirical analysis. The sorption properties of the composite also decrease with the concentration of the mercerizing and acetylating agent. The improved properties observed were as a result of the increase in affinity between the rubber matrix and the chemically treated groundnut shell fillers. From this research work, it is recommended that chemically treated groundnut shell powder, particularly at 20% concentration can be employed for articles such as shoe soles, footmats and hoses that require less stress during service life.

Keywords: Modified, Shell, Mercerization, Acetylation, Composite, Cross-linking, Sorption, Fillers, Matrix.

CHAPTER ONE

INTRODUCTION

1.1 Background of Study

Agro-base resources, also referred to as lignocelluloses, are resources that contain cellulose, hemicelluloses, and lignin. Lignocelluloses include wood, agricultural residues, water plants, grasses, and other plant substances (Rowell, 1998). The upsurge in the interest of natural fibres in biocomposites has grown because of their lightweight, nontoxic, low cost and easy to recycle. The emergence of polymers in the beginning of the 19th century ushered a new era of research with a new option of using the natural fibres in a more diversified fields. Many people have tried to use various agricultural by-products as fillers in compounding polymers. These fillers are either used raw or modified. This resulted in a large number of modifications to bring it at par with and even superior to synthetic fibre. Because of such tremendous changes in the quality of natural fibres, they are fast emerging as a reinforcing material in composites (Rowell, 1998). Fowler et al. (2006) stated that materials from renewable resources are being sought after as a replacement not only as the reinforcement elements, but also the matrix phases of composite materials. It is not surprising; therefore, that a large number of researchers judging from the volume of reports in the scientific literatures are working in the area. Fowler et al. (2006)

Rubbers as one of the classes of polymers have found great important applications in engineering, sport, leisure and domestic applications. In its raw state, rubbers may not be good enough for any useful application, so there is the need for the inclusion of additives which help to enhance their properties. Among these additives are varieties of different fillers. Carbon black is the major filler used in the rubber industry. Today there are lots of researches going on to find alternatives for it (Ayo et al., 2011). Advances are being made in the use of agricultural by products, such as rice husk, dika-nut shell, groundnut shell, melon husk etc in the manufacture of rubber composites (Ekebate et al., 2010). These materials are used in their raw form or modified before use.

A better understanding of the chemical composition and surface adhesive bonding of natural fibres is necessary for developing natural fibre reinforced composites. The composition of natural fibre include; cellulose, hemicellulose, lignin, pectin, fat, waxes and water soluble substances (Li et al., 2007). The natural fibre exhibit a high hydrophilicity due to attraction or interaction between hydroxyl groups of fibre components and water molecules. The interaction between fibre and water originates from the non-crystalline region and extends to the crystalline region (Bledzki et al., 2008). The uptake of water by hygroscopic substances such as cellulose and hemicellulose is a hydration process involving accessible hydroxyl groups. Water molecules absorbed by cellulose molecules form cellulose hydrate and the reactions are exothermic which provides the driving force for further absorption (Pizzi and Eaton, 1987). The high moisture content sensitivity of lignocellulose fibre causes dimensional instability and limits the use of these fibres as reinforcement in composite materials. In this present work groundnut shell is chosen because of it’s availability. Additionally, previous work by Ayo et al., (2011) gave results which indicated that it has a great promise as filler.Chemical treatment of the fibre can stop the moisture absorption process, clean the fibre surface, and chemically modify the surface or increase the surface roughness, by decreasing the hydroxyl groups which may be involved in hydrogen bonding within the cellulose molecules (Scandola et al., 2000). Research on a cost effective modification of natural fibres is a necessity since it is the main attractions for today’s market of bio-fibres. However, in Nigeria, these fibres are regarded as agricultural waste and are abundantly available. Imanah and Okieiemen (2010) found out that rubber seed shell is reinforcing but nothing has been reported on the use of groundnut shell as filler for rubber products.

1.2 Problem Statement of Study

In recent years, interest has grown in the use of natural fibres in the development of product biocomposites, probably because they give rise to light weight, non-toxic, low cost and easy to recycle products. On the other hand, lack of good interfacial adhesion and poor resistance to moisture absorption makes the use of natural fibres to be unattractive. Moisture absorption can result in swelling of the fibres which may lead to micro -cracking of the composite and degradation of mechanical properties. Chemical treatment of the fibres can reduce the moisture absorption process, clean the fibres surface, and chemically 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

1.3 Objectives of Study

The main objectives of this project work is to study the physico-mechanical properties of natural rubber filled with treated groundnut shell powder for shoe sole production.

The specific objectives are:

i. to determine the effects of mercerization and acetylation on groundnut shell characteristics.

ii. to determine some mechanical properties of the products such as tensile strength, modulus, elongation at break, hardness, abrasion resistance, compression set, flex fatique and impact strength.

iii. to determine the effect of relevant solvents on the swelling behaviour of the products.

1.4 Justification of Study

Natural fibre represents a good renewable and biodegradable alternative to the most common synthetic reinforcing materials. It is expected that the success of this research work will help to reduce the price of rubber products. It has the potential of widening rubber products for a variety of different applications. It will also provide additional income to farmers as groundnut shell will no longer be wasted but useful in the production of rubber articles.

1.5 Scope of Study

This work would be limited to production of shoe sole (rubber vulcanizate) using mercerized and acetylated ground nut shell powder as filler and carrying out tests on the products to evaluate the cure characteristics, mechanical properties and swelling behaviour in relevant solvents.

CHAPTER TWO

LITERATURE REVIEW

2.1 Elastomers

The modern elastomer industry was founded on the naturally occurring product isolated from the latex of the tree Hevea brasiliensis. It was used by South Americans and Indians and was called caoutchouc from the Indian name but later sampling rubber, when it was discovered by J.P priestly that the material was able to rub out pencil marks (Ruys et al., 1999). Whelan and Lecks (1997) defined elastomer or rubber as a material that is capable of undergoing very great recoverable deformation when stresses are applied. Smith (1993) in his own definition, stated that rubber or elastomer is a material which at room temperature can be stretched repeatedly to at least twice its original length and upon immediate release of the stress will return with force to its original length.

2.1.1 Characteristics of Elastomers

Elastomers are characterised by:

a. Rapid and considerable stretching under tension with elongations in the range of 500 – 1000% at low damping (i.e. little loss of energy).
b. High tensile strength and high modulus (stiffness) when fully stretched.
c. Rapid retractions with snap or rebound behaviour.
d. Fully recovering of original dimensions upon the release of stress, exhibiting resilience and low permanent set.
e. Increase in modulus with increasing temperatures

The molecular requirement for rubber- like behaviour was reported by Blow and Hepburn (1971) as follows:

i. The materials must be high molecular weight polymers.
ii. The temperatures must be above Tg to obtain high local segmental mobility.
iii. The materials must be amorphous in its stable (unstressed) state for same reason as in ii.
iv. It must contain a network of cross-links to restrain gross mobility of its chain.

Rubbers are loosely described as materials which show elastic properties (Smith, 1993). Such materials are generally long chain molecules known as “polymers” and the combination of elastic and polymer has led to the alternative name of ‘elastomers’ (Smith, 1993).

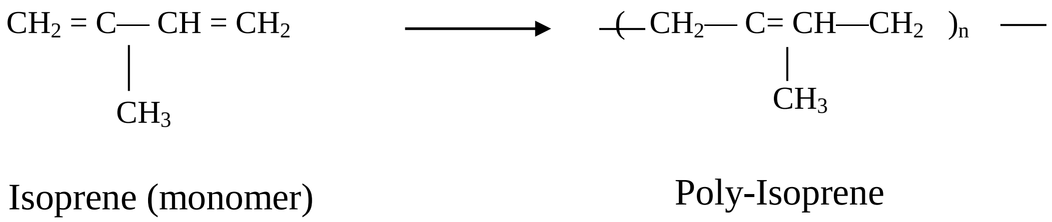
2.1.2 Classification of Rubbers

Rubbers are classified as:

a. Natural or synthetic i.e by source
b. General purpose or special purpose i.e by application (Chukwu, 2002).

2.2 Natural Rubber

Natural rubber is source from many species of tropical plants. The most outstanding commercially available is the Hevea brasilinesis (Driver, 1979). It is indigenous to South America (Brazil). They grow well in Malaysia, Indonesia, India, Ivory Coast and Nigeria (Ekebafe et al., 2010). The other variants of Hevea brasiliensis are the Gutta percha and Balata. Gulta percha is obtained from latex of trees grown mainly in Malaysia and Indonesia. Balata, on the other hand is obtained from the latex of trees grown mainly in Central America. The hydrocarbon components of natural rubber consist of over 85% of linear cis-1, 4 poly-isoprene and the remaining being trans isomers (Chukwu, 2002). Most commercial natural rubbers have mooney viscosity value of about 60 ±when freshly coagulated (Ekebafe et al., 2010). Commercial rubbers obtained from cloned blends may have average molecule weights of 1.0 - 1.5 x 1.6 and number average molecular weight of 3.0 x 10^5 - 5.0 x 10^5.



$$\mathrm{CH_2 = \underset{\displaystyle CH_3}{\underset{|}{C}} - CH = CH_2 \longrightarrow -\!\left(CH_2 - \underset{\displaystyle CH_3}{\underset{|}{C}} = CH - CH_2 \right)_n -}$$

Figure 2.1: formular of Poly-Isoprene (Chukwu, 2002)

2.2.1 Production of Natural Rubber

On wild or in the plantation, the Hevea trees are up to 30metres tall above ground level and deciduous in nature (Ihuezor and Ayo, 2010). In order to obtain the latex, the trees are tapped using tapping knife, which create systematically controlled cuts on the bark of the hevea tree. The latex, milky in colour flows from the cuts on the bark of the tree and it is collected in small cups. If anticoagulant such as ammonia is added to the small cups prior to collection of the latex retained for a reasonable period and enables the taper store enough quantity of the latex in plastics cans up to 40 litres in volumetric scale. When the taper had gathered enough quantity of latex, it is sent to a central processing unit where the latex is diluted to solid content of about 15 - 20% and coagulated naturally or by the use of acids usually formic or acetic acid (Ihuezor and Ayo, 2010). The coagulum either as sheet or lump is further processed into solid dry rubbers. Essentially, local tapers allow their latex to coagulate under natural conditions. Conventionally, field latex and cup lumps can be processed into the different types of dry rubber viz.:

2.2.1.1 Crepe Rubber (CR)

Crepe rubber is obtained by treating the latex with a bleaching agent and then coagulated with an acid. The coagulum is then passed through a series of rollers driven at frictional speed. The sheets obtained are then dried by circulation of warm air (45 - 50^{o}C) for about 7 - 10days.

2.2.1.2 **Ribbed Smoked Sheet (RSS)**

The production of ribbed smoked sheet basically involves the coagulation of latex from 30 - 45% dry rubber content (Ekabafe *et al.,* 2010). The latex is first sieved and acid coagulated to obtain coagulum free from microbial attack before and during drying in some houses. The coagulated latex in partitioned aluminum through is then passed through evenly derived ribbed tools to obtain the ribbed sheet. The thickness of the sheet is within the range, 2mm- 5mm thick and the drying period of one week is advocated at a temperature range of 40 - 60^{o}C depending on the thickness of the sheet (Ekebafe, 2010). The smoke for drying is generated from burning wood, coconut shells etc. At the expiration of drying period, the dried sheets are taken to inspection sections for visual examination, any defects, such as undried portion, void, blister or burnt portion are cut off with the aid of a pair of scissors by the quality control staff. Light or dark brown coloured ribbed smoked sheets (depending on the age of trees and colonial variety from which the latex are obtained are then baled into 101kg (one hundred and one kilogram) of square or rectangular shape, rubbed with talcum powder to prevent self adhesion and stored at room temperature awaiting sales or shipment.

2.2.1.3 Technically Specified Rubber (TSR)

In this group of rubbers, coagulated latex is converted using slab-cutters, pre-breakers, turbo mills, creepers, hammer mills, granulator extruders and shealers to reduce the size of the lumps to granules for easy drying. Some quantity of castor oil (diluted) is added at the last stage prior to loading into the drier boxes so as to reduce or eliminate self adhesion of the rubber granules. At the drier end, the stainless steel boxes which comprises of 12 partitions aided with perforated stainless steel trays are carefully loaded with granulated rubber. Before loading the rubber granules filled stainless steal boxes into the drier, the temperature of the oven must attain 100 - 150°C. The total drying period for crumbs rubber had been calculated and found to be between 4 - 5 hours (Asore, 2000). The dried crumb rubber are weighed into 33.33kg or 35kg and compressed into rectangular shape bales which are covered and packaged with transparent polyethylene films. The polyethylene wraps bales are then loaded into wooden pallets. To classify this type of dry natural rubber as technically specified rubber, samples are cut from the alternate opposite edge of the rectangular bale at a regular interval of every six bales and these samples are taken to laboratory for quality assessment tests. The test result is then used for grading the rubbers.

2.2.2 Grades of Natural Rubber

Natural rubber is available in many grades related to its dirt content and precise methods of production. Popular grades are ribbed smoke sheet (RSS), crepe rubber and technically specified rubber such as standard Malaysian rubber (SMR), standard Indonesia rubber (SIR), standard African rubber (SAR) and Nigerian standard rubber (NSR). The sub grades are RSS1 - RSS5, SMR5, 10, 20 and SMR 50 and NSR5, 10, 20 and NSR 50. They are graded based on dirt content, ash content, volatile matter, plasticity retention index (PRI) and nitrogen content. The lower the ash content, dirt content and volatile matter, the cleaner the grade, and therefore the more expensive. Another special grade of natural rubber is the standard Malaysian rubber constant viscosity (SMR CV). This grade has 0.15% of hydroxylamine salt added to prevent a cross linking phenomenon known as storage hardening; which will cause an increasing viscosity during storage.

Table 2.1: Standard Malaysian Rubber Specification (Bryson, 1967)

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**	**0.60**	**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**
Wallace rapid plasticity	**-**	**-**	**30**	**-**	**30**	**30**	**30**
Plasticity retention Index	**60**	**60**	**60**	**50**	**50**	**40**	**30**

2.2.3 Chemical Composition and Structure of Natural Rubber

The natural rubber latex is a colloidal dispersion of ethylene polymeric materials called rubber hydrocarbon (RHC) in an aqueous medium (Asore, 2010). It is milky in colour and has dry rubber content of 30 - 45% when it is obtained fresh from the tree. The typical composition of hevea latex is given in Table 2.2 below:

Table 2.2: Composition of Natural Ruber (Ihuezor and Ayo, 2010)

Total solid content	36%
Proteinous substances	1.5%
Resinous substances	1 – 2.5%
Ash	< 1.0%
Sugar	1.0%
Water	60%

The acetone content of natural rubber is 2.7%. The latex particulars are negatively charged and have an iso-electric point of 4.5pH value. In order to maintain it liquid phase, the pH of the latex must not fall below this iso-eletric point value. Hence natural rubber latex is stabilized using alkaline chemicals such as potassium hydroxide, casein solution ammonia water etc. the presence of a proton in the latex medium destabilizes the ionic stability of the latex and causes the latex to coagulate into lumps. Natural rubber also has some level of micro-gel content such as aldehyde groups (Ekebafe, 2010). The micro-gel content is about 0.5% relative to total weight of the rubber molecule. This aldehyde groups is capable of reacting with other compatible chemical agencies or its reactive nature aids in providing sites for cross-linking or as a point where the chain is weak and susceptible to fracture. The aldehyde and the carbonyl group can cross-link leading to hardening of bulk dry rubber that occurs on storage. The hydro carbon component of natural rubber (Hevea brassiliensis) is predominantly cis-1, 4 polyisoprene. The Gutta percha is a highly thermoplastic polymer used in areas such as golf ball manufacture. It is a polymer of isoprene with a converse possibility of geometrical isomerism of mainly trans-1, 4 polyisoprene.

2.2.4 Processing Behaviour of Natural Rubber

The processing of natural rubber into finished products can be classified into three main stages, viz: mastication/ mixing, forming and vulcanization. The natural rubber at its raw state is more or less useless for the production of engineering materials. In order to make good the viability of the rubber, some physical and mechanical properties boosting ingredients have to be incorporated into the natural rubber matrix. This process of mixing compounding ingredients into the rubber can only be affected by initial reductions of the molecular weight of the dry raw natural rubber. The mechanical and physico-chemical working on the natural rubber leading to the reduction of the high mooney viscosity so as to facilitate the incorporation of property boosting additives prior to easy forming process is known as “mastication” (Asore, 2000).

Mastication is carried out in two- roll mill or in an internal mixer. The process of mastication is time and energy consuming. Generally, viscosity and breakdown characteristics during mastication and milling are dependent on clones and consequently, it is advisable to blend natural rubber lots from different producers or suppliers (Asore, 2000). Natural rubber has the ability to produce good light bale round the rolls of two-roll mill machine. Natural rubber has been known to give excessive heat building up during milling and mixing. This is the reason for the inclusion of efficient cooling facilities in natural rubber processing equipment. Natural rubber should be masticated to constant viscosity prior to any further subsequent processing. Thus, mechano-chemical degradation help in no small measure to even out colonial variation that could be inherent with natural grades wider processing (Ihuezor and Ayo, 2010).

The second stage in dry rubber processing is forming. Thus involves forming the rubber mixes into the required shape of the designed product's dimensions. Forming process include: extrusion, calendaring, and moulding. Extrusion through a die gives tubes or profile shapes. The extrudates have adequate dimensional stability in their uncured state with little or no tendency for them (extrudates) to collapse on their own weight. This has been attributed to the high "green" strength of natural rubber (Ihuezor and Ayo, 2010). Calendaring between rolls leads to the formation of rubber sheets or rubber coated fabric. The high building tack characteristics of natural rubber inherited from the inherent resinous materials of the rubber composite endears it to both tyre manufacturers as well as producers of conveyor and drive belts. Moulding is usually done in a compression moulding press. The product takes the shape of the mould. It is in this machine that vulcanization can take place.

2.2.5 Properties of Natural Rubber

Natural rubber has some excellent properties which make it useful in many applications. Some of these properties are as follows:

i. Because of its high regular structure, natural rubber is capable of crystallization when stretched or strained at low temperature.
ii. The strain induced crystallization characteristics of natural rubber has a reinforcing effect on natural rubber than in the synthetic rubbers. Abrasion and wear resistance are improved by the presence of silica fillers or some grades of carbon black fillers (Asore, 2000). Chukwu et., al (2011) observed in their work, “effect of stearic acid level on the mechanical properties of natural rubber vulcanizate” that the abrasion resistance of natural rubber can be improved by using stearic acid at a higher level (above 4phr). Brydson (1979) attributed the outstanding abrasion resistance, resilience, low hysteresis and low chain flexibility to its regular structure.
iii. Resistance to petroleum oils is poor while resistance to alcohols and ketones is much better. Natural rubber vulcanizates are unaffected by most aqueous reagents but strong oxidizing agents, such as nitric acid, causes degradation.
iv. Thermal oxidative degradation of natural rubber occurs at elevated temperatures. Thermal oxidation is defined as the degradation of polymeric materials at elevated or high temperature in the presence of atmospheric oxygen. Natural rubber being a polymer of high molar mass also undergoes reactions with atmospheric oxygen at elevated temperature. This interaction has been known to be a major deficiency of natural rubber, causing the deterioration in the mechanical properties of the rubber on ageing (Ihuezor

and Ayo, 2010). Natural rubber has a high temperature heat ageing resistance limit for continuous use in the region of 75^{o}C.

v. The thermal oxidative degradation involving such unsaturated compounds with methene groups like natural rubber, result in chain scission along the polymer back bone causing a reduction in molecular mass and loss of mechanical properties.

vi. Poor UV and Ozone resistance due to it unsaturation. It is an established fact that ozone goes for unsaturation in polymeric materials (Ihuezor and Ayo, 2010). Since natural rubber has double bond (unsaturation) in it structure, it makes the rubber vulnerable to ozone attack which causes cracks on natural rubber vulcanizate.

vii. Natural rubber has very good low temperature resistance, down into the region of -57^{O}C. This property makes it suitable for use as an elastomeric product in the refrigerator.

viii. Natural rubber also has very good electrical insulation properties.

2.2.6 Applications of Natural Rubber

Natural rubber is used in applications 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 e.tc. (Asore, 2010). Natural rubber also has important application in the production of latex dip products such as balloon, surgical gloves or sanitary rubber products due to its strain induced crystallization and self- reinforcing properties. Natural rubber can be used for making adhesive tapes, rubber solution or art gum.

2.3 Groundnuts (Arachis hypogaea)

The groundnut is a leguminous plant. It originates in Brazil, from where it was introduced into West Africa by Portuguese traders (Onwueme, 1978). The plant is an annual crop. The seed germinates in about 5days after planting, flowering occurs in 1½ months, and the crop is ready for harvest in 4 - 5 months. It is a low, herbaceous annual with an upright central stem and several lateral branches which may be upright in the bunch types. The central stem is up to 20cm tall. The stems are hairy, and as they mature, they become hollow at their centre. The leaves are borne alternately on the stem. Each of the leaf is composed of four leaf-lets privately arranged (so that there are two leaflets close to the tip and two tars from the tip). The leaflets are attached to the stem by means of a long, thin petiole. The flowers arise in the leaf axils, and occur mainly at the base of the stem. Each flower has the typical leguminous flower structure five united sepals, five yellow petals made up of a standard, two wing and two keel petals; ten stamens joined to form tube, and an ovary made up of a single carpel with marginal placentation. Each ovary may have up to five ovules. Self pollination occurs in most cases. After fertilization, the region immediately behind the ovary begins to elongate and grow downward. This region called the gynophores (Onwueme, 1978) pushes the ovary into the soil and it is within the soil that the fruit matures. The mature fruit is an indehiscent pod (one that does not open of its own accord) containing 1-4 seeds. Each seed is ovoid (egg-life) in shape and is composed of a papery testa, two thick whitish cotyledons, the plumule and the radicle. The groundnut plant has a well- developed tap root system with numerous lateral roots. There are very few root hairs. Root nodules are present on the tap root and most of the lateral roots.

2.4 Natural Fibres

Agro- based resources, also referred to as lignocellulosics, are resources that contain cellulose, hemicellulose, and lignin. Lignocellulosics include wood, agricultural residues, grasses and other plant substances. When considering lignocellulosics as possible engineering materials, there are several very basic concepts that must be considered.

First, lignocellulosics are hygroscopic resources that were designed to perform, in nature, in a wet environment (Rowell, 1998).

Secondly, nature is programmed to recycle lignocellulosics in a timely way through biological, thermal, aqueous, photochemical and mechanical degradations. In simple terms nature builds a lignocellulosic from carbon dioxide and water and has all the toils to recycle it back to the starting chemicals (Rowell, 1998).

Table 2:3: Degradation Reactions in Lignocellulosics (Ray *et al,* 2001)

DEGRADATION TYPE	**AGENTS**
Biological degradation enzymatic reactions chemical reactions mechanical.	Fungi Bacterial, Insects, Termites Oxidation, Hydrolysis, Reduction
Fire degradation paralysis reaction	Oxidation, Hydrolysis, Reduction
Water degradation	Chewing, Lighting, Sun
Water interactions	Acetylation, Hydrolysis, Oxidation, Rain, Sea, Ice, Acidrain,Dew swelling, shrinking, Freezing, cracking ultraviolet radiation, water, heat, wind oxidation, hydrolysis erosion
Weather degradation	Acids, bases, salts
Chemical reactions mechanical	Oxidation, reduction, delydration, hydrolysis dust, wind, hail, snow, sand
Chemical degradation	Freezing, cracking ultraviolet radiation
Mechanical degradation mechanical, Chemical reactions	Stress cracks, fracture, abrasion

2.4.1 Classification of Fibres

Natural fibres can be classified according to their origin as follows:

i. Animal fibre

ii. Mineral fibre

iii. Plant fibre

2.4.1.1 Anima Fibre:

These are fibres taken from hairy animals e.g. sheep’s wool, goat hair (cashmere, mohair), alpaca hair, horse hair, etc. Fibre collected from dried saliva of bugs or insect during the preparation of cocoons e.g. silk from silk worms or fibres from birds’ e.g. feathers.

2.4.1.2 Mineral Fibres:

These are naturally occurring fibre or slightly modified fibre from minerals. They are categorized into the following:

a. Asbestos: This is the only naturally occurring mineral fibre. The various classes of asbestos fibres are serpentine, amphiholes and anthophyllite.
b. Ceramic fibres: examples are glass fibres, silicon carbide and boron carbide.

2.4.1.3 Plant fibres:

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

2.4.2 Applications of natural fibre composite

Natural fibre composite can be very cost effective material for the following applications:

Building and construction industry: panels for partition and false ceiling, partition boards, wall, floor window and door frames, roof tiles, mobile or prefabricated buildings which can be used in times of natural calamities such as floods, cyclones, earthquakes e.tc.

Storage devices: post-boxes, green storage silos, bio-gas container e.tc.

Furniture: chair, table, shower, bath unit e.tc. Electric devices: electric appliances, pipes e.tc.

Everyday applications: lamp shades, suit cases, helmets, e.tc.

Transportation: automobile and railway coach interior, boat e.tc.

The reasons for the application of natural fibre in the automotive industry include, low density, which may lead to weight reduction of 10 to 30%, acceptable mechanical properties and good acoustic properties, favourable processing properties such as favourable accident performance, high stability, less splintering and eco-balance for part production and occupational health benefits compared to glass fibres during production. No off-gassing of toxic compounds (in contrast to phenol resin bonded wood and recycle cotton fibre parts). Price advantages both for the fibres and the applied technologies (Mizahur et al., 2007).

2.4.3 Advantages of natural fibre composite

The main advantages of natural fibre composites are: low specific weight, resulting in a higher specific strength and stiffness than glass fibres. It is a renewable source, the production requires little energy, and CO_2 is used while oxygen is given back to the environment. It is producible with low investment at low cost, which makes the material an interesting product for low wage countries, reduced wear of tooling, healthier working condition, and no skin irritation. Thermal recycling is possible while glass causes problem in combustion furnaces (Thillai et al., 2010).

2.4.4 Modification of Nature Fibres

The interest in using natural fibres in composites has increased in recent years due to their light weight, non-abrasive, non-toxic, low cost and biodegradable properties. However, lack of good interfacial adhesion, low melting point and poor resistance to moisture absorption, make the use of natural fibre reinforced composites less attractive. Pretreatments of the fibre can clean the fibre surface, chemically modify the surface, stop the moisture absorption process and increase the surface roughness (Kalia et al., 2009). Due to the presence of hydroxyl group in natural fibres, they are amenable to modification. The hydroxyl groups may be involved in the hydrogen bonding within the cellulose molecules thereby reducing the activity towards the matrix (Kalia et al., 2009). Chemical modifications may activate these groups or can introduce new moieties that can effectively interlock with the matrix. Some of the chemical treatment of fibres are; mercerization, isocyanine, Acetylation, acrylation, peroxide, benzylation etc.

The influence of different treatment such as mercerization, acetylation, benzoylaton and silanation on the mechanical properties of isora fibre reinforced natural rubber composites was investigated by Mathew et al (2004). They observed a marked improvement of properties after chemical modification. In another study involving biodegradable matrix, Joseph et al. (2005) employed heterogeneous esterification reactions on flax fibres to improve fibre/matrix adhesion. The authors observed an increase in strength for the chemically treated composites. The influence of 4, 4-thidiophenol (TDP) on the interfacial properties of flax fibre reinforced poly (3-hydroxyl butyrate) was studied by Wong et al (2004). Scanning electron microscopic studies revealed good adhesion between fibre and matrix while FTIR confirms the presence of hydrogen bonds between additives and matrix. The interface modification and mechanical properties of newsprint, kraft pulp and hemp fibre reinforced polyolefin composite product was investigated by Sain et al. (2005). The effects of low molecular weight, maleated type coupling agent on the mechanical properties of this natural fibre filled polypropylene composite was also investigated and it was found that the optimum level of coupled agent was found to be around 3 to 4 % by weight of the composite.

In an interesting study using cardanol based bio-composites, Maffezolli et al (2004) used silane coupling agent to improve the adhesion between the natural fibre and matrix. The fibres used were hemps, ramie, flax and jute fibres. The authors observed that void content decreased in composites containing chemically treated fibres. An attempt to study the mechanical characteristics of hybrid system was performed by Mishra et al. (2003). The composite system used was sisal/ glass fibre and pineapple/glass fibre reinforced polyester composites. The composites were prepared by varying the concentration of glass fibre and by subjecting the bio-fibre to different chemical treatments. The modifications employed were mercerization, cyanoethylation and acetylation. The surface modification of sisal fibres such as alkaline treatment was found to produce optimum tensile and impact strengths while cyanoethylation resulted in the maximum increase in flexural strength of the hybrid composite (Mishra et al., 2003). It is apparent from the various literatures that chemical treatment has a profound influence on the properties of fibre-reinforced composites (Ahmedna, 1997)

2.4.4.1 Mercerization of Natural Fibres

This is the alkali treatment of natural fibres, a common method to produce high-quality fibres (Ray et al., 2001). Mercerization leads to fibrillation which causes the breaking down of the composite fibre bundle into smaller fibres. Mercerization reduces fibre diameter, thereby increasing the aspect ratio which leads to the development of a rough surface topography that results in better fibre matrix interface adhesion and an increase in mechanical properties (Kalia et al., 2009) and (Joseph et al., 2001). Moreover, mercerization increases the number of possible reactive sites and allows better fibre wetting.

$$\text{Fibre} - \text{OH} + \text{NaOH} \longrightarrow \text{fibre O-Na} + \text{H}_2\text{O} \qquad 2.1$$

2.4.4.2 Acetylation of Natural Fibre

Pretreatment of fibres with acetic anhydride substitutes the polymer hydroxyl groups of the cell wall with acetyl groups, modifying the properties of these fibres so that they become hydrophobic (Murray, 1998 and Rowell, 1991). Acetylation is based on the reaction of cell wall hydroxyl groups of lignocellilosic materials with acetic or propionic anhydride at elevated temperature. Hydroxyl groups that react with the reagent are those of lignin and hemicelluloses (amorphous materials), whereas the hydroxyl groups in cellulose (crystalline materials) are being closely packed with hydrogen bonds, preventing the diffusion of reagent and thus result in very low extents of reaction (Rowell, 1998). Acetylation of natural fibre is well known esterification method causing plasticization of cellulosic fibres. Polymer hydroxyl groups of the cell wall with acetyl groups modify the properties of these polymers so that they become hydrophobic which could stabilize the cell wall against moisture, improving dimensional stability and environmental degradation (Bledzki et al., 2008). Reduction of about 50% of moisture uptake for acetylated jute fibres and of up to 65% for acetylated pine fibres have been reported (Bledzki et al., 1999). Seena et al (2003) investigated the effect of acetylation in banana fibres reinforced phenol formadehyde composites and reported that the tensile strength, modulus and impact strength are found to improve compared to the non-treated banana fibre composites (Seena et al., 2003).

Liu et al., (1994) studied the effect of acetylation in natural fibre composites (cotton, rayon, wood, with polystyrene as matrix) and they show by using micro-debonding test that acetylated fibres had increased interfacial shear strength. Furthermore, they reported that acetylation increased surface free energy of the fibres (Liu et al., 1994).

Acetylation is beneficial in reducing the moisture absorption of natural fibres.

$$\text{Fibre} - \text{OH} + \text{CH}_3\text{CO}^- \longrightarrow \text{fibre- OOCCH}_3 + \text{H}^+ \qquad 2.2$$

2.4.4.3 Benzoylation of Natural Fibres

In benzoylation treatment, benzoyl chloride is most often used in fibre treatment (Rowell, 1998). The inclusion of benzoyl (C_6H_5CO) group in the fibre is responsible for the decreased in hydrophilic nature of the treated fibre (Mohanty et al., 2007).

2.4.4.4 Silane treatment (SiH_4)

Silane is used as coupling agent to let glass fibre adhere to polymer matrix, stabilizing the composite materials. Silane coupling agents may reduce the number of hydroxyl groups in the fibre-matrix interface.In the presence of moisture, hydrolysable alkozy group leads to the formation of silanols. Silanol reacts with hydroxyl group of the fibre, forming stable covalent bonds to the cell wall that are chemisorbed unto the fibre surface. As a result of the hydrocarbons chains provided by the application of silane restrain the swelling of the fibre by creating a crosslink network due to covalent bonding between the matrix and the fibre. The reaction schemes are given as follows (Li et al., 2004).

$$CH_2CHSi(OC_2H_5)_3 \longrightarrow CH_2CHSi(OH)_3 + 3C_2H_5OH \qquad 2.3$$

$$CH_2CHSi(OH)_3 + Fibre\text{-}OH \longrightarrow CH_2CHSi(OH)_2O\text{-}fibre + H_2O \qquad 2.4$$

2.4.4.5 Peroxide treatment

Peroxide is a molecule with the functional group ROOH which contain the divalent ion O-O. Organic peroxides tend to decompose easily to free radicals of the form RO*: RO* then react with the hydrogen group of the matrix and cellulose fibres. For example, the peroxide initiated free radical reaction between polyethylene matrix and cellulose fibre is shown by the following.

$$RO\text{-}OR \longrightarrow 2RO^* \qquad 2.5$$

$$RO^* + PE\text{-}H \longrightarrow ROH + PE \qquad 2.6$$

$$RO^* + Cellulose\text{-}H \longrightarrow ROH + Cellulose \qquad 2.7$$

$$\text{PE + Cellulose} \longrightarrow \text{PE + Cellulose} \qquad 2.8$$

Benzoyl peroxide $(C_6H_5C0)_2O_2$ and dicumyl peroxide $(C_6H_5C(CH_3)_2O)_2$ are chemicals in the organic peroxide family that are used in natural fibre surface modifications. In peroxide treatment, fibres are coated with benzoyl peroxide or Dicumyl Peroxide in acetone solution for about 30minutes after alkali pretreatment (Sreekala et al., 2000, and Sreekala et al., 2002). Sreekala et al. (2000) observed that the decomposition of the peroxide was favoured at high temperature for the peroxide treated oil palm fibre reinforced polyphenol formaldehyde composites could withstand tensile stress to a higher strain level. Amar (2005) studied the Benzoyl peroxide and Dicumyl Peroxide treatment on short sisal fibre polyethylene composites. The tensile strength values of composites increase with increase in concentration of peroxide up to a certain level (4% for dicumyl peroxide and 6% for Benzoyl peroxide) and then remain constant. As a result of peroxide treatment, the hydrophilicity of the fibres decreased (Dubey et al., 2011) and the tensile properties increased (Debnah et al., 2003).

2.4.4.6 Other chemical treatments

Zafeirpoulos et al, (2002) have reported that treatment of natural fibre with steric acid in ethyl alcohol solution was investigated earlier it was reported that this treatment removed non-crystalline constituents of the fibres and change in the fibre surface topography occurs. Zafeirpoulos et al. (2002) also observed that treated flax fibres were more crystalline than the untreated ones and stearation decreased the fibre surface free energy. Sodium chlorite ($NaClO_2$) usually is used in bleaching fibres. However, it could delignify lignocellulosics. Studies have been conducted wherein it was used in fibre surface treatment for composites. Mishra et al, (2002) dipped untreated sisal fibre for use in sisal-polystyrene biocomposite in sodium chlorite solution with a liquor ratio of 25:1 at 75^0C for 2hours. Tensile strength of bleach fibre-polystyrene composite was less than other chemical treated fibre composite which may be due to the fact that delignification of the fibre lowered its tensile strength (Mishra et al., 2002). But it was reported that flexural strength was better for bleach fibre composite because of lower stiffness and more flexible character of fibre after delignification. After delignification, the polymer replaces the role of lignin in fibres and makes composites more hydrophobic and tougher (Mishra et al., 2002). Similar results on tensile strength of bleached composites using sodium chlorite was also reported by Li et al. (2004) on flax fibre/polyethylene composites.

2.5 Polymer Composites

Composites are materials that comprise strong load carrying material (known as reinforcement) embedded in weaker material (know as matrix). Reinforcement provides strength and rigidity, helping to support structural load. The matrix maintains the position and orientation of the reinforcement. Significantly, Constituents of the composites retain their individual, physical and chemical properties; yet together they produce a combination of qualities which individual constituents would be incapable of producing along (Saira et al., 2007). Materials that have especially useful combination of properties often are mixture of two or more quite different constituents. One component may be light and strong but too brittle to be used alone. Another constituent may be tough and ductile though without sufficient strength. When suitably combined, these composites display excellent properties. Composite are produced when two or more materials are used together to give a combination of properties that cannot be attained otherwise. Composite materials may be selected to give unusual combinations of stiffness, strength, weight, high temperature performance, corrosion, resistance, hardness, or conductivity. According to Bledzki et al. (1998) wood is a natural three dimensional polymeric composite that consists primarily of cellulose, hemicelluloses and lignin. Wood is a natural composite. Other examples of natural composites are bone teeth and abalone shell.

Historically, the use of reinforcing mud walls in houses with bamboo sheets, glue laminated wood by the Egyptians (1500BC) and laminated metals in the forging of swords (1800AD) are known. An example of a material that is a composite at a macro-scale would be steel reinforced concrete. Composites that are at a micro-scale include such materials as carbon or glass fibre reinforced plastics.

2.5.1 Overview of Composites

The first composite materials may have been bricks fashioned by the ancient Egyptians from mud and stray (Fried, 2005). Commercialization of composites can be traced to early 20th century. Modern composites were used in 1930s, where glass fibre reinforced resins were made. Boats and aircrafts were built out of these glass composites. Since the 1970s, the application of composites have widely increased due to development of new fibres such as carbon, boron and aramid, leading to new composite systems with matrices made of metal and ceramics. The volume and number of applications of composite materials have grown steadily, penetrating and conquering new markets relentlessly. Modern composite materials constitute a significant proportion of the engineered materials market ranging from every day products to sophisticated nitche applications while composite have already proven their worth as weight saving materials, the current challenge is to make them cost effective. The efforts to produce economically attractive composite components have resulted in several innovative manufacturing techniques currently being used in the composite industry. Best results may be achieved through the use of composites in conjunction with traditional material (Iannace et al., 2001).

2.5.2 Definition of Composite

From literatures, many people have defined composite. Some of the definitions are given below:

i. Van Suchetclen defined composite as heterogeneous materials consisting of two or more solid phases, which are in intimate contact with each other on a microscopic scale. They can also be considered as homogeneous materials on a microscopic scale in the sense that any portion of it will have the same physical properties (Mohanty et al., 2004).

ii. Saira et al. (2007) define composite as materials that comprise of strong load carrying material (reinforcement) embedded in weaker material (matrix).

iii. Another definition is that given by Jentiz which states that, composites are multifunctional material system that provide characteristics not obtainable from any discrete material. They are cohesive structures made by physically combining two or more compatible materials, different in composition and characteristics and some times in form (Zafeiropoulosa et al., 2002).

iv. Beghezan defined composite as compound materials which differ from alloys by the fact that the individual components retain their characteristics but are so incorporated into the materials as to take advantage only of their attributes and not their short comings, in order to obtain improved materials (Mohanty et al., 2001).

v. Philips (1987) defined composite as a material consisting of a large number of fibres (fine filaments) embedded in a continuous phase or matrix, which gives it a definite shape and a durable surface.

vi. Fowler et al. (2006) defined composite as a material consisting of two or more distinct constituents or phases which when married together result in a material with entirely different properties from those of the individual components.

Typically, a man-made composite would consist of a reinforcement phase of stiff strong material, frequently fibrous in nature, embedded in a continuous matrix phase. The latter is often weaker and more compliant than the former. Two of the main functions of the matrix are to transmit externally applied loads, via shear stresses at the interface, to the reinforcement and to protect the latter from environmental and mechanical damage (Fowler et al., 2006).

2.5.3 Classification of Composites

Composites can be grouped into categories based on the nature of the matrix each type possesses (Amar et al., 2005). Under this group, we have:

2.5.3.1 Polymer Matrix Composites (PMCS)

This is the most common advanced composites (Saira et al., 2007). This composite consists of a polymer thermoplastic or thermosetting reinforced by fibre. These materials can be fashioned into variety of shapes and sizes. They provide great strength and stiffness along with resistance to corrosion. The reason for these being most common is their low cost, high strength and simple manufacturing principles.

2.5.3.2 Metal Matrix Composites (MMCS)

Metal matrix composites, as the name implies, have a metal matrix. Examples of matrices in such composites include aluminum, magnesium and titanium. Typical fibres include carbon and silicon carbide. Metals are mainly reinforced to suit the needs of design. For examples, the elastic stiffness and strength of metals can be increased, while large co-efficient of thermal expansion, thermal and electrical conductivities of metals can be reduced by the addition of fibres such as silicon carbide

2.5.3.3 Ceramic Matrix Composites (CMCS)

These are composite that have ceramic matrix such as alumina, calcium, alumino silicate reinforced by silicon carbide. The advantages of ceramic matrix composite include high strength, hardness, high service temperature limits for ceramics, chemical inertness and low density (Saira et al., 2007). There are four classes of ceramic matrices: glass (easy to fabricate because of low softening temperature including borosilicate and alumino silicates), conventional ceramics (silicon carbide, silicon nitride, aluminum oxide and zirconium oxide are fully crystalline) cement and concreted carbon components.

2.5.3.4 Carbon-Carbon Composites (CCS)

Carbon- carbon composites used carbon fibres in a carbon matrix. Carbon-carbon composites are used in very high temperature environments of up to 600^{o}F, and are twenty times stronger and thirty times higher than graphite fibres. Also, composites can be categorized as particulate composite, fibre reinforced composite and laminar composite. This division is based on the shapes of the materials. Concrete, a mixture of cement and gravel, is a particular composite; fibre glass embedded in a polymer is a fibre reinforced composite; and plywood, having alternating layers of wood veneer, is a laminar composite.

2.5.4 Particulate Composite

The particulate composites are designed to produce unusual combinations of properties rather than to improve strength. The particulate composites contain large amounts of coarse particles that do not block-slip effectively. The rule of mixture can be used to predict the properties of the composite. For example, the density of a particulate composite is given as:

$$\Sigma_c = V_m + V_f \qquad 2.9$$

Where Σ_c is the density of the composite, V_m and V_f are the volume fractions of each component, i.e. matrix and the reinforcing materials (Asore et al, 2010).

2.5.5 Fibre- Reinforced Composites

These are composites that are reinforced with fibres. The matrix provides protection for the fibre surface and minimizes diffusion of species such as oxygen or moisture that can degrade the mechanical properties of fibres. First as in particulate composite, the rule of mixture can be used to predict the density of fibre- reinforced composites.

$$\sum_c = F_m \sum_m + F_f \sum_f \qquad 2.10$$

Where the subscripts m and f refer to the matrix and the fibre respectively. The modulus of elasticity parallel to the fibre is given as:

$$E_c = F_m E_m + F_f E_f \qquad 2.11$$

While the modulus perpendicular to the fibre is given as:

$$\frac{1}{E_c} = \frac{F_m}{E_m} + \frac{F_f}{E_f} \qquad 2.12$$

2.5.5.1 Natural fibre reinforced composite

Natural fibres such as sisal, flax and jute possess good reinforcing capabilities with polymers. These fibres are relatively inexpensive, originate from renewable and possess favourable values of specific strength and specific modulus. Natural fibre reinforced composites come from the renewable materials and can be mechanically recycled. Some of the recent studies on the natural fibre reinforced composites have been cited in this work

2.5.5.2 Banana fibre reinforced composites

Effect of chemical modifications on the dynamic mechanical properties of banana fibre reinforced polyester composite was studied (Amar, 2005). A number of silane coupling agents were used to modify the banana fibres. Joseph et al studied the environmental durability of chemically banana fibre reinforced phenol formaldehyde composites. They observed that silane, sodium hydroxide and acetylation treatments improved the resistance of the banana/phenol formaldehyde composites on outdoor exposure and soil burial. Durbey et al. (2011) investigated the thermo-physical properties of banana sisal hybrid reinforced composites as a function of a chemical modification. Sisal and banana fibres were subjected to mercerization and polystyrene maleic anhydride treatment. They observed that chemical modification resulted in an increase of 43% in the thermal conductivity when compared with untreated composites (Debnah et al., 2003).

2.5.5.3 Flax fibre reinforced composite

Most studies concerning the chemical modification of flax fibres have been reported earlier by many researchers. Wang et al. (2003) investigated the chemical modification of flax fibres by alkali treatment. The study concentrated on optimizing parameters such as time and concentration of sodium hydroxide to develop a continuous process for the treatment and fabrication of unidirectional flax fibre epoxy composites. The authors observed a specific improvement in the mechanical properties of the resulting material. Treatment with 4% sodium hydroxide solution for 45seconds increased the transverse strength of the composite by up to 30%. Wang et al. (2003) investigated the effects of different chemical modifications on the properties of flax fibre reinforced rotationally moulded composites. The chemical modifications carried out were mercerization, peroxide treatment and benzoylation treatment. The modified fibres were then extruded with the polymer matrix to form the composite and an improvement in interfacial adhesion was observed. Zafeiropoulos et al investigated the effect of chemical modification on the tensile strength of flax fibres. The authors tried acetylation and stearation and found that the tensile strength of flax fibre did not exhibit any drastic improvement. The scanning electron microscope examination of the fractured surfaces revealed that acetylated fibres exhibited a different mode of failure from the other fibres, suggesting that the treatment alters the bulk properties along with the surface properties (Bledzki et al., 1999).

2.5.5.4 Hemp fibre reinforced composite

Bledzki et al. (1999) have studied the influence of chemical treatment on the properties of hemp fibre reinforced epoxy and polypropylene composites. The effects of different mercerization parameters such as concentration of alkali (NaOH), temperature, duration time and tensile stress applied to the fibres on the structure and properties of hemp fibres were studied and judged via the cellulose I-II lattice conversion. It was observed that the mechanical properties of the fibres can be controlled in a broad range using appropriate parameters during mercerization treatment. Debnah et al. (2003) investigated the effect of alkali treatment on the mechanical and thermal properties of hemp fibre reinforced polyester composites. The scanning electron microscope photomicrograph of the longitudinal surface of untreated fibre bundles shows the presence of wax, oil ad surface impurities. Waxes and oils provide a protective layer to the surface of the fibres. The longitudinal view of the 6% sodium hydroxide treated fibre shows a very clean surface. Its surface topography shows the absence of surface impurities which were present in the untreated fibre. The individual ultimate fibres also show a slight separation which was not apparent in the untreated hemp fibre (Li et al, 2004).

2.5.5.5 Isora fibre reinforced fibre composites

In an interesting study, researchers have used a novel fibre (isora fibre) I natural rubber. Isora fibre resembles jutes in appearance but surpasses it in strength, durability and lustre. The effect of different chemical treatments such as acetylation, benzoylation treatment with toluene diisocyanate (TDI) and silane coupling agents on the mechanical properties of isoral fibre and composites were analysed. Isora fibre was seen immense potential as reinforcement in natural rubber. The variation in tensile strength with chemical modification can be observed that treatment with NaOH and TDI exhibited higher tensile strength among other chemical modifications (Sreekala et al., 2000).

2.5.5.6 Pineapple fibre reinforce composite

Green composites were fabricated using pineapple leave fibres and soy-based resin. The addition of polyester amide grafted glycidyl methacrylate (PEA-g-GMA) as compatibilizer was seen to increase the mechanical properties of composites. Tensile and flexural strength of composites containing treated fibres were found to be 35 and 50MPa respectively whereas those of composites containing untreated fibres were found to be 30 and 45MPa respectively. Sodium hydroxide solutions (1, 3, and 7% w/v) and benzoyl peroxide (1, 3 and 5 weight % of fibres) were used to treat the surface of fibres . It was found that all surface modification enhanced adhesion and tensile properties. The treatment with 5% sodium hydroxide and 1% benzoyl peroxide provided the best improvement of strength (28 and 57% respectively) of composite when compared with that of untreated fibre composite (Dubey et al., 2003).

2.5.5.7 Sisal fibre reinforced composites

Amar, (2005) carried out the alkali treatment of sisal fibres and analyzed the changes with respect to the diameter and internal structure such as cellulose content, crystallinity index, and micro-fibril angle. Alkalization was found to change the internal structure of sisal fibres which exhibited approximately same specific stiffness as that of steel. The crystalline nature of the treated fibre was also found to increase due to alkaline treatment. His results indicated that the structure of sisal fibre can be chemically modified to attain properties that will make the fibre useful as a replacement for synthetic fibres. Thillai et al. (2010) studied the effects of chemical modifications on the structure and morphology of sisal fibres by nuclear magnetic resonance spectroscopy. Mercerization, acetylation and resorcinol/hexamethylene tetramine treatments were applied to sisal fibres in order to improve their adhesion in composite materials. The results show that the fibre/ acetylation of fibres prior to treatment with 20/10g/L hexamethylene tetraamine solution for 15minuts was the best treatment since the fibres obtained exhibited the biggest effective surface area available for chemical interaction and mechanical interlocking with the matrix (Debnah et al., 2003).

2.5.6 Laminar Composites

Laminar composites are built of layers of different materials. These layers may be sheets of different metals, with one metal providing strength and the other providing hardness or corrosion resistance. Layers may also include sheets of fibre- reinforced materials bonded to metal or polymer sheets or even to fibre (Asore et al., 2010).

2.6 Methods of Making Composites

The techniques used to manufacture composites are based largely on existing techniques for processing plastics (Fowler et al., 2006). These include press moulding, hand lay up, filament winding, protrusion¸ extrusion, injection moulding, compression moulding, resin transfer moulding and sheet moulding compounding. The majority of current bio-composite materials are processed by compounding and extrusion.

Asore et al. (2010) highlighted the following as the methods of making composites:

2.6.1 Spray up:

In this method, both fibres and resins are sprayed onto the mould. The layers are densified with rollers as for hand lay up. Gel coats are used for good surface finish. Polyesters or epoxy thermosetting resins are usually used.

2.6.2 Hand lay up:

This is the simplest method of making continuous fibre-reinforced composites. In this method, fibres are laid onto a mould by hand, and the resin is painted on and allowed to cure. This method is versatile, very labour intensive and has little capital investment.

2.6.3 Protrusion:

This method is used for very strong aligned composites. The fibres are impregnated with resin and pulled through a mould shaped to produce the desired cross-section in the product. The mould is then heated to promote setting after it has impregnated the fibres.

2.6.4 Mixing:

This method is used for making particulate filler-reinforced polymer composites. In this method, the filler, polymer and other additives are mixed on a two roll mill, internal mixer or in an extruder. After mixing, the composite is then vulcanized.

2.6.5 Filament Winding:

It consists of winding continuous filament over a suitable shaped mandrel. The filaments are in bundles and usually consist of thousands of individual fibres and are referred to as roving (fibre glass) or tow (carbon). The fibres are impregnated with resin before they go into a mandrel for the wet winding process. In the dry winding process, prepreg are used. Epoxy resins are often used for the matrix though polyesters and other resins may be used.

2.7 Application of Composites

Several years ago, nearly all resources for the production of commodities and many technical products were materials divided from natural textiles (Saira et al, 2007). As early as 1908, the first composite materials were applied for the fabrication of large quantities of sheets, tubes and pipes for electronic purpose.

In 1940, composites fibre glass was employed to reinforce plastics and advantageously used in nose radar domes to protect aircraft antennas.

In 1950, reinforced plastics were employed to aircraft propeller blades. Saving in both weight and cost gained by the use of composite materials is also impressive. Boeing 727 jet introduced in 1960 used 5000 lbs (2273kg) of reinforced plastics. Hence replacement of metal by composite resulted in 33% reduction in weight.

By 1996, Airplane seats and fuel tanks were made of polymeric binders. The use of natural fibres within composite applications is being pursued extensively throughout the world. Consequently, natural fibre composite materials are being used for making many components in the automotive sector.

Table 2.4: Application for Polymer Composites (Fried, 2005)

Industry	**Millions of LBS**	**Percentage**
Aerospace and military	41.1	1.54
Appliances and business	153.3	5.75
Construction	495.4	18.6
Consumer products	170.9	6.41
Corrosion resistant equipment	350.8	13.2
Electrical and electronics	234.8	8.81
Marine	432.8	16.2
Transportation	703.6	26.4
Others	82.2	3.09
Total	**2664.9**	**100**

2.8 Rubber Compounding Ingredients

Rubber compounding as we know it today is the result of the considerable work, effort and contributions of countless workers in this field, since the discovering of vulcanization in 1839 (Evans, 1981). The manufacture of rubber products 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 for use in many given applications.

Rubber is visco-elastic in nature and this tendency gives rise to creep which is adverse to engineering and other applications. They exhibit thermoplastic behaviour within a limited range of temperatures and are soluble in a wide range of organic solvents. These factors impose severe limitations on the usefulness of the rubber material.

The objectives of rubber compounding are to produce an acceptable balance between properties in finish products to satisfy service requirement, processing characteristics for efficient utilization of available equipment, and to achieve the desirable properties and processability at the lowest possible cost. Today's compounder or rubber chemist must be competent in the use and application of both natural and synthetic materials and to do this to best advantage requires the following (Evans, 1981):

a. An understanding of the plant and processing methods available.

b. A thorough knowledge of both the chemical and physical properties of the raw material available.

c. Knowledge of the vulcanizing systems available in order to bring out, develop and maximize the ultimate properties of the materials used.

d. An understanding of the in-process and final testing of the finished products, so as to ensure consistency.

e. Lastly, the capability of producing material that will process well in the factory and of the right price to be commercially viable.

A practical compounding formulation has the following basic ingredients.

2.8.1 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 soft plastic material to a strong, non plastic and even hard substance

2.8.2 Vulcanizing Agent

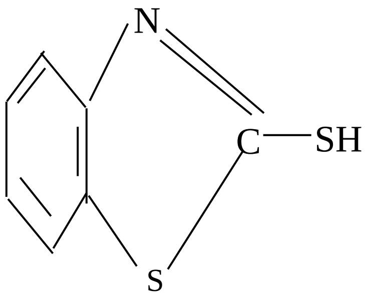
These are ingredients added to the base polymer to help effect cross-linking of the polymer chain. The most important vulcanizing agent is still sulphur (Sharma, 2006). Other elements from the same group in the Periodic Table as sulphur, such as selenium and tellurium (and their derivatives) will also function in a similar manner. These are used in specialized applications where good heat resistance is required.

Natural rubber, styrene butadiene rubber, polyisoprene, butyl rubber and nitrile rubber (just to name a few) all react with sulphur and sulphur bearing chemicals to achieve crosslink of chains. However, with neoprenes, metallic oxides such as zinc oxide and magnesium oxide serve as the vulcanizing agents.

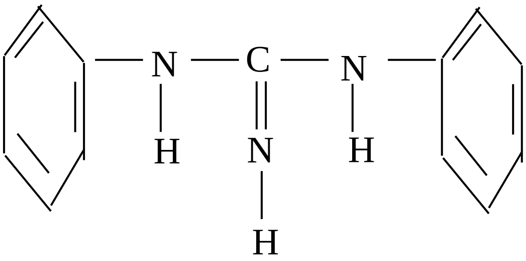
2.8.3 Accelerators

These are ingredients used in compounding to increase 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. Accelerators are divided into five classes:

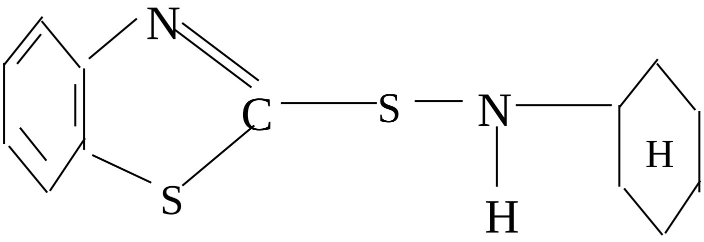
i. **Thiazoles:** Thiazoles derivatives are versatile accelerators used alone or in combination with other accelerators in a compounding formulation. It gives moderate vulcanization rate and scorch time. Example is 2-mercaptobenzothiazole (MBT).



ii. **Guanidines:** These are secondary accelerator which is used with other accelerators of thiazoles class. The thiazole-guanidine combinations are frequently used for technical goods. Example is N, N- diphenyl guanidine.

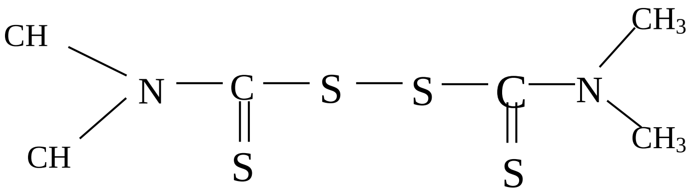


iii. **Sulphenamides**: These groups of accelerators play a dual role in the vulcanization. They provide longer scorch time which avoid premature cross-linking during vulcanization and processing. They are good choice when furnace black is used because of the heater. Example is N-cyclohexy 1-2- benzthiazyl sulphenamide (CBS).



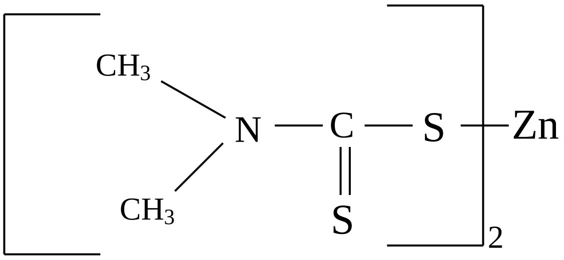
(CBS)

iv. **Thiurams**: These classes of accelerators are used as ultra fast accelerators with normal amount of sulphur. Example is tetra methyl thiuriam disulphide (TMTD).



TMTD

v. **Dithiocarbamates:** They are class of accelerators that are used as ultra fast accelerators. Example is zinc dimethyl dithio carbamate (ZDMC).



2.8.4 Activators

Activators are used to increase the effect of accelerators. Examples of activators are zinc oxide, stearic acid, litharge, magnesium oxide, amine soap etc (Sharma, 2006). Zinc oxides, stearic acid (or other fatty acid) are generally found in all recipes based on natural rubber, styrene butadiene rubber, butyl rubber, isoprene, where they are used as activating materials and produce a uniform rate and state of cure in the compound. However, they also appear in poly-chloroprene compounds but for different reasons such that, the fatty acid helps as an anti-roll sticking additive, whereas the zinc oxide is the vulcanizing agent.

2.8.5 Anti-degradants

It is almost universally necessary to add anti-degradants to any polymer to impact improved and satisfactory ageing properties in the cured compound. Anti-degradants retard deterioration of rubber compound initiated by oxygen, Ozone, light, heat, metal impurities and mechanical flexing. Some polymers, such as polychloroprene and especially butyl and ethylene propylene diene monomer already have well to excellent built in ageing characteristics, but even with this chamit, it is usual and advisable to add small quantities of these rubber chemicals for maximum results. Anti-degradants are divided into anti-oxidants and anti-oxidants.

Anti-oxonants are chemicals which diffuse to the surface and react with the Ozone thereby protecting the rubber from attack. Commonly used anti-ozonants are Para phenylene diamine (PPD) and micro crystalline waxes.

Anti-oxidants are chemicals which extend the life of rubber products by first reacting with polymeric free radicals and stopping propagation of polymer oxidation. The earlier antioxidants used to help natural rubber life prolongation were based on various aromatic amines and phenols, and even today such materials are still used. It is usual to use quantities of the order of 1 - 100 parts of rubbers, but the amount obviously depend on the service requirements of the product and also upon the actual basic polymer in the formulation. Some antioxidants are specific to the type of protection which they impart (Evans, 1981). They can be used to improve heat resistance, flex cracking, or improved resistance to weathering.

2.8.6 Processing Aids

Rubber chemicals within this grouping include pertizers, softeners (Oils and Waxes) and plasticizers. A processing aid plays one or more of the rules included in the following list:

i. Speed up the rate of polymer breakdown and also controls the degree of breakdown.

ii. Helps to disperse the other compounding ingredients, especially blacks.
iii. Helps to reduce nerve within the compound, and shrinkage during subsequent processing.
iv. Can impact building tack to the compound.
v. Improve and more stable compound Processing, especially in the compound Preparation (blanking) and moulding areas.

Natural rubber is greatly assisted in its breakdown during mastication by the addition of peptizing agents. These chemicals act as catalysts for oxidative breakdown during the milling and internal mixer mastication operations.

2.8.7 Fillers

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

Reinforcing fillers are those that improve properties such as modulus, tensile strength, abrasion resistance and flex fatigue.

Examples are phenolic resins, carbon black, silicates etc.

The semi reinforcing fillers also impact reinforcing properties into the composite (Vulcanizate) but with all average rates as it stands the gap between reinforcing and non-reinforcing fillers. Examples are antimony oxide, treated whitening etc.

The non reinforcing fillers are also called cheapeners or extenders. They reduce cost and are non strength impacting. Examples are barum sulphate

($BaSO_4$), mica powder, calcium carbonate ($CaCO_3$), etc. Fillers may also be classified as black and non-black types.

The non-black is the pure silicates. It is of interest to know that carbon black as an ingredient is still the outstanding reinforcement material for general application. When considering the choice of filler, it is necessary to ensure its suitability in the service environment of the product (Evans, 1981). As an obvious example, if chemical resistance is required, and in particular resistance to acid conditions, than whiting (calcium carbonate) is unsuitable whereas inert materials such as silica and silicates (China clay, talc) are ideal. For extreme acid conditions, then barytes (Barium sulphate) is more suitable.

2.8.8 Miscellaneous Compounding Ingredients

In addition to other major compounding additives already discussed, some specific materials or ingredients are also introduced into the rubber formulation recipe to impart some special purpose which is not normally required in the majority of rubber compound. Some of these ingredients are enumerated below:

2.8.8.1 Colourants:

Titanium oxide is the major white pigment used in rubber compounding. Inorganic pigments such as iron, cadmium, chromium, or strontium oxides and antimony sulphides find application in rubber compounding, particularly in stocks to be vulcanized in open steam. These classes of ingredients improve the asthetic properties of the vulcanizates. Carbon black apart from performing its primary function also acts as a colourant.

2.8.8.2 Blowing Agents:

These are ingredients used to produce sponge-rubber (open cell) or micro cellular rubber products (close cell). A good blowing agent should fulfill the following requirements (Chukwu, 2002).

i. Contain a large amount of releasing gas.
ii. Non toxic.
iii. Decomposition products should not have a bad odour.
iv. Should disperse well in the rubber.
v. Be low priced

Generally, sodium bicarbonate, along with fatty acid release carbon dioxide under vulcanizing conditions. This is used in compounding continuous cell sponge. Nitrogen releasing materials are used in unicellular rubbers, generally with urea which acts as a neutralizer for the odours formed by decomposition of the nitrogen bearing materials. Examples of organic chemical blowing agents include: Azo compounds like azodicarbonamides hydrazine derivatives like, benzene 1,3-disulphurydrazide, P-toluene sulphonyl hydroxide etc and N-Nitroso compounds.

2.8.8.3 Deodorants:

Small quantities of about 0.1pphr of aromatic substances are added to some rubber compounds to neutralize their characteristics odour, or to impart a pleasing scent to the finished product. Vanderbilt RODO No. 6 is used as a neutralizing agent, RODO

No.4 imparts a clean fresh scent and RODO No. 10 is used when a pleasing floral odor is desired.

2.8.8.4 **Antimicrobials**:

Antimicrobial properties may be important for article like rubber footwear, hygienic rubber goods etc to prevent spreading of pathogens. The same goes for articles that are used in homes, hospitals and other health sectors. Suitable antimicrobial products are salicylaldehyde and dihydroxy dichlorodiphenyl methane derivatives.

2.8.8.5 **Factice:**

Factice are unsaturated oils that have reacted with sulphur or similar materials (Chukwu, 2002). The reaction that occurs during factification corresponds to hard rubber vulcanization. Factices give dimensional stability to extruded articles, reduce mould fill time and cure cycle time, improve the ozone resistance of the rubber compound, give a smooth velvety feel to rubber articles, reduce migration of oils and plasticizers to the surface of low diameter stocks, absorb large amount of mineral oil and liquid plasticizer on the mill and in the Banbury mixer, and have the ability to flow or promote flow under mechanical pressure (Lovely et al., 2006).

2.9**Vulcanization System**

Technically, the most traditional and potential systems for the vulcanization of rubbers include those based on (Ihuezor and Ayo, 2010):

i. Accelerated sulphur system
ii. Organic peroxides
iii. Tellurium and selenium
iv. Urethane ‘Novor’ system
v. Radiation cure
vi. Others

2.8.1 Accelerated Sulphur System

Generally the reaction between natural rubber and elemental sulphur is relative slow of temperature normally used for vulcanization (150^{0}C- 200^{0}C). The process is also inefficient in that between 40 - 55 sulphur atoms become chemically combined with the rubber for each cross-links formed (Ihuezor and Ayo, 2010). Only 6 - 10 of these sulphur at most are actually the cross-links while the remaining sulphur atoms being present as cycle supplied units.

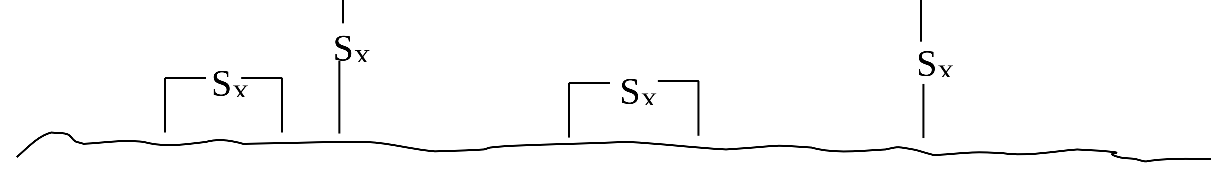


Figure 2.2: Network of Accelebrated Sulphur Vulcanization System for Natural Rubber.

This extensive main chain modification and the production of polysulphic network affect both the physical and the chemical properties of the resultant vulcanizate. It leads to reduced strain induced and low temperature crystallization, hence the need for accelerator in vulcanizing rubbers. However, the addition of typical accelerations to the compound recipe, substantially increase the rate of reaction between natural rubber and sulphur as a vulcanizing agent. Accelerating effects are shown by wide range of organic compound of which typical examples are mercaptobenzo thiazole (MBT), tetramethyl thiouram disulphide (TMTD), zinc dimethyl thiocarbonate etc.

Basically, accelerated sulphur system can be classified into three modes, viz: conventional system, efficient vulcanization system and semi efficient vulcanization system.

a. **Conventional System:** This is also known as unaclelerated sulphur vulcanization system. This involved the use of high sulphur level (2 - 3.5phr) and low level of accelerator 0.3 – 1.2phr (Chukwu, 2010). This type of vulcanization system impart the polysulphidic cross-links into the vulcanizate polysulphidic cross-links (S_X) are associated with high mechanical strength. Vulcanizate, high compression set and high rate of primary creep, and stress relaxation at elevated temperature (Chukwu, 2002). The cross-links are very weak and liable (bond energy of less than 64kglm) and as a result they are not stable at elevated temperature.

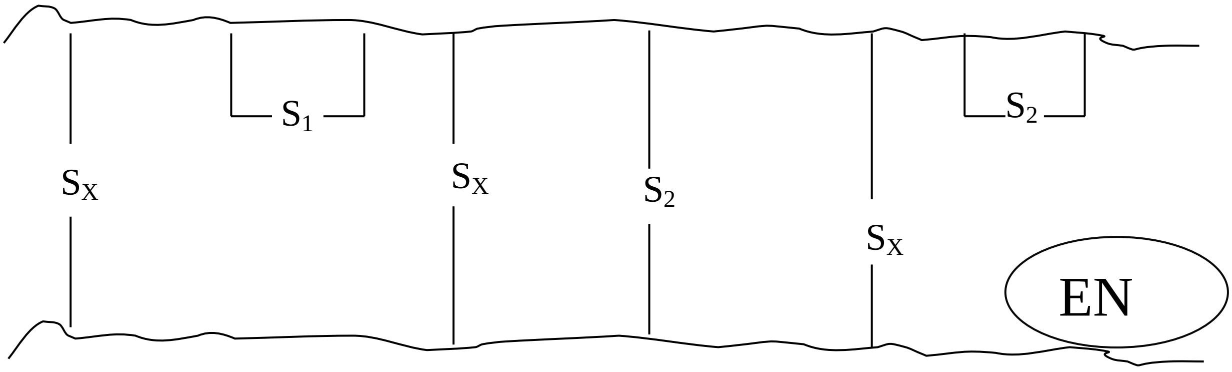


Figure 2.3: Network Structure for Conventional System

S_X – Polysulphidic network

S_1 - Mono sulphidic network

S_2 - Disulphici network

ENM -Extra – network materials

b. **Efficient Vulcanization System:** This type of sulphur vulcanization is achieved by the use of low sulphur level, typically 0.25- 0.70phr and high accelerator levels, typically 2 - 2.5phr (Chukwu, 2002). It gives predominantly the monosulphidic cross-links and much less chain modification, hence they are known as “efficient” vulcanization system. These types of networks produces vulcanizates which are resistant to oxidative ageing and high temperature compression set because of the high thermal stability of monosulphidic cross-links (Akpa, 2005). The limitation of this type of vulcanization system is that it gives vulcanizate which have poor resistance to tearing, fatigue and wear resistance than the conventional system.

$$\text{Efficiency value} = \frac{\text{No of sulphur combined}}{\text{No of chemical cross-links Produced}}$$

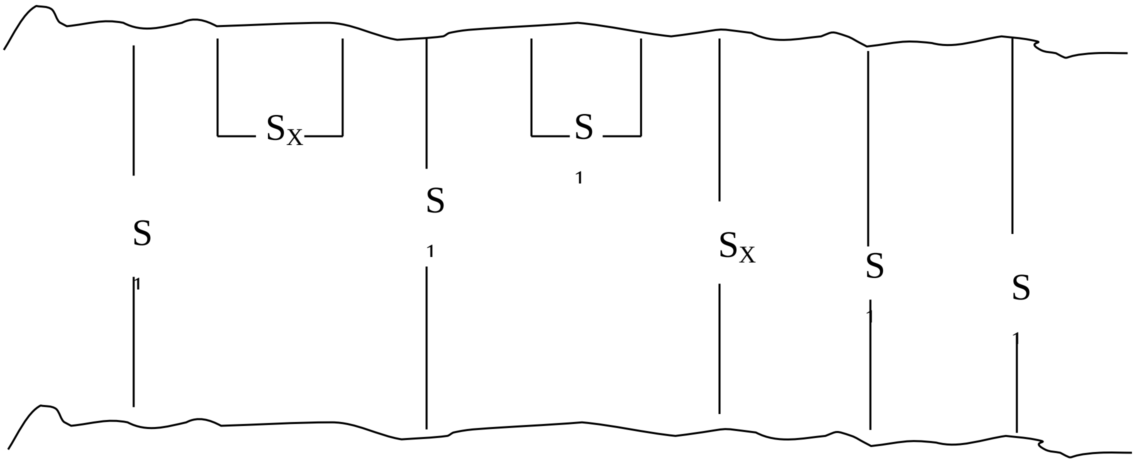


Figure 2.4: Network Structure for Efficient Vulcanization System.

c. **Semi- Efficient vulcanization system**: This system of vulcanization is achieved by using intermediate sulphur level of 1 - 2phr or accelerator. The vulcanizates obtained have physical properties intermediate between those of conventional and efficient vulcanization systems. The network formed comprises of mono and polysulphidic cross-links.

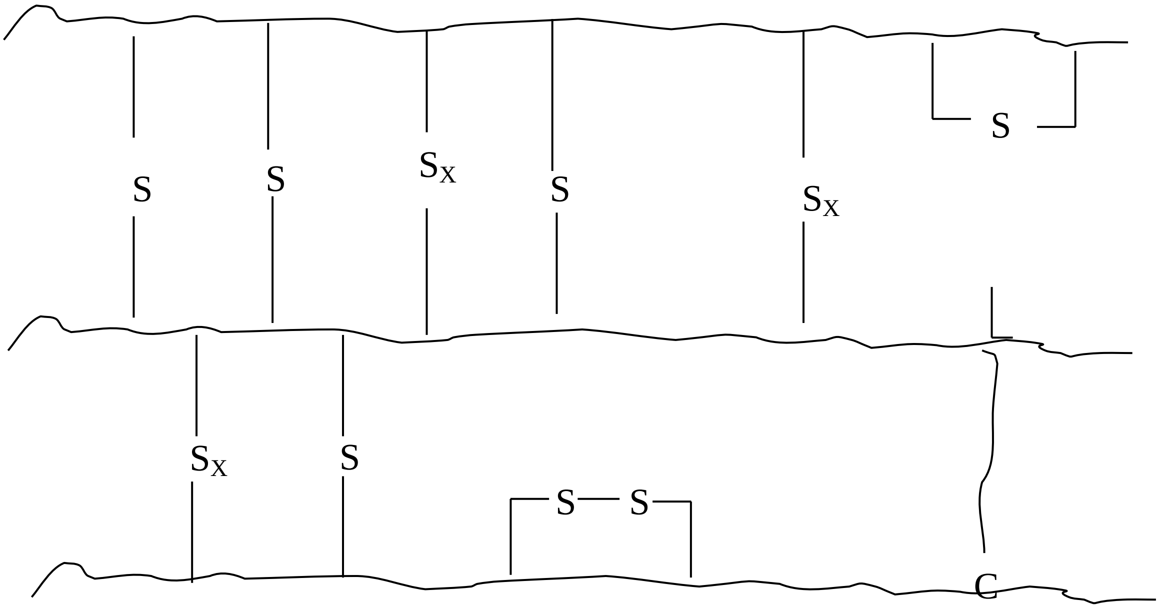
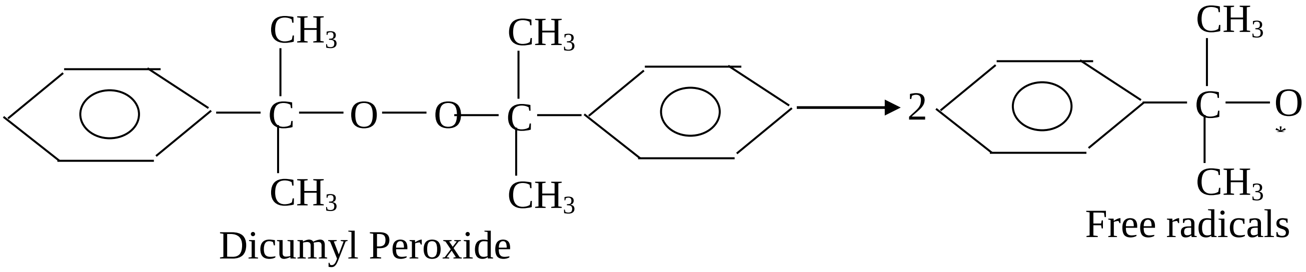


Figure 2.5: Network Structure for Semi Efficient Vulcanization System

2.8.2 Peroxide Vulcanization System

In the vulcanization of natural rubber, peroxide (organic peroxide) gives vulcanizate with outstanding resistance to ageing, compression set and creep. This type of vulcanizing agent does not enter into the polymer chain but produces free radicals which cause the formation of carbon- carbon cross-links with adjacent polymer chains. The carbon cross-links formed are quite stable. The peroxides are used in the production of heat stable vulcanizates of most diene polymers such as styrene butadiene rubber, natural rubber and butadiene rubber etc. Example of organic peroxide is dicumnyl peroxide. Peroxides are mostly used in the vulcanization of saturated rubber like silicon rubber. The peroxide decomposed to form free radicals which are able to remove some of the hydrogen atoms from the methyl group thereby permitting the carbon atoms of two adjacent chains to couple and form cross-links.



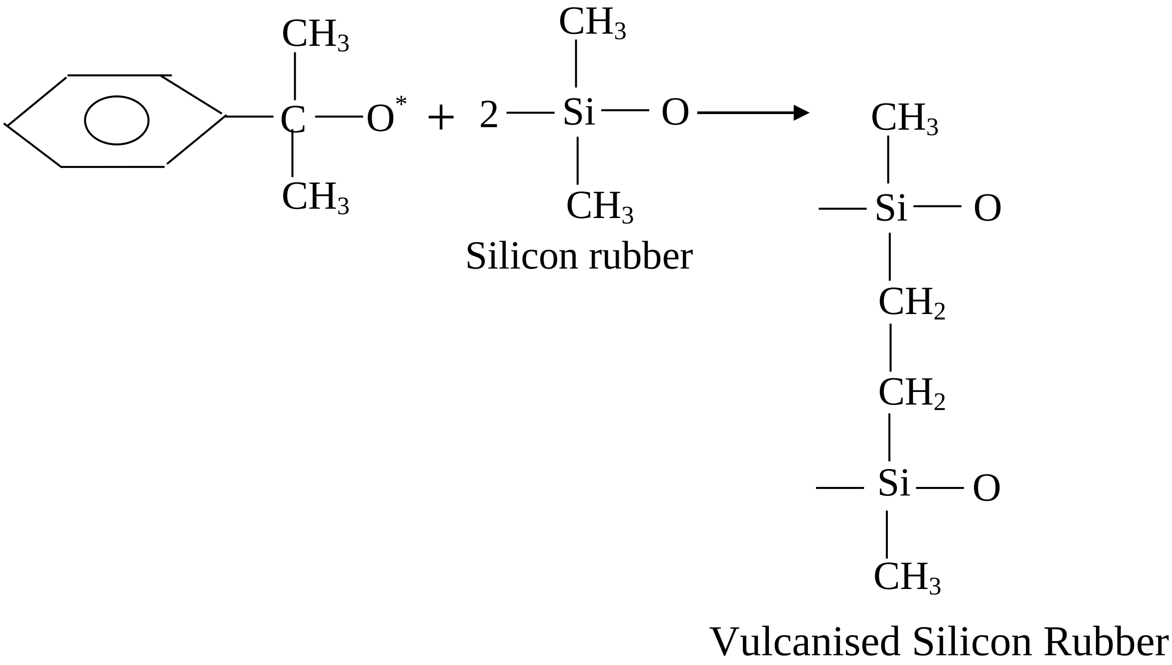


Figure 2.6: Network Structure for Peroxide Vulcanization System

2.8.4 Tellurium and Selenium

They are elements occupying the same group in the Periodic Table as sulphur. Their expensive nature coupled with repulsive odour and toxicity has limited the use of these elements as vulcanizing agents for natural rubber compounds. Nevertheless, they have been known to give natural rubber vulcanizate some increased heat resistance, well above that possible for conventionally vulcanized rubber compound.

2.8.4 Urethane “Novor” System

It was developed by the Malaysia rubber producers’ research association (MRPRA) for the cross-linking of natural rubber compound for a wide variety of applications. It is actually based on the products of the addition reaction of a nitroso-phenol and di-isocyanate. They can be used alone (novor system in which a case a dosage of 6 - 7phr is recommended) or in combination with sulphur (in the ratio of 19/10, 80/20, 70/30 60/40, 50/50 of the novor to sulphur). Typical example includes novor 924 and 750. The principal benefits of novor system are good ageing resistance, and an outstanding resistance to reversion.

2.8.5 Radiation Cure System

This involves the exposure of natural rubber compound to high energy radiation, typically about 40mrad. It gives carbon-carbon cross-links of the natural rubber vulcanizate which posed adequate and outstanding ageing resistance. In principle, this process has the attraction of providing a vulcanizate which could be free of extractable, perhaps toxic materials (Brydson, 1979).

$$\underset{\text{Rubber hydrocarbon}}{RH} \xrightarrow{\text{40Mrad}} R^{*} + {}^{*}H$$

$$H^{*} + RH \longrightarrow R^{*} + H_{2(g)}$$

$$R^{*} + R^{*} \longrightarrow \underset{\text{(Crosslink natural rubber)}}{R—R}$$

2.8.6 Metallic Oxide Vulcanization System

Metallic oxides are non-sulphur vulcanizing agents used for non-olefinic elastomers. For a cross-link to be effected, the elastomer must contain some active groups by which cross-links may occur. Carboxylated nitrile rubber, styrene butadiene rubber and polychlorophrene rubber can be cross-linked by the use of zinc oxide. Other metallic oxides such as magnesium oxide (MgO) and lead oxide

(PbO) are also used. Polychloroprene is vulcanized with zinc oxide taking advantage of the reactivity of the chlorine atom with the zinc oxide. For the vulcanization of polychloroprene, about 5phr of zinc oxide is recommended (Chuckwu, 2002).

2.9 Cross-linking

Cross-linking converts rubber from a linear polymer to a three dimensional network. Cross-linking provides anchoring points for the chains and these anchor points restrain excessive movement and maintain the position of the chains in the network. When a polymer sample is cross-linked, it improve the dimensional stability, lower the creep, increases resistance to solvents, it become less prone to heat and the Tg is raised. All these effects tend to be intensified as the crosslink density is increased. There are different types of cross-links:

i. Monosulphidic cross-links
ii. Disulphidic cross-links
iii. Polysulphidic cross-links
iv. Carbon-carbon cross-links

2.9.1 Monosulphidic Cross-links

This is the main crosslink obtained in an efficient vulcanization system. It gives vulcanizates which are resistant to oxidative ageing and high temperature compression set and stress relation properties are also maintained at minimum values. Resistance to tearing, fatigue and wear, and to a lesser extent, tensile strength is generally lower than that from a polysulphidic network.

2.9.2 Disulphidic Cross-links

Little is known about the properties of these cross-links mainly because it is very difficult to prepare a network in which disulphides are predominant (Chukwu, 2002). In both conventional and efficient sulphur vulcanizates, the proportion of disulphidic cross-links is seldom more that 20 - 30%.

2.9.3 Polysulphidic Cross-links

This is a crosslink in which two polymer chains are bridged by a chain of three or more sulphur atoms. It is most common in a conventional sulphur vulcanizate. It accounts for not less than 60% of the total cross-links inserted at optimum cure (Chukwu, 2002). They are associated with high mechanical strength. They are not as thermally stable as other cross-links. Vulcanizates produced using this type of crosslink generally have good tensile strength; tear resistance and fatigue provided heat is not involved during service life of the resultant vulcanizate, high compression set and high rate of creep and stress relaxation at elevated temperature.

2.9.4 Carbon-Carbon Cross-links

These types of cross-links result from peroxide curing systems. This network of cross-links is very stable at elevated temperatures. They give maximum resistance to creep and stress relaxation and compression set is low.

2.10 Swelling Behaviour

Solvent polymer compatibility problems are repeatedly encountered in industry. Choice of composite is of prime importance, as contact with highly compatible fluids may cause serious swelling and impair the operation of the system. The wrong selection can have far reaching consequences; the initial choice of materials for the seals in the landing gear of the DC-8 aircraft resulted in serious jamming because the seals became swollen when in contact with the hydraulic fluid (Wang, 2003). The extent of swelling of polymers in solvents depends on the solubility parameter of the polymer and the solvent. Where the solubility parameters of the polymer is close to that of the solvent, much swelling is expected (Ruys et al., 1999). Another factor which affects the swelling is the cross-linking density. The fewer the void for the liquid, particles to fill, hence reduced swelling.

CHAPTER THREE

3.0 MATERIALS AND METHOD

3.1 Materials

The major materials required in this work are groundnut shell, natural rubber and the compounding ingredients. The preparation of treated groundnut shell powder, characterization of the filler, compounding, cure characteristics, vulcanization and the various tests carried out were carefully discussed.

Table 3.1: Materials and their Sources

Materials	Sources
Natural Rubber	Famad Rubber Industry, Benin City
Groundnut Shells	Auchi, Edo State
Sodium hydroxide	British Drug House (BDH), England
Tetramethyl thiuram disulphide (TMTD)	British Drug House (BDH), England
Mercarpto benzothiazole sulphenamide (MBTS)	British Drug House (BDH), England
Stearic acid	British Drug House (BDH), England
Sulphur	British Drug House (BDH), England
Trimethylquinoline (TMQ)	British Drug House (BDH), England
Zinc Oxide	British Drug House (BDH), England
Mineral Processing Oil	British Drug House (BDH), England
Tetraoxo sulphate (Vi) acid	British Drug House (BDH), England
Acetic anhydride	Sigma Andriech, Germany
Glacial acetic acid	Sigma Andriech, Germany

3.1.1 Machines and Equipments

Tensile Properties

Machine: Instron Universal Tensometer

Model: SSTM - Smart -1 - Series - 20KN

Manufacturer: Scientific Instrument Co. Ltd., U.S.A

Flexural Properties

Machine: Flex Tensometer

Model: LCH - 150KN

Manufacturer: Vecomtech Co. Ltd., Viet Nam

Abrasion Resistance

Machine: Taber Oscillating Abrasion Tester

Model: 6160 - F735

Manufacturer: Taber Co. Ltd., Canada

Compression Set

Machine: High Energy Compressor

Model: CTM - 2P - 200 - 2000KN (200Tons)

Manufacturer: Interlaken Technologies Co. Ltd., Thailand

Cure Characteristics

Machine: Mosanto Rheomter

Model: MDR 2000 Series

Manufacturer: Interlaken Technologies Co. Ltd., Thailand

Fourier Transform Infrared Spectroscopy

Machine: Fourier Transform Infra-Red Spectrometer

Model: Subpart ZZZZ-MACT-320

Manufacturer: Pine Equipments Co. Ltd., U.S.A

Hardness

Machine: Wallace Hardness Tester

Model: c8007/25

Manufacturer: Interlaken Technologies Co. Ltd., Thailand

3.2 Method

3.2.1 Mercerization Process

Groundnut shells were pounded in a mortar to fine particle size. After which, 40g each of them were soaked in 5, 10,15, 20, 25, and 30% sodium hydroxide solutions for 1hour at room temperature. The solutions were then filtered and thoroughly washed with distilled water, dried at room for 48 hours follow with oven drying at 70^{O}**C** for 2 hours.

$$\text{Fibre} - \text{OH} + \text{NaOH} \rightarrow \text{Fibre} - \text{ONa} + H_2O \qquad 3.1$$

3.2.3 Acetylation Process

Pounded groundnut shells were immersed in 20% sodium hydroxide solution for 1hour at room temperature. The alkaline treated shells were then soaked in 5% glacial acetic acid for 1hour at room temperature. The mixture was filtered and 40g each of the filtered groundnut shell were soaked in 5, 10, 15, 20, 25 and 30%s acetic anhydride containing one drop of concentrated sulphuric acid for five minutes. The solutions were then filtered again and thoroughly washed with distilled water; dried at room temperature for 48 hours followed with oven drying at 70^{o}C for 2 hours.

$$\text{Fibre} - \text{OH} + CH_3CO^- \rightarrow \text{Fibre} - OOCH_3 + H^+ \qquad 3.2$$

3.3 Characterization of Filler

The powdered groundnut shell was characterized as follow in terms of bulk density and moisture absorption at relative humidity of 60%, thermal stability and chemical constituents.

3.3.1 Bulk Density Determination

The bulk density was determined according to the method described by Ishak and Baker (1995). Accurately weighed samples were poured into a uniform cylinder of cross section 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 thus:

$$\text{Bulk density} = \frac{\text{Mass}}{\text{Volume}} \qquad 3.3$$

3.3.2 Moisture Absorption Determination

The moisture adsorptions at relative humidity of 60°C of the untreated and treated shell powder were determined using the method described by Wang (2004) Samples were kept in a refrigerator for 24hours. After which the samples were removed and weighed. The percentage moisture absorption was calculated thus:

$$Moisture\ Content\ (\%) = \frac{Initial\ Weight\ -\ Final\ Weight}{Initial\ Weight} \times 100\,. \qquad 3.4$$

3.3.3 Thermal Stability Determination

The thermal stability test of treated and untreated groundnut shell powders were conducted using the flammability test as described by R.R. Costa (2008)

3.3.4 Chemical Composition Determination

The powdered groundnut shell was characterizes in terms of the lignin content, hemicellulose content, ash content and cellulose content.

3.3.4.1 Lignin Content Determination

The lignin content in groundnut shell was determined according to ASTMD1106 – 56 (1997) as follows: a one gram, oven dried sample of extractive free groundnut shell was placed in a 150cm^3 beaker. 15cm^3 of cold Sulphenic acid 72% was added slowly while stirring and mixed well. The reaction proceeded for 2hours with frequent stirring in a water bath maintained at 20^{o}C. The content of the flask was filtered after washing with distilled water into a glass crucible of known weight. The residue was washed free of acid with 500cm^3 of hot water and them over dried at 103+2%. Crucibles was then cooled in desiccators and weighed until a constant weight was obtained.

The following formula was used to obtain the lignin content.

$$\text{Lignin content (\%)} = \frac{W_4W_3}{(100-w_2) \times (100 - w_1)} \tag{3.5}$$

Where;

W_1 = Alcohol toluene extractive content (percent)

W_2 = Weight of oven-dried extractive-free sample (grams)

W_3 = Weight of oven-dried crucible (grams)

W_4 = Weight of oven-dried residue and crucible (grams)

3.3.4.2 Hemicellulose Determination

Hemicellulose in powder groundnut shell was determined using the method described by ASTMD1104-56 (1978). A two-gram sample of oven dried extractive free powdered grounded not shell was weighed and placed into a $250cm^2$ flask with a small watch glass cover. The specimen was then treated with $150mcm^3$ of distilled water, $0.2cm^2$ of cold glacial acetic acid, and one gram of nacho, and placed into a water bath maintained between 70^oC – 80^oC. Every hour for 5 hours $0.22cm^3$ of cold glacial acetic acid and one gram of nodes were added and the contents of the flask were stirred constantly. At the end of 5 hour, the flasks were placed in an ice water bath until the temperature of the flasks was reduced to 10^oC and the contents of the flask weight. The residue was washed free of odour the $500cm^3$ of cold distilled wiper and the residue change colour from yellow to white. The crucible was then oven-dried at 103 ± 2^oC, then cooled in a desiccator, and weighed until a constant weight was reach. The following formula was used to determine the hemicelluloses content in powered groundnut shell.

$$\text{Hemicelluloses (\%)} = \frac{W_4 - W_3}{(1000w_2) \times (100 - w_1)} \qquad 3.6$$

Where;

W_1 = alcohol - toluene extractive content (percentage).

W_2 = weight of oven - dried extractive - free sample (grams)

W_3 = weight of oven - dried crucible (grams).

3.3.4.3 Cellulose Content Determination

Cellulose in powdered groundnut shell was determined according to ASTMD 1103-60 (1978). A three gram oven dried sample of holocellulose extracted from the powdered groundnut shell was placed in a 250cm3. Erlenmeyer flask with a small watch glass cover was used. The flasks were placed into water bath that was maintained at 20°C. The sample was then treated with 50cm^3 of 17.5 percentage sodium hydroxide and thoroughly mixed for one minute and allowed to react for 30mins and 50cm^3 distill water was added. The contents of the flask were filtered into a glass crucible of known weight. The residue was washed first with 50cm^3 of 8.3 percent NaOH, then with 40cm^3 of 10% acetic acid. The residue was washed free of acid with 1000cm3 of hot water. The crucible was oven-dried in an oven at 103± 2°C, then cooled in desiccator, and weighed until a constant weight was reached. The formula used to obtain the cellulose content is:

$$\text{Cellulose (\%)} = \frac{W_4 - W_3}{(1000w_2) \times W_1} \qquad 3.7$$

Where:

W_I = Holocellulose content (percentage)

W_2 = Weight of oven - dried holocellulose sample (grams)

W_3 = Weight of oven - dried crucible (grams)

W_4= Weight of oven - dried residue and crucible (grams)

3.3.5 Fourier Transform Infrared Test

The Fourier Transform Infrared of the powdered samples was carried out using the Fourier's Transform Infrared Spectrometer

3.4 Characterization of Natural Rubber

The Natural Rubber was characterized as follows:

3.4.1 Dirt Content

The process involves homogenizing 20g of natural rubber in a Two-roll Mill (nip setting 0.33mm) and a test piece of 10g was weighed out and cut into pieces. The piece of rubber is placed in a conical flask containing 250ml of mineral turpentine and 1ml of RPA No.3 is added. The Flask with its content will be placed in the oil bath and heated to about 135^{o}C for 4hours. On complete dissolution the hot solution will be filtered through a previous weighed, clean and dry sieve by decantation. The dirt in the flask will be washed into the sieve with a jet of warm mineral turpentine. The sieve with the dirt will dried in an oven at 90^{o}C - 100^{o}C.

$$\text{Dirt Content (\%)} = \frac{\text{Weight of Dirt}}{\text{Weight of test portion}} \times 100 \qquad 3.9$$

3.4.2 Volatile Matter

From a homogenized sample, a test portion of 10g was weighed out and passed twice through the Two-roll Mill. The milled test piece was folded loosely and placed on a properly labeled watch glass. This was fed into an oven maintained at 100^{o}C for 4hours after which the test piece was removed and cooled for 30mins. The volatile matter is expressed as percentage of the test portion.

$$\text{Volatile Matter (\%)} = ((A-B)/A) * 100 \qquad 3.10$$

Where:
A = Weight of Test portion before drying
B = Weight of test portion after drying

3.4.3 Ash Content

A test portion of 5g will be weighed out from the homogenized piece and wrapped in an ash less filter paper. The wrapped test portion was placed in a covered crucible which has been previously ignited and weighed. The crucible with its contents was introduced into a muffle furnace controlled at a temperature of 550°C for 5hours. The crucible will then be removed and allowed to cool in desiccators and weighed.

$$\text{Ash (\%)} = \frac{\text{Weight of Ash}}{\text{Weight of test portion}} \times 100 \qquad 3.11$$

3.4.4 Plasticity Retention Index

The unaged (P_o) and aged (P_{30}) plasticity of rubber are those measured on a Wallace Rapid Plastometer using unaged test piece and test aged in an air oven for 30mins at 140°C respectively. It is expressed as:

$$\text{PRI (\%)} = \frac{\text{Aged Plasticity } (P_{30})}{\text{Aged Plasticity (Po)}} \times 100 \qquad 3.12$$

3.5 Processing of the Composite

This involves Compounding of natural rubber with powdered groundnut shell filler. The formulation used for the compounding of the natural rubber (NSR 10) with the treated and untreated groundnut shell filler is given in Table 3.2

Table 3.2: Formulation for Compounding Natural Rubber (Asore, 2000).

Ingredient	**Parts per hundred rubber**
Natural rubber	100
Fillers (GNS)	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 seven was used to multiply the weight of the ingredients in parts per hundred of the rubber. After mixing, the rubber composite was stretched out. Mixing follow ASTMD 3184-80 standard

3.5.1 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°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 (GNS)	10
Addition of MBTS	1
Addition of TMTD	1
Processing Oil	1
Addition of Sulphur	2
Total	**22**

3.5.2 Cure Characteristics

The cure characteristics were determined using the Mosanto Rheometer, MDR 2000 model at 150^{o}C. The cure time predicted by the Mosanto rheographs was used as a guide to obtain vulcanizates for the test specimen.

3.5.3 Compounded Composite Curing

The curing of test pieces was done in a compression moulding machine. The curing was carried out at 140^{o}C for 15mins.

3.5.4 Mechanical Properties of the Composite

The mechanical properties of the composites formed were determined using standard task procedures.

3.5.4.1 Tensile Properties Determination

The tensile properties were determine on an Instron Universal Tensometer using dumbbell test pieces of dimension (45 x 5 x 5 x 2) as contained in ASTMD 412- 87 method. The machine measures both the tensile stress and the tensile strain, and modulus elongation at break. The tensile stress is the strength of pull in the area between the notch marks. It is based on the original cross sectional area. The tensile strain is a measure of how the test sample has been stretched by the pull.

3.5.4.2 Hardness Test Determination

The hardness of the sample was determined by adopting the standard dead load method. The standard dead load method of measurement covers rubbers in the range of 30 to 85 international rubber hardness degrees (IRHD). The test was carried out in accordance with ASTMD 785 (1983).

3.5.4.3 Compression Set Determination

The procedure adopted for the measurement of compression set was based on ASTM 385. High energy Compressor machine was used. Compression set evaluated 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. The test sample was cut to standard dimension and compressed between two parallel steel plates under a stress of 2.8Mpa. It was then conditioned for a selected time of 22 hours at 70^{o}C after which the sample was removed and allowed recovering at room temperature for 30 minutes. The compression set is the difference between the original thickness of the sample and the thickness after test expressed as a percentage of the original thickness.

$$\text{Compression set } (\%) = \frac{t_o - t_r}{t_o} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. 3.13$$

Where:

t_o is the initial thickness of the sample

t_r is the recovered thickness of the sample

3.5.4.4 Flex Fatigue Determination

The measurement was carried out in accordance to the procedure described in ASTMD 430 using the Flex Tensometer machine, which functions by inducing surface cracking of the rubber vulcanizates sample.

3.5.4.5 Abrasion Resistance Determination

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

$$Abrasion\ \mathrm{Re}\,sis\tan ce = \frac{Weight\ \ Loss\ \ of\ \ the\ S\tan dard}{Weight\ Loss\, of\ \ the\ Sample} \times 100 \qquad 3.14$$

3.5.4.6 Impact Test Determination

The impact test was carried out by supporting the sample at both ends and placed horizontally with the impact applied midway between the two supports. A pendulum of known mass fall through a known height, strike the specimen as it continued its swing or return. The difference between the initial height and the height it reached after impact on the test sample is the impact strength of the sample. Thus the difference between the height is proportional to the energy absorbed.

3.6 Swelling Analysis

Circular specimen of diameter 20mm were punched out from the vulcanized sheets and weighed. Specimens of known weights were immersed in the solvents (acetone, toluene and xylene) in different diffusion bottles, kept at room temperature. The samples were removed at periodic intervals, dried using tissue papers and the new weights recorded. The experiment was carried out at intervals of two hours until no further increase in solvent uptake was noticed.

3.6.1 Mole Percentage Uptake of the Solvent

The mole percentage uptake of the solvents, Q for the samples was determined using equation:

$$Q = \frac{[(W_1 - W_0)/M] \times 100}{W_0} \qquad 3.15$$

Where:
W_1 and W_0 are the weights of the specimen after and before swelling.

M = molar mass of the solvents

3.6.2 Swelling Index

The swelling index is calculated using the equation:

$$SwellingIndex(\%) = \left(\frac{As}{W}\right) \times 100 \qquad 3.16$$

Where:

A_s = Amount of solvent absorbed by the sample

W = Initial weight of the sample before swelling

3.6.3 Swelling Coefficient

The swelling coefficient which is an index of the ability with which the samples swells are determined by the equation:

$$\text{Swelling coefficient } (\alpha) = (A/M_s) \text{ x } 1/d \qquad 3.17$$

Where:

A is the weight of the solvent sorbed at equilibrium swelling

M is the mass of the sample before swelling and

d is the density of the solvent used.

3.6.4 Cross-linking Density

Cross-linking density was evaluated as the difference between the maximum and minimum torque rise calculated from the rheographs (Oladimeji et al, 2004).

3.7 Statistical Techniques for Empirical Analysis of Experimental Data

This section explains the Statistical methods applied in the experimental data analysis (data treatment) to establish the significant relationships among the concentrations of samples, the mechanical properties, swelling behaviour and cross linking densities. The results obtained during the experimentation using initial treatments are analysed using Analysis of Variance (ANOVA) techniques.

3.7.1 Analysis of Variance (ANOVA) Technique

Analysis of Variance is a statistical technique used to test the significant relationship between or among variables. The significant difference may occur in the raw results, mean difference or variance of the variables. In this technique, data are usually partitioned into sum of squares total (SST), sum of squares treatment (SSTr), sum of squares error (SSE) and mean sum of squares (MSS). The test follows F-test which is the ratio of the Mean Sum of Squares Treatment to the Mean Sum of Squares Error. The test statistic is tested at 5% critical value using P-value of the result outputs as the analysis is conducted electronically.

ANOVA procedure is used to test the significant relationship among concentration of mechanical properties (Tensile Strength, Modulus, Elongation at Break, Hardness, Compression Set, Abrasion Resistance, Flex fatigue) and vulcanizate types (Acetylated and Mercerized) based on initial treatment. It is used in the test of significant relationship among swelling behaviour of Vulcanizate types using initial treatment indicators. The ANOVA procedure is adopted in the test of significant relationship among swelling behaviour of Vulcanizate types based on Xylene and Tuolene reagents based on initial treatment. The cross linking densities of Acylated and mercerized vulcanizate categories significant relationship are performed using ANOVA. Comparison test statistics such as Least

Significant Difference (LSD) Test and Duncan Multiple Range (DMR) Test are adopted to investigate the existence of significance in the result outputs.

3.7.2 Algorithm of Analysis of Variance (ANOVA)

Step1: Obtain the data design and calculate sum of squares

Sum of squares total

$$SST = \sum_{i=1}^{r}\sum_{j=1}^{v} x_{ij}{}^{2} - \frac{G^2}{N} \qquad G^2 = \sum Y^2 \qquad N = r.v$$

Sum of squares concentration

$$SSTr(concentration) = \sum_{i=1}^{r} \frac{C^2}{r} - \frac{G^2}{N}$$

Sum of squares vulcanizate types

$$SSTr(Vulcanizates) = \sum_{i=1}^{r} \frac{VT^2}{v} - \frac{G^2}{N}$$

Sum of Squares Error

$$SSError = SST - SS(conc) - SS(vulcanizate)$$

Step2: Calculated Mean Sum of Squares

Mean sum of squares Concentration

$$MSTr(concentration) = \frac{SSTr(Concentration)}{r-1}$$

Mean sum of squares Vulcanizate

$$MSTr(Vulcanizate) = \frac{SSTr(Vulcanizate)}{v-1}$$

Mean sum of squares Error

$$MSE(Error) = \frac{SSError}{r-1}$$

Step3: Compute the F-calculated values;

$$Fcal(Concentration) = \frac{MS(Concentration)}{MSError}$$

$$Fcal(Vulcanizate) = \frac{MS(Vulcanizate)}{MSError}$$

Step 4: Compute the F-tabulated

$Ftab = F_{(r-1)}\alpha$, for concentration

$Ftab = F_{(r-1)}\alpha$, for vulcanizate

$Ftab = F_{(r-1)(v-1)}\alpha$, for mean sum of squares error

Step 5: Decision Rule

- If $Fcal < Ftab$, there is significant relationship (differences exist)
- If $Fcal > Ftab$, there is no significant relationship (no differences exist i.e the are the same or similar)

Step 6: Draw conclusion and make reports about the findings based on the decision rule.

3.7.3 Data Interpretations

The interpretation of ANOVA will be based on the value of F-test statistic if the analysis is manually done but electronic analysis using statistical software employs Probability value associated with the F-test compare with the level of significance or critical value of 5%.

3.7.3.1 Decision Rule for electronic result

- If $P-Value < 0.05$, there is significant relationship (differences exist)

- $P - Value > 0.05$, there is no significant relationship (no differences exist i.e. they are the same or similar). If differences exist or the results are significant, further investigation is carried out as to identify the actual significant using Comparing Treatment Test Statistic such as LSD Test and DMR Test. This thesis will employ the used of statistical software to analyze the data based on ANOVA procedure. The software used during the analysis of variance (ANOVA).

The thesis will also employ the used of statistical package to design coding for the ANOVA procedure. The package that will be adopted for these analyses is **Excel Programming Office 2010**. Also statistical software employs to analyze results based on the concentration of samples, the mechanical properties, swelling behaviour and cross linking densities for the ANOVA is **Statistical Package for the Social Sciences (SPSS)** version **20.0**.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Results

Results of the tests carried out are shown in Tables 4.1- 4.10:

Table 4.1: Characterization of Natural Rubber

Grade	NSR -10
PRI	70%
Dirt Content	0.08%
Ash Content	0.6%
Volatile Matter	0.8%

Table 4.2: Physico-Chemical Properties of the Treated Groundnut Shell

Concentration (%)	Cellulose (%)	Moisture Absorption (%)	Lignin Content (%)	Thermal Stability (g/s)	Hemicellulose (%)	Bulk Density (g/cm^3)
5	[12.75] (14.43)	[8.90] (8.79)	[17.89] (16.08)	[2.8] (2.4)	[19.08] (16.65)	[0.91] (0.85)
10	[15.12] (17.56)	[8.60] (8.20)	[14.21] (13.55)	[2.5] (2.0)	[18.77] (15.12)	[0.71] (0.69)
15	[16.89] (19.24)	[8.55] (8.01)	[13.47] (11.23)	[2.3] (1.9)	[17.54] (13.31)	[0.62] (0.54)
20	[20.09] (24.33)	[8.50] (7.64)	[12.96] (10.07)	[2.1] (1.8)	[17.08] (12.75)	[0.56] (0.45)
25	[21.83] (26.22)	[7.20] (6.15)	[10.06] (9.98)	[1.9] (1.6)	[14.46] (11.88)	[0.50] (0.40)
30	[28.95] (32.11)	[6.10] (5.83)	[8.12] (7.66)	[1.7] (1.4)	[9.22] (7.35)	[0.45] (0.30)

Key: Acetylated Fibre ( )
Mercerized Fibre [ ]

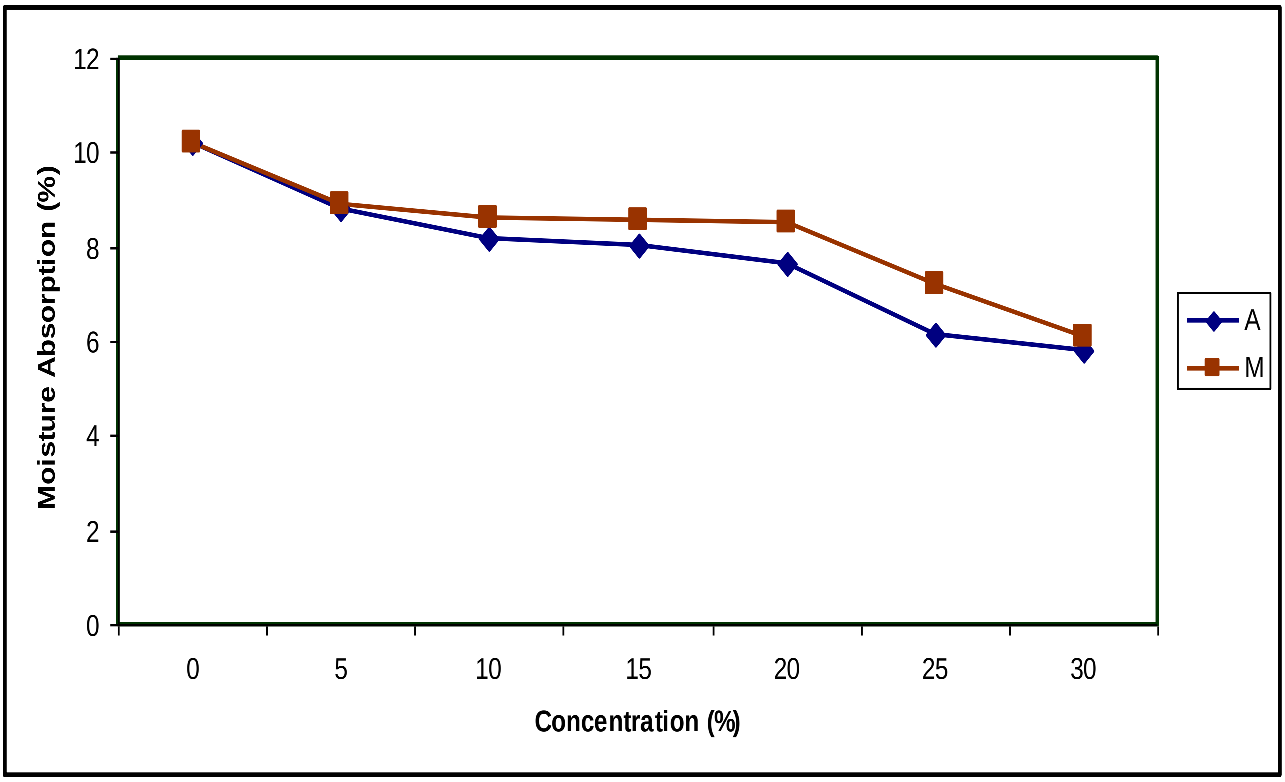


Figure 4.1: Moisture Absorption of the treated Groundnut Shell Fillers

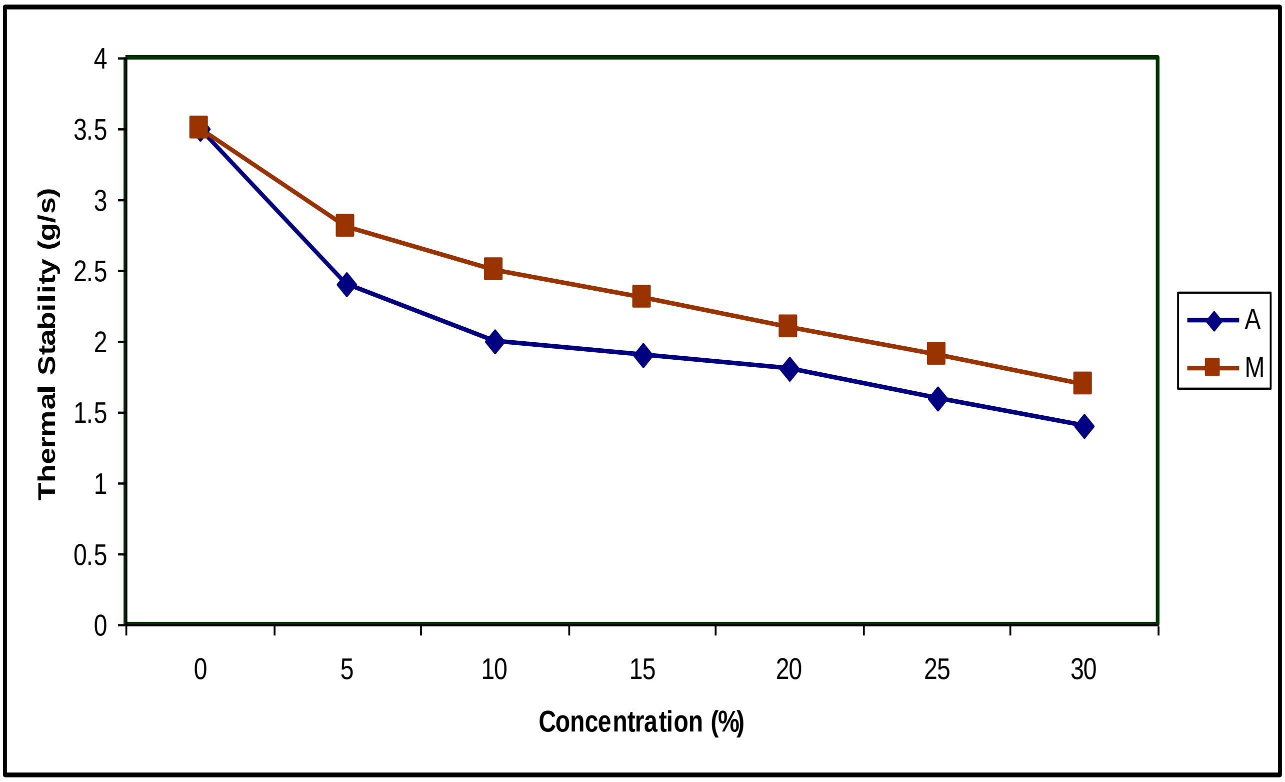


Figure 4.2: Thermal Stability of the treated Groundnut Shell Fillers

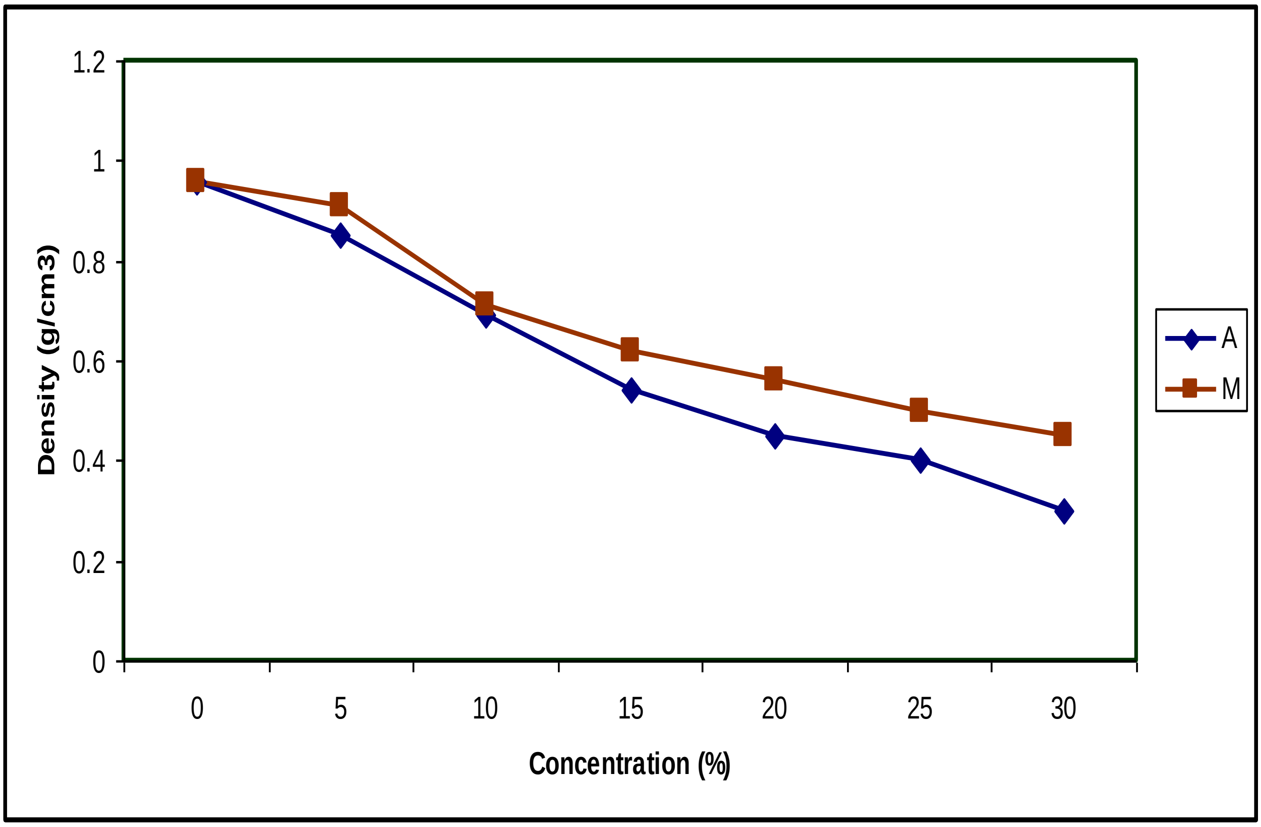


Figure 4.3: Density of the treated Groundnut Shell Fillers

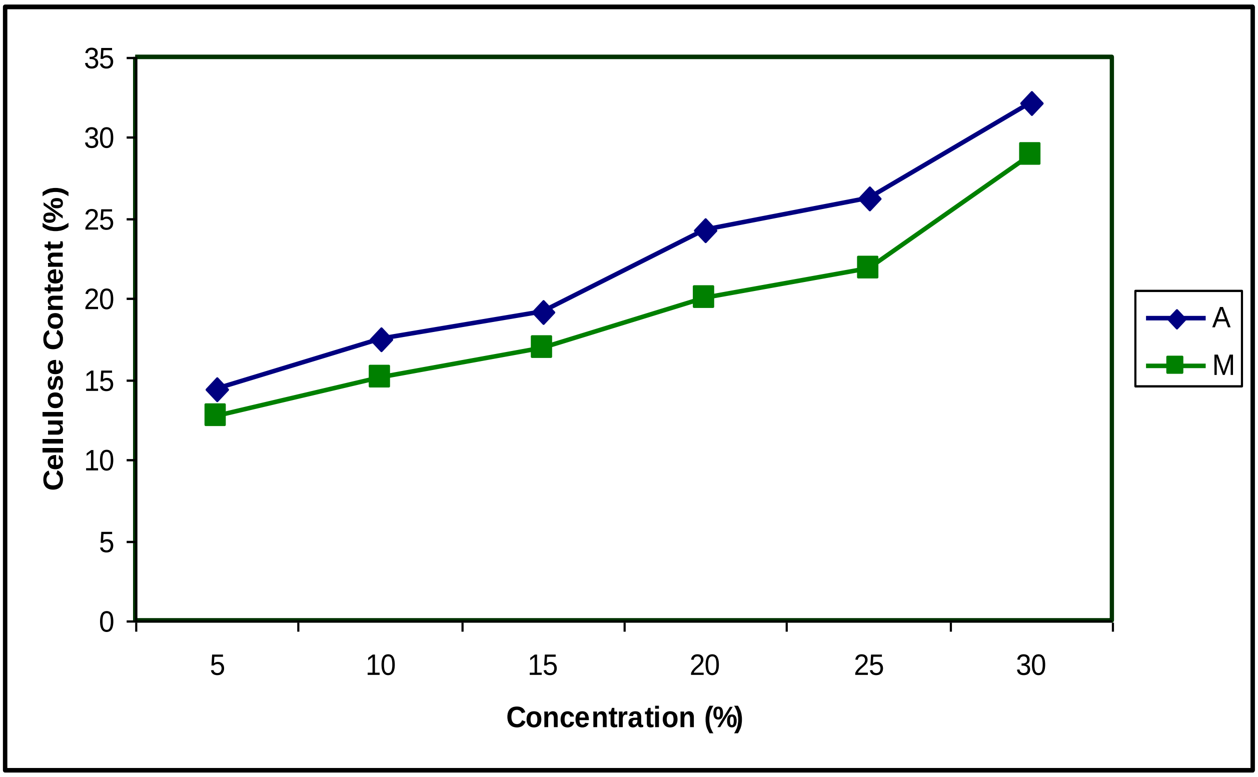


Figure 4.4: Cellulose Content of the treated Groundnut Shell Fillers

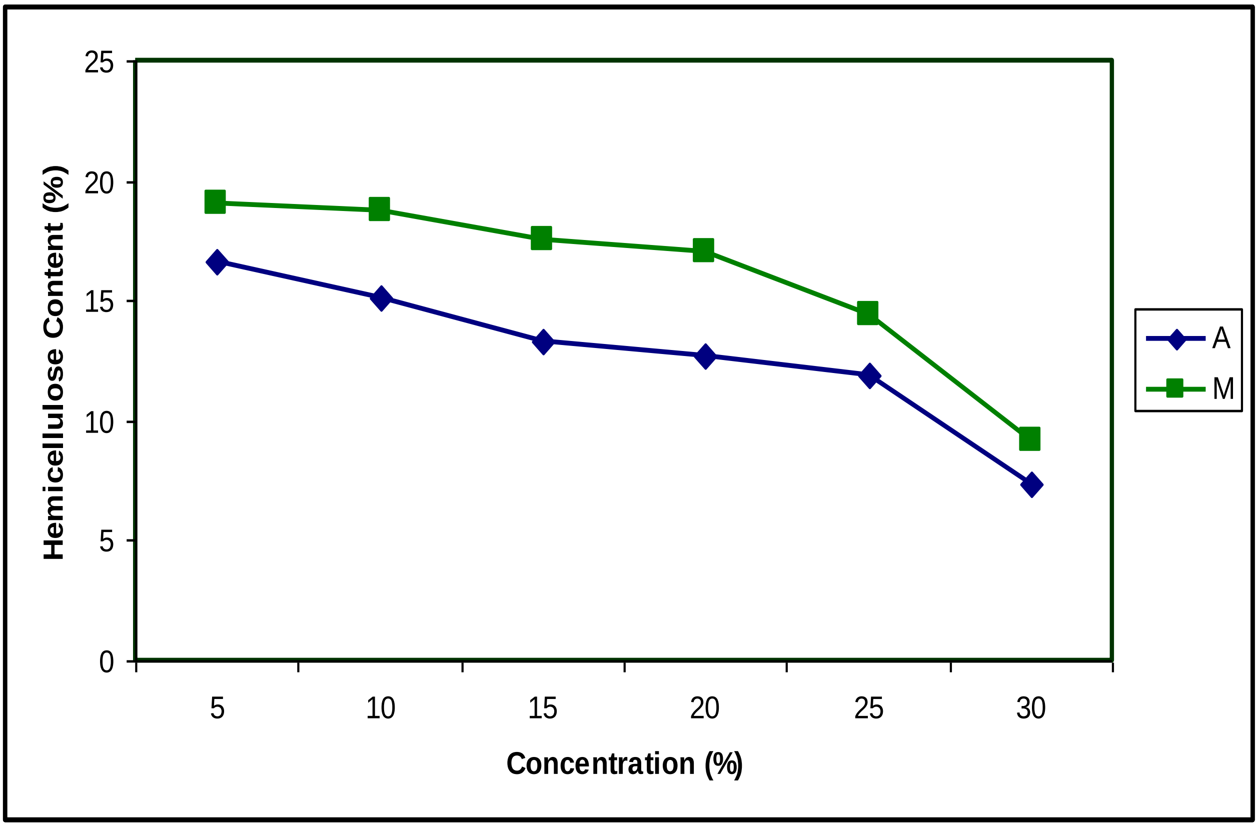


Figure 4.5: Hemicellulose Content of the treated Groundnut Shell Fillers

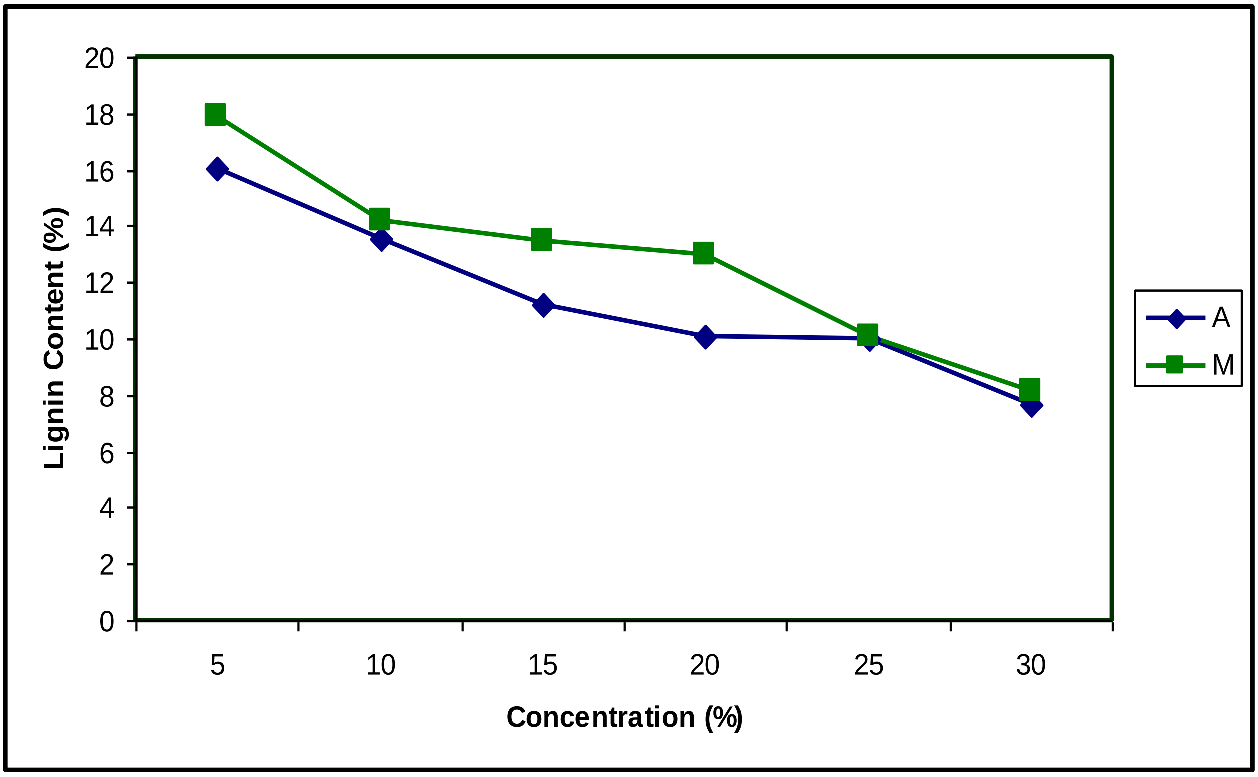


Figure 4.6: Lignin Content of the treated Groundnut Shell Fillers

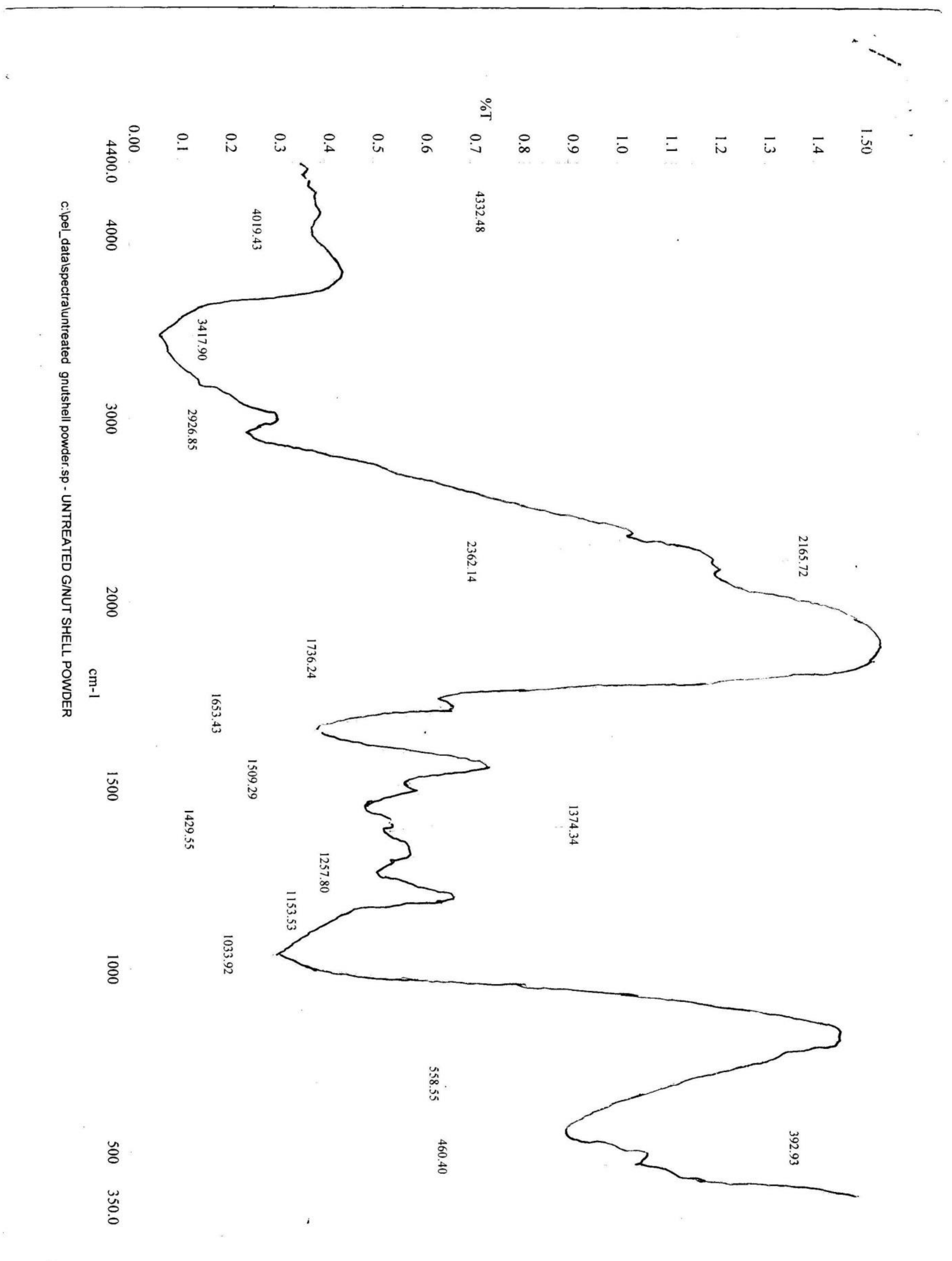


Figure 4.7: FTIR Spectra of Untreated Groundnut Shell Fillers

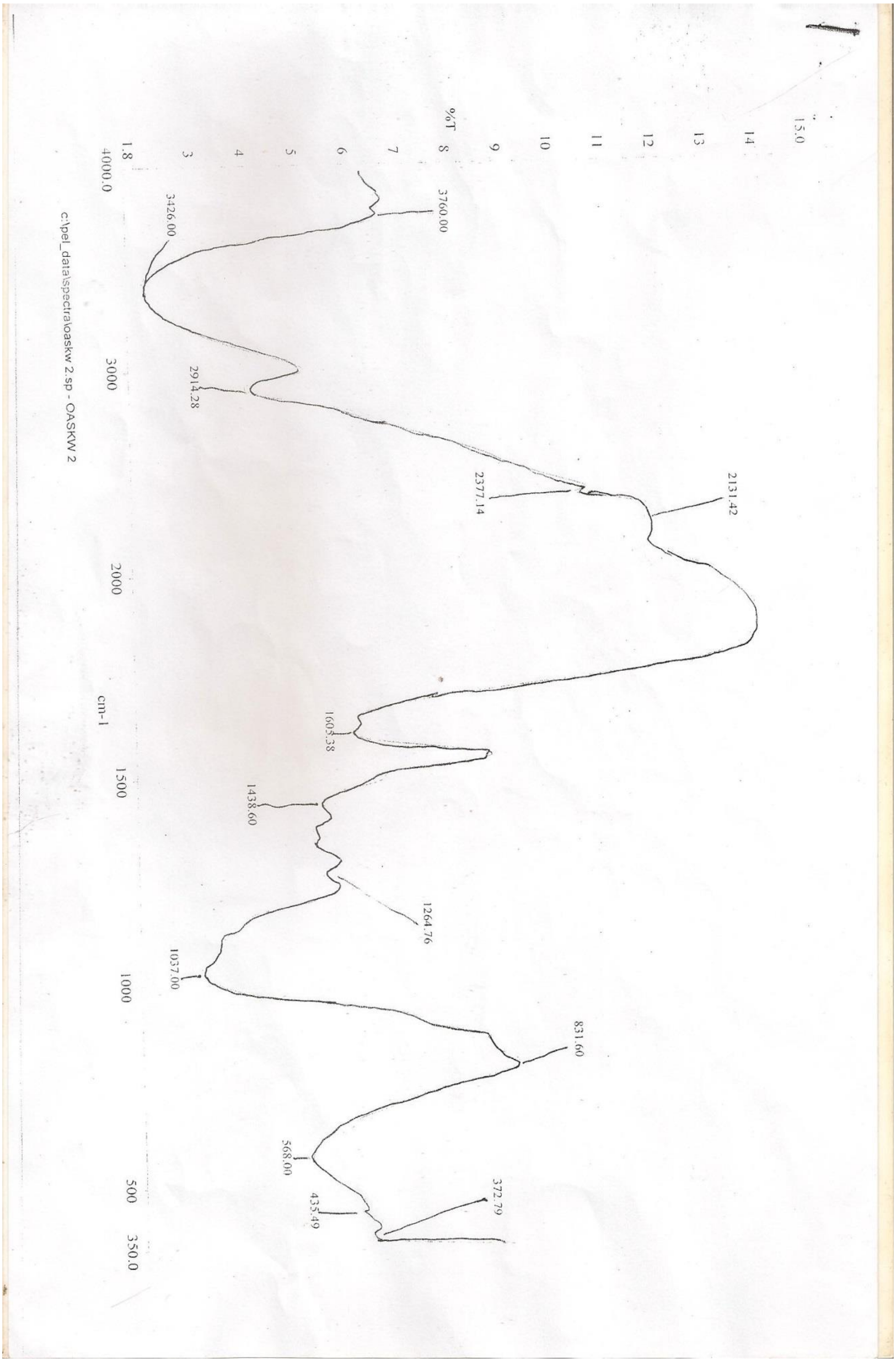


Figure 4.8: FTIR Spectra of Mercerized Groundnut Shell Fillers

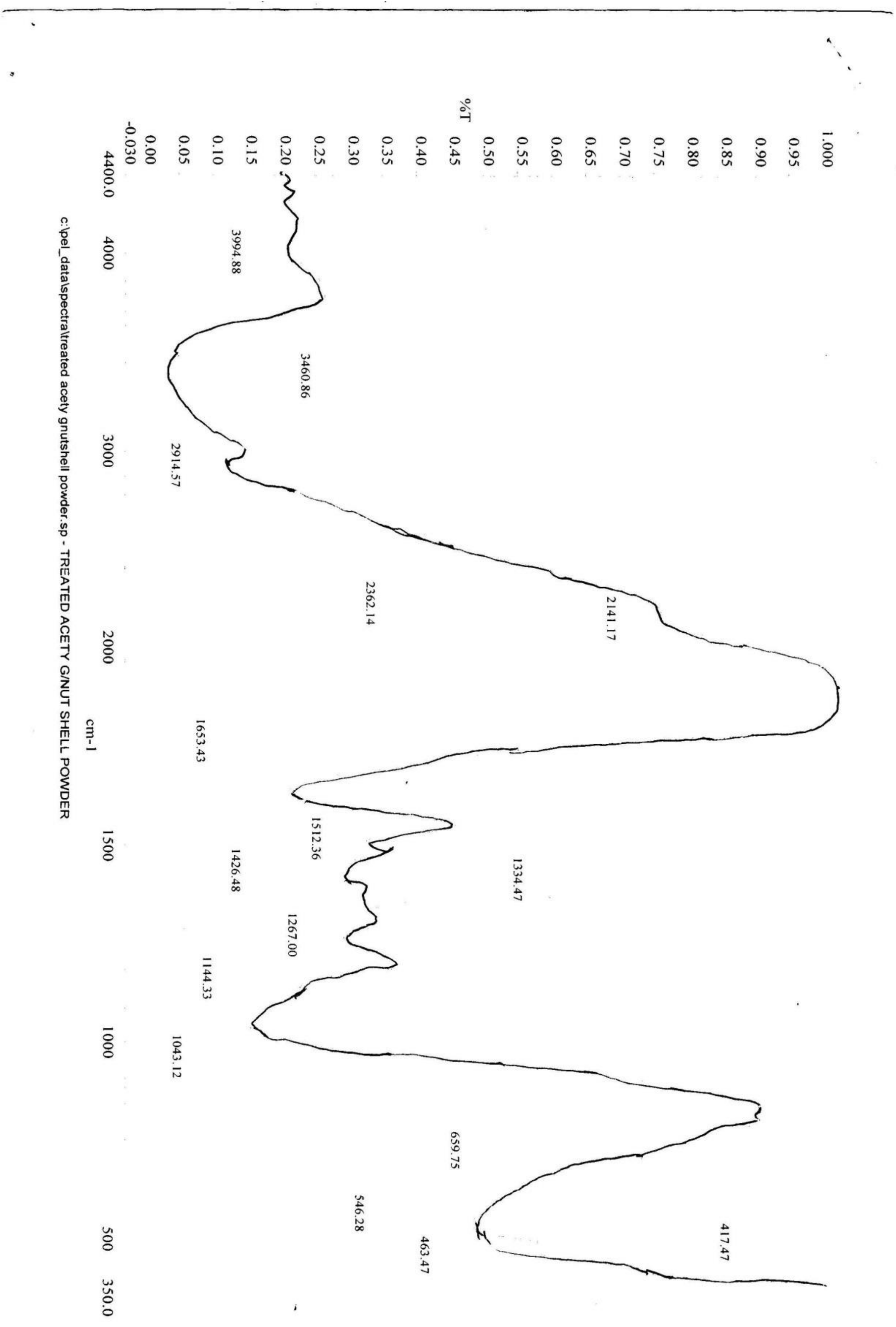


Figure 4.9: FTIR Spectra of Acetylated Groundnut Shell

Table 4.3: Infra-red Characteristics of Untreated Groundnut Shell Powder

Wave number (cm^{-1})	**Functional Group**	**Characteristics**
3417.90	Alcohol O-H	Stretching
2926.85	Methylene Asymmetric C-H	Stretching
2362.14	Combination C-H	Stretching
2165.72	Combination and Overtone O-H	Stretching bands
1653.43	C=C	Stretching
1429.55	Methylene	Stretching
1153.53	In-Plane C-H	Stretching
1033.92	In-Plane C-H	Stretching
558.55	Out of plane C-H	In plane bending
460.40	= C – G	Bending
392.93	Out of plane C-H	Stretching
3417.90	Alcohol O-H	Stretching
2926.85	Methylene Asymmetric C-H	Stretching
2362.14	Combination C-H	Stretching
2165.72	Combination and Overtone O-H	Stretching bands

Table 4.4: Infra-red Characteristics of the Treated Groundnut Shell Powder

Wave number (cm-1)	**Functional Group**	**Characteristics**
3460.86	Alcohol O-H	Stretching
2914.14	O-H	Stretching
2362.14	Combination C-H	Stretching
2141.17	Combination and overtone O-H	Stretching bands
1653.43	C=C	Stretching
1426.48	C-O-H	In plane bending
1334.47	Methyl symmetrical C-H	Bending
1300 – 1000	Aliphatic C-O	Stretching
Wave number (cm-1)	Functional Group	Characteristics
3460.86	Alcohol O-H	Stretching
2914.14	O-H	Stretching

4.2 Discussion

4.2.1 Results of Filler Characterization

The chemical structure of the groundnut shell powder and the chemically treated groundnut shell powder components are shown in Figures 4.7 - 4.9; the FTIR spectra of groundnut shell powder show a strong characteristic carbonyl absorption peak at 1736.24cm^{-1}. This was attributed to the acetyl and uronic ester groups of the hemicelluloses or the carboxylate groups of the ferulic and p-coumeric acids of lignin and hemicellulose (Kamel, 2007). The peaks at 1509.29 and 1429.55 cm^{-1} in the groundnut shell powder show the aromatic C =C stretch of the aromatic rings of the lignin (Donescu et al., 2008, Laka and Chernyavskaya, 2007). 1653.43cm^{-1} C=C stretching confirm the presence of the lignin aromatic rings. Alcohols and phenols produce characteristics infrared bands the to O-H stretching at 3417.90cm^{-1} and C-O stretching at 1257.80 and 1033.92cm^{-1} which are both sensitive to hydrogen bonding (Kamel, 2007 and Donescu et al, 2008).

The FTIR spectra of acetylated groundnut shell powder shows the removal of pectins, lignin and hemicelluloses resulting from the varnishing characteristic band at 1736.24cm^{-1} (carbonxylic groups), prominence of 1605.51cm^{-1} (acetyl group) and reduction in the intensity of 1257.80cm^{-1} (methyl ester groups) 1509.29 and 1429.55cm^{-1} (aromatic C=C stretch) indicating the treatment had removed some amount of pectin, lignin and hemicelluloses. Equally this was in accordance with the chemical changes in the surface and it's crystalline in literature (Nakagaito et al, 2005).

The results in Table 4.2 shows that the weight of the acetylated groundnut shell and that of the untreated after taking the bulk density of both are almost the same 0.49g/cm^3 for the acetylated and 0.5g/cm^3 for the untreated shell. This is due to the treatment given to the acetylated powdered shell. The density decreases with increase in concentration of the treating agents.

There was decrease in the moisture absorption for the acetylated treated shells. Reduction of about 50% moisture up take for acetylated jute fibres has been reported by Bleezki and Gassan (1999).

The materials tested were assumed to be thermally homogeneous. The heat flow showed the rate of consumption of the material as a function of time. It shows that chemical treatment can increase the thermal stability of the treated shell as a result of the consumption rate of the material per minutes i.e. burning test

(Mizahur et al, 2007). The reason for these is the fact that chemical treatment confers on the shell powder hydrophobicity and increase tensile strength of the material.

The results of the chemical constituents presented in Table 4.2 and Figure 4.4 - 4.6 show a progressive decrease in percentage of lignin and hemicellulose while there was a significant increase in percent of the cellulose content. This is expected because more lignin and hemicellulose are gradually removed as a result of the chemical treatment thereby increasing the yield of cellulose in the fibre

Table 4.5: Cure Characteristics of the Vulcanizates

Conc. (%)	**Cure time (mins)**	**Maximum Torque (kg-cm)**	**Minimum Torque (kg-cm)**
0	6.42	23.99	4.78
5	(7.33) [3.41]	(29.31) [24.47]	(9.27) [8.97]
10	(6.33) [3.08]	(32.01) [28.38]	(3.95) [4.90]
15	(3.07) [3.43]	(35.64) [29.04]	(11.56) [8.71]
20	(4.36) [3.38]	(47.05) [30.28]	(5.97) [7.32]
25	(4.29) [3.18]	(35.27) [22.95]	(6.85) [7.58]
30	(3.47) [4.43]	(31.06) [19.86]	(7.52) [7.98]

Key: Acetylated Compounded Rubber ( )

Mercerized Compounded Rubber [ ]

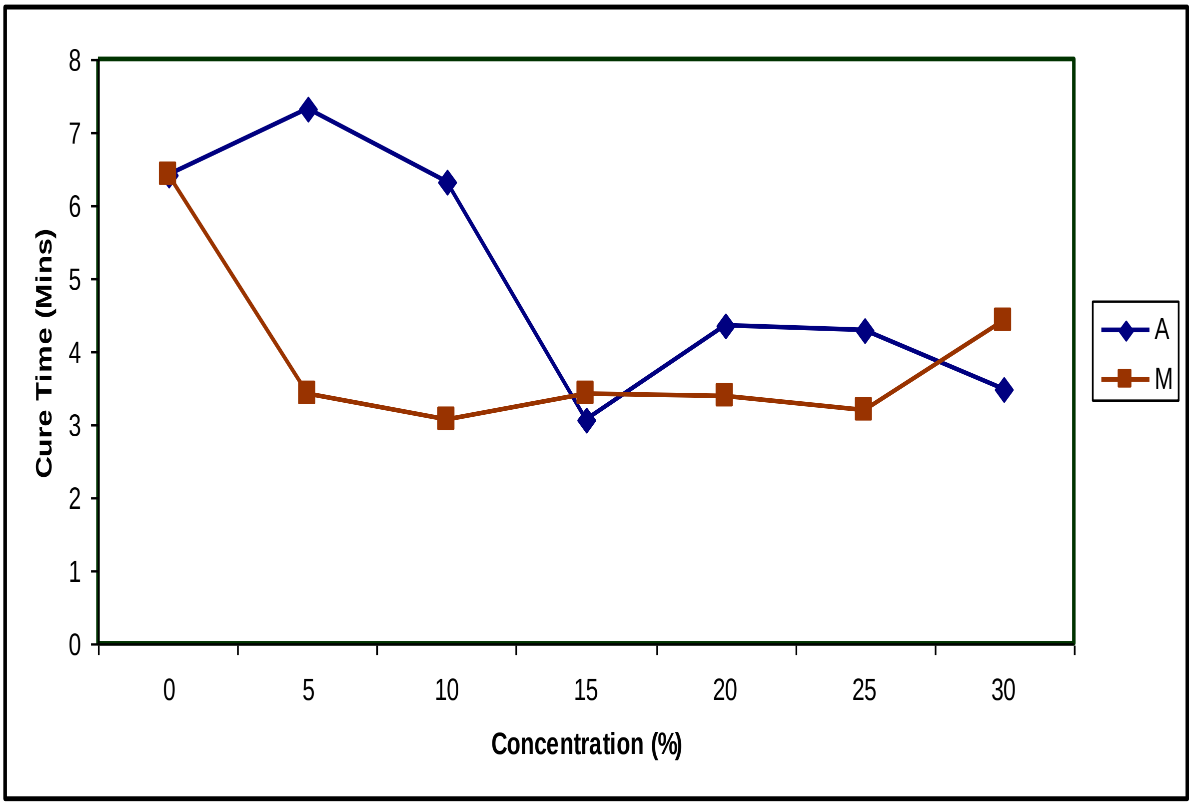


Figure 4.10: Cure Time of the treated Groundnut Shell filled Vulcanizates

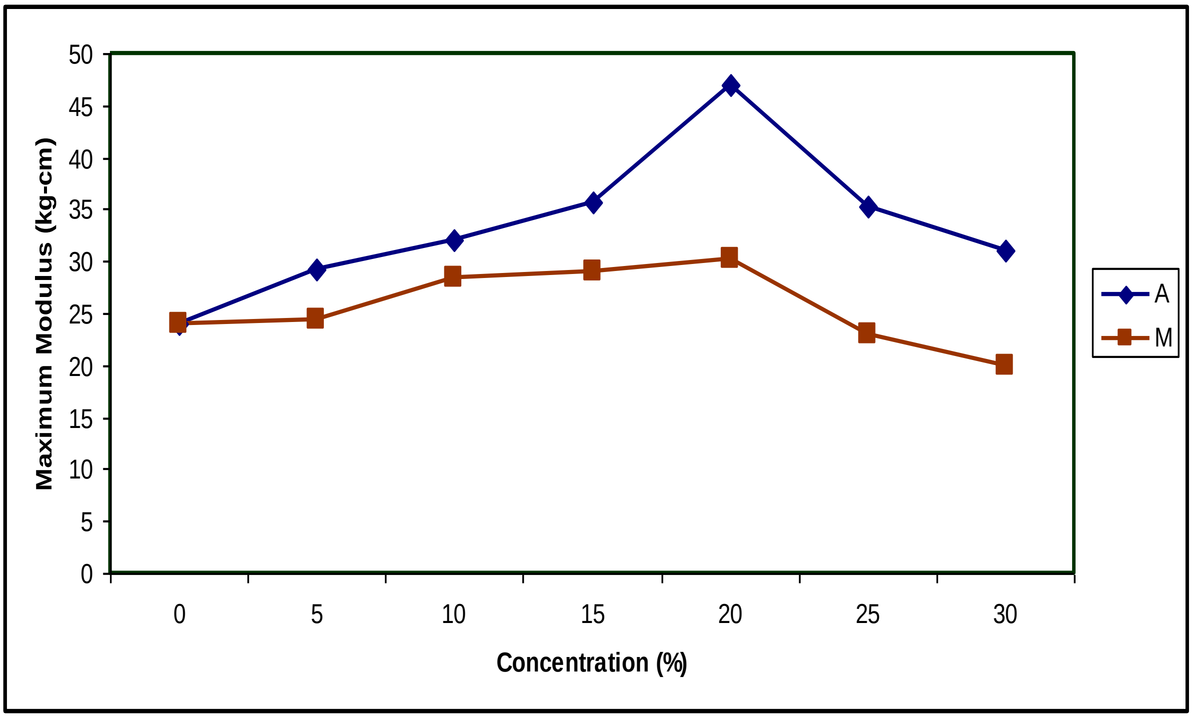


Figure 4.11: Maximum Torque of the treated Groundnut Shell filled Vulcanizates

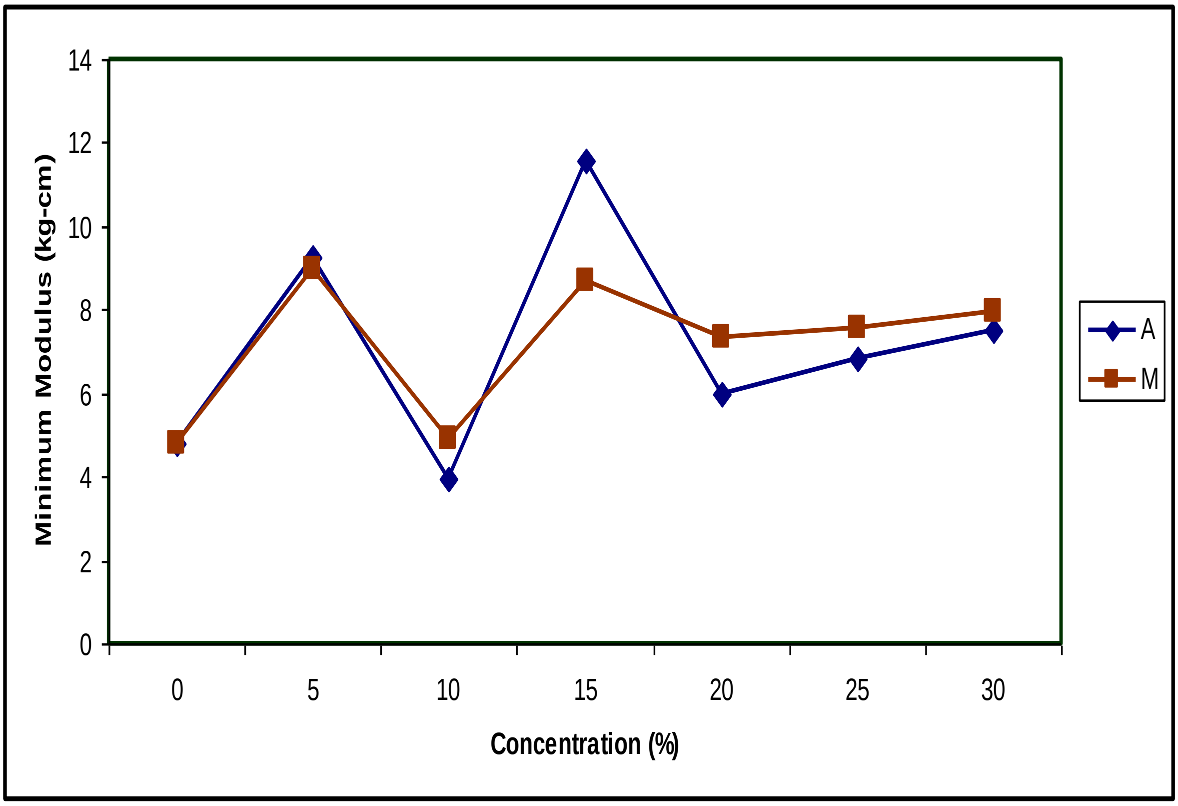


Figure 4.12: Minimum Torque of the treated Groundnut Shell filled Vulcanizates

4.2.2 Results of Cure Characteristics

The results in Table 4.5 present values for cure time, maximum torque and minimum torque of the gum; treated and untreated vulcanizates. The minimum torque gives an indication of the filler content in the rubber while the maximum torque in the rheograph is a measure of the cross linking density and stiffness in the rubber. In general, for all the mixes, the torque initially decreased, then increases and finally levels off. The initial decrease in torque was due to the softening of the rubber matrix while the increase is due to the cross-linking of the rubber. The level-off is an indication of complete curing. It is found that the presence of fibres increases the maximum torque (Eichhom et al., 2001 and Mizahur et al., 2001). It has been revealed that upon treatment maximum torque increases indicating greater cross-linking due to better adhesion between the groundnut shell and the matrix. Maximum torque value is exhibited by the vulcanizate treated via acetylation indicating maximum cross-linking for acetylated vulcanizates. The cure time does not show any systematic trend upon treatment (Nakagaito et al., 2005).

Table 4.6: Mechanical Properties of the Vulcanizates

Property	Concentration (%)						
	UT	**5**	**10**	**15**	**20**	**25**	**30**
Tensile Strength(MPa)	18.30	(21.30) [19.50]	(24.00) [20.40]	(29.00) [25.90]	(31.50) [28.00]	(27.50) [23.00]	(25.00) [21.60]
Modulus (MPa)	1.40	(2.43) [1.86]	(2.86) [2.15]	(3.52) [2.90]	(3.85) [3.10]	(3.47) [1.84]	(3.21) [1.68]
Elongation at Break (%)	548	(496) [513]	(476) [510]	(451) [488]	(381) [472]	(401) [514]	(440) [526]
Hardness (IRHD)	48.00	(61.00) [54.00]	(63.00) [60.00]	(67.00) [63.00]	(68.00) [65.00]	(65.00) [49.00]	(64.00) [48.00]
Compression Set (%)	22.00	(16.00) [18.00]	(14.00) [16.00]	(12.00) [14.00]	(11.00) [13.00]	(14.00) [19.00]	(16.00) [20.00]
Abrasion Resistance (%)	31.55	(31.80) [31.60]	(36.40) [34.50]	(40.20) [38.00]	(42.50) [39.30]	(37.10) [36.80]	(36.20) [33.40]
Flex fatigue (kc x 10^3)	8.989	(8.060) [8.910]	(7.360) [8.675]	{6.330} [6.672]	{5.360} [5.860]	{6.317} [8.700]	{7.340} [8.915]
Impact strength (j/m^2)	980	(946) [968]]	(939) [950]	(912) [936]	(870) [895]	(890) [920]	(898) [932]

Key: Acetylated Vulcanizates ( )
Mercerized Vulcanizates [ ]

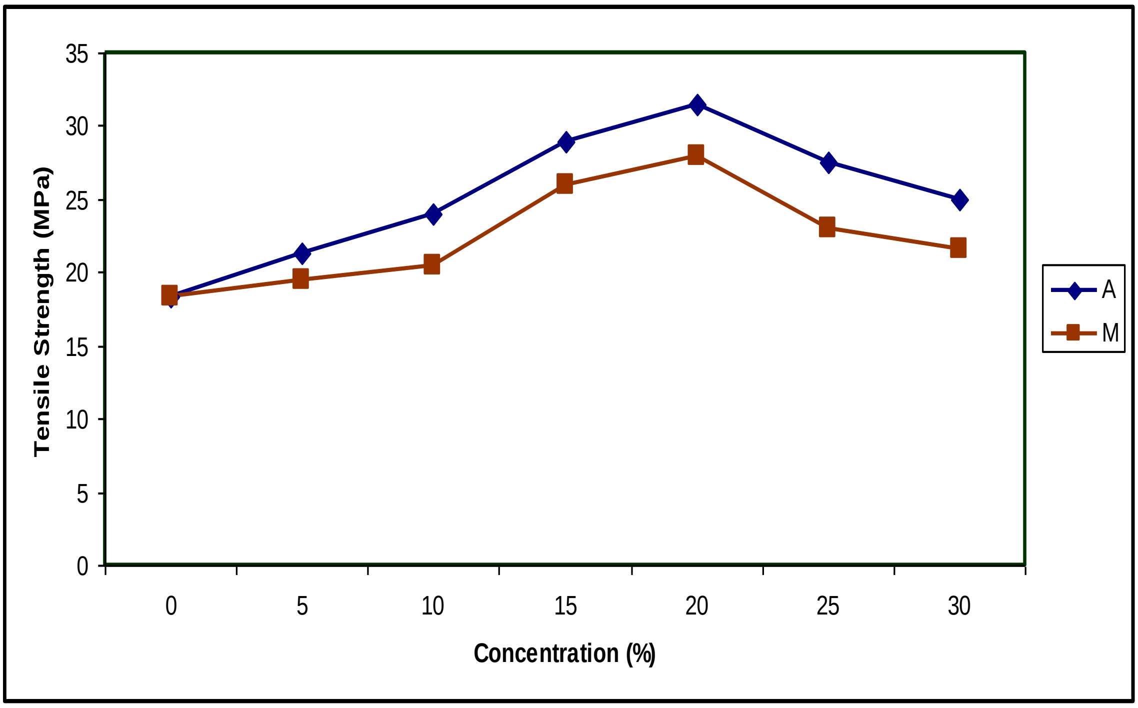


Figure 4.13: Tensile Strength of the treated Groundnut Shell filled Vulcanizates

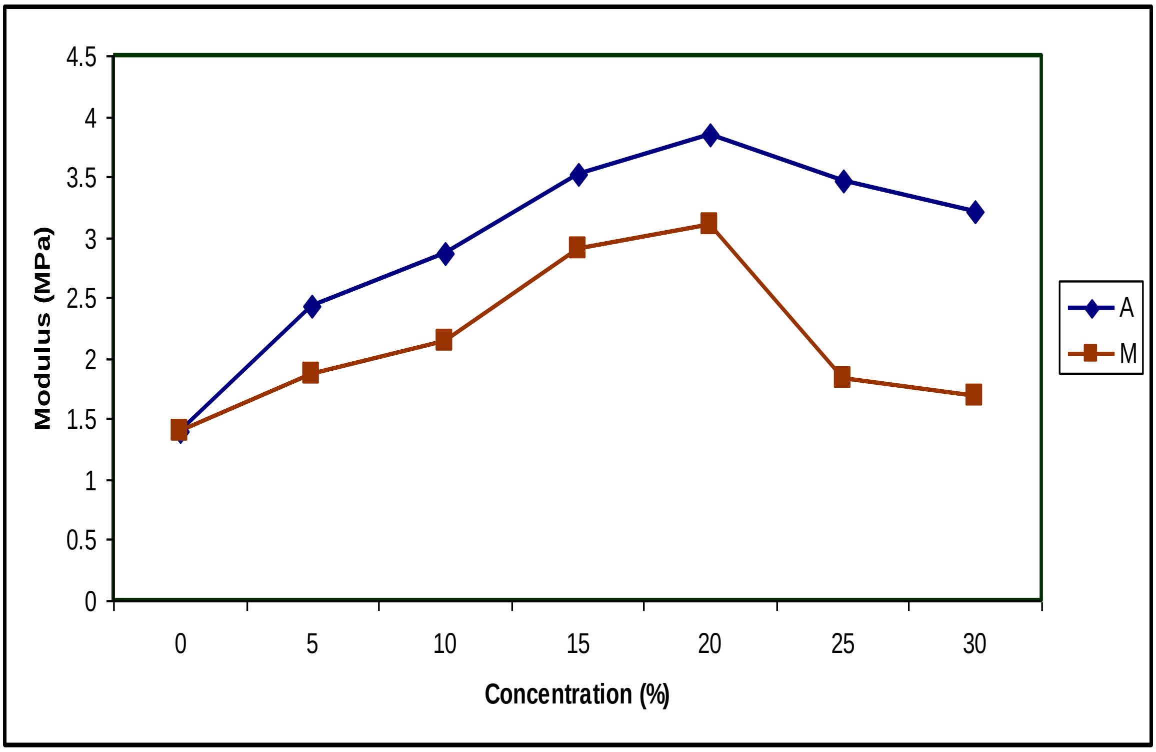


Figure 4.14: Modulus of the treated Groundnut Shell filled Vulcanizates

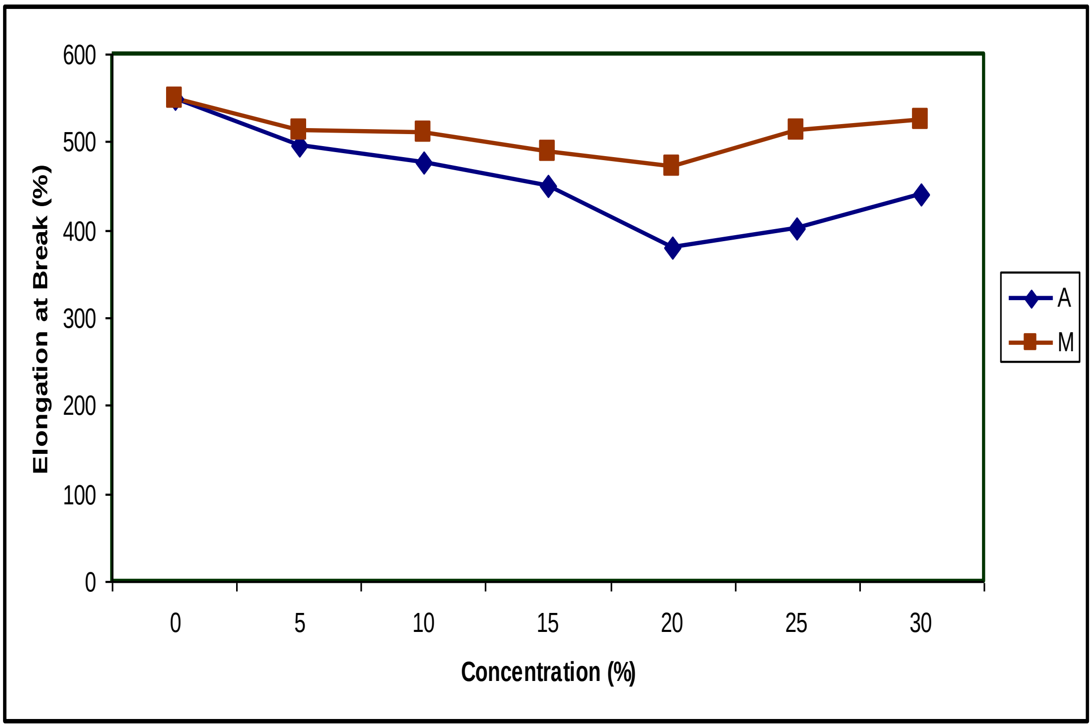


Figure 4.15: Elongation at Break of the treated Groundnut Shell filled Vulcanizates

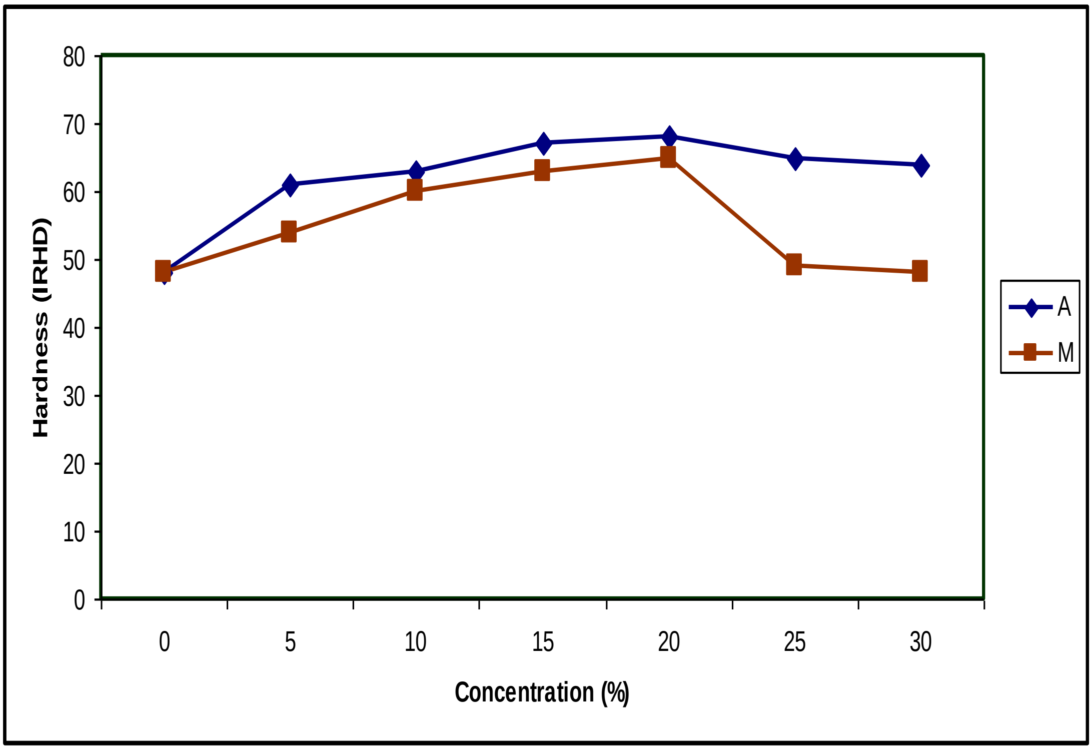


Figure 4.16: Hardness of the treated Groundnut Shell filled Vulcanizates

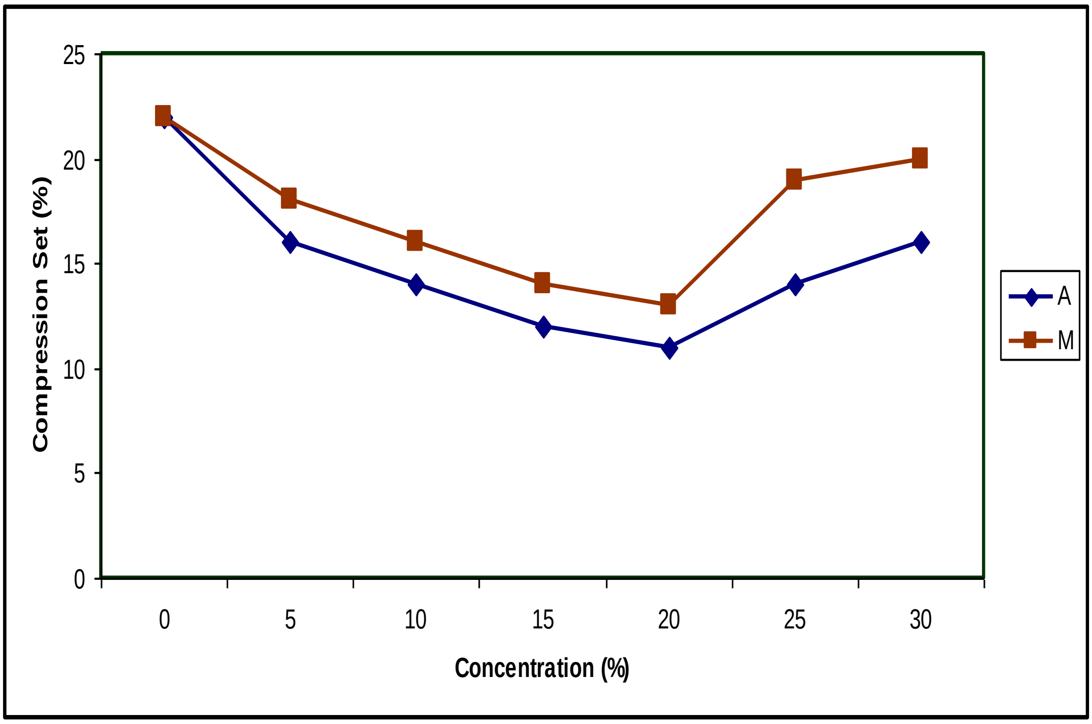


Figure 4.17: Compression Set of the treated Groundnut Shell filled Vulcanizates

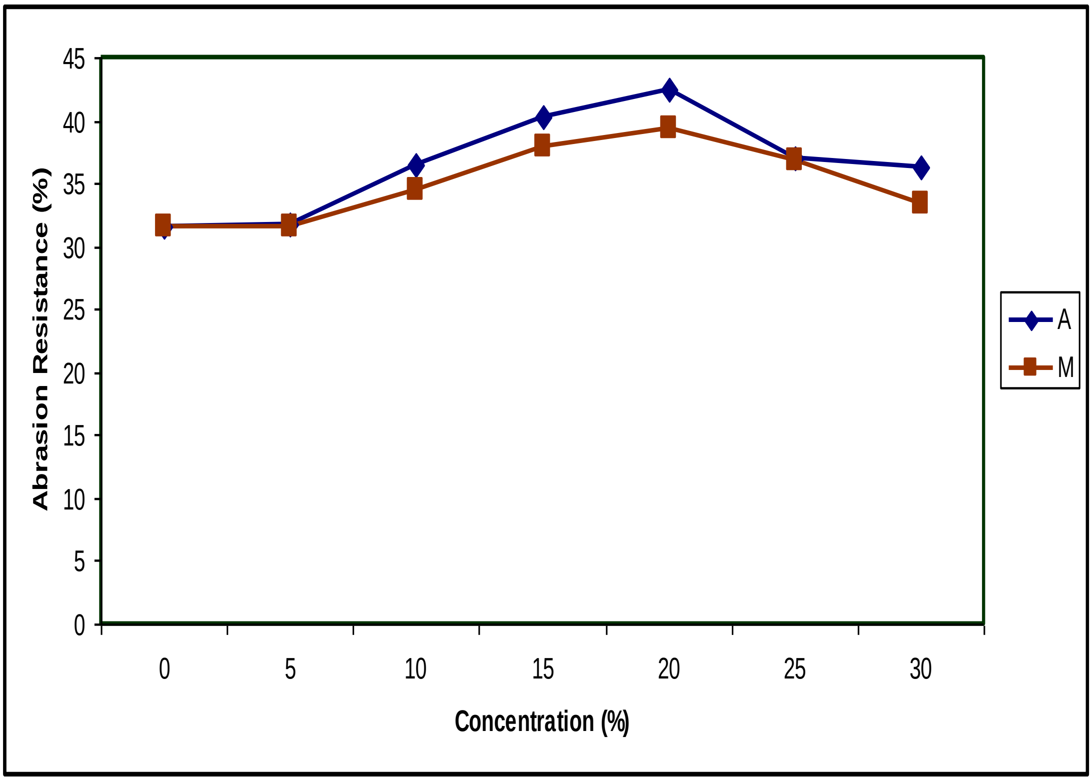


Figure 4.18: Abrasion Resistance of the treated Groundnut Shell filled Vulcanizates

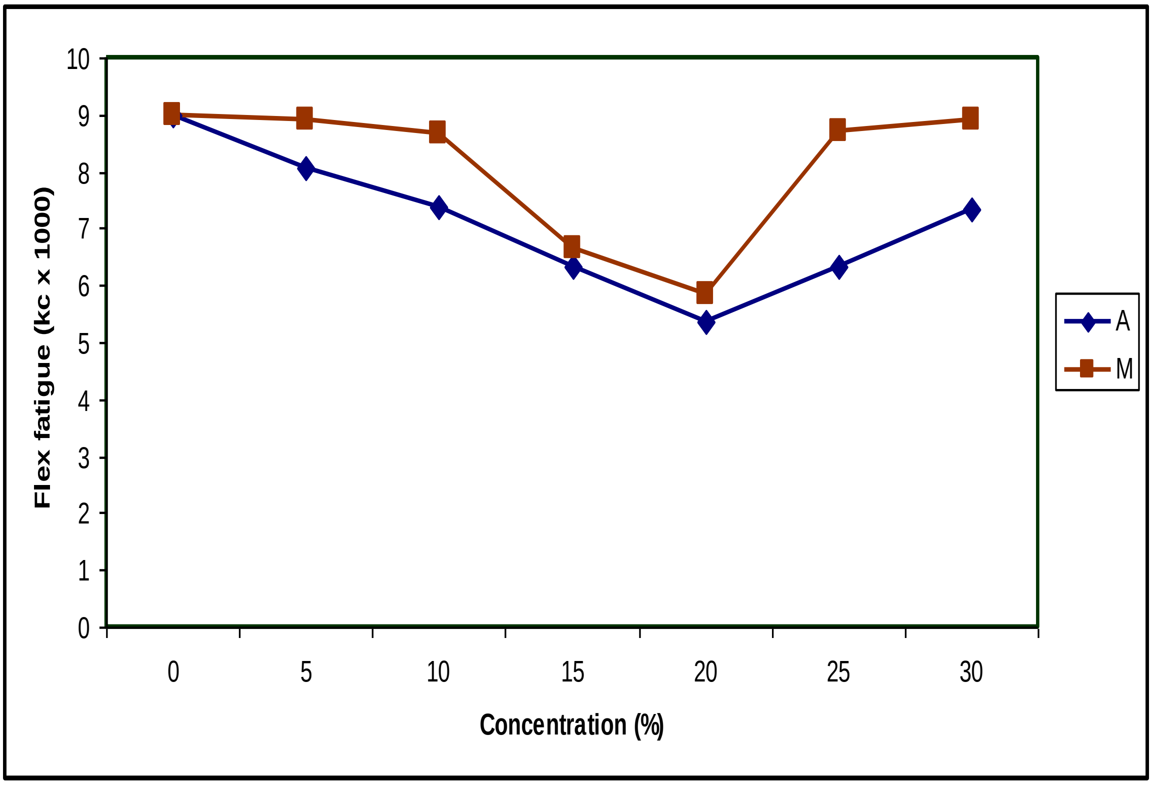


Figure 4.19: Flex fatigue of the treated Groundnut Shell filled Vulcanizates

4.2.3 Results of Mechanical Properties

The variation of the tensile strength of the untreated and treated vulcanizates is shown in Figure 4.13. The two factors that are apparent are that the vulcanizates containing the treated groundnut shell powder possessed greater tensile strength when compared to untreated vulcanizates and also that vulcanizates treated with acetylating agents show better tensile strength than the one treated with mercerizing agent. Sreekala et al. (2000) reported that chemical treatment leads to fibre fibrillation i.e breaking down of fibre bundles into smaller fibres which increases the effective surface area available for contact with the matrix. Chemical treatments of fibres in natural fibre reinforced compounds often showed improved tensile properties owing to the increased fibre-matrix adhesion. Tensile properties can be explained on the basis of the changes in chemical interactions at the fibre-matrix interface. Acetylation and mercerization results in improvement in the interfacial bonding by giving rise to additional sites of mechanical interlocking thereby promoting more polymer-fibre interpenetration at the surface; hence the increase in the tensile strength observed (Jorts et al., 2005). However at high concentration of treatment, the tensile strength for both acetylated and mercerized filled composites decreases caused by the high concentration treatment since the lignocellulose shell undergo degradation leading to lowering of the tensile strength.

The variation of modulus with chemical modification is shown in Table 4.6. It is clear that the modulus of a well bonded composite as a result of treatment arises from the fact that the load transfer between the fibre and the matrix occur through the strong fibre matrix interface. Hence one can see that the modulus of the chemically treated composites exhibit higher modulus values than the untreated composites. It also shows that it was due to the presence of a strong interface between the treated fibres and matrix (Onyeagoro 2012).

Figure 4.15 shows the variation of elongation at break of the untreated and treated composites. It can be seen that the elongation at break for treated composites is lower than that for the untreated composites. The elongation at break of the compounds filled with chemically modified fibre was attributed to the changes in the chemical structure and bonding ability of the fibre. The decrease in elongation was due to better strength and stiffness achieved from strong adhesion between treated fibre and rubber matrix, however; higher extension is obtained from weak interfacial adhesion(Onyeagoro et al., 2013).

The hardness results presented in Table 4.6 shows a progressive increase with the filler type up to 20% concentration for both treated fillers. This results is expected because the treatment increases the interaction between the rubber matrix and the filler hence; the increase in hardness. However, at higher concentration, the fibres are destroyed chemically leading to poor interaction. At higher interaction, the elasticity of the rubber chain decreases resulting in more rigid vulcanizates (Ekebafe et al., 2009).

The results in Table 4.6 also show the values of flex fatigue as a function of filler type (mercerized and acetylated filler). The value decreases with increase in concentration of the acetylating and mercerizing agents used for the filler treatment. The decrease is as a result of stiffening of the polymer chain due to the adherence of the filler to the polymer matrix. Flexural strength is the ability of the material to withstand bending forces applied perpendicular to its longitudinal axis. The stress induced due to the flexural load is combination of compressive and tensile stresses. The effects of acetylation of groundnut shell on the flexural strength are found to be increasing up to 20% acetylation after which it decreased rapidly. The improvement of flexural strength properties of treated fibre composites is likely to be due to removal of the outer surface, increase cellulose content And effective surface area, increase interfacial adhesion and physical and chemical changes induced by fibre. The variation of abrasion resistance with filler type is presented in Table 4.6. It shows a progressive increase with increase in concentration of the acetylating and mercerizing agents used for the filler treatment. This observation may be as a result of improved affinity between the rubber and the fillers.

The compression set results presented in Table 4.6 shows a progressive decrease with the filler type before it starts rising again. Compression set is affected by the affinity of the rubber for the filler surface energy of the filler (Nemour, 1986).

The impact strength of a composite is influenced by many factors, including the toughness properties of the reinforcement, the nature of the interfacial region and frictional work involved in pulling out the fibre from the matrix. The nature of the interfacial region is of extreme importance in determining the toughness of the composite. It was observed that the impact strength decreases slowly with increasing concentration of the treating agents which is due to strong interface and decrease in toughness of the composites.

Table 4.7: Swelling Behaviour of the Vulcanizates in Acetone

Sample Concentration (%)	Swelling Index (%)	Swelling Coefficient (%)	% mole uptake of the solvents
UT (0)	554	4.995	6.986
5	[346.40] (380.20)	[4.378] (4.806)	[5.963] (6.545)
10	[322.60] (354.10)	[4.079] (4.474)	[5.555] (6.096)
15	[286.00] (309.60)	[3.615] (3.909)	[4.923] (5.329)
20	[229.50] (246.00)	[2.900] (3.109)	[3.950] (4.236)
25	[278.20] (297.40)	[3.516] (3.760)	[4.789] (5.122)
30	[292.40] (323.80)	[3.696] (4.092)	[5.033] (5.574)

Key: Acetylated Vulcanizates [ ]
Mercerized Vulcanizates ( )

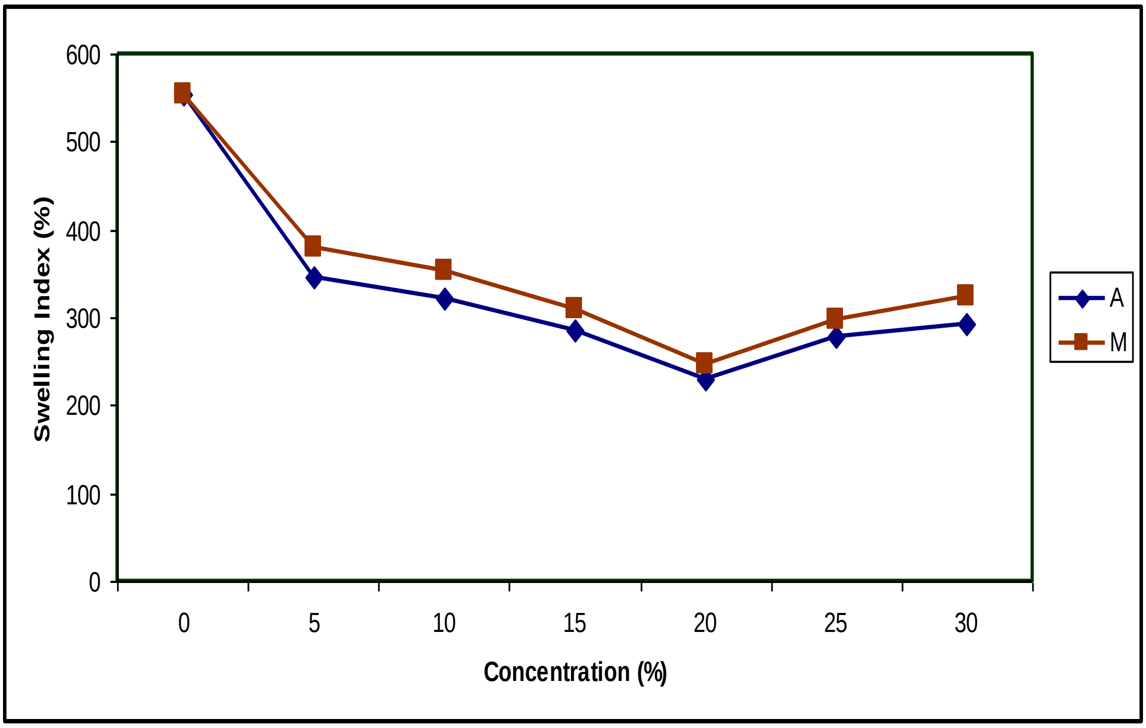


Figure 4.20: Swelling Index of the Vulcanizates in Acetone

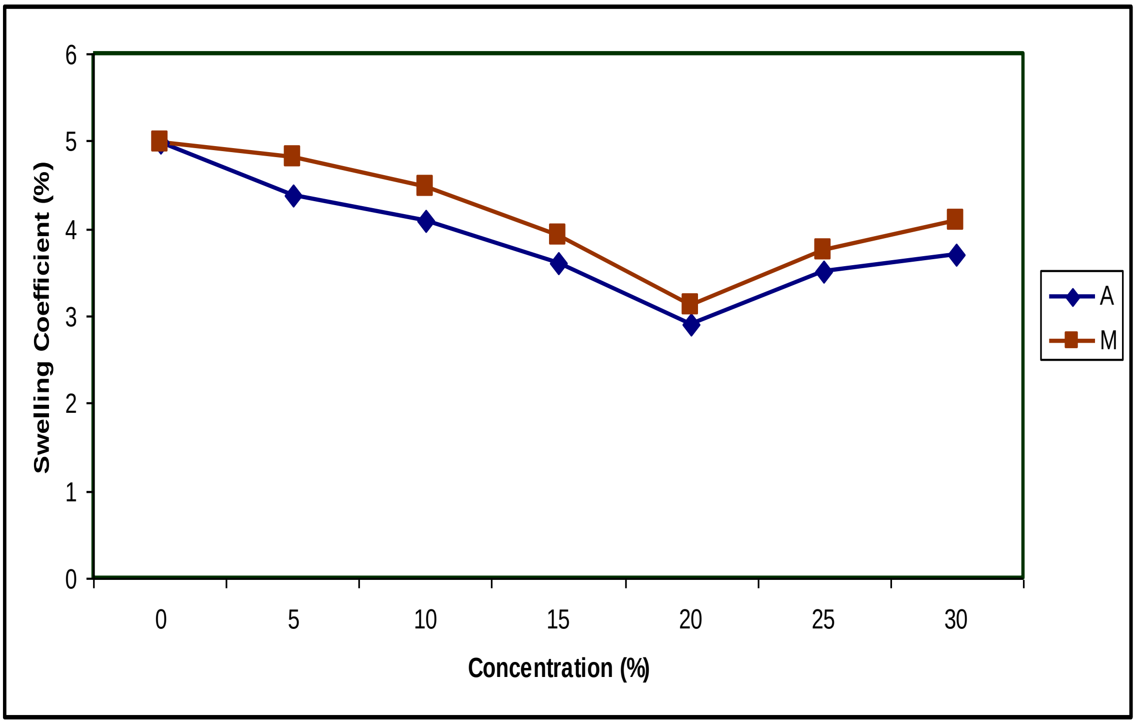


Figure 4.21: Swelling Coefficient of the Vulcanizates in Acetone

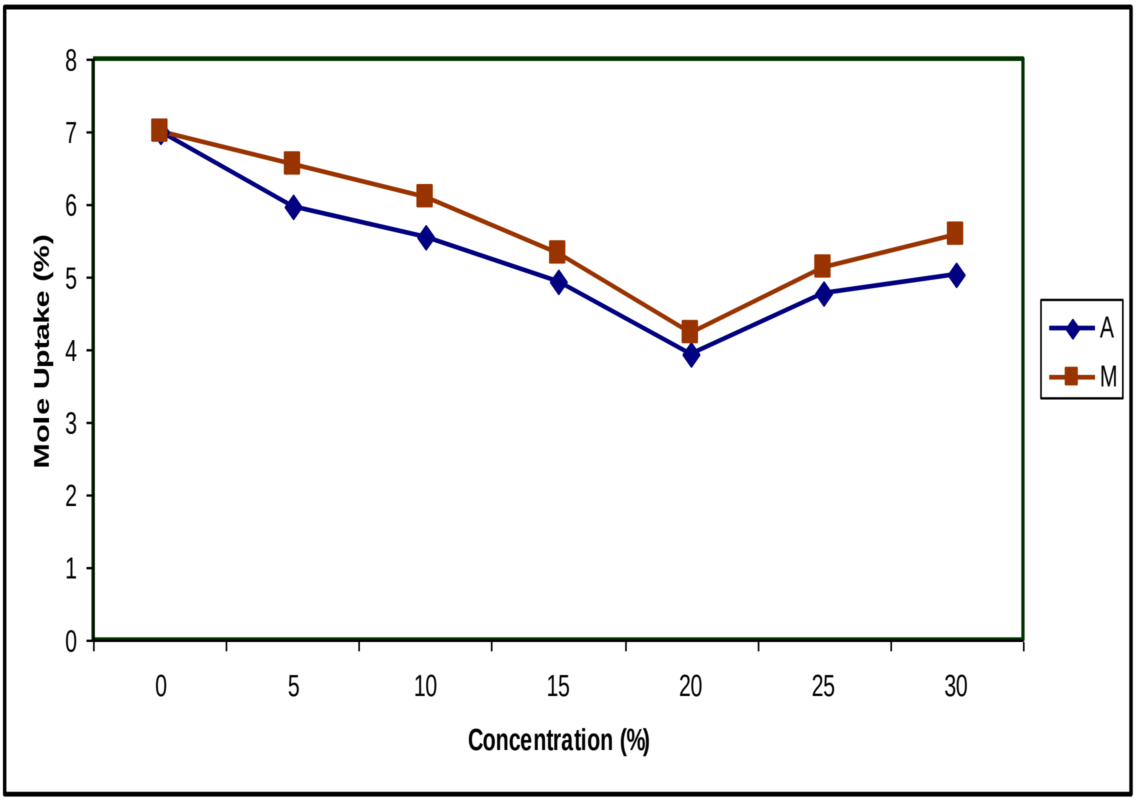


Figure 4.22: Mole Uptake of the Vulcanizates in Acetone

Table 4.8: Swelling Behaviour of the Vulcanizates in Xylene

Sample Concentration (%)	**Swelling Index (%)**	**Swelling Coefficient (%)**	**Mole uptake of the solvents (%)**
UT (0)	540	5.112	5.086
5	[384.00] (417.30)	[4.443] (4.848)	[3.616] (3.930)
10	[342.80] (408.60)	[3.967] (4.745)	[3.229] (3.848)
15	[300.20] (385.30)	[3.475] (4.476)	[2.828] (3.690)
20	[246.40] (342.00)	[2.852] (3.973)	[2.321] (3.221)
25	[308.50] (376.40)	[3.572] (4.371)	[2.907] (3.544)
30	[346.00] (380.00)	[4.005] (4.413)	[3.260] (3.578)

Key: Acetylated Vulcanizates [ ]
Mercerized Vulcanizates ( )

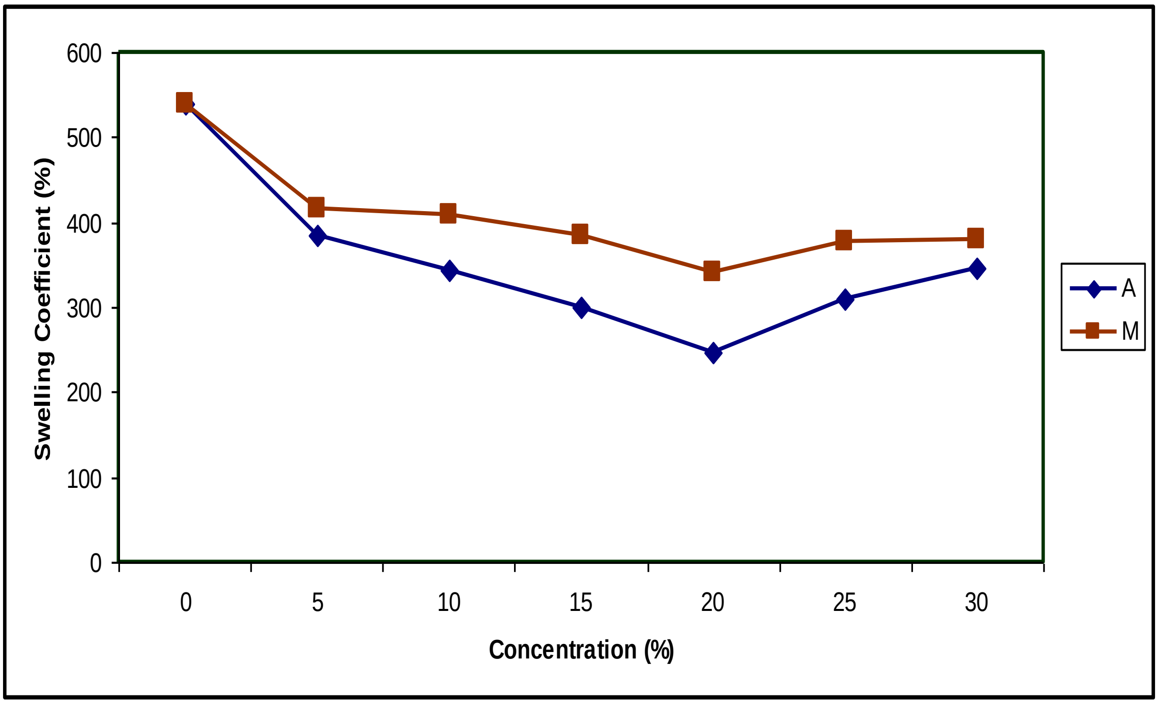


Figure 4.23: Swelling Index of the Vulcanizates in Xylene

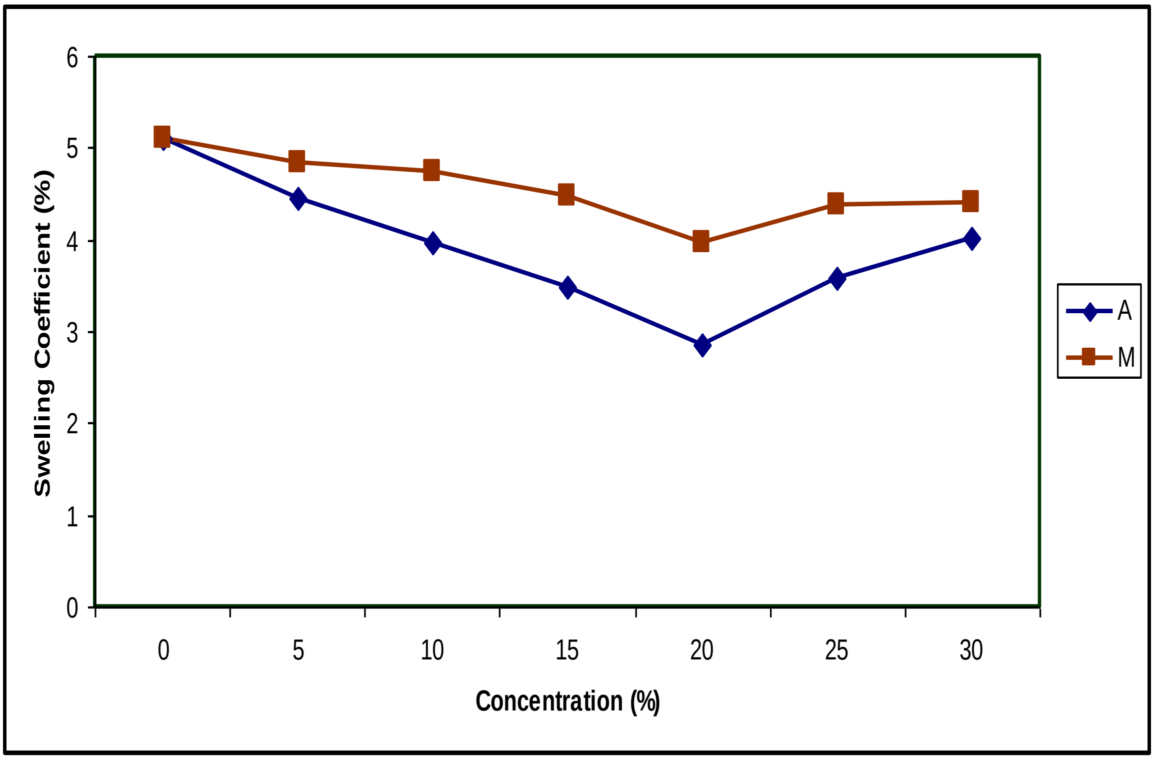


Figure 4.24: Swelling Coefficient of the Vulcanizates in Xylene

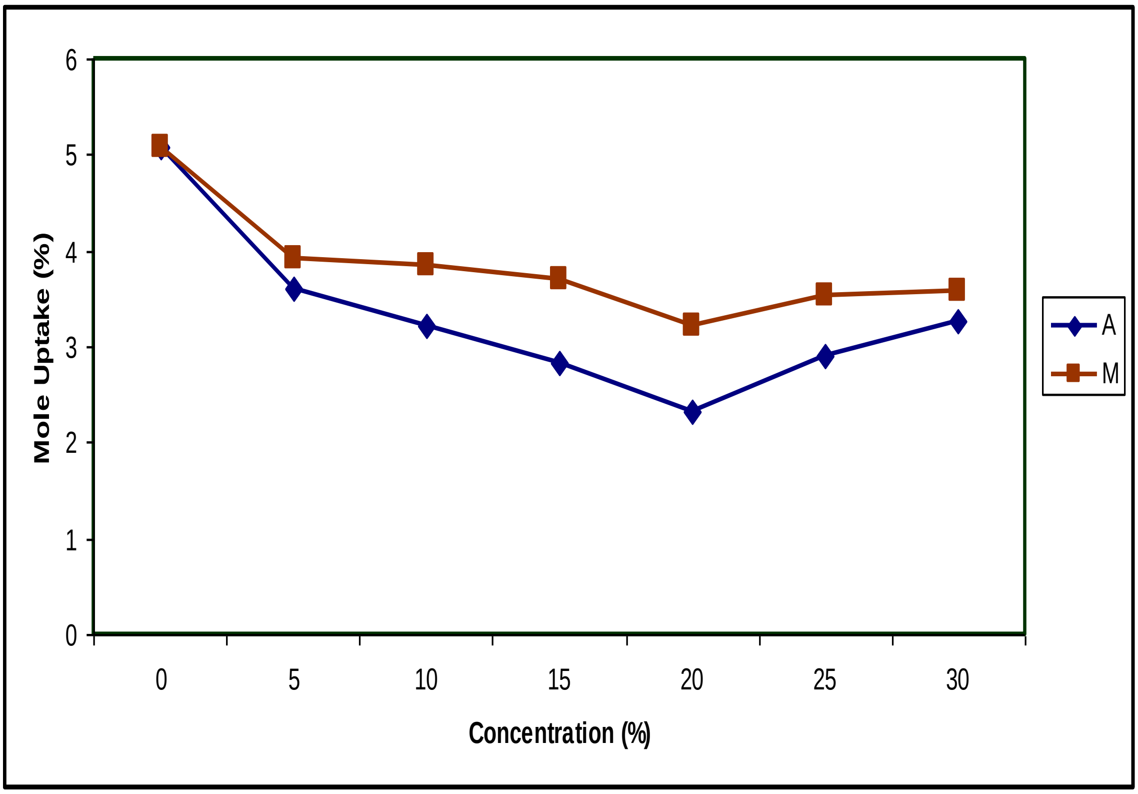


Figure 4.25: Mole Uptake of the Vulcanizates in Xylene

Table 4.9: Swelling Behaviour of the Vulcanizates in Toluene

Sample Concentration (%)	**Swelling Index (%)**	**Swelling Coefficient**	**% mole uptake of the solvents**
UT (0)	528.50	4.898	4.887
5	[368.20] (411.80)	[4.233] (4.750)	[3.997] (4.468)
10	[326.40] (400.60)	[3.753] (4.619)	[3.544] (4.347)
15	[294.00] (382.00)	[3.380] (4.406)	[3.191] (4.145)
20	[235.60] (365.40)	[2.709] (4.216)	[2.557] (3.966)
25	[296.90] (390.60)	[3.412] (4.506)	[3.221] (4.238)
30	[333.40] (391.20)	[3.833] (4.507)	[3.619] (4.240)

Key: Acetylated Vulcanizates [ ]
Mercerized Vulcanizates ( )

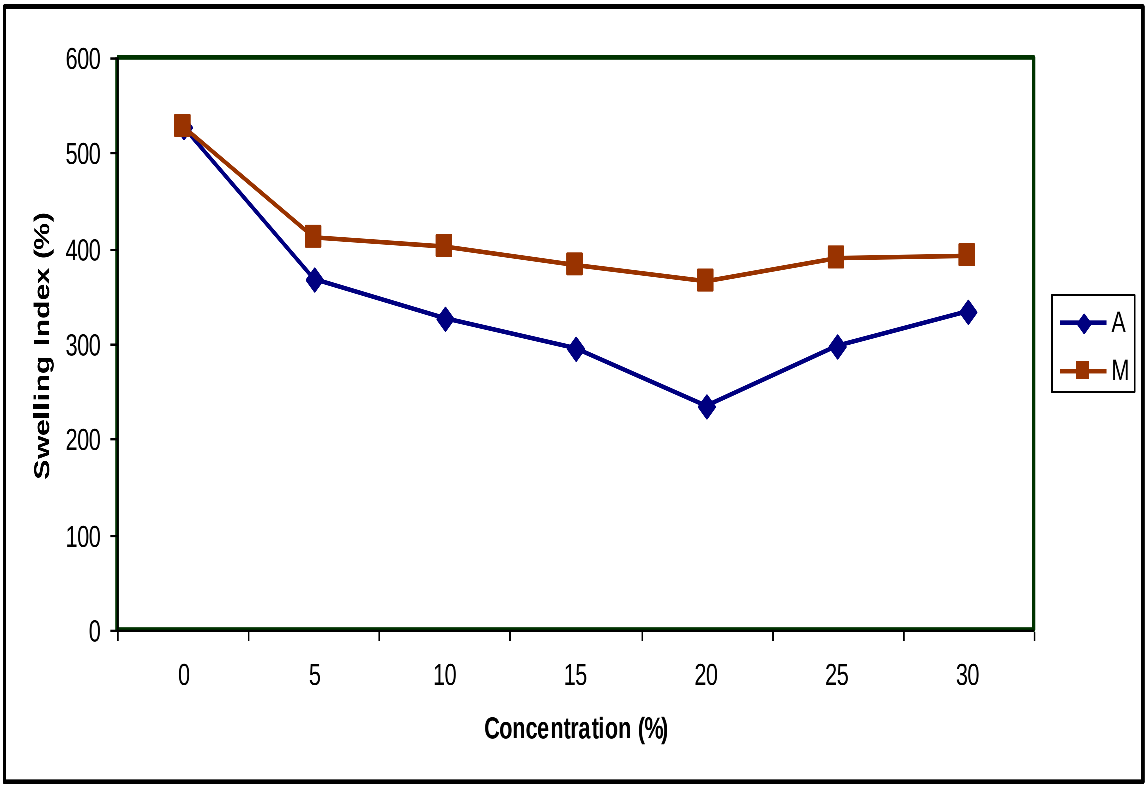


Figure 4.26: Swelling Index of the Vulcanizates in Toluene

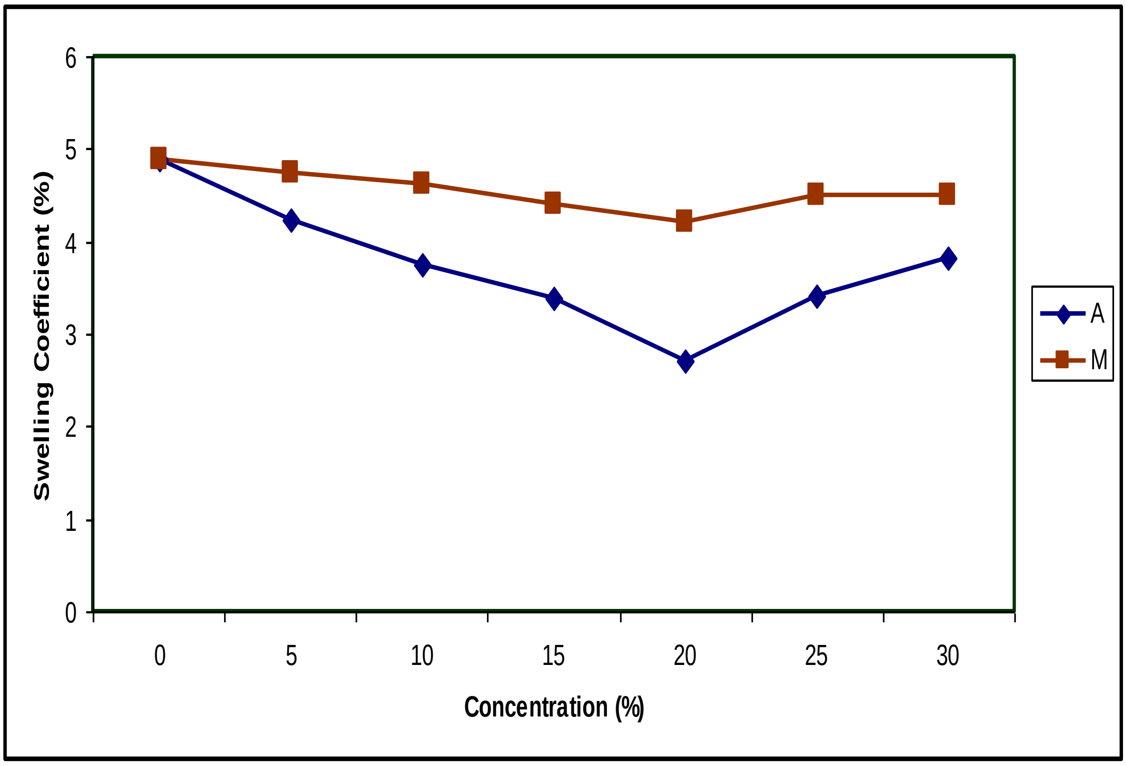


Figure 4.27: Swelling Coefficient of the Vulcanizates in Toluene

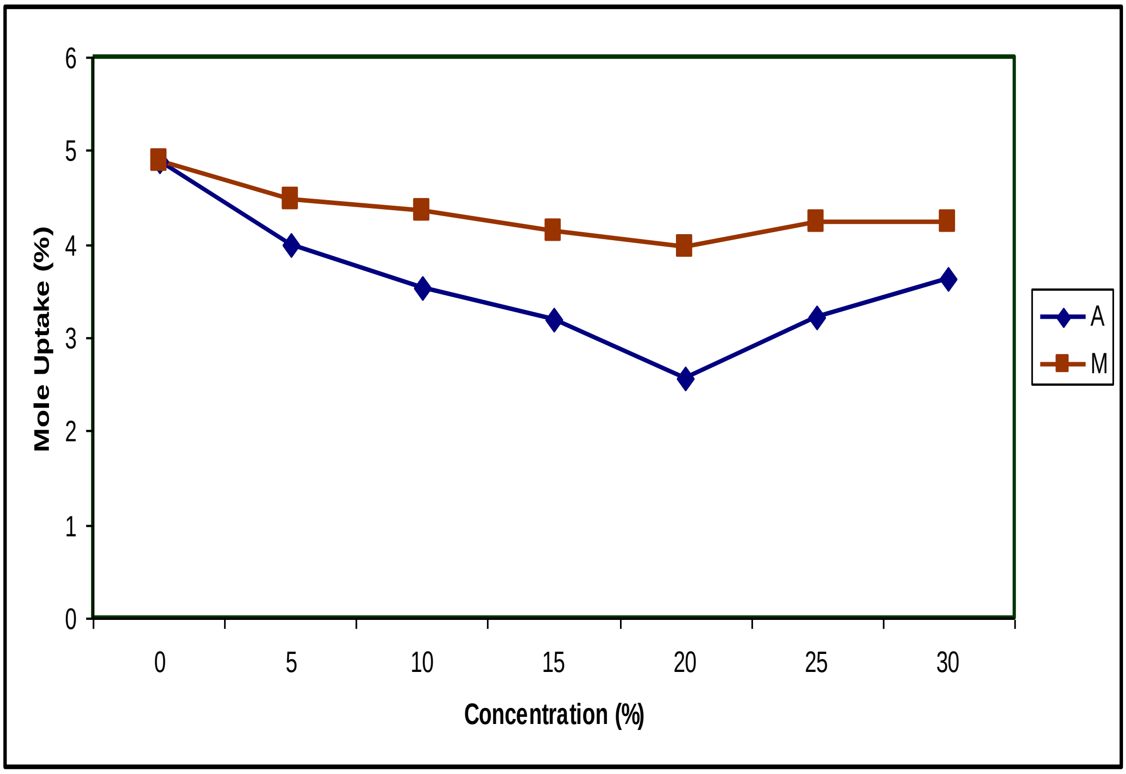


Figure 4.28: Mole Uptake of the Vulcanizates in Toluene

Table 4.10: Cross-linking Density of the Vulcanizates

Sample	**Cross-linking Density (Kg/cm)**
5	(15.50) [20.04]
10	(23.48) [28.06]
15	(20.33) [24.08]
20	(22.96) [41.08]
25	(15.37) [28.42]
30	(11.88) [23.54]
UT	19.21

Key: Acetylated vulcanizates [ ]
Mercerized vulcanizates ( )

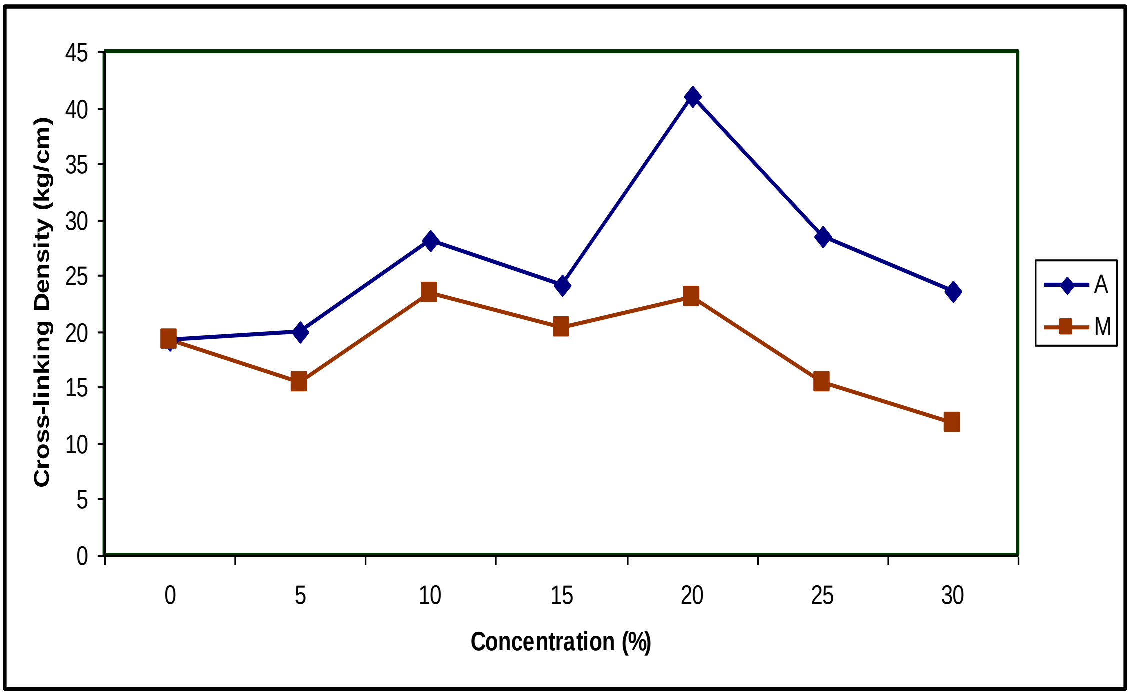


Figure 4.29: Cross-linking Density of the Vulcanizates

4.2.4 Results of Sorption Experiments

The results of the sorption behaviour of the vulcanizates presented in Table 4.7 - 4.10 show the influence of chemical treatments. In the entire composite samples, it was observed that the mole percentage uptake of the solvents decreases with increase in concentration of the acetylating and mercerizing agents. This shows that chemical treatments increases the interfacial adhesion between rubber and fibres and thus increase the cross-link density. This prevents entry of the solvents. The acetylated fibres show better results than the mercerized fibres which is in agreement with previous work by Ekebafe et al (2011).

The results presented show highest percentage swelling for acetone for both acetylated filler-filled and mercerized filler-filled vulcanizates. This is expected because the solubility parameter of acetone is closest to natural rubber than other solvents used in this research work. The solubility parameter of the relevant solvents used include; acetone (9.77 $(cal/cm^3)^{0.5}$), Xylene (8.85 $(cal/cm^3)^{0.5}$) and toluene (8.91 $(cal/cm^3)^{0.5}$) (Wang, 2004). In all the relevant solvents used the percentage swelling of the vulcanizates decreases with chemical treatments of the fibres. The swelling index percentage also follows the same trend. The diffusion mechanism in rubbers is essentially connected with the ability of the polymer to provide pathways for the solvent to progress in the form of randomly generated voids. As the voids formation decreases with the addition of fibres, the solvent uptake also decreases (Ekebafe, et al., 2011). The densities of the solvents used in this research work are as follows; toluene (0.870g/ml), acetone (0.791g/ml) and xylene (0.864g/ml) respectively.

Analysis of Variance of Mechanical Properties based on Mathematical Model
Tensile Strength (MPa)

Between-Subjects Factors

		Value Label	N
Concentration (%)	1.00	Conc 5%	2
	2.00	Conc 10%	2
	3.00	Conc 15%	2
	4.00	Conc 20%	2
	5.00	Conc 25%	2
	6.00	Conc 30%	2
Vulcanizate Category	1.00	Acetylated Vulcanizates	6
	2.00	Mercerised Vulcanizates	6

Tests of Between-Subjects Effects

Dependent Variable: Tensile Strength (MPa)

Source	Type I Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	153.128[a]	6	25.521	65.975	.000
Intercept	7335.907	1	7335.907	18964.000	.000
Conc	120.128	5	24.026	62.108	.000
VT	33.001	1	33.001	85.310	.000
Error	1.934	5	.387		
Total	7490.970	12			
Corrected Total	155.063	11			

a. R Squared = .988 (Adjusted R Squared = .973)

Homogeneous Subsets

Tensile Strength (MPa)

	Concentration (%)	N	Subset				
			1	2	3	4	5
Duncan[a,b]	Conc 5%	2	20.4000				
	Conc 10%	2		22.2000			
	Conc 30%	2		23.3000			
	Conc 25%	2			25.2500		
	Conc 15%	2				27.4500	
	Conc 20%	2					29.7500
	Sig.		1.000	.137	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.
The error term is Mean Square(Error) = .387.

a. Uses Harmonic Mean Sample Size = 2.000.

b. Alpha = 0.05.

Graphs of Mechanical Properties based on Mathematical Modeling

Tensile Strength (MPa) Untreated UT=18.3

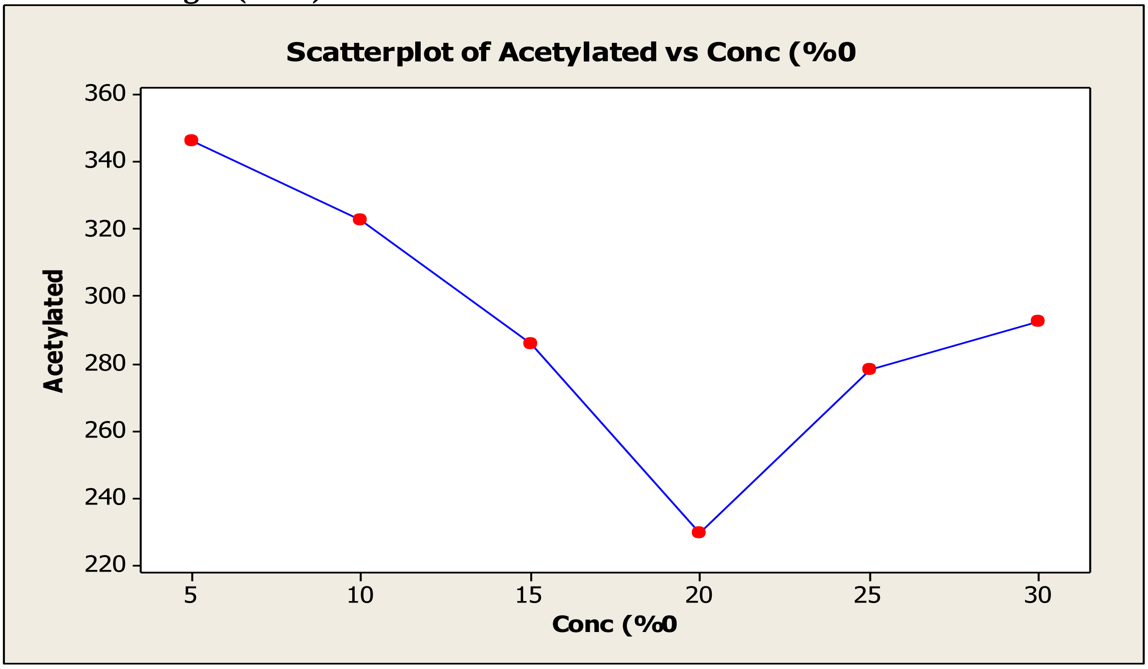


Figure 4.30A: Tensile Strength of Acetylated Groundnut Shell filled Vulcanizates

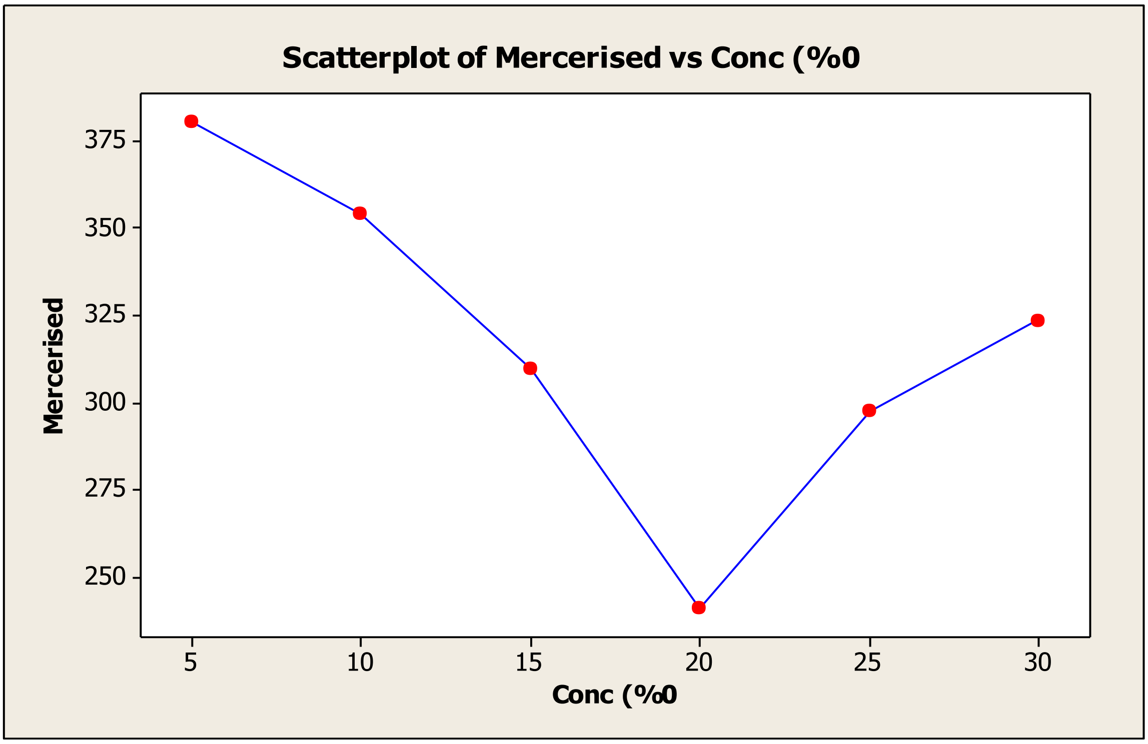


Figure 4.30B: Tensile Strength of Mercerized Groundnut Shell filled Vulcanizates

Modulus (MPa)

Between-Subjects Factors

		Value Label	N
Concentration (%)	1.00	Conc 5%	2
	2.00	Conc 10%	2
	3.00	Conc 15%	2
	4.00	Conc 20%	2
	5.00	Conc 25%	2
	6.00	Conc 30%	2
Vulcanizate Category	1.00	Acetylated Vulcanizates	6
	2.00	Mercerised Vulcanizates	6

Tests of Between-Subjects Effects

Dependent Variable: Modulus (MPa)

Source	Type I Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	5.342[a]	6	.890	7.758	.020
Intercept	90.036	1	90.036	784.506	.000
Con	2.529	5	.506	4.408	.065
VC	2.813	1	2.813	24.510	.004
Error	.574	5	.115		
Total	95.953	12			
Corrected Total	5.916	11			

a. R Squared = .903 (Adjusted R Squared = .787)

Homogeneous Subsets

Modulus (MPa)

	Concentration (%)	N	Subset		
			1	2	3
Duncan[a,b]	Conc 5%	2	2.3500		
	Conc 30%	2	3.2450	3.2450	
	Conc 10%	2	2.9050	2.9050	
	Conc 25%	2	3.5550	3.55550	3.5550
	Conc 15%	2		3.5551	3.5551
	Conc 20%	2			3.8850
	Sig.		.205	.082	.066

Based on observed means.

The error term is Mean Square(Error) = .115.

a. Uses Harmonic Mean Sample Size = 2.000.

b. Alpha = 0.05.

Modulus (MPa) Untreated UT=22

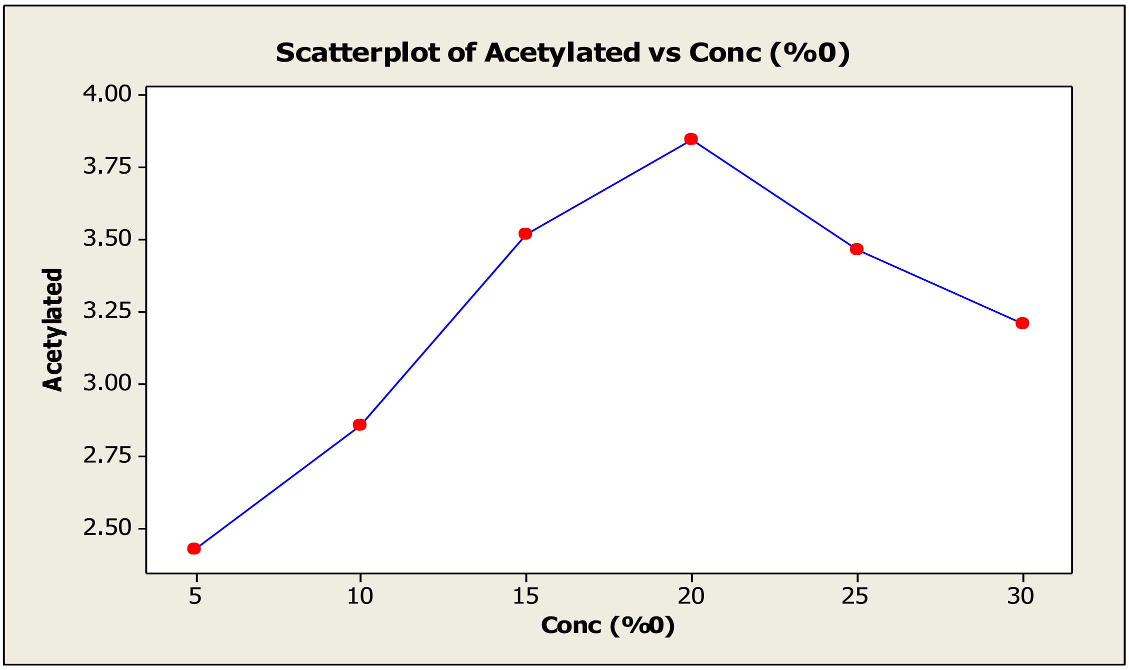


Figure 4.31A: Modulus of Acetylated Groundnut Shell filled Vulcanizates

Figure 4.31B: Modulus of Mercerized Groundnut Shell filled Vulcanizates

Elongation at Break (%)

Between-Subjects Factors

		Value Label	N
Concentration (%)	1.00	Conc 5%	2
	2.00	Conc 10%	2
	3.00	Conc 15%	2
	4.00	Conc 20%	2
	5.00	Conc 25%	2
	6.00	Conc 30%	2
Vulcanizate Category	1.00	Acetylated Vulcanizates	6
	2.00	Mercerised Vulcanizates	6

Tests of Between-Subjects Effects

Dependent Variable: Elongation at Break (%)

Source	Type I Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	13392.333[a]	6	2232.056	2.144	.210
Intercept	2724627.000	1	2724627.000	2617.485	.000
Concentration	4427.000	5	885.400	.851	.568
VCT	8965.333	1	8965.333	8.613	.032
Error	5204.667	5	1040.933		
Total	2743224.000	12			
Corrected Total	18597.000	11			

a. R Squared = .720 (Adjusted R Squared = .384)

Homogeneous Subsets

Elongation at Break (%)

	Concentration (%)	N	Subset
			1
Duncan[a,b]	Conc 25%	2	447.5000
	Conc 20%	2	461.5000
	Conc 15%	2	469.5000
	Conc 30%	2	483.0000
	Conc 10%	2	493.0000
	Conc 5%	2	504.5000
	Sig.		.148

Based on observed means.

The error term is Mean Square(Error) = 1040.933.

a. Uses Harmonic Mean Sample Size = 2.000.

b. Alpha = 0.05.

Elongation at Break (%) Untreated UT=548

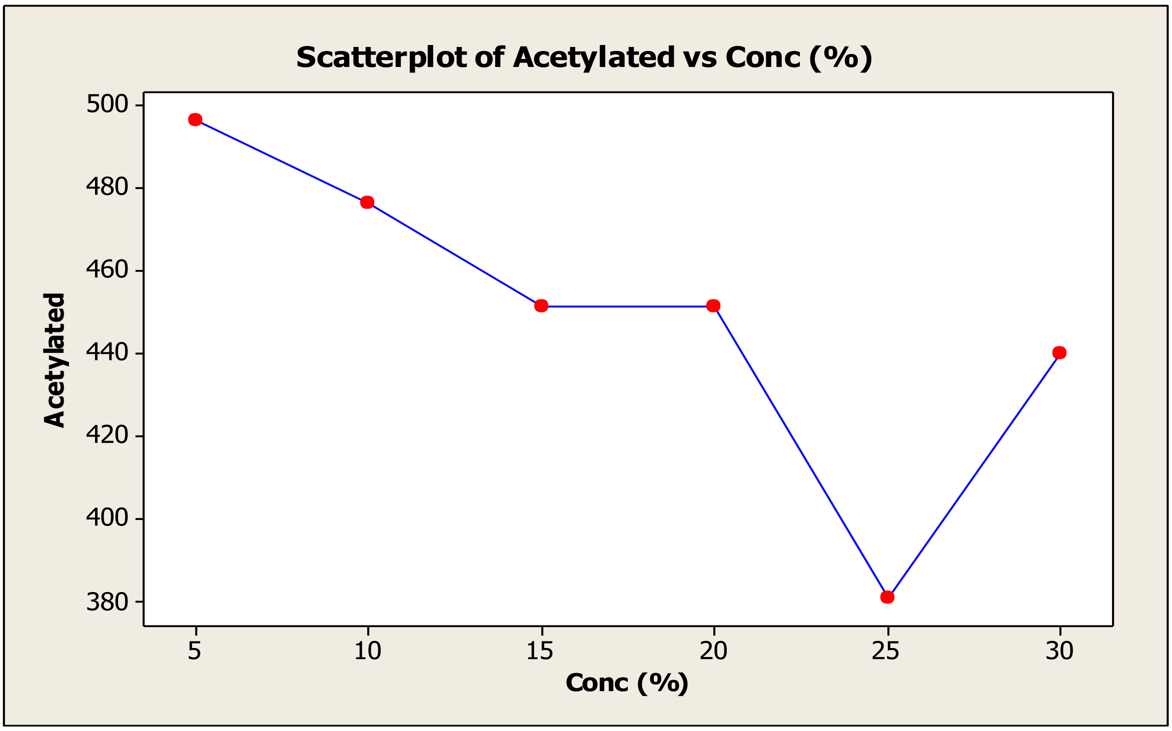


Figure 4.32A: Elongation at Break of Acetylated Groundnut Shell filled Vulcanizates

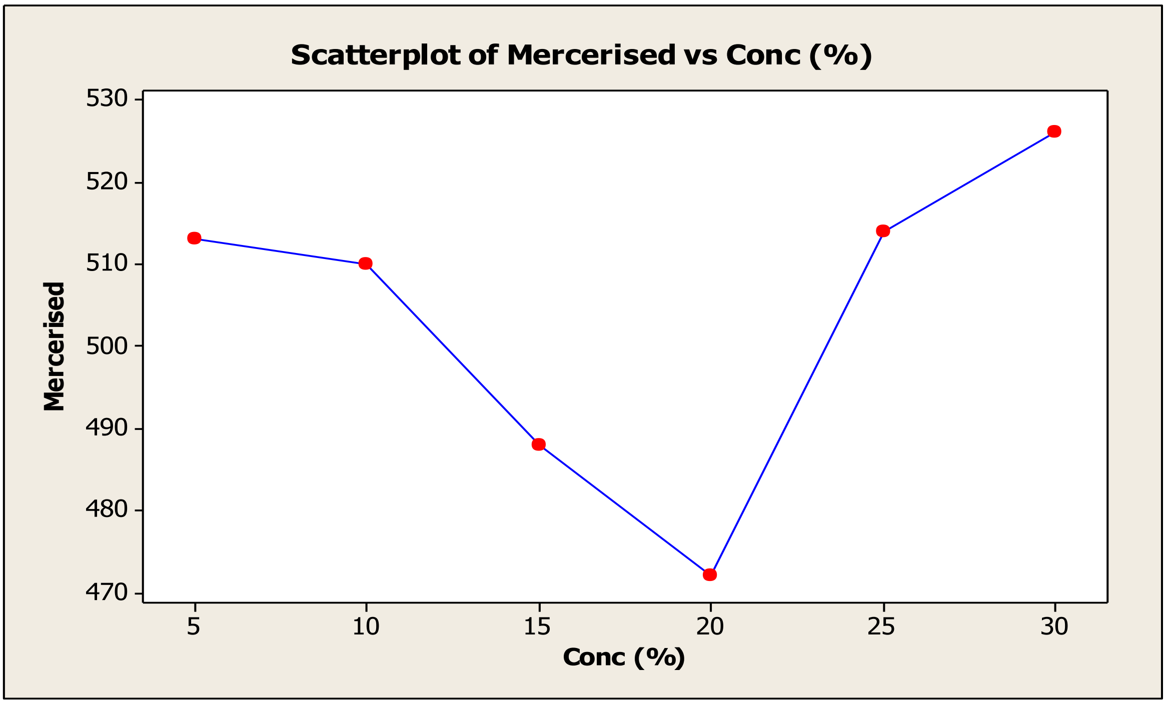


Figure 4.32B: Elongated at Break of Mercerized Groundnut Shell filled Vulcanizates

Hardness (IRHD)

Between-Subjects Factors

		Value Label	N
Concentration (%)	1.00	Conc 5%	2
	2.00	Conc 10%	2
	3.00	Conc 15%	2
	4.00	Conc 20%	2
	5.00	Conc 25%	2
	6.00	Conc 30%	2
Vulcanizate Category	1.00	Acetylated Vulcanizates	6
	2.00	Mercerised Vulcanizates	6

Tests of Between-Subjects Effects

Dependent Variable: Hardness (IRHD)

Source	Type I Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	397.500[a]	6	66.250	3.400	.100
Intercept	44044.083	1	44044.083	2260.603	.000
Concentration	197.417	5	39.483	2.027	.228
VT1	200.083	1	200.083	10.269	.024
Error	97.417	5	19.483		
Total	44539.000	12			
Corrected Total	494.917	11			

a. R Squared = .803 (Adjusted R Squared = .567)

Homogeneous Subsets

Hardness (IRHD)

	Concentration (%)	N	Subset
			1
Duncan[a,b]	Conc 30%	2	56.0000
	Conc 25%	2	57.0000
	Conc 5%	2	57.5000
	Conc 10%	2	61.5000
	Conc 15%	2	65.0000
	Conc 20%	2	66.5000
	Sig.		.072

Based on observed means.

The error term is Mean Square(Error) = 19.483.

a. Uses Harmonic Mean Sample Size = 2.000.

b. Alpha = 0.05.

Hardness (IRHD) Untreated UT=48

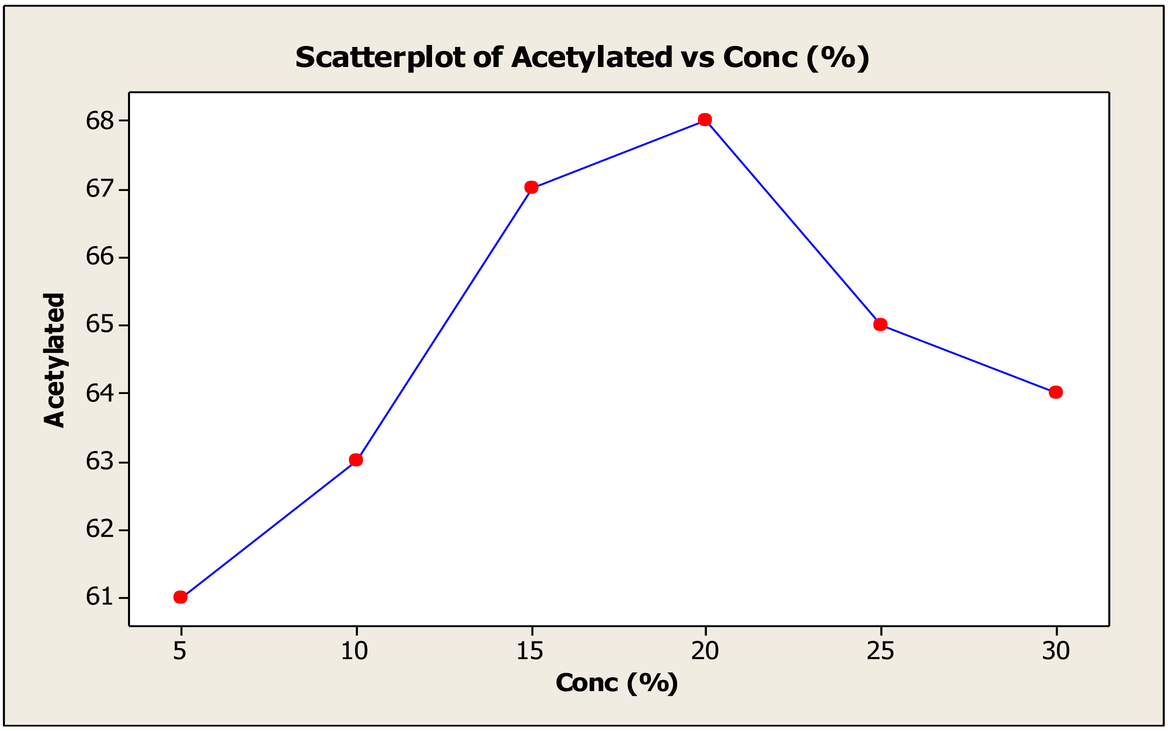


Figure 4.33A: Hardness of Acetylated Groundnut Shell filled Vulcanizates

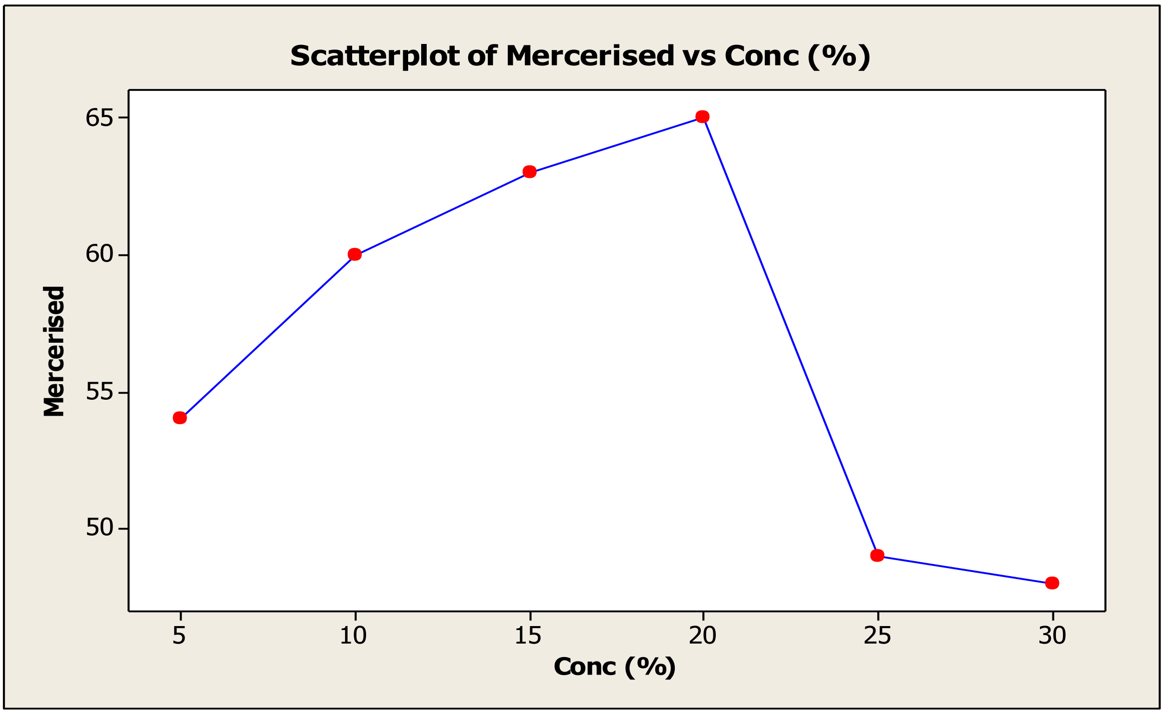


Figure 4.33B: Hardness of Mercerized Groundnut Shell filled Vulcanizates

Compression Set (%)

Between-Subjects Factors

		Value Label	N
Concentration (%)	1.00	Conc 5%	2
	2.00	Conc 10%	2
	3.00	Conc 15%	2
	4.00	Conc 20%	2
	5.00	Conc 25%	2
	6.00	Conc 30%	2
Vulcanizate Category	1.00	Acetylated Vulcanizates	6
	2.00	Mercerised Vulcanizates	6

Tests of Between-Subjects Effects

Dependent Variable: Compression Set (%)

Source	Type I Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	79.833[a]	6	13.306	15.063	.005
Intercept	2790.750	1	2790.750	3159.340	.000
Concent	55.750	5	11.150	12.623	.007
VT2	24.083	1	24.083	27.264	.003
Error	4.417	5	.883		
Total	2875.000	12			
Corrected Total	84.250	11			

a. R Squared = .948 (Adjusted R Squared = .885)

Homogeneous Subsets

Compression Set (%)

	Concentration (%)	N	Subset			
			1	2	3	4
Duncan[a,b]	Conc 20%	2	12.0000			
	Conc 15%	2	13.0000	13.0000		
	Conc 10%	2		15.0000	15.0000	
	Conc 25%	2			16.5000	16.5000
	Conc 5%	2			17.0000	17.0000
	Conc 30%	2				18.0000
	Sig.		.336	.087	.094	.181

Based on observed means.

The error term is Mean Square(Error) = .883.

a. Uses Harmonic Mean Sample Size = 2.000.

b. Alpha = 0.05.

Compression Set (%) Untreated UT=22

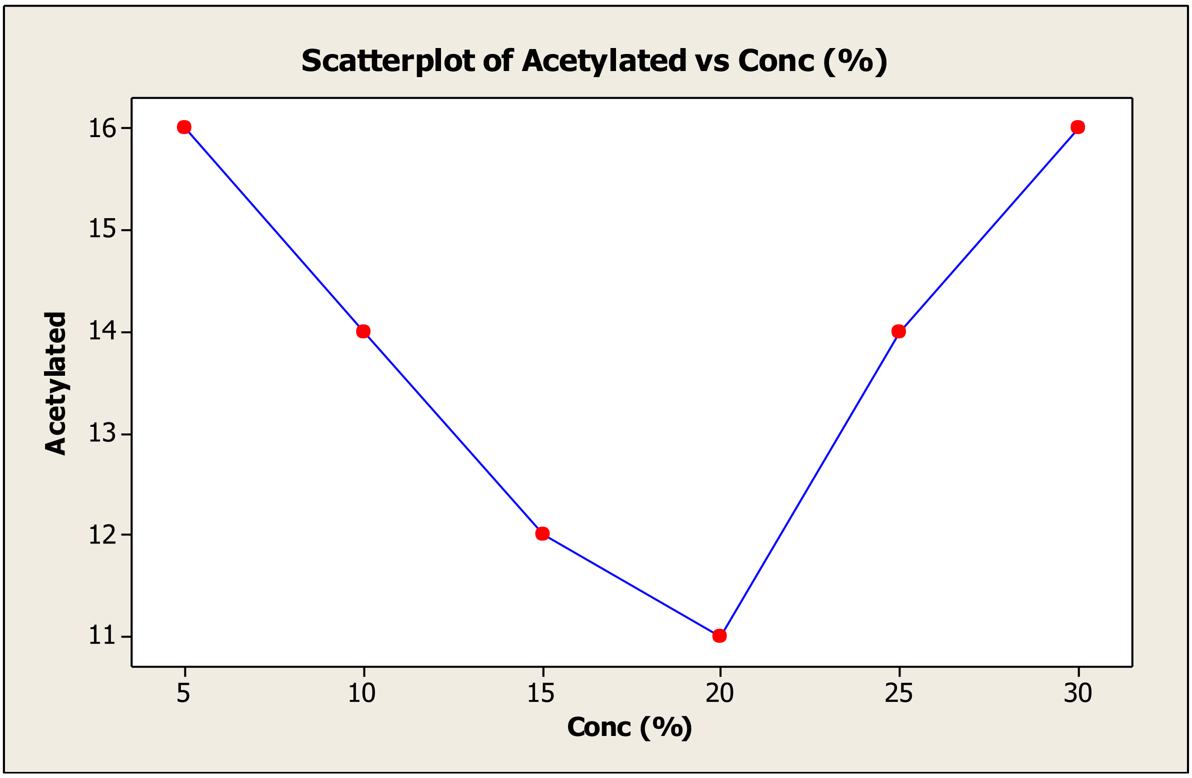


Figure 4.34A: Compression Set of Acetylated Groundnut Shell filled Vulcanizates

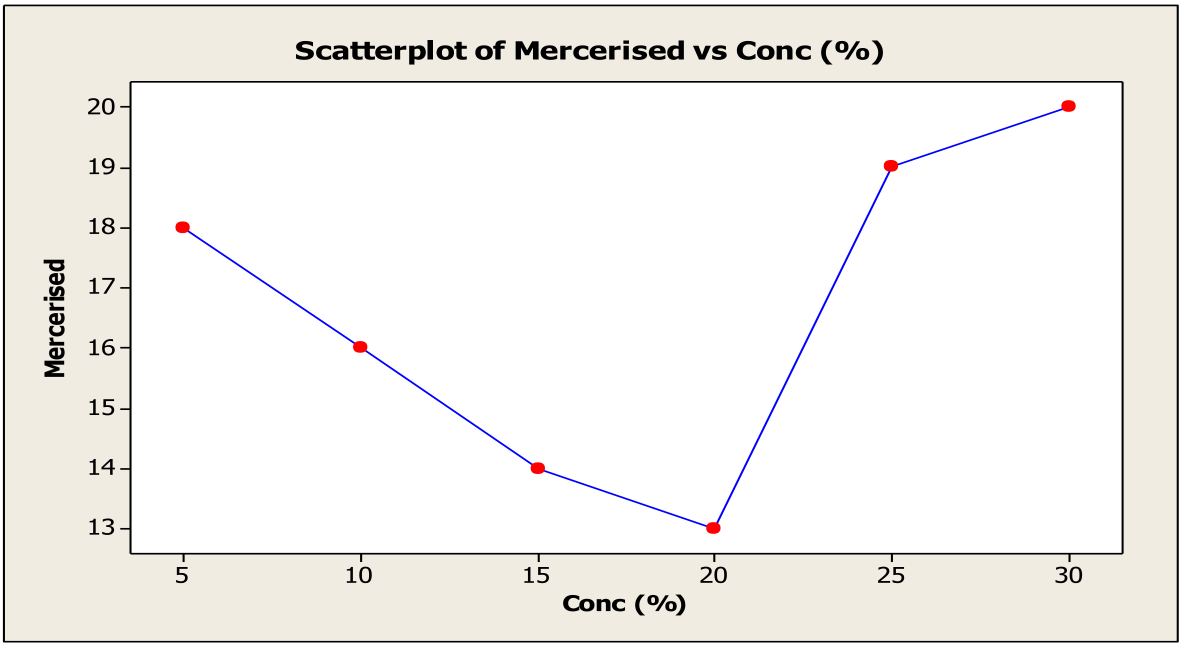


Figure 4.33B: Compression Set of Mercerized Groundnut Shell filled Vulcanizates

Abrasion Resistance (%)

Between-Subjects Factors

		Value Label	N
Concentration (%)	1.00	Conc 5%	2
	2.00	Conc 10%	2
	3.00	Conc 15%	2
	4.00	Conc 20%	2
	5.00	Conc 25%	2
	6.00	Conc 30%	2
Vulcanizate Category	1.00	Acetylated Vulcanizates	6
	2.00	Mercerised Vulcanizates	6

Tests of Between-Subjects Effects

Dependent Variable: Abrasion Resistance (%)

Source	Type I Sum of Squares	Df	Mean Square	F	Sig.
Corrected Model	119.728[a]	6	19.955	29.746	.001
Intercept	16008.907	1	16008.907	23864.210	.000
Concentration	111.228	5	22.246	33.161	.001
VT3	8.501	1	8.501	12.672	.016
Error	3.354	5	.671		
Total	16131.990	12			
Corrected Total	123.082	11			

a. R Squared = .973 (Adjusted R Squared = .940)

Homogeneous Subsets

Abrasion Resistance (%)

	Concentration (%)	N	Subset		
			1	2	3
Duncan^{a,b}	Conc 5%	2	31.7000		
	Conc 30%	2		34.8000	
	Conc 10%	2		35.4500	
	Conc 25%	2		36.9500	
	Conc 15%	2			39.1000
	Conc 20%	2			41.1500
	Sig.		1.000	.052	.054

Based on observed means.

The error term is Mean Square(Error) = .671.

a. Uses Harmonic Mean Sample Size = 2.000.

b. Alpha = 0.05.

Abrasion Resistance (%) Untreated UT=31.55

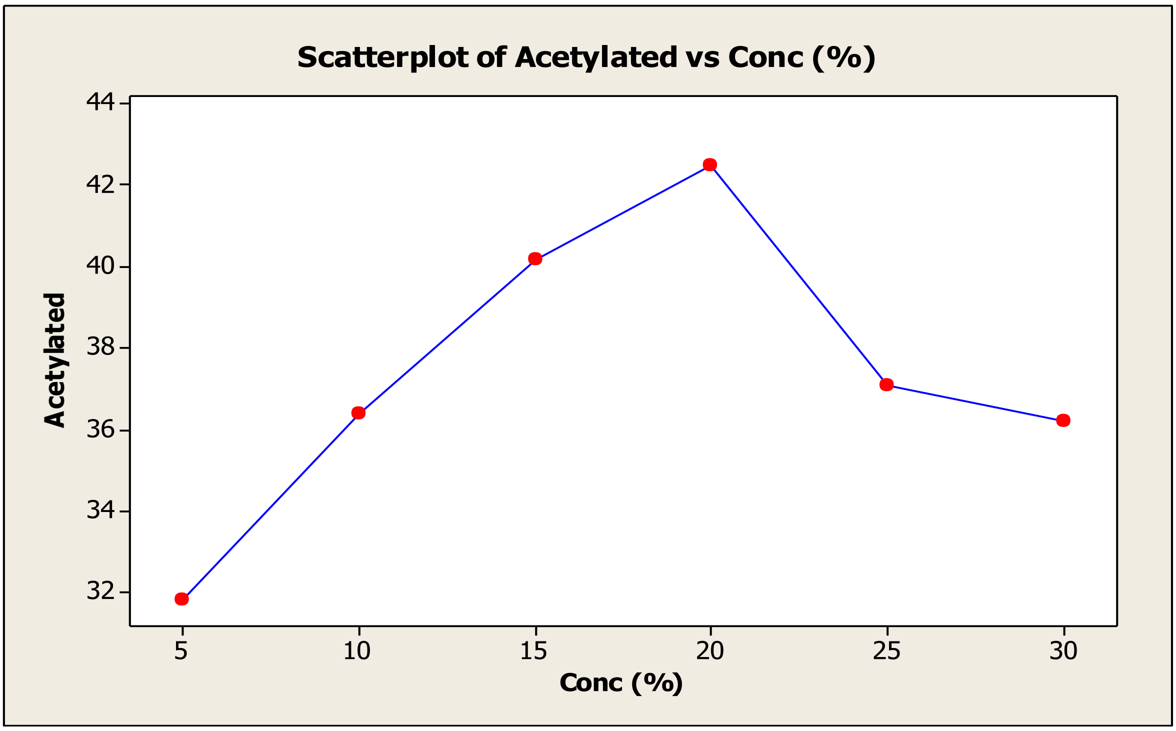


Figure 4.34A: Abrasion Resistance of Acetylated Groundnut Shell filled Vulcanizates

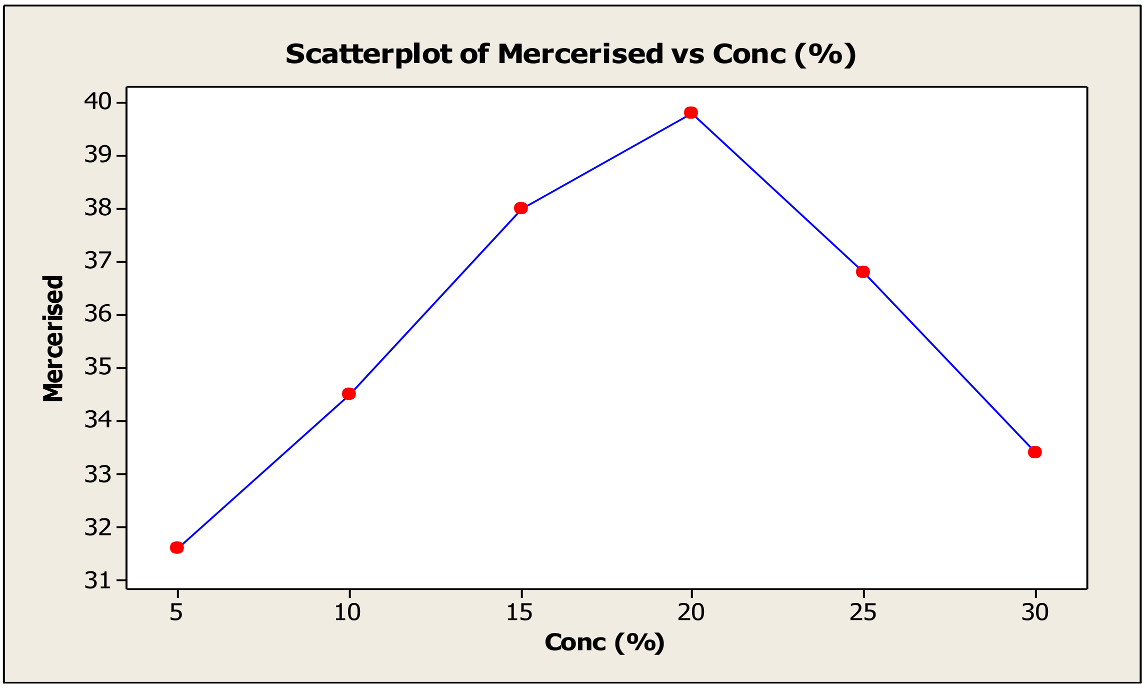


Figure 4.34B: Abrasion Resistance of Mercerized Groundnut Shell filled Vulcanizates

Flex Fatique (Kc x 10^3)

Between-Subjects Factors

		Value Label	N
Concentration (%)	1.00	Conc 5%	2
	2.00	Conc 10%	2
	3.00	Conc 15%	2
	4.00	Conc 20%	2
	5.00	Conc 25%	2
	6.00	Conc 30%	2
Vulcanizate Category	1.00	Acetylated Vulcanizates	6
	2.00	Mercerised Vulcanizates	6

Tests of Between-Subjects Effects

Dependent Variable: Flex Fatique (Kc x10^3)

Source	Type I Sum of Squares	Df	Mean Square	F	Sig.
Corrected Model	16.259[a]	6	2.710	9.367	.013
Intercept	652.673	1	652.673	2256.198	.000
Concentration	12.216	5	2.443	8.446	.018
VT4	4.043	1	4.043	13.975	.013
Error	1.446	5	.289		
Total	670.378	12			
Corrected Total	17.705	11			

a. R Squared = .918 (Adjusted R Squared = .820)

Homogeneous Subsets

Flex Fatique (Kc x10^3)

	Concentration (%)	N	Subset		
			1	2	3
Duncan^{a,b}	Conc 20%	2	5.61000		
	Conc 15%	2	6.50100	6.50100	
	Conc 25%	2		7.50850	7.50850
	Conc 10%	2			8.01750
	Conc 30%	2			8.12750
	Conc 5%	2			8.48500
	Sig.		.159	.120	.141

Based on observed means.
The error term is Mean Square(Error) = .289.
a. Uses Harmonic Mean Sample Size = 2.000.
b. Alpha = 0.05.

Flex Fatique (Kc x 10^3) Untreated UT=8.989

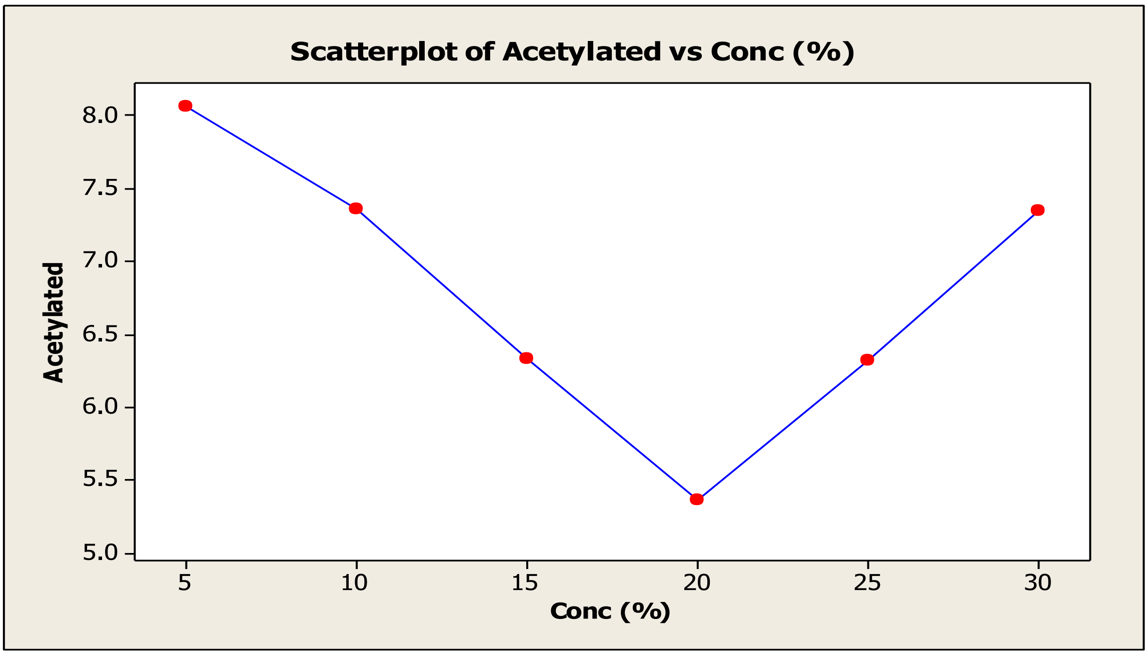


Figure 4.35A: Flex fatigue of Acetylated Groundnut Shell filled Vulcanizates

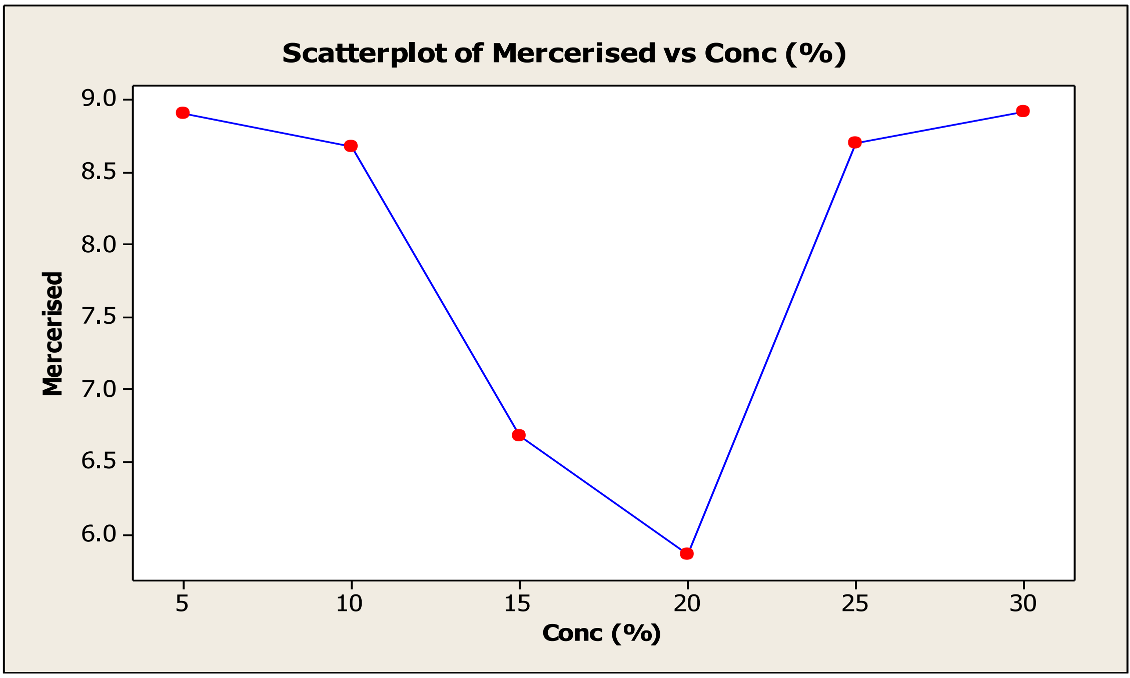


Figure 4.35B: Flex fatigue of Mercerized Groundnut Shell filled Vulcanizates

Analysis of Variance of Swelling Behaviour
Swelling Index in Acetone
Between-Subjects Factors

		Value Label	N
Concentration (%)	1.00	Conc 5%	2
	2.00	Conc 10%	2
	3.00	Conc 15%	2
	4.00	Conc 20%	2
	5.00	Conc 25%	2
	6.00	Conc 30%	2
Vulcanizate Category	1.00	Acetylated Vulcanizates	6
	2.00	Mercerised Vulcanizates	6

Tests of Between-Subjects Effects
Dependent Variable: Swelling Index in Acetone

Source	Type I Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	21357.588[a]	6	3559.598	95.007	.000
Intercept	1116849.067	1	1116849.067	29809.006	.000
Con	19465.047	5	3893.009	103.905	.000
VT1	1892.541	1	1892.541	50.512	.001
Error	187.334	5	37.467		
Total	1138393.990	12			
Corrected Total	21544.923	11			

a. R Squared = .991 (Adjusted R Squared = .981)

Homogeneous Subsets

Swelling Index in Acetone

	Concentration (%)	N	Subset				
			1	2	3	4	5
Duncan[a,b]	Conc 20%	2	235.2500				
	Conc 25%	2		287.8000			
	Conc 15%	2		297.8000	297.8000		
	Conc 30%	2			307.9500		
	Conc 10%	2				338.3500	
	Conc 5%	2					363.3000
	Sig.		1.000	.163	.158	1.000	1.000

Based on observed means.

The error term is Mean Square(Error) = 37.467.

a. Uses Harmonic Mean Sample Size = 2.000.

b. Alpha = 0.05.

Swelling Behaviour

Swelling Index Untreated UT=554

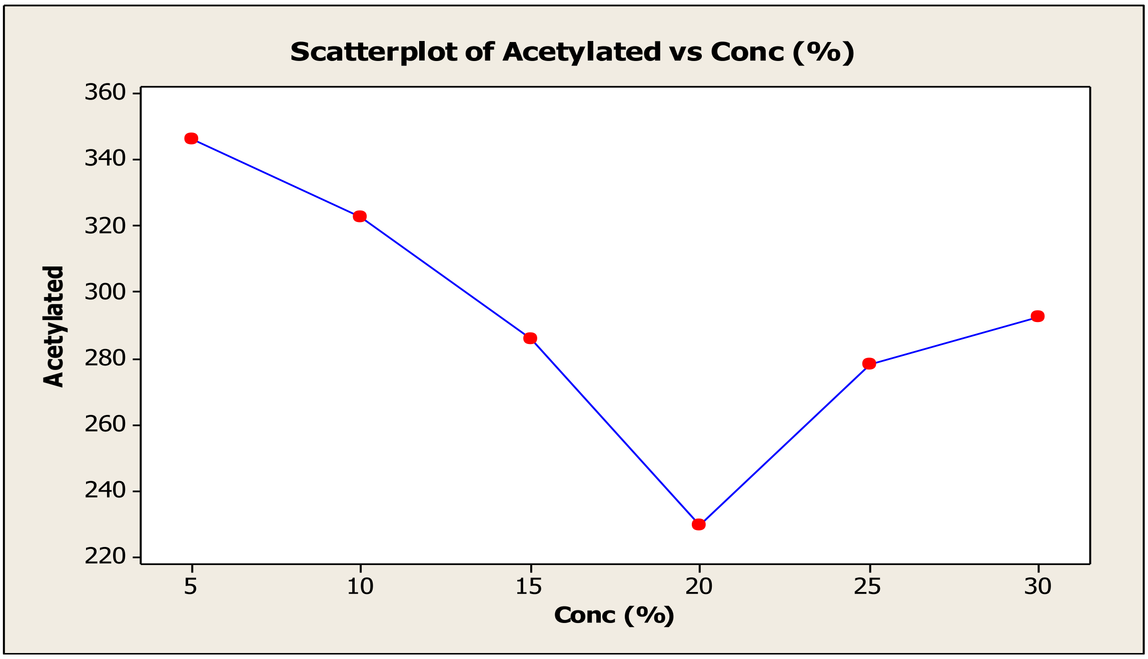


Figure 4.36A: Swelling Index of Acetylated Groundnut Shell filled Vulcanizates in Acetone

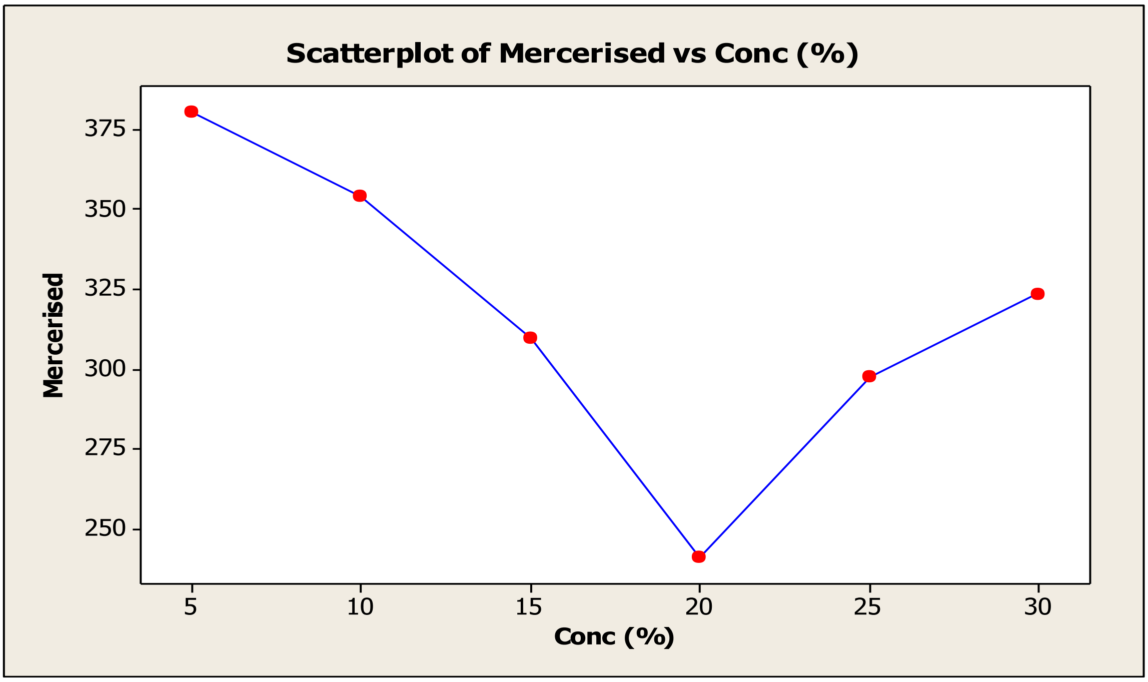


Figure 4.36B: Swelling Index of Mercerized Groundnut Shell filled Vulcanizates in Acetone

Analysis of Variance of Swelling Coefficient in Acetone

Between-Subjects Factors

		Value Label	N
Concentration (%)	1.00	Conc 5%	2
	2.00	Conc 10%	2
	3.00	Conc 15%	2
	4.00	Conc 20%	2
	5.00	Conc 25%	2
	6.00	Conc 30%	2
Vulcanizate Category	1.00	Acetylated Vulcanizates	6
	2.00	Mercerised Vulcanizates	6

Tests of Between-Subjects Effects

Dependent Variable: Swelling Coefficient in Acetone

Source	Type I Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	3.325[a]	6	.554	133.562	.000
Intercept	178.903	1	178.903	43124.469	.000
Concentration	3.002	5	.600	144.746	.000
VT2	.322	1	.322	77.641	.000
Error	.021	5	.004		
Total	182.249	12			
Corrected Total	3.345	11			

a. R Squared = .994 (Adjusted R Squared = .986)

Homogeneous Subsets

Swelling Coefficient

	Concentration (%)	N	Subset				
			1	2	3	4	5
Duncan[a,b]	Conc 20%	2	3.0045				
	Conc 25%	2		3.6380			
	Conc 15%	2		3.7620	3.7620		
	Conc 30%	2			3.8940		
	Conc 10%	2				4.2765	
	Conc 5%	2					4.5920
	Sig.		1.000	.112	.096	1.000	1.000

Based on observed means.

The error term is Mean Square(Error) = .004.

a. Uses Harmonic Mean Sample Size = 2.000.

b. Alpha = 0.05.

Swelling Co-efficient Untreated UT=4.995

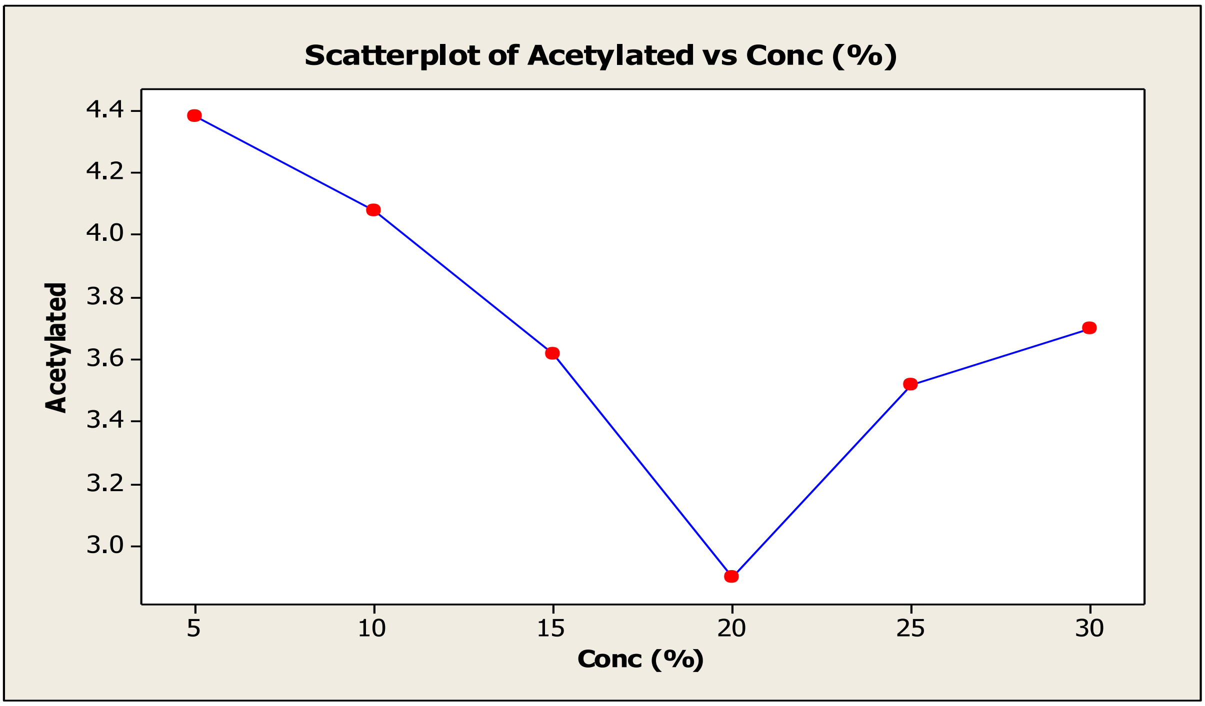


Figure 4.37A: Swelling Coefficient of Acetylated Groundnut Shell filled Vulcanizates in Aceton

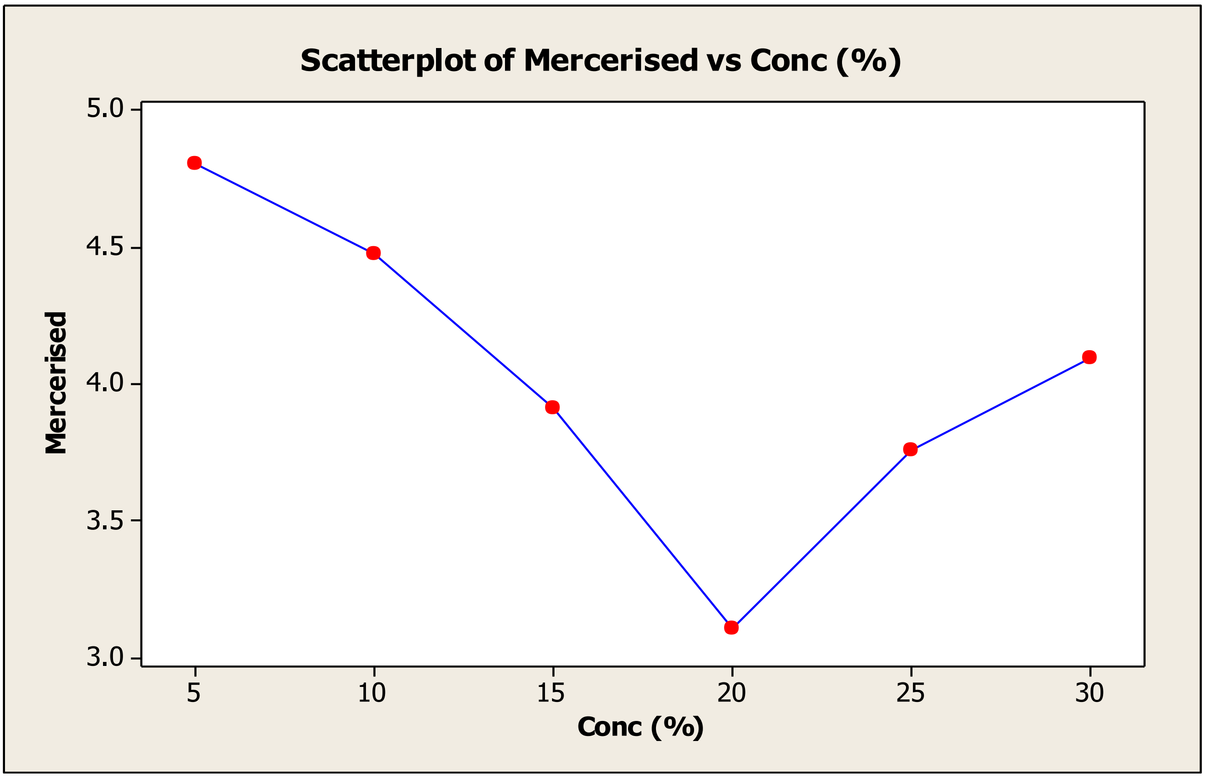


Figure 4.37B: Swelling Coefficient of Mercerized Groundnut Shell filled Vulcanizates in Acetone

Analysis of Variance of %Mole Uptake of Solvent

Between-Subjects Factors

		Value Label	N
Concentration (%)	1.00	Conc 5%	2
	2.00	Conc 10%	2
	3.00	Conc 15%	2
	4.00	Conc 20%	2
	5.00	Conc 25%	2
	6.00	Conc 30%	2
Vulcanizate Category	1.00	Acetylated Vulcanizates	6
	2.00	Mercerised Vulcanizates	6

Tests of Between-Subjects Effects

Dependent Variable: % Mole Uptake of Solvent

Source	Type I Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	6.167[a]	6	1.028	134.383	.000
Intercept	331.959	1	331.959	43400.751	.000
Concentration	5.565	5	1.113	145.504	.000
VT3	.603	1	.603	78.780	.000
Error	.038	5	.008		
Total	338.164	12			
Corrected Total	6.205	11			

a. R Squared = .994 (Adjusted R Squared = .986)

Homogeneous Subsets

% Mole Uptake of Solvent

	Concentration (%)	N	Subset				
			1	2	3	4	5
Duncan[a,b]	Conc 20%	2	4.0930				
	Conc 25%	2		4.9555			
	Conc 15%	2		5.1260	5.1260		
	Conc 30%	2			5.3035		
	Conc 10%	2				5.8255	
	Conc 5%	2					6.2540
	Sig.		1.000	.109	.098	1.000	1.000

Based on observed means.

The error term is Mean Square(Error) = .008.

a. Uses Harmonic Mean Sample Size = 2.000.

b. Alpha = 0.05.

Mole Uptake Solvent Untreated UT=6.986

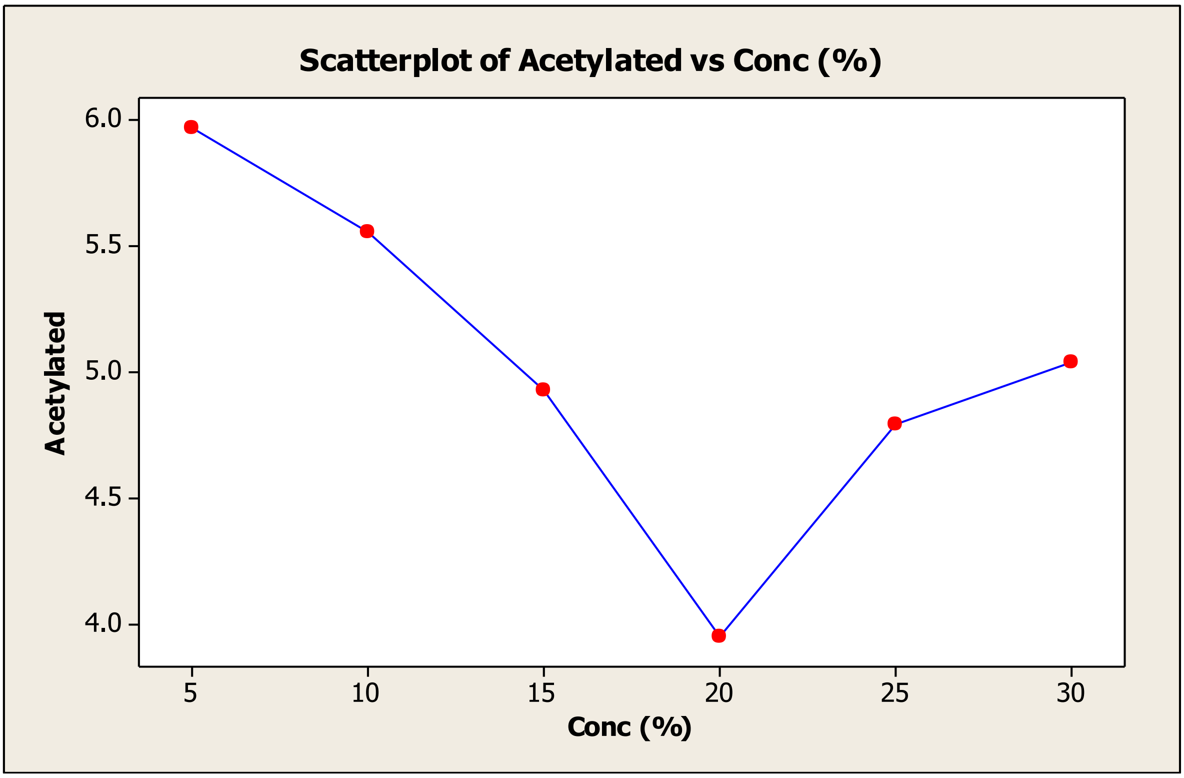


Figure 4.38A: Mole Uptake of Acetylated Groundnut Shell filled Vulcanizates in Acetone

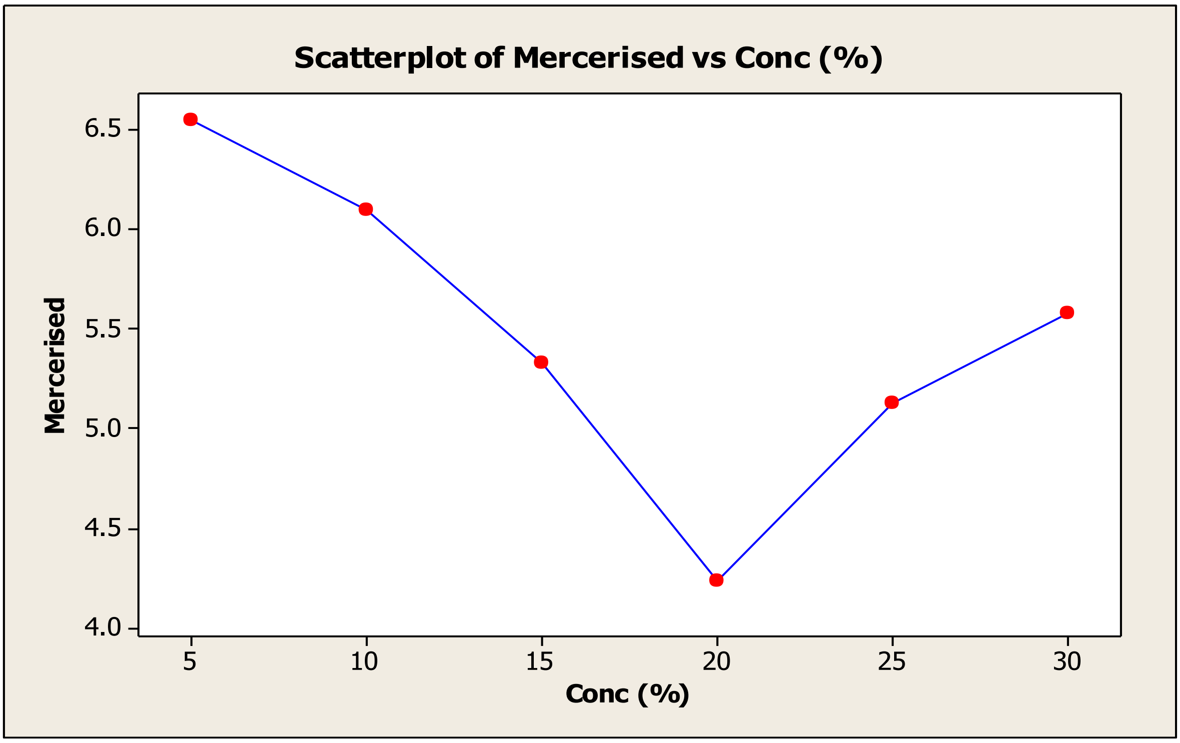


Figure 4.38B: Mole Uptake of Mercerized Groundnut Shell filled Vulcanizates in Acetone

Analysis of Variance of Xylene

Between-Subjects Factors

		Value Label	N
Concentration (%)	1.00	Conc 5%	2
	2.00	Conc 10%	2
	3.00	Conc 15%	2
	4.00	Conc 20%	2
	5.00	Conc 25%	2
	6.00	Conc 30%	2
Vulcanizate Category	1.00	Acetylated Vulcanizates	6
	2.00	Mercerised Vulcanizates	6

Tests of Between-Subjects Effects

Dependent Variable: Swelling Index

Source	Type I Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	28904.638[a]	6	4817.440	10.530	.010
Intercept	1467271.267	1	1467271.267	3207.313	.000
Con	9132.437	5	1826.487	3.993	.077
VT1	19772.201	1	19772.201	43.220	.001
Error	2287.384	5	457.477		
Total	1498463.290	12			
Corrected Total	31192.023	11			

a. R Squared = .927 (Adjusted R Squared = .839)

Homogeneous Subsets

Swelling Index

	Concentration (%)	N	Subset	
			1	2
Duncan[a, b]	Conc 20%	2	300.5000	
	Conc 15%	2	338.0000	338.0000
	Conc 25%	2	343.7500	343.7500
	Conc 30%	2		362.3000
	Conc 10%	2		363.5000
	Conc 5%	2		390.0000
	Sig.		.107	.068

Based on observed means.

The error term is Mean Square(Error) = 457.477.

a. Uses Harmonic Mean Sample Size = 2.000.

b. Alpha = 0.05.

Swelling Behaviour of the Vulcanizate in Xylene

Swelling Index Untreated UT=540

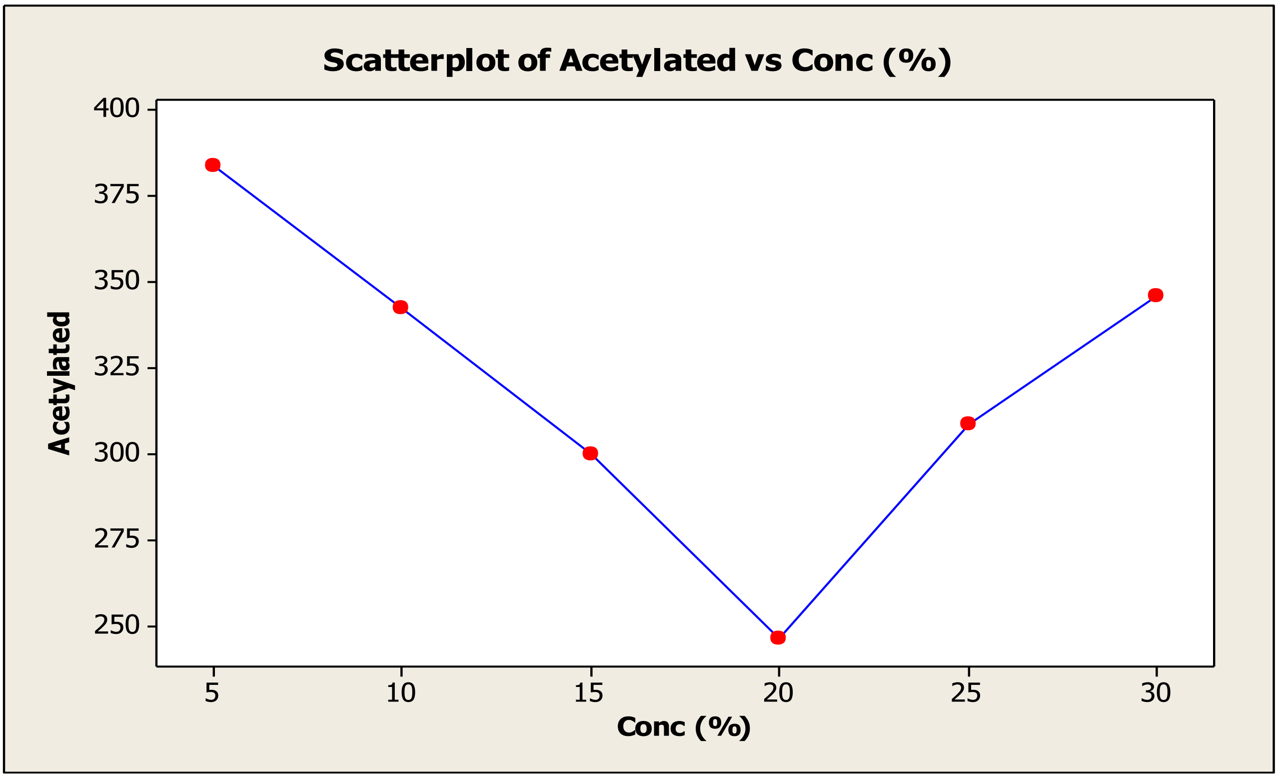


Figure 4.39A: Swelling Behaviour of Acetylated Groundnut Shell filled Vulcanizates in Xylene

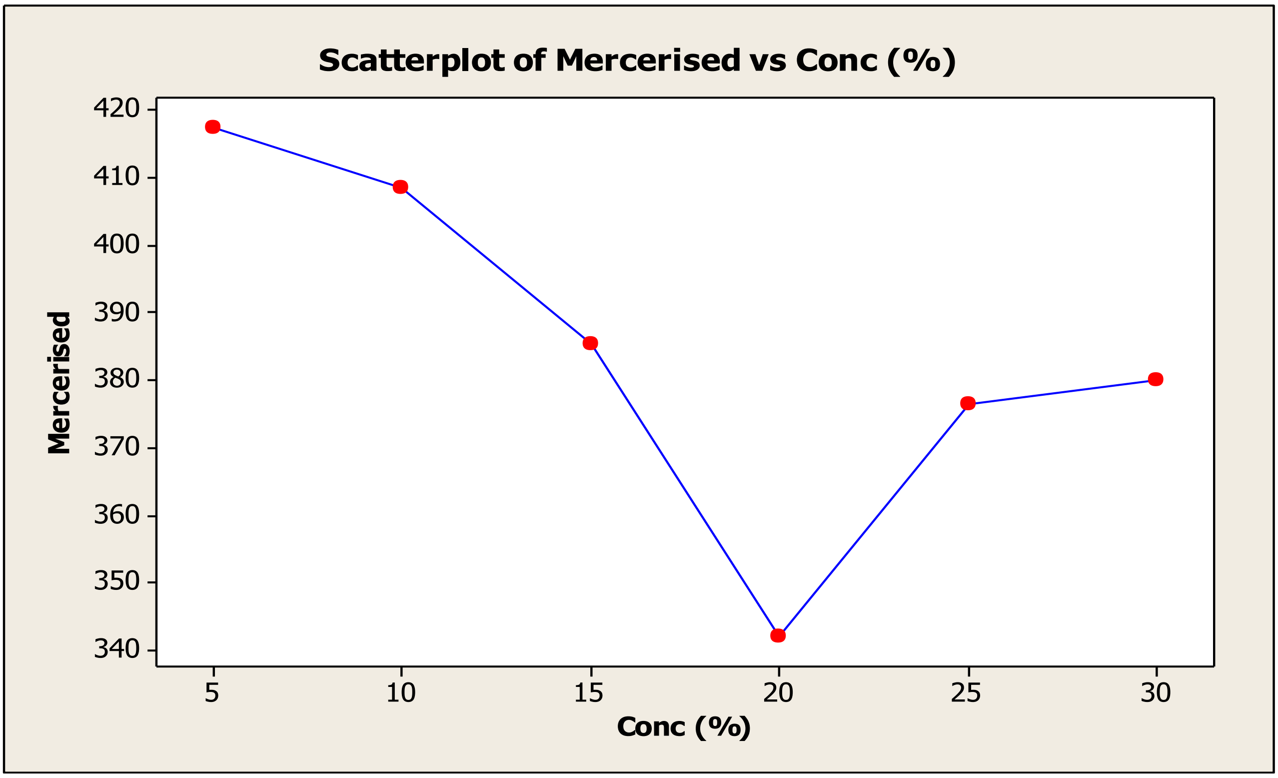


Figure 4.39B: Swelling Behaviour of Mercerized Groundnut Shell filled Vulcanizates in Xylene

Analysis of Variance of Swelling Coefficient in Xylene

Between-Subjects Factors

		Value Label	N
Concentration (%)	1.00	Conc 5%	2
	2.00	Conc 10%	2
	3.00	Conc 15%	2
	4.00	Conc 20%	2
	5.00	Conc 25%	2
	6.00	Conc 30%	2
Vulcanizate Category	1.00	Acetylated Vulcanizates	6
	2.00	Mercerised Vulcanizates	6

Tests of Between-Subjects Effects

Dependent Variable: Swelling Coefficient in Xylene

Source	Type I Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	3.325[a]	6	.554	133.562	.000
Intercept	178.903	1	178.903	43124.469	.000
Concentration	3.002	5	.600	144.746	.000
VT2	.322	1	.322	77.641	.000
Error	.021	5	.004		
Total	182.249	12			
Corrected Total	3.345	11			

a. R Squared = .994 (Adjusted R Squared = .986)

Homogeneous Subsets

Swelling Coefficient

	Concentration (%)	N	Subset				
			1	2	3	4	5
Duncan[a,b]	Conc 20%	2	3.0045				
	Conc 25%	2		3.6380			
	Conc 15%	2		3.7620	3.7620		
	Conc 30%	2			3.8940		
	Conc 10%	2				4.2765	
	Conc 5%	2					4.5920
	Sig.		1.000	.112	.096	1.000	1.000

Based on observed means.

The error term is Mean Square(Error) = .004.

a. Uses Harmonic Mean Sample Size = 2.000.

b. Alpha = 0.05.

Swelling Co-efficient Untreated UT=528.5

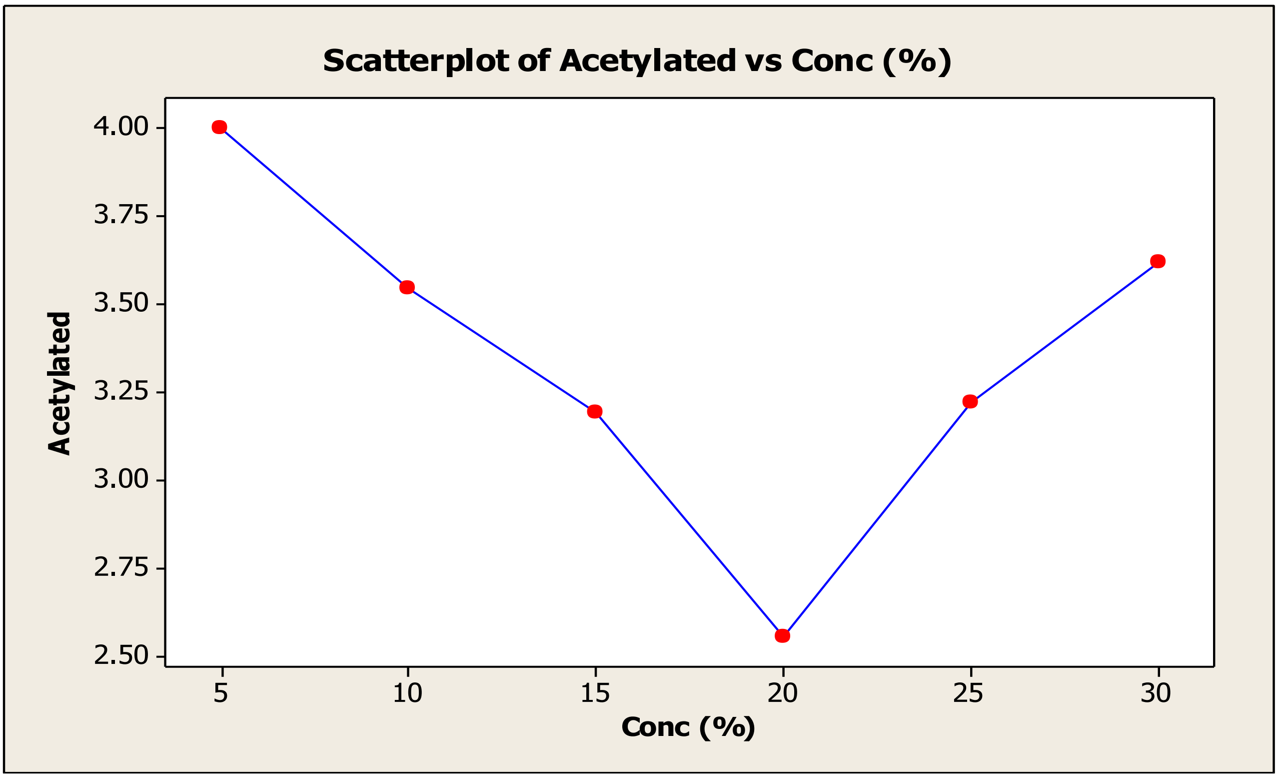


Figure 4.40A: Swelling Coefficient of Acetylated Groundnut Shell filled Vulcanizates in Xylene

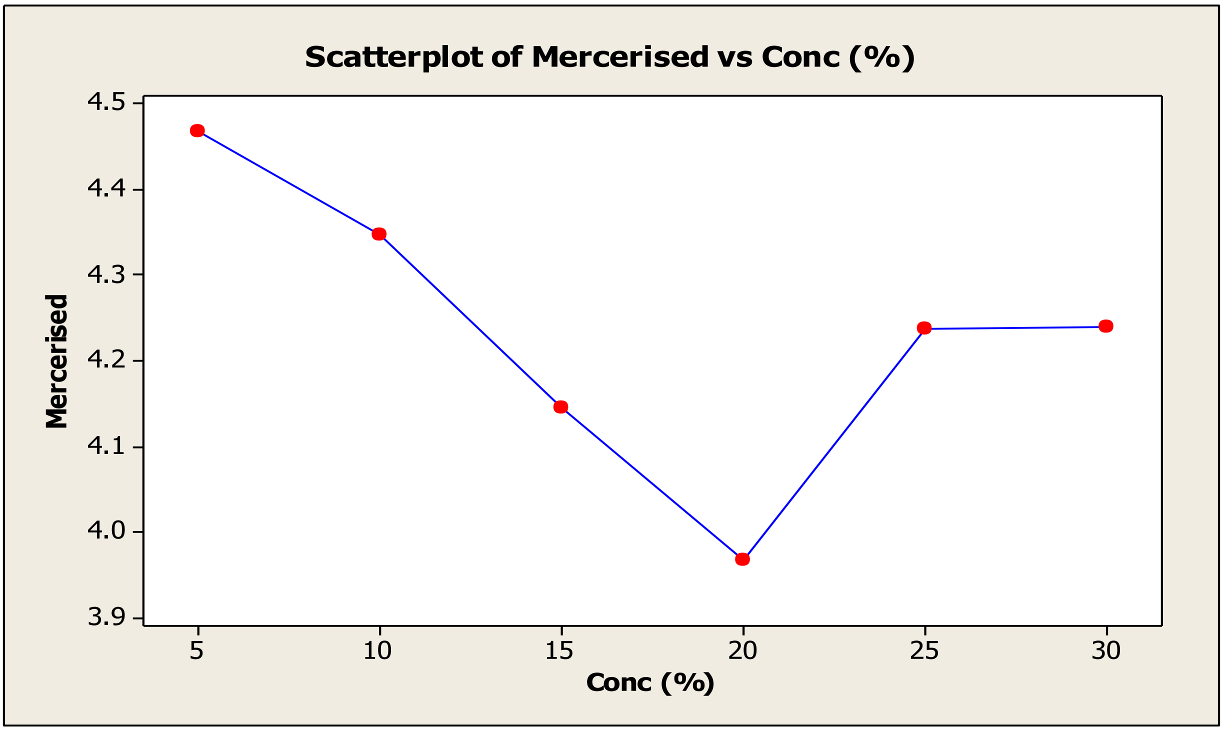


Figure 4.40B: Swelling Coefficient of Mercerized Groundnut Shell filled Vulcanizates in Xylene

Analysis of Variance of %Mole Uptake of Solvent

Between-Subjects Factors

		Value Label	N
Concentration (%)	1.00	Conc 5%	2
	2.00	Conc 10%	2
	3.00	Conc 15%	2
	4.00	Conc 20%	2
	5.00	Conc 25%	2
	6.00	Conc 30%	2
Vulcanizate Category	1.00	Acetylated Vulcanizates	6
	2.00	Mercerised Vulcanizates	6

Tests of Between-Subjects Effects

Dependent Variable: % Mole Uptake of Solvent

Source	Type I Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	6.167[a]	6	1.028	134.383	.000
Intercept	331.959	1	331.959	43400.751	.000
Concentration	5.565	5	1.113	145.504	.000
VT3	.603	1	.603	78.780	.000
Error	.038	5	.008		
Total	338.164	12			
Corrected Total	6.205	11			

a. R Squared = .994 (Adjusted R Squared = .986)

Homogeneous Subsets

% Mole Uptake of Solvent

	Concentration (%)	N	Subset				
			1	2	3	4	5
Duncan^{a,b}	Conc 20%	2	4.0930				
	Conc 25%	2		4.9555			
	Conc 15%	2		5.1260	5.1260		
	Conc 30%	2			5.3035		
	Conc 10%	2				5.8255	
	Conc 5%	2					6.2540
	Sig.		1.000	.109	.098	1.000	1.000

Based on observed means.

The error term is Mean Square(Error) = .008.

a. Uses Harmonic Mean Sample Size = 2.000.

b. Alpha = 0.05.

Mole Uptake of Solvent Untreated UT=5.086

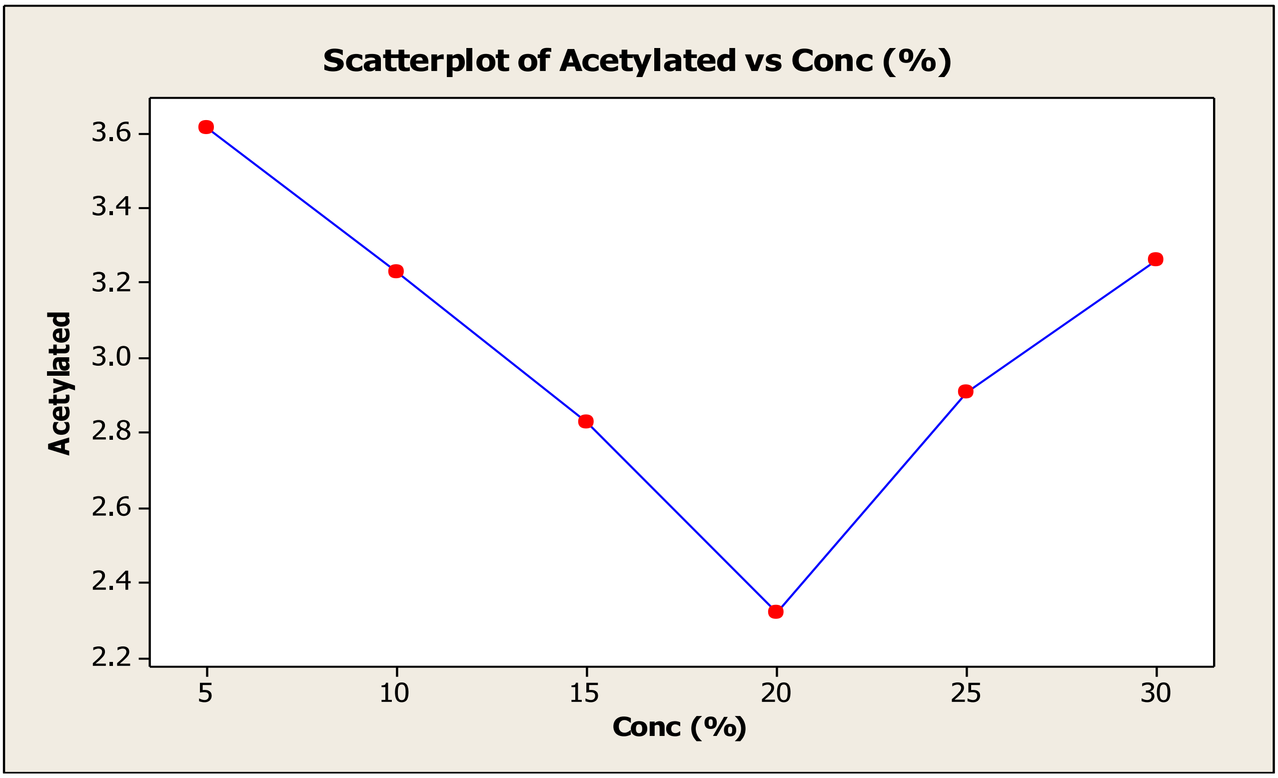


Figure 4.41A: Mole Uptake of Acetylated Groundnut Shell filled Vulcanizates in Xylene

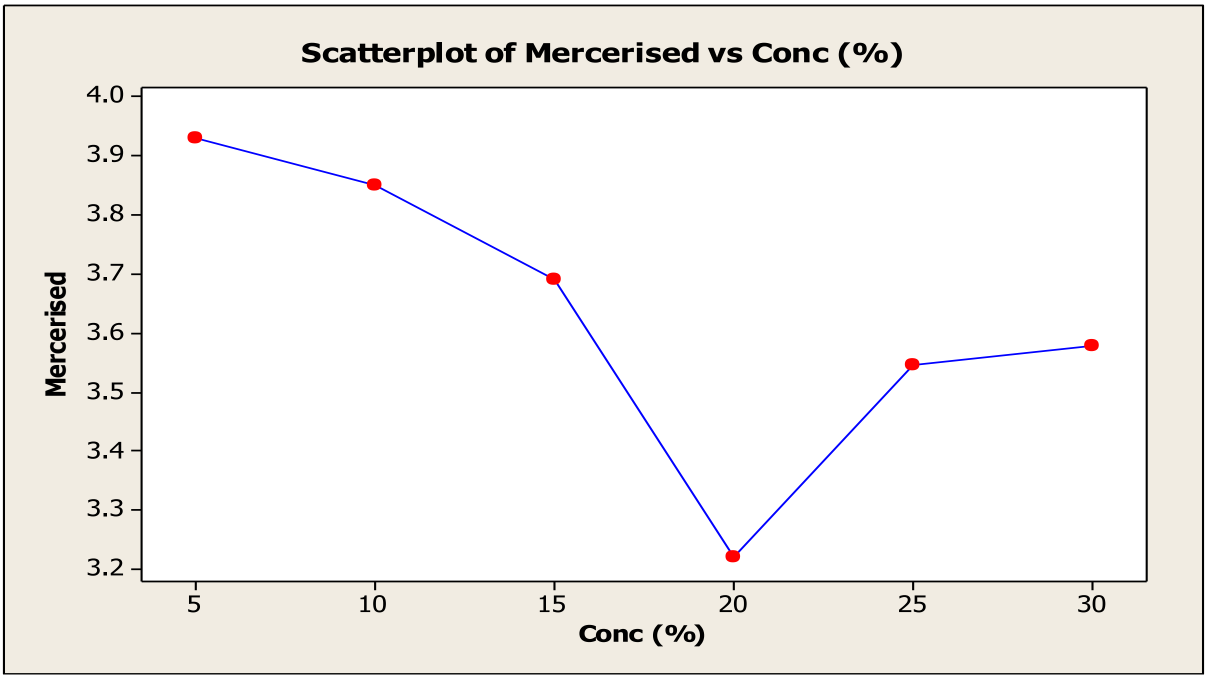


Figure 4.41B: Mole Uptake of Mercerized Groundnut Shell filled Vulcanizates in Xylene

Analysis of Variance of Toluene

Between-Subjects Factors

		Value Label	N
Concentration (%)	1.00	Conc 5%	2
	2.00	Conc 10%	2
	3.00	Conc 15%	2
	4.00	Conc 20%	2
	5.00	Conc 25%	2
	6.00	Conc 30%	2
Vulcanizate Category	1.00	Acetylated Vulcanizates	6
	2.00	Mercerised Vulcanizates	6

Tests of Between-Subjects Effects

Dependent Variable: Swelling Coefficient

Source	Type I Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	3.898[a]	6	.650	10.695	.010
Intercept	194.601	1	194.601	3203.624	.000
Conc	1.205	5	.241	3.969	.078
VT2	2.692	1	2.692	44.322	.001
Error	.304	5	.061		
Total	198.802	12			
Corrected Total	4.202	11			

a. R Squared = .928 (Adjusted R Squared = .841)

Homogeneous Subsets

Swelling Coefficient

	Concentration (%)	N	Subset	
			1	2
Duncan[a,b]	Conc 20%	2	3.4625	
	Conc 15%	2	3.8930	3.8930
	Conc 25%	2	3.9590	3.9590
	Conc 30%	2		4.1700
	Conc 10%	2		4.1860
	Conc 5%	2		4.4915
	Sig.		.108	.068

Based on observed means.

The error term is Mean Square(Error) = .061.

a. Uses Harmonic Mean Sample Size = 2.000.

b. Alpha = 0.05.

Swelling Behaviour of the Vulcanizate in Tuolene

Swelling Index Untreated UT=4.898

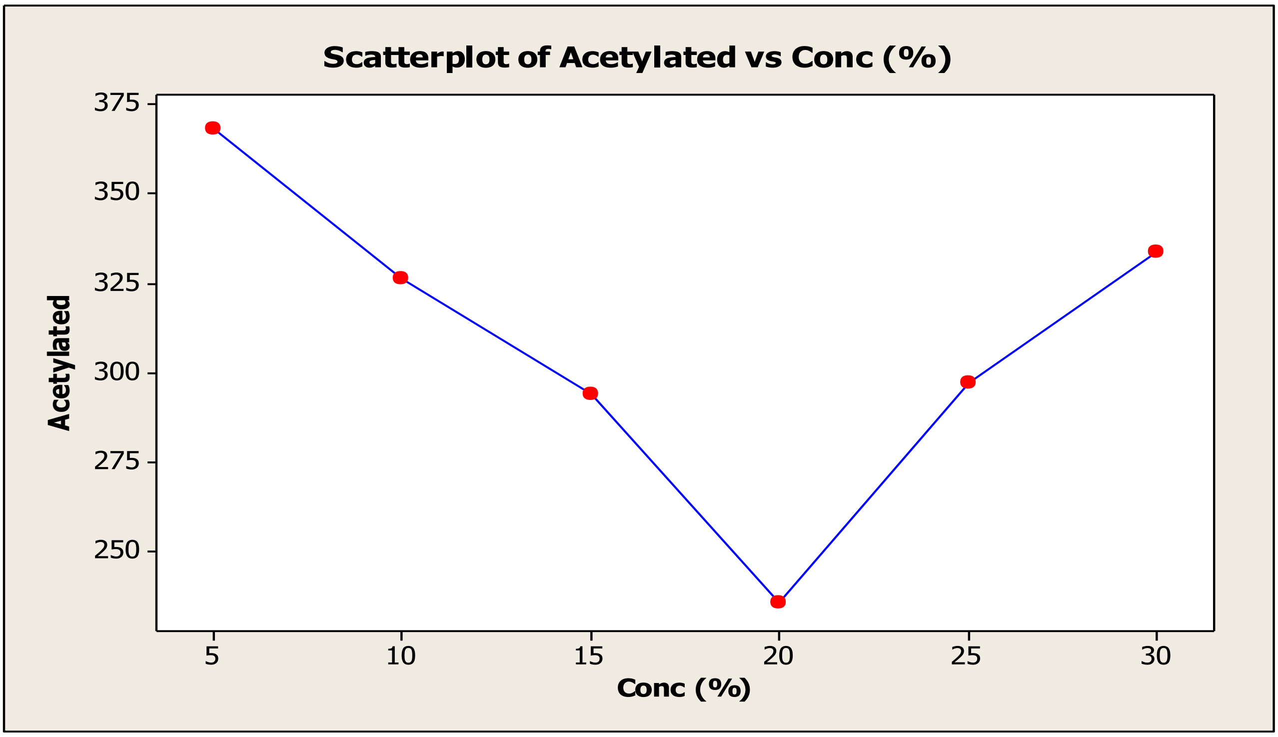


Figure 4.42A: Swelling Index of Acetylated Groundnut Shell filled Vulcanizates in Toluene

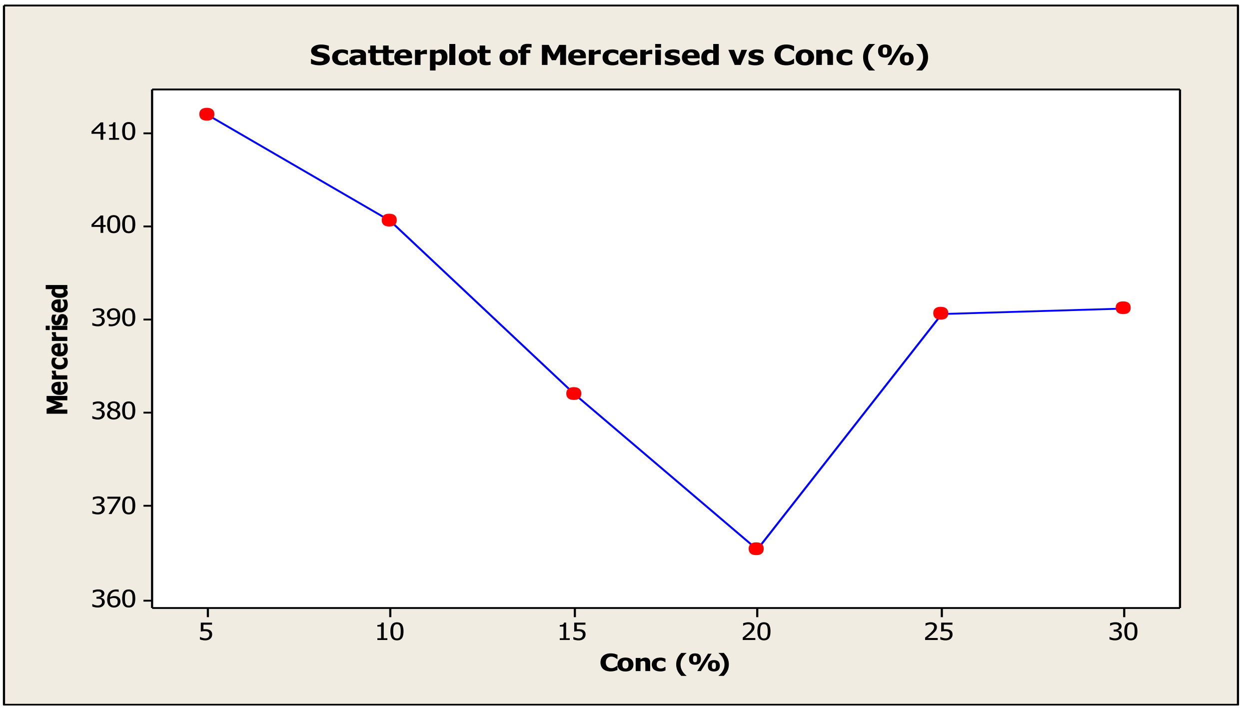


Figure 4.42B: Swelling Index of Mercerized Groundnut Shell filled Vulcanizates in Toluene

Analysis of Variance of Swelling Coefficient in Toluene

Between-Subjects Factors

		Value Label	N
Concentration (%)	1.00	Conc 5%	2
	2.00	Conc 10%	2
	3.00	Conc 15%	2
	4.00	Conc 20%	2
	5.00	Conc 25%	2
	6.00	Conc 30%	2
Vulcanizate Category	1.00	Acetylated Vulcanizates	6
	2.00	Mercerised Vulcanizates	6

Tests of Between-Subjects Effects

Dependent Variable: Swelling Coefficient in Toluene

Source	Type I Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	3.325[a]	6	.554	133.562	.000
Intercept	178.903	1	178.903	43124.469	.000
Concentration	3.002	5	.600	144.746	.000
VT2	.322	1	.322	77.641	.000
Error	.021	5	.004		
Total	182.249	12			
Corrected Total	3.345	11			

a. R Squared = .994 (Adjusted R Squared = .986)

Homogeneous Subsets

Swelling Coefficient

	Concentration (%)	N	Subset				
			1	2	3	4	5
Duncan[a,b]	Conc 20%	2	3.0045				
	Conc 25%	2		3.6380			
	Conc 15%	2		3.7620	3.7620		
	Conc 30%	2			3.8940		
	Conc 10%	2				4.2765	
	Conc 5%	2					4.5920
	Sig.		1.000	.112	.096	1.000	1.000

Based on observed means.

The error term is Mean Square(Error) = .004.

a. Uses Harmonic Mean Sample Size = 2.000.

b. Alpha = 0.05.

Swelling Co-efficient Untreated UT=4.887

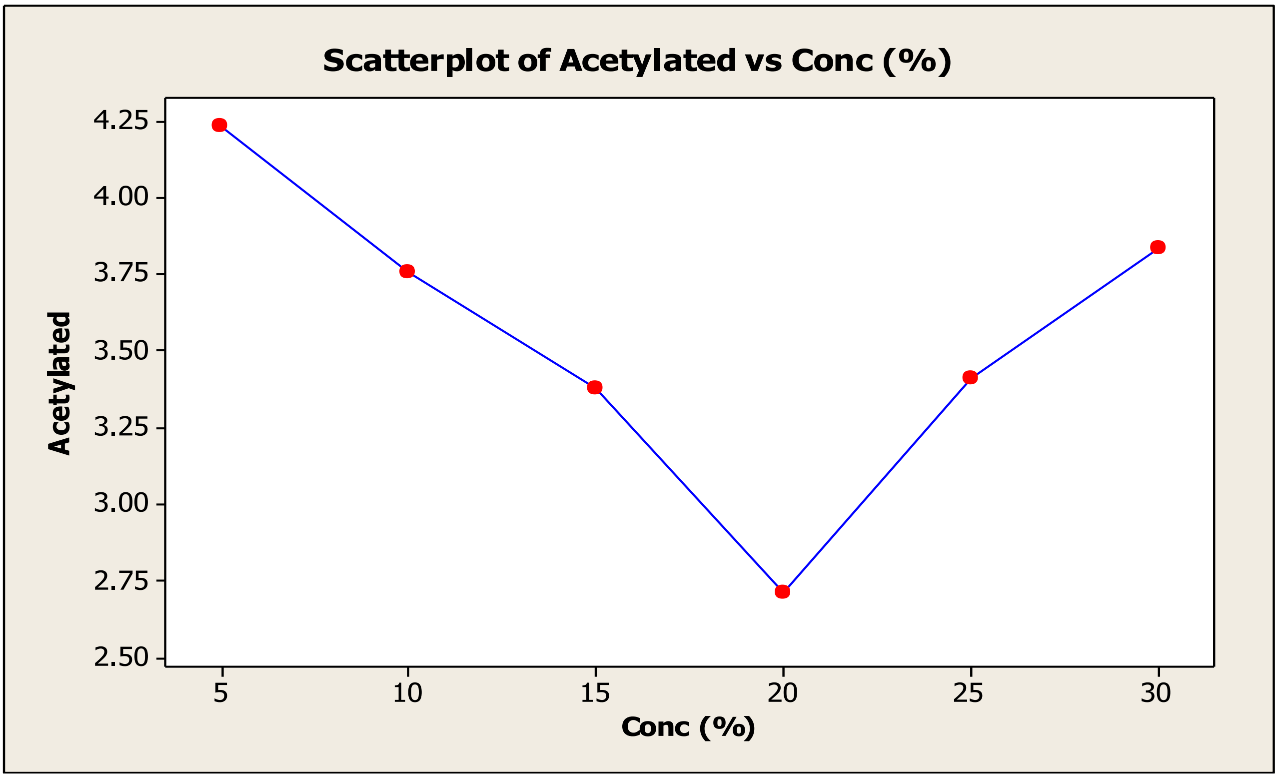


Figure 4.43A: Swelling Coefficient of Acetylated Groundnut Shell filled Vulcanizates in Toluene

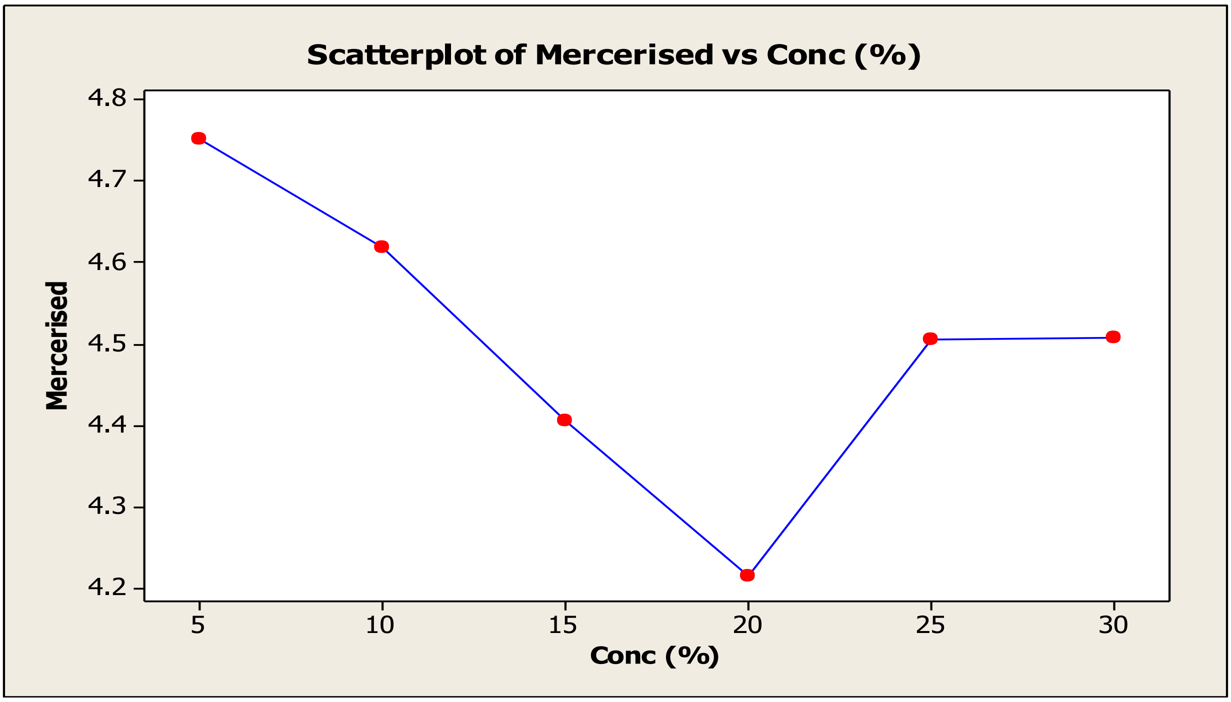


Figure 4.43B: Swelling Coefficient of Mercerized Groundnut Shell filled Vulcanizates in Toluene

Analysis of Variance of %Mole Uptake of Solvent

Between-Subjects Factors

		Value Label	N
Concentration (%)	1.00	Conc 5%	2
	2.00	Conc 10%	2
	3.00	Conc 15%	2
	4.00	Conc 20%	2
	5.00	Conc 25%	2
	6.00	Conc 30%	2
Vulcanizate Category	1.00	Acetylated Vulcanizates	6
	2.00	Mercerised Vulcanizates	6

Tests of Between-Subjects Effects

Dependent Variable: % Mole Uptake of Solvent

Source	Type I Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	6.167[a]	6	1.028	134.383	.000
Intercept	331.959	1	331.959	43400.751	.000
Concentration	5.565	5	1.113	145.504	.000
VT3	.603	1	.603	78.780	.000
Error	.038	5	.008		
Total	338.164	12			
Corrected Total	6.205	11			

a. R Squared = .994 (Adjusted R Squared = .986)

Homogeneous Subsets

% Mole Uptake of Solvent

	Concentration (%)	N	Subset				
			1	2	3	4	5
Duncan^{a,b}	Conc 20%	2	4.0930				
	Conc 25%	2		4.9555			
	Conc 15%	2		5.1260	5.1260		
	Conc 30%	2			5.3035		
	Conc 10%	2				5.8255	
	Conc 5%	2					6.2540
	Sig.		1.000	.109	.098	1.000	1.000

Based on observed means.
The error term is Mean Square(Error) = .008.
a. Uses Harmonic Mean Sample Size = 2.000.
b. Alpha = 0.05.

Mole Uptake Untreated UT=5.112

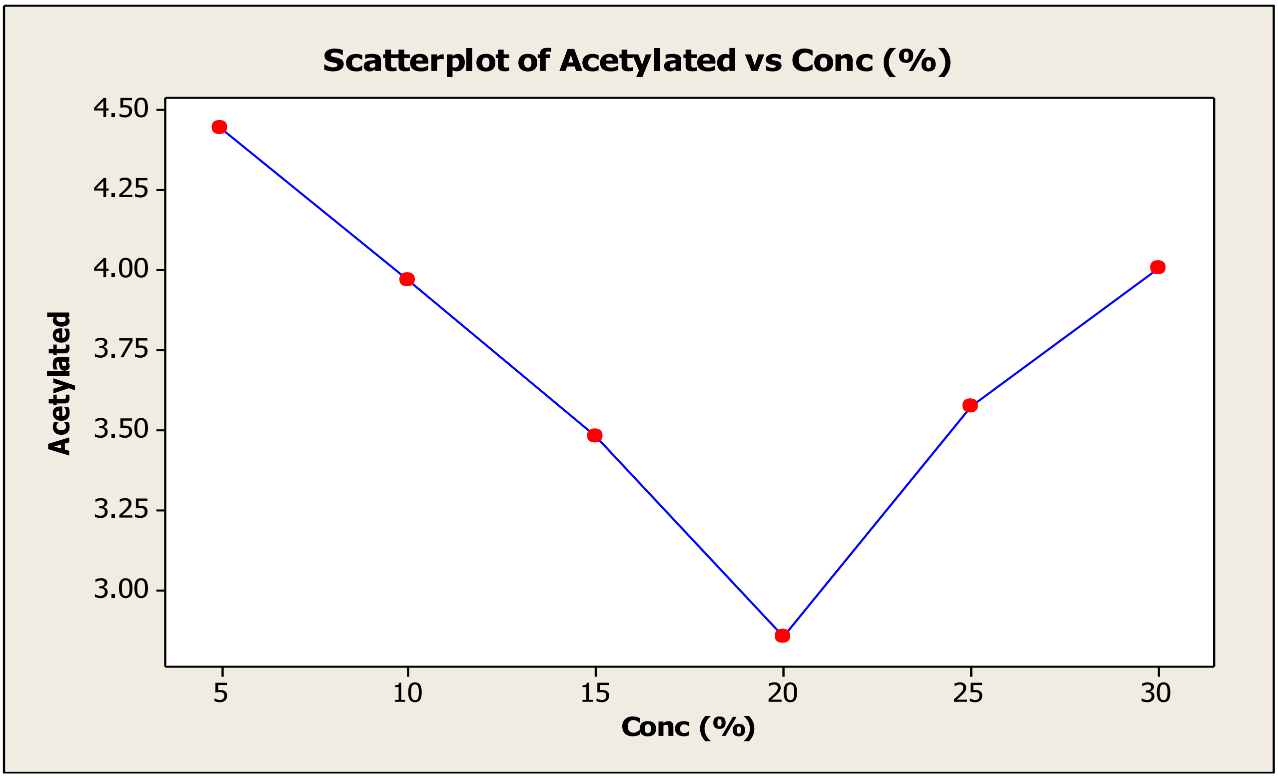


Figure 4.44A: Mole Uptake of Acetylated Groundnut Shell filled Vulcanizates in Toluene

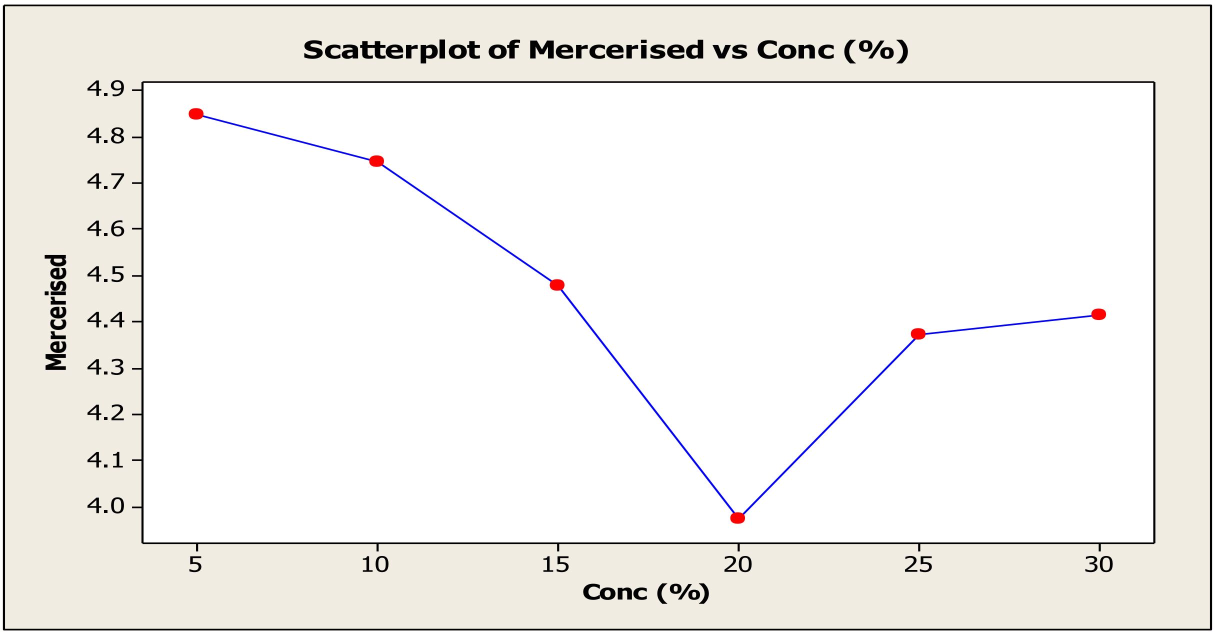


Figure 4.44B: Mole Uptake of Mercerized Groundnut Shell filled Vulcanizates in Toluene

Analysis of Variance of Cross Linking Densiity

Between-Subjects Factors

		Value Label	N
Concentration (%)	1.00	Conc 5%	2
	2.00	Conc 10%	2
	3.00	Conc 15%	2
	4.00	Conc 20%	2
	5.00	Conc 25%	2
	6.00	Conc 30%	2
Vulcanizate Category	1.00	Acetylated Vulcanizates	6
	2.00	Mercerised Vulcanizates	6

Tests of Between-Subjects Effects

Dependent Variable: Cross linking density

Source	Type I Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	550.855[a]	6	91.809	5.302	.044
Intercept	6290.172	1	6290.172	363.255	.000
Concent	292.314	5	58.463	3.376	.104
VT4	258.541	1	258.541	14.931	.012
Error	86.581	5	17.316		
Total	6927.608	12			
Corrected Total	637.436	11			

a. R Squared = .864 (Adjusted R Squared = .701)

Homogeneous Subsets

Cross linking density

	Concentration (%)	N	Subset	
			1	2
Duncan[a,b]	Conc 30%	2	17.7100	
	Conc 5%	2	17.7700	
	Conc 25%	2	21.8950	21.8950
	Conc 15%	2	22.2050	22.2050
	Conc 10%	2	25.7700	25.7700
	Conc 20%	2		32.0200
	Sig.		.122	.067

Means for groups in homogeneous subsets are displayed.
Based on observed means.
The error term is Mean Square(Error) = 17.316.

a. Uses Harmonic Mean Sample Size = 2.000.

b. Alpha = 0.05.

Cross Linking density of the Vulcanizates

Cross-linking density (kg/cm) Untreated UT=19.21

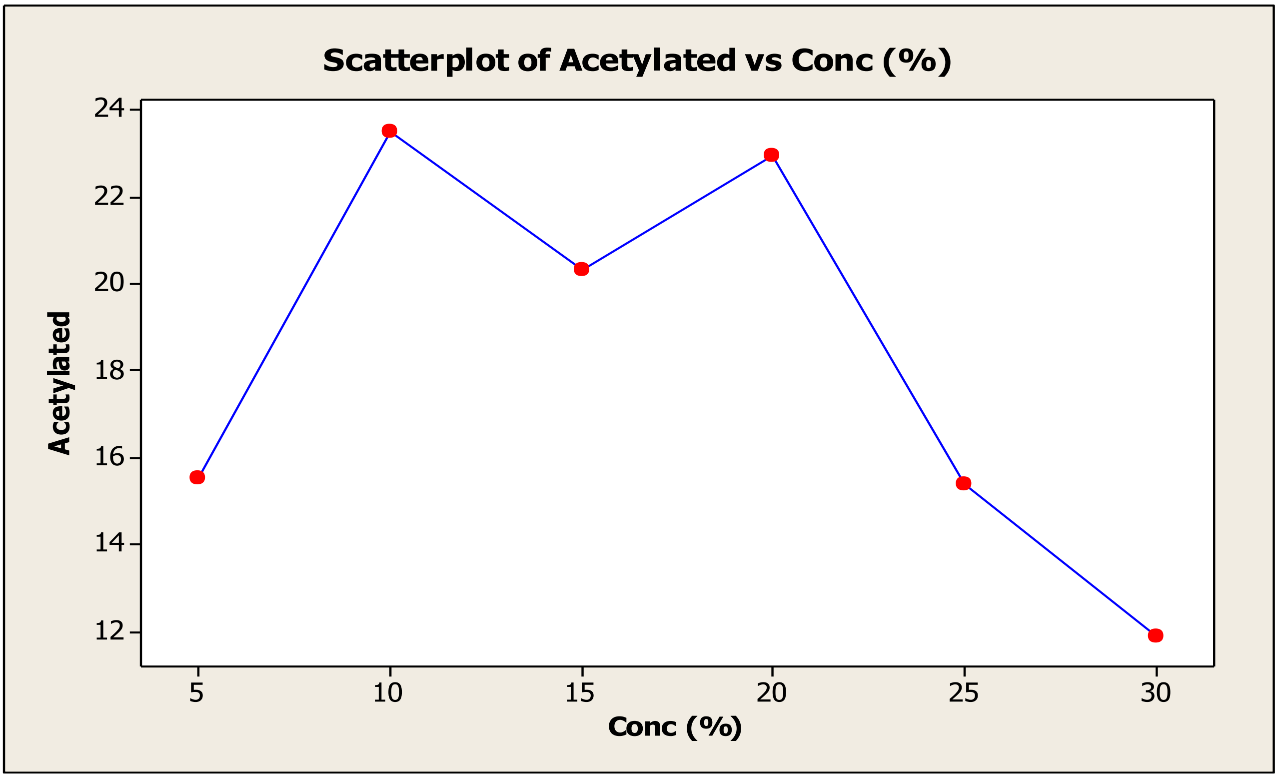


Figure 4.45A: Cross - linking Density of Acetylated Groundnut Shell filled Vulcanizates

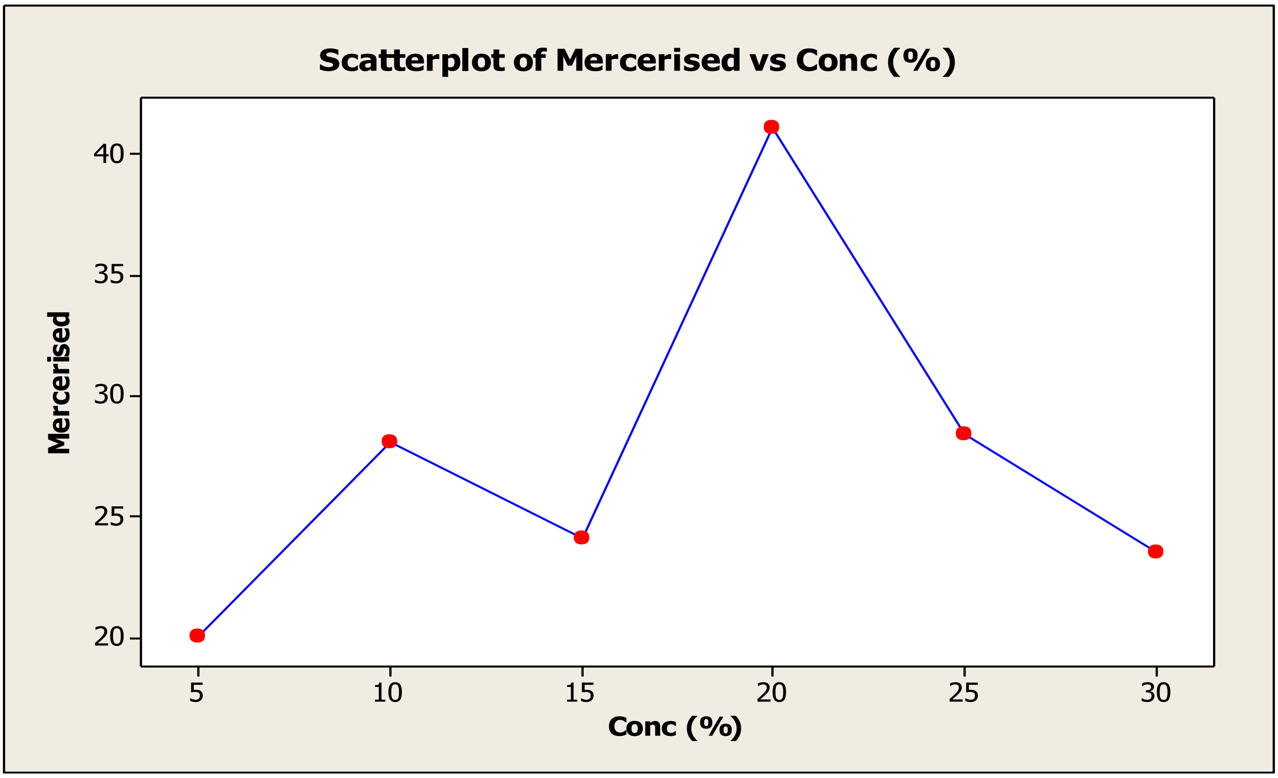


Figure 4.45B: Cross - linking Density of Mercerized Groundnut Shell filled Vulcanizates

Table 4.11: Correlation Coefficient Values for Statistical Model (R^2)

Properties	R^2 Values
Tensile Strength	0.988
Modulus	0.903
Elongation at break	0.720
Hardness (IRH)	0.803
Compression set q_0	0.948
Abrasion resistance q_0	0.973
Flex Fatigue	0.918
Swelling index in acetone	0.991
Swelling coefficient in acetone	0.994
q_0 mole uptake of acetone	0.994
Swelling index in xylene	0.927
Swelling coefficient in xylene	0.994
q_0 mole uptake of xylene	0.994

4.2.5 Results of Statistical Analysis

The graphs of concentration (%) and vulcanisates types (acetylated and mercerized) based on their respective initial treatment for mechanical properties, swelling behavior and cross-linking density using statistical packages known as minitab 16.0 was used to show the trend and visual behavior of concentration based on the identified properties.

From the results of the mathematical modeling (statistical) analysis shown in Figures 4.29 - 4.45 reveals that the empirical results are in agreement with the various test analysis carried out in this research work which further proved that chemically treated groundnut shell fillers have better reinforcing effect on the statistic if the analysis is manually done but electronic analysis using statistical software employs Probability value associated with the F-test compare with the level of significance or critical value of 5%.

From the correlation coefficient values, the statistical model is justified for all the properties except for elongation at break, hardness and cross-linking density where the values for R2 are less than 0.9. When R2 is greater than or equal to 0.9, convergence occurs and the model is not justified (Anthon and Barrett, 2002).

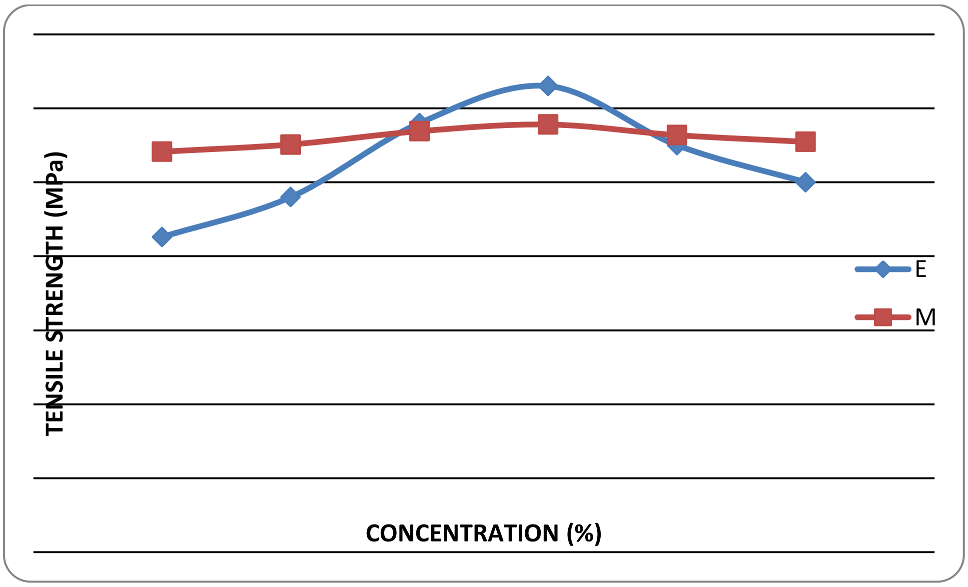


Figure 4.46: Graph of tensile strength experimental & model values versus for acetylated sample.

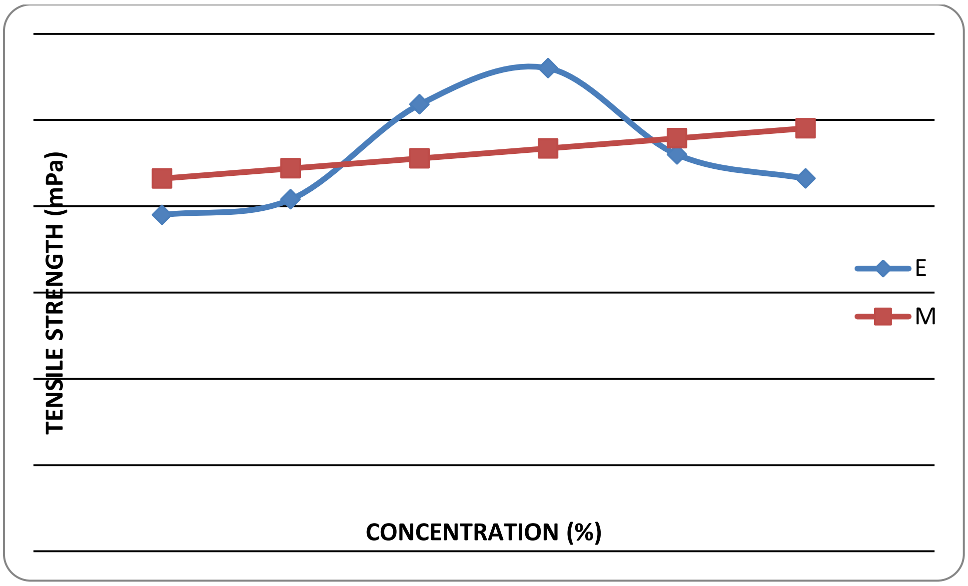


Figure 4.47: Graph of tensile strength experimental & model values versus for Mercerized sample.

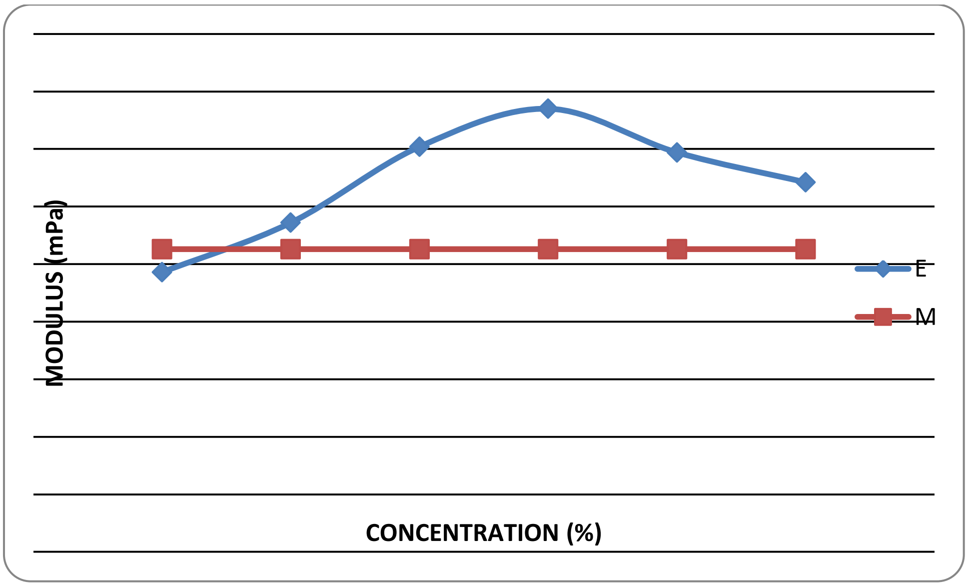


Figure 4.48: Graph of modulus experimental & model values versus for acetylated sample.

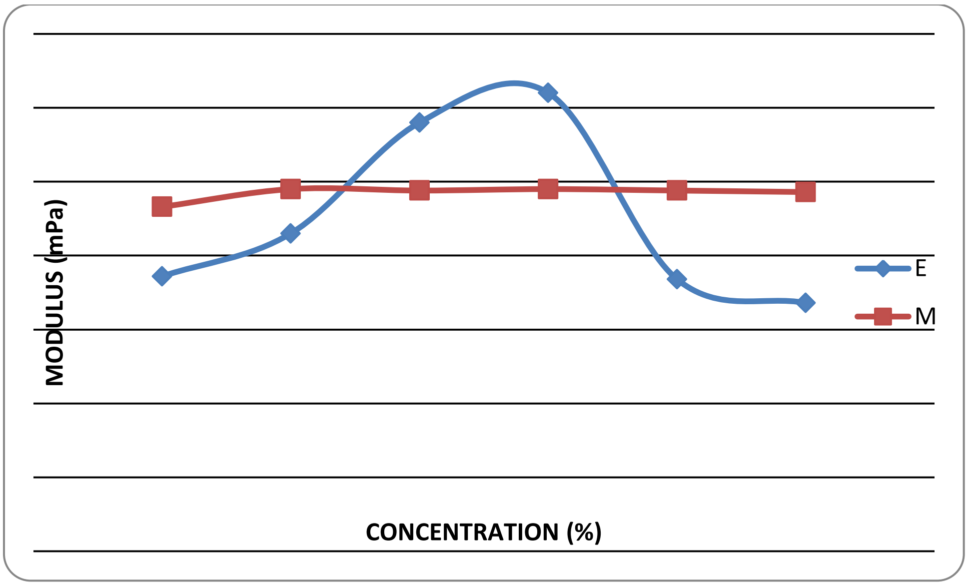


Figure 4.49: Graph of Modulus experimental & model values versus for Mercerized sample.

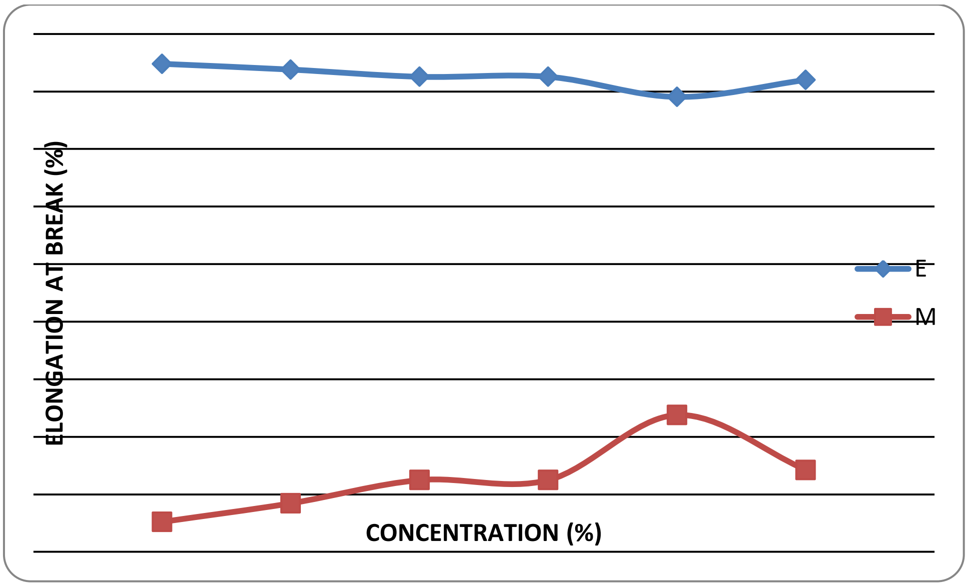


Figure 4.50: Graph of Elongation at Break (%) experimental & model values versus for acetylated sample.

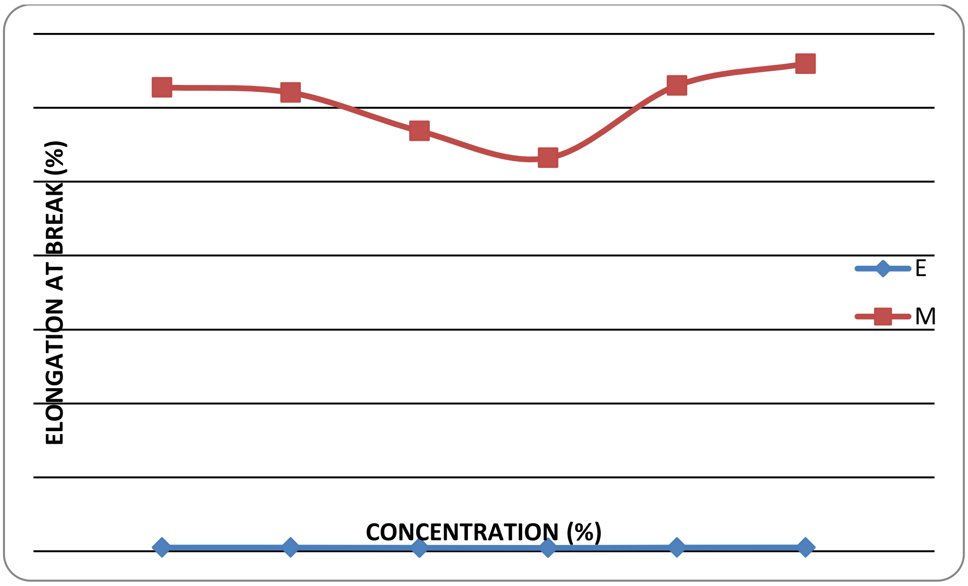


Figure 4.51: Graph of Elongation at Break (%) experimental & model values versus for Mercerized sample.

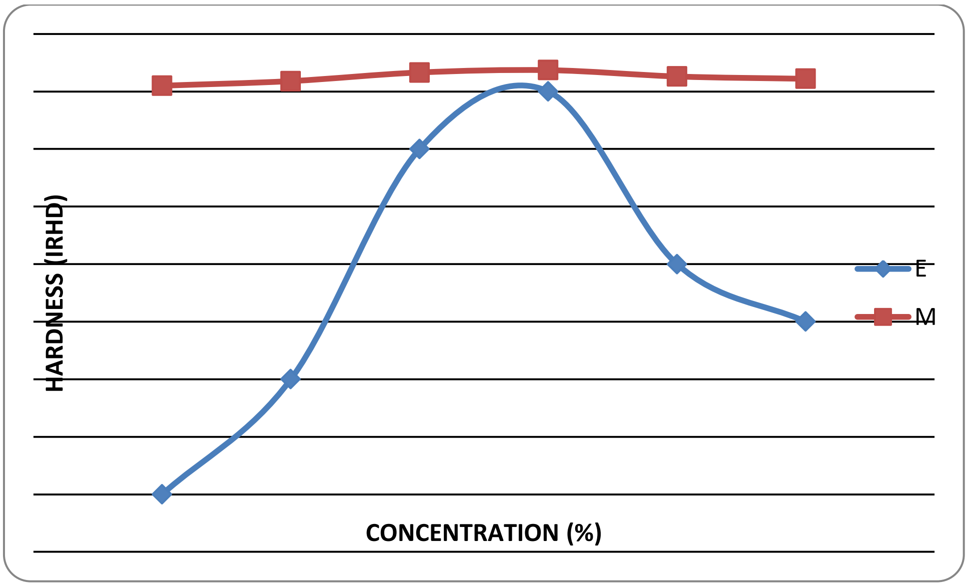


Figure 4.52: Graph of Hardness experimental & model values versus for acetylated sample.

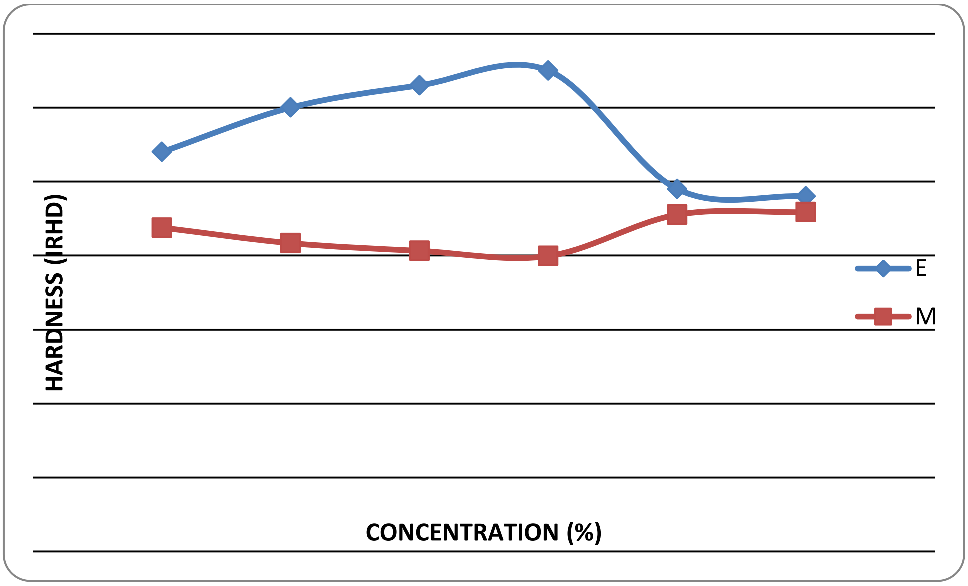


Figure 4.53: Graph of Hardness experimental & model values versus for Mercerized sample.

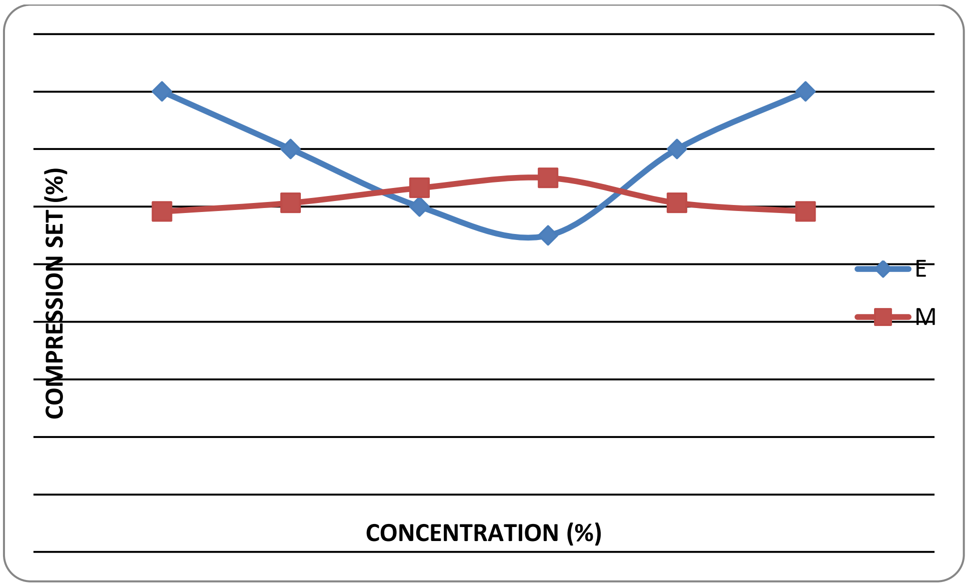


Figure 4.54: Graph of Compression set experimental & model values versus for acetylated sample.

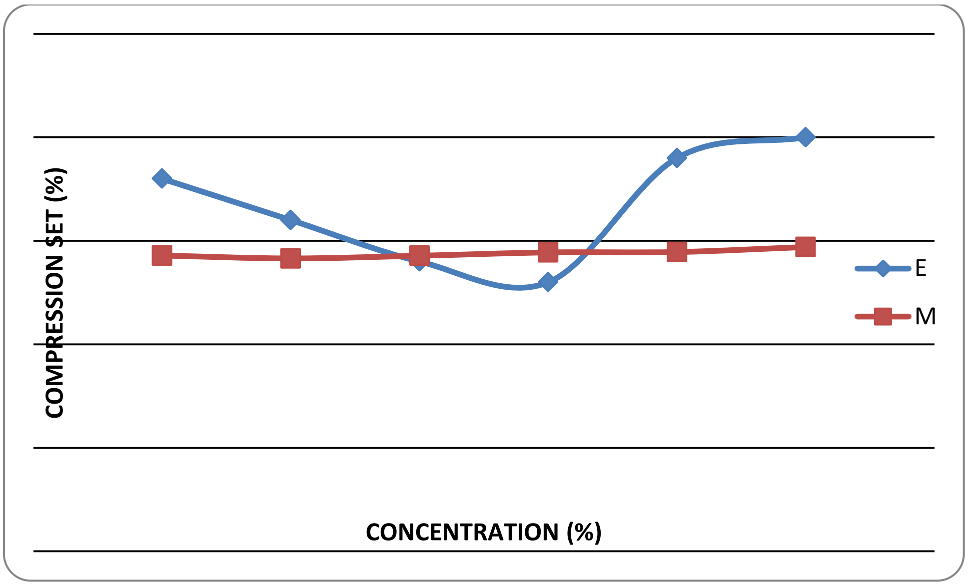


Figure 4.55: Graph of Compression set experimental & model values versus for Mercerised sample.

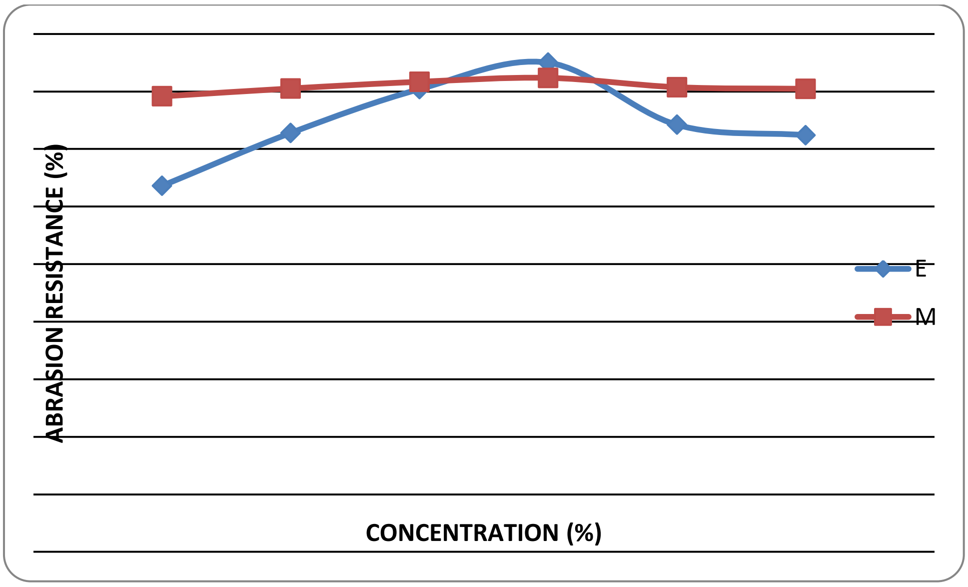


Figure 4.56: Graph of Abrasion resistance experimental & model values versus for acetylated sample.

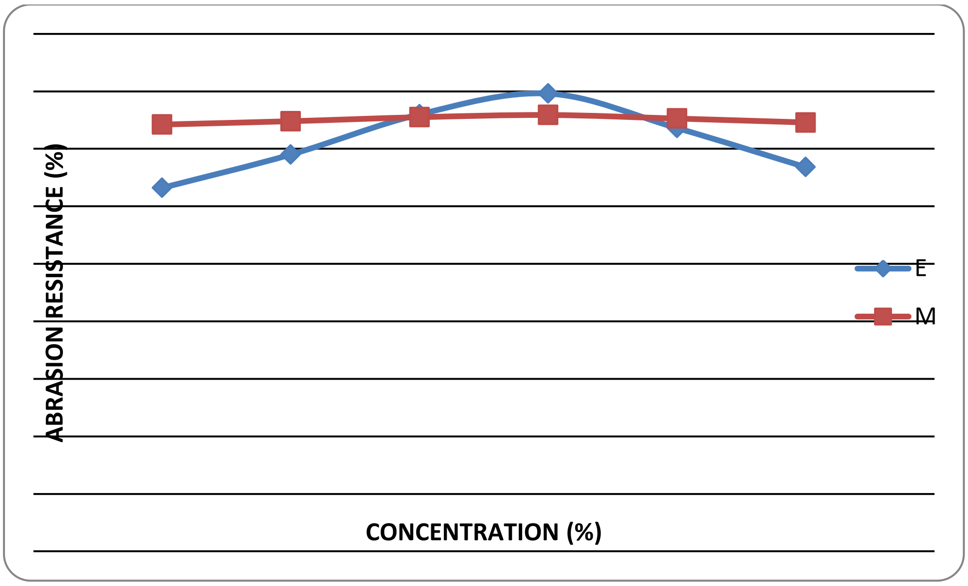


Figure 4.57: Graph of Abrasion resistance experimental & model values versus for Mercerised sample.

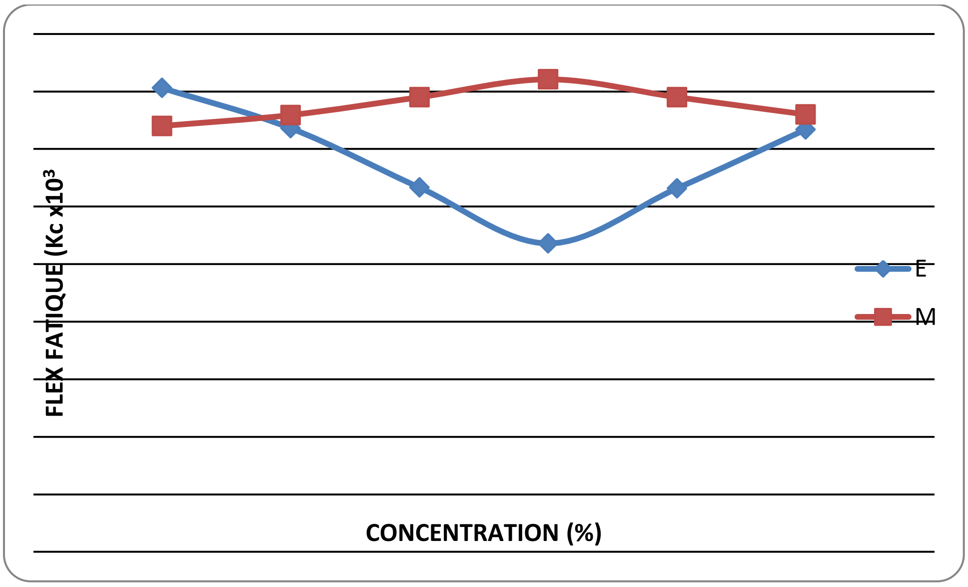


Figure 4.58: Graph of Flex Fatique experimental & model values versus for acetylated sample.

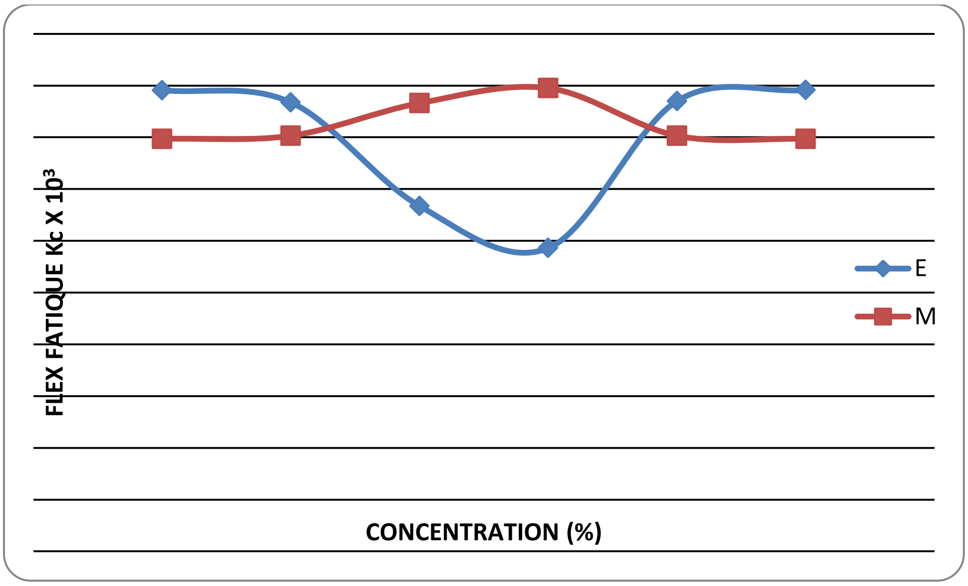


Figure 4.59: Graph of Flex Fatique experimental & model values versus for Mercerised sample.

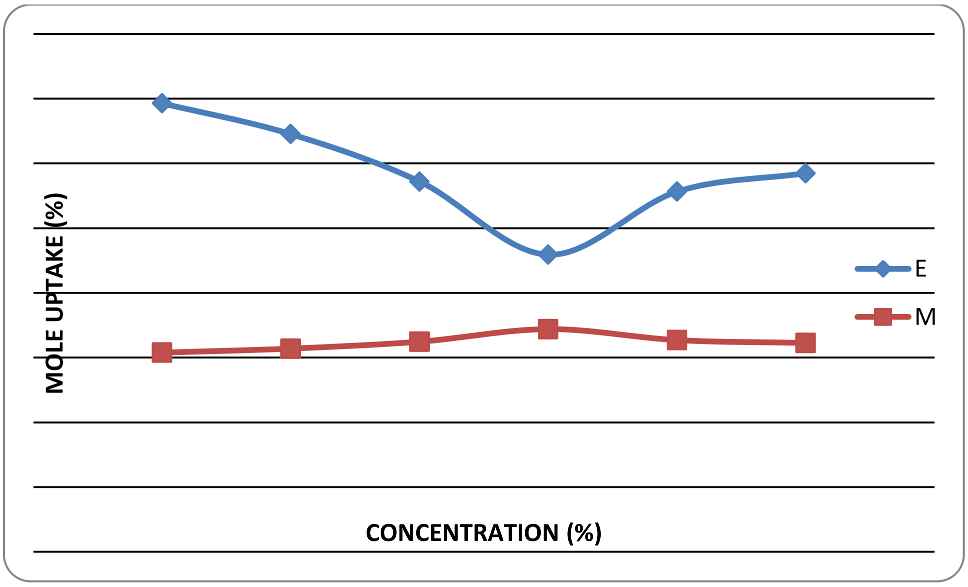


Figure 4.60: Graph of Mole uptake experimental & model values versus for acetylated sample.

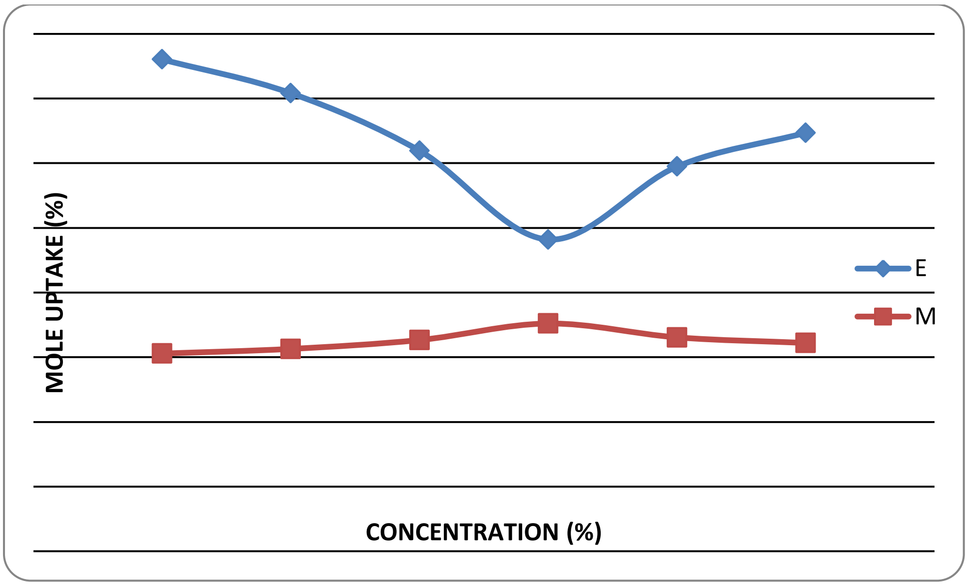


Figure 4.61: Graph of Mole uptake experimental & model values versus for Mercerised sample.

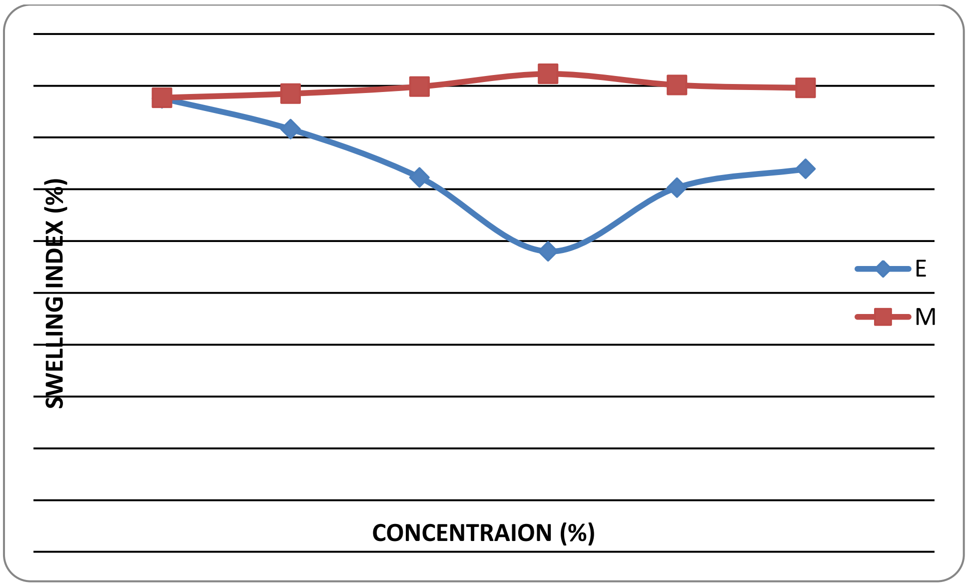


Figure 4.62: Graph of Swelling Index experimental & model values versus for acetylated sample.

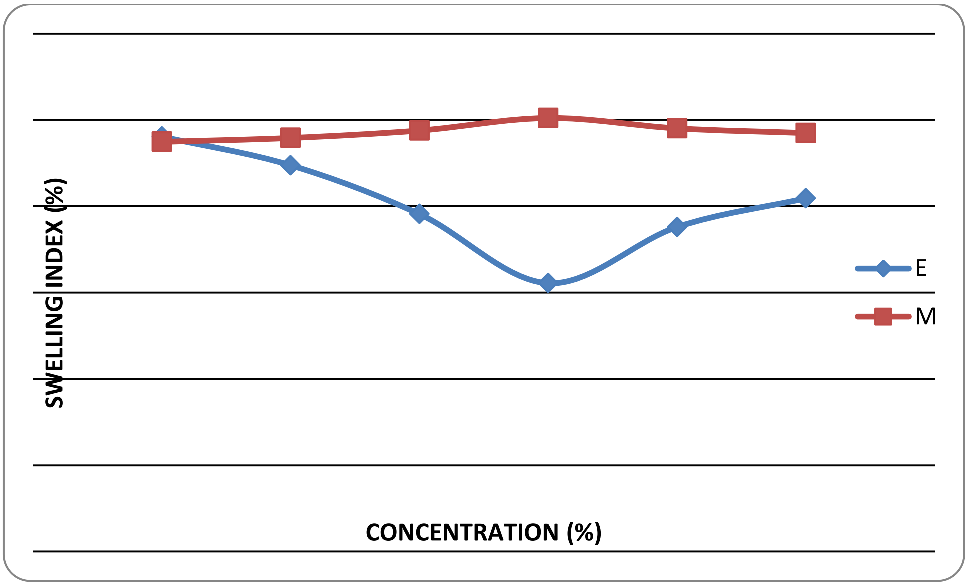


Figure 4.63: Graph of Swelling Index experimental & model values versus for Mercerised sample.

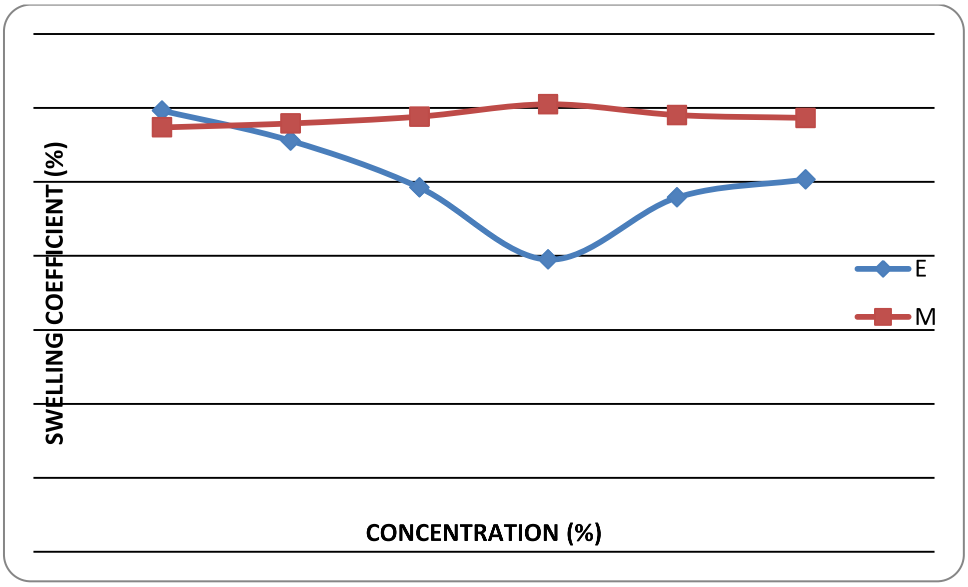


Figure 4.67: Graph of Swelling Coefficient experimental & model values versus for acetylated sample.

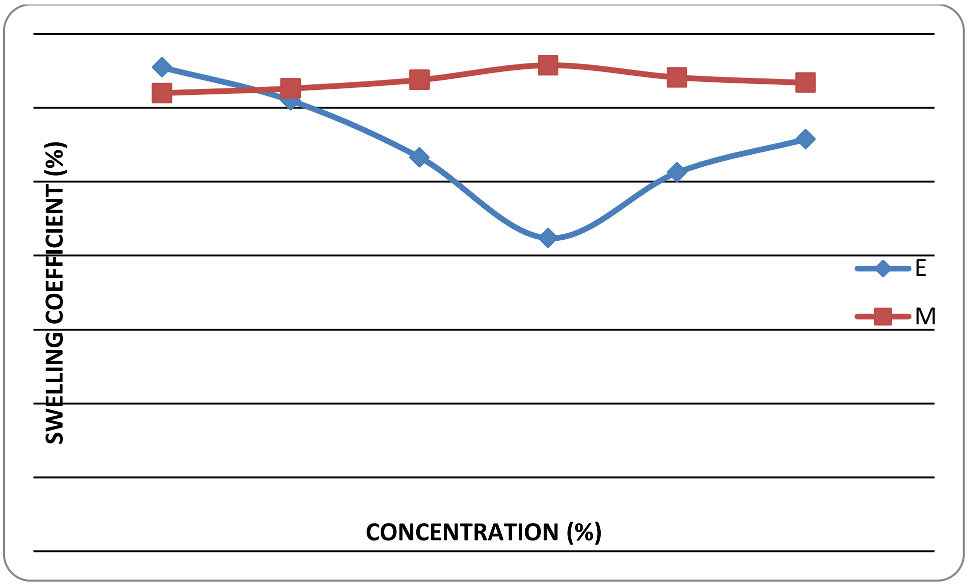


Figure 4.68: Graph of Swelling Coefficient experimental & model values versus for Mercerised sample.

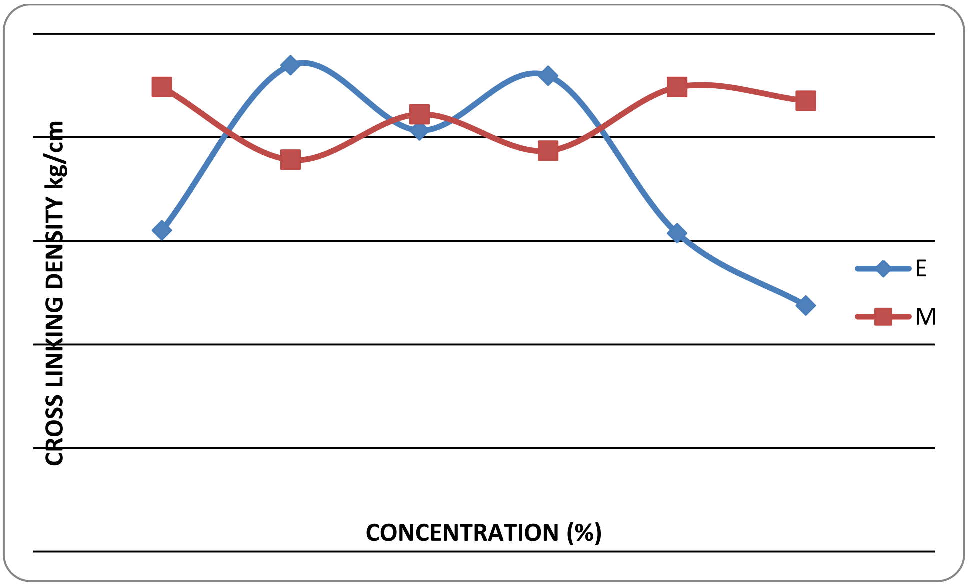


Figure 4.69: Graph of Cross linking density experimental & model values versus for acetylated sample.

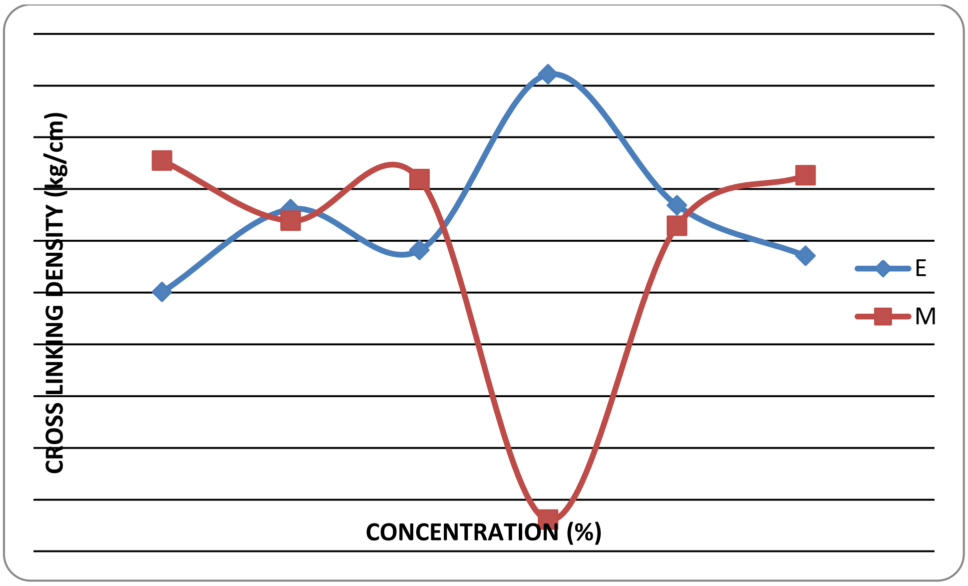


Figure 4.70: Graph of Cross linking density experimental & model values versus for mercerised sample.

Table 4.12: Corrolation Coefficient Values (R^2) for Mathematical Model

Properties	R^2 for Acetylated	R^2 for Mercerised
Tensile strength (mPa)	0.2094	0.1094
Modulus (mPa)	0.4026	0.0211
Elongation at break	0.5961	0.5261
Hardness (IRHD)	0.3942	0.2033
Compression set (%)	0.9150	0.7863
Abrasion resistance (%)	0.1470	0.1213
Flex fatigue	0.8712	0.6232
% mole uptake	0.5330	0.4900
Swelling index (%)	0.5326	0.5080
Swelling coefficient (%)	0.5330	0.5080
Crosslinking density (kg/cm)	0.8141	0.5037

4.2.6 **Result of Mathematical Modelling**

The mathematical modeling result above shows the relationship that exists between the experimental and the estimated values. The correlation coefficient was used. When R^2 is greater than or equal to 0.9, convergence is said to occur and the model is justified. But when R^2 is less than 0.9, divergence occurs and the model is not justified (Anthon and Barrett, 2002).

The mathematical model is not justified because R^2 values are less than 0.9. The model is only justified for compression set of acetylated filler.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The aim of this work is to find out the effects of chemical treatment of fillers on the physico-mechanical properties of natural rubber composites. The preliminary results of the assessment revealed that groundnut shell is hydrophilic due to the presence of the hydroxyl group from cellulose and lignin. Chemical treatment reduces the hydrophilicity of the fibre by decreasing the hydroxyl groups in the fibres. It also shows that groundnut shell is a potential substitute for carbon black , based on the fact that chemical treatment of groundnut shell have achieved some degree of success in making a good interface between the filler and the rubber,improved mechanical properties and sorption behaviour. Most of the chemical treatment from literature reviewed indicates decrease in the strength properties at high concentration levels because of the disintegration of the non-cellulosics materials. Mercerization and acetylation studied from this work shows that at low concentration, treatment lead to strong covalent bond formation, increase fibre matrix adhesion and thereby enhancing the composite strength.

5.2 Recommendations

This project work reveals certain outstanding properties of groundnut shell treated with different chemicals and at different concentrations. In order to establish and/or modify these findings, the following recommendations have been put forward:

i. Chemically treated groundnut shell can be used in place of fibre glass in many polymers because of its reinforcing effects and very low water absorption.
ii. Chemically treated groundnut shell (particularly at 20% concentration) can be employed for articles such as shoe soles, foot-mats and hoses that require less stress during service life.
iii. A blend of two different fillers should also be studied so as to find the best way and the most economical use of groundnut shell as filler in rubber composites.
iv. This study leaves a wide scope for future investigations. Chemically treated groundnut shell should be used for other polymers. However, other treatments such as benzolation, peroxide etc should be used as treatment on groundnut shell and similar analysis carried out on the composite.

5.3 contributions to knowledge

The production of natural rubber based shoe soles from chemically treated groundnut shell powder has been carefully investigated. The contributions to knowledge include:

i The development of local content material from groundnut shell powder (hydrophobic filler) that can be used in many rubber applications

ii The successful production of shoe sole from chemically treated groundnut powder.

iii A model equation for the compression set was obtained. The equation is

$y=0.028686x2 - 1.0057x+20.6$

Where y= Compression set, x= Experimental value

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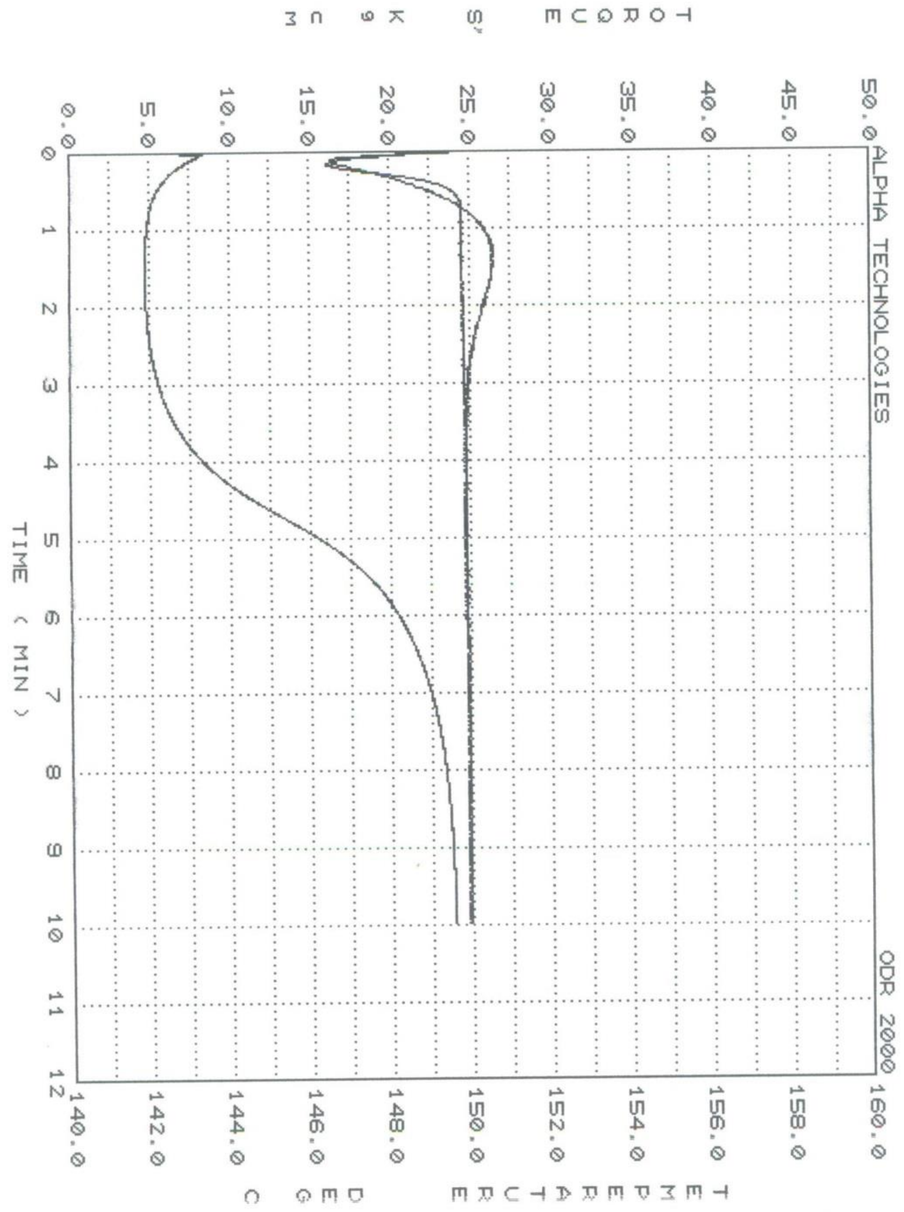
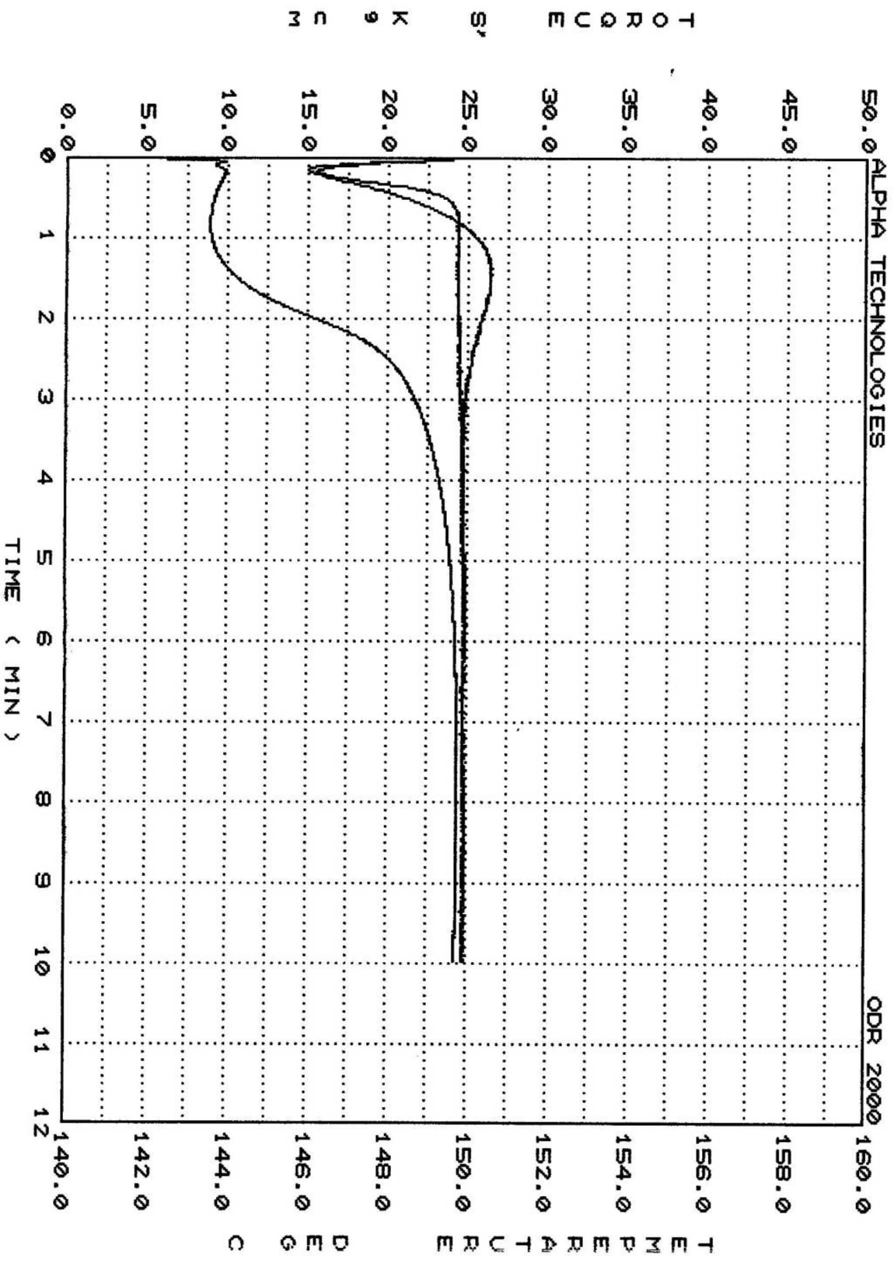
APPENDIX



```
------------------------------------------------------------  20aih2161
^ Temp: 150.0 C                               ML:     4.78 Kg-cm
v Temp: 150.0 C                               MH:    23.99 Kg-cm
tS1:     3:07 m:s     tS2:     3:35 m:s
t10:     3:33 m:s     t50:     4:52 m:s     t90:     6:42 m:s
------------------------------------------------------------------------
```

G1

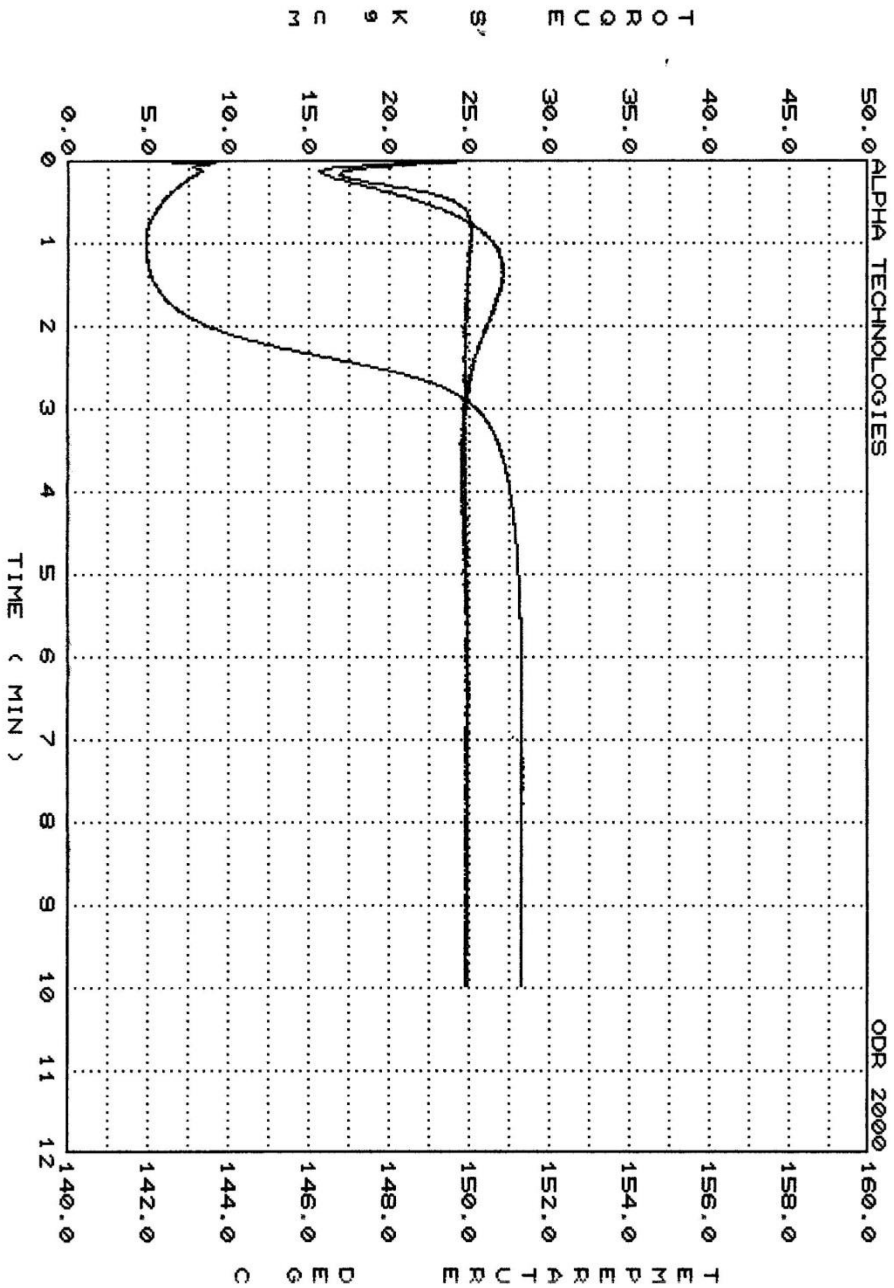
Cure Characteristics of the Untreated Groundnut Shell Filler



```
------------------------------------------------------------  20aih2161
^ Temp:  150.0 C                          ML:     8.97 Kg-cm
v Temp:  150.0 C                          MH:    24.47 Kg-cm
tS1:     1:22 m:s    tS2:     1:34 m:s
t10:     1:29 m:s    t50:     2:06 m:s    t90:     3:41 m:s
------------------------------------------------------------------------------
```

5M

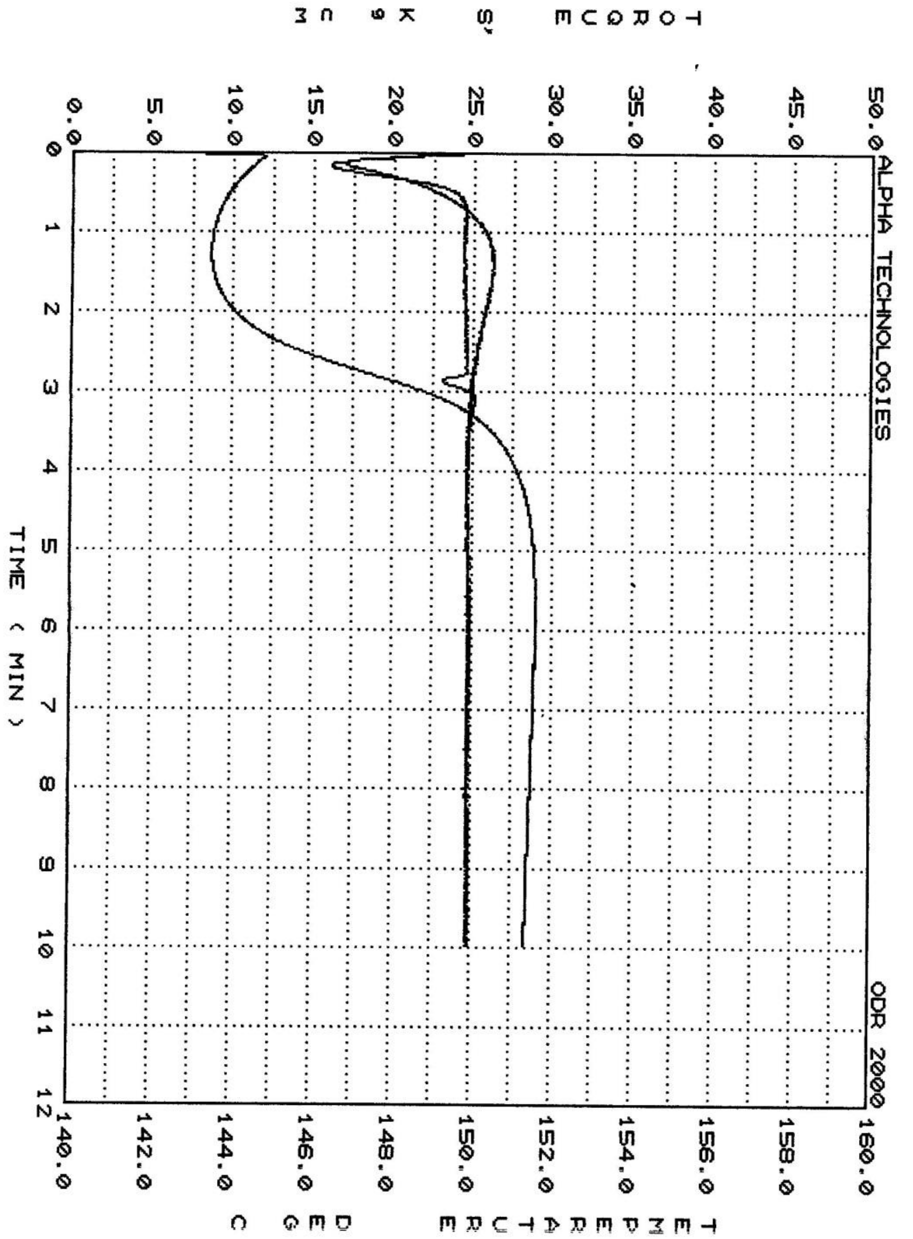
Cure Characteristics of 5% Mercerized Groundnut Shell Filler



```
-------------------------------------------------------------  20aih2161
^ Temp: 150.0 C                          ML:     4.90 Kg-cm
v Temp: 150.0 C                          MH:    28.38 Kg-cm
tS1:     1:38 m:s     tS2:     1:49 m:s
t10:     1:52 m:s     t50:     2:24 m:s     t90:     3:08 m:s
-------------------------------------------------------------------------------
```

10M

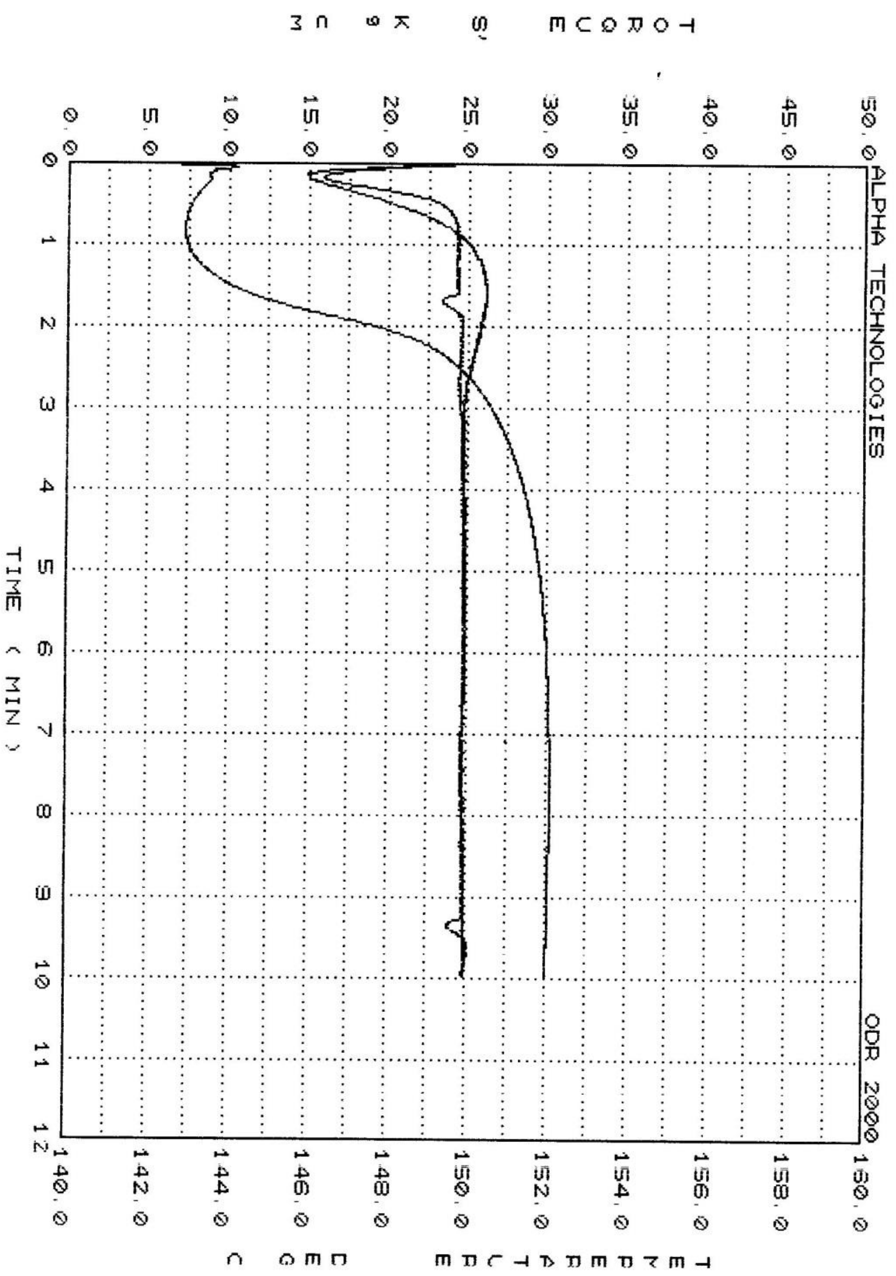
Cure Characteristics of 10% Mercerized Groundnut Shell Filler



```
------------------------------------------------------------  20aih2161
^ Temp: 150.0 C                          ML:     8.71 Kg-cm
v Temp: 150.0 C                          MH:    29.04 Kg-cm
tS1:     1:54 m:s    tS2:     2:07 m:s
t10:     2:07 m:s    t50:     2:49 m:s    t90:     3:43 m:s
--------------------------------------------------------------------------------
```

15M

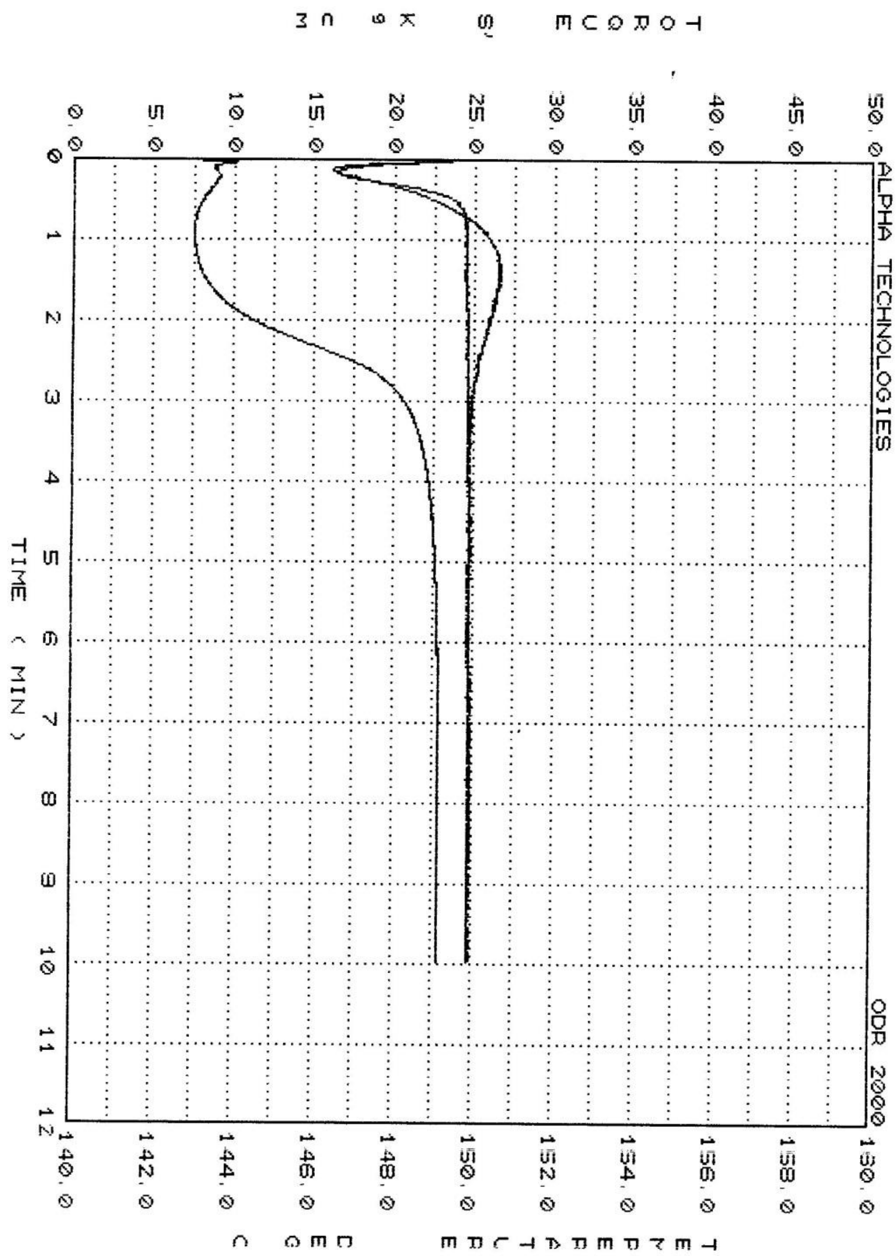
Cure Characteristics of 15% Mercerized Groundnut Shell Filler



```
------------------------------------------------------------   20aih2161
^ Temp: 150.0 C                                  ML:     7.32 Kg-cm
v Temp: 150.0 C                                  MH:    30.28 Kg-cm
tS1:      1:16 m:s     tS2:     1:25 m:s
t10:      1:27 m:s     t50:     1:59 m:s         t90:     3:38 m:s
```

20M

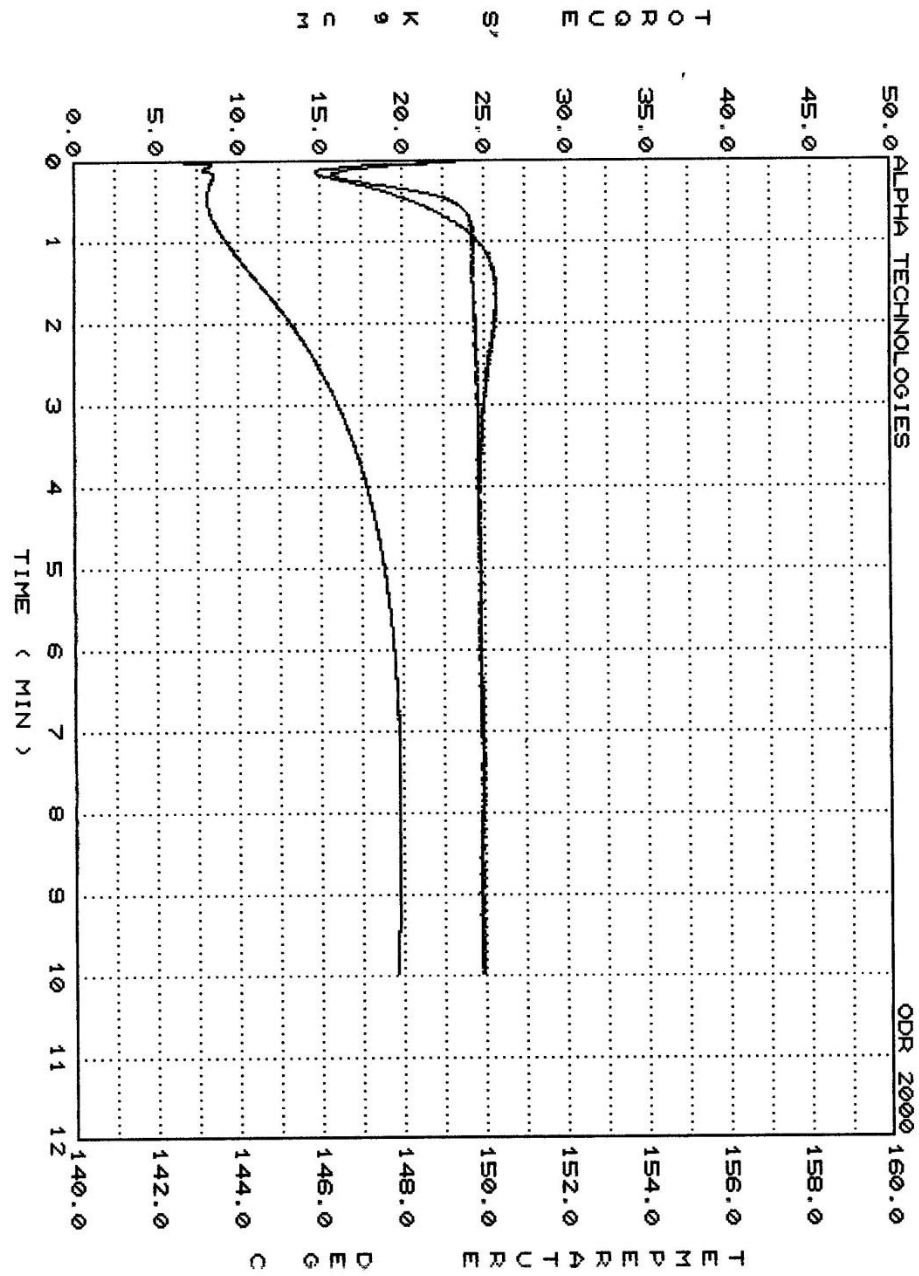
Cure Characteristics of 20% Mercerized Groundnut Shell Filler



```
------------------------------------------------------------  20aih2161
^ Temp: 150.0 C                         ML:    7.58 Kg-cm
v Temp: 150.0 C                         MH:   22.95 Kg-cm
tS1:     1:36 m:s   tS2:    1:48 m:s
t10:     1:43 m:s   t50:    2:21 m:s    t90:    3:18 m:s
```

25M

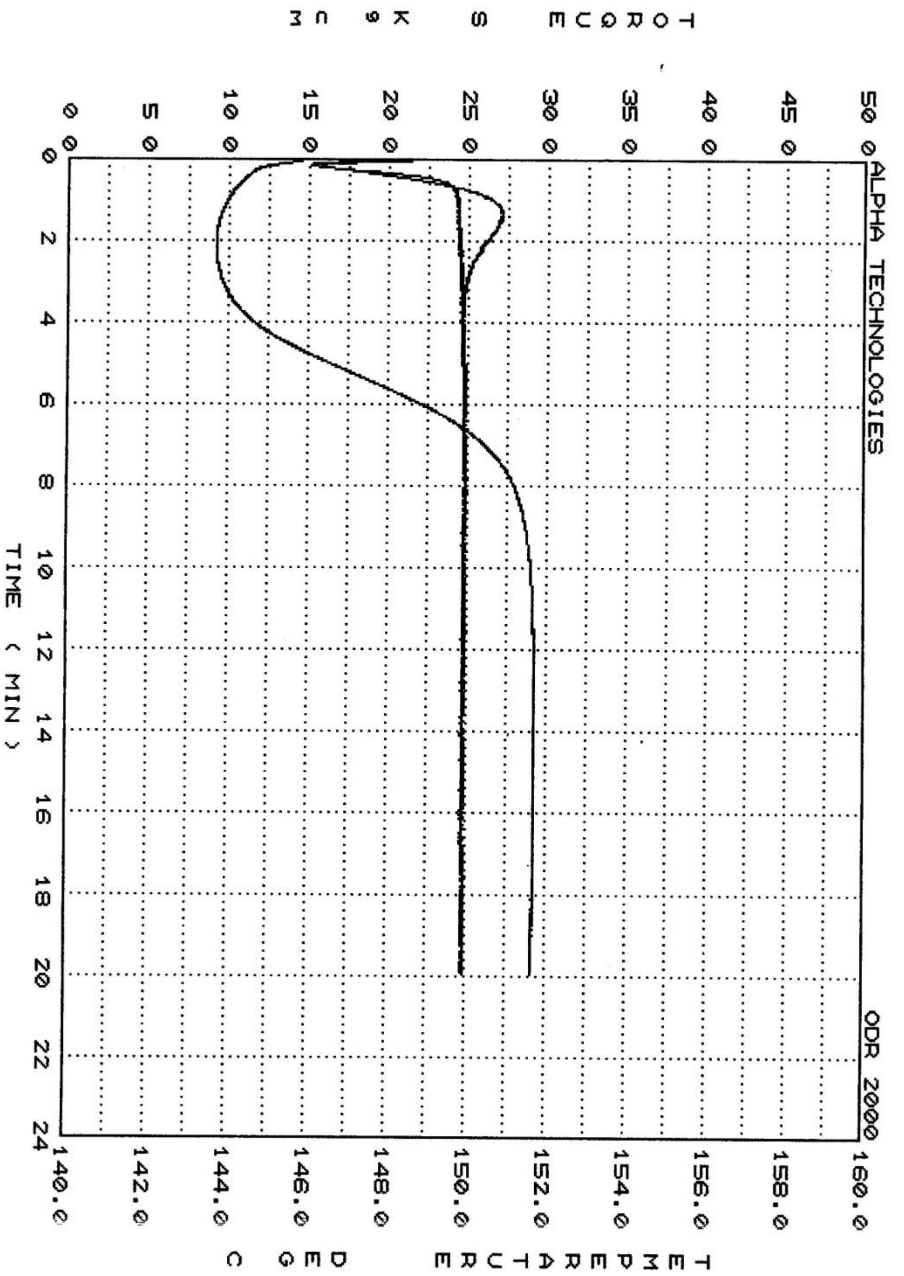
Cure Characteristics of 25% Mercerized Groundnut Shell Filler



```
------------------------------------------------------------ 20aih2161
^ Temp:  150.0 C                           ML:      7.98 Kg-cm
v Temp:  150.0 C                           MH:     19.86 Kg-cm
tS1:     0:54 m:s    tS2:     1:11 m:s
t10:     0:57 m:s    t50:     2:12 m:s    t90:     4:43 m:s
-------------------------------------------------------------------------------
```

30M

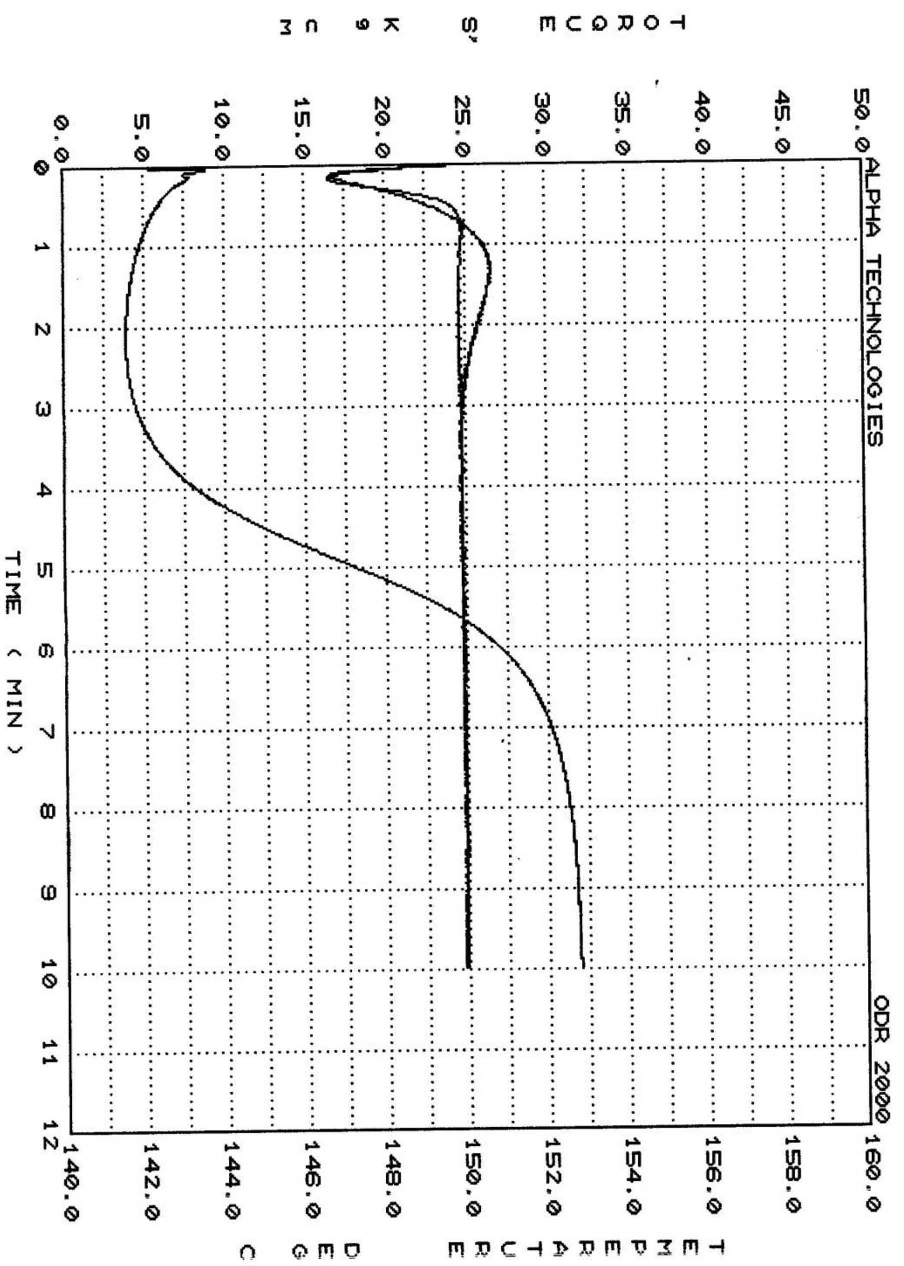
Cure Characteristics of 30% Mercerized Groundnut Shell Filler



```
------------------------------------------------------------  20aih2161
^ Temp: 150.0 C                                ML:     9.27 Kg-cm
v Temp: 150.0 C                                MH:    29.31 Kg-cm
tS1:     3:27 m:s     tS2:     3:54 m:s
t10:     3:54 m:s     t50:     5:31 m:s        t90:     7:33 m:s
------------------------------------------------------------------------------
```

5A

Cure Characteristics of 5% Acetylated Groundnut Shell Filler



-- 20aih2161

^ Temp: 150.0 C   ML: 3.95 Kg-cm

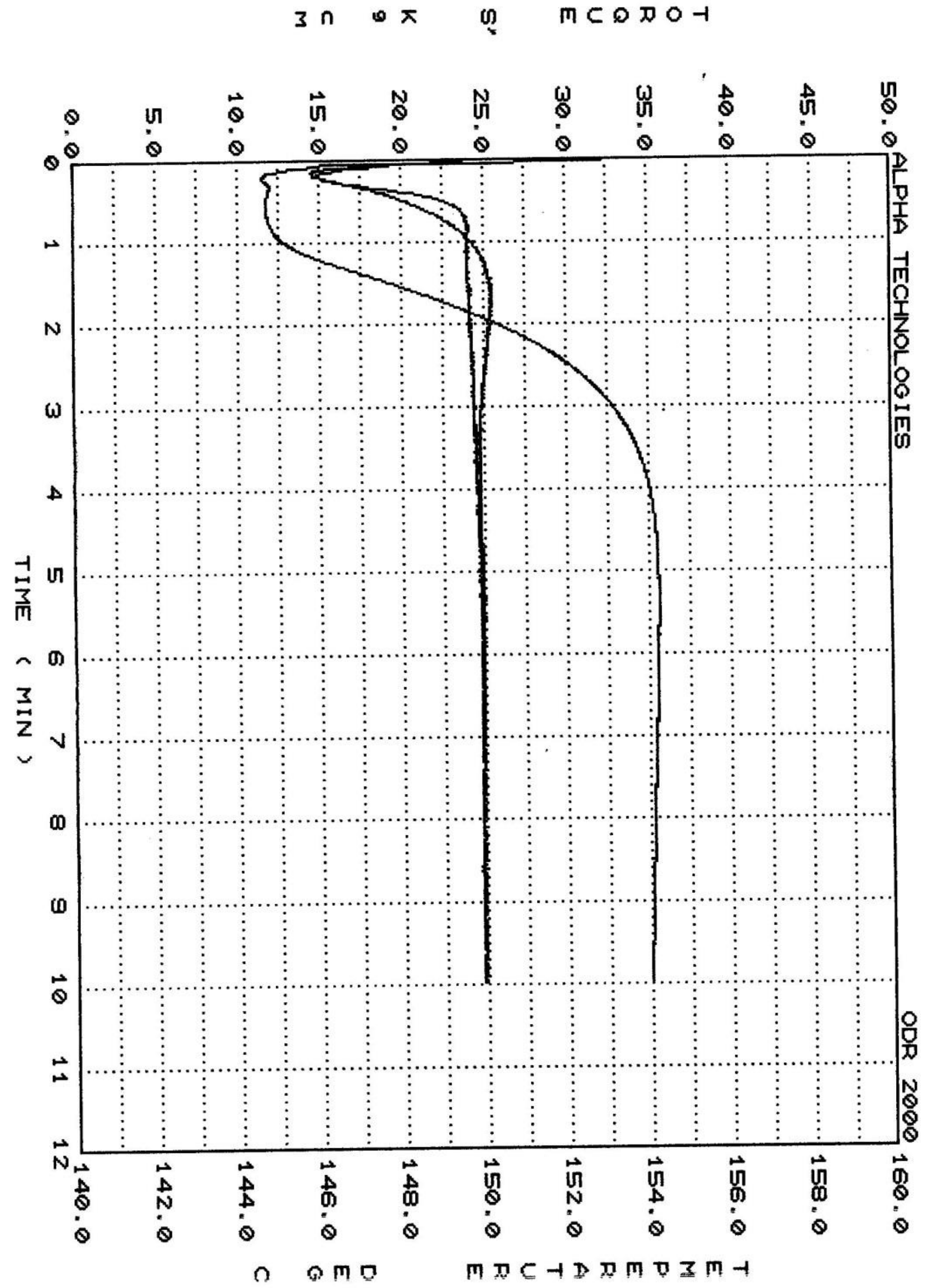
v Temp: 150.0 C   MH: 32.01 Kg-cm

tS1: 3:12 m:s   tS2: 3:33 m:s

t10: 3:44 m:s   t50: 5:00 m:s   t90: 6:33 m:s

10A

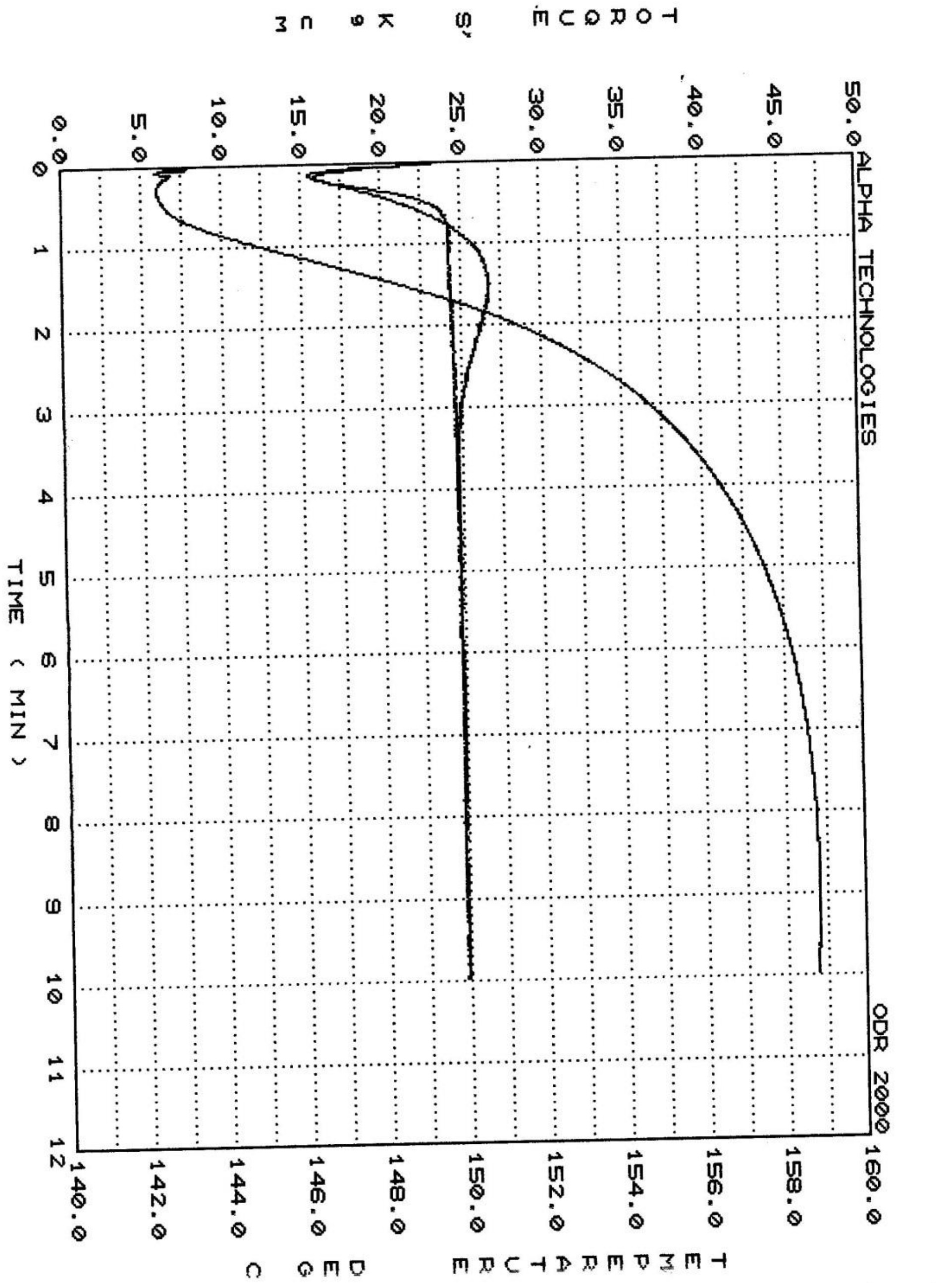
Cure Characteristics of 10% Acetylated Groundnut Shell Filler



```
---------------------------------------------------------------  20aih2161

^ Temp:  150.0 C                              ML:    11.56 Kg-cm

v Temp:  150.0 C                              MH:    35.64 Kg-cm

tS1:     0:57 m:s      tS2:     1:06 m:s

t10:     1:08 m:s      t50:     1:49 m:s      t90:     3:07 m:s
--------------------------------------------------------------------------------
```

15A

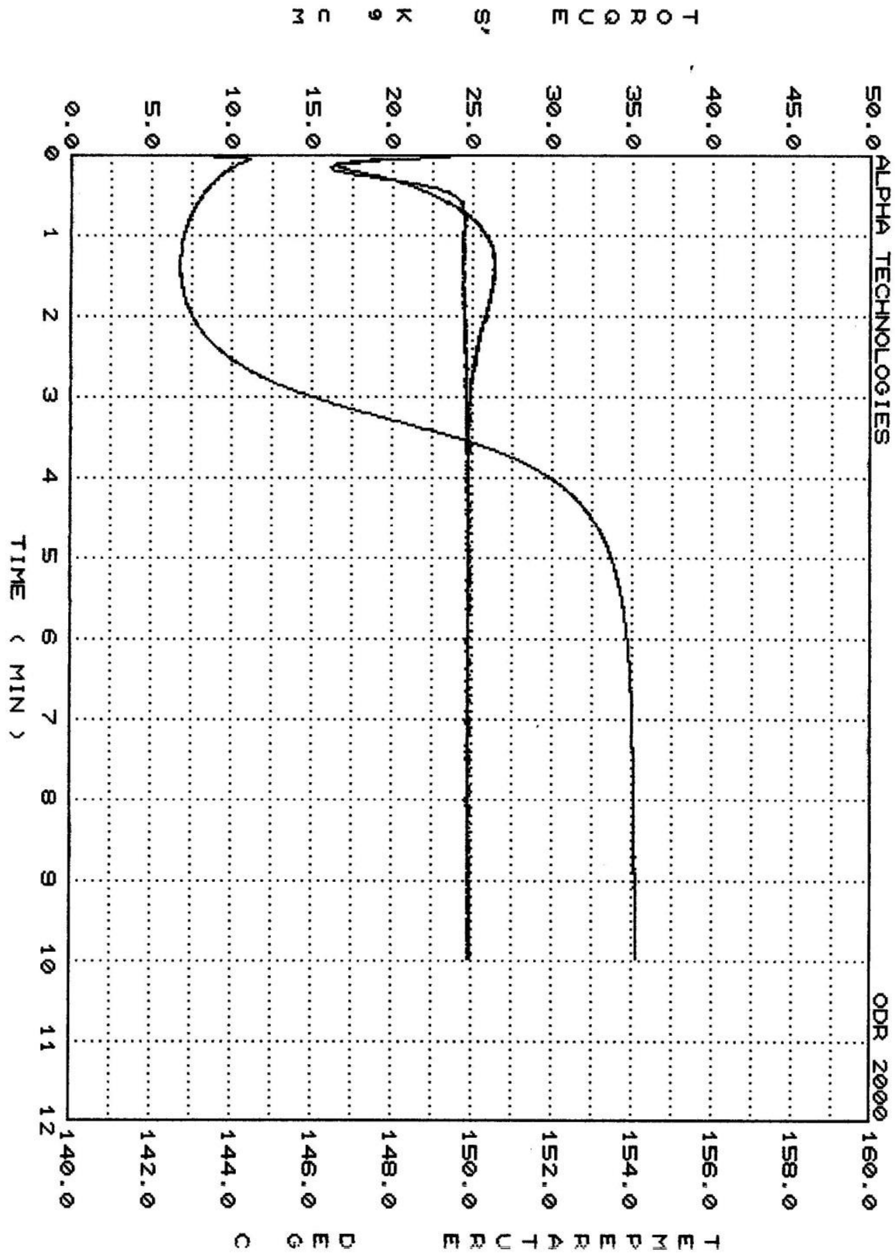
Cure Characteristics of 15% Acetylated Groundnut Shell Filler



```
--------------------------------------------------------  20aih2161

^ Temp: 150.0 C                       ML:    5.97 Kg-cm

v Temp: 150.0 C                       MH:   47.05 Kg-cm

tS1:     0:36 m:s    tS2:    0:43 m:s

t10:     0:52 m:s    t50:    1:51 m:s    t90:    4:36 m:s
------------------------------------------------------------------
```

20A

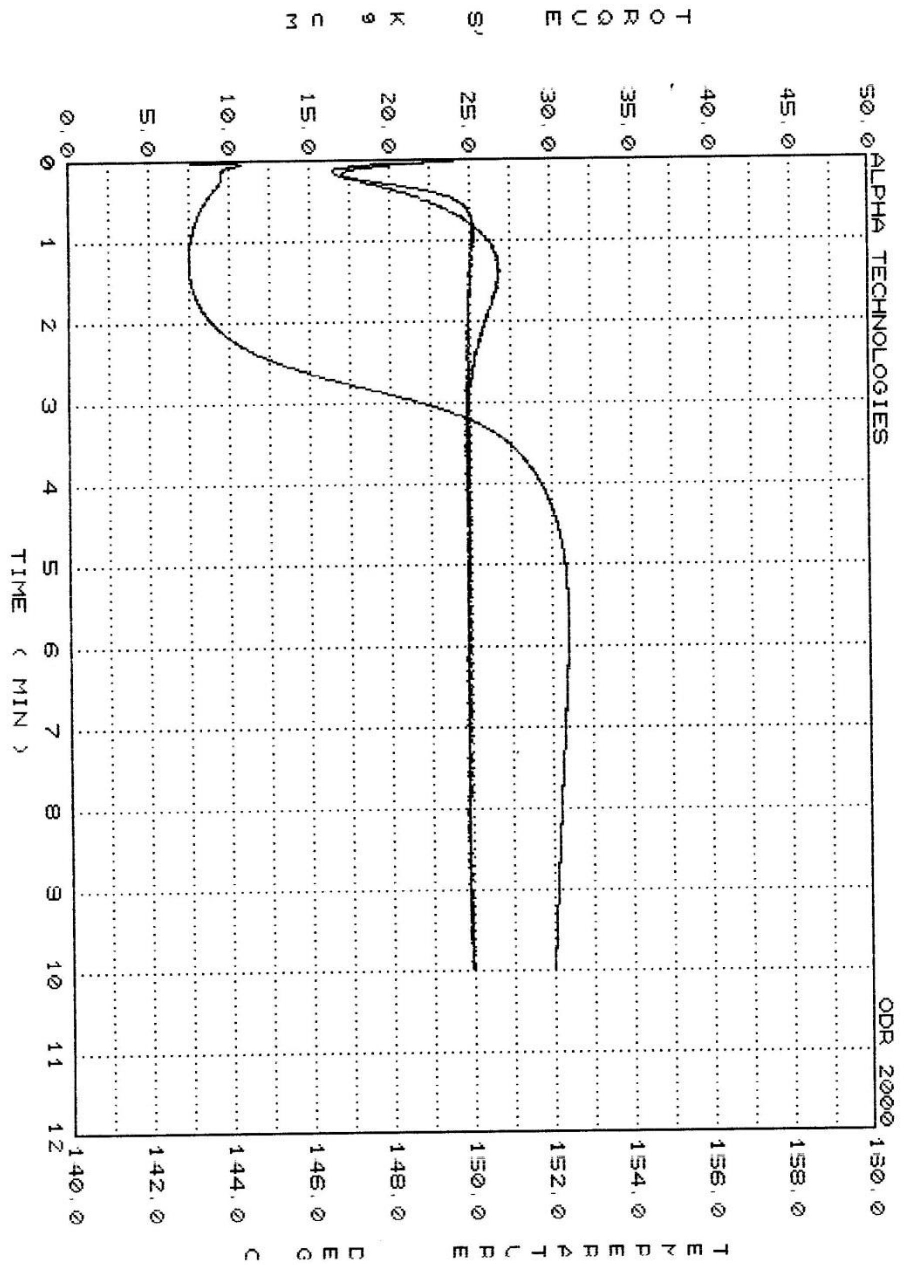
Cure Characteristics of 20% Acetylated Groundnut Shell Filler



```
--------------------------------------------------------------  20aih2161
^ Temp: 150.0 C                         ML:     6.85 Kg-cm
v Temp: 150.0 C                         MH:    35.27 Kg-cm
tS1:     2:06 m:s    tS2:     2:21 m:s
t10:     2:29 m:s    t50:     3:21 m:s    t90:     4:29 m:s
--------------------------------------------------------------------------------
```

25A

Cure Characteristics of 25% Acetylated Groundnut Shell Filler



```
------------------------------------------------------------  20aih2161

^ Temp: 150.1 C                              ML:     7.52 Kg-cm

v Temp: 150.1 C                              MH:    31.06 Kg-cm

tS1:      1:54 m:s     tS2:     2:07 m:s

t10:      2:10 m:s     t50:     2:52 m:s     t90:     3:47 m:s
```

30A

Cure Characteristics of 30% Acetylated Groundnut Shell Filler