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MICRO-STRUCTURAL PROPERTIES OF NATURAL RUBBER REINFORCED WITH MERCERIZED RICE HUSKS

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ABSTRACT

Micro-structural properties of natural rubber filled with alkaline treated rice husks were studied. Rice husk was obtained, washed off and was treated using sodium hydroxide solution at a concentration of 20%. The dried rice husk was ground to fine particles and sieved through a mesh of 75µm. The characterization results showed excellent values of pH (8.72), moisture content (1.85%) and bulk density (0.65g/ml). The surface structural properties of the treated rice husk filled vulcanizates present adequate dispersion of treated rice husk in the filled vulcanizates when compared to the untreated rice husk filled and the unfilled natural rubber vulcanizates. However, the results of the alkaline treated rice husks filled vulcanizates showed excellent morphological property when compared with the untreated and the unfilled samples which revealed that chemical modifications help to improve the inherent properties in natural fibres and hence better polymer-fibre interactions.

Keywords: Alkaline, fibres, husks, sieve, vulcanizate

INTRODUCTION

Emergence of polymer in the beginning of the 19th century ushered a new area of research with a new option of using natural fibres in more diversified fields. This renewed interest in natural fibres has resulted in a large number of modifications carried out to obtain properties when compared to synthetic fillers. Because of such tremendous changes in the quality of natural fibres, they are fast emerging as a reinforcing material in composites. Fillers, as one of the major additives used in natural rubber compounds are either used raw or modified. These fillers function to modify the physical and to some extent, the chemical properties of the vulcanizates [1]. Combining a polymer with another material, such as glass, carbon, or another polymer, it is often possible to obtain unique combinations or levels of properties [2]. Therefore, the objectives of producing such a material like polymeric composites are because of high strength, stiffness, dimensional stability by embedding particles or fibers in a matrix. Moreover, a cost is playing a very important role in economic side since it is available in good prices in the markets. This goal is increasingly important as petroleum supplies become costlier and less reliable [3]. Today, there are lots of research going on to find an alternative for it. Advances are being made into the use of other agricultural by- products, such as guinea corn husk, rice husk, groundnut shell, rubber seed shell, sawdust etc. These materials are used in their raw form or modified. The importance of fillers in rubber production cannot be over-emphasized. It is the most widely used in terms of volume in the rubber industry [4].

The objectives of study are:

i. To obtain and characterize alkaline treated rice husks for natural rubber compounding.
ii. To study the effect of alkaline treated rice husks on filler characteristics.
iii. To investigate the effect of alkaline treated rice husks on the morphological properties of natural rubber vulcanizates.

MATERIALS AND METHOD

Materials

The materials used in this research work are presented in Table 2.1.

Table 2.1: Materials and their Sources

Materials	Sources
Natural Rubber (NSR-10)	Rubber Research Institute, Iyanomoh, Benin
Rice Husk (RH)	Zaria, Kaduna State
Tetramethyl thiuram disulphide (TMTD)	British Drug House (BDH), England
Mercarptobenzothiazole sulphenamide (MBTS)	Sigma Andriech, Germany
Stearic acid	Sigma Andriech, Germany
Sulphur	British Drug House (BDH), England
Trimethylquinoline (TMQ)	Sigma Andriech, Germany
Zinc Oxide	British Drug House (BDH), England
Paraffin Wax	Sigma Andriech, Germany
NaOH	Sigma Andriech, Germany
Distilled Water	SUNPAT Table Water, Zaria

Equipment and Machines

The equipment used during this study includes;

i. Fourier Transform Infra-Red Spectrometer, Subpart ZZZZ-MACT-320, Pine Equipment Co. Ltd., U.S.A.
ii. Phenom, ProX, Phenom World, Eindhoven, Netherlands.

iii. Two Roll Mill, Manufactured by British Company Limited, England mills were used in mixing the rubber composite.

iv. Hydraulic press, Elektron Technology Series, UK was used for curing the rubber composite.

Collection of Filler (Rice Husks)

Rice Husks were collected from Samaru rice mill, Zaria and were washed to remove possible impurities, dried, crushed and sieved using a 75µm screen gauge.

Alkaline Treatment Process

The fillers were soaked into 20% sodium hydroxide solutions for 3hrs at room temperature. After which the fillers were thoroughly washed with distilled water, dried at room temperature for 24hrs, followed by oven drying at 150^{o}C for 1hr.

Characterization

Moisture Content

The method is used to determine the percentage of water in a sample by drying the sample to a constant weight. The moist sample was weighed and recorded as initial weight of sample. The wet sample was dried to a constant weight at a temperature of 125^{o}C in an oven. The sample was allowed to cool, reweighed and recorded as the final weight of the sample.

$$\text{Moisture Content (\%)} = \frac{\text{Initial Weight} - \text{Final Weight}}{\text{Initial Weight}} \times 100$$

Bulk Density

Bulk density of the various alkaline treated rice husk was determined by the tapping procedure. Accurately weighed samples were poured into a uniform cylinder of cross sectional area and were then tapped several times until there was no change in the volume occupied [5]. This volume was then recorded and the bulk density calculated.

pH

The pH of the alkaline treated rice husk was determined using ASTMD 1512 method by immersing 1.0g samples in 20.0mL of deionized water in a 250mL beaker. The mixture was stirred for 15mins and the pH meter used to obtain reading directly from solution [5].

Fourier Transform Infrared Test

The Fourier Transform Infrared of the powdered samples was studied using the Fourier's Transform Infrared Spectrometer.

Processing of the Composites

This involved the compounding of natural rubber with rice husk particles using the formulation given in Table 2.2

Table 2.2: Formulation for Compounding Natural Rubber.

Ingredient	Parts per hundred rubber (phr)
Natural rubber	100
Rice Husk (RH)	Variable (10 - 50)
Zinc Oxide	5.0
Stearic acid	2.5
Sulphur	1.5
MBTS	1.5
TMTD	3.5
Processing Oil	5.0

Mixing Procedure

The rubber mixes were prepared on a laboratory size two roll mill according to the mixing cycle showed in Table 2.3 following ASTMD 3184 - 80 Standard [5].

Table 3.3: Mixing Steps and Mixing Time

Mixing Steps	Time (Minutes)
Natural rubber mastication	3
Addition of Stearic acid	0.5
Addition of Zinc Oxide	0.5
Addition of filler	3
Addition of MBTS	0.5
Addition of TMTD	0.5
Processing Oil	0.5
Addition of Sulphur	1.5
Total	**10**

Composite Curing

The curing of test pieces was done in a compression moulding machine at 115^{o}C and 2bar for 5 mins.

Micro-Structural Analysis

Specimen samples, usually nonconductive were made conductive by introducing about 5nm gold onto it and were cut into specified dimension using a sputter cutting machine. The samples were then placed on the column of the Scanning Electron Microscope (SEM) where the image were focused using navigation camera and transferred to electron mode in accordance to the desired magnification.

RESULTS AND DISCUSSION

The experimental results are presented in Figures 3.1 - 3.5.

Table 3.1: Characteristics of the Powdered Rice Husk

Parameter	Rice Husk (RH)	Treated Rice Husk (TRH)
Moisture content (%)	2.30	1.85
pH of slurry	5.86	8.72
Particle size distribution (μm)	75	75
Bulk Density (g/ml)	0.97	0.65

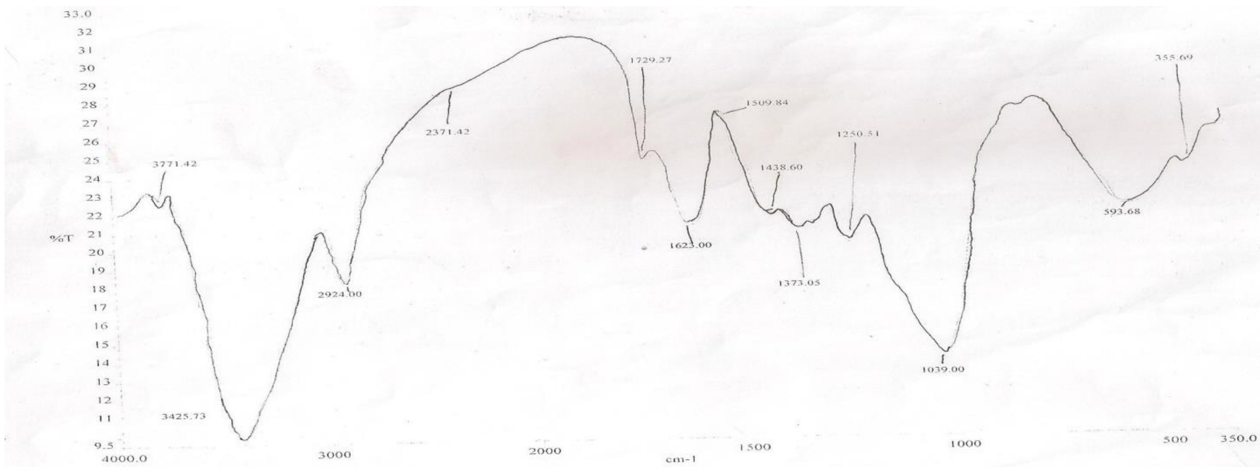

Figure 3.1: FTIR Characteristics of Rice Husk

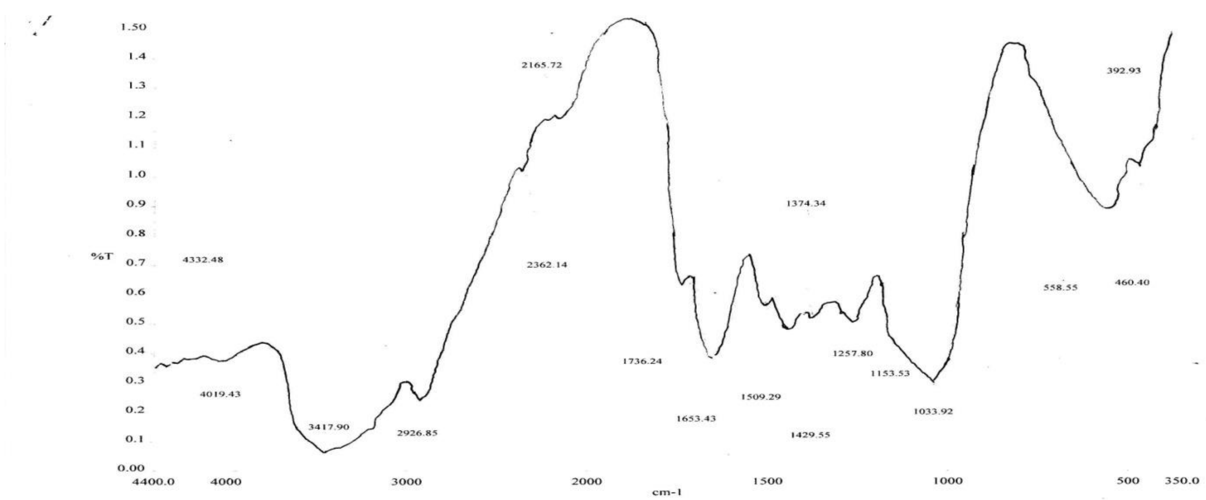

Figure 3.2: FTIR Characteristics of Treated Rice Husk

Figure 3.3: Surface Morphology of Unfilled Natural Rubber Vulcanizate

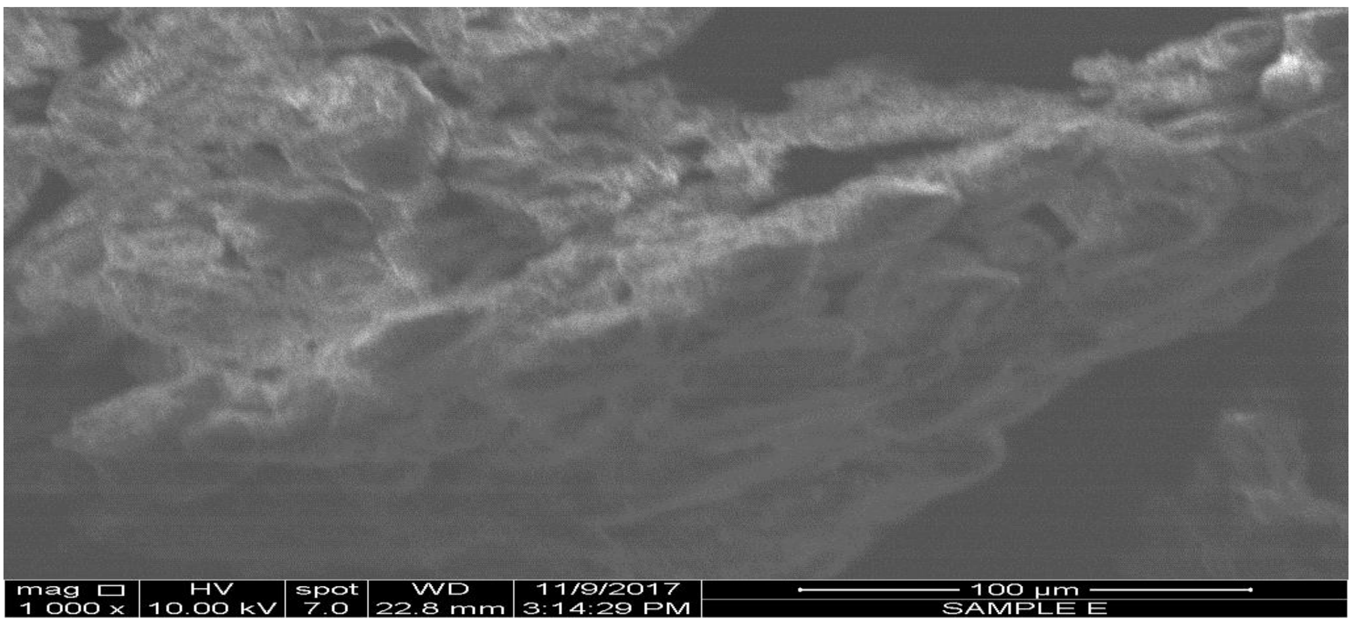

Figure 3.4: Surface Morphology of Rice Husk filled Natural Rubber Vulcanizate

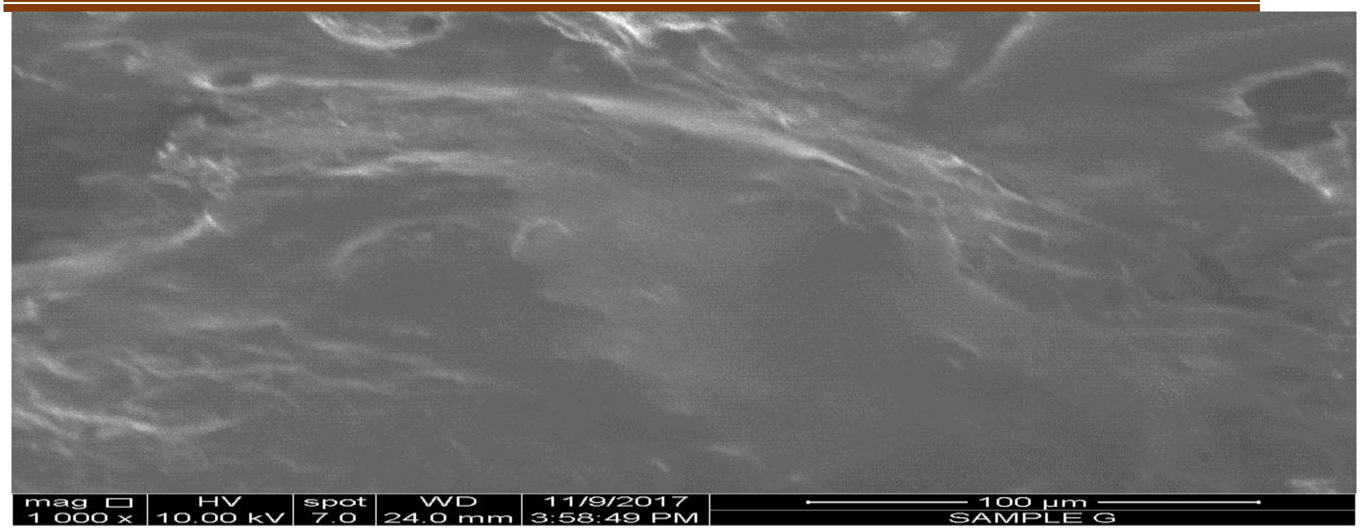

Figure 3.5: Surface Morphology of Treated Rice Husk filled Natural Rubber Vulcanizate

Table 3.1 showed the relationship between moisture contents of rice husk as a function of the chemical modification. The moisture content decreases with chemical modification from 2.30 - 1.85% for unmodified to chemically modified rice husk respectively. However, the amount of water present in a sample decreases as with chemical modification. The moisture content of the filler is often used to predict the degree of defects arising from shrinkage during curing particularly for products processed at elevated temperatures [6].

Bulk density is principally influenced by the particle size and structure of the fibre [6]. Lower particle sizes lowers bulk density and therefore improve the interaction between the polymer matrices and the reinforcing fillers [5]. This inherent properties enhances processing of the vulcanizates and improve quality of the final product since desirable properties for fibre include tensile strength, modulus, durability, low bulk density, good mouldability and recyclability [7]. The bulk densities of both unmodified and chemically modified rice husk are presented in Table 3.1. The bulk density for unmodified rice husk samples was 0.97g/ml while that of the chemically modified was 0.65g/ml.

The pHs of the powdered fillers for both unmodified and chemically modified powdered rice husk was 5.86 and 8.72 respectively and are presented in Table 3.1. However, pH at acidity level tends to slow cure rate and hence reduce the cross-links density.

The FTIR results in Figures 3.1 and 3.2 showed the spectra of untreated rice husk (RH) and chemically treated rice husks (TRH) respectively. The spectra showed three significant changes. Four hydroxyl-stretching frequencies of natural untreated RH were also, observed at (3417, 2926, 2362, and 2165 cm^{-1}). The band at 3417 cm^{-1}attributed to hydroxyls coordinated with the magnesium [8]. Bands at 2926 and 2362 cm^{-1} attributed to the symmetric and antisymmetric stretching modes of molecular water coordinated with the magnesium at the edges of the channels [9]. The band at 3417cm^{-1} is due to the water in the untreated rice husk structure [10]. The hydroxyl stretching vibrations of absorbed water is at 1653 cm^{-1}. The band at 1429 cm^{-1} is due to the stretching vibration of magnesium oxygen. The bands from 558 cm^{-1} to 392 cm^{-1} are due to hydroxyl deformation [11]. Compared with that of treated rice husk, the FTIR spectrum of rice husk did not changed except that the intensity of the band at 1653 cm^{-1} was weaker and at 1334 cm^{-1} disappeared which might be attributed to impurities which were presented in rice husk. The intensities of the untreated rice husk bands at 3417, 2926, 2362, 1653, 1429, and 588 cm^{-1} to 392 cm^{-1} decreased, even some bands disappeared with the treatment. The dehydration of untreated rice husk is followed by the loss of the peak intensity of the hydroxyl bands of water. Dehydroxylation is followed by the decrease in the peak intensity of the band 3417 cm^{-1}. The FTIR spectra of the hydroxyl stretching bands of untreated rice husk disappeared with the chemical treatment process. Figures 3.1 and 3.2 clearly showed the decrease in the intensity of these bands with the chemical treatment. However, the band at 1300 cm^{-1} remains prominent and is also, attributed to Si–O stretching [12]. The intensities of the 460 and 392 cm^{-1} bands are also, maintained. These two bands are not lost because they are associated with the OH translation peak and O–Si–O bend vibration peak, respectively [13].

Scanning electron microscope produces images of a sample by scanning it with a focused beam of electrons, which interact with atoms in the sample producing various signals that contain information about the sample surface topography and composition [14]. The electron beam is usually scanned in a raster scan pattern and the beam position positioned is combined with the dictated signal to produce images with resolution better than 1nm [8]. The most common scanning electron microscope (SEM) mode is detection of secondary electrons emitted by atoms excited by the electron beam. The number of secondary electron that can also, be detected depends among others, the angle in which the beam meets the specimen [15]. The micro-structural result obtained revealed that at 1000x magnification, the plate showed similar pore areas but relatively lower than the filled matrices [16]. For both rice husk filled systems at 30% loadings, the composites showed irregular surface defects and cracks while the unfilled natural rubber matrix was quite plane. The observation may be due to complex filler interactions and compaction within the composite material [17]. The morphologies of the fracture surface for both matrices of the NR, NR/RH and NR/TRH composites were examined by Scanning electron microscope (SEM). Figure 4.3 showed the SEM micrograph of NR. The fractured section of NR was smooth, while those of NR/RH and NR/TRH composites showed many irregularities as presented in Figures 3.4 and 3.5 respectively. The micrographs revealed that the TRH-particles were also, well dispersed within the rubber matrix when compared to RH-filled, thus contributing to the improved properties investigated in the study. The NR matrix was in gray, the RH and TRH filler in white which were dispersed uniformly in NR. The composite exhibited fibrous morphology and great deal of fibres congregate into bundles. Most fibres were fractured and only a few fibrils were pulled out from the NR matrix which implies that the adhesion between TRH and the NR matrix is good [16]. The results demonstrated that the fractured surface of NR/RH was the roughest with deeper tearing lines and angular cracking. In addition, the interface between hybrid TRH and the natural rubber matrix was not so clear. However, the fracture surface of NR/TRH composite was a few smaller holes, which indicated that the interfacial adhesion was still strong. Higher crack propagation energy was required to fracture the composite [15]. The interfacial bonding between TRH and the rubber matrix was strong, thus resulting in higher values of tensile properties.

CONCLUSION

The assessment of modified rice husk for natural rubber compound has been carefully studied. The main aim is to examine how chemically modification of rice husks affects its filler characteristics properties and hence the micro-structural properties of the filled natural rubber vulcanizate. The experimental results showed that chemically modified rice husk is reinforcing filler for natural rubber compound when compared to unmodified rice husks filler. The results revealed that micro-structural properties of the natural rubber vulcanizates are greatly influenced by filler modification and are therefore significant factors in determining the nature and type of fillers for rubber products and service performance applications.

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