

Mechanical Characteristics and Regression Models of Rice Husk Silica Reinforced Natural Rubber Composites

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ABSTRACT: Carbon black and silica fillers have been widely used as reinforcing fillers in tyres and engine mounts. However, both fillers are non-renewable and with REACH legislation in Europe, the USA and elsewhere, where some of these fillers are termed hazardous due to the presence of polyaromatic hydrocarbons (PAHs), there is a need to search for sustainable alternative fillers to wholly or partially replace carbon black as a filler. This research studied rice husks-derived silica (RHS) as a filler in natural rubber (NR). The characteristics of RHS at 50 phr to 90 phr filler loading levels were examined to determine its suitability as a substitute for unsustainable carbon black (N772) fillers used in the rubber industry. Bound rubber content, crosslink density, tensile strength, young modulus, tear strength, shore A hardness, compressive set, and elongation at break were measured. Regression models were generated and the correlation of determination (R^2) values was obtained. The RHS composites resulted in maximum tensile strength of 13.20 MPa at 90 phr, tear strength of 119 MPa at 90 phr, shore A hardness of 69 at 90 phr, compressive set of 6.72% at 80 and 90 phr, elongation at break of 453.60% at 80 phr, bound rubber content of 92.14% at 50 phr and crosslink density of 3.87×10^{-2} mol/cm³ at 70 phr. The results obtained were within the range of those obtained for the carbon black filled composites across various loading levels. The R^2 value of mechanical characteristics for the RHS and N772 samples respectively were 50.06% and 62.18% (bound rubber content), 97.62% and 99.85% (tensile strength), 98.44% and 63.97% (tear strength), 89.16 and 97.40% (Shore A hardness), 32.90% and 91.80% (compressive set), and 50.91% and 46.91% (elongation at break). Rice husk-derived Silica filled natural rubber composites showed favourable mechanical properties and can substitute traditional fillers in tyres, rubber engine mounts, bushings, seals and doormats.

KEYWORDS: Carbon Black, Composite, Filler, Natural Rubber, Rice Husk Silica

[Received March. 26, 2023; Revised July 3, 2023; Accepted July 13, 2023]

Print ISSN: 0189-9546 | Online ISSN: 2437-2110

I. INTRODUCTION

Carbon black and commercial silica which are the predominant fillers used in the rubber industry are non-sustainable and non-biodegradable. The use of carbon black has been found to create harmful byproducts during manufacture (Dominic *et al.*, 2020) and results in complicated health issues as revealed by the Fact sheet of the New Jersey Department of Health Hazardous Substance (NJDOH, 2016). Research and manufacturing in recent times pay much attention to environmentally compatible and sustainable materials and systems (Abdulrahman *et al.*, 2015; Anosike-Francis *et al.*, 2022; Ofem and Ubi, 2020; Shrestha *et al.*, 2010;

Ubi and Abdulrahman, 2013), hence the need to seek a sustainable biobased alternative to the existing traditional fillers. In the rubber industry, fillers such as carbon black and silica are usually used for reinforcement and enhancement of the properties of products. Fillers perform essential functions in rubber composites, accounting for a reasonable percentage of variation in the mechanical and physical properties of their products (Sattayanurak *et al.*, 2019).

Rice husks have been reported to be very rich in silica (Iluppalla *et al.*, 2020; Shiva *et al.*, 2023; Ubi *et al.*, 2022; Ullal *et al.*, 2022) making them suitable for use in various applications where commercial silica is used. The current disposal methods of rice husks in developing nations offer

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several challenges (Ubi *et al.*, 2018), but the most significant difficulty faced today is developing creative uses for the residues that are produced (Suhot *et al.*, 2021). Rice husk as an agricultural residue has been reported to be rich in silica (Ubi *et al.*, 2018) and is currently used as a cheap yet effective material in the engineering manufacturing of several products, including its use in the construction industry for the production of cement (Chandrasekhar *et al.*, 2003; Nair *et al.*, 2008), generation of energy (Habeeb and Mahmud, 2010; Liu *et al.*, 2013), pigments and coatings (Nair *et al.*, 2008), absorbent (Mane *et al.*, 2007), insulators (Gonçalves and Bergmann, 2007), electronics (Adam *et al.*, 2010; Chaudhary *et al.*, 2004), and composites (Arjmandi *et al.*, 2015; Sae-Oui *et al.*, 2002; Soltani *et al.*, 2015) for varying applications. In tyre manufacturing, it has been established that silica-reinforced rubber composites offer low rolling resistance, enhanced safety, better energy savings and high wet grips compared with those filled with carbon black (Luginsland, 2000; Rodgers and Waddell, 2005; Sattayanurak *et al.*, 2019), thereby leading to higher efficiency in fuel saving.

Masłowski *et al.* (2019) explored the use of agricultural waste from cereal straw as a potential biobased filler to replace carbon black and commercial silica fillers used in rubber composites. Findings from their study revealed that the crosslink densities of carbon black, silica and straw increased with increasing filler loading. The elongation at break for the samples decreased with filler loading while the tensile strength of carbon black (15.6 MPa, 17.4 MPa and 19.2 MPa) and the straw (18 MPa, 20.7 MPa and 21.8 MPa) increased with filler loadings at 10, 20 and 30 phr. The tensile strength of the silica filled samples however did not follow the same pattern as that of the straw and carbon black when the filler loading was increased at 10, 20 and 30 phr which yielded tensile strength values of 13.4 MPa, 6.2 MPa and 7.9 MPa respectively. However, the tear strength of the straw increased with filler loading while that of carbon black and silica decreased with increasing filler loading. They reported shore A hardness values within the range of 25 and 45 across the various filler loadings which increased for all samples with increasing filler loading. Chigondo *et al.* (2013) investigated the use of fibres from maize stalk as a substitute filler material for non-biodegradable inorganic fillers in natural rubber composites. Findings from their study established that the use of maize stalk fibres was effective in reinforcing natural rubber at various filler loadings with the 20 phr loading resulting in the optimum having a tensile strength of 22.4 MPa, an elongation at break of 404% and a shore A hardness of 55. Chigondo *et al.* (2013) reported that the tensile strengths of the maize stalk filled natural rubber composites increased with increasing filler loading. The commercial silica filled natural rubber composites also increased with increasing filler loading across all loading levels, while the elongation at break decreased with increasing filler loading. They further stated that the results obtained in their investigation were comparable with those of commercial silica filled composites. Similar studies on silica-rich bagasse fibre ash (BFA) in natural rubber matrix composites showed that BFA can perform excellently as a replacement to commercial-based silica and carbon black with filler loadings of not more than 15 phr yielding better

properties (Kanking *et al.*, 2012). The resulting mechanical and swelling properties showed that BFA had better compatibility for addition with precipitated silica against carbon black when desired to be used as a blend.

In a study involving the utilisation of rice husk ash and carbon black as fillers in rubber, it was noticed that the addition of rice husk ash from 0 to 40 phr resulted in increased hardness and a reduction in the tensile and tear strength alongside the curing time and viscosity (Arayaprane *et al.*, 2005). The results from the research by Arayaprane *et al.* (2005) also established that the young modulus and abrasion loss did not change significantly. Observations of good mechanical properties compared with traditional carbon black and silica-filled composites have been established by researchers (Arayaprane *et al.*, 2005; Chaudhary *et al.*, 2004; Ishak and Bakar, 1995; Ismail *et al.*, 2001). Reports from the researchers suggested that rice husk ash as a cheap filler in rubber can only be applied when improving the mechanical characteristics of a composite is not the main aim of its addition. Several researchers (Arayaprane *et al.*, 2005; Chaudhary *et al.*, 2004; Ishak and Bakar, 1995; Ismail *et al.*, 2001) who have modified the rice husk ash through various means including chemical treatments have reported favourable and comparable properties of the rice husk ash when compared with commercial silica or carbon black. They reported that silica obtained from rice husk ash possessed a high specific surface area, more silica content and a reduced moisture content compared to commercial silica. The curing time for the RHA-filled natural rubber composites was shorter than that of commercial-based silica and the general mechanical properties including the abrasion resistance, tear strength, resilience, tensile strength and compression set of the rubber composites were better compared to the traditional silica-filled rubber composites, however, they reported that the hardness was lower.

In a study (Chuayjuljit *et al.*, 2003), the properties of silica obtained from rice husk ash were compared with those of commercial silica. The results from the study showed that the silica prepared from rice husk ash was composed of fine particles but yielded a reduced porosity compared with the commercial silica, thereby leading to a less specific surface area. However, they reported the possibility of gaining favourable properties from rice husk ash when used as a substitute for commercial silica. Chuayjuljit *et al.* (2003) also noted that the mechanical properties were reduced with increasing silica content and concluded that it was most likely due to the lower bulk density that silica possesses and the high value of average particle size.

It has been established that for rice husk silica to be a more marketable product, it has to contain more amorphous silica than crystalline silica (Javed *et al.*, 2009). Hemicellulose and cellulose in rice decompose within 277 – 350°C while the lignin decomposes gradually at a temperature ranging from 370 to 600°C leaving silica ash. The burning of rice husk above 600°C in an oxygen-free furnace removes all the carbon, resulting in fine particles that are almost pure silica. This method of producing carbon-free rice husk however emits some carbon dioxide during the process, but it is carbon neutral and all emitted carbon dioxide goes back annually into the rice paddies. With this problem solved, rice husk ash would not

make any difficulty in making it into mainstream applications thus coming out with very low carbon content. Burning of rice husk in a furnace before its use as a filler reduces the hydrophilic property of rice husk thereby yielding favourable mechanical properties from the silica produced. Combustion of rice husk at temperatures below 700°C results in amorphous ash while combustion carried out at temperatures above 800°C results in crystalline silica (Bakar *et al.*, 2016; Hossain *et al.*, 2018). The high reactivity of amorphous silica makes it preferable to its crystalline counterpart. Despite the advantages and excellent properties of utilizing silica as reinforcement in rubber composites, it has been established that silica possesses compatibility issues when combined with rubber, thereby yielding poor filler-rubber interaction and weakly distributed particles in the composites. The weak dispersion is due to the very strong filler-filler interaction or hydrophilic silica which is a result of the hydrogen bonding between the hydroxyl group on the surface of the silica. To mitigate this challenge, findings from several studies have established that effective silanization including the use of coupling agents such as bis(3-triethoxysilylpropyl) tetra sulfide (TESPT) which by nature is a donor of sulphur (Jeong *et al.*, 2016; Jin *et al.*, 2020) yields excellent results. Also, in cases of safe scorch during processing, bis (3-triethoxysilyl propyl) disulphide (TESPD) has been recommended (Luginsland, 2000).

This study focused on exploring the use of silica derived from rice husks as an alternative filler to unsustainable petro-based fillers used in the rubber industry. The use of silica derived from rice husk as a filler in rubber composites promises significant potential in addressing the biobased sustainability requirements of rubber-based products while meeting required performance metrics.

II. MATERIALS AND METHODS

A. Materials

Rice husk was collected from a mill in Zaria, Nigeria. This research adopted the approach of Ahmed *et al.* (2014) and Chuayjuljit *et al.* (2001) in the extraction of high-purity silica from rice husks. The rice husks were treated with 0.4M HCl and burned in an oven at 600°C for 6 hours. The N772 grade of carbon black, all additives, curing aid, coupling agents and accelerators used during rubber mastication were procured from chemical reagent stores in Lagos and Zaria, Nigeria. The natural rubber grade employed in this investigation was the CV-60. The compounding of samples was done on a two-roll mill at 70°C and roller speed ratio of 1:1.25, at 24 rpm, according to ASTM D3182-07 standard. All samples were cured at 130°C using a pressure of 2.5 MPa for 20 minutes. The RHS and N772 fillers were independently utilised to reinforce the rubber at 50, 60, 70, 80 and 90 phr. The choice of filler loading in the range of 50 to 90 phr was adopted from established findings of Bokobza and Banks (2017) and Ngolemasango *et al.* (2008) who observed that high filler loadings within the selected range are needed to achieve excellent mechanical and physical properties of rubber composites. Table 1 presents the steps and duration of the mastication process.

Table 1: The phases of compounding the fillers and additives

PHASE	TIME OF ADDITION (MINUTES)	ACTIVITY
1		CV-60 is cut, added to a two-roll mill and masticated
2	2	ZnO (activator), stearic acid (processing aid) and anti-oxidants were added
3	4	Half of the filler, part of the processing aid added
4	6	Addition of the remaining filler and remaining processing aid added
5	8	Half of the Sulphur (curing agent) added
6	10	The remainder of Sulphur added
7	12	Material cut and re-banded 6 times.
8	14	Compound sheeted out, dumped, labelled and conditioned

B. Characterisations

1) Bound rubber content

Bound Rubber Content (BRC) was performed to ascertain the surface activity between the fillers and natural rubber. The BRC presents the portion of the natural rubber which cannot be removed by a good solvent such as toluene hence quantifying the rubber's adsorption on the surface of the filler. BRC depends on the quantity of filler loading in the composite, the structure, and the surface property (Mark *et al.*, 2013; Mazlina, 2013). A high BRC implies a stronger rubber with outstanding filler interaction. The BRC was calculated using the expression in Eqn. 1.

$$\text{BRC (\%)} = \frac{W_{fr} - W \left[\frac{m_f}{m_f + m_r} \right]}{W \left[\frac{m_r}{m_f + m_r} \right]} \times 100 \quad (1)$$

where W_{fr} is the weight of the filler and natural rubber after extraction, W is the weight of the compound before extraction, m_f is the filler weight in the compound and m_r is the weight of rubber in the compound.

2) Crosslink density

The crosslink density was determined in conformity with the ASTM D471-16a standard and was computed using the Flory-Rehner equation expressed in Eqn. (2).

$$V_{cd} = \frac{1}{2M_c} = - \frac{\ln(1-V_r) + V_r + \chi V_r^2}{2\rho_r V_s \left(\sqrt[3]{V_r} - \frac{V_r}{2} \right)} \quad (2)$$

where V_{cd} is the crosslink density (mol/cm³), M_c is the average molecular weight of rubber between crosslinks (g/mol), V_r is the volume fraction of the swollen rubber obtained from the mass and densities of rubber and toluene as shown in Eqn. (3), χ is the Flory Huggins rubber-toluene interaction parameter determined as shown in Eqn. (4), V_s is the molar volume of toluene (106.27 cm³/mol) and ρ_r (g/cm³) is the density of the natural rubber.

$$V_r = \frac{\frac{W_1 - W_f}{\rho_r}}{\frac{W_1 - W_f}{\rho_r} + \frac{W_2 - W_1}{\rho_s}} \quad (3)$$

Where W_1 is the weight in grams of the composite before swelling, W_2 is the weight in grams of the composite after swelling, W_f is the filler weight in grams and ρ_s (g/cm³) is the density of toluene.

$$\chi = \beta + \frac{V_s}{RT} (\sigma_p - \sigma_s)^2 \quad (4)$$

Where β is 0.34 (lattice constant for polymer-solvent blends), R is the gas constant, T in kelvin is the absolute temperature given as 293.15K, σ_p (MPa^{1/2}) is the solubility parameter of the rubber sample which is 16.7 MPa^{1/2} for natural rubber, σ_s (MPa^{1/2}) is the solubility parameter of toluene which is 18.0 MPa^{1/2} (Kim *et al.*, 2020).

3) Compression set

The compression set was determined using a compression set apparatus following method A of the ASTM D395 standard and calculated using Eqn. (5).

$$CS = \frac{t_o - t_1}{t_o} \times 100 \quad (5)$$

Where t_o is the initial thickness of the composite in millimetres, t_1 is the thickness of the sample in millimetres after recovery.

4) Shore A hardness

The Shore A hardness of the samples was determined in compliance with the ASTM D2240 standard using a Mover Durometer Hardness Tester with model number 5019.

5) Tensile and tear test

The tensile test was performed using a Hounsfield Monsanto Tensometer (386083-W9) in line with method A of the ASTM D412 Type C standard, and the measurement was based on the tensile stress at break. A tear test was also conducted in compliance with method A of the ASTM D624 – 00 standards to ascertain the resistance of the composite to tearing.

III. RESULTS AND DISCUSSION

The Brunauer, Emmett and Teller (BET) specific surface area of RHS and N772 was 235.702 m²/g and 37 m²/g respectively having an average particle size of 2.125 μ m and 0.15 μ m respectively. Chuayjuljit *et al.* (2001) reported a similarly high value of the BET specific surface area for RHS which they found to be 182 m²/g while Mahmud *et al.* (2016) obtained a BET surface area of 234.6 m²/g with a pore diameter of 5.3 nm. Pongdong *et al.* (2015) reported an average particle size of RHS to be approximately 3.83 μ m as against the commercial silica which he reported to be 0.018 μ m. The results obtained for the particle size of RHS in this research are in contrast with reports from Boonmee *et al.* (2019) who reported the average particle size of RHS to be between 13.21 μ m to 76.25 μ m and Bakar *et al.* (2016) who stated that average particle sizes of RHS range between 0.50 to 0.70 μ m for combustion temperatures between 500°C to 900°C, however the BET surface area of HCl treated RHS combusted at 600°C which they reported to be 218 m²/g and that treated with H₂SO₄ which was 209 m²/g conforms to results obtained in this research. In agreement with Pongdong *et al.* (2015), the large particle size and specific surface area of RHS do not deter it from its great potential as a reinforcement material that improves desired properties in rubber composites.

The BRC of the rice husk silica filled composite was maximum at the 50 phr filler loading while the N772 filled samples had a maximum BRC value at 90 phr as shown in Figure 1. The BRC results obtained in this study agreed with

findings published by Wolff *et al.* (1993) who established that bound rubber content is higher for materials with greater specific surface area and gets lower with increasing filler loading as observed at the 80 and 90 phr RHS filler loading. Fillers with large specific surface areas give a greater interfacial area with the rubber per unit volume at a given loading value, hence an increase in the bound rubber content. However, when the loading becomes much, agglomeration of the filler particles is eminent as each struggle for attention from the matrix leading to a drop in the BRC as exhibited by the RHS filler. It was observed that during mastication of the compounds, larger particles were broken down thereby exposing new active surfaces to the rubber matrix. These surfaces are also likely to alter the bound rubber content depending on the filler loading level. A study by Sattayanurak *et al.* (2019) on silica (Si) and carbon black (CB) natural rubber composites revealed that fillers with high specific surface area have a synergistic effect on the overall performance of silica-filler rubber composites. Sattayanurak *et al.* (2019) reported a decrease in the bound rubber content of Si/CB reinforced natural rubber composites with increasing filler loading from 20 phr. The correlation of determination (R²) value and the model equations for the BRC of the individual fillers as shown in Figure 2 presents an R² value for the N772 and RHS fillers as 62.2% and 50.06% respectively. This demonstrates that 62.2% and 50.06% of the variation in N772 and RHS loading respectively is connected to the regression model while approximately 38% and 50% of the variation in the respective models are accounted for by other factors. The low R² values, therefore, suggest that apart from filler loadings, additional factors such as surface area, particle size and coupling agents are likely to influence the bound rubber content of the composites.

The sample with 90 phr N772 resulted in a maximum crosslink density of 4.09×10⁻² mol/cm³ while RHS filled samples showed a maximum crosslink density of 3.87×10⁻² mol/cm³ at 70 phr. The crosslink density of N772 filled samples grew continuously with an increase in filler loading while the RHS filled composite showed an inconsistent increase and drop with increment in their filler loading. The high crosslinks exhibited by the RHS filled composites when compared with that of filled N772 can be attributed to the impurities present in RHS in the form of metallic oxides which promotes crosslinking reactions (Pongdong *et al.*, 2015). The RHS used in this research as reported previously (Ubi *et al.*, 2022) contained a significant amount of magnesium oxide (MgO), calcium oxide (CaO), and alumina (Al₂O₃). These metallic oxides have been reported to result in favourable properties of natural rubber, with MgO and CaO serving as activators thereby enhancing crosslinking (Heideman & Noordermeer, 2005; Qamarina & Kawahara, 2014) while Al₂O₃ improves the tear strength, tensile strength, modulus and ageing resistance of natural rubber composites (Fu *et al.*, 2012). These along with the variation in particle size and surface area of RHS when compared with that of N772 is responsible for the inconsistent increase and decrease in the crosslink densities of the RHS reinforced composites as observed in Figure 3.

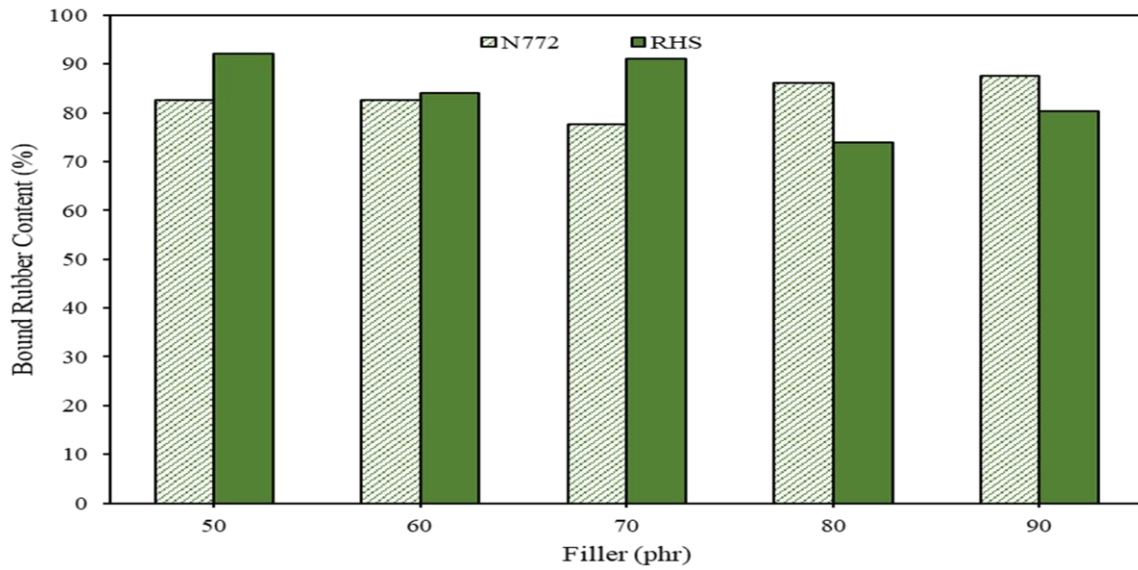


Figure 1: Bound Rubber Content of N772 and RHS filled NR composites

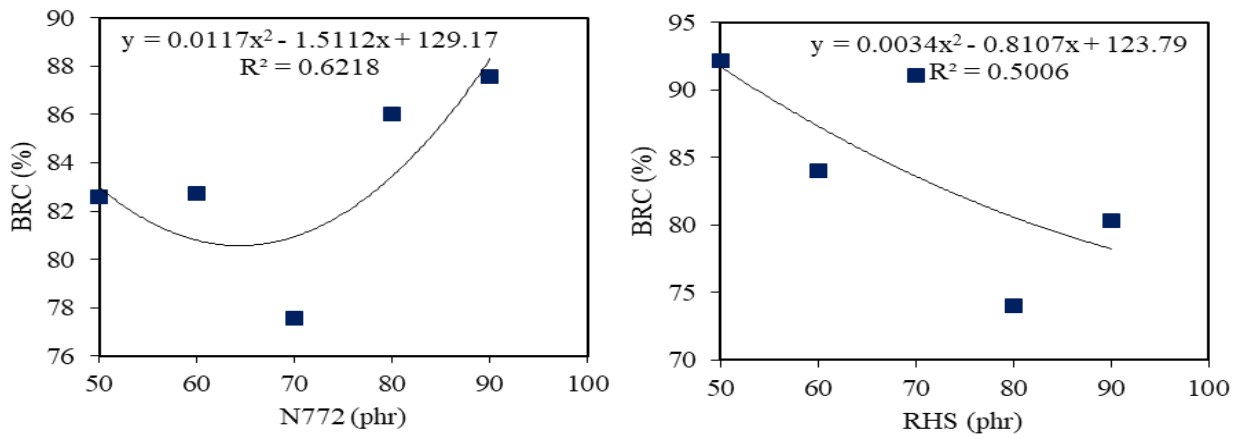


Figure 2: Line fit plots of the fillers with regression models for BRC

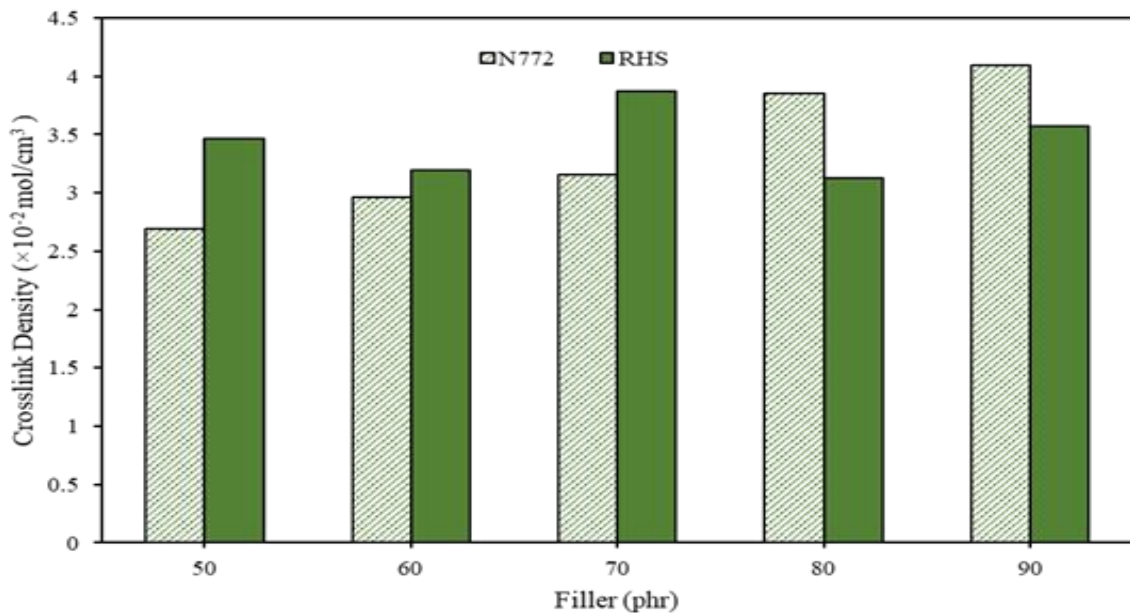
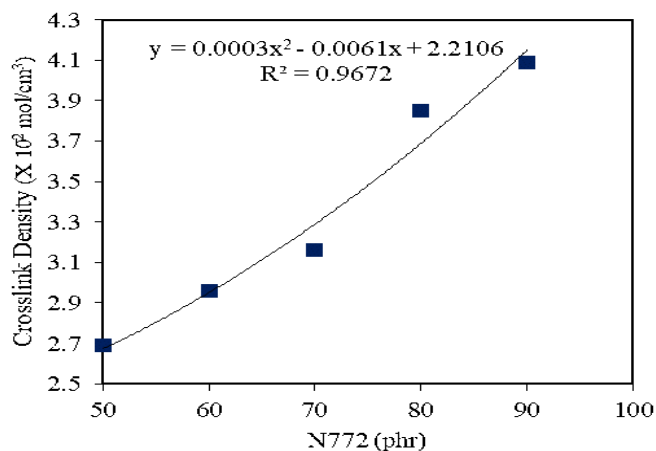


Figure 3: Crosslink density of N772 and RHS filled NR composites

The crosslink densities obtained for the carbon black reinforced samples conform with the report of researchers (Kim *et al.*, 2020; Masłowski *et al.*, 2019) who observed an increase in crosslink density with increasing filler loading for the carbon black filled composites. For commercial silica filled composites, Kim *et al.* (2020) observed a decrease in crosslink density with increasing filler loading, however in this research, the RHS samples decreased from 50 to 60 phr, increased to a value of $3.87 \times 10^{-2} \text{ mol/cm}^3$ at 70 phr before decreasing and increasing again at 80 and 90 phr respectively. Figure 4 shows the plot fits and regression model for the composites. The N772-filled samples resulted in an R^2 value of 96.72% with an adjusted R^2 value of 93.45%, implying that the model sufficiently explains the relationship existing between all parameters involved. However, the RHS-filled composites showed a comparatively low R^2 value of 0.71% meaning that over 99% of the crosslink density of the samples is accounted for by other factors aside from the filler loading. This is expected owing to changes in specific surface area, particle size, effect of activators and the need for coupling agents to promote the interaction between silica and natural rubber.

Apart from filler loading, a significant contributor to the crosslink density is the accelerators and curing agents such as sulphur (Kaewsakul *et al.*, 2013), which when high yield a material with high crosslinks. Heavily crosslinked elastomers have very severe constraints on the mobility of rubber chains, hence their inability to release energy in the form of heat created during deformation via molecular motion thereby leading to ease in brittle fracture at low strain. In actual applications, the crosslink density must be high to a good degree to avoid failure from viscous flow, however, it must also be soft enough to avoid brittle fracture.



account for the relationship that exists between the parameters in the models.

The tensile strength of the composites is seen to rise with filler loading from 50 to 90 phr as shown in Figure 7. The results obtained for the RHS filled samples exhibited higher tensile strength compared with those of the N772 filled samples for all loadings except at 50 phr. This aligns with the reports of Subeh *et al.* (2020) who stated that materials with large surface areas generate high tensile strength capabilities. However, the tensile strength in this research did not decline for filler loadings after 60 phr as reported by Subeh *et al.* (2020). The tensile test results obtained for the RHS and N772 single filled samples also aligned with observations reported by Masłowski *et al.* (2019) who noted that the tensile strength of carbon black (18 MPa, 20.7 MPa and 21.8 MPa) and cereal straw (15.6 MPa, 17.4 MPa and 19.2 MPa) filled natural rubber composites increased with increase in filler loadings at 10, 20 and 30 phr. However, the values they obtained for the tensile strength of the silica filled natural rubber composites (13.4 MPa, 6.2 MPa and 7.9 MPa) at the same filler loading levels did not increase with an increase in the filler loading which also is at variance with observations made by Chigondo *et al.* (2013) silica filled natural rubber composites.

The R^2 value for the tensile strength was 99.85% and 97.62% for the N772 and RHS fillers respectively with a corresponding R^2 adjusted value of 99.70% and 95.24%. These data demonstrate that filler loading is a primary element responsible for predicting the tensile strength property of natural rubber composites having single fillers. Figure 8 shows the fit plots for the tensile strength to the filler loading of the samples.

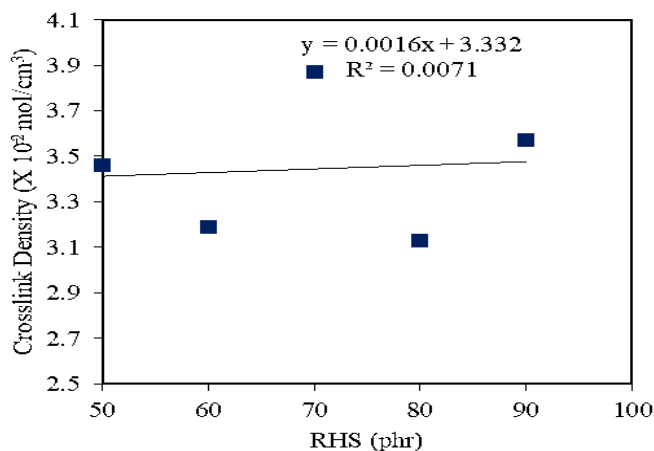


Figure 4: Line fit plots of the fillers and regression models for crosslink density

The shore A hardness illustrated in Figure 5 shows increasing hardness with an increase in the filler loadings for all samples owing to the increase in the bond between the fillers and rubber chains, hence resulting in the reduction in movement of filler-matrix chains, which accounts for hard and rigid composites.

At 60 and 70 phr, similar hardness was experienced for each compound. The R^2 value of the samples as illustrated in Figure 6 was above 89% indicating that the regression models

The rise in modulus with increasing filler loading is partly due to the effect of RHS filler particles in the composite as established by several studies (Ahmed *et al.*, 2014; Pongdong *et al.*, 2015; Subeh *et al.*, 2020). The study of Pongdong *et al.* (2015) asserted that large specific surface area of silica particles is responsible for the high tensile strength and modulus of resulting composites. Similarly, Boonmee *et al.* (2019) reported that materials with smaller particle sizes result in lower values of tensile and tear strengths. The immobility of

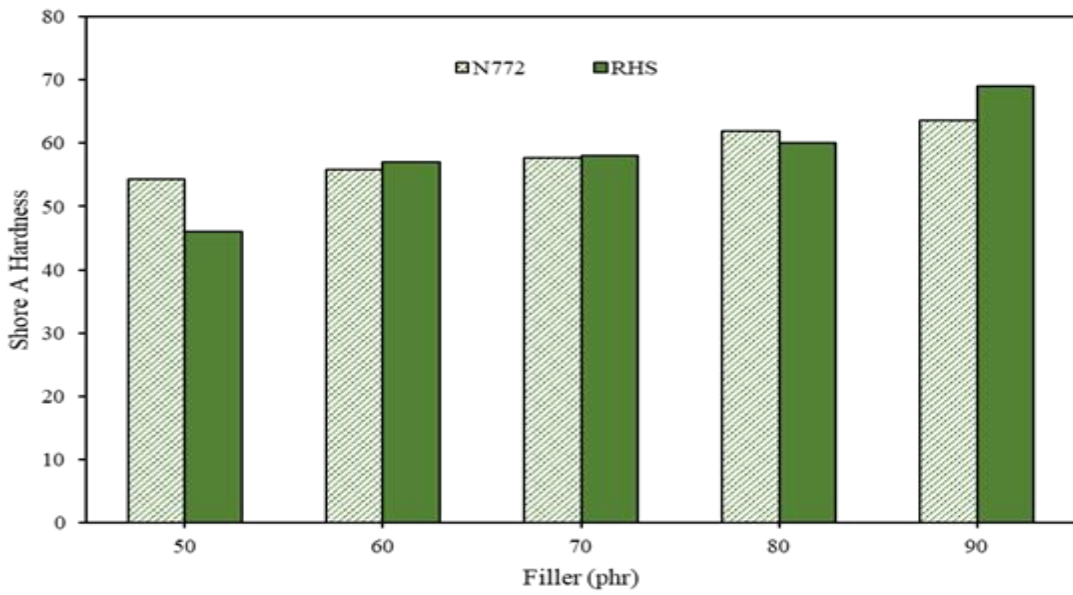


Figure 5: Shore A of N772 and RHS filled NR composites

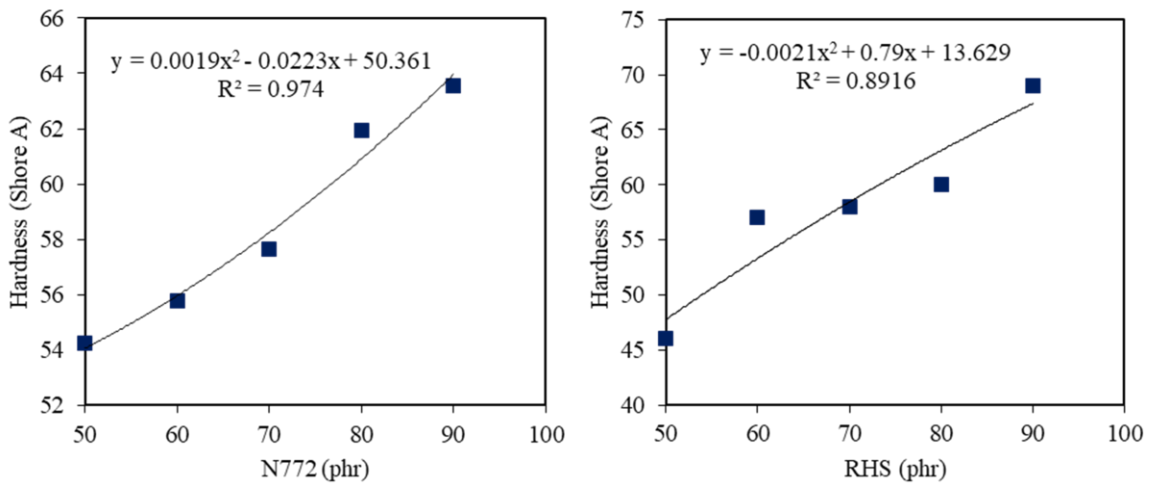


Figure 6: Line fit plots of the fillers and regression models for shore A hardness

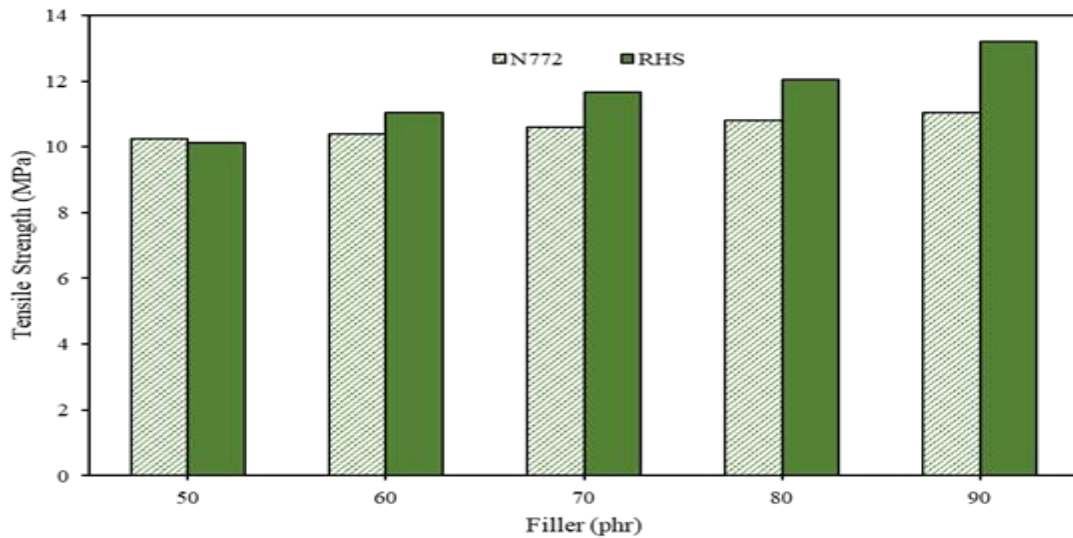


Figure 7: Tensile strength of N772 and RHS filled NR composites

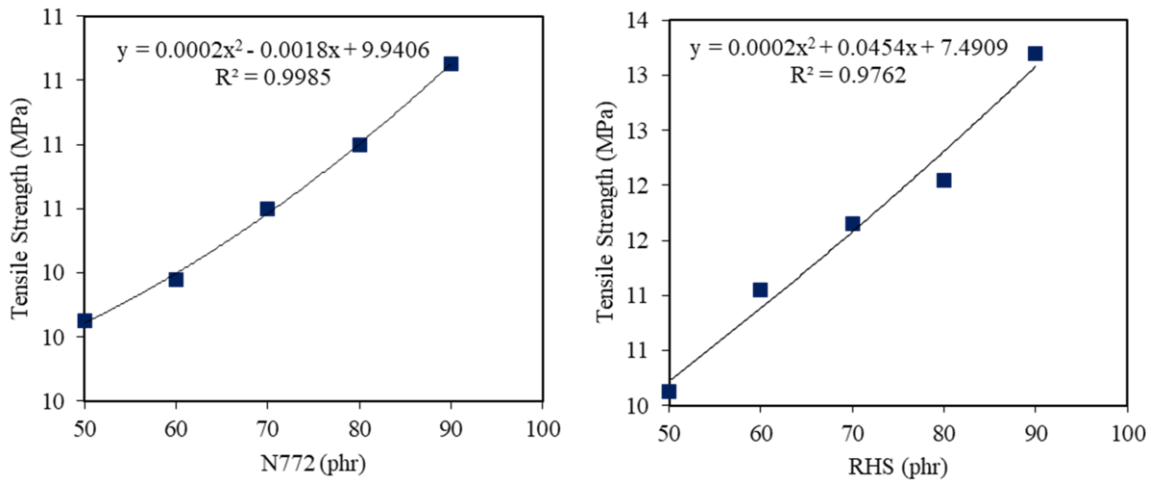


Figure 8: Line fit plots of the fillers and regression models for tensile strength

natural rubber chains at higher filler loading levels also contributes to the modulus behaviour of the composites.

The tear strength results for carbon black did not conform to the reports of Masłowski *et al.* (2019) who reported a decrease in tear strength for carbon black and silica single-filled natural rubber composites with increasing filler loading. However, the results obtained for the tear strength in this study aligned with their observation on the cereal straw investigated which showed an increase in tear strength with increasing filler loading. The tear strengths and tensile strength of the samples in this research followed a similar trend and conformed with the reports of Ahmed *et al.* (2014). Figure 9 shows the tear strength of the samples while Figure 10 shows the line fit plot and models. The low R^2 value of 63.97% for the N772 filled composites compared with that of RHS filled composite may be attributed to various predictors and uncontrollable experimental noise since a similar mean value was achieved for repeated trials. A similar low R^2 value of 54.79% was obtained for the tensile modulus of N772 and 81.44% for RHS as shown in Figure 11a.

The elongation at break of RHS filled composites decreased with increasing filler loading level except at 80 phr which possessed the highest value of 453.60 MPa. This decrease in the percentage elongation at break with increasing filler loading conforms to observations reported by Masłowski *et al.*, (2019) for carbon black, silica and cereal straw filled natural rubber composites which they investigated. Kim *et al.* (2020) and Chigondo *et al.* (2013) similarly reported a reduction in the elongation at break with higher filler loading levels for carbon black and commercial silica. The R^2 values for the elongation were low and are similar to results reported by Barrera *et al.* (2018) who stated that the regression model was observed to be weak in explaining variability, consequently revealing the dependence of the elongation on variables aside from filler loading. Figure 11b shows the fit curves and model for the elongation.

For the compressive set, its increase with increasing filler loading for the N772 filled samples composites corresponds with results reported by Subeh *et al.* (2020) who attributed this

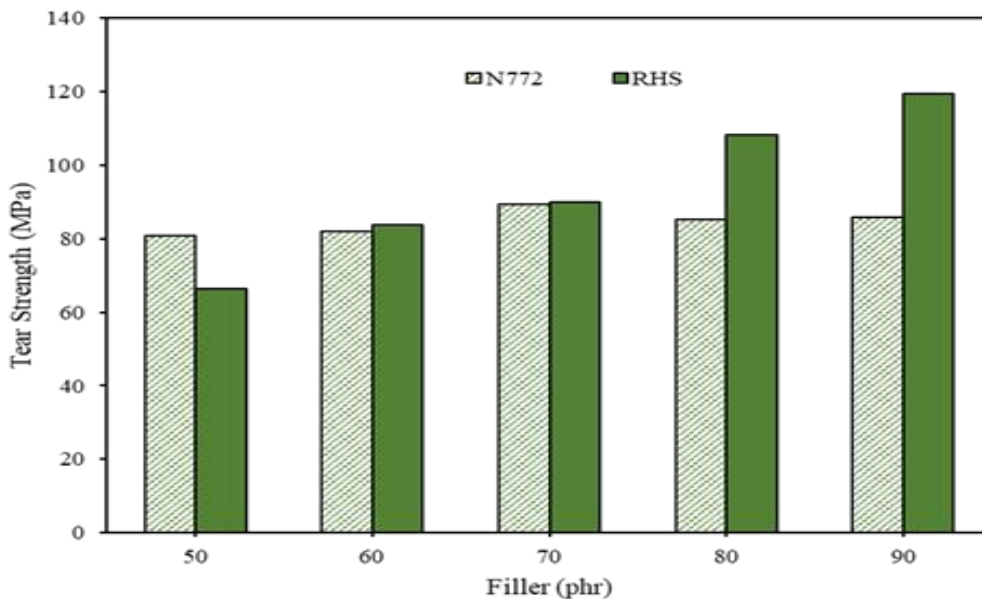


Figure 9: Tear strength of N772 and RHS filled NR composites

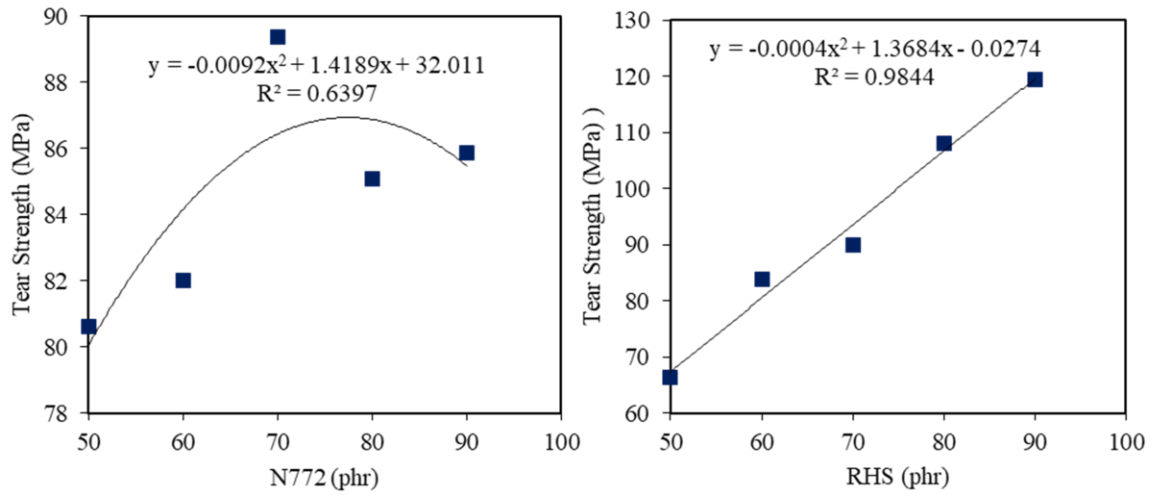


Figure 10: Line fit plots of the fillers and regression models for tear strength

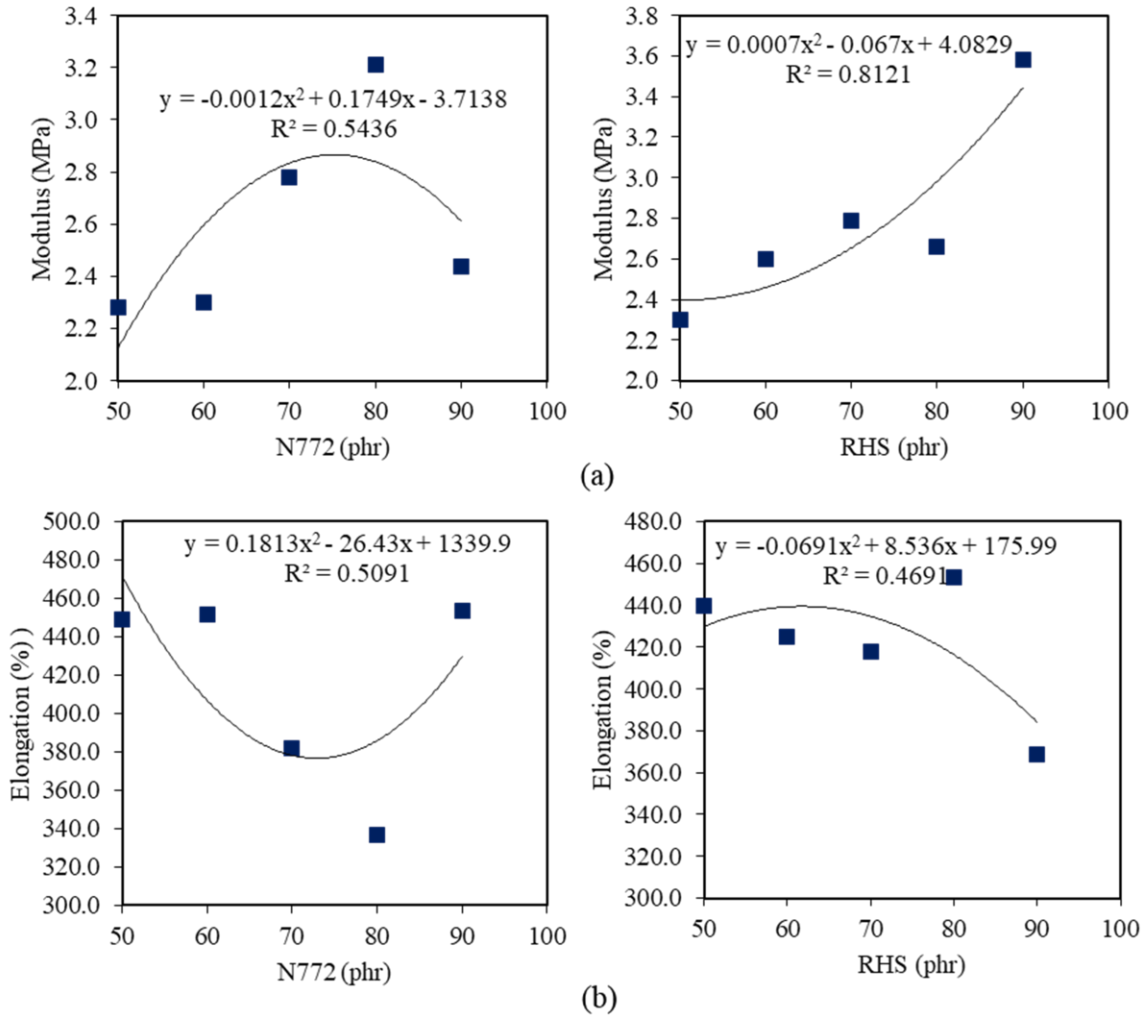


Figure 11: Line fit plots and models of N772 and RHS single-filled composites for (a) tensile modulus (b) elongation

behaviour to the rise in the entanglement and increased crosslink density, decrease in the movement of rubber chains and the rigidity of the composite. The compressive set obtained for the RHS samples however does not rise with filler loading and is within the same range of values greater than the maximum recorded for the N772 filled compounds as indicated in Figure 12. This characteristic demonstrated may be partly owing to the large particle size and surface area of the RHS.

The investigations by Subeh *et al.* (2020) gave a compressive set of approximately 3% for carbon black N220 single filler composites at 60 phr, while at the same filler loading in this research for the N772 and RHS single filler composites, a compressive set of 4.52% and 6.8% were obtained respectively. The R^2 values for the compressive set as depicted in Figure 13 were low for RHS and may be mostly related to differences in the specific surface area, filler structure and particle size.

IV. CONCLUSION

Introducing rice husk-derived silica as a filler in rubber composites offers enormous advantages and can serve as a cost-effective and sustainable substitute to the present traditional fillers employed in the manufacture of rubber products.

The mechanical characteristics of the rice husk-derived silica reinforced natural rubber composites showed excellent properties across all loading levels when compared with those of carbon black (N772 grade). The R^2 values of the rice husk-derived silica-reinforced composites sufficiently showed the ability of the regression models to predict the tensile strength, shore A hardness, tear strength and young modulus of the composites. However, low R^2 values were observed for the compressive set, elongation at break, crosslink density and bound rubber content of the rice husk-derived silica reinforced natural rubber composites.

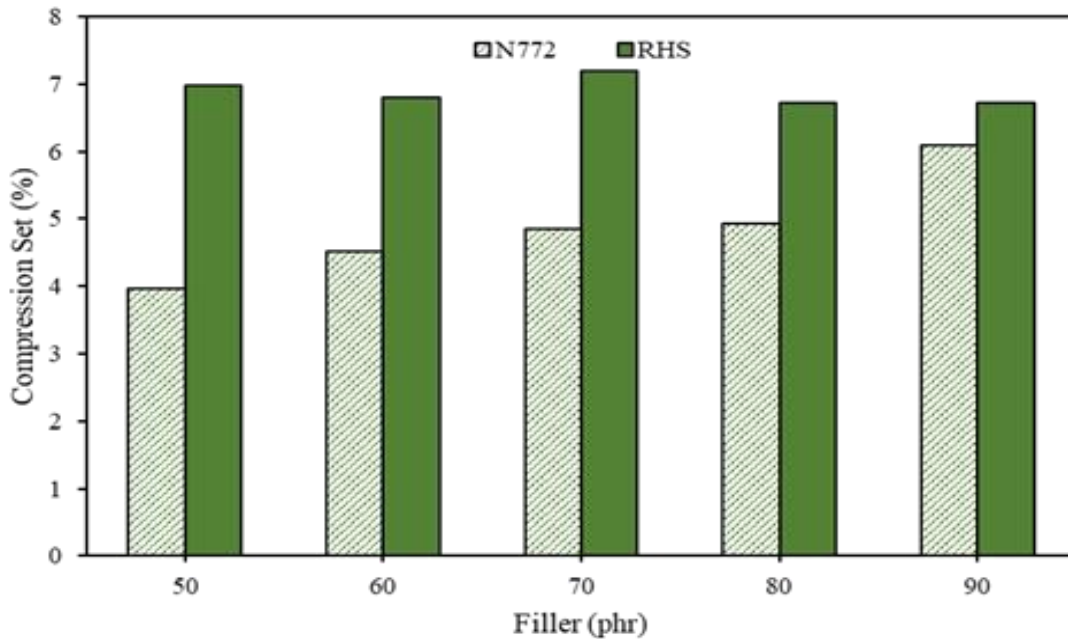


Figure 12: Compressive set of N772 and RHS filled NR composites

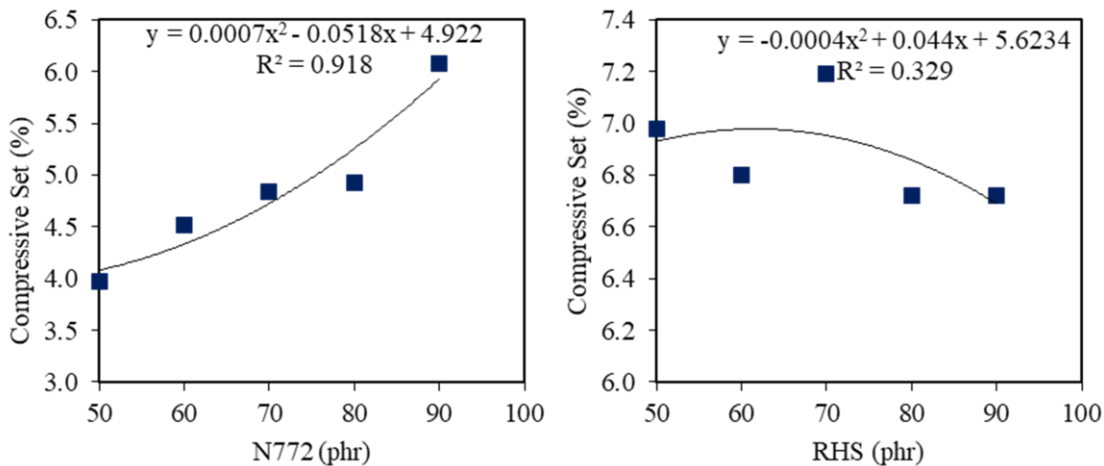


Figure 13: Line fit plots of the fillers and regression models for the compressive set

The low R2 values obtained for the regression models of these properties were weak in explaining the relationship that exists between the variables, hence these properties depend largely on other factors aside from filler loading levels.

Results obtained in this research established that rice husk-derived silica is a viable alternative to the traditional non-sustainable fillers used in the rubber industry. Properties of rice husk-derived silica-filled composites can be improved by reducing the particle size to nano-size and also by incorporating RHS as a blend with carbon black in rubber composites. Products such as tyres, rubber engine mounts, bushings, seals, doormats and several others involving elastomers can perform effectively when the elastomers are reinforced with rice husk-derived silica, thereby not only satisfying the biobased earth and sustainability requirements but also promising energy savings during processing.

AUTHOR CONTRIBUTIONS

P. A. Ubi: Conceptualization, Methodology, Investigation, Data Curation, Writing- Original draft. **N. A. Ademoh:** Supervision, Validation, Writing- Review and Editing. **A. S. Abdulrahman:** Supervision, Resources, Writing- Review and Editing. **A. B. Hassan:** Supervision, Resources. **J. D. Dashe:** Investigation, Resources. **O. S. Wasiu:** Investigation, Resources. **F. Ngolemasango:** Supervision, Methodology, Writing- Review and Editing.

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