ChemSearch Journal 12(1): 78 – 84, June, 2021
Publication of Chemical Society of Nigeria, Kano Chapter

Received: 08/04/2021 Accepted: 18/05/2021
http://www.ajol.info/index.php/csj

Use of Neem *(Azadirachta Indica)* Seeds as Filler in Natural Rubber Compounding

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ABSTRACT

The importation of carbon black (a petroleum product) for the reinforcement of Natural Rubber (NR) is very expensive. Therefore, the need to source alternative materials locally becomes necessary. Neem seed (NS) was evaluated as reinforcing fillers in the compounding of NR. NS were collected, cleaned, dried, milled and some part of it was carbonized at 250^{0}C. The Carbonized Neem Seed (CNS) and Uncarbonized Neem Seed (UNS) powders were sieved using 90µm mesh size and then characterized. These were then used as fillers in varying proportions (0%, 15%, 30%, 50% and 100%) with Carbon Black (CB) for the compounding of NR. The physicomechanical properties including tensile strength, elongation at break of the vulcanizates were determined. Scanning Electron Microscopy (SEM) was also used to analyze the morphology of the blend in the vulcanizates with 100% CNS, UNS and CB. The loss on ignition for the CNS was found to be 89.5 while that of UNS was 69.8. The physicomechanical analysis carried out on the vulcanizates showed better properties for the carbonized samples than the uncarbonized ones. The 15% and 30% CNS reinforced better than 100% CB as shown in the results. The SEM result showed a better dispersion of the CB into the vulcanizate with 100% CNS and UNS.

Keywords: Carbonization, Natural Rubber Vulcanizates, Neem Seed, Properties

INTRODUCTION

Natural rubber (NR) is a material with outstanding physical properties, such as high mechanical strength, low heat build-up, excellent durability, impact and tear resistance, as well as the potential to be recycled (Daniel *et. al.*, 2009). In engineering and domestic applications, raw dry rubber is seldom used in its natural state. As a result, many ancillary materials known as additives are added to rubber compounds for them to be satisfactorily processed and vulcanized to boost application properties. Vulcanizing agents, accelerators, activators and/or retarders, fillers, and anti-degradants are some of the additives used in rubber manufacturing (Onyeagoro, 2012)

Carbon black has long been recognized as the most widely used reinforcing filler in the rubber industry. The increasing concern about its environmental effects (such as non-renewable petroleum origin, dark colour, toxicity, and emissions) and the stringent environmental legislation around the world has to lead a growing interest in the use of efficient sustainable natural resources, thus, researchers have been working to develop alternative reinforcements that are environmentally friendly and perform as well as their synthetic equivalents (Onyeagoro, 2012). In line with the aforementioned, natural fibers are considered fine, reusable, and biodegradable alternative to synthetic reinforcement because of their low cost, easy availability, ease of chemical and mechanical alteration, and excellent basic mechanical properties (Lovely *et.al.*2006). Neem seed is therefore suggested as an alternative biofiller of renewable origin.

Neem (*Azadirachta indica*) of the Meliaceae family is an evergreen tree indigenous from the Indian subcontinent and South-East Asian countries. In Nigeria, neem is also known as "Dongon-yaro". In South-Western Nigeria, the seeds are found as waste litters on the floor under the trees.

This study aims to reinforce natural rubber with neem seed and determine its physicochemical properties which would be compared with the commonly used carbon black.

MATERIALS AND METHODS

Materials

Neem seeds were obtained from the Bells University of Technology, Ota, Ogun State. Crumb rubber was sourced from Alagbado, Lagos State. Chemicals used were of analytical grades.

Sample Preparation and Characterization

Sand particles and moisture were removed from the Neem seeds by air drying. The dried shells were milled to a fine powder and sieved through a mesh of 90µm. A portion of the sieved powder was carbonized using a slightly modified version of the procedure defined by Ishak and Baker (1995).Carbonized Neem Seed (CNS) and Uncarbonized Neem Seed (UNS) were characterized by following the methods described in the ASTM 1509 in terms of moisture content, loss on ignition, pH**, v**olatile matter, and ash content.

Compounding and Physico-mechanical Properties of the Vulcanizates

The mixing was done on a standard laboratory two-roll mill (160x 320mm) with the formula shown in Table 1.The vulcanizates' tensile properties were calculated using a dumbbell test specimen (Type II) and a Universal tensile tester model at a crosshead speed of 500mm/min, as stated in ASTM D-412-87 (Method A). The tensile strength, elongation at break and modulus elasticity at maximum load values of the specimen were determined from the stress-strain curves. Abrasion Resistance Test was done using a DN abrasion tester Model FE5000.The hardness test was carried out using the procedure described in BS 903-A26. The equipment used was Rex Durometer Model OS-2A. Rubbers with an International Rubber Hardness Degree of 30 to 85 are covered by the standard dead load system of measurement (IRHD).

SEM-EDX analysis was carried out to give the morphological information of the vulcanizates filled with 100% CNS, UNS and CB respectively. This was done using PhenomProX fitted with Energy Dispersive X-Ray Spectroscopy (EDX) Analyzer.

Table 1: Filler reinforced natural rubber composites compounding formula

Materials (g)	A 15% UNS	B 30% UNS	C 50% UNS	D 100% UNS	E 15% CNS	F 30% CNS	G 50% CNS	H 100% CNS	I 100% CB
Natural rubber	100	100	100	100	100	100	100	100	100
Zinc oxide	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Processing oil	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
MBTS	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Trimethylquinoline	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Carbon black	34	28	20	0	34	28	20	0	40
Neem seed	6	12	20	40	6	12	20	40	0

UNS- Uncarbonized Neem Seed; CNS- Carbonized Neem Seed; CB- Carbon Black, MBTS –Mercapto Benzothiazole Sulphenamide

RESULTS AND DISCUSSION

Characterization of Neem seeds

Moisture Content is an indication of the proportion of water in the sample. The amount of moisture in the uncarbonized seeds was found to be 8.70% which is higher than that of carbonized seed. This implies that the moisture content of the sample was reduced during carbonization. The higher the moisture content, the higher the tendencies for the test materials to absorb water and humidity from the surrounding which can easily cause shrinkage and distortion of vulcanizates (Akinlabi, 2007). Therefore the carbonized sample when used in rubber compounding should be less susceptible to shrinkage.

Loss on Ignition is a measurement of the material's carbon content. The loss on ignition value for the carbonized seed is 89.5% while that of the uncarbonized seed is 69.8%, showing that there will be more available bonds for cross-linking in the carbonized seed. The high LOI for both samples, when compared to other bio fillers (rubber seed -59.3 (Ekebafe *et al*., 2010);eggshell **–** 47.8 (Akinlabi *et al*., 2018)), is an indication that it is likely to serve as a good filler with a good network system with natural rubber.

Ash Content indicates the trace elements or extraneous foreign matter. The result (Table 2) indicates that the trace elements or extraneous foreign matter in the uncarbonized samples are more than that of the carbonized sample.

Volatile Matter indicates the presence of foreign materials. The volatile matter content of uncarbonized seed was found to be higher than carbonized seed (Table 2). Some of the foreign matters have been removed during the carbonization of the seed.

pH is a measure of the degree of acidity or alkalinity. The pH values also indicate the presence of hydrogen. The presence of hydrogen in filler does not enhance the curing of such vulcanizates when compounded with sulphur. Therefore, acidic fillers are not desirable for rubber vulcanizates.

Acidity causes shrinkage and would not make the rubber cure on time. The pH of the uncarbonized sample was found to be weakly acidic (5.6) and the carbonized sample was weakly alkaline (8.9). The ideal pH for natural rubber vulcanizates is from neutral to alkaline. The result shows that the carbonized seed filler should cure on time.

Table 2: Results from the characterization of Neem seed

Parameter	UNS	CNS	100% Carbon Black (Akinlabi *et. al.*, 2018)
Moisture Content	8.07	6.08	2.51
Volatile matter	6.92	4.20	0.5
Loss on ignition	69.8	89.5	92.8
Ash	7.20	4.31	6.2
pH of slurry	5.60	8.90	6.5

XRF Analysis

The XRF results in Table 3 show the presence of sulphur (a good vulcanizing agent) which can also assist in the reinforcement of the Natural rubber vulcanizates. This is an indication that the neem seed is expected to confer greater rigidity and stronger interaction with the NR matrix. Also, the presence of calcium is observed from the result. This implies that neem seed has the tendency of serving as reinforcing filler in rubber compounds.

Table 3: X-Ray Fluorescence analysis result of Neem seed

Element (%)	UNS	CNS
Fe_2O_3	0.0743	0.1145
CuO	0.0009	0.0013
NiO	0.0349	0.0734
ZnO	0.0017	0.0027
Al_2O_3	0.0728	0.0691
MgO	0.3463	0.5931
Na_2O	0.0	0.0389
S	0.2510	0.3146
P_2O_5	0.3727	0.7360
CaO	0.5472	0.8247
K_2O	2.9748	6.0650
MnO	0.0201	0.0344
Rb_2O	0.0120	0.0168
SrO	0.0040	0.0056
Br	0.00025	0.0008
Cl	0.0899	0.1814
Cr_2O_3	0.0899	0.0003
V_2O_5	0.0016	0.000285
Sn	0.000289	0.035

Physico-Mechanical Properties of Vulcanizates

Tensile Strength (TS) - The tensile strength of natural rubber vulcanizates filled with the UNS and CNS is shown in Figure 1.The highest TS was observed for vulcanizate with 15% CNS (38.40) while the lowest TS was for vulcanizate of 100% UNS (7.73). It was observed from the result that at a lower percentage of seed (15% for UNS and 15% & 30% for CNS), a higher value of TS than that of the CB was obtained. Neem seed either carbonized or uncarbonized in low percentage with CB produced a better link with the NR than 100%

CB. This implies that the incorporation of NS at a low percentage helped in the reinforcement of the vulcanizates. At a higher percentage of the seed, there was a weak intermolecular force between the NR and the Neem seed.From figure 1, it is obvious that TS for the vulcanizates with CNS was higher than that of UNS at all percentages. This is likely due to a higher percentage of carbon in the CNS than the UNS as shown from the result of loss on ignition (89.5 for CNS and 69.8 for UNS), which helped to reinforced the vulcanizates more. This is because more bonds are available for cross-linking in the CNS, hence, the observed high tensile strength value for vulcanizates with CNS. High TS for the CNS can also be attributed to the higher composition of reinforcing elements in it than that of UNS (i.e. S – 0.3146CNS; 0.2510UNS and CaO – 0.8247CNS; 0.5472UNS).

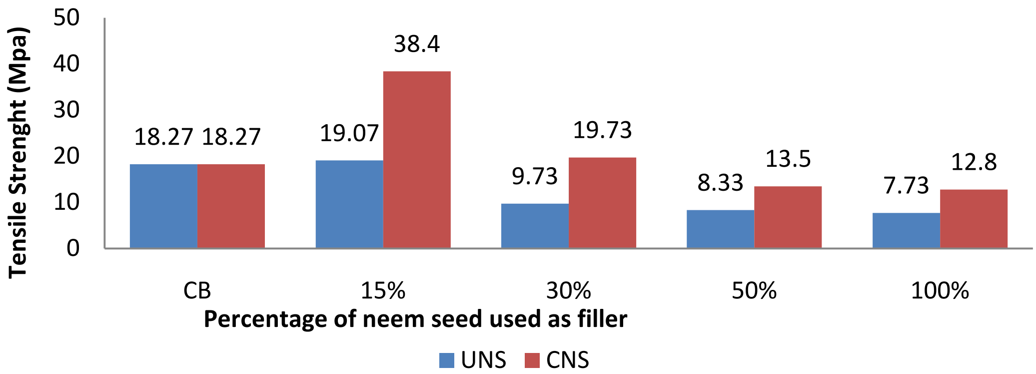

Figure 1: Tensile strength of vulcanizates filled with UNS and CNS

Elongation at Break - The Elongation at break of NR vulcanizates filled with the uncarbonized and carbonized neem seed is shown in Figures 2.Elongation at Break shows the extent of flexibility of the materials at specific applied forces. The result of elongation at break ranges from 73.35 (100% UNS vulcanizate) to 486.25 (15% CNS vulcanizate). The result indicates that vulcanizates with a low percentage of NS (15% UNS and 15% &30%CNS) are more flexible implying a better network in the vulcanizate produced. A higher percentage of NS impacted a softening effect on the vulcanizates. Reduction in Elongation at Break was also clarified in terms of filler adherence to the polymer process, which resulted in the stiffening of the polymer chain and thus resistance to stretch when the strain was applied (Chigondo *et al.*, 2013).

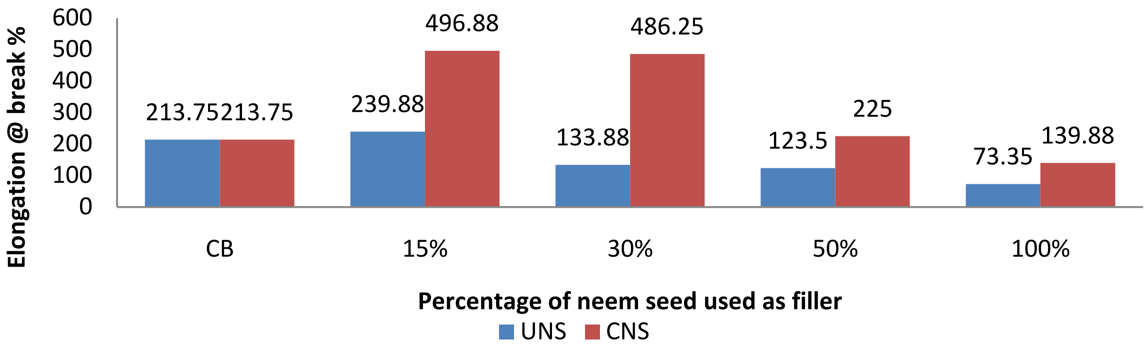

Figure 2: Elongation at break of vulcanizates filled with UNS and CNS

Modulus Elasticity- The modulus elasticity of natural rubber vulcanizates filled with the UNS and CNS is shown in Figure 3. A similar result as in the case of Elongation at break was observed for modulus elasticity (i.e.15% and 30% had better modulus elasticity than 100% Carbon black).

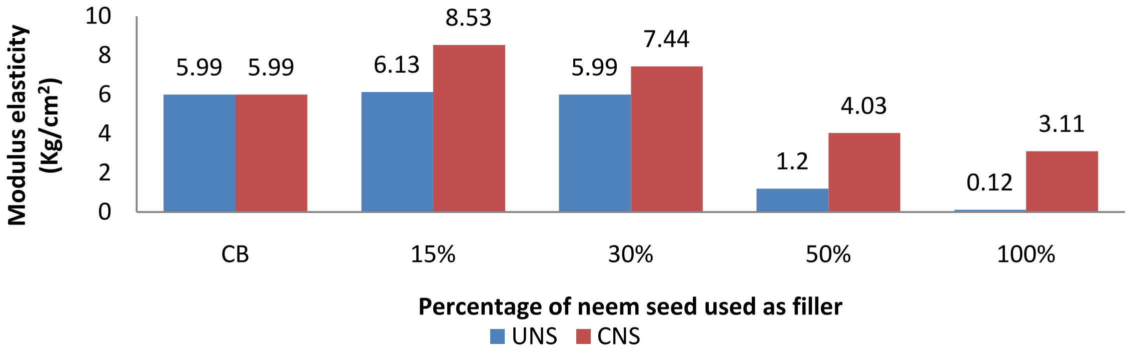

Figure 3: Modulus Elasticity of vulcanizates filled with UNS and CNS

Abrasion Resistance - Abrasion resistance refers to the rubber's ability to withstand mechanical action such as scratching, grinding, or erosion that seeks to strip material from its surface over time. It is an important property that determines the useful life of rubber products (Akinlabi *et al*., 2018). At 15% for both carbonized and uncarbonized, high abrasion resistance was observed. This suggests that there is high dispersion of the filler into the NR.

At higher percentage, a low abrasion resistance was observed indicating that there is a lower crosslink between the NR and the Neem seed when compared to CB. The abrasion resistance of vulcanized rubber has an optimal value with increasing crosslinking density (Do *et al.*, 2020).

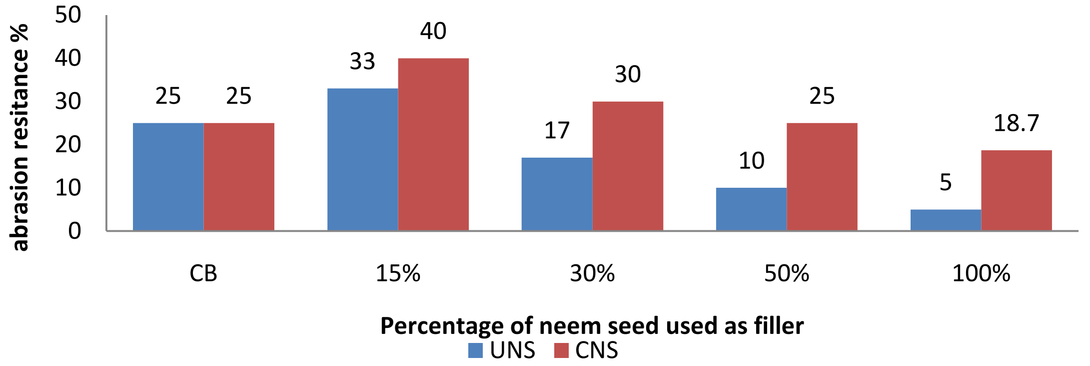

Figure 4: Abrasion resistance of vulcanizates filled with UNS and CNS

Hardness - The hardness of natural rubber vulcanizates filled with the uncarbonized and carbonized neem seed is shown in Figure 5. The resistance to indentation is the description of hardness. It was found that the hardness value range from 7.5 for 100% UNS-filled vulcanizate to 29.1 for 15% CNS. Hardness value reduced as the ratio of neem seed was increased. Due to the low crosslink density between the Natural Rubber and Neem seed at a high percentage, the hardness reduced.

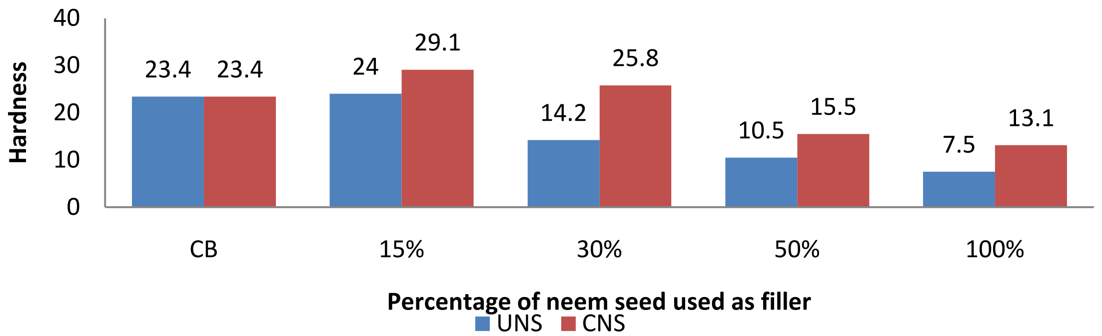

Figure 5: Hardness of vulcanizates filled with UNS and CNS

SEM – EDX Analysis

The SEM analysis of natural rubber vulcanizates filled with the 100% UNS, CNS and CB respectively is shown in Figure 6 with a summary of elements presented in Table 4.

Scanning Electron Microscopy gave the details on the morphology of the vulcanizates. From the result, Carbon black has the best dispersion followed by the carbonized seed, with uncarbonized seed showing uneven dispersion. This explains why the 100% Carbon black showed better physico-mechanical properties than 100% CNS and UNS. The presence of more Carbon in the CB vulcanizates as shown in Table 3 gives better crosslinks and therefore better physicomechanical properties.

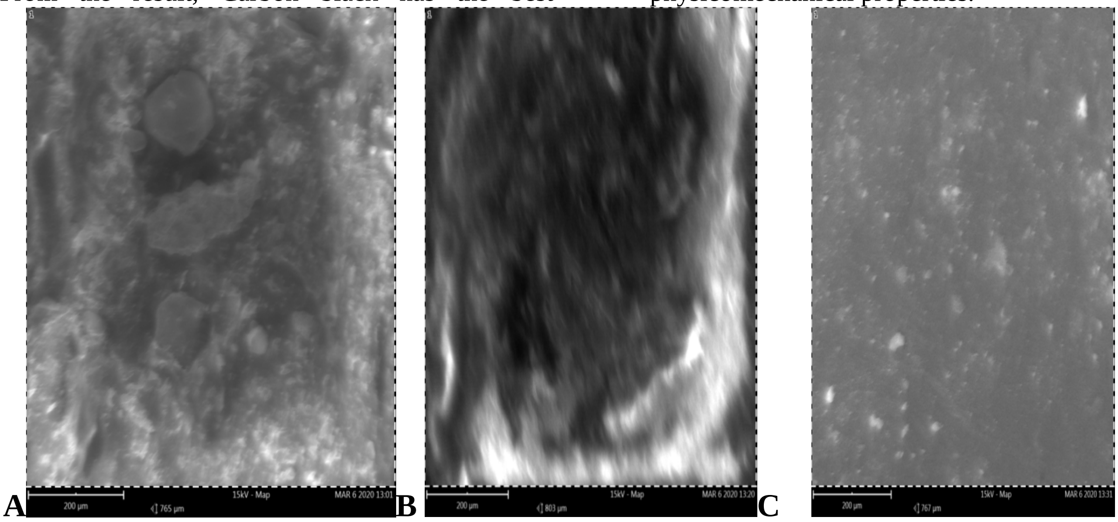

Figure 6: SEM image of vulcanizate filled with (A) 100% UNS (B) 100% CNS (C) 100% CB

Table 4: SEM-EDX Analysis of vulcanizates filled with uncarbonized neem seed, carbonized neem seed and carbon black

Element	Vulcanizates with 100%UNS	Vulcanizates with 100%CNS	Vulcanizates with 100%CB
Si	16.94	15.03	7.18
C	38.62	44.43	59.62
K	6.68	5.32	3.17
S	7.83	8.80	10.26
Ca	5.85	7.46	4.37
Cl	5.07	3.70	3.15
Al	0.00	5.49	3.41
Ag	1.53	0.86	1.36
Mg	3.73	2.87	2.27
Ti	1.77	0.00	0.00
P	2.19	2.11	2.18
Fe	1.20	0.00	2.27
O	1.99	1.38	0.00
Na	0.84	1.18	0.94
Ni	0.66	0.77	1.19

CONCLUSION

The research work has revealed the potential of neem seed as filler in natural rubber compounding. The investigated physico-mechanical properties were comparable to those of carbon black, with better properties when a low percentage of seed (15&30%) was used to fill the vulcanizates. This shows that the seed when used with Carbon black at a low percentage can help achieved enhanced properties for the vulcanizates.

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