

Utilization of Agricultural Wastes as Filler in Natural Rubber Composite: Opportunities for Property Enhancement, Sustainable Waste Management, and Waste-To-Wealth Conversion

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Abstract

In this research, rubber composite was produced with natural rubber, modified periwinkle shell, carbon black (reference filler) and other additives using Banbury mixer, two-roll mill and compression moulding machine at the filler contents of 0 - 20 pphr and subjected to some physical property assessment. Mechanical property results of rubber/carbonized and uncarbonized periwinkle shell powder composite respectively obtained at the maximum filler content revealed improvement in tensile strength, modulus, hardness, abrasion resistance, specific gravity and reduction in elongation at break, flame retardancy, water absorption and compression set. Morphological analysis of composite samples with SEM provided evidence of uniform dispersion and interfacial interactions. Rubber/carbon black composite exhibited better improvement, but modified periwinkle shell is a substitute to carbon black in shoe soles and foot mats. The research provides means to manage periwinkle shell waste and convert it to wealth.

Keywords: *Natural Rubber; Composites; Periwinkle Shell; Mechanical Property; Wastes Management.*

1.0 INTRODUCTION

The combination or blending of two or more materials such as filler and matrix with other additives of different characteristics to obtain a material possessed with enhanced and specific multifunctional properties is regarded as hybrid composites. Rubber composite which is a polymer composite is a typical example of hybrid composite, and it involves the introduction of fillers and other additives into the polymer matrix to modify the processing characteristics of the matrix and provide the essential or required multifunctional properties¹⁻³. Thus, the involvement of filler from different sources and other additives in processing of rubber to finished products has improved the mechanical properties, end-use rubber applications and their service properties as well. Also, there is significant reduction in the material cost with enhanced quality control resulting from adequate and proper filler selection during rubber processing⁴⁻⁸. In rubber technology, the sources of rubber matrix are majorly from synthetic sources via polymerization reaction and natural sources via tapping techniques. The sources of rubber, their mode of processing, filler addition and environmental conditions have significant role to play in the individual characteristics of rubber, their limitations and usefulness. In addition, the effect of filler on rubber matrix is governed by nature of filler surface, availability of varying functional groups presents within the filler molecular structure and their compatibility (interfacial interaction properties) to build or form a spatial network with rubber matrix⁹⁻¹¹. In polymer industries, inorganic fillers such as calcium carbonate, talc, mica, glass

fibres, carbon fibres, etc. are extensively utilized to re-adjust the behaviour or performance of polymers in service environment. Thus, particulate fillers from inorganic sources provide temperature or heat resistance, rigidity or stiffness to polymer matrix but their high cost together with abrasive response to the processing equipment are their challenging factors. Fillers from agricultural wastes receive tremendous acceptance from polymer-based industries due to their advantages of low densities, cost effectiveness, high filling levels, non-abrasiveness, low energy consumption, biodegradability and availability over wide choice of applications¹²⁻¹⁷.

In this study, modified periwinkle shell powder was introduced to natural rubber matrix as filler to attain optimal balance of mechanical properties with reduction in the cost of ingredients as well as transformation of agricultural wastes into useful product. Periwinkle (*Littorina littorea*), a marine gastropod mollusk, belongs to small edible sea animal species. It has a dark brown shell which constituent over 70% of the animal weight, the shell has no identified applications and litters our markets and homes as agricultural wastes¹⁸. Hence, the inclusion of periwinkle shell powder in NR composites is therefore hoped to transform wastes to wealth, solve environmental pollution problem, identify material application of periwinkle shell and produce biodegradable and compostable composites.

Natural rubber (NR) is a biodegradable and renewable material with useful applications in automobile, defence, medical, pharmaceuticals, domestics, sports and household products as result of its excellent features such as resilience, abrasion resistance, elasticity, tensile strength and modulus. These remarkable characteristics effect possessed by NR was accrued from induced crystallization due to straining effect on the molecular structure. However, NR is susceptible to ultraviolet, ozone and oxidizing agent attack with minimal resistance to some solvents attack¹⁹⁻²³. These shortcomings contribute immensely in the limitation of NR utilization in many industrial products and applications. Natural rubber filled composites are polymorphous material containing soft and hard regions and recently they have garnered lots of interest due to their enormous display of intermediary characteristics and ease of production with reduced cost. For instance, Barrera and Cornish (2017)¹⁶ reported that rubber composite produced by combination of natural rubber and renewable filler with nano-size characteristics possessed high performance with reduction in the dependency on petroleum products, and also rubbers from different sources possess different macromolecular structure and the presence of multiple fillers within the rubber matrix exhibits uncommon, combined properties which cannot be achieved by single conventional fillers. Utrera-Barrios et al. (2012)¹⁰ noted that combination of conventional and in situ generated fillers in rubber composite improved the mechanical properties of the composites. Surya, Marpongahtun and Hayeemasae (2023)⁸ noted that introduction of silane with natural rubber -silica composite improved hardness, tensile and morphology behaviours of the rubber composite. De Carvalho et al., (2024)⁴ reported the introduction of polyurethane filler within the natural rubber and styrene/butadiene rubber matrix respectively improved mechanical and reinforcing property together with increase in cross-link density as a barrier against solvents. Phuhiangpa et al., (2020)²⁴ reported that the use of calcium carbonate as filler natural rubber composite has great potential in modifying the properties of rubber products. Teh et al. (2006)²⁵ noted that presence of organoclay improved the tensile strength, rheological and tear properties, crosslink density of the natural rubber nanocomposite whereas weight-swelling ratio decreased. Chandrana et al. (2015)²⁶ investigated the effect of different fillers on curing, mechanical properties and morphology studies of different natural rubber composites and reported bio-filler materials exhibited more suitable mechanical performance improvement in rubber applications. Sivaselvi et al. (2021)

reported the improvement on mechanical properties (tension, abrasion and wear resistance) of natural rubber composite with carbon black (N220) and silica as fillers. Dechojarassri et al. (2017)¹ investigated the impact of waste tire rubber, rice husk ash and starch sludge along with commercial reinforcing fillers (carbon black and silica) on mechanical properties of natural rubber composites in the presence of malleated natural rubber or silane as a coupling agent, and reported that rice husk ash gave higher tensile strength compared to starch sludge and waste tire but has similar strength to silica and malleated natural rubber was better than silane.

There has not been much research done with regards to use of sea animal shell as fillers for rubber matrix in polymer composite. Therefore, this research reports the preparation of natural composite with different forms of periwinkle shell particles sourced locally. In addition, the prepared composite samples obtained were subjected to characterization for determination of some mechanical properties of the resultant composite. We hereby report that the use of modified periwinkle shell powder as filler from agricultural wastes for natural rubber filled composite has not been researched on.

2.0 EXPERIMENTAL

2.1 Materials Used

The materials used are; Analytical reagents (Stearic acid, Zinc oxide, Mercapto benzothiazole disulphide (MBTS), Tetramethyl Thiuram Disulphide (TMTD), Paraffin oil, Sulphur), rubber crump, periwinkle shell, Equipment used include the following; grinding mill, display tray (for displaying the sample), electronic digital weighing balance, Sieve (45µm), carbonizing furnace, two roller mill, press moulding machine, mould (male and female part), universal testing machine, compressor machine, abrader, SEM tester, durometer

2.2 Preparation materials

The material preparations done in the research include the following;

(a) Preparation of periwinkle shell powder

The periwinkle shell, an agricultural waste, used for the research was obtained from Federal University of Technology Owerri, Imo State and identified in the Department of Crop Science, Federal University of Technology Owerri, Imo State. Weighed quantity of fresh periwinkle shell obtained was thoroughly washed with distilled water to remove dirt and dried thoroughly. The prepared shell sample was pulverized to fine powdered samples using locally fabricated milling machine. The particulate sample was seized to a mesh of 45 µm, afterwards it was carbonized at 800 °C for 3 h and kept for preparation of rubber composite.

(b) Preparation of natural rubber composites

The rubber composite samples were produced with formulation presented in Table 1.

Table 1: Compounding formulation rubber (parts per 100 parts of rubber by weight) composite

Ingredients	NR/CB	NR/UCPSP	NR/CPSP
Natural rubber	100	100	100
Zinc oxide	5	5	5
Stearic acid	2.5	2.5	2.5
Carbon black, CB (330HAF)	3, 7, 10, 13, 16, 20	—	—
UCPSP	—	3, 7, 10, 13, 16, 20	—
CPSP	—	—	3, 7, 10, 13, 16, 20

Oil	3	3	3
MBTS	1.5	1.5	1.5
TMTD	2	2	2
Sulphur	3	3	3

UCPSP - Uncarbonized periwinkle shell powder; CPSP - Carbonized periwinkle shell powder

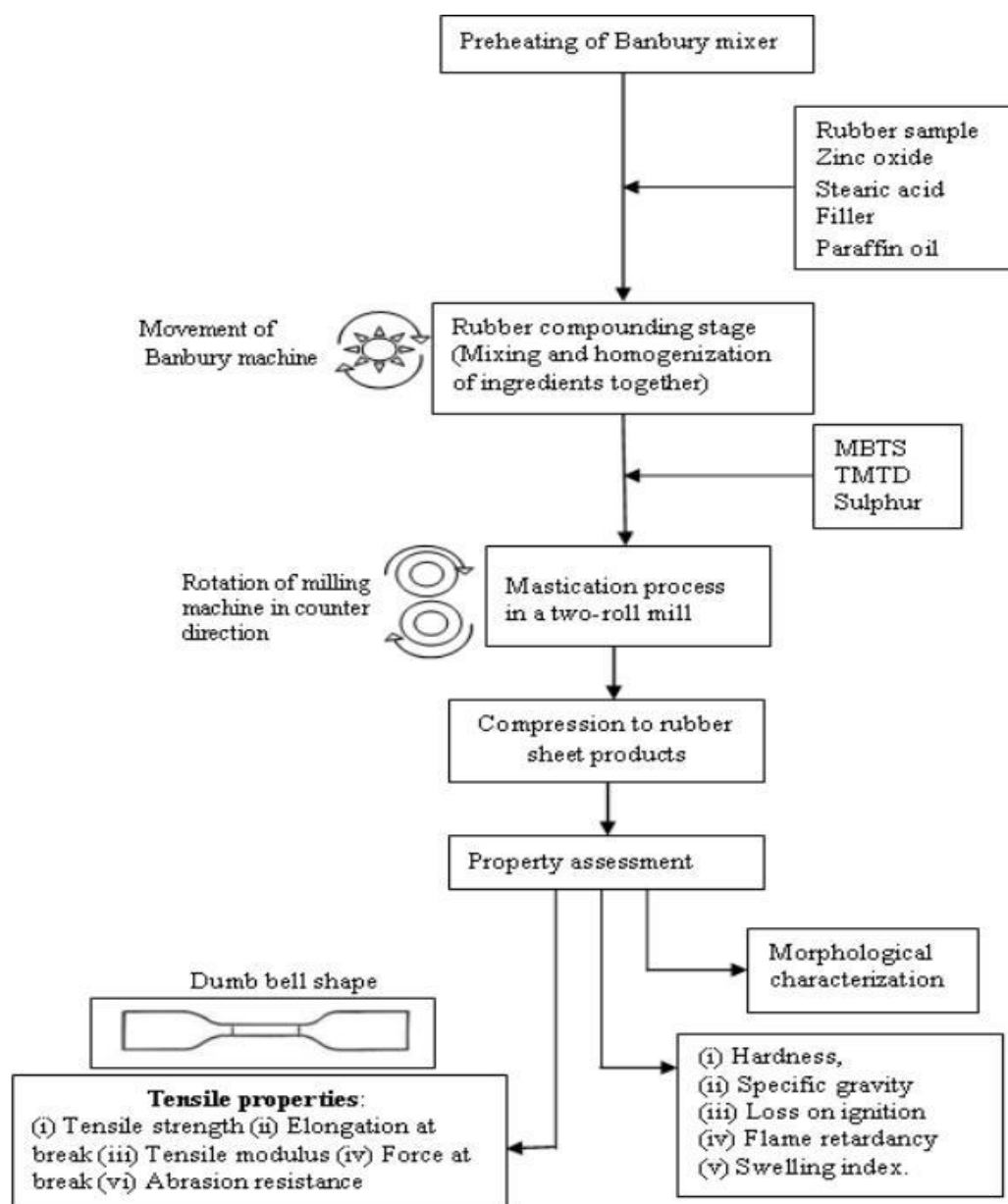


Fig 1: Experimental process flow design or rubber compounding, mastication, compression and property assessment

The experimental procedure was according to the experimental process flow design shown Figure 1. Weighed amount of natural rubber sample together with other compounding ingredients excluding sulphur and accelerators were placed in a Banbury mixer preset at 145 - 150 °C for the mastication of the ingredients. The mixture produced was transferred to a two-roll mill rotating in counter direction to transform it from irregularly shaped mass to suitable sheet. Before the introduction of the sulphur and accelerators there was reduction in the

temperature of two roll mill from 160 - 80 °C to prevent premature curing of the compound mix. Finally, the resultant mixture obtained was placed in mould and compressed with hydraulic press at 127 °C and 4 MPa for 10-15 min and compressed sheet was obtained. The above process was repeated for other filler contents of carbon black, uncarbonized and carbonized periwinkle shell powder respectively. The vulcanized product samples obtained were subjected to characterization and analysis in triplicates and mean values were recorded.

3.0 RESULTS AND DISCUSSION

3.1 Mechanical property response of natural rubber filled composite

Mechanical properties of a material are regarded as the characteristics possessed by the material that describe or define its behaviour under various forms of mechanical loading, and it is influenced by the nature of the materials (matrix), nature and content of filler, processing conditions, service environment, etc. These properties are crucial for understanding and interpretation of material's behaviour during practical applications and are determined using some tests and measurements. The mechanical properties investigated using standard procedure in the course of this study include the following; tensile strength, elongation at break, tensile modulus, hardness and compression set. Other end-use properties assessed include; flame retardancy, water absorption rate and specific gravity.

(a) Tensile strength

This is an essential mechanical property parameter that provides information on the utmost amount of tensile (pulling or stretching) stress a material can sustain or withstand before deformation sets in and determines the suitability of a material under various structural and load bearing applications. In the course of this research, the characteristics of uncarbonized periwinkle shell powder (UCPSP) and carbonized periwinkle shell powder (CPSP) have been assessed along with carbon black which was used as control filler in this work and are illustrated in Figure 1. Data on Figure 2 revealed that presence of filler (CB, UCPSP and CPSP) content within the rubber matrix caused the tensile strength of the composite to increase reaching the maximum tensile strength of 38.2896, 33.5944 and 28.4567 N/mm². There exist some results in rubber composites presented in scientific literature showing the increase tensile strength with increase in filler^{26, 28, 29}. The order of increment in the tensile strength result obtained is as follow; NR/CB > NR/CPSP > NR/UCPSP. Generally, it is believed that the three main factors that contributed immensely to the trend observed include the surface area of the filler, dispersion and interfacial interaction. Thus, increased surface area (that is, smaller particle size) of filler encourages the improvement or enhancement on the tensile strength of the composite. Also, better or good filler dispersion within the matrix structure as well as good matrix-filler interaction has the potentials to modify the physical and chemical characteristics of the matrix with significant improvement on the tensile strength of the composite. On comparing the characteristics of the fillers employed, it was observed that the carbon black (reference filler) exhibited considerable increase in the rubber filled composite in terms of tensile strength compared to UCPSP and CPSP, thus suggesting that the filler performance may be attributed to its carbon content. Hence, high carbon content value of filler associates with better reinforcing potentials of filler in a composite³⁰. The present study revealed that the observed increment in tensile strength of the rubber composite is the resultant additional reinforcement effect on polymer matrix phase of the composite which depends on the nature of polymer, filler geometry and interfacial interaction. The interfacial interactive forces expected caused the degree of reinforcement on the rubber composite to increase and the better

strength property shown by carbonized periwinkle shell powder could be attributed to its geometry. This is because irregularity within filler shape does not support improvement on the composite strength as well as possess the poor ability during transfer of stresses to polymer matrix.

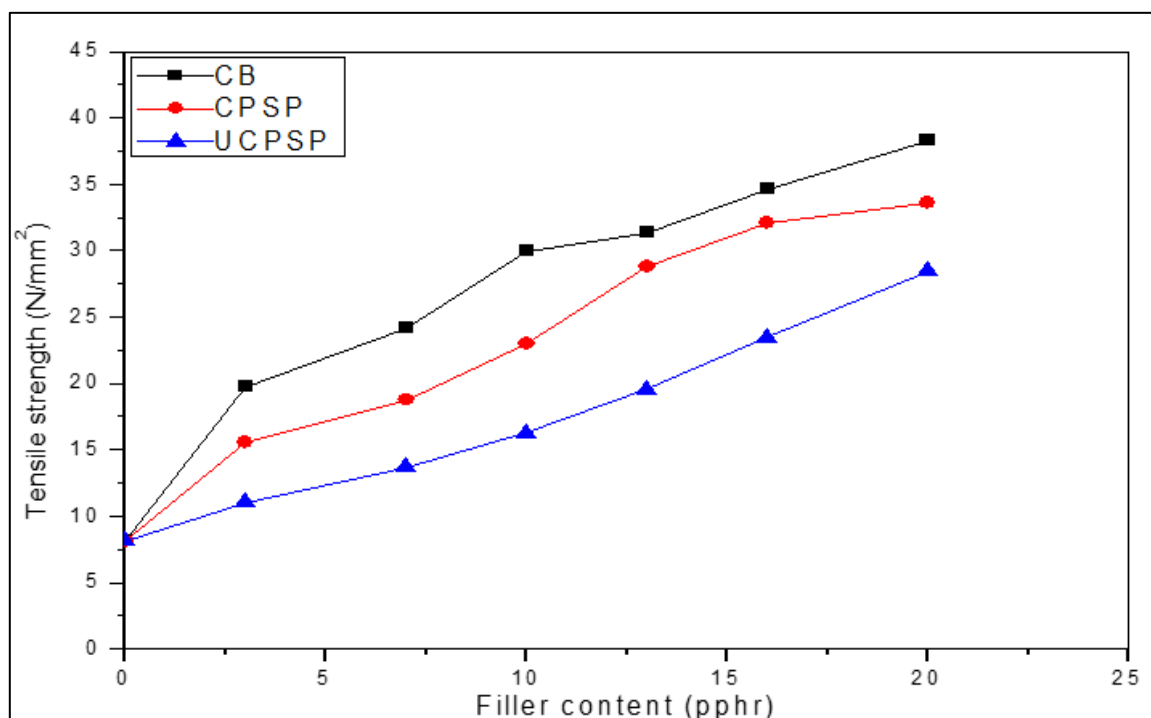


Fig 2: Filler content effect on tensile strength of natural rubber filled composite

(b) Elongation at break

This is a parameter that evaluates the material's ability or response to withstand or sustain deformation under tensile stress before failure sets in. It is essential in the prediction of ductility and flexibility as well as provides useful insights on the mechanical performance and durability of the composites, thus making it a critical factor to consider in engineering design and material selection. In addition, it gives information about the strain experienced by a material subjected to tensile test. High elongation at break implies that a material that can significantly stretch to a certain limit before breaking whereas low elongation at break suggests an expectant fractures potential with little deformation due to the brittle nature of the material.

The results of elongation at break (EB) for the natural rubber filled composite with respect to effect of filler content and variation respectively is presented in Figure 3. It is observed that unfilled natural rubber exhibited EB of 721.7224 % and the addition of filler into the rubber vulcanizate caused the EB value to decrease irrespective nature of the filler.

A close inspection revealed that response of carbon black filler on rubber vulcanizate had better effect of EB value compared to UCPSP and CPSP. It was expected that presence of the fillers within the rubber vulcanizate would stiffen the rubber chains, thereby restricting the movement of polymer chains to a certain degree. However, a contrary trend was observed, that is, decrease in EB value with increase in filler content. This result is an evident that all the fillers used did not impact observable stiffened characteristic effect on the rubber vulcanizate that would resist the elongation on application of strain effect. The EB result obtained is similar to some findings reported in the literature²⁶.

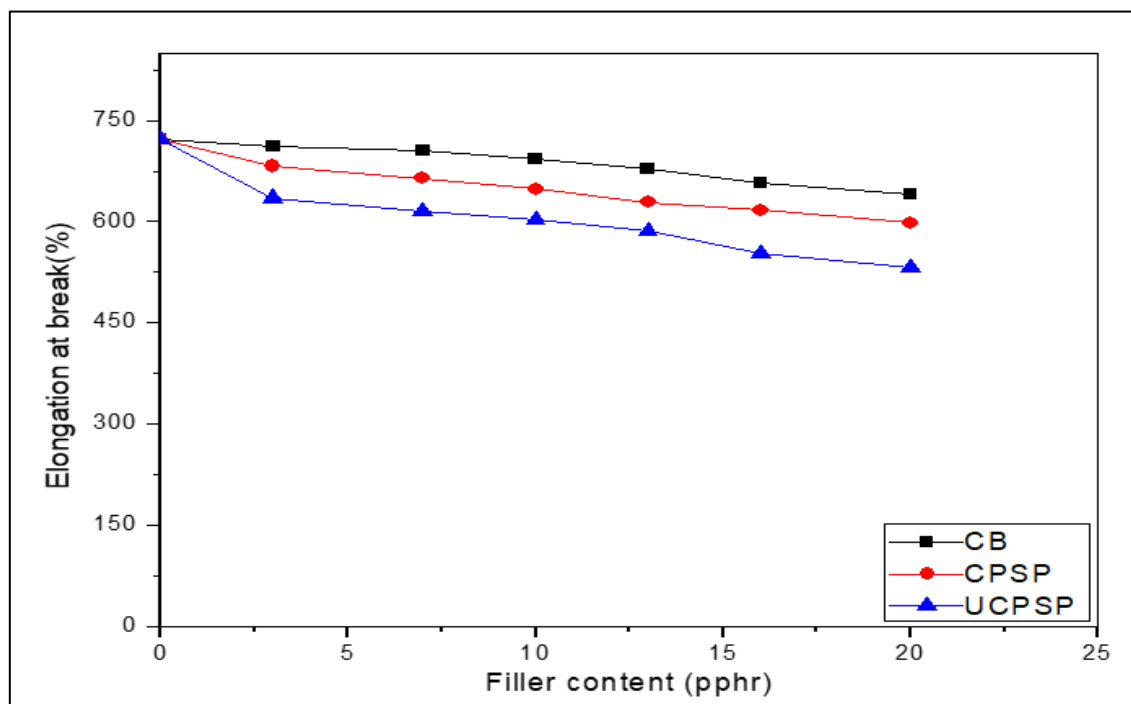


Fig 3: Filler content effect on elongation at break of natural rubber filled composite

(c) Tensile modulus

This is a characteristic parameter that evaluates the stiffness of a material subjected to deformation under tensile stress. It is affected by some factors such as nature or type of filler, content of filler, nature rubber matrix, filler dispersion, etc. Figure 4 presents the result of filler content effect on tensile modulus of natural rubber filled composite as shown below.

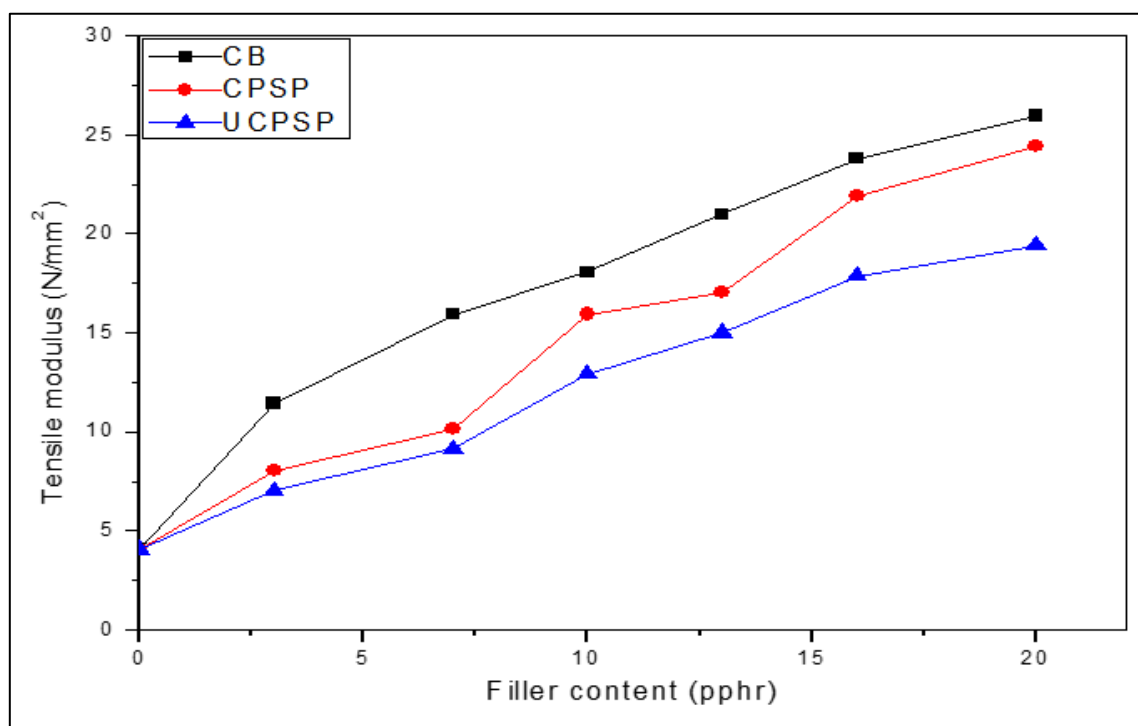


Fig 4: Filler content effect on tensile modulus of natural rubber filled composite

It was observed that presence of filler within the rubber vulcanizate increased steadily the tensile modulus of the natural rubber filled composites for all the filler content. The effect of carbon black on the tensile modulus property of the composite was more pronounced compared to CPSP and UCPSP. The expected observation suggests existence of good matrix/filler interaction which is an essential factor to consider in predicting modulus and support the evidence that natural rubber vulcanizate and carbon black always form strong adsorptive bond with each other. In addition, it could be inferred from the Figure 3 that carbon black possess high surface area which gave room for greater stiffness in the composites, thus indicating the role of surface activity characteristics in polymer/filler interaction. The tensile modulus result of rubber composite observed in this work coincides with some existing reports on natural rubber/filler composites^{31, 32}.

(d) Hardness property of natural rubber filled composite

This is an essential parameter that measures the ability of the composite to resist deformation and Figure 5 presents the results of filler content effect on the hardness performance of rubber/filler composite. It is revealed that natural rubber vulcanizate has the hardness value of 37.4307 shore A while the presence of carbon black and periwinkle shell powder respectively at different contents or amounts exhibited appreciable increase in the hardness value of the composites. The observed trend is an indication that fillers used in this work contributed to enhanced impact strength and abrasion of the natural rubber vulcanizate. There are some studies in the field of rubber/filler composites that have reported general improvement on hardness performance of natural rubber vulcanizate by filler addition^{33, 34}. In addition, carbon black introduced better hardness improvement of natural rubber filled composite compared to UCPSP and CPSP, thus suggests the evidence of more uniform dispersion and better carbon black/rubber vulcanizate interaction.

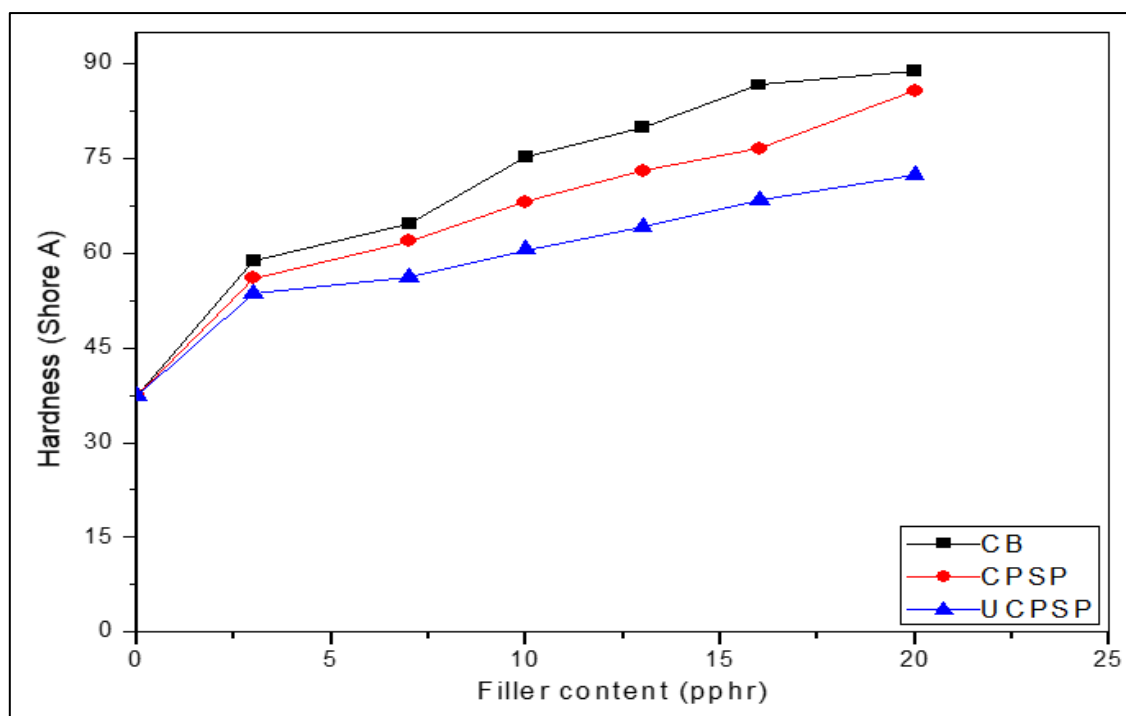


Fig 5: Filler content effect on hardness property of natural rubber filled composite

(e) Abrasion resistance property

The abrasion resistance of a composite material is regarded as the capability of a composite material withstand or resist tear and wear (or degradation) on the surface of the composite caused because of mechanical action or effect such as scrapping, rubbing, erosion etc. It is an essential parameter in determination of end-use application of composite material specifically in a service environment where the surface of materials is subjected or exposed to friction and contact with other surfaces which may lead to surface damage, material loss, loss of aesthetic value, etc. It is determined by some of the following factors; nature of polymer matrix, nature of filler, interfacial interaction of bonding between the matrix and filler, surface treatment, process of manufacturing, etc. The result filler content effect on abrasion resistance of rubber/ filler composites in this study is presented in Figure 6. Information from Figure 6 revealed that carbon black and modified periwinkle shell respectively improved the abrasion resistant characteristics of the natural rubber filled composites produced as the filler content increased. Thus, natural rubber composite with carbon black, carbonized and uncarbonized periwinkle shell powder exhibited the abrasion resistance of 40.3456, 37.4758 and 34.5768 mm³/rev respectively at the maximum filler content or 20 pphr. The observable trend could be credited to the extent of filler dispersion with the matrix and ability of the filler to create the lubricating effect on the composite surface which reduced the impact of rubbing or scratching effect on the surface.

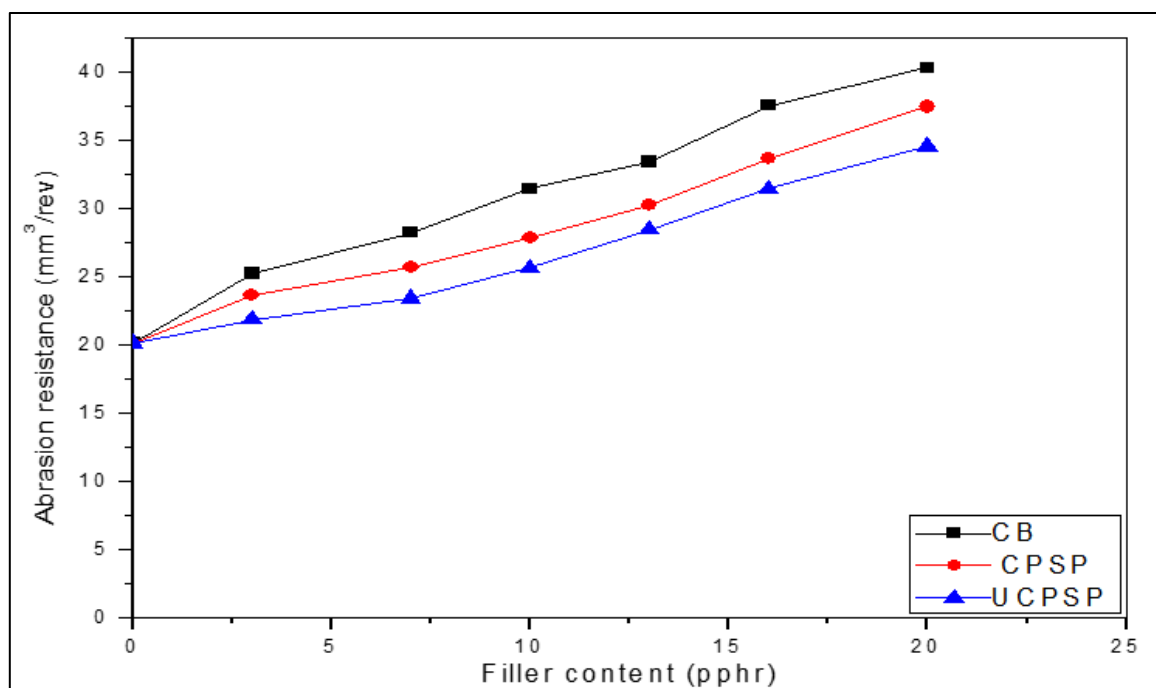


Fig 6: Filler content effect on abrasion resistance of natural rubber filled composite

(f) Compression set property

In this study, ASTM D395 standard testing method was employed to evaluate the compression set of rubber composite samples and the results obtained are presented in Figure 7. The compression set of a natural rubber composite is an essential mechanical parameter that measures the capability of the rubber composite to return to its original size (thickness) after being subjected to compressive effect for a prolonged period.

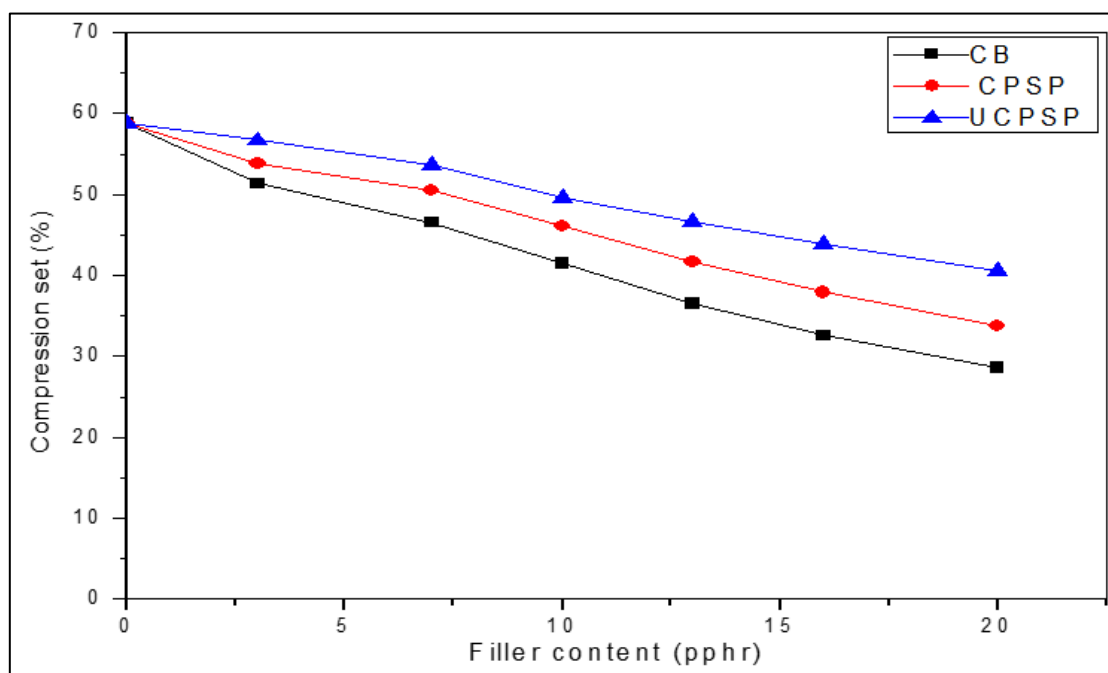


Fig 7: Response of filler content on compression set of natural rubber filled composite

It is a useful parameter in considering the end-user applications of rubber composite in terms of long-term performance or stability and durability specifically in service environment where materials are subjected to repeated or continuous compressive action. This parameter is affected by some factors such as rubber formulation (which include the followings; nature of rubber, type and nature of filler, additives, etc.), curing process and environmental conditions (which include; temperature, compression time or duration and humidity).

It is evident that the percentage of compression set of the natural rubber composite was lowered by the addition of carbon black and modified periwinkle shell in the natural rubber vulcanizate reduced the percentage compression set of the natural rubber composite. Also, the reduction trend observed in the composite was dependent on filler content. The order of percentage compression set value of the rubber composites obtained is as follows: uncarbonized periwinkle shell powder > carbonized periwinkle shell powder > carbon black. Evidently, the results of compression set revealed that curing performance of the composites and the order is as follows: carbon black > carbonized periwinkle shell powder > uncarbonized periwinkle shell powder. It is noteworthy that the rubber composite has been adequately cured has a lower set parameter for compression

(g) Flame retardancy property

This is an essential parameter used to measure the ability of the rubber composite to retard the burning rate when subjected to open flame. Figure 8 presents the response of filler on natural rubber vulcanizates. Critical inspection of data in Figure 8 revealed that presence of modified periwinkle shell powder and carbon black respectively decreased the burning rate of natural rubber vulcanizates. Thus, the observed response was dependent on filler content. In addition, it is clear that flame retardant performance is particularly good though it is outweighed by carbon black. This characteristic property could be attributed to greater dispersion of filler particles within the rubber vulcanizates.

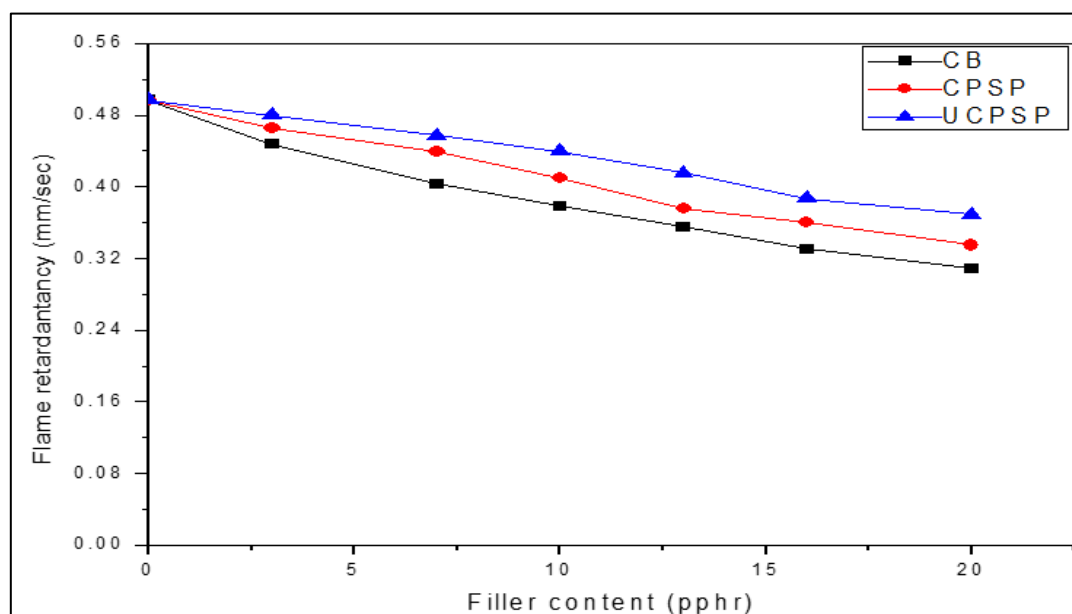


Fig 8: Filler content effect on flame retardant property of natural rubber filled composite

(h) Water absorption rate (%)

The natural rubber filled composite samples produced were placed in glass beaker containing distilled water, kept at room temperature and allowed to stay for the 90 days. The rate of water absorption or swelling index was monitored and determined. The results of swelling behaviour for the different natural rubber filled composites are presented in Figure 9 as shown below.

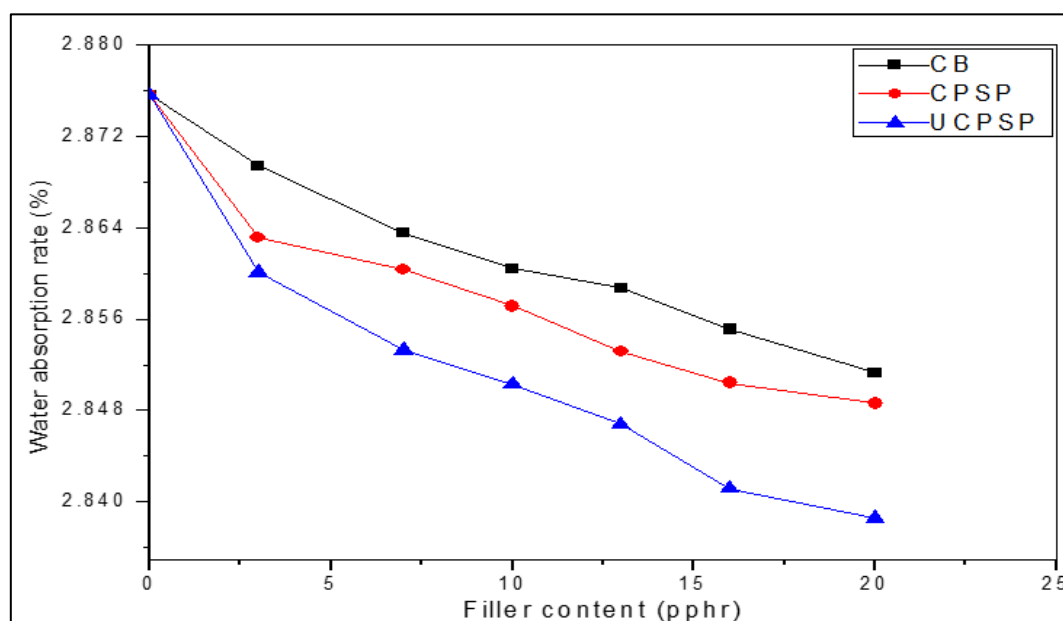


Fig 9: Filler content effect on water absorption rate of natural rubber filled composite

It is observed that percentage water absorption rate of the composite samples produced decreased as the filler content increased. Also, it is worthy to note that reduction in swelling behaviour observed is an indication that filler particles closed the free volume within the rubber

matrix, created greater and uniform crosslinking of rubber matrix and kept the rubber chains closer and intact. Also, rubber /carbon black composite took least amount of water when compared with rubber /modified periwinkle shell composite. In addition, the variations in the water absorption rate observed between carbon black and modified periwinkle shell fillers points out to the water liking/disliking characteristics of the fillers.

(i) Specific gravity

The response of carbon black and modified periwinkle shell on the specific gravity of rubber/filler composite is presented in Figure 10. Critical evaluation of data on Figure 10 revealed that increase in the quantity of filler introduced in the composite samples resulted to composite with increased density compared to unfilled composite samples. This characteristic trend observed presents similar result with the one given by Mishra and Shimpi³⁵ who reported a gradual increase in density of rubber composites due to filler quantity increase in a composite between styrene-butadiene rubber and CaCO_3 as a filler and linseed oil as an extender. The increase in density of the composite due to increase in filler content is an indication there exist good surface activity relationship between the rubber matrix and filler at the 45 μm particle size. This also suggests that smaller particulate fillers introduce more uniformly dispersed phase into the rubber matrix with the rubber chains being more intact during crosslinking activity. In addition, rubber composite with carbon black recorded higher specific gravity followed by carbonized and uncarbonized periwinkle shell powder respectively. This result could be attributed to the fact that carbon black has more or better compatibility, interfacial interaction and uniform dispersion with natural rubber compared to modified periwinkle shell powder.

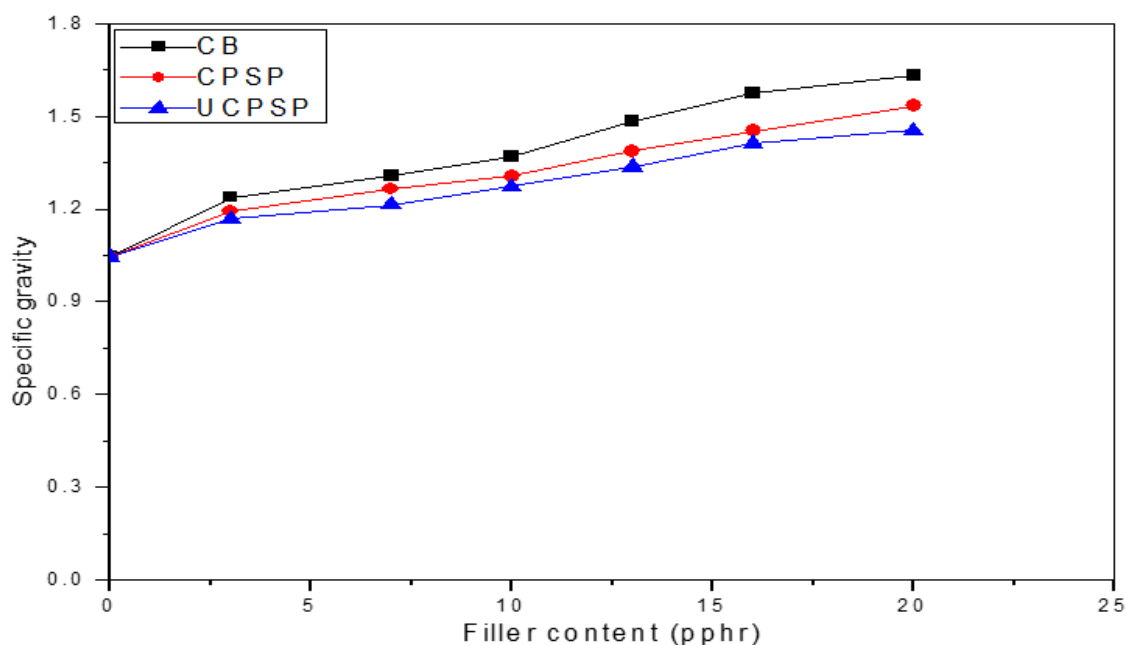


Fig 10: Response of filler content on specific gravity of natural rubber filled composite

3.2 Structural characterization analysis

The rubber composite samples produced were subjected to morphological characterization using scanning electron microscope and the results obtained are presented in Figure 11. This was performed to evaluate the extent of dispersion of filler within the rubber matrix, nature of mixing among the filler, other additives and rubber matrix within the

composite and extent of interfacial interaction occur within the composite. Figure 11(a) represents the internal morphological structure of unfilled rubber composite, that is, the rubber composite produced in the absence of filler. It is observed that there is evidence of proper homogeneousness between the rubber matrix and other additives introduced into the matrix, and properly bonding structure. Figure 11(b) represents the internal morphological structure of natural rubber/uncarbonized periwinkle shell powder composite. Critical inspection of Figure 11(b) revealed loose interfacial interaction within the internal structure of the composites. In Figure 11(c) and (d) respectively, there is evidence of better interfacial interaction, uniform dispersion and homogeneous mix between the filler particles and rubber matrix, but Figure 11(d) presents better result.

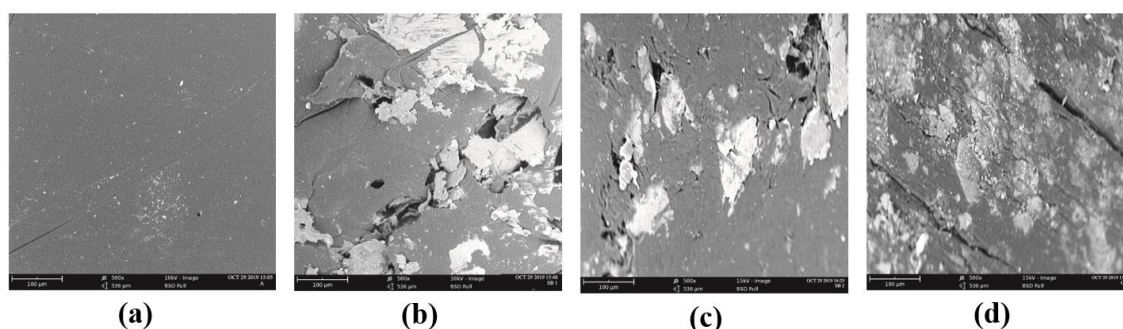


Fig 11: Morphological characterization result of rubber and its composite: (a) Unfilled natural rubber (b) NR/UCPSP (c) NR/CPSP and (d) NR/CB

4.0 CONCLUSION

This presents the natural rubber composites produced with carbonized, uncarbonized periwinkle shell powder and carbon black (reference) respectively and results of some characterized properties of the composites. Tensile properties of natural rubber filled composite such as tensile strength and modulus, hardness, abrasion resistant and compression set values exhibited appreciable values compared to unfilled rubber vulcanizate at all filler content considered. However, results of natural rubber/carbon black composite outweighed the tensile strength and modulus, hardness, abrasion resistance and compression set (curing property) values of both the unfilled rubber vulcanizate and NR/modified periwinkle shell powder composites. A close inspection on the end-use properties of the rubber composite showed that carbon black filler possessed greater advantage in flame retardancy, water absorption rate, specific gravity over the modified periwinkle shell in the production of rubber composites. In addition, the result of morphological analysis revealed the extent of uniform dispersion, homogeneous mix and interfacial bonding between the filler and rubber matrix. Our experimental results revealed that although carbon black possess better potentials compared to modified periwinkle shell in the development of rubber, but the agricultural filler can serve as a substitute or replacement filler in the development of rubber shoe sole and foot mat. In addition, the study provided a means to transform the wastes generated from handling periwinkle shell to useful engineering materials

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Conflict of Interest

The authors hereby state that there are no conflicts of interest regarding the completion of this work

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