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EFFECT OF CELLULOSIC MICRO- AND NANO- SIZED FILLERS ON STRENGTH AND MICROSTRUCTURE OF RUBBER COMPOSITES

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Abstract

The tensile strength of polymer composites is basically influenced by the geometry (size and shape) of the reinforcing material as well as interfacial interaction and bonding between the polymer matrix and reinforcing phase. This work compares the effect of microfillers to nanofillers of coconut husk, bamboo and cotton linter on the tensile strength and microstructure of vulcanized rubber matrix. The various composites were formulated and prepared using filler loading of 5, 10, 15, 20, 25 and 30 parts per hundred of rubber (pphr) in rubber matrix for both micro- and nano- fillers of the various biomass through friction shearing and compression moulding processes. Results revealed that the tensile strength of the nanocomposites predominantly increased from 1.85 MPa for neat sample to maximum values of 3.83, 3.16 and 3.85 MPa respectively for composites with 25pphr of coconut husk cellulosic nanoparticles (NR-CHNC$_{25}$), 30pphr of bamboo cellulosic nanoparticles (NR-BNC$_{30}$) and with 25pphr of cotton linter cellulosic nanoparticles (NR-CLNC$_{25}$) conversely, the tensile strength of their counter microcomposites changes from 1.85MPa for neat sample to maximum values of 1.68, 1.67 and 2.46 MPa for composites with 10pphr of coconut cellulosic microparticles (NR-CHMC$_{10}$) 15pphr of bamboo cellulosic microparticles (NR-BMC$_{15}$) and 30pphr of cotton linter cellulosic microparticles (NR-CLMC$_{30}$) respectively within the loading range employed in this experiment. Scanning Electron Microscope (SEM) images of microcomposites showed cases of microfiller debonding and pull-out from the rubber matrix. Hence the improved tensile strength of nanocomposites over their counterpart microcomposites was attributed to the larger surface area provided by nanofillers for interfacial bonding and effective stress transfer.

1.0 INTRODUCTION

The use of agricultural residue/resource for value added materials offer dual role of converting waste to wealth and environmental protection. Coconut husk, bamboo and cotton lint are lignocelluloses biomass that can be utilized in the preparation of rubber composites due to the high strength and stiffness of their cellulose components [1-3]. However, the hydrophilicity of cellulose due to polar hydroxyl groups makes it interaction with non- polar rubber matrix difficult at microstructure level [2,4]. The use of these materials as nanofillers or nano-size particles can offer large active surface area for adequate surface bonding and interaction with rubber matrix at microstructure level [5-7]. The factors that determine the influence of fillers on the tensile strength of rubber matrix are particle size, shape, surface activity and strength of the particulate filler, note that the categories of fillers that are able to distribute applied

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stress within the rubber matrix will increase tensile strength at optimal loading range.

Surface activity relates to the compatibility of the fillers with rubber matrix and the ability of the rubber to adhere to the filler [8-9]. Fillers with smaller particle sizes provides large active surface area for interfacial interaction and bonding.The strength of materials is controlled by their microstructures, pore geometries and chemical compositions of their constituents [10-11]. The constitutive relationship of microstructure greatly influences the behavior of the bulk material [5, 13]. The precise relationship between strength and microstructure of polymer materials /composites is imperfectly understood. However, a fair knowledge is necessary to predict the type of modification in microstructure required for the preparation of composites with optimum strength.

The microstructure of vulcanized rubber composites is made up of randomly dispersed particles or fibres in rubber matrix, hence, the factors that will determine the resultant microstructure and strength of rubber composites are the conformation of rubber chain, geometrical characteristics of particles/fibres, green strength of the rubber and filler, volume fraction of filler in rubber matrix, and nature of filler disposition within the rubber matrix. These factors determine the potential and magnitude of stress distribution within the rubber matrix and consequently the strength of the composites. These factors form the basis for the hypothesis and theoretical modeling of rubber composites [13]. Therefore, this work compares the effects of cellulosic microparticle and nanoparticles used as fillers on the tensile strength and microstructure of rubber composites.

2.0 MATERIALS AND METHODS

2.1 Materials

Dry natural rubber crumb, Stearic acid, Mercaptobenzothiazoledisulfide (MBTS), Trimethyl-quinolone (TMQ), and Zinc oxide were supplied by Tony West rubber factory, Lagos Nigeria. The specifications of the dry rubber according to the supplier were ≤ 0.05% dirt content, ≤ 1.00% volatile content, ≤ 0.7 % nitrogen content, ≤ 0.6 % ash content, minimum of 30 initial plasticity, minimum of 60 plasticity retention index (PRI) and blackish brown in colour. Other compounding ingredients were of rubber processing commercial grade and were used as received. The cellulosic microparticles and nanoparticles used in this experiment were obtained from treated coconut husk, bamboo and cotton linter through mechanical process according to a method already described [14]. The particle size distributions of 32 - 175, 68 – 311 and 620 to 5408 nm for bamboo, coconut husk and cotton linter sources respectively were used as nanofillers while their corresponding micro-fillers were ≤ 125 μm.

2.2 Preparation of Nanocomposites and Microcomposites

Composites of nanoparticles and microparticles (coconut husk, bamboo and cotton linter) and natural rubber as the matrix were prepared using two roll mixing mill in accordance with ASTM D3184-80 method, followed by *in-situ* moulding and curing [15]. The mixing/compounding of the rubber with microfillers/nanofillers and other ingredients such as the vulcanizing and protective agents was performed on a two roll mixing mill. The formulation used in this experiment is presented in Table 1. Note that, three different composites with three reinforcements (coconut husk, bamboo and cotton linters) at nano- and micro-particles levels each were prepared with compositions of 0, 5, 10, 15, 20, 25, 30 parts per hundred (pphr) each. The compounded composites were moulded and vulcanized into appropriate test shapes at 140^{o}C for 13 minutes using compression moulding technique.

Table 1: Formulation of composites

Sample Code	NR	X_j	ZnO	SA	TMQ	MBTS	Sulpur
Neat NR	100	0	5	2	1	2	3
NR – X_5	100	5	5	2	1	2	3
NR – X_{10}	100	10	5	2	1	2	3
NR – X_{15}	100	15	5	2	1	2	3
NR – X_{20}	100	20	5	2	1	2	3
NR – X_{25}	100	25	5	2	1	2	3
NR- X_{30}	100	30	5	2	1	2	3

NR – natural rubber, ZnO – zinc oxide, SA – stearic acid, TMQ – trimethylquinolone, MBTS – mercaptobenzothiazoledisulfide, X = coconut husk cellulosic nanoparticles (CHNC), bamboo cellulosic nanoparticles (BNC), cotton linter cellulosic nanoparticles (CLNC), coconut husk cellulosic microparticles (CHMC), bamboo cellulosic microparticles (BMC), cotton linter cellulosic microparticles (CLMC) and subscript – fillers volume in phr.

2.3 Tensile Strength and Morphology Study

The tensile strength of various micro- and nano-composites was evaluated in accordance with ASTM D 412 using Universal Instron model 3366 machine (UK). Dumbbell shaped specimens with dimensions of 50 x 8 x 4 mm were used to perform the experiment at a loading speed of 80mm/min. The morphology of the fillers and composites samples were studied with the aid of Scanning Electron Microscope (SEM

Phenon World model Prox, Switzerland)), Transmission Electron Microscope (TEM model JEM-2100, USA) and Atomic Force Microscope (AFM easyScan,Nanosurf Switzerland). Point tests sample preparation method in accordance to ASTM was adopted for microscopic analysis.

3.0 RESULTS AND DISCUSSIONS

3.1 Morphology of Nanoparticles

The morphology of nanofillers was investigated with the aid of TEM and SEM, the objective was to study the shapes and packing patterns of various particles. The TEM and SEM images of coconut husk, bamboo and cotton linter based nanofillers are shown in Figures 1-3 respectively.

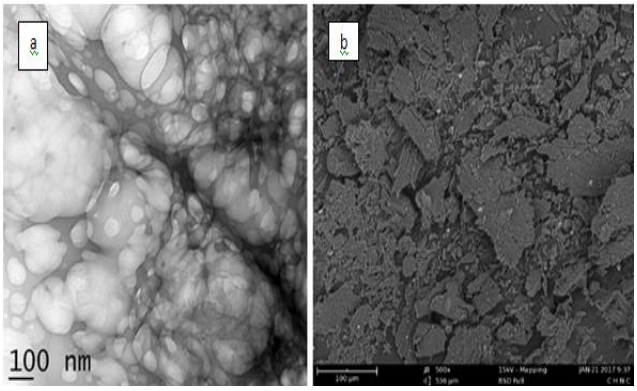

Figure 1: (a) TEM (b) SEM of nanofiller from coconut husk

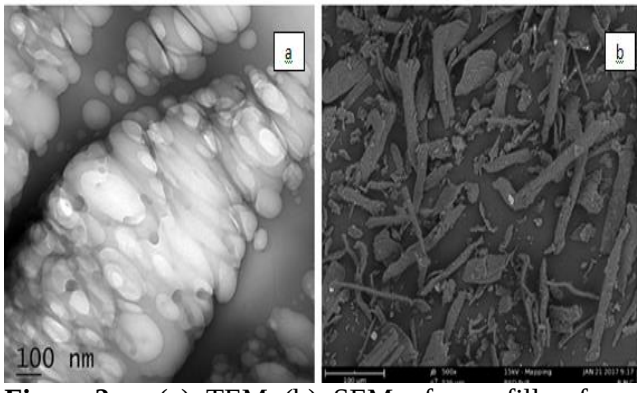

Figure 2: (a) TEM (b) SEM of nanofiller from bamboo

Considering the scale and resolution of particle projection, The SEM images present aggregated particles (microscale) while the individual dispositions of particles were presented by TEM at nanoscale. Coconut husk nanofiller SEM micrograph resembles broken pieces of plate with little or no spatial arrangement suggesting a close packing behavior with high aggregation tendencies probably due to the hyper-active nature of nanoparticle surfaces [16]. The SEM pictures of bamboo and cotton linter nanofillers gave similar look of rope-like or fibrous filaments of varying dimensions. Microgram of cotton linter particle is particularly observed to be curled with adequate spatial arrangements; this is an indication of high potential for self twisting and entanglement [17].

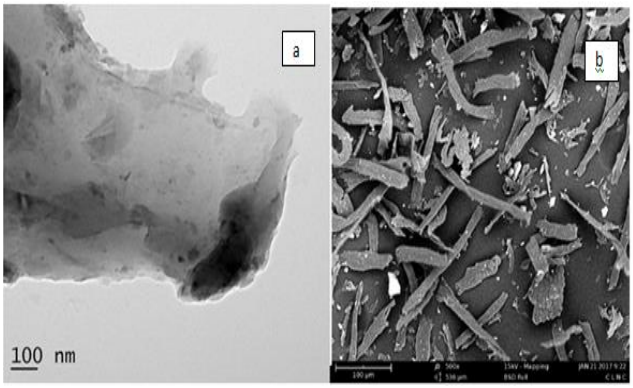

Figure 3: (a) TEM (b) SEM of nanofiller from cotton linter

The TEM images present a clearer picture of the morphology of individual particles within the aggregates such that particles of coconut and bamboo were predominantly ellipsoid while that of cotton linter were fish like in shape. TEM images of coconut and bamboo nanofillers also revealed particles of different geometrical characteristics (varying shapes and sizes). This variation in geometrical properties of the particle is caused by varying shear forces experienced by the particle during ball milling process [18-19].

3.2 Microstructure of Composite Formation

The idealized microstructure of rubber composite formation is illustrated in Figure 4.

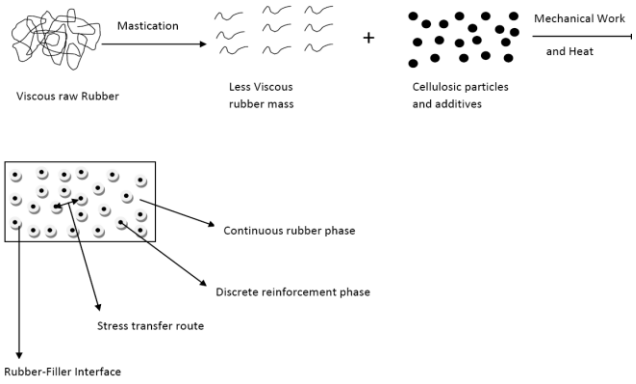

Figure 4: Rubber composite formation

As projected in Figure 4, vulcanized rubber composites are considered to be a system where reinforcement particles (fillers) are embedded in cross-linked rubber matrix [20]. The geometrical characteristics and distribution/orientation pattern of

the fillers within the rubber matrix will dictate the overall microstructure of the rubber composites [5]. For instance smaller particle will offer greater surface area and adhesion index than larger particles, similarly an irregular shaped particle will leave an air gap at interface, this air gap represent zero stress which constitute point of failure when load is applied. The formation of rubber matrix-filler network rather than filler-filler or matrix-matrix networks is important for effective stress distribution within composite microstructure. Therefore the most important aspect of processing is to achieve reduction of the size of filler particles aggregation to the ultimate size necessary for the formation of micro-structural networks that are essential for reinforcement [20-21].

3.3 Tensile Strength of Microcomposites and Nanocomposites

The effects of micro- and nano-fillers obtained from coconut husk, bamboo and cotton linter on tensile strength are presented in Figures 5-7 respectively, while the effect of nanofiller types on tensile strength is presented in Figure 8.

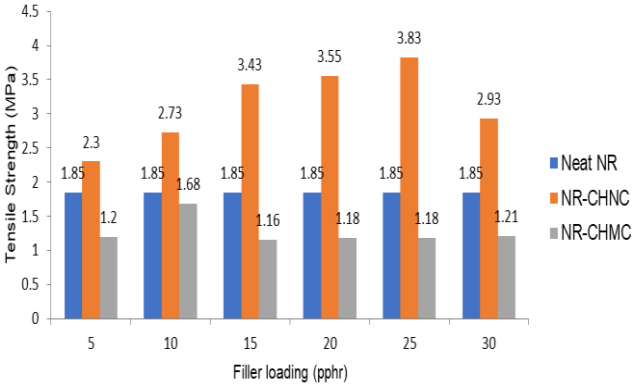

Figure 5: Effect of coconut husk micro and nanoparticles on the tensile strength of rubber composite

In the case of coconut husk composites, the inclusion of micro-sized particles was found to reduce the tensile strength of their resultant microcomposites (NR-CHMC) when compared to the reference neat NR sample and their corresponding counterpart nanocomposites (NR-CHNC). Typically, the highest value of tensile strength for NR-CHMC was obtained at loading of 10 pphr and was 1.68 MPa. This value is less than the tensile strength of the neat NR which was 1.85 MPa. On the other hand, tensile strength values obtained for nanocomposites (NR-CHNC) sample in all loading points (5, 10, 15, 20, 25 and 30 pphr) were far higher than their corresponding microcomposites. Similar trends for nanocomposites and microcomposites of bamboo were also observed.

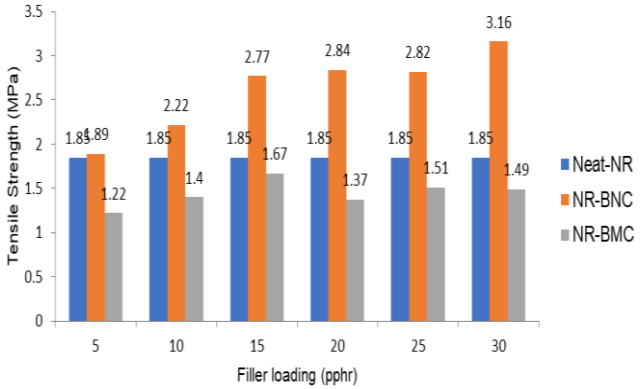

Figure 6: Effect of bamboo micro and nanoparticles on the tensile strength of rubber composite

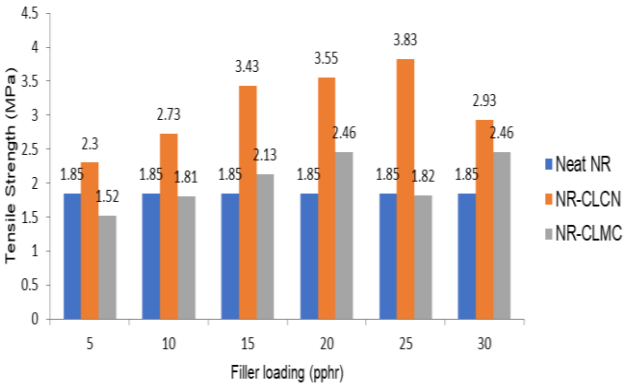

Figure 7: Effect of cotton linter micro and nanoparticles on the tensile strength rubber composite

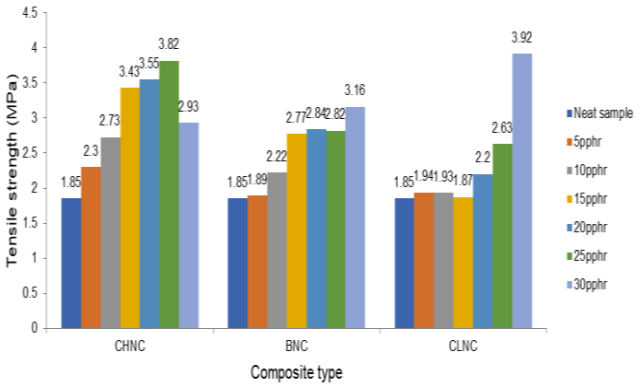

Figure 8: Effect of nanofiller Type on tensile strength of rubber composites

The highest value of tensile strength for the microcomposite samples was 1.67MPa and was obtained at 15 pphr, which is again lower than that of neat NR and nanocomposite samples. This implies that micro-particles of coconut husk and bamboo could not reinforce natural rubber matrix used in this experiment. Gumel *et al.* (2013) [22] reported similar trend of decrease in tensile strength of natural rubber microcomposites with increasing loading of treated wooden micro-cellulosic particle. However, the micro-fillers of cotton lint were found to reinforce rubber matrix at certain loading points, though their

level of reinforcement were lower than their counterpart nanocomposite samples at all loading points. The loading points where reinforcement took place for it micro-fillers were 15, 20 and 30 pphr and their corresponding tensile strength values were 2.13, 2.46 and 2.46 respectively as against the 1.85 MPa for neat NR sample.

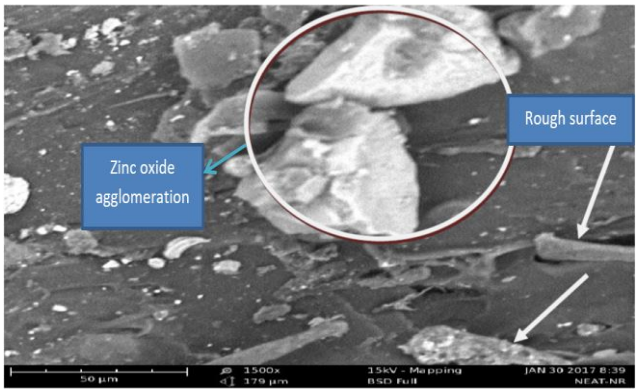

Figure 9: SEM micrograph of Neat NR

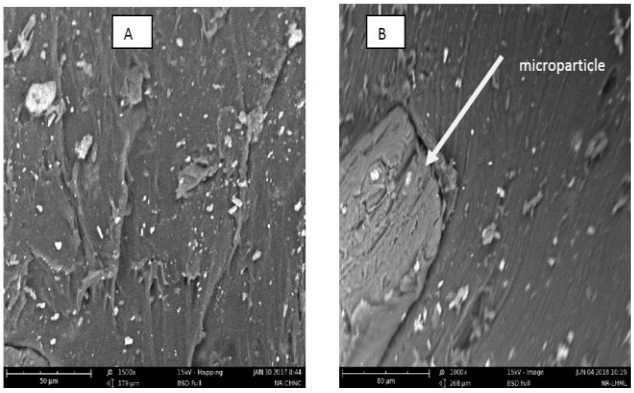

Figure 10: SEM Micrograph of coconut husk composites (a) NR-CHNC$_{25}$ (b) NR-CHMC$_{25}$

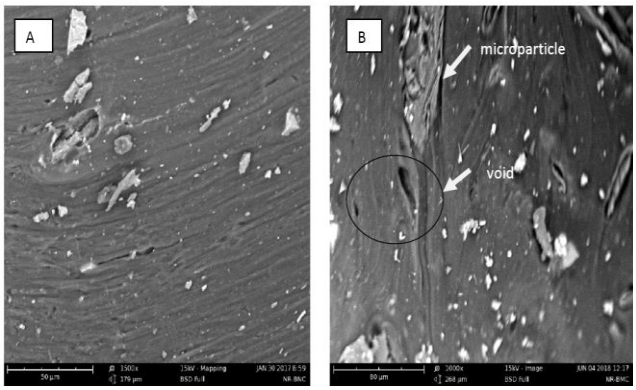

Figure 11: SEM micrograph of bamboo composites (a) NR-BNC$_{25,}$ (b) NR-BMC$_{25}$

3.4 Morphology of Rubber Composites

The SEM images of reference neat rubber is presented in Figure 9 while the corresponding images of 25 pphr of micro- and nanocomposites of coconut husk, bamboo and cotton linter are presented in Figures 10, 11 and 12 respectively. Similarly, the AFM images of surface topography and phase contrast of reference neat rubber, coconut husk, bamboo and cotton linter are shown in Figures 13, 14, 15 and 16.

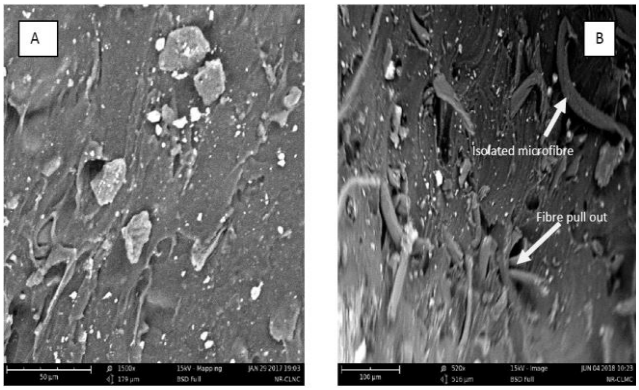

Figure 12: SEM Micrograph of cotton linter composites (a) NR-CLNC$_{25,}$ (b) NR-CLMC$_{25}$

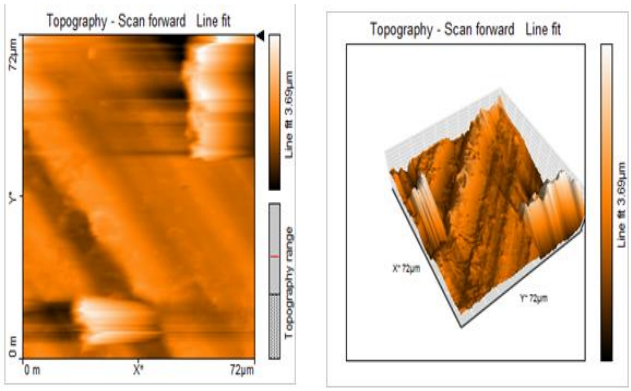

Figure 13: AFM micrograph of Neat NR (a) Topography (b) Phase contrast

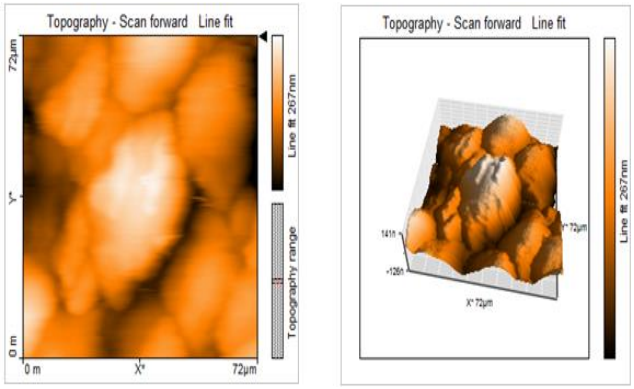

Figure 14: AFM Micrograph of coconut husk composites (a) Topography (b) Phase contrast

From the SEM images, presented in Figure 9 the neat sample is observed to be characterized by voids and lumps of micro-scaled dispersion of zinc oxide and other modifying ingredients used during the rubber formulation and compounding. Similar observation has been reported by other researchers [20]. In the case of coconut husk based microcomposite and

nanocomposite, the SEM image of microcomposite (NR-CHMC$_{25}$) revealed separation of coconut husk microparticles from the rubber matrix, whereas the image of the counterpart nanocomposites (NR-CHNC$_{25}$) was observed not to possess clear particle separation. This debonding of particles from rubber matrix of the microcomposite is the reason for its low tensile strength (1.18 MPa) when compared to its counterpart nanocomposites with much higher tensile strength of 3.83 MPa.

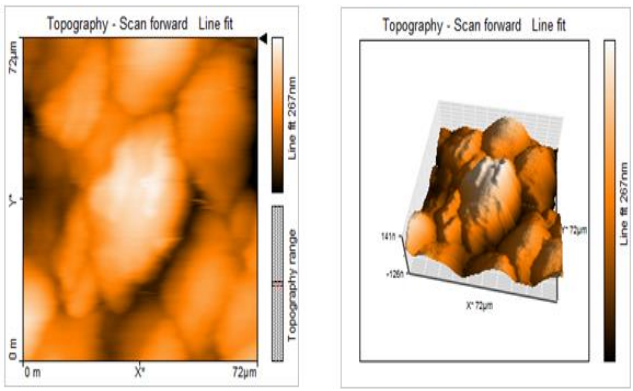

Figure 15: AFM micrograph of bamboo composites (a) Topography (b) Phase contrast

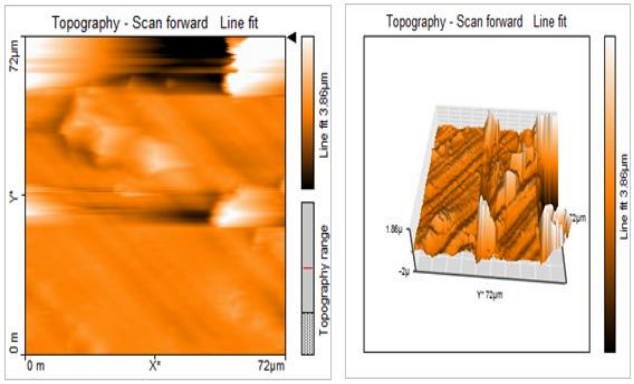

Figure 16: AFM Micrograph of cotton linter composites (a) Topography (b) Phase contrast

The different colour sections seen in all AFM images represent different material environments within the rubber composites. Hence, the dominant colours of composites samples represent the rubber matrix and the filler. The stacked yellow section of the phase contrast of neat sample represents aligned rubber chains in three-dimensional structure of crosslinked rubber. The inclusions of nanoparticles into the rubber matrix as it is in the case of composites (see Figures 14 - 16) were found to have altered the initial arrangement of the neat rubber structure. On the overall, the AFM topography and phase contrast showed a fair region of uniform dispersion of particles as well as a region of particles aggregation around regimented rubber matrix.

4.0 CONCLUSIONS

Tensile strength predominantly increased with inclusion of the cellulosic nanofillers into the rubber matrix while the reverse was the case with microparticles addition. The use of Atomic Force Microscope (AFM) and Scanning Electron Microscope (SEM) to study the microstructure of composite samples revealed better particle – matrix interaction for composites of coconut husk and bamboo than of cotton linter based composites. The authors recommend the study of hybrid effect of these biomass such as coconut/bamboo, coconut/cotton linter or bamboo cotton linter based nanofillers on the properties natural rubber matrix.

5.0 ACKNOWLEDGMENT

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