

Mechanical Properties of Maize Stalk Nano-particle Reinforced Epoxy Composites

**Johnson Olumuyiwa Agunsoye, Adeola
A. Bamigbaiye, Sefiu Adekunle Bello &
Suleiman Bolaji Hassan**

**Arabian Journal for Science and
Engineering**

ISSN 2193-567X

Arab J Sci Eng
DOI 10.1007/s13369-020-04345-5



Your article is protected by copyright and all rights are held exclusively by King Fahd University of Petroleum & Minerals. This e-offprint is for personal use only and shall not be self-archived in electronic repositories. If you wish to self-archive your article, please use the accepted manuscript version for posting on your own website. You may further deposit the accepted manuscript version in any repository, provided it is only made publicly available 12 months after official publication or later and provided acknowledgement is given to the original source of publication and a link is inserted to the published article on Springer's website. The link must be accompanied by the following text: "The final publication is available at link.springer.com".



Mechanical Properties of Maize Stalk Nano-particle Reinforced Epoxy Composites

Johnson Olumuyiwa Agunsoye¹ · Adeola A. Bamigbajye¹ · Sefiu Adekunle Bello² · Suleiman Bolaji Hassan¹

Received: 27 July 2019 / Accepted: 14 January 2020
© King Fahd University of Petroleum & Minerals 2020

Abstract

This study addresses challenges of maize stalk wastes via conversion into nano-particles for producing epoxy composites at different levels of reinforcements. Mechanical tests were conducted on the produced epoxy composites. The result obtained reveals that development of epoxy polymer is synonymous with metallic crystal nucleation and growth. Epoxy composites have composite grains finer than those of the epoxy polymer. The hardness value increased from 2.2 HV of the pristine epoxy polymer to 10.35 and 17.83 HV at 2 wt% UCMSnp and CMSnp additions, respectively. The improvement in the hardness values is equal to about 370 and 710%, respectively; likewise, the tensile strengths. Better mechanical performance of the epoxy/carbonized maize stalk nano-composites than its counterpart containing uncarbonized maize stalk nano-particles is attributed to residual carbon in the carbonized maize stalk nano-particles known with high strength.

Keywords Nano-particle · Composite · Maize stalk · Carbonization · Ball milling

1 Introduction

Nowadays, there is an increasing trend for the use of natural fillers because of government legislation on environmental issue. The non-biodegradability, high initial processing cost, non-recyclability, high energy consumption, machine abrasion and health hazards associated with synthetic fillers [1] have prompted the use of natural reinforcement for developing new composite. The natural fillers are inexpensive, renewable, recyclable, biodegradable and have low density with favourable properties [2]. Also, huge amounts of maize stalks are generated as wastes from annual maize productions. Being wastes, they constitute nuisance on farmlands preventing farmers from easy access to the land as a part of preparations for the next cropping practice. The common practice among farmers especially in African continent to solve this problem is the burning of the maize stalks. The practice removes the maize stalks, and farmers have access to the farmland for the next farming/cropping exercises, but

the maize stalk burning contributes to green-house effect and enhances global warming. Possible applications of maize stalks and other agricultural wastes to address the identified problems have been reviewed by many authors [3–5]. Extraction of silica from the maize stalks for tooth-paste [6], desiccant [7], solar panel [8, 9] and other applications is found in the literature. Process of silica extraction from maize stalks is good, but calcination of the maize stalk before silica extraction wastes huge amount of carbonaceous materials from the maize stalk and amount of silica obtained from the extraction is very small. Therefore, an alternate conversion of maize stalks with little or no waste of its components to produce useful engineering materials such as uncarbonized maize stalk nano-particles for composite production is imperative.

Attempts to produce economically attractive composite components have resulted in several ingenious composite manufacturing methods currently being used. The potentials of agricultural waste as reinforcing fillers can be further harnessed by processing into nanometric level since particles within the nanoscale possess superior properties such as ductility, combined high strength and toughness of nano-particles which are very rare with materials within micro level.

In the pursuit of high performance, advanced composites for engineering applications, carbon has been discovered as

✉ Sefiu Adekunle Bello
bellosaafiu@gmail.com; adekunle_b@yahoo.com

¹ Department of Metallurgical and Materials Engineering,
University of Lagos, Lagos, Nigeria

² Department of Materials Science and Engineering, Kwara
State University, Malete, Nigeria



a major element in the revolution of material science. The synthesis of carbon black is expensive because of its dependence on fuel [10]. Researchers, over time, have explored an alternative method for producing carbon from agricultural waste [11, 12]. Carbon black can be obtained from agricultural products such as bamboo, jute, cotton, flax, which are carbonaceous in nature and receive high attention as alternative fillers because of their low cost and abundance [13]. Previous studies conducted on production of carbon black from agricultural waste as reinforcement in composite including bamboo, oil palm shell [14], rice husk [15] and coconut shell [16]; wood apple shell and maize stalk [17] show an increment in carbon level and consequently an impact in the expansion of thermoset polymer industry.

Among the different natural fillers that can be carbonized, maize stalk appears to be an emerging and promising material. The use of maize stalk as a filler material in polymer composites presents an interesting alternative for polymer reinforcement due to its natural abundance, high lignocellulose content, low density, renewability and no health risk. Furthermore, maize stalk is one of widely available underutilised agricultural wastes and to the best of authors' knowledge, there seems to be limited research on its conversion to nano-particles as reinforcements for composite fabrication. Moreover, nano-particles can be produced via bottom up and top-down approaches [18]. Synthesis of nano-particles for composite productions has been achieved through top-down approach using ball milling technique [19–21]. The literature reveals different sizes of nano-particles obtained at varied milling durations using balls of different materials and sizes. For instance, a minimum size of 22 nm was obtained after 15 h of wet attritor milling of Al6061 at 180 revolution per minute (rpm) by Hanna and his co-researcher [22]. Similarly, Bello and his researchers [23] reported average size of 119.2 ± 0.85 , 72.1 ± 0.22 and 49.84 ± 0.48 nm of coconut shell nano-particles obtained at 16, 46 and 70 h of milling, respectively, using tumbler ball mill rotating at 194 rpm and ceramics balls of size range 5–60 mm.

This present investigation is focused on effects of maize stalk-based carbon nano-particles on the mechanical properties and morphology of epoxy composites. The maize stalk nano-particles used in this study were produced using jack mill operating for 70 h at 10 charge ratios based on findings from optimization of milling parameters found in the literature [4]. Authors' previous studies have revealed synthesis and characterization of aluminium nano-particles using coconut shell-based carbon particles as milling interphase [5, 24]; production of coconut shell nano-particles using different techniques [19, 23]; development of epoxy/aluminium composites [25] with a focus on flexural properties [26] and statistical optimization of tensile properties [27]. Then, epoxy containing coconut shell particles with a focus on mechanical properties [28, 29] formed a part of

authors' previous studies. The present investigation is unique and different from the previous studies in which natural rubber [30] and polyester were used as the matrix [17, 31]. This work explores the use of maize stalks as precursor for carbon nano-particles synthesis and development of epoxy composite using maize stalk nano-particles as reinforcements. This study focuses on effect of maize stalk particles on mechanical properties of the epoxy composite which is unique and different from morphology and thermal properties of epoxy/maize stalk fibres composites reported in [32]. Epoxy resin (LY 556) used in the study is different from epoxy resin MAX 16/18A used as the matrix in the previous studies [25, 27, 28]. The idea is to address threats emanating from wastes generated from annual agricultural productions in Nigeria for possible conversion into wealth.

2 Materials and Methods

2.1 Materials

Materials used are maize stalk obtained locally from a farm in the Ikorodu area of Lagos state. Epoxy resin (LY556) and hardener were purchased from Tony Chemical Enterprises, 18 Oyebola Street, Ojota Lagos, Nigeria. Epoxy resin is diglycidyl ether of bisphenol A which is curable at room temperature, and the hardener is aromatic amine.

2.2 Methods

2.2.1 Maize Stalk Processing

Waste maize stalks were cleaned and dried in the sun for about 2 days, then broken into smaller sizes and pulverized into powder (Fig. 1) using a pulverizer (RPMP/01 Model) operated at 3500 rpm and 1.5 Hp and classified using a standard sieve set, in accordance with BS1377:1990. Particles of an average size of 105 μm were selected as feeds for carbonized (CMS) and uncarbonized (UMS) maize stalk nano-particles synthesis.

2.2.2 Carbonization of Maize Stalk Particles

A total of 5 kg of maize stalk powders was placed in a $15 \times 14 \times 10 \text{ cm}^3$ rectangular steel mould and carbonized in the absence of air at a temperature of 1100 °C for 5 h in an electric furnace (Vecstar LF3 Model) at Heat Treatment Laboratory, Department of Metallurgical and Materials Engineering, University of Lagos, Nigeria, to obtain carbon particles (See Fig. 1).





Fig. 1 a Chopped maize stalk b pulverized maize stalk c carbonized maize stalk



Fig. 2 A jar mill

2.2.3 Maize Stalk Nano-particle Production

The nano-particle production method used was mechanical ball milling according to [23] with little modification. The samples (carbonized and uncarbonized maize stalk) were weighed and poured in a jar mill (see Fig. 2) containing alumina balls of different sizes as the grinding media. Milled maize stalk carbon samples were collected at 34, 46, 60 and 70 h of milling. Those particles obtained at 70 h of milling were used as reinforcement for composite development.

2.2.4 Characterization of Maize Stalk Nano-particles

A multipurpose field emission transmission electron microscope (TEM), Model: JEM 2100F was used to view ultra-thin (< 100 nm) samples of the nano-particle reinforcements to obtain quantitative measurement of grain size and morphology. The samples were prepared by drying the nano-particles on a copper grid coated with a thin film of carbon, after which the transmission electron microscope operating at an accelerating voltage of 100 keV with an AMTXR41-B 4-megapixel (2048 × 2048) bottom mount CCD camera was used to focus a beam of electron through the sample. Scanning electron microscopy (SEM), Model JSM 6510A equipped with an energy-dispersive spectrometer (EDX) was

used to analyse the reinforcement samples. Scanning was done with an electron beam operated at 15 kV. The signals and images produced due to secondary and back scattered electrons gave information about the structure of the reinforcement sample. The energy-dispersive spectroscopy analysed the elemental composition of the samples.

2.2.5 Production of Epoxy/Maize Stalk Nano-particle Reinforced Composites

Epoxy/maize stalk reinforced composites were produced by mixing epoxy resin (LY 556) with hardener in ratio of 2 to 1. Uncarbonized maize stalk (UMS) nano-particles equivalent to 2% weight of measured diglycidyl ether of bisphenol A (DGEBA) was added and mixed thoroughly to ensure even dispersion of the powder in the resin. The mixture was then poured into the fabricated mould and left to cure for 24 h after which it was removed. The same procedure was repeated for 4, 6, 8, 10 and 12 wt% additions of uncarbonized maize stalk nano-particles and 2–12 wt% additions of carbonized maize stalk nano-particles.

2.2.6 Characterization of Epoxy/Maize Stalk Nano-particle Reinforced Composites

Microstructural properties of the epoxy/maize stalk particle composites were examined. An Instron Universal Machine was used to gradually stretch the samples using a uniaxial tensile load at a cross-head speed of 10 mm/min until failure occurred. This experiment was done in Engineering Materials Development Institute (EMDI), Akure, Nigeria in accordance with ASTM D 3039. The specimens used were the dog bone-shape with a gauge length 50 mm, width of 10 mm and 8 mm thickness. The sample was tightened and held vertically between the top and bottom grips of the machine. An extensometer was attached, and the test was run. The procedure was repeated for all composite samples. Micro-hardness property test was conducted in accordance



with ASTM E 384 standard to measure the resistance of the developed composites to plastic deformation/indentation. A Vickers's hardness tester (Model MMT-X7A) was used. A load of 50gf was applied on the examined sample through an indenter for a dwelling time of 10 s. The diagonals of the indentation were measured, and the micro-hardness value (HV) was computed. The same procedure was repeated for other composite samples. Before the analysis, the cut sample surfaces were prepared by mechanical grinding on an abrasive paper of 400 grit size for about 5 min followed by surface polishing for another 3 min.

3 Results and Discussion

3.1 Microstructure and Chemical Composition of Maize Stalk Nano-particles

Uncarbonized maize stalk nano-particles (UMSnp) appear as flakes having different sizes (Fig. 3). Their shapes are oval, irregular, pearl-like and tube-like structures. Many particles are fused together and exist in agglomerated forms. The literature [4, 12] reveals similar observation on coconut shell nano-particles. The shapes have influence in their relative packing within the matrix when used as reinforcement for composite production. Chemically, UMSnp contains carbon (C), titanium (Ti), oxygen (O), sodium (Na), magnesium (Mg), aluminium (Al), silicon (Si), phosphorus (P), sulphur (S), chlorine (Cl), potassium (K), calcium (Ca), iron (Fe) and barium (Ba) as shown in energy-dispersive X-ray spectrograph. The level of carbon content is higher when

compared with that of uncarbonized coconut shell (Fig. 3). Carbon particles, being very strong, have been added to many polymers to improve their impact and other mechanical properties [28]. Elements such as S, P, Fe, Ti are hard and strong. They have the tendency to improve the strength of the matrix individually or interact with other elements during curing of the polymeric matrix to produce hard and strong compounds which are load carriers and improve load bearing capacity of the composites [19, 23, 33].

Similarly, carbonized maize stalk nano-particles (CMSnp) appear in agglomerated networks of different shapes. Physical fusion of the CMSnp is more pronounced (Fig. 4) than what is observed with UMSnp. These could be resulted from the presence of hard phases in the CMSnp. Vacuum carbonization has been reported in the literature to remove moisture and volatile contents of carbonaceous materials, leaving behind residual brittle/hard carbon and ash containing ceramics oxides [34]. The hard phases broke more easily than the uncarbonized carbonaceous materials such as the maize stalk used in this present study. Therefore, carbonized maize stalk attains a threshold size above which physical combination of carbonized maize stalk particles occurs at a shorter milling duration than that for uncarbonized maize stalk particles. This is in perfect agreement with inferences in [4]. Smaller % weight fraction of O and higher % weight fraction of C in Fig. 4 when compared with Fig. 3 affirms elimination of moisture and volatile contents raising composition of the remaining phases. Similar finding was read in a published article [12]. Transmission electron microscopic image in Figs. 5a, b confirms agglomeration both in uncarbonized and carbonized nano-particles. Image

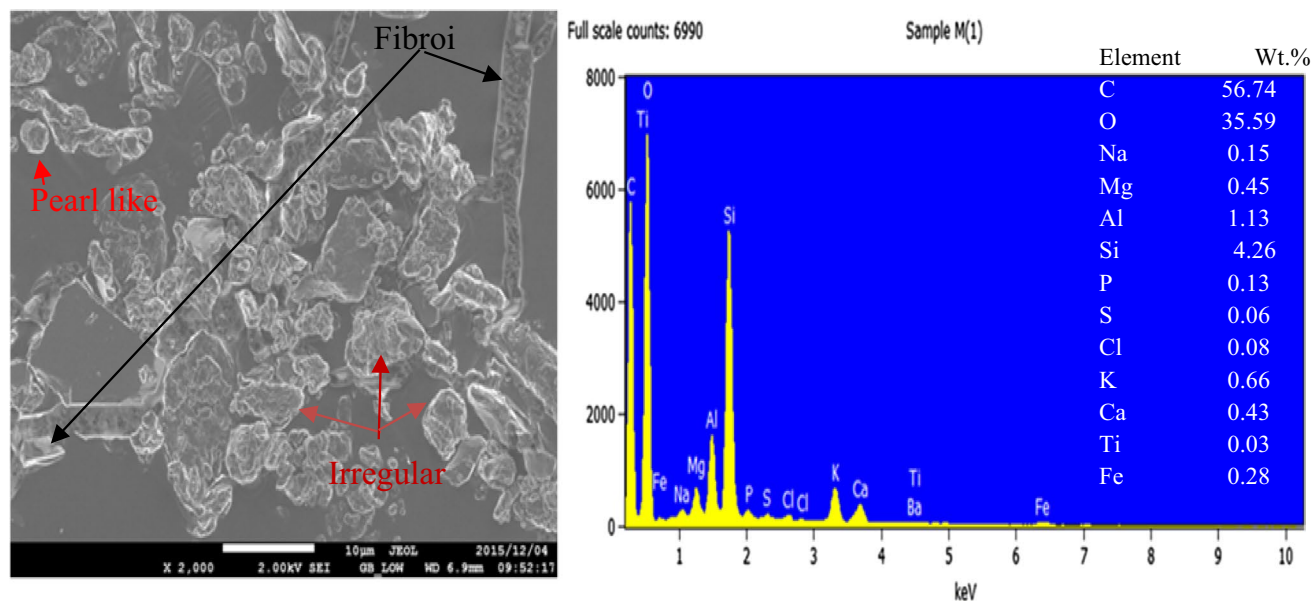


Fig. 3 SEM/EDS of uncarbonized maize stalk nano-particles obtained at 70 h

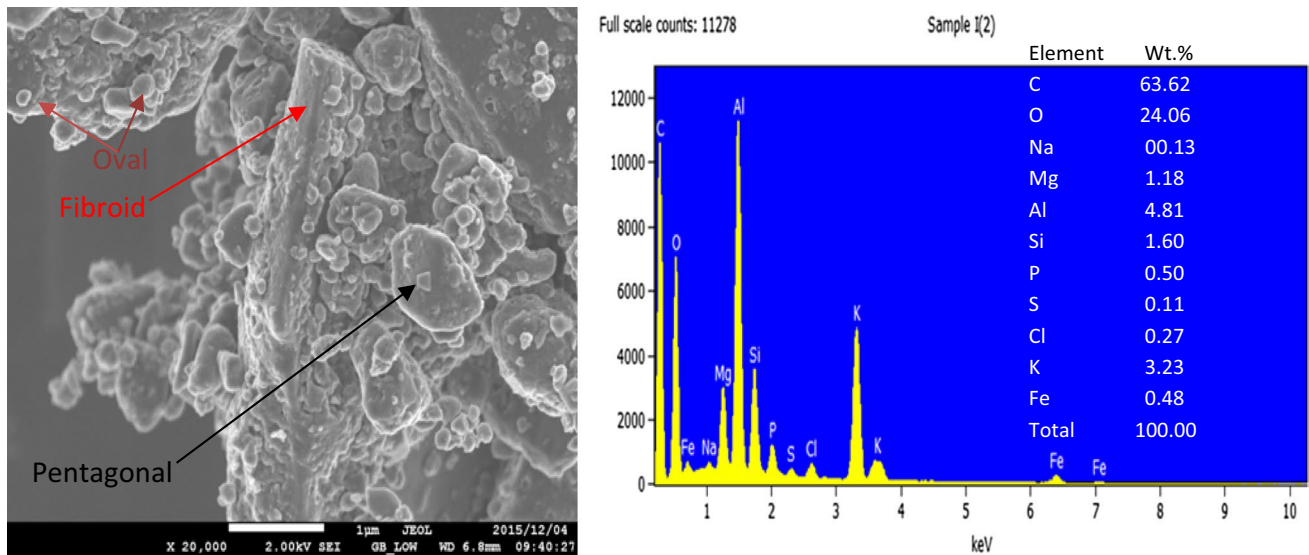


Fig. 4 SEM/EDS of carbonized maize stalk (CMS) nano-particles

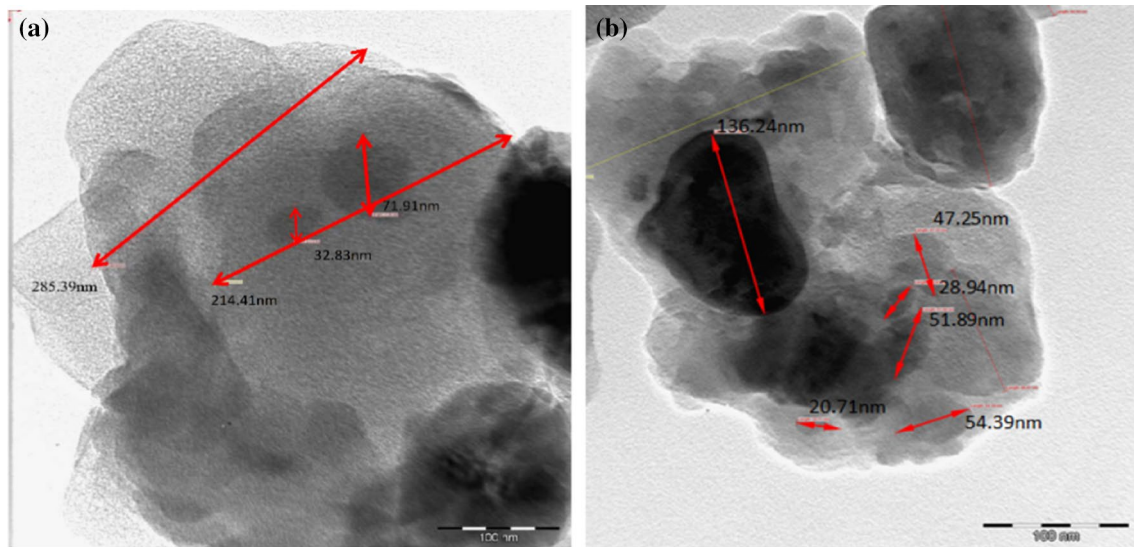


Fig. 5 TEM images of **a** uncarbonized maize stalk nano-particles; **b** carbonized maize stalk nano-particles

size determination discloses sizes of UCMSnp varying from 32.53 to 285.39 nm with an average size of 106.81 nm while those of CMSnp range from 20.71 to 136.24 nm, and its average size is 56.57 nm. Therefore, the developed composite is a dispersion strengthening composites because of nano-particles (maize stalk) used as reinforcement.

Different studies are found in the literature on particle production by ball milling technique covering both metallic and non-metallic materials. Broadness of MgB_2 XRD peak signifying a decrease in grain size with an increase in milling duration was found in [35]. Cryogenic milling at 180 rpm for 15 h using 6.4 mm steel balls of Al 6061

was reported by Hanna et al. [22]. Their finding indicated the decrease in Al 6061 grain size with an increase in milling duration, and minimum sizes of 20 and 23 nm were obtained from XRD and TEM, respectively. Attritor milling of poly (amide imide)/water suspension using 0.5 mm yttria-stabilized zirconia and 1 mm $\alpha\text{-Al}_2\text{O}_3$ balls was disclosed and findings revealed an exponential curve describing relationship between milling time and poly (amide imide) particle sizes and highest loading mass of 20% volume of the attritor drum/vial gave the best milling output [36]. Authors' previous study revealed an average sizes of 201.6 ± 14.73 , 122.6 ± 16.83 and 107.1 ± 4.61 nm



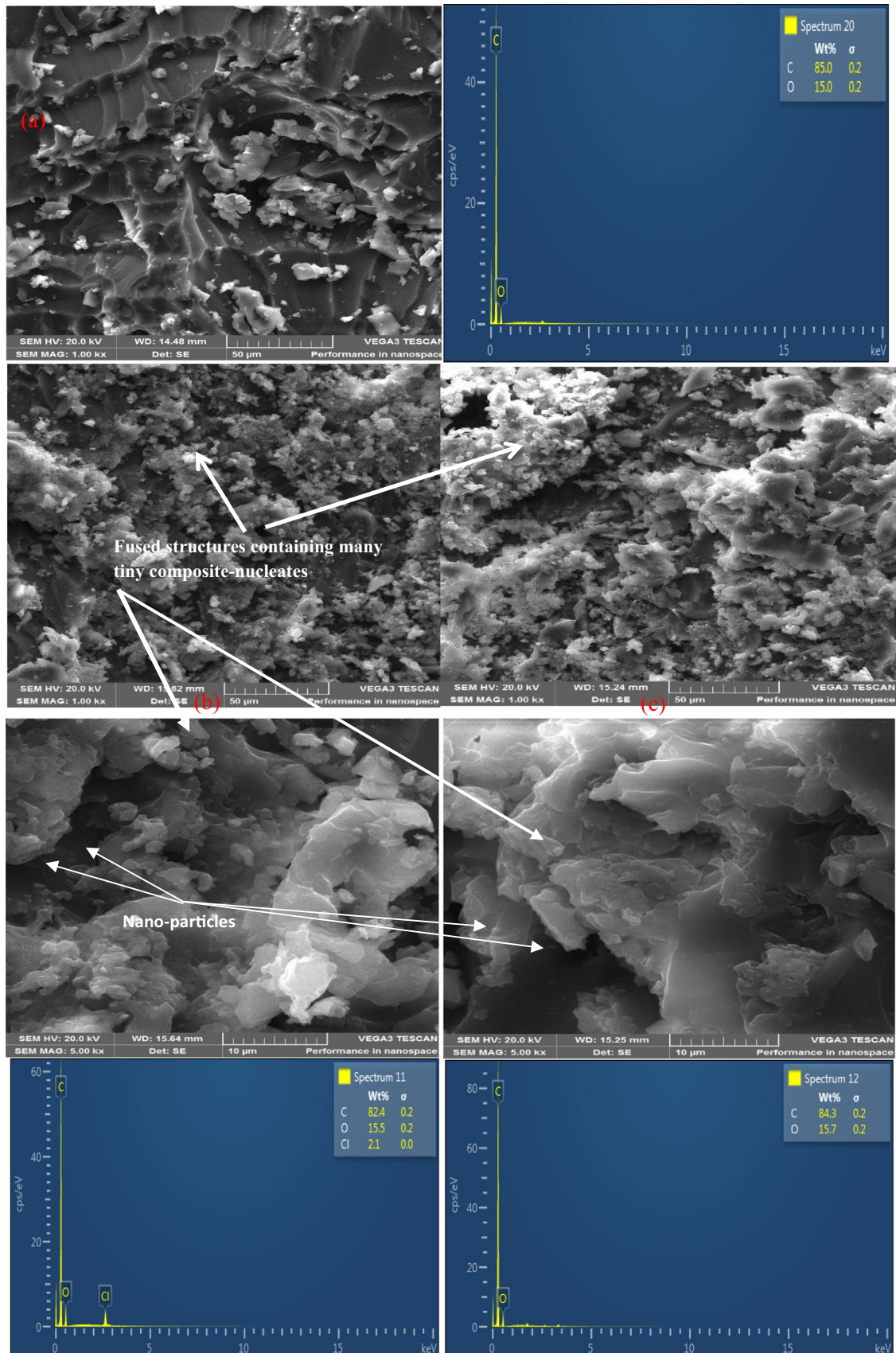


Fig. 6 SEM/EDX of **a** epoxy **b** uncarbonized maize stalk/epoxy composite 1000 and 5000 magnifications **c** carbonized maize stalk/epoxy composite at 1000 and 5000 magnifications

of aluminium nano-particles obtained at 8.5 charge ratios for 16, 46 and 70 h of milling, respectively [5]. Moreover, reduction in % transmittance after 70 h of milling at 194 rpm of aluminium powders using 5–30 mm ceramic balls was previously reported [24]. In studying an effect of charge ratios on sizes of coconut shell nano-particles, Gaussian function was developed by Bello and his co-researchers [4] for determining sizes of coconut shell nano-particles at different charge ratios. A minimum size was predicted by the function when milling the coconut shell powders for 70 h at 13.49 ± 0.6 charge ratios [4]. Average sizes of 119.2 ± 0.85 , 72.1 ± 0.22 and 49.84 ± 0.48 nm were obtained from SEM/software by milling uncarbonized coconut shell powders for 16, 46 and 70 h at 10 charge ratios using tumbler ball mill as read in [23]. Also, average sizes of coconut shell-based carbon nano-particles at 10 charge ratio and 16, 46 and 70 h of milling were reported as 55.01, 31.76 and 12.29 nm, respectively [12]. Size range (20.71–136.24 nm) of CMSnp and 32.53–285.39 nm for UCMSnp perfectly agrees with previous studies already cited. Whether metallic or organic particles, each particle component has different sizes at any instance of milling due to different ball impacts or attritions on each of them, justifying the size ranges as disclosed in this present work and in all cited published articles in this write-up to avoid repetition. Moreover, study of comminution properties of maize stalk-based carbon expands knowledge on top-down approach to synthesis of organic nano-particles. Despite many studies on mechanical alloying (metallic materials) [22, 36–42], additional studies are still reported in this field to date. Besides nano-particle synthesis, ball milling helps in preparing particle surfaces for ease of adhesion with matrix molecules to enhance interfacial bonding of the particles with the matrix. Also, particle surface treatment of graphene through silane-functionalization resulting in improvement in its interfacial bonding with epoxy and enhancement in mechanical properties of the epoxy/graphene composites has been found in the literature [43, 44]. However, ball milling of maize stalks in this study to miniaturize the maize stalk particles and to prepare their surfaces for ease of adhesion with epoxy molecules is unique and different from previous silane-functionalization found in [43–46].

3.2 Microstructure and Chemical Properties of the Developed Composite

Monomers of epoxy resin and those of the hardener interacted chemically giving rise to formation of epoxy

molecules which cross-link during curing process to produce solid structure [47] in Fig. 6a. This structure appears dendritic and similar to metallic structures developed from nucleation and growth of dendrites [48]. The presence of epoxy grains of different geometries separated by pronounced boundaries perfectly describes metallic alloy structure, implying that the development of epoxy molecules during the curing occurs like that of the metallic alloys which is crystalline meanwhile epoxy molecule is expected to be amorphous because it is a thermoset [49]. From this observation, the epoxy molecules can be described as semi-crystalline if not a perfect crystal. Besides, there are tiny second phase particles which are disjointed from the basic thermosetting structures. Since no reinforcements were added to the control epoxy, the second phase particles may be epoxy molecules which were not linked with the main structure during the gelation process. The disjointed epoxy molecules act like excess reinforcement particles after the matrix saturation which create discontinuity within the matrix and may impair the mechanical properties of the epoxy polymer [50, 51].

Structures (Fig. 6b, c) developed after addition of the reinforcement particles (UCMSnp and CMSnp) are finer than that with epoxy polymer. Interaction of the reinforcement with epoxy polymer molecules might induce formation of many tiny/fine composite blend nucleates that cross-link to produce thermosetting composites with refined structures. Different fused structures having many composite-nucleates linked or connected are evidence for the formation of the fine nucleates during gelation of the epoxy mixture. However, differences in microstructures in Figs. 6b, c can be attached to variation in features of the maize stalk particles added to the epoxy as reinforcement. Chemically, epoxy/UCMSnp composite structure contains different proportion of carbon (C), oxygen (O) and chlorine (Cl). Carbon and oxygen belong to epoxy resin and UCMSnp while chlorine (Cl) may form part of the volatile components of the UCMSnp rather than the hardener because of its absence in the structures of epoxy polymer and epoxy/CMSnp composites. Since CMSnp were produced at elevated temperature as indicated under Sect. 2 of this presentation, chlorine containing component of the maize stalk might have been volatilised during the carbonization process. This inference agrees perfectly with the literature [12, 52]. Therefore, both epoxy polymer and epoxy/CMSnp composite are chemically similar but their structural differences can cause differences in their responses when loaded mechanically. Moreover, response of the epoxy/CMSnp composite to mechanical loading is expected to be different from those of epoxy polymer and the epoxy/UCMSnp composites due to their chemical and geometric differences.



3.3 Mechanical Properties of Epoxy/Maize Stalk Composites

Hardness values of epoxy composites increase correspondingly with an increment in per cent weight addition of nanoparticulate reinforcement additions. The hardness value increased from 2.2 HV of the pristine epoxy polymer to 10.35 and 17.83 HV at 2 wt% UCMSnp and CMSnp additions, respectively. The improvement in the hardness values is equal to about 370 and 710%, respectively. Above 2 wt% of UCMSnp, the % increase from a level of reinforcement to another decreases. For instance, from 2 to 6 wt%, the increase is about 23% while from 6 to 8 wt%, there is about 9% increase but about 44% increase from 8 to 12 wt% opposes the decreasing percentage trend though the 44% increase is still much smaller than 370% obtained from 0 to 2 wt%. This implies that although generally there is an increase in the hardness values, degree of improvement over

one level of reinforcement to another decreases. This agrees with similar work in the published articles [27, 53]. This is a piece of evidence for an approach of the reinforcement saturation level above which the matrix become incapacitated to bind all reinforcement particles together. Moreover, such level of reinforcement that can induce the matrix saturation does not reach in this study (see Fig. 7). About 2, 9 and 15% increase corresponding to 2–6, 6–8, 8–12 wt%, respectively, for epoxy/CMSnp composites reveal similar observations with both composites. Moreover, the hardness values of epoxy/CMSnp composites are greater those of epoxy/UCMSnp composites at all levels of reinforcements.

Tensile strengths of epoxy composites are greater than that of the epoxy polymer at all levels of reinforcements (see Fig. 8). Enhancement in tensile strength is like that in Fig. 7. The improvement in the tensile strength can be described by the presence of the nano-particles added to the epoxy matrix causing development of new structures having many refined epoxy composites grains with numerous barriers such as the grain boundaries in the metallic structures [54, 55]. During uniaxial loading such as that in the tensile test, there is a disturbance within the composite structure leading to formation of very tiny pores known as crazes [26]. More crazes were forming as the loading continued. Craze propagation and growth are less inhibited in epoxy polymer because of coarse-grain structures unlike those of fine grain structures of epoxy/UCMSnp and epoxy/CMSnp composites having numerous barriers which are potential resistances to prevent ease of craze propagation and growth. Therefore, both composites exhibit a prolong yielding elongation which requires additional stress to cause further deformation such as strain or work hardening in the metallic crystal [26, 56]. This forms a basis for the increment in the tensile strengths of the epoxy composites with a consequent reduction in tensile strain as shown in Fig. 8b. Higher tensile strength of the

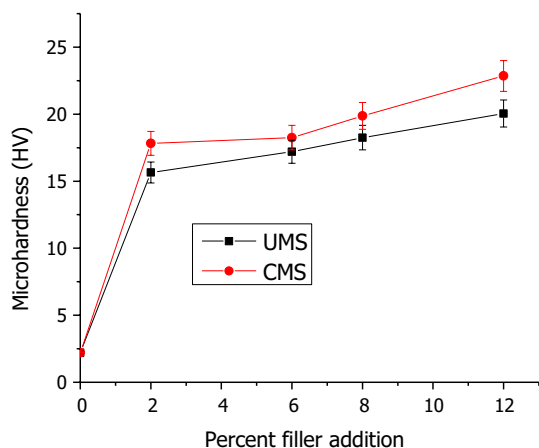


Fig. 7 Microhardness values of epoxy composites

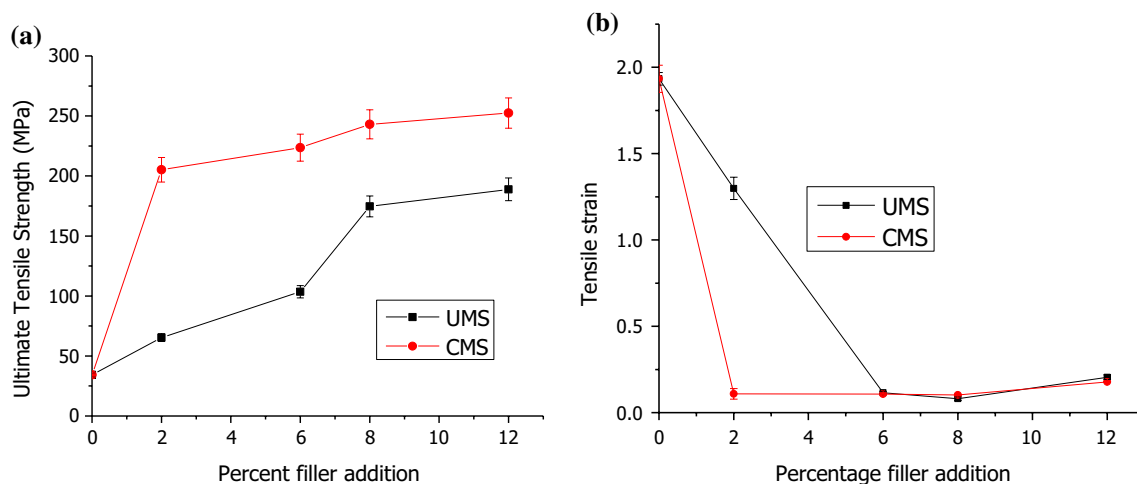


Fig. 8 Tensile properties of epoxy composites **a** strength **b** strain



epoxy/CMSnp composite than those of the epoxy/UCMSnp composites is attributable to greater stiffening of the epoxy polymer by the CMSnp that contains mainly carbon having high strength [34]. Its presence in the matrix improves load bearing capacity of the epoxy more than that of the UCMSnp. Different facts are found in the literature concerning properties of epoxy particulate composites. An increase in tensile strength up to 10 wt% with a maximum tensile strength at 1 wt% (about 24% increase) of 870 μm sized aluminium particle to epoxy resin (PL 411) cured with PH 861 hardener and a decrease in tensile strength due to 80 μm sized copper particles addition to epoxy were found in [57].

An increase in hardness values from 5 wt% and above of Al and Cu addition was reported by the same authors [57]. Moreover, Pargi et al. [58] reported a continual increase in flexural strength, modulus and hardness values of epoxy (DER 331 cured with polyamine hardener)/copper composites with approximated 67, 82 and 186% increases, respectively, at 40 vol% and mixed particle size. Study of Bello et al. [25] on effects of aluminium particle sizes on mechanical properties of epoxy (MAX16/18A cured with MAX16/18B)/aluminium composite established approximated 10% maximum increase at 6 wt% of 56 μm sized aluminium particle added to epoxy; 38% highest increase at 10 wt% addition of 55.5 nm sized aluminium particle addition with 28 and 56% increase at 10 wt% each of both aluminium particles additions to the epoxy, respectively. In addition, empirical model developed by Bello et al. [27] for estimating tensile strength of epoxy/aluminium particulate composite affirmed 16.5% discrepancies between the predicted and experimental tensile strengths. The particle volume fraction and bifunctional interaction between particle size and volume fraction of the aluminium particles were reported to have significant influences on the tensile properties [27]. Findings from this research were compared with those of [25, 26, 57] because of particulate nature of metals used as reinforcement since the literature and the present study contributed to development of particulate composite technology. Furthermore, addition of maize stalk fibres at 25 wt% to natural rubber was reported with about 44% improvement in tensile strength and 43% reduction in % elongation [30]. Approximated 49, 357 and 190% increase in tensile strength, tensile modulus and hardness values, respectively, but 16% reduction in impact energy was reported on polyester reinforced carbonized maize stalk particles [31]. Ojha and his co-researcher [16] reported respective 168 and 35% enhancement in tensile strength and hardness values due to 15 wt% wood apple particles addition to epoxy. Hassan et al. [28] showed about 44, 85 and 14% increase in tensile strength, hardness values and impact energy, respectively, and attributed the increase to homogeneous distribution of coconut shell particles within the epoxy matrix and their good adhesion to the matrix. Also, approximated 10

and 48% improvements in tensile modulus and strength of epoxy/graphene oxide composite were reported by Wan and his co-researcher [44]. Generally, increase in tensile strength and hardness values found in this study perfectly agrees with [16, 17, 25, 27, 28, 30, 31, 33, 43–46, 57–59] but decrease in tensile strength with an increase in copper and chopped coconut shell fibres additions to epoxy was found in [57, 59]. Also, the maximum value of 250 MPa obtained at 12 wt% of UCMSnp is a marked improvement from the value obtained with epoxy composite containing maize stalk microparticles in the previous study [17]. This can be linked to the fineness of the present nano-particles reinforcement which result in better interfacial bonding between the particles and the epoxy matrix giving rise to property enhancement.

4 Conclusion

In this study, epoxy polymeric nano-composites containing uncarbonized and carbonized maize stalk nano-particles as reinforcements were produced. Maize stalk nano-particles exist in fused networks having different geometries. Epoxy composites have dendrite-like structures with finer grains than those of the epoxy polymer. There is an increment in tensile strength and hardness values up to 12 wt% additions of maize stalk nano-particles. Epoxy/carbonized maize stalk nano-composites show better mechanical properties than the epoxy/uncarbonized maize stalk nano-composites. Degree of improvement in mechanical properties decreases from a level of reinforcement to the other.

Funding No funding was received on this work. It is self-sponsored.

Compliance with Ethical Standards

Conflict of interest Authors declare no conflict of interest on this work.

Ethical Approval Authors declare that all third parties' rights in line with ethical standards are respected.

Informed Consent This research does not involve human participant nor animal.

References

- Williams, T.; Hosur, M.; Theodore, M.; Netravali, A.; Rangari, V.; Jeelani, S.: Time effects on morphology and bonding ability in mercerized natural fibers for composite reinforcement. *Int. J. Polym. Sci.* **2011**, 1–9 (2011). <https://doi.org/10.1155/2011/192865>
- Mohanty, A.K.; Misra, M.; Drzal, L.T.: Sustainable bio-composites from renewable resources: opportunities and challenges in the green materials world. *J. Polym. Environ.* **10**(1), 19–26 (2002). <https://doi.org/10.1023/A:1021013921916>



3. Adebisi, J.A.; Agunsoye, J.O.; Bello, S.A.; Ahmed, I.I.; Ojo, O.A.; Hassan, S.B.: Potential of producing solar grade silicon nanoparticles from selected agro-wastes: a review. *Sol. Energy* **142**, 68–86 (2017). <https://doi.org/10.1016/j.solener.2016.12.001>
4. Bello, S.A.; Agunsoye, J.O.; Adebisi, J.A.; Hassan, S.B.: Optimisation of charge ratios for ball milling synthesis: agglomeration and refinement of coconut shells. *Eng. Appl. Sci. Res. (EASR)* **42**(4), 262–272 (2018). <https://doi.org/10.14456/easr.2018.36>
5. Bello, S.A.; Agunsoye, J.O.; Adebisi, J.A.; Kolawole, F.O.; Raji, N.K.; Hassan, S.B.: Quasi crystal Al (1xxx)/carbonised coconut shell nano-particles: synthesis and characterisation. *MRS Adv.* **3**(42–43), 2559–2571 (2018). <https://doi.org/10.1557/adv.2018.369>
6. Joiner, A.: A silica toothpaste containing blue covarine: a new technological breakthrough in whitening. *Int. Dent. J.* **59**(5), 284–288 (2009)
7. Joshi, H.H.; Gertz, R.E.; da Gloria Carvalho, M.; Beall, B.W.: Use of silica desiccant packets for specimen storage and transport to evaluate pneumococcal nasopharyngeal carriage among Nepalese children. *J. Clin. Microbiol.* **46**(9), 3175–3176 (2008)
8. Adebisi, J.A.; Agunsoye, J.O.; Bello, S.A.; Kolawole, F.O.; Ramakokovhu, M.M.; Daramola, M.O.; Hassan, S.B.: Extraction of silica from sugarcane bagasse, cassava periderm and maize stalk: proximate analysis and physico-chemical properties of wastes. *Waste Biomass Valoriz.* **10**, 617–629 (2019). <https://doi.org/10.1007/s12649-017-0089-5>
9. Adebisi, J.A.; Agunsoye, J.O.; Bello, S.A.; Ramakokovhu, M.M.; Daramola, M.O.; Hassan, S.B.: Proximate analysis and physico-chemical properties of sugarcane bagasse, cassava periderm and maize stalk. In: Paper Presented at the IWAN, India
10. Sri-Aprilia, N.A.; Abdul Khalil, H.P.S.; Bhat, A.H.; Dungani, R.; Hossain, M.S.: Exploring material properties of vinyl ester biocomposites filled carbonized *Jatropha* seed shell. *BioResources* **9**(3), 4888–4898 (2014). <https://doi.org/10.15376/biores.9.3.4888-4898>
11. Bledzki, A.K.; Mamun, A.A.; Volk, J.: Barley husk and coconut shell reinforced polypropylene composites: the effect of fibre physical, chemical and surface properties. *Compos. Sci. Technol.* **70**(5), 840–846 (2010). <https://doi.org/10.1016/j.compscitech.2010.01.022>
12. Bello, S.A.; Agunsoye, J.O.; Adebisi, J.A.; Kolawole, F.O.; Suleiman, B.H.: Physical properties of coconut shell nano-particles. *Kathmandu Univ. J. Sci., Eng. Technol.* **12**(1), 63–79 (2016)
13. Khalil, H.P.S.A.; Noriman, N.Z.; Ahmad, M.N.; Ratnam, M.M.; Fuaad, N.A.N.: Polyester composites filled carbon black and activated carbon from bamboo (*Gigantochloa scortechinii*): physical and mechanical properties. *J. Reinf. Plast. Compos.* **26**(3), 305–320 (2016). <https://doi.org/10.1177/0731684407065066>
14. Abdul Khalil, H.P.S.; Firoozian, P.; Bakare, I.O.; Akil, H.M.; Noor, A.M.: Exploring biomass based carbon black as filler in epoxy composites: flexural and thermal properties. *Mater. Des.* **31**(7), 3419–3425 (2010). <https://doi.org/10.1016/j.matdes.2010.01.044>
15. Samantrai, S.P.; Raghavendra, G.; Acharya, S.K.: Effect of carbonization temperature and fibre content on the abrasive wear of rice husk char reinforced epoxy composite. *Proc. Inst. Mech. Eng., Part J: J. Eng. Tribol.* **228**(4), 463–469 (2014). <https://doi.org/10.1177/1350650113516435>
16. Ojha, S.; Acharya, S.K.; Raghavendra, G.: A novel approach to utilize waste carbon as reinforcement in thermoset composite. *Proc. Inst. Mech. Eng., Part E: J. Process Mech. Eng.* **230**(4), 263–273 (2014). <https://doi.org/10.1177/0954408914547118>
17. Hassan, S.B.; Oghenevweta, E.J.; Aigbodion, V.S.: Potentials of maize stalk ash as reinforcement in polyster composites. *J. Miner. Mater. Charact. Eng.* **11**(4), 445 (2012)
18. Pokropivny, V.; Lohmus, R.; Hussainova, I.; Pokropivny, A.; Vlassov, S.: Introduction to nanomaterials and nanotechnology. Tartu University Press, Tartu (2007)
19. Bello, S.A.; Hassan, S.B.; Agunsoye, J.O.; Kana, M.G.Z.; Raheem, I.A.: Synthesis of uncarbonised coconut shell nanoparticles: characterisation and particle size determination. *Tribol. Ind.* **37**(2), 257–263 (2015)
20. Hassan, S.B.; Agunsoye, J.O.; Bello, S.A.: Ball milling synthesis of Al (1050) particles: morphological study and particle size determination. *Ind. Eng. Lett.* **5**(11), 22–27 (2015)
21. Kolawole, F.O.; Kolawole, S.K.; Agunsoye, J.O.; Bello, S.A.; Adebisi, J.A.; Soboyejo, W.O.; Hassan, S.B.: Synthesis and characterization of cassava bark nano-particles. *MRS Adv.* **3**(42–43), 2519–2526 (2018). <https://doi.org/10.1557/adv.2018.412>
22. Hanna, W.; Maung, K.; El-Danaf, E.A.; Almajid, A.A.; Soliman, M.S.; Mohamed, F.A.: Nanocrystalline 6061 Al powder fabricated by cryogenic milling and consolidated via high frequency induction heat sintering. *Adv. Mater. Sci. Eng.* **2014**, 1–9 (2014). <https://doi.org/10.1155/2014/921017>
23. Bello, S.A.; Agunsoye, J.O.; Hassan, S.B.: Synthesis of coconut shell nano-particles via a top down approach: assessment of milling duration on the particle sizes and morphologies of coconut shell nano-particles. *Mater. Lett.* **159**, 514–519 (2015). <https://doi.org/10.1016/j.matlet.2015.07.063>
24. Bello, S.A.; Agunsoye, J.O.; Adebisi, J.A.; Anyanwu, J.E.; Bamigbade, A.A.; Hassan, S.B.: Potential of carbonised coconut shell as a ball-milling interface for synthesis of aluminium (1xxx) nanoparticles. *Ann. Fac. Eng.* **15**(2), 149–157 (2017)
25. Bello, S.A.; Agunsoye, J.O.; Adebisi, J.A.; Suleiman, B.H.: Effects of aluminium particles on mechanical and morphological properties of epoxy nano-composites. *Acta Period. Technol.* **48**, 25–38 (2017)
26. Bello, S.A.; Agunsoye, J.O.; Adebisi, J.A.; Raji, N.K.; Adeyemo, R.G.; Alabi, A.G.F.; Hassan, S.B.: Flexural performances of epoxy aluminium particulate composites. *Eng. J.* **22**(4), 97–107 (2018). <https://doi.org/10.4186/ej.2018.22.4.97>
27. Bello, S.A.; Agunsoye, J.O.; Adebisi, J.A.; Adeyemo, R.G.; Hassan, S.B.: Optimization of tensile properties of epoxy aluminium particulate composites using regression models. *J. King Saud. Univ. Sci. Press* (2018). <https://doi.org/10.1016/j.jksus.2018.06.002>
28. Hassan, S.B.; Agunsoye, J.O.; Bello, S.A.; Adebisi, J.A.; Agboola, J.B.: Microstructure and mechanical properties of coconut shell reinforced epoxy composites In: *Materials Science and Technology 2018 (MS&T18)*. Greater Columbus Convention Center, Columbus, pp. 1312–1318. Materials Science and Technology (2018)
29. Agunsoye, J.O.; Odumosu, A.K.; Dada, O.: Novel epoxy-carbonized coconut shell nano-particles composites for car bumper application. *Int. J. Adv. Manuf. Technol.* **102**(1–4), 893–899 (2019). <https://doi.org/10.1007/s00170-018-3206-0>
30. Fidelis, C.; Piwai, S.; Benias, C.N.; Guyo, U.; Mambo, M.: Maize stalk as reinforcement in natural rubber composites. *Int. J. Sci. Technol. Res.* **2**(6), 263–271 (2013)
31. Hassan, S.B.; Oghenevweta, J.E.; Aigbodion, V.S.: Morphological and mechanical properties of carbonized waste maize stalk as reinforcement for eco-composites. *Compos. B Eng.* **43**(5), 2230–2236 (2012). <https://doi.org/10.1016/j.compositesb.2012.02.003>
32. Saravana Bavan, D.; Mohan Kumar, G.C.: Morphological and thermal properties of maize fiber composites. *Fibers Polym.* **13**(7), 887–893 (2012). <https://doi.org/10.1007/s12221-012-0887-0>
33. Sarki, J.; Hassan, S.B.; Aigbodion, V.S.; Oghenevweta, J.E.: Potential of using coconut shell particle fillers in eco-composite materials. *J. Alloy. Compd.* **509**(5), 2381–2385 (2011). <https://doi.org/10.1016/j.jallcom.2010.11.025>



34. Peters, S.T.: Handbook of Composites, 2nd edn. Springer, Dordrecht (1998)
35. Yang, F.; Yan, G.; Wang, Q.Y.; Xiong, X.M.; Li, S.Q.; Liu, G.Q.; Feng, J.Q.; Pang, Y.C.; Li, C.S.; Feng, Y.; Zhang, P.X.: The effect of high-energy ball milling on the microstructure and properties of Ti-doped MgB₂ bulks and wires. *Phys. Proc.* **65**, 157–160 (2015). <https://doi.org/10.1016/j.phpro.2015.05.090>
36. Wolff, M.F.H.; Antonyuk, S.; Heinrich, S.; Schneider, G.A.: Attritor-milling of poly(amide imide) suspensions. *Particuology* **17**, 92–96 (2014). <https://doi.org/10.1016/j.partic.2013.11.005>
37. Breitung-Faes, S.; Kwade, A.: Nano particle production in high-power-density mills. *Chem. Eng. Res. Des.* **86**(4), 390–394 (2008). <https://doi.org/10.1016/j.cherd.2007.11.006>
38. Dewa, M.D.K.; Wiryolukito, S.; Suwarno, H.: Hydrogen absorption capacity of Fe–Ti–Al alloy prepared by high energy ball milling. *Energy Proc.* **68**, 318–325 (2015). <https://doi.org/10.1016/j.egypro.2015.03.262>
39. Liu, T.; Shen, H.; Wang, C.; Chou, W.: Structure evolution of Y₂O₃ nano-particle/Fe composite during mechanical milling and annealing. *Prog. Nat. Sci.: Mater. Int.* **23**(4), 434–439 (2013). <https://doi.org/10.1016/j.pnsc.2013.06.009>
40. Loh, Z.H.; Samanta, A.K.; Sia Heng, P.W.: Overview of milling techniques for improving the solubility of poorly water-soluble drugs. *Asian J. Pharm. Sci.* **10**(4), 255–274 (2015). <https://doi.org/10.1016/j.ajps.2014.12.006>
41. Zhang, S.; Liu, J.; Feng, J.; Li, C.; Ma, X.; Zhang, P.: Optimization of FeSe superconductors with the high-energy ball milling aided sintering process. *J. Mater.* **1**(2), 118–123 (2015). <https://doi.org/10.1016/j.jmat.2015.04.004>
42. Zhang, X.; Mu, H.; Huang, X.; Fu, Z.; Zhu, D.; Ding, H.: Cryogenic milling of aluminium–lithium alloys: thermo-mechanical modelling towards fine-tuning of part surface residual stress. *Proc. CIRP* **31**, 160–165 (2015). <https://doi.org/10.1016/j.procir.2015.03.055>
43. Wan, Y.-J.; Tang, L.-C.; Yan, D.; Zhao, L.; Li, Y.-B.; Wu, L.-B.; Jiang, J.-X.; Lai, G.-Q.: Improved dispersion and interface in the graphene/epoxy composites via a facile surfactant-assisted process. *Compos. Sci. Technol.* **82**, 60–68 (2013). <https://doi.org/10.1016/j.compscitech.2013.04.009>
44. Wan, Y.-J.; Gong, L.-X.; Tang, L.-C.; Wu, L.-B.; Jiang, J.-X.: Mechanical properties of epoxy composites filled with silane-functionalized graphene oxide. *Compos. A Appl. Sci. Manuf.* **64**, 79–89 (2014). <https://doi.org/10.1016/j.compositesa.2014.04.023>
45. Tang, L.-C.; Wan, Y.-J.; Peng, K.; Pei, Y.-B.; Wu, L.-B.; Chen, L.-M.; Shu, L.-J.; Jiang, J.-X.; Lai, G.-Q.: Fracture toughness and electrical conductivity of epoxy composites filled with carbon nanotubes and spherical particles. *Compos. A Appl. Sci. Manuf.* **45**, 95–101 (2013). <https://doi.org/10.1016/j.compositesa.2012.09.012>
46. Tang, L.-C.; Wan, Y.-J.; Yan, D.; Pei, Y.-B.; Zhao, L.; Li, Y.-B.; Wu, L.-B.; Jiang, J.-X.; Lai, G.-Q.: The effect of graphene dispersion on the mechanical properties of graphene/epoxy composites. *Carbon* **60**, 16–27 (2013). <https://doi.org/10.1016/j.carbon.2013.03.050>
47. Bello, S.A.: Development and Characterisation of Epoxy-Aluminium-Coconut Shell Particulate Hybrid Nano-composites for Automobile Applications. University of Lagos, Lagos (2017)
48. William Jr., D.C.: Materials Science and Engineering an Introduction, 7th edn. Wiley, Hoboken (2007)
49. Dotan, A.: Biobased Thermosets, pp. 577–622 (2014). <https://doi.org/10.1016/b978-1-4557-3107-7.00015-4>
50. Agunsoye, J.O.; Aigbodian, V.S.: Bagasse filled recycled polyethylene bio-composites: morphological and mechanical properties study. *Results Phys.* **3**, 187–194 (2013). <https://doi.org/10.1016/j.rinp.2013.09.003>
51. Asuke, F.; Aigbodian, V.S.; Abdulwahab, M.; Fayomi, O.S.I.; Popoola, A.P.I.; Nwoyi, C.I.; Garba, B.: Effects of bone particle on the properties and microstructure of polypropylene/bone ash particulate composites. *Results Phys.* **2**, 135–141 (2012). <https://doi.org/10.1016/j.rinp.2012.09.001>
52. Abiko, H.; Furuse, M.; Takano, T.: Reduction of adsorption capacity of coconut shell activated carbon for organic vapors due to moisture contents. *Ind. Health* **48**, 427–437 (2010)
53. Akram, M.; Taha, I.; Ghobashy, M.M.: Potential of carbon particle reinforced polypropylene formed in situ through the pyrolysis of carboxymethylcellulose. *Compos. Commun.* **1**, 6–14 (2016). <https://doi.org/10.1016/j.coco.2016.07.005>
54. Bello, S.A.; Raheem, I.A.; Raji, N.K.: Study of tensile properties, fractography and morphology of aluminium (1xxx)/coconut shell micro particle composites. *J. King Saud. Univ. Eng. Sci.* **29**, 269–277 (2017). <https://doi.org/10.1016/j.jksues.2015.10.001>
55. Aigbodian, V.S.; Hassan, S.B.; Oghenevwe, J.E.: Microstructural analysis and properties of Al–Cu–Mg/bagasse ash particulate composites. *J. Alloy. Compd.* **497**(1–2), 188–194 (2010). <https://doi.org/10.1016/j.jallcom.2010.02.190>
56. Mohammad, S., Laurentiu, N., Anwarul, H.: Development of High-Strength and Highly Ductile Hypo-Eutectic Al–Si Alloys by Nano-refining the Constituent Phases. In: Paper Presented at the TMS. The Minerals, Metals and Materials Society
57. Srivastava, V.K.; Verma, A.: Mechanical behaviour of copper and aluminium particles reinforced epoxy resin composites. *Am. J. Mater. Sci.* **5**(4), 84–89 (2015). <https://doi.org/10.5923/j.materials.20150504.02>
58. Pargi, M.N.F.; Teh, P.L.; Hussieny, S.; Yeoh, C.K.; Abd Ghani, S.: Recycled-copper-filled epoxy composites: the effect of mixed particle size. *Int. J. Mech. Mater. Eng.* **10**(1), 3 (2015). <https://doi.org/10.1186/s40712-015-0030-2>
59. Ozsoy, N.; Ozsoy, M.; Mimaroglu, A.: Comparison of mechanical characteristics of chopped bamboo and chopped coconut shell reinforced epoxy matrix composite materials. *Eur. Int. J. Sci. Technol.* **3**(8), 15–20 (2014)

