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Research Article

Vehicle bumper fascia prototyping using sustainable nanocomposites

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ABSTRACT

Eggshells and date seeds are wastes which contribute to land pollution. Their conversions to useful materials are important to save the environment from the health hazards associated with rotten eggshells and possible impacts from the date seed wastes. This study focuses on conversion of eggshells and date seeds into reinforcing particles for producing sustainable polymeric and metallic nanocomposites for prototyping a vehicle bumper fascia. Eggshell nanoparticles were incorporated into low-density polyethylene up to 12 wt%. Metallic nanocomposites were produced using Al–Cu–Mg sourced from aluminium alloy scraps and date seed particles and then, heat treated. The developed nanocomposites were analysed chemically, structurally, and mechanically. The structural integrity of the polymeric nanocomposites was confirmed by the scanning electron microscope. Enhancements in impact energy, tensile and flexural strengths at 12 wt% of eggshell nanoparticle additions to the very low-density polyethylene are 1.5, 110.4 and 47.7 %, respectively. 1 wt% date seed particle reinforced Al–Cu–Mg that has highest impact energy after annealing treatment is selected for the mould parts fabrication for forming the bumper fascia. Property comparison of the produced polymeric nanocomposites with those of existing bumper fascia materials affirms that the tensile strength and impact energy of the nanocomposite that contains 12 wt% eggshell nanoparticles are suitable for the automobile bumper fascia. Hence, fabrication of the bumper fascia using the VLDPE/12 wt% eggshell nanocomposite was fruitful.

1. Introduction

Focuses are made over years for developing new materials to provide numerous choices with a material to replace another in an application. The materials replacement in automobiles evolves to address high fuel cost, gas emission, environment and safety rules which relate to vehicle lightweight system. The vehicle lightweights are approaches to reduce the overall automobile weight with consequent benefits of lowering automobile fuel consumption, gas emission and impact on pedestrians in an accident [1]. Materials replacement is one of the vehicle lightweight approaches in addition to structural optimisation and advanced manufacturing techniques. Size, shape and topology structural optimizations were reported with 7 % reduction in automobile weight, numerous number of rivets adding to vehicle weight was reported to have been eliminated by spot welding aluminium vehicle structure and 50 % reduction was attributed to use of lightweight materials for replacing the conventional automobile materials [2]. Therefore, development of lightweight materials like engineering composite is one of priorities in automobile industries. Moreover, the present research concentrates on polymeric nanocomposites developed from very low-density polyethylene and eggshell nanoparticles. Also, date seed particles reinforced Al–Cu–Mg were developed to enable formation of bumper fascia using the metallic nanocomposite moulds. Therefore, this study focuses on green productions of both polymeric and metallic composites.

Initially, reinforcement has been sourced from synthetic materials for composite fabrications. This includes an incorporation of graphene into polystyrene with improvements in mechanical properties as it was

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reported in Ref. [3]. An enhancement in the tensile strength due to multiwall carbon nanotube additions to polyurethane was disclosed in Ref. [4] and many articles in literature, affirming an increase in the mechanical properties of the polymers due to synthetic reinforcements addition. Despite the advantage of the synthetic reinforcement, high cost of such reinforcement has contributed to high expensive cost of the composites and limit their applications.

Sourcing of reinforcement from agricultural wastes such as eggshells and date seed has advantages of removing wastes from the environments, value addition to the wastes and development of ecofriendly composites that will enable widespread applications of compsites in the luxurious and passengers' vehicles. Polymer reinforcement was sourced from eggshell because it contains majorly calcium carbonates [5,6] which are hard and have high potential to increase load bearing capacity of the low-density polyethylene. It was reported in Ref. [5,7] that chemically, eggshell contains 95 % calcium carbonate and the remnant accounts for collagen, protein, and polysaccharides. Eggshells being waste from both domestic and industries, are readily available. Sourcing of polymer reinforcement from eggshells could emerge more ecofriendly polymeric nanocomposites than using commercial calcium carbonate as reinforcement which is more expensive. Although eggshell contains 5 % impurity, its % purity (95 %) is not much far from about 98 % purity [8] of the commercial calcium carbonate.

In addition, date seeds are hard materials which have high potential to improve mechanical properties of Al–Cu–Mg matrix. Its uses as reinforcing materials will reduce land pollution. Therefore, this research establishes a wealth creation from wastes in addition to production of new materials for automobile applications. Needs for recycling of eggshells to address their consequent challenges after rotting and to establish an alternate wealth creation from wastes were justified in a review, creating a gap to be bridged by the present research [9].

Moreover, research articles reviewed as thus have established different directions on usage of agricultural wastes as polymer reinforcements. Use of bagasse as reinforcement in recycled low density polyethylene [10], wood apple shell in epoxy [11], wood apple shell based carbon in epoxy [12], jute and banana fibre for reinforcing epoxy [13], banana and sisal fibre in epoxy [14], barley husk and coconut shell fibres for filling polypropylene [15], eggshell in high density polyethylene [16,17], chicken eggshell for modifying polypropylene [18] were documented in literature. Beside application of eggshell nanoparticles as reinforcement in polymer for engineering new nanocomposites, reports have indicated their usages as absorbents for removing heavy metals from wastewater, sorbents for capturing carbon dioxide, heterogeneous catalyst for manufacturing biodiesel and wall painting [6,19].

Bumper is a vehicle component forming front and rear parts and protect passengers and vehicle in the event of collision with other vehicles or obstacles. It contains bumper beam, energy absorber and fascia. Bumper beam is the shock absorbing part of a vehicle. It is fixed to the front and rear of vehicle with the aids of bracket. It functions as a crash box via impact absorption in the axial direction [20]. Energy absorber damps the impact energy by an elastic deflection at the transverse fixing point and the fascia being the covers to the other bumper components, provides the aesthetics and resists aerodynamic drag. Initially, bumper components were made from heavy steel because of high impact absorption requirements in case of collisions with obstacles but on the other hands, heavy steel bumpers were reported with havocs on pedestrians involved in collision with vehicles leading to various legislations [21,22] across the globe mandating pedestrian's safety [23] as one of important factors to be considered in designing automobile bumpers. Impact test simulation was carried out by different researchers at 40 km/h using leg form impactor to determine maximum impact that is friendly to the pedestrian in case of any collision with the vehicle at low speed and to specify suitable materials for manufacturing bumpers that are saved to the pedestrian [20,24]. Moreover, productions of vehicle bumpers from soft and light materials were reported [22,25]. Beside impact test simulations, previous research on vehicle bumpers was focused on polymeric composite for bumper applications. Tensile strength of about 150 MPa, approximated tensile elastic modulus of 7.5 GPa, flexural strength of 230 MPa, flexural elastic modulus of 12.0 GPa and impact energy of 30 J/m of kenaf-glass fibre reinforced epoxy for passenger car bumper beam compared with glass fibre reinforced thermoplastic of 70 MPa tensile strength, 5.4 GPa tensile elastic modulus, 150 MPa flexural strength, 5.0 GPa flexural elastic modulus and 50 J/m impact energy was reported in Ref. [25]. In addition, tensile strength of 18.58 MPa, flexural strength of 130 MPa and impact energy of 15.5 J of aluminium nanoparticle reinforced epoxy compared with mechanical properties of Toyota Sienna (13.4 MPa tensile strength, 138 MPa flexural strength, and 22 J impact energy) and Nissan Almera (7 MPa tensile strength, 60 MPa flexural strength, and 24 J impact energy) bumper cover was disclosed in Ref. [24]. Therefore, studies on date seed particle reinforced Al–Cu–Mg and very low-density polyethylene containing eggshell nanoparticle and their uses for developing native technology for prototyping automobile bumper fascia are scarce. Authors' previous study focused on the recycled LDPE that contains eggshell particles for the bumper fascia and properties comparison between 10 wt% eggshell nanoparticle reinforced recycled and very LDPE [26]. However, this study concentrates on very low-density polyethylene that is reinforced with eggshell nanoparticles for bumper fascia productions and Al–Cu–Mg having date particles for mould fabrications. Date seed reinforced Al–Cu–Mg was heat treated with an aim of enhancing its impact energy to make it suitable for the targeted application (mould fabrication). This is important and new since such scientific data on the very low-density polyethylene and Al–Cu–Mg are scarce in literature. Eggshell nanoparticle reinforced low-density polyethylene bumper being thermoplastic can be recycled after the bumper service expiration and used as matrix for producing new composites. This is an advantage of the low-density polyethylene-based bumper over the bumper fabricated from thermoset-based composites. In addition, it could be cheaper than the bumper produced from epoxy-based composites since the epoxy is more expensive than the low-density polyethylene. Its superior properties to those of the recycled low-density polyethylene can spur its applications in luxurious vehicles with enhanced safety from the higher energy absorption.

In processing eggshell nanoparticles and very low-density polyethylene, there is a need for a wet interphase to stick the particles to the polymer pellets to achieve a homogenous nanocomposite with little or no particle segregation since both are solid at room temperature. Further, this is important to ensure a nanocomposite with a high structural integrity that emanates from a good adhesion between the eggshell nanoparticles and very low-density polyethylene. Importance of the strong adhesion between the reinforcement and the matrix is explained in the review article in literature [27].

Choice for palm kernel oil among other vegetable oils was made in this study to hold eggshell nanoparticles and low-density polyethylene pellets together because it is cheaper when compared to coconut oil or any of other vegetable oil. Vegetable oil contains fatty acids (RCOOH) [28]. The COOH group of the acid is polar and has affinity for the carbonate group in the eggshell while the nonpolar aliphatic group attaches to the polymer. Therefore, it performs the role of the plasticizer as reported in Ref. [29,30] while holding the particles and polymer pellets together. Hence, this study aims at developing polymeric nanocomposites for bumper fascia applications with focuses on some mechanical properties relevant to the targeted applications. Moreover, the polymeric composite developed is targeting the bumper fascia prototype, and there is a need for metallic composites with optimum combination of properties to produce metallic mould parts for forming the bumper facia prototype. This study also covers investigation of effect of date seed microparticle and heat treatment on the mechanical properties of the Al–Cu–Mg composite to obtain the composite with the optimum properties for forming the polymeric nanocomposite bumper fascia. Therefore, this study used both Al–Cu Mg and very low-density

polyethylene as independent matrix and date seed microparticle as reinforcement in Al–Cu–Mg and eggshell nanoparticles as reinforcement in the very low-density polyethylene, making this study to be novel. The whole study is unique and different from previous study on eggshell nanoparticle reinforced low-density polyethylene in which properties of the recycled low-density were compared with properties of the very low-density polyethylene [26]. However, this present study aims at enhancements in the properties of the very/new low-density polyethylene due to eggshell nanoparticles additions from 2, 4, 6, 8, 10 to 12 wt% which have not been reported in literature before this study. The objective of this study is to know a proportion of eggshell nanoparticles (within the range, from 2 to 12 wt%) in the very low-density polyethylene that will give composite with optimum properties for the bumper fascia application and other possible automobile parts. Moreover, this study forms a part of an ongoing project. Addition of eggshell nanoparticles above 12 wt% to the very low-density polyethylene is a subject for a further study to be communicated in a future article.

2. Methods

2.1. Synthesis and characterisation of eggshell and date seed particles

Eggshell nanoparticles of an average size of 76.25 nm were used in this study. This value was determined following the instruction described in Ref. [30] on particle size determination from TEM image. Detailed synthesis of the eggshell nanoparticles is in line with the report in Ref. [26]. The eggshell nanoparticles were used to reinforce very low-density polyethylene. Date seeds were turned into powders using a disc grinder which were classified using a set of sieves arranged in decreasing order of mesh sizes and vibrated with a sine shaker. The date seed retained in 150 μm sized sieve was used as reinforcement for developing metallic nanocomposites.

2.2. Materials and nanocomposite development

2.2.1. Polymeric nanocomposite development

Very low-density polyethylene (VLDPE) used as a matrix and absolute ethanol were obtained from G Tek Materials Procurement, Ibadan, Oyo State, Nigeria. Melt flow index and density of the very low-density polyethylene are 190 °C/2.16 kg and 0.925 gcm^{-3}, respectively. 2 wt% of eggshell nanoparticles was added to 15 cm^3 of absolute ethanol and stirred mechanically at 200 revolution per minute to produce a slurry of eggshell nanoparticles. The slurry was poured on 500g of VLDPE in the tumbler ball mill rotating at 200 rpm for thorough mixing of VLDE and the slurry. The mixture was heated in a flask at 85 °C to evaporate the ethanol using hotplate (Stuart UC 152). Then, 5 drops of palm kernel oil were added and stirred to stick eggshell nanoparticles to the VLDPE pellets. The mixture was processed at 150 °C using polymer mill to produce VLDPE/eggshell nanocomposite plates which were hot pressed at 90 °C and pressure of 0.5–1.5 Nmm^{-2} to form standard samples for analysis. The described procedure for producing polymeric nanocomposite is called composite mix-compressive sheet moulding. Different grades of low-density polyethylene/eggshell nanocomposites were produced. In each grade, 500 g of low-density polyethylene were used. Weighed quantities of eggshell nanoparticles were added to the matrix in each case. At 2 wt%, 10 g of the eggshell nanoparticles were added to 500 g of low-density polyethylene. The processes were repeated to produce other nanocomposite grades with additions of corresponding masses of eggshell nanoparticles equivalent to 4, 6, 8, 10 and 12 wt% of eggshell nanoparticles to the matrix.

2.2.2. Development of metallic nanocomposites

Date seed particle renforcd Al–Cu–Mg was developed using a stir cast technique. Al–Cu–Mg lumps sourced from Al cans, Cu scraps and Mg ribbon were remelted at 900 °C inside a crucible using a gas fired pit furnace and poured in a sand mould whose cavities have shapes and sizes conforming to standard dimensions for mechanical tests. The process was repeated with addition of 56 μm sized date seed particles equal to 0.5, 1, 2, 4 and 8 % by weight. Melt-date seed particles were stirred thoroughly prior to pouring into the sand mould prepared in line with [31]. Then, the metallic composites samples produced were heated to 500 °C at 100 °C per hour and held at the temperature for 5 h before furnace and air cooling. Fig. 1a presents pictures of materials and procedures for producing both polymeric and metallic composite. Moreover, Fig. 1b demonstrates flowcharts for bumper fascia prototyping.

2.3. Characterisations of the developed nanocomposites

2.3.1. Fourier transform infrared spectroscopic (FTIR) analysis

The representative samples of the very low-density polyethylene and its nanocomposite in powdery form were subjected to FTIR analysis to study chemical properties of the polymer and its nanocomposites. The test was carried out using Shimadzu FTIR machine. A disc containing the sample (a polymer or a composite at a time) was placed on the sample holder and scanning was done at 4 cm^{-1} resolution for 45 times to make sure the spectra data obtained are accurate. Averages of the wavenumbers and light absorbances were used to plot the spectrograph. In addition, scanning was done in the transmission mode in the mid-infrared range having wavenumbers from 500 to 4000 cm^{-1}.

2.3.2. X-ray diffraction analysis

X-Ray diffraction analysis was conducted at Nigerian Geological Survey Agency, Kaduna on the pristine low-density polyethylene and the low-density polyethylene containing 12 wt% eggshell nanoparticles. This test was performed by directing an X-ray beam at each sample under analysis and measuring the scattered intensity as a function of the positions (2theta). Before the analysis, samples were pressed into the sample holder. Scanning was carried out at room temperature (25 °C) in a continuous mode between angle 0° and 80° (2θ) at a step size of 0.0026° with the aid of the Empyrean X-ray diffractometer (manufactured by Malvern Panalytical, United Kingdom) set at 45 kV and 40 mA using Cu anode with Goniometer radius, distant focus divergence slit and irradiated length of 240, 91 and 4 mm, respectively. Peaks were fitted using X'pert High Score software. The slits were fixed with Fe filtered Cu Kα radiation. The phases were identified using X'Pert High Scores Plus software attached with International Centre for Diffraction Data Powder Diffraction Files Databases.

2.3.3. Microstructural analysis

Morphology of the low-density polyethylene/eggshell nanocomposites were examined using ASPEX 3020 scanning electron microscope (SEM, manufactured/supplied by Aspex Corporation, Delmont, Pennsylvania, United States) model SIRIUS50/3.8 at Department of Materials Science and Engineering, Kwara State University, Malete, Nigeria.

Each of the samples was placed on SEM mount with the aids of double-sided adhesive tape. Samples held on the mount were placed inside SEM stage and scanned at 15.1 kV accelerating voltage.

2.3.4. Mechanical examinations

2.3.4.1. Mechanical test of polymeric nanocomposites. Mechanical tests were performed on the developed representative polymeric composite samples (Fig. 1a) and those samples (Fig. 2) cut from the existing bumper fascia selected from commonly available vehicles in Nigeria per ASTM D638-14 [32] for tensile property, ASTM D7264/D7264M − 15 [33] for flexural property using Testometric Materials Testing Machine (supplied from Unit 1 Lincoln Business Park, Lincoln Close, Rochdale, Lancashire, England) at NCHAM Laboratory, Ganmo, Ilorin Kwara State, Nigeria, ASTM D256-10[34] (ASTM D256-10[34], 2018) for impact energy test using Hounsfield Balanced Impact Tester (Manufactured by

Fig. 1a. Pictures of materials and procedures for production of composites: (a) eggshells (b) date seed particles (c) mixture ready for pouring (d) roll mill extruder (e) hot compressive moulding machine (f) developed polymeric nanocomposite samples (g) Al–Cu–Mg lumps (h) broken sand mould to remove the as cast metallic nanocomposites (i) the as cast samples (j) putting samples inside the tube furnace for the heat treatment.

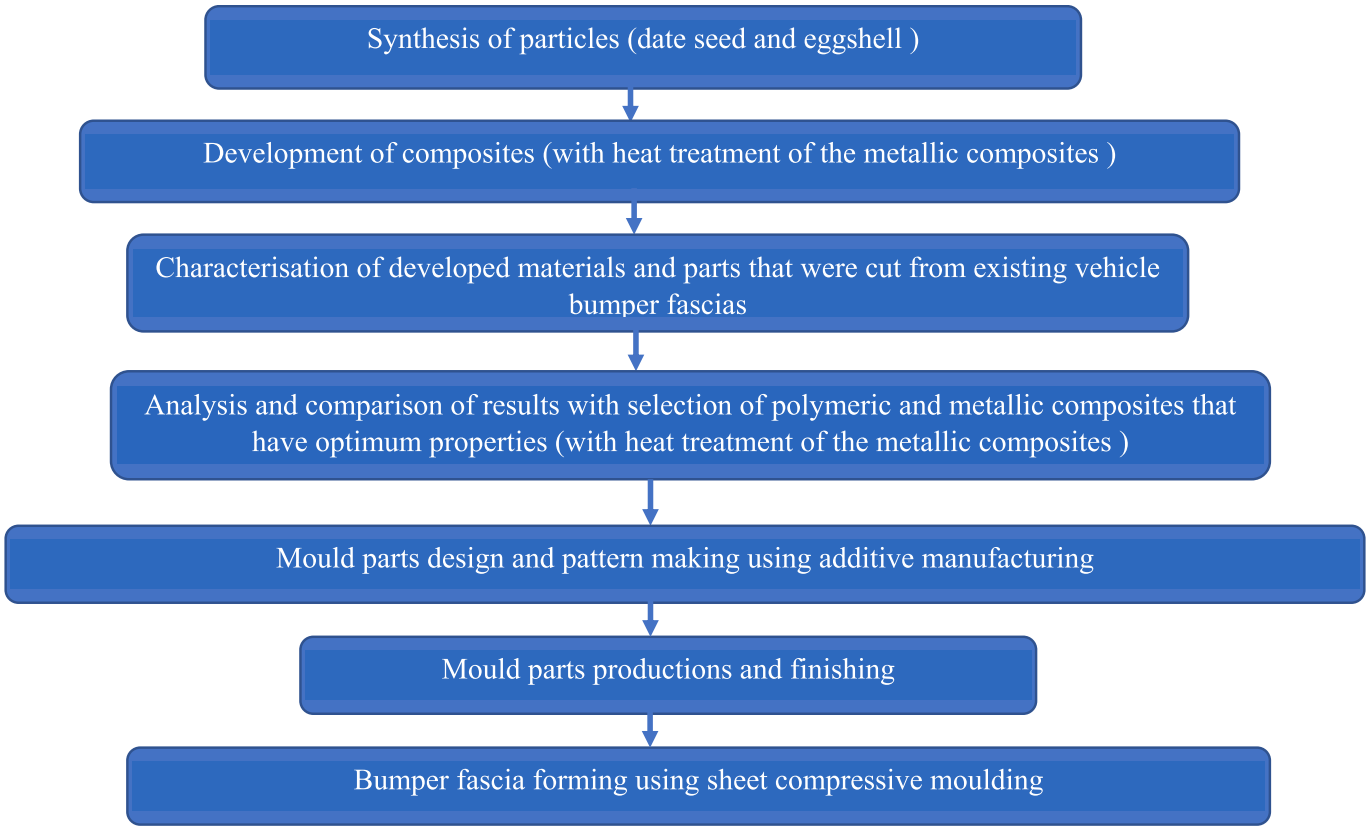

Fig. 1b. Graphical procedures of materials development, characterisation and bumper fascia prototyping.

Tensometer Limited, 81 Morland Road, Croydon, Surrey) at Materials Testing Laboratory, Obafemi Awolowo, University, Ife Osun State Nigeria, with slight modifications and hardness values of the developed polymeric nanocomposites were determined using Vickers hardness tester (model: LV-700AT) at Department of Metallurgical and Materials Engineering Laboratory, University of Lagos.

2.3.4.2. Mechanical investigation of metallic composites. Moreover, to determine the metallic composites that is suitable for the mould fabrication, both as cast and heat-treated samples of the metallic composites were tested mechanically. Tensile test was conducted per ASTM E8/E8M-16ae1 [35]. Each cylindrical shape having a dog bone shape of 120 mm gauge length and 7 mm diameter were loaded at a strain rate of $10^{-}4\ s^{-1}$ till the sample failed.

Tensile strength and other additional tensile parameters were automatically exported from the Testometric Materials Testing Machine using excel sheet. In addition, impact energy was determined per ASTM E23-18 [36] and ASTM E92-17 [37] for the hardness values

Fig. 2. Selected vehicles models serving as sources of bumper fascia for benchmarking the properties of the developed polymeric nanocomposites.

determination for the metallic composites.

3. Results and discussion

3.1. Size of eggshell nanoparticles

TEM image of the eggshell nanoparticles is presented in Fig. 3a. Average size of the eggshell nanoparticles determined from the previous study containing eggshell nanoparticles and recycled low-density polyethylene is 76.25 nm. Moreover, eggshell nanoparticles exist in globules of different shapes and sizes. Each network or globule is formed from fusion of many individual eggshell nanoparticles. The eggshell nanoparticle aggregates suggest their dissolution in ethanol and subsequent wet milling to separate them into many individual particles prior to processing of polymeric nanocomposites.

3.2. Chemical properties of the polymeric nanocomposites

Chemical properties of the very low-density polyethylene and its nanocomposites are presented by the Fourier transform Infrared spectrograph (Fig. 3b). Four major peaks have been identified for both polymer and its composites, however, with differences in the wavenumbers and absorbances at which the peaks appear. The variations could be attributed to the chemical reaction between the eggshell nanoparticles and polymer molecules that give rise to new molecules having the same functional groups with those of the polymer molecules affirming their similar chemical properties. Moreover, differences in the absorbances indicate variation in the optical properties of polymer and composite molecules. Moreover, minor peaks at 1747.93 and at 1158.16 cm^{-1} confirming formations of new compounds in the nanocomposite as those peaks are not found in the very low-density polyethylene. In addition, molecule at 2018.74 cm^{-1} is only found in the polymer. This affirms the attributed chemical reaction between the polymer molecule and eggshell particle phases. Disappearance of the peak at 2018.74 cm^{-1} in the nanocomposite FTIR spectrum could imply that it reacted and formed a new compound/bond having different properties from the polymer molecule at the peak. This finding agrees with literature [38]. In addition, peak at 2916.5/2916.49 cm^{-1} and 1471.91/1471.9 as detected in the polymer/composite is linked to asymmetric CH_2 stretching. The peak at 2850.29/2850.20 is assigned to symmetric CH_2 stretching, while the peak at 718.03/717.89 cm^{-1} belongs to C═C asymmetric stretch alkene family. The peak interpretation is in line with [38,39] and those bonds confirm polyethylene. Broadness of the peaks in the functional group side affirm the low-density polyethylene.

3.3. X-ray profiles of polymeric nanocomposites

X-ray diffractograms of the pristine low-density polyethylene have peaks fitted with detected compounds (Fig. 4). Pentaerythritol ($C_5H_{12}O_4$) observed at position of 20.5274°, 35.4325°, 42.1678°, 46.1747° and 52.2759°; tri-methylene di-phosphonic acid ($C_3H_{10}O_6P_2$)

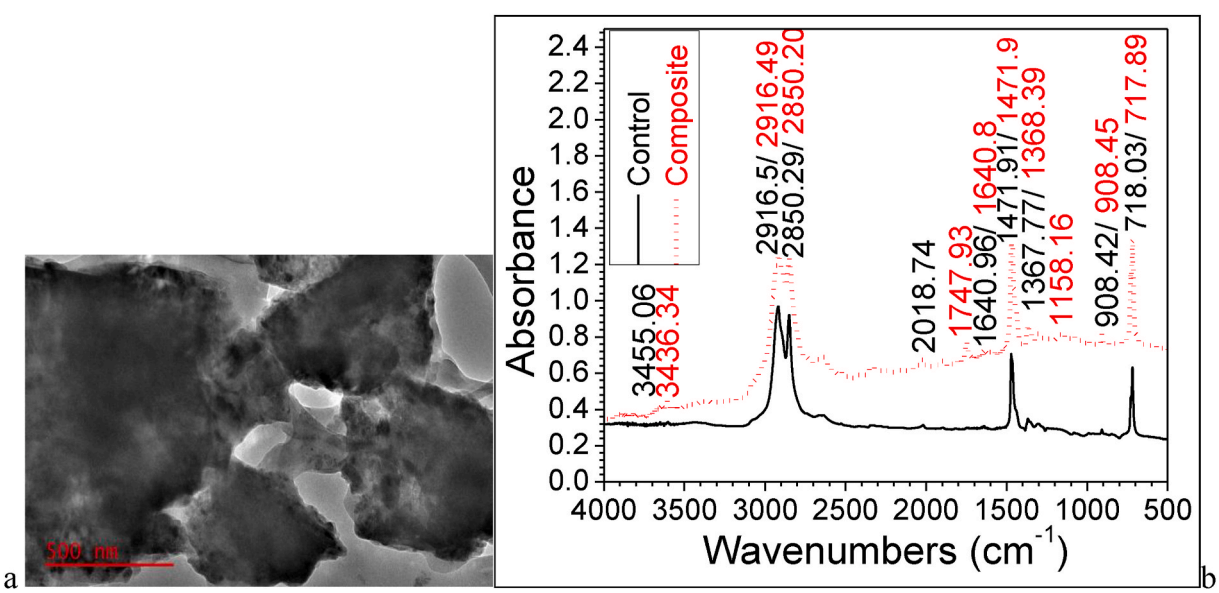

Fig. 3. (a) Transmission electron microscopic image of the eggshell nanoparticles (b) Fourier transform infrared spectrographs of the polymeric nanocomposite.

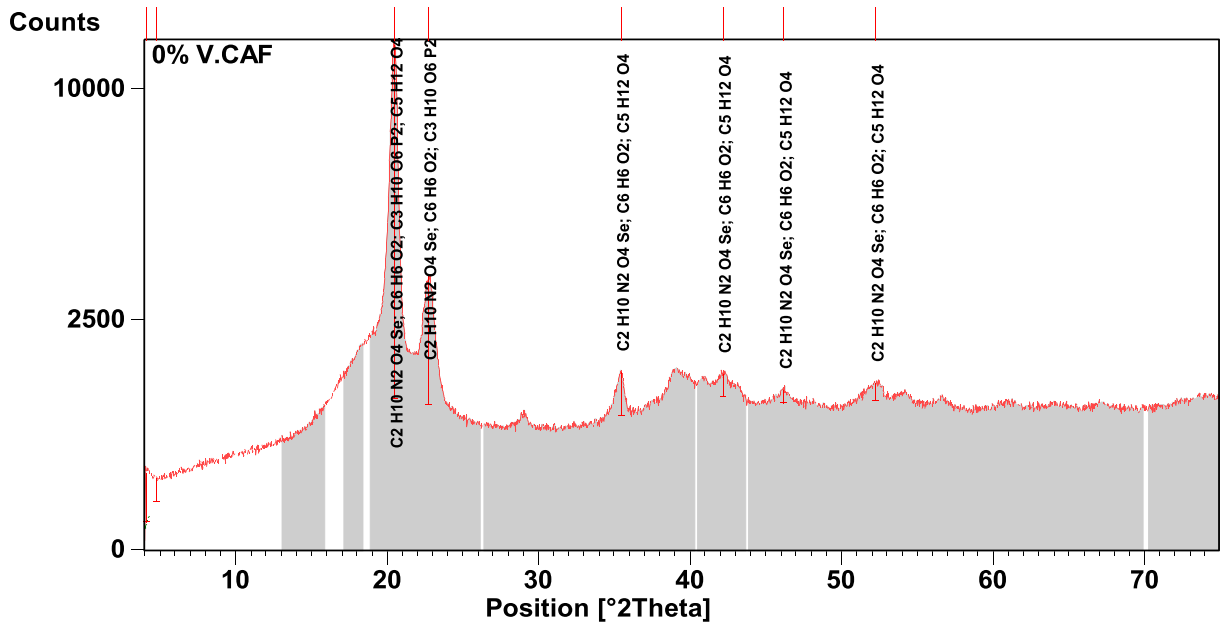

Fig. 4. X-ray diffractogram of the (a) pristine very low-density polyethylene.

at 20.5274° and 22.7464°; $GG-Hydroquinone ($C_6H_6O_2$) and ethylenediamine hydrogen selenite ($C_2H_{10}N_2O_4Se$) at 20.5274°, 22.7464°, 35.4325°, 42.1678°, 46.1747° and 52.2759° are the phases observed with various XRD peaks of the low-density polyethylene. In details, phases observed with a peak at 20.5274° possess intensity of 10894.35 cts, full width half maximum (FWHM) of 0.4517° and interplanar spacing (d-spacing) of 4.32677 Å. In addition, phases identified with the peak at 22.7464° have intensity of 2530.53 cts, FWHM of 0.6376° and d-spacing of 3.90945 Å; those observed at 35.4325° are characterized by intensity of 625.66 cts, FWHM of 0.4251 and d-spacing of 2.53345 Å. Intensity of 358.86 cts, FWHM of 0.8502 and d-spacing of 2.14307 Å belong to the phases confirmed with the peak at 42.1678°. Moreover, intensity of 182.26 cts, FWHM of 0.8502 and d-spacing of 1.96601 Å attribute the phases appeared on the peak at 46.1747°. Moreover, phases of the peak at 52.2759° have intensities of 262.85 cts, FWHM of 1.0368° and 1.74856 Å. Ethylene, the monomer of polyethylene is expected to be confirmed with the XRD peaks. However, Pentaerythritol ($C_5H_{12}O_4$), tri-methylene di-phosphonic acid ($C_3H_{10}O_6P_2$) and ethylenediamine hydrogen selenite ($C_2H_{10}N_2O_4Se$) are ethylene products resulted from interaction of ethylene with palm kernel oil added to the low-density polyethylene during processing which makes it wettable with eggshell nanoparticles. The compounds detected from eggshell nanoparticle reinforced low-density polyethylene are different from those of the very low-density polyethylene polymer (control).

Moreover, very low-density polyethylene/eggshell nanocomposites has 1,6-Anhydro-$GB-D-galactopyranose ($C_6H_{10}O_5$) observed at 18.6706, 34.0828 and 45.1908°; Johachidolite $CaAl(B_3O_7)$ detected at 34.0828 and 45.1908°; Poly($GB-hydroxynonanoate) $(C_9H_{16}O_2)_n$ found at 4.1510 and 34.0828°; Magnesium toluenesulfonate hexahydrate ($C_{14}H_{14}MgO_6S_2.6H_2O$) at 18.6706°, 20.9689°, 34.0828° and 45.1908° and 1,2-Diphenylcyclohexene ($C_{18}H_{18}$) at 18.6706°, 20.9689° and 34.0828° (Fig. 5). Varied compounds detected with the low-density

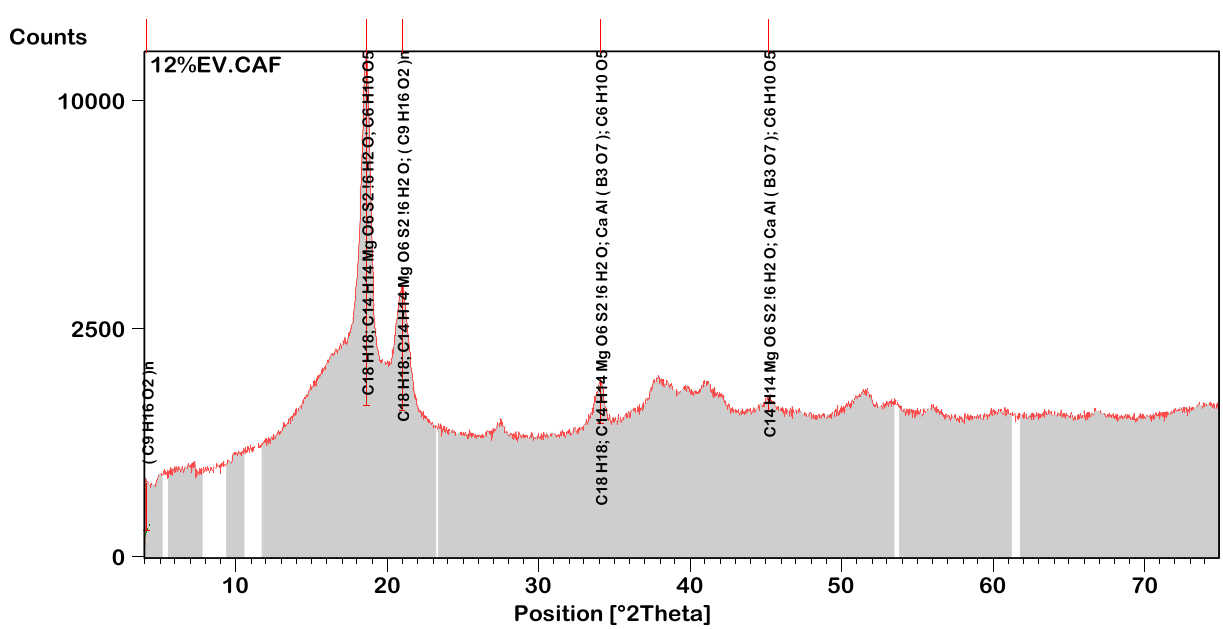

Fig. 5. X-ray diffractogram of the very low-density polyethylene having 12 wt% eggshell nanoparticle additions.

polyethylene and its nanocomposites establishes chemical interaction between phases of the low-density polyethylene and eggshell nanoparticles giving rise to formation of new compounds as it is established by new peaks and peak parameters of the FTIR spectrograph in Fig. 3b. New compounds identified with the polymeric nanocomposites are distinguished from those of the control very low-density polyethylene. Structural features of the XRD peaks (Table 1) establish broadness of the peaks due to eggshell nanoparticle additions to the very low-density polyethylene as FWHM of the low-density polyethylene polymer is smaller than that of the corresponding peak of the nanocomposites. Broader peaks of the nanocomposites propose refinement of the structure due to reinforcing particle additions to the very low-density polyethylene. Smaller d-spacing of the nanocomposite phases at 4.1497°/4.1510° and 20.5274°/20.9689° than those of the very low-density polyethylene indicate close packing of the nanocomposite phases which could be linked with fine grain structure of the nanocomposites. This establishes fair dispersion of the eggshell nanoparticles within the low-density polyethylene as the d-spacing of the nanocomposite phases at 35.4325°/34.0828° and 46.1747/45.1908 are greater than those of the control.

3.4. Microstructural properties of polymeric nanocomposites

Furthermore, unreinforced very low-density polyethylene polymer contains layered structures with a layer appears displaced over another (Fig. 6a). The structure has many fused polymeric grains conforming to continuous undulating layered structure (Fig. 6a) with extended polymer grains. Being a continuous structure, when loaded, there could be no room for local deformation since the polymer would collectively act as a single solid. Therefore, it has a high potential to prevent deformation from the external load, but extent of the resistance is limited due to absence of reinforcing particles. Energy dispersive X-ray spectroscope confirmed only C in the unreinforced low-density polyethylene (Fig. 6b). Considering the eggshell nanoparticles interaction with the low-density polyethylene, distinctions are observed when their microstructures (Fig. 7a–d) are compared with those of the pristine low-density polyethylene. There are numerous composite grains in Fig. 7 networking together to form a rigid composite structure. Pattern of grains arrangement in this case has no resemblance from that of the very low-density polyethylene. This implies that the addition of the eggshell nanoparticles greatly modified the structure of the very low-density polyethylene. Grains are observed connecting with one another forming composite structure with a strong bond with one another. Therefore, very low-density polyethylene having 12 wt% eggshell nanocomposites have a high integrity structure containing continuous polymeric composites having numerous tiny dendritic grains interlocking one another in well-defined patterns analogous to a metallic crystalline structure.

Moreover, orientation and spatial configuration of each grain with even dispersion of eggshell nanoparticles are showing clearly in the magnified image in Fig. 7b–c. Observation from the SEM micrograph agrees with finding from XRD in Fig. 5. A good material performance relies on integrity of its microstructure. With high integrity of microstructure of the very low-density polyethylene/12 wt% eggshell nanocomposite, its excellent performance under mechanical loading is expected. Energy dispersive X-ray spectroscope affirmed C, O and Ca as the major elements found in the very low-density polyethylene/12 wt% eggshell nanocomposites. Polyethylene is a hydrocarbon. Presence of C attributes to the presence of the polyethylene since hydrogen cannot be detected by EDX due to its lightness. Ca and C belong to eggshell nanoparticles. Other elements may affirm palm kernel oil used to join the eggshell nanoparticles to the very low-density polyethylene pellets and small amounts of minerals forming part of the eggshells.

Table 1
Peak features of the X-ray diffractograms of both low-density polyethylene and nanocomposite.

Low density polyethylene		
Position (°2theta)	FWHM (°2theta)	d-spacing [Å]
4.1497	0.1594	21.29342
4.7995	0.8502	18.41220
–	–	–
20.5274	0.4517	4.32677
22.7464	0.6376	3.90945
35.4325	0.4251	2.53345
42.1678	0.8502	2.14307
46.1747	0.8502	1.96601
52.2759	1.0368	1.74856
Low density polyethylene nanocomposite		
Position (°2theta)	FWHM (°2theta)	d-spacing [Å]
4.1510	0.1653	21.28675
–	–	–
18.6706	0.4684	4.75266
20.9689	0.7164	4.23665
–	–	–
34.0828	0.4408	2.63062
–	–	–
45.1908	1.0752	2.00483

FWHM-Full width half maximum; d-spacing- interplanar spacing.

3.5. Mechanical properties of polymeric nanocomposites

3.5.1. Tensile properties of polymeric nanocomposites

Generally, addition of eggshell nanoparticles to the very low-density polyethylene improves tensile properties of the produced polymeric nanocomposites. Figs. 8 and 9a indicate a progressive increase in the tensile strength and modulus equal to 110.4 and 499.4 %, respectively at 12 wt% eggshell nanoparticle additions. An increase in tensile elongations is also observed at 2 wt% after which a decrease prevails as shown in Fig. 9c and e. Theoretically, greater mechanical properties of the polymeric nanocomposites can be explained by dispersion strengthening mechanism using microstructure in Figs. 6 and 7. There is no segregation of eggshell nanoparticles found in the very low-density polyethylene/12 wt% eggshell nanocomposite as microstructure in Fig. 7 demonstrates. It implies an even dispersion of the reinforcing nanoparticles which are all united by the low-density polyethylene matrix. When the composite is under uniaxial load like in the tensile test, the low-density polyethylene matrix transfers the load to every eggshell nanoparticle connected to it and share the loading constraints. Therefore, united nanoparticles collectively resist the deformation from the externally applied load. This continues till their resistance is overcome afterwards the composite yielding begins with initiation of micro-voids (crazes). The micro-voids advance and grow via dilation by tensile pulls meanwhile the craze advancement/growth is impinged at every approach of the nanoparticles, causing delay in the craze propagation. Therefore, additional stress is needed to cause further movement and coalescences of the crazes to produce macro-voids leading to polymeric nanocomposite necking at the ultimate stress. After necking, stress drops since resistance to deformation is low due to debonding of the reinforcing eggshell nanoparticles from the low-density polyethylene matrix. Moreover, in the low-density polyethylene polymer, craze propagation and growth are rapid since there is no reinforcing eggshell nanoparticle or second phase compounds to block the craze (see Fig. 6). This explains why tensile properties of the low-density polyethylene are smaller than those of the low-density polyethylene/eggshell nanocomposites. Increase in the tensile properties is linked with greater resistances to deformation due to an increase in the number of connected particles within the matrix as the wt% of eggshell nanoparticle addition increases (see Fig. 7). This explanation is in line with literature [26]. Moreover, tensile properties of the developed nanocomposites were benchmarked with those of the existing vehicle bumper fascia. It is observed that the maximum tensile strength, 13.8 Nmm^{-2} obtained in this study is at 12 wt% eggshell nanoparticle additions to the low-density polyethylene.

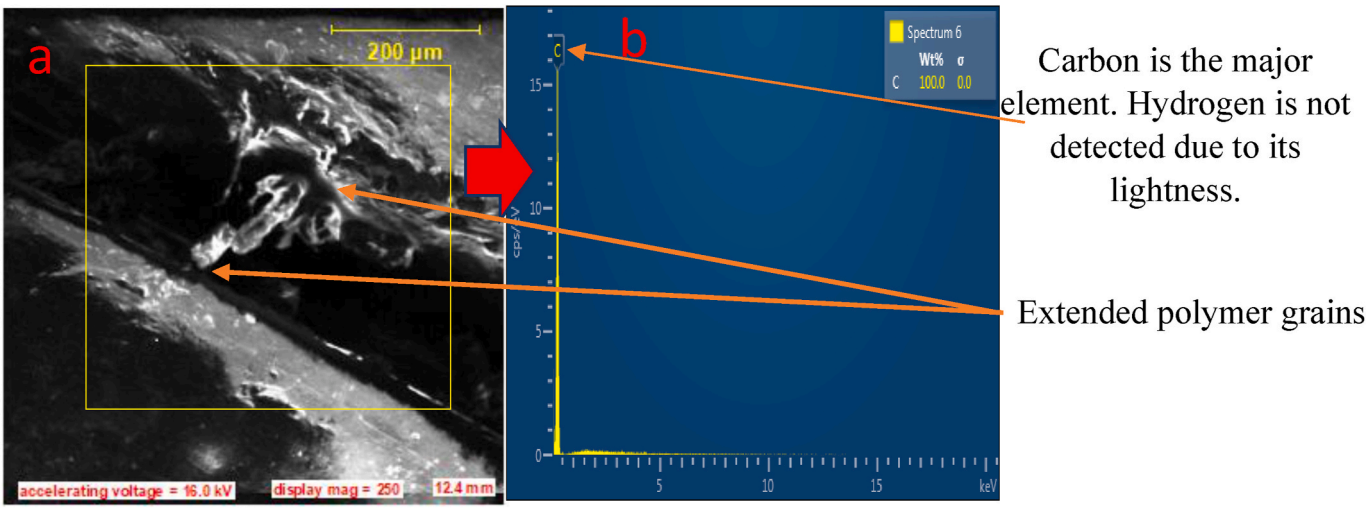

Fig. 6. SEM/EDX of unreinforced new low-density polyethylene (a) micrograph (b) elemental composition.

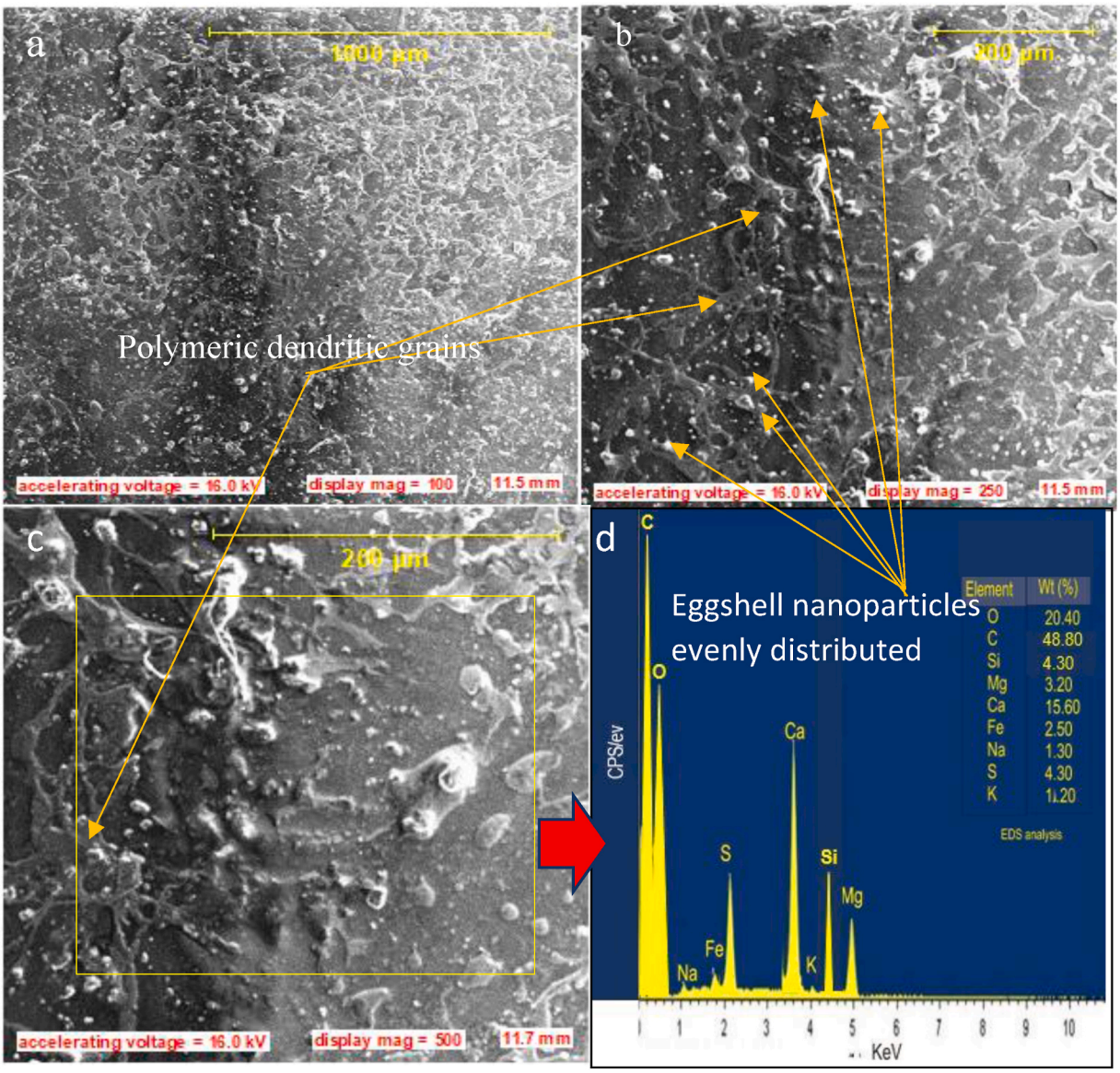

Fig. 7. SEM/EDX of new low-density polyethylene containing 12 % eggshell nanoparticles (a) X 100 (b) X 250 (c) X 500 (d) elemental composition.

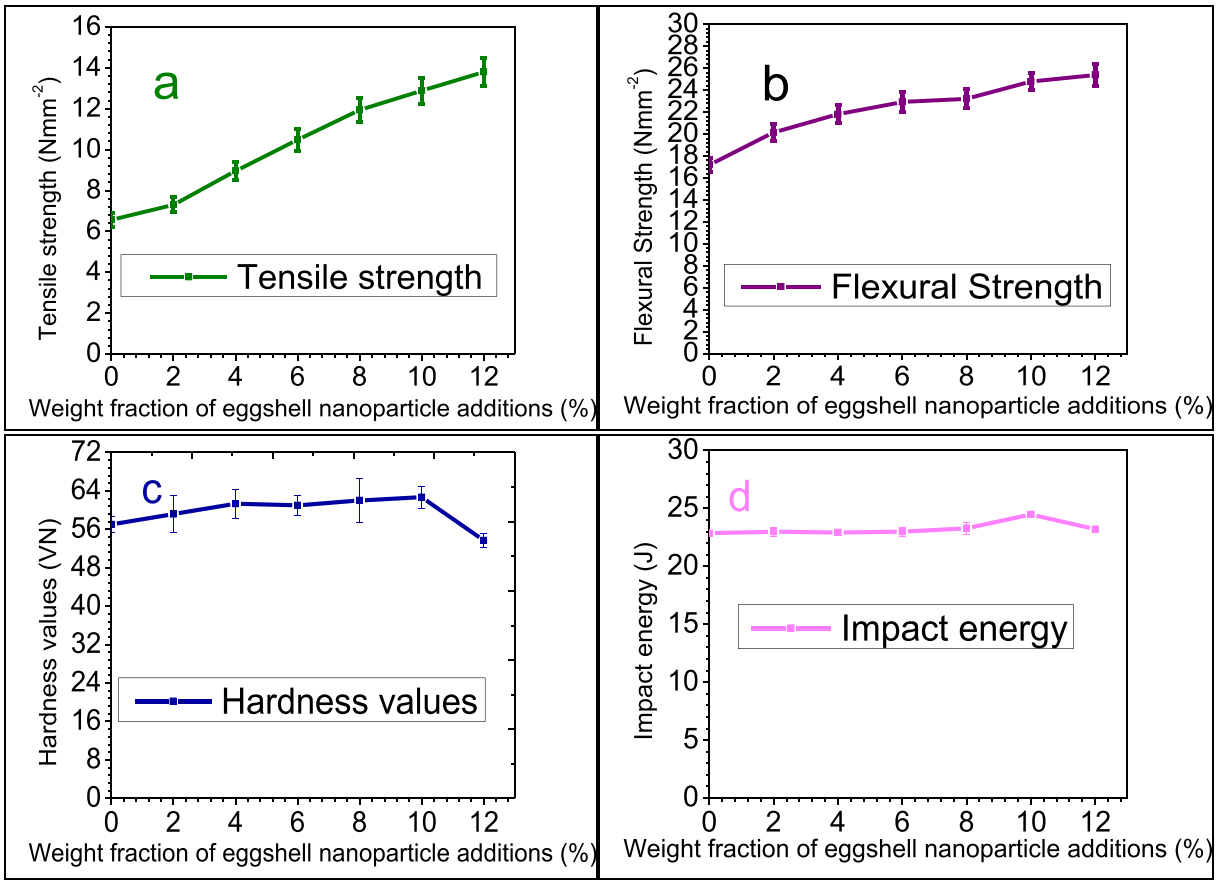

Fig. 8. Mechanical properties of the low-density polyethylene-eggshell nanocomposites (a) tensile strength, (b) flexural strength, (c) hardness values, and (d) impact energy.

Tensile modulus of the polymeric nanocomposite containing 12 wt% of eggshell nanoparticles is 751.36 Nmm^{-2} and its tensile elongation is 3.065 %. Tensile strength of the XLE 2010 model Toyota Sienna bumper fascia is 12.23 Nmm^{-2} and that of 2010 model Nissan Almera is 6.44 Nmm-2 as reported in Ref. [24]. Moreover, tensile strength of the existing bumper fascia investigated in this study is presented in Table 2. 1st, 2nd and 3rd are the tensile strength of the analysed samples cut from each of the respective bumper fascia. Average or mean value of the three tensile strength values is presented in the 6th column of the table while their standard deviation in the 7th column. Tensile strength, 13.4 ± 1.4 Nmm^{-2} of 2005 Table 3 Model Toyota Sienna is in line with 12.23 Nmm^{-2} already reported in literature for 2010 model of the same vehicle [26]. Moreover, LEXUS RX300 has the highest tensile strength and percentage elongation values (Tables 2 and 4). Honda 2002 has the highest tensile elastic modulus among the three-vehicle bumper fascia (Table 3). By comparing with the properties of 12 wt% eggshell nanoparticle reinforced low-density polyethylene, its 13.8 ± 0.7 Nmm^{-2} is greater than each of Nissan Almera, Toyota Sienna 2002, 2010 and Honda 2002 but it is less than that of the LEXUS RX300. Moreover, its elastic modulus 751.36 Nmm^{-2} is the least by comparing with those of the Honda 2002, SIENNA 2005 and LEXUS RX300 while its percentage elongation (3.065 %) is the greatest comparing with those of the existing vehicle bumper fascia. Upon this, it is inferred that tensile properties of 12 wt% eggshell nanoparticle reinforced very low-density are superior to those of the existing materials for the vehicle bumper fascia.

3.5.2. *Flexural properties of polymeric nanocomposites*

Moreover, an increase in flexural strength is also noted up to 12 wt% corresponding to 47.7 % (Fig. 8b). Flexural modulus of elasticity increases with increasing nanoparticle additions to the low-density polyethylene (Fig. 9b). Since the percentage increase in flexural modulus at 10 wt% and 12 wt% of eggshell nanoparticle addition are 16.9 and 7.1 %, respectively, this implies the degree of enhancement in the flexural strength start declining from 10 wt% of eggshell nanoparticle addition though flexural modulus at 12 wt% is still greater than that of the control but maximum is obtained at 10 wt%. Since flexural strength and modulus are two different parameters for evaluating a bending tendency of a material, the difference noticed in the flexural strength and modulus enhancement is possible. This could be due to changes in flexural deflections (Fig. 9d) of the nanocomposites as wt% of eggshell nanoparticle increases. Smaller values of the flexural deflections at 4, 6, 8 and 10 wt% justify the increase in flexural modulus of the eggshell/low-density polyethylene nanocomposites within the loading range. Smallest value of the flexural deformation at 12 wt% has effect of raising the flexural strength up since the higher the strength, there is a tendency for a decrease in the strain (material's ductility). The increase and decrease patterns observed with both tensile elongations and flexural deflections are attributed to nature of phases formed from interactions of the very low-density polyethylene molecules and $CaCO_3$ from eggshell nanoparticles (see Fig. 5). Although, most tensile elongations of nanocomposites are smaller than that of the pristine low-density polyethylene, maximum tensile elongation is ascertained at 2 wt% eggshell nanoparticle addition to the low-density polyethylene, corresponding to the loading level at which the tensile modulus of the nanocomposite is minimum. This agrees with formula in Equation (1) [40] relating tensile strength (σ), modulus of elasticity (E) and tensile elongation (ε) of a material deformed plastically; n is strain hardening coefficient.

$$Strength\ \sigma = E\varepsilon^{n} \quad (1)$$

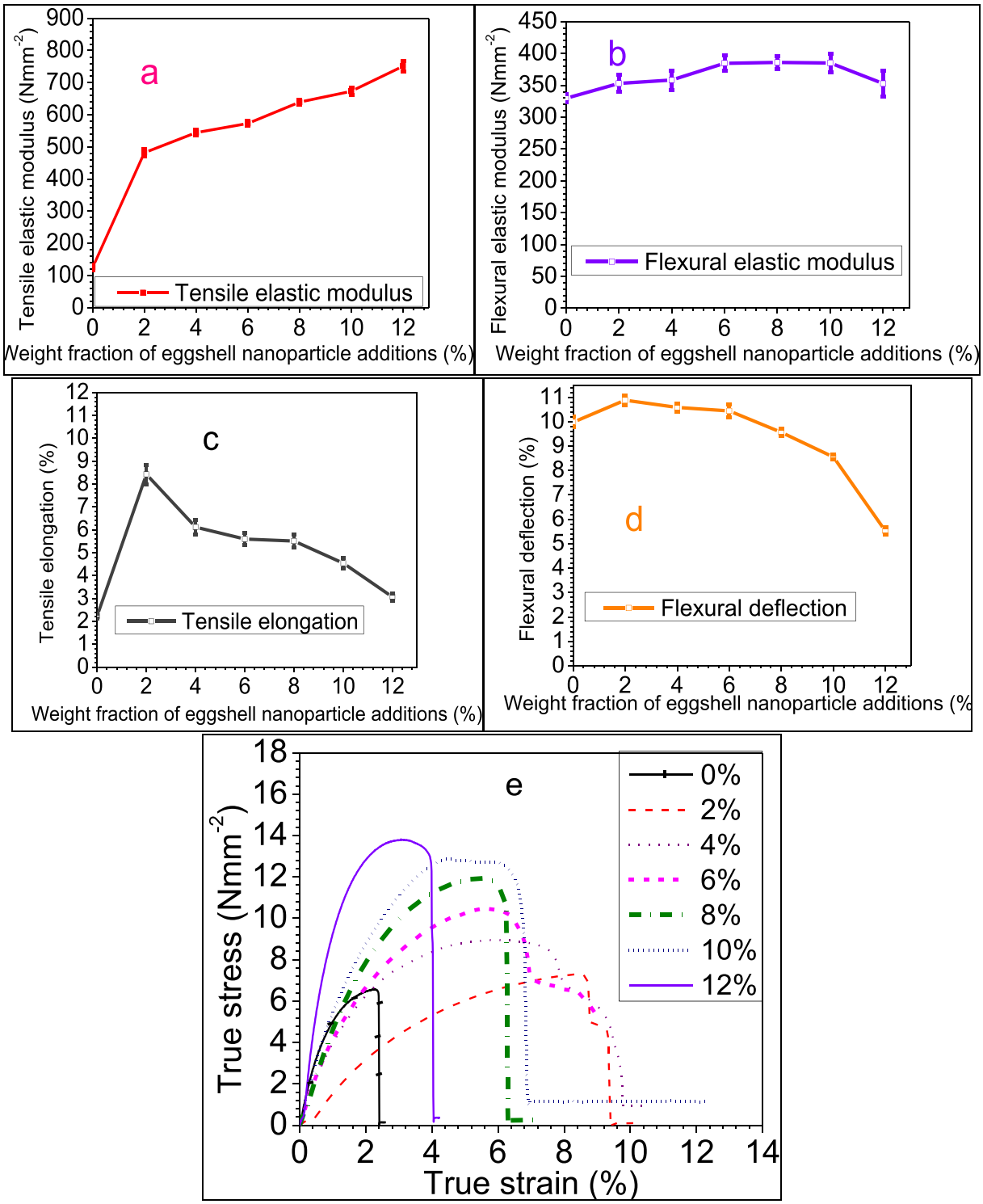

Fig. 9. Mechanical properties of the low-density polyethylene-eggshell nanocomposites (a) tensile elastic modulus, (b) flexural elastic modulus, (c) tensile elongation (d) flexural deflections (e) combined tensile true stress-strain curves at different eggshell nanoparticles additions.

Enhancement in the flexural properties is linked with even dispersion strengthening effect (See Fig. 7) leading to greater load/stress bearing capacities of the composite due to eggshell nanoparticles additions. However, the decrease in the flexural deflection above 2 wt% could be linked with inability of the respective low-density polyethylene nanocomposites to bear the elongation during bending over appreciable period at the fracture stress prior to eventual failure or breakage of the sample.

Moreover, flexural properties of the existing bumper fascia vary from a vehicle to another. RX300 has a flexural strength of 1.91 ± 0.18 Nmm^{-2}, SIENNA 2005 has 5.3 ± 0.7 Nmm^{-2}, while Honda 2002 has 1.7 ± 0.2 Nmm^{-2} (Table 5). These values are much less than 135.16 Nmm^{-2} and 58.30 Nmm^{-2} reported for 2010 Model Toyota SIENNA and Almera NISSAN, respectively in Ref. [24]. By comparing the flexural strength of the developed polymeric nanocomposite, its flexural strength of 25.4 ± 0.96 falls within those of existing vehicle bumper fascia. It is greater

Table 2
Tensile strength of already existing vehicle bumper fascia.

TENSILE STRENGTH (Nmm^{-2})						
S/N	SAMPLES	1ST	2ND	3RD	AVERAGE	Standard deviation
1	HONDA 2002	13.334	13.404	13.409	15.076	2.88312
2	SIENNA 05	12.664	14.987	12.532	13.394	1.380489
3	RX 300	16.660	18.426	19.584	18.224	1.472617

than each of RX300, SIENNA 2005 and Honda 2002 but least when compared with both Toyota SIENNA, and Nissan ALMERA 2010. Information on flexural modulus of materials for the bumper fascia is scarce as such has not been found in literature. Moreover, those of the LEXUS RX300, TOYOTA SIENNA 2005 and HONDA 2002 are presented in Table 6. Each of those values are smaller than 352.747 ± 20 Nmm^{-2} of 12 wt% eggshell nanoparticle reinforced very low-density polyethylene.

3.5.3. Impact energy and hardness values

In addition, impact energies of the composites are nearly the same with that of the very low-density polyethylene up to 8 wt% eggshell nanoparticle addition (Fig. 8d), but a noticeable increase is found at 10 wt% which is 7 % higher than that of the low-density polyethylene meanwhile a continuous slight increase in the hardness values was recorded equal to 10 % enhancement at 10 wt% eggshell nanoparticle addition (Fig. 8c). Above 10 wt%, the composite hardness value is smaller than that of the very low-density polyethylene. The smaller value of the hardness at 12 wt% of eggshell nanoparticle addition could be linked with impact energy at the same level of reinforcement which its value is greater than that of the control (very low-density polyethylene).

Small increase observed with the impact energy implies that eggshell additions to the low-density polyethylene does not impair the impact energy. This may account for slight improvement in the hardness since a hard material rarely absorbs energy. Therefore, it is noteworthy that the eggshell/very low-density polyethylene nanocomposites have impact energies comparable with that of the very low-density polyethylene despite their greater hardness than that of the low-density polyethylene polymer. Therefore, the eggshell/very low-density polyethylene nanocomposites are tough and moderately hard. The combined toughness and hardness of the nanocomposites enable them as candidate materials for vibration damping application like a vehicle absorber, cases for electronic/electrical gadgets, dashboard, or bumper cover/fascia.

For benchmarking purpose, impact energy of the bumper fascia in literature was reviewed. It was reported that TOYOTA Sienna (XLE 2010 model) bumper fascia has impact energy of 21.8 J. The 2010 model NISSAN Almera has 25.54 J [24]. Impact energy of the TOYOTA SIENNA 2005 determined in this study is 40.99 ± 0.2 J. HONDA 2002 has an impact energy of 40.3 ± 0.8 J and LEXUS RX300 has 41.12 ± 0.34 J. The impact energy of 12 wt% eggshell nanoparticle reinforced very low-density polyethylene is 23.2 ± 0.1 J which is the least by comparing with those of RX300, SIEANNA 2005 and HONDA 2002 and 2010 model NISSAN Almera though it is greater than that of TOYOTA SIENNA 2010 model. It is also greater than the impact energy (21.69 J) of 10 wt% eggshell nanoparticle reinforced recycled low-density polyethylene reported in Ref. [26] which implies that the present material is superior to the previous one, making it a better candidate for the application. The developed 12 wt% eggshell nanoparticle reinforced very low-density polyethylene is suitable for the bumper fascia of some of the vehicles whose properties are compared with those of the developed material. Moreover, it is important to note that the highest flexural strength and impact energy of the bumper fascia of the existing vehicles are 135.16 [26] and 41.09 J (Table 7), respectively which are higher than those of the 12 wt% eggshell nanoparticle reinforced very low-density polyethylene in this study. Therefore, further study is recommended until a polymeric material having greater flexural strength and impact energy are obtained.

3.5.4. Benchmarking findings of this study with properties of polymeric composite in literature

Moreover, this study has established enhancements in mechanical properties of the very low-density polyethylene due to eggshell

Table 4
Tensile elongation of already existing vehicle bumper fascia.

Percentage elongation (%)						
S/N	SAMPLES	1ST	2ND	3RD	AVERAGE	SD
1	HONDA 2002	2.424	4.171	4.933	3.843	1.286439
2	SIENNA 05	3.687	8.638	4.314	5.546	2.696053
3	RX 300	5.055	2.726	4.129	3.970	1.172648

Table 5
Flexural strength of already existing vehicle bumper fascia.

Ultimate Flexural Strength (Nmm-2)						
S/N	SAMPLES	1ST	2ND	3RD	AVERAGE	SD
1	RX 300	1.824	1.780	2.118	1.907	0.184028
2	SIENNA 05	6.042	4.846	4.973	5.287	0.656668
3	HONDA 2002	1.928	1.547	1.613	1.696	0.203589

Table 6
Flexural modulus of already existing vehicle bumper fascia.

BENDING MODULUS (Nmm^{-2})						
S/N	SAMPLES	1ST	2ND	3RD	AVERAGE	SD
1	RX 300	110.758	211.233	83.880	135.290	67.12734
2	SIENNA 05	136.381	121.264	114.970	124.205	11.00423
3	HONDA 2002	45.067	26.134	43.219	38.140	10.43822

Table 7
Impact energies of already existing vehicle bumper fascia.

SAMPLE	IMPACT ENERGY (J)			Average	Standard
	A	B	C		
SIENNA 2005	41.10	41.07	40.80	40.99	0.17
HONDA 2002	40.66	39.44	40.80	40.30	0.75
LEXUS RS 300	41.09	40.80	41.48	41.12	0.34

Table 3
Tensile elastic modulus of already existing vehicle bumper fascia.

YOUNG MODULUS (Nmm^{-2})						
S/N	SAMPLES	1ST	2ND	3RD	AVERAGE	SD
1	HONDA 2002	1043.194	1262.167	1033.084	1112.815	129.441
2	SIENNA 05	969.450	999.666	906.152	958.423	47.72267
3	RX 300	938.076	1039.499	985.827	987.801	50.74012

nanoparticles additions. However, different reports or findings have been encountered in literature. For instance, potentials of softwood, barley husk and coconut shell as reinforcing fibres in polypropylene were studied and compared; it was reported that the tensile strength of the barley husk composite were 10 and 24 % greater than of the softwood and coconut shell based composites, respectively [15]. No report was found on the tensile strength of the unreinforced polypropylene composite making it difficult to ascertain whether the used reinforcement in Ref. [15] either improves or degrades the tensile property of the polypropylene. In addition, 17, 4.3 and 35.5 % improvements in respective tensile strength, flexural strength and impact energy were found in Ref. [13] due to equal proportions of banana-jute fibres addition to epoxy. Similarly, 125.6, 214.3, 188.5, 145.7 and 64.3 % gains in respective tensile strength, tensile modulus, flexural strength, flexural modulus and impact energy of the low-density polyethylene reinforced with 20 % palm fibres with 62.9 % reduction in the tensile elongation were presented in Ref. [41]. Also, 40 wt% bagasse fibre addition to high density polyethylene was come across in Ref. [42] with 122 % enhancement in the tensile modulus. Improvements in mechanical properties in this study as presented above are in line with literature [43]. Also, the hardness increase due to eggshell nanoparticle additions to the very low-density polyethylene in this study perfectly agrees with findings on the hardness values of the low-density polyethylene reinforced with 75 μm sized bean pod ash particles however reduction in impact energy was reported by the authors [44] which contradicts slight impact energy increase in this study. The different behaviour in respect of impact energy in the present study and that of the previous study could be linked with variations in the reinforcing particles, size differences (75 μm and 76.25 nm) and weight percentage of particles addition. Smaller size of the eggshell nanoparticle may contribute to better impact property of the low-density polyethylene/eggshell nanocomposites since conventional brittle material at microscale becomes tough/soft at nanoscale level; this property relates to cold welding of the ceramic nanoparticles as established in literature [45,46]. Moreover, difference in weight percentage of the particle addition could also be responsible for differences in the impact behaviour. Impact energy of the low-density polyethylene/bean pod ash composites are 34.4, 34.2, 34 and 33.9 kJ/m^2 at 0, 5 10 and 15 %, respectively which implies that there is no significant impact energy differences between the polymer and the nanocomposites up to 15 wt% bean pod ash addition to the low-density polyethylene but at higher weight percentage additions like that at 30 wt%, 11.2 % reduction was reported by the authors [44].

There is a possibility for reductions in the impact energy of the low-density polyethylene nanocomposites in this study above 12 wt% eggshell nanoparticle addition since impact energy at 12 wt% is smaller than that at 10 wt% eggshell nanoparticle additions. Moreover, findings from author's previous study on the eggshell nanoparticle reinforced recycled low-density polyethylene indicate a maximum tensile strength of 10.68 Nmm^{-2} which is less than 13.8 Nmm^{-2} maximum tensile strength obtained in this study. Impact energy and flexural strengths of the eggshell nanoparticle reinforced recycled low-density polyethylene having tensile strength of 10.68 Nmm^{-2} are 21.69 J and 21.964 Nmm^{-2}, respectively as it was reported in Ref. [26] meanwhile those of the nanocomposite having tensile strength of 13.8 Nmm^{-2} in this study are 23.2 J and 25.39 Nmm^{-2}. Greater values of the impact energy, tensile and flexural strengths of the nanocomposite in this study than those of the previous study affirms better performance of the very low-density polyethylene as a matrix for the eggshell nanoparticles than that of the recycled low-density polyethylene though economically, the very low-density polyethylene is more expensive. Based on the better technical properties of the 12 wt% eggshell nanoparticle reinforced very low-density polyethylene, it can be a better candidate for fabricating the automobile bumper fascia than the 10 wt% eggshell nanoparticle reinforced recycled low-density polyethylene in the previous study.

It is noted that the cost of production of the 12 wt% eggshell nanoparticle reinforced very low-density polyethylene is greater than that of the 10 wt% eggshell nanoparticle reinforced recycled low-density polyethylene [26] since the recycled low-density polyethylene is cheaper than the very low-density polyethylene. Despite the high cost, its superior mechanical properties to those of the recycled low-density based nanocomposite attributes to an improved safety of the vehicle and its passengers without compromising the pedestrian safety. This spurs its use for the luxurious vehicles associated with high safety and comfort.

Also, since the eggshell contains calcium carbonate, it is very important to compare its degree of reinforcement with that of the commercial or synthetic calcium carbonate to establish its value and encourage its uses as reinforcement in polymer. According to Ref. [47], at 3 and 5 wt% addition of synthetic calcium carbonate, yield strength of the low-density polyethylene increased from 8.5 ± 0.03 to 9.1 ± 0.15 and 9.2 ± 0.09, respectively. The increments are equal to respective 7.06 and 8.24 % which are lower than 18.75 and 46 % increase obtained by interpolation in Fig. 8a at 3 and 5 wt% eggshell nanoparticle additions to the very low-density polyethylene, respectively.

3.6. Mechanical properties of metallic composites

3.6.1. Tensile strength of metallic composites

Date seed particle addition to Al–Cu–Mg causes enhancement in the tensile strength up to 8 wt%. Since the black curve in Fig. 10a appears almost parallel to the horizontal axis above 1 wt%, it implies that the tensile strengths of Al–Cu–Mg harbouring 2, 4 and 8 wt% of date seed particles are nearly the same as that of 1 wt%. This establishes that there is none significant improvement in the strength above 1 wt%, tending to the matrix saturation level. Similar enhancement in the tensile strength was reported in literature due to eggshell particle addition to AA 2024 [48], calcined eggshell particle to AA 2014 [49], palm kernel shell addition to Al-Mg-Mn [50] and coconut shell particle additions to Al-Cu-Mg [31]. After annealing (furnace cooling) treatment, there is an improvement in the tensile strength of the control Al–Cu–Mg alloy from 124.23 Nmm^{-2} to 145.72 Nmm^{-2} while that of 0.5 wt% date seed particle reinforced Al–Cu–Mg also increased. Respective tensile strengths of the as cast and annealed samples at 1, 2 and 4 wt% of the date seed particles addition remain nearly the same implying that the annealing treatment has no positive nor negative effects on the tensile strength of those samples. The tensile strength of 8 wt% date seed reinforced Al–Cu–Mg decreased after the annealing treatment. It is likely that the annealing treatment produces a structure with lower dislocation density which gives room for the deformation of the 8 wt% date seed reinforced Al–Cu–Mg at lower tensile stress than that of the as cast sample. Moreover, the tensile strengths of normalised samples are greater than those of the cast. Matrix saturation level at 1 wt% of the date seed particles is likely to cause a decrease observed in the tensile strength of the normalised samples above 1 wt%. This is like the observation with the tensile strength of the cast samples. An improvement in the tensile strength due to normalising treatment observed in this study is similar to some findings in literature [51].

Tensile elastic modulus of the as cast composite samples increased up to 4 wt% after which a reduction in the elastic modulus begins (Fig. 10b). Those of the normalised samples increase up to 8 wt% while the annealed samples have their tensile elastic modulus p to 2 wt% after which the reduction in the elastic modulus decreases. Summarily, the as cast sample has the highest elastic modulus at 4 wt% of the date seed addition to Al–Cu–Mg alloy.

3.6.2. Impact energy of the metallic composite

An improvement in the impact energy to a certain level of date seed addition to Al –Cu–Mg is noticed generally for all samples (Fig. 10c). For the as cast samples, the decrease in the impact energy is noticed above 0.5 wt%. The reduction in the impact energy prevails above 1 wt% of date seed additions for the annealed and normalised samples. Moreover, it is noted that the impact energy of the annealed sample at 1 wt% of the

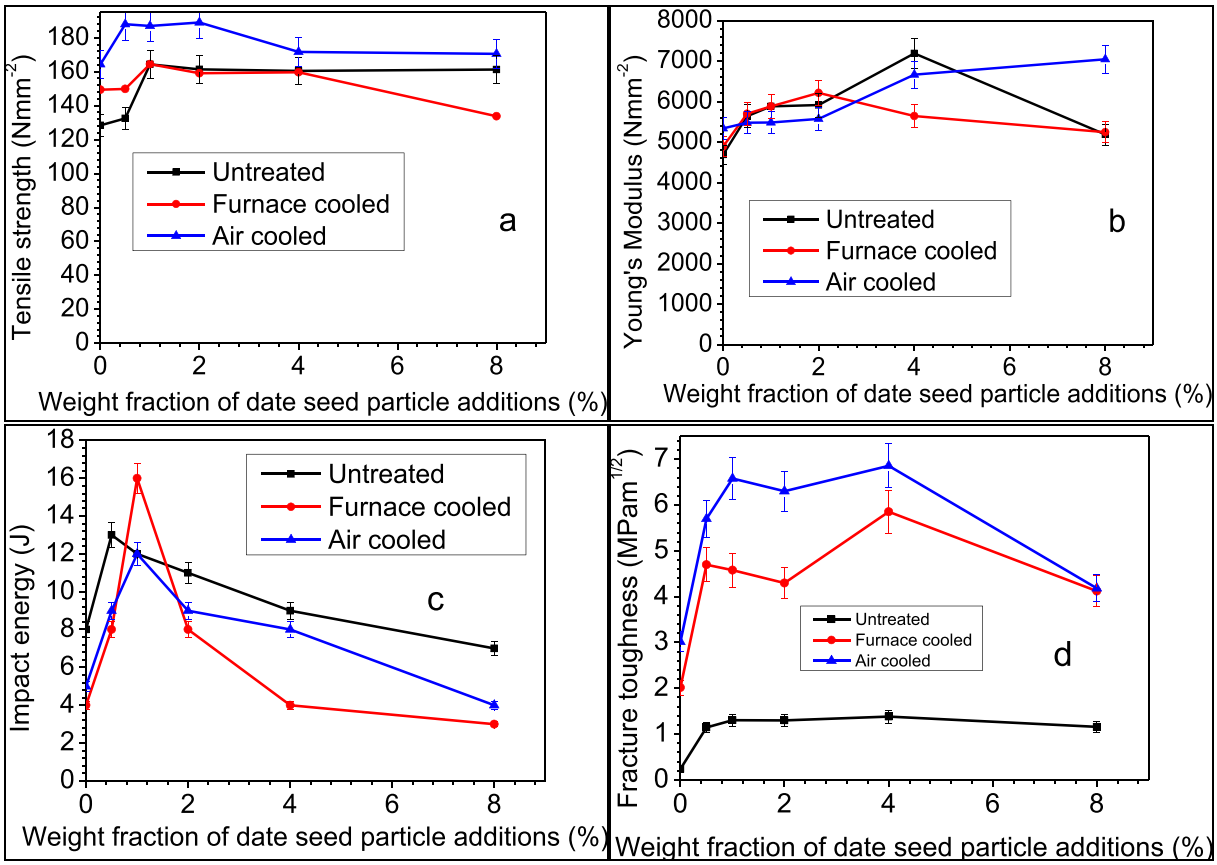

Fig. 10. Mechanical properties of date seed particle reinforced Al–Cu–Mg for facia mould parts fabrication (a) tensile strength (b) modulus of elasticity (c) impact energy (d) fracture toughness.

date seed particle addition to the Al–Cu–Mg has the highest impact energy value. The smallest impact energy values of the normalised samples could be attributed to its strength which is the highest among others. This can be likened to the hardness of those samples. That is higher rate of cooling of the normalised sample compared to the annealing may spur its lower impact energy value due to inherent increase in hardness values as the rate of cooling increases. Moreover, it is noted that the annealing (furnce cooling) treatment is beneficial to 1 wt % date seed particle reinforced Al–Cu–Mg as the annealing treatment increased its impact energy from 12.23 J of the as cast at 1 wt% date seed reinforced Al–Cu–Mg to 16.31 J with about 14.78 % increase.

3.6.3. Fracture toughness of the metallic composite

Fracture toughness increases with wt% of date seed addition to Al–Cu–Mg. An observation with the fracture toughness of the as cast samples is like those of the tensile strength of the as cast samples. There is none a significant increase in the fracture toughness of the as cast samples beyond 0.5 wt%. Both annealing and normalising significantly improved the fracture toughness with the highest value is noted with the normalised sample at 4 wt% date seed particle additions. The improvement in the fracture toughness and impact energy in this study is like some findings in the literature [52].

Since metallic composite is targeting a mould parts fabrication for forming bumper fascia prototype, the impact energy value appears to be a fundamental property for selecting a material for the mould fabrication. Therefore, annealed sample having 1 wt% of the date seed is selected for the mould fabrication because of its highest value of the impact energy. Moreover, the mould was designed using SOLIDWORK2018 from a vehicle blueprint. The detailed dimension of the bumper fascia is presented in Fig. 11b while the wireframe geometric model of the mould part is presented in Fig. 11c and d demonstrates a printing of the mould part pattern.

The pattern was used to make sand moulds (Fig. 12a) for casting 1 wt % date seed reinforced Al–Cu–Mg mould parts (Fig. 12b–d) which were annealed using the procedures in section 2.2 of this article. The finished mould parts were used for forming the bumper fascia (Fig. 12e)

4. Conclusions

The following conclusions were made based on experimental investigation in the study.

1. Compounds detected in the eggshell nanoparticle reinforced very polyethylene are different from those in the very low-density polyethylene.
2. Interplanar spacing of the crystals in the polymeric nanocomposites is shorter to that of the polymer implying closer packing of the composites' phases than those of the polymer.
3. Eggshell nanoparticle reinforced very low-density polyethylene were manufactured using sheet compression moulding.
4. Unreinforced very low-density polyethylene polymer contains layered structures with a layer appears displaced over another.
5. The very low-density polyethylene's structure has a high potential to prevent deformation from the external load, but extent of the resistance is limited due to absence of reinforcing particles while the composite has a rigid structure having distributed particles within the matrix.
6. The tensile strength of the polymeric nanocomposites increases up to 12 wt% of the eggshell nanoparticle additions
7. A decrease in impact energy and flexural modulus were found above 10 wt% of eggshell nanoparticle additions.

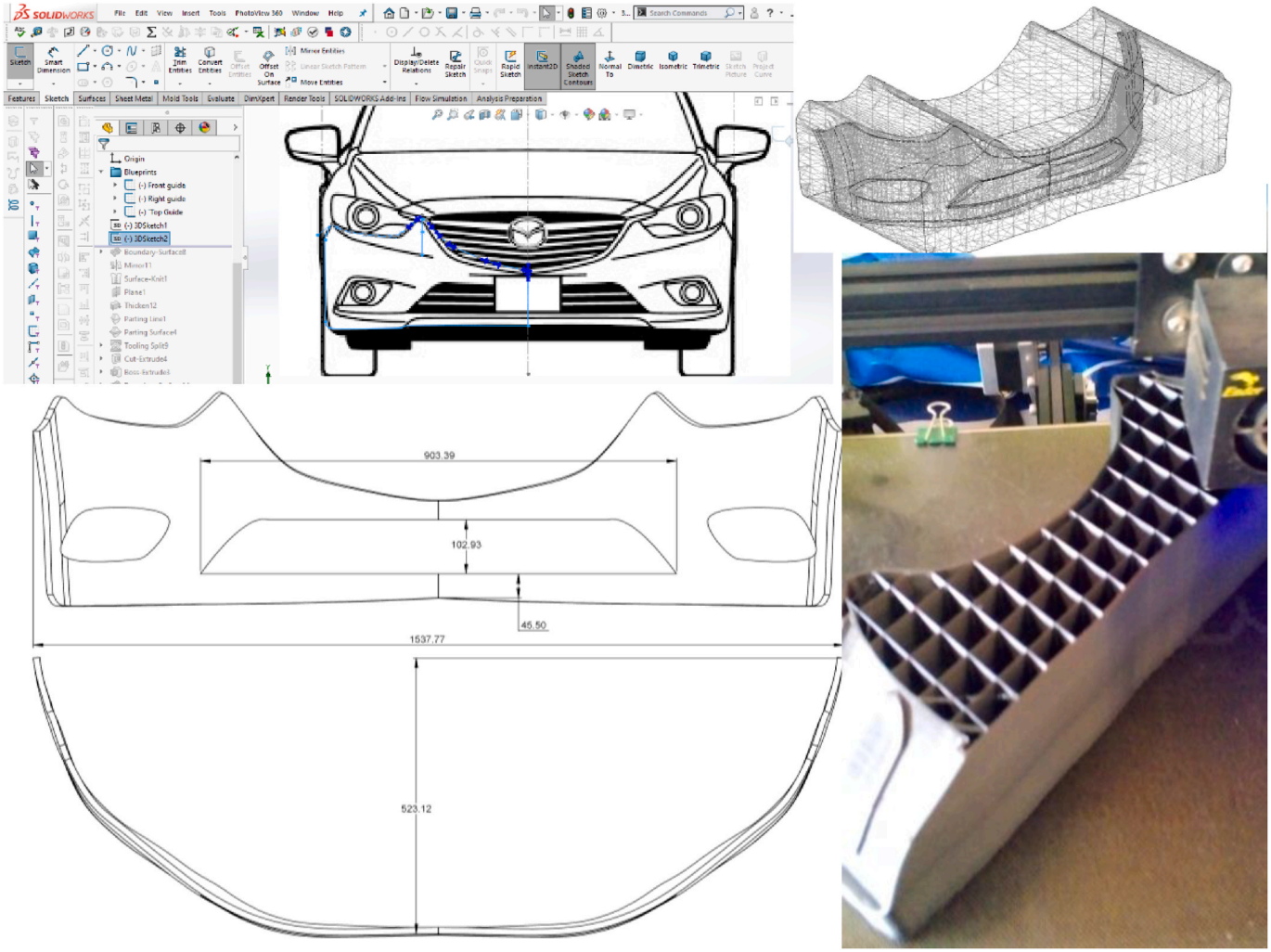

Fig. 11. Design and printing of mould parts (a) a vehicle blueprint for a bumper fascia design (b) detailed dimension of the bumper fascia (c) wireframe geometric model of a mould part (d) 3d printing of a mould part.

Fig. 12. Fabrication of bumper fascia prototype (a) mould pattern (b) pouring of metalli composite melt into the mould (c) As cast mould part [cope] (d) mould part (drag) (e) as formed bumper fascia prototype (f) trimmed bumper fascia prototype(g) painted bumper fascia prototype.

8. An increase in the tensile modulus up to 12 wt% eggshell nanoparticle addition is noted with polymeric nanocomposites.
9. Tensile strength, flexural strength and impact energy of the very low-density polyethylene/12 wt% eggshell nanocomposites fall between minimum and maximum values of the respective properties of the existing materials for the bumper fascia.
10. Tensile strength of Al–Cu–Mg alloy is improved due to date seed addition and heat treatment.
11. Annealed Al–Cu–Mg having 1 wt% of date seed particles is considered for the mould parts fabrication.
12. Bumper fascia prototype was successfully formed using the fabricated 1 wt% date seed particle reinforced Al–Cu–Mg.

CRediT authorship contribution statement

Sefiu Adekunle Bello: Writing – original draft, Supervision, Methodology, Funding acquisition, Conceptualization. **Sodiq Olamide Olaitan:** Methodology. **Mohammed Kayode Adebayo:** Investigation. **Lateef Olayinka Akinwande:** Project administration. **Funsho Olaitan Kolawole:** Writing – review & editing. **Maruf Yinka Kolawole:** Formal analysis. **Abdulmumuni Ariboh Suberu:** Data curation. **Fawaz Afolami Arowoduye:** Investigation. **Muhiz Akangbe:** Resources. **Roseline Ifeoluwa Michael:** Investigation. **Timothy Adeyi:** Writing – review & editing.

Availability of data and material

Materials for this study are available and it will be released on request.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] J. Rowe, 1 - introduction: advanced materials and vehicle lightweighting, in: J. Rowe (Ed.), Advanced Materials in Automotive Engineering, Woodhead Publishing, 2012, pp. 1–4.
[2] G. Belingardi, A.T. Beyene, E.G. Koricho, B. Martorana, 12 - lightweight solutions for vehicle frontal bumper: crash design and manufacturing issues, in: V. Lopresto, A. Langella andS. Abrate (Eds.), Dynamic Response and Failure of Composite Materials and Structures, Woodhead Publishing, 2017, pp. 365–393.
[3] T. Aized, M. Imran, H. Raza, M.R. Raza, G.A. Gohar, A. Iqbal, Effect of nano-filler graphene on nano-composite system of polystyrene-graphene, Int. J. Adv. Des. Manuf. Technol. 95 (9) (2018) 3707–3715, https://doi.org/10.1007/s00170-017-1456-x.
[4] G.A. Gohar, A. Akhtar, H. Raza, G. Mustafa, M. Fatima, H.U. Rehman, M.W. Aslam, A.u. Haq, W. Manzoor, Achieving enhanced tensile properties of polyurethane-multiwall carbon nanotubes nanocomposites, Nano Express 4 (4) (2023) 045013, https://doi.org/10.1088/2632-959X/ad100b.
[5] J.O. Agunsoye, S.A. Bello, S.I. Talabi, A.A. Yekinni, I.A. Raheem, A.D. Oderinde, T. E. Idegbekwu, Recycled aluminium cans/eggshell composites: evaluation of mechanical and wear resistance properties, Tribology in Industry 37 (1) (2015) 107–116. http://www.tribology.rs/journals/2015/2015-1/14.pdf.
[6] L. Habte, N. Shiferaw, D. Mulatu, T. Thenepalli, R. Chilakala, J. Ahn, Synthesis of nano-calcium oxide from waste eggshell by sol-gel method, Sustainability 11 (11) (2019) 3196, https://doi.org/10.3390/su11113196.
[7] P. Toro, R. Quijada, M. Yazdani-Pedram, J.L. Arias, Eggshell, a new bio-filler for polypropylene composites, Mater. Lett. 61 (22) (2007) 4347–4350, https://doi.org/10.1016/j.matlet.2007.01.102.
[8] J. Zhang, J. Fang, J.-L. Wu, J. Wu, N.-L. Zhou, H. Mo, Z.-M. Ma, J. Shen, Processing characteristics of low-density polyethylene filled with calcium carbonate of different size distributions, J. Appl. Polym. Sci. (2010), https://doi.org/10.1002/app.32308 n/a-n/a.
[9] S. Owuamanam, D. Cree, Progress of bio-calcium carbonate waste eggshell and seashell fillers in polymer composites: a Review, Journal of Composites Science 4 (2) (2020) 70, https://doi.org/10.3390/jcs4020070.
[10] V.S. Aigbodion, S.B. Hassan, J.O. Agunsoye, Effect of bagasse ash reinforcement on dry sliding wear behaviour of polymer matrix composites, Mater. Des. 33 (2012) 322–327, https://doi.org/10.1016/j.matdes.2011.07.002.
[11] S. Ojha, G. Raghavendra, A. Samir Kumar, Effect of filler loading on mechanical and tribological properties of wood apple shell reinforced epoxy composite, Adv. Mater. Sci. Eng. 2014 (2014) 1–9, https://doi.org/10.1155/2014/538651.
[12] S. Ojha, S.K. Acharya, G. Raghavendra, A novel approach to utilize waste carbon as reinforcement in thermoset composite, Proc. IME E J. Process Mech. Eng. 230 (4) (2014) 263–273, https://doi.org/10.1177/0954408914547118.
[13] M. Boopalan, M. Niranjanaa, M.J. Umapathy, Study on the mechanical properties and thermal properties of jute and banana fiber reinforced epoxy hybrid composites, Compos. B Eng. 51 (2013) 54–57, https://doi.org/10.1016/j.compositesb.2013.02.033.
[14] R. Badrinath, T. Senthilvelan, Comparative investigation on mechanical properties of banana and sisal reinforced polymer based composites, Procedia Materials Science 5 (2014) 2263–2272, https://doi.org/10.1016/j.mspro.2014.07.444.
[15] A.K. Bledzki, A.A. Mamun, J. Volk, Barley husk and coconut shell reinforced polypropylene composites: the effect of fibre physical, chemical and surface properties, Compos. Sci. Technol. 70 (5) (2010) 840–846, https://doi.org/10.1016/j.compscitech.2010.01.022.
[16] W. Sutapun, P. Pakdeechote, N. Suppakarn, Y. Ruksakulpiwat, Application of calcined eggshell powder as functional filler for high density polyethylene, Polym.-Plast. Technol. Eng. 52 (10) (2013) 1025–1033, https://doi.org/10.1080/03602559.2013.769578.
[17] I.O. Oladele, O.G. Agbabiaka, A.A. Adediran, A.D. Akinwekomi, A.O. Balogun, Structural performance of poultry eggshell derived hydroxyapatite based high density polyethylene bio-composites, Heliyon 5 (10) (2019) e02552, https://doi.org/10.1016/j.heliyon.2019.e02552.
[18] j. s. dhaliwal, g. s. kapur, shashikant, Chicken eggshell as a biofiller, in polypropylene: composites Society of Plastics Engineers (SPE) (2013), https://doi.org/10.2417/spepro.005251.
[19] P. Nikhil, P. Sudheer, P.J. Joy, T. Sruthi, M. Vangalpati, Synthesis and characterization of nanoparticles using egg shell, Mater. Today Proc. 26 (2020) 3246–3249, https://doi.org/10.1016/j.matpr.2020.02.907.
[20] M.M. Davoodi, S.M. Sapuan, D. Ahmad, A. Aidy, A. Khalina, M. Jonoobi, Concept selection of car bumper beam with developed hybrid bio-composite material, Mater. Des. 32 (10) (2011) 4857–4865, https://doi.org/10.1016/j.matdes.2011.06.011.
[21] J.A. Carroll, A.H. Barrow, J. B, B. Robinson, Client project report cpr1825 pedestrian legform test area assessment final report, Europe: Transport Research Laboratory, European Commission, DG Enterprise 121/PP/2011/FC (2014) 1–106.
[22] Brussels, TTIP-car Safety Analysis in the EU and US in Relation to US and EU Regulatory Standrads Crash Testing *Indutrial Transformation and Advanced Value Chains*, automotive and mobility industries: European Commision, 2016, pp. 1–538.
[23] R. Fredriksson, Pedestrian Protection Accident Data, Experimental Tests and Numerical Simulations of Car-To-Pedestrian Impacts, Department of Public Health Karolinska Institutet, Stockholm, Sweden, 2011, pp. 1–114.
[24] S.A. Bello, J.O. Agunsoye, J.A. Adebisi, R.G. Adeyemo, S.B. Hassan, Optimization of tensile properties of epoxy aluminum particulate composites using regression models, J. King Saud Univ. Sci. 32 (1) (2020) 402–411, https://doi.org/10.1016/j.jksus.2018.06.002.
[25] M.M. Davoodi, S.M. Sapuan, D. Ahmad, A. Ali, A. Khalina, M. Jonoobi, Mechanical properties of hybrid kenaf/glass reinforced epoxy composite for passenger car bumper beam, Mater. Des. 31 (10) (2010) 4927–4932, https://doi.org/10.1016/j.matdes.2010.05.021.
[26] S.A. Bello, N.K. Raji, M.Y. Kolawole, M.K. Adebayo, J.A. Adebisi, K.A. Okunola, M. O. AbdulSalaam, Eggshell nanoparticle reinforced recycled low-density polyethylene: a new material for automobile application, Journal of King Saud University - Engineering Sciences 35 (6) (2023) 406–414, https://doi.org/10.1016/j.jksues.2021.04.008.
[27] M.D. Bukhari, G.A. Gohar, A. Akhtar, S. Ullah, M. Akram, J. Abid, H. Raza, Adhesion Theories and effect of surface roughness on energy estimation and wettability of polymeric composites bonded joints: a-review, VW Applied Sciences 2 (2019) 74–86, https://doi.org/10.36297/vw.applsci.v2i1.37.
[28] A.A. Abdelmalik, Chemically modified palm kernel oil ester: a possible sustainable alternative insulating fluid, Sustainable Materials and Technologies 1–2 (2014) 42–51, https://doi.org/10.1016/j.susmat.2014.06.001.
[29] J.A. Brydson, Plastics Materials, seventh ed., Butterworth Heinman, Oxford, 1999.
[30] S.A. Bello, M.Y. Kolawole, Recycled plastics and nanoparticles for green production of nano structural materials, in: O.V. Kharissova, L.M.T. Martínez, andB.I. Kharisov (Eds.), Handbook of Nanomaterials and Nanocomposites for Energy and Environmental Applications, Springer International Publishing, Cham, 2021, pp. 599–630.

[31] S.A. Bello, Coconut shell particle reinforced Al-Cu-Mg nanocomposites for cavity die mould parts applications, Int. J. Eng. Res. Afr. 61 (2022) 79–94, https://doi.org/10.4028/p-29l8h7.
[32] ASTM D638-14, Standard Test Method for Tensile Properties of Plastics, ASTM International, West Conshohocken, PA, 2014.
[33] ASTM D7264/D7264M-15, Standard Test Method for Flexural Properties of Polymer Matrix Composite Materials, ASTM International, West Conshohocken, PA, 2015.
[34] ASTM D256-10(2018), Standard Test Methods for Determining the Izod Pendulum Impact Resistance of Plastics, ASTM International, West Conshohocken, PA, 2018.
[35] ASTM E8/E8M-16ae1, Standard Test Methods Fortension Testing of Metallic Materials, ASTM International, West Conshohocken, PA, 2016.
[36] ASTM E23-18, Standard Test Methods for Notched Bar Impact Testing of Metallic Materials, ASTM International, West Conshohocken, PA, 2018.
[37] ASTM E92-17, Standard Test Methods for Vickers Hardness and Knoop Hardness of Metallic Materials, ASTM International, West Conshohocken, PA, 2017.
[38] S.A. Bello, O.E. Egbanubi, A.G.F. Alabi, Emerging hybrid particle-reinforced high-density polyethylene nanocomposite for bone replacement, Polym. Bull. 81 (2) (2024) 1743–1766, https://doi.org/10.1007/s00289-023-04791-9.
[39] G.H. Jeffery, J. Basset, J. Mendham, R.C. Denney, VOGEL's Textbook of Quantitative Chemical Analysis, 5 ed., Longman Scientific and Technical, New York, 1989.
[40] G.E. Dieter, Mechanical Metallurgy, McGraw-Hill Book Company, New York, 1961.
[41] D.R. Mulinari, J.R. Guedes, B.G. Simba, Low density polyethylene composites reinforced with Australian King Palm fibers: mechanical and thermal properties, Polym. Bull. 74 (11) (2017) 4549–4559, https://doi.org/10.1007/s00289-017-1963-9.
[42] D.R. Mulinari, H.J.C. Voorwald, M.O.H. Cioffi, M.L.C.P. da Silva, Cellulose fiber-reinforced high-density polyethylene composites—mechanical and thermal properties, J. Compos. Mater. 51 (13) (2016) 1807–1815, https://doi.org/10.1177/0021998316665241.
[43] J.O. Agunsoye, S.A. Bello, L.O. Adetola, Experimental investigation and theoretical prediction of tensile properties of Delonix regia seed particle reinforced polymeric composites, Journal of King Saud University - Engineering Sciences 31 (1) (2019) 70–77, https://doi.org/10.1016/j.jksues.2017.01.005.
[44] C.U. Atuanya, R.O. Edokpia, V.S. Aigbodion, The physio-mechanical properties of recycled low density polyethylene (RLDPE)/bean pod ash particulate composites, Results Phys. 4 (2014) 88–95, https://doi.org/10.1016/j.rinp.2014.05.003.
[45] V. Pokropivny, R. Lohmus, I. Hussainova, A. Pokropivny, S. Vlassov, Introduction to Nanomaterials and Nanotechnology, Tartu University Press, 2007.
[46] R. Moreno, B. Ferrari, Nanoparticles Dispersion and the Effect of Related Parameters in the EPD Kinetics, 2012, pp. 73–128.
[47] P.A. Zapata, H. Palza, B. Diaz, A. Armijo, F. Sepulveda, J.A. Ortiz, M.P. Ramirez, C. Oyarzun, Effect of caco(3) nanoparticles on the mechanical and photo-degradation properties of LDPE, Molecules 24 (1) (2018), https://doi.org/10.3390/molecules24010126.
[48] S.P. Dwivedi, S. Sharma, R.K. Mishra, Characterization of waste eggshells and $CaCO_3$ reinforced AA2014 green metal matrix composites: a green approach in the synthesis of composites, Int. J. Precis. Eng. Manuf. 17 (10) (2016) 1383–1393, https://doi.org/10.1007/s12541-016-0164-z.
[49] S. Jannet, R. Raja, S. Rajesh Ruban, S. Khosla, U. Sasikumar, N.B. Sai, P.M. Teja, Effect of egg shell powder on the mechanical and microstructure properties of AA 2024 metal matrix composite, Mater. Today Proc. 44 (2021) 135–140, https://doi.org/10.1016/j.matpr.2020.08.546.
[50] J.O. Agunsoye, J.E. Anyanwu, S.A. Bello, S.B. Hassan, Effect of particle sizes on some mechanical properties of kernel shell reinforced Al-Mg-Mn Composites, Nano Hybrids and Composites 35 (2022) 19–32, https://doi.org/10.4028/p-t85e9s.
[51] S.B. Hassan, V.S. Aigbodion, The effect of thermal ageing on microstructure and mechanical properties of Al–Si–Fe/Mg alloys, J. Alloys Compd. 486 (1) (2009) 309–314, https://doi.org/10.1016/j.jallcom.2009.06.131.
[52] S.A. Bello, I.A. Raheem, N.K. Raji, Study of tensile properties, fractography and morphology of aluminium (1xxx)/coconut shell micro particle composites, Journal of King Saud University - Engineering Sciences 29 (2017) 269–277, https://doi.org/10.1016/j.jksues.2015.10.001.