Key Engineering Materials
ISSN: 1662-9795, Vol. 1001, pp 67-82
doi:10.4028/p-lh2kYq
© 2024 Trans Tech Publications Ltd, All Rights Reserved
Submitted: 2023-12-21
Revised: 2024-07-23
Accepted: 2024-07-25
Online: 2024-12-18

Structural and Some Mechanical Properties of Parquetina Nigrescens Pod Nanoparticles Reinforced Mixed Matrix Membrane for Dental Applications

Sefiu Adekunle Bello[1,a*], Bolwatife Olukunle[1,b], Raphael Gboyega Adeyemo[2,c], Funsho Olaitan Kolawole[3,d], Mohammed Kayode Adebayo[1,e], Abdul Ganiyu Funsho Alabi[1,f], Sikiru Ottan Abdulraman[1,g]

[1]Department of Materials Science and Engineering, Kwara State University, Malete, Nigeria

[2]Gateway (ICT) Polytechnic, Saapade, Ogun State, Nigeria

[3]National Institute for Space Research, Associated Laboratory of Sensors, and Materials Av dos Astronautas 1758, São José dos Campos, SP, Brazil, 12227-010

[a*]belloshaafiu@gmail.com, [b]boluolu1@gmail.com, [c]adeyemoralph@gmail.com, [d]fkopresido82@gmail.com, [e]mohammed.adebayo14@kwasu.edu.ng, [f]abdulganiyu.alabi@kwasu.edu.ng, [g]sikiru.abdulraman@kasu.edu.ng

Keywords: Polylactic acid (PLA), Structural features, *Parquetina nigrescens*, Pod nanoparticles.

Abstract. Polylactic acid (PLA) is a biocompatible, and biodegradable thermoplastic. It is renewable being produced by bacterial fermentation of potatoes, sugarcane, or corn starch. PLA has been attempted in many applications to replace petroleum-based polymers because some of its mechanical properties are excellent and it can be processed easily but low toughness and thermal stability are setbacks from one application to another. To improve on mechanical properties of the PLA to be suitable as biomaterials for dental and other applications, this study focuses on synthesis of *Parquetina nigrescens* pod nanoparticles (PNPNP) as reinforcements in the PLA to engineer new nanocomposites for biomedical applications. Chemical, structural and some mechanical properties were investigated. TEM result indicates an average size of 14.14 nm of the PNPNP used for reinforcing the PLA. Fourier Transform Infrared Spectrograph establishes a reduction in the amount of light transmitted by the PLA. This is due to PNPNP additions with changes in the wavenumbers of the observed peaks affirming formation of new compounds due to interactions of the PLA molecules and PNPNP. X-ray diffractograms reaffirms new compound formations. Moreover, there are enhancements in mechanical properties up to 3% by weight of PNPNP addition to the PLA with about 92% improvement in the impact toughness.

1. Introduction

A denture is a removable replacement for the surrounding tissues and missing teeth. There are two types of dentures which are complete and partial denture bases [1]. Denture materials are biomaterials. A material, either synthetic or naturally utilized in medical applications for the purpose of performing a body function or replacing a part or tissue of the body is known as a biomaterial. Biomaterials are created with the intention that it will interact at the interface of biological systems during application. Use as a delivery system for drug or biological factor is a function of biomaterials [2].

The field of engineering involved in the study and production of biomaterials is Biomedical engineering, which is a multidisciplinary field that combines varieties including biomaterials bioinformatics, biomechanics, instrumentation, biology, computer science, and medicine to proffer solutions to engineering related health problems. Optimal integration between the body and any biomedical device is highly required, making biomaterial important to biomedical engineering to achieve a successful design. If there is rejection of the biomedical device by the immune system, or

All rights reserved. No part of contents of this paper may be reproduced or transmitted in any form or by any means without the written permission of Trans Tech Publications Ltd, www.scientific.net. (Research Gate for subscription journals-20/12/24,03:58:17)

if the biomaterial releases toxin or becomes unstable in the body, this totals as a failure of the device.

There have been recent advancements in materials science. Nanotechnology which has been birthed through these advancements has improved healthcare in areas such as tissue engineering and drug delivery [3]. Polylactic acid (PLA) is a versatile biopolymer which is biodegradable and shows thermoplastic behaviour. PLA and its composites have been used in biomedical applications such as orthopaedic retainers, and bone replacement. In the dentistry world, tooth loss is rampant and over the years, different materials have been processed for tooth replacement, but PLA has been considered a viable option in term of its properties and cost for the purpose of the experiment. The research process inculcates the size effect theory; the smaller the material the lesser the imperfection encountered with the material, and this can be used to improve the mechanical properties of the PLA. Nanoparticles have been proven to enhance the properties of their matrix phase. It also comes with ease while combining the mixture (individual parts of the composite). This research investigates the effects of a filler material (*Parquetina nigrescens* pod particles) on the mechanical properties of PLA for optimum performance of PLA as a biomaterial for denture application.

Polylactic acid which also known as *polylactide* (PLA) is a thermoplastic polyester possessing a backbone formula: $(C_3H_4O_2)n$ or $[–C(CH_3)HC(=O)O–]n$. It is formally obtained from the polymerization (condensation) of lactic acid $C(CH_3)(OH)HCOOH$ involving the loss of water. Another method is a preparation by ring-opening polymerization of lactide $[–C(CH_3)HC(=O)O]_2$, the cyclic dimer of the basic repeating unit [4]. PLA is synonymous in terms of mechanical properties to polyethylene terephthalate (PET) but possesses a significantly lower maximum continuous use temperature. Poly(L-lactide) (PLLA) happens to be the most important PLA. It occurs as a semi-crystalline polymer with ~37% crystallinity, a glass transition temperature (Tg) of ~67°C and it melts at a temperature (Tm) of ~180°C [4]. PLA undergoes processes like other thermoplastic polymers such as extrusion, blow moulding, injection moulding, or fibre spinning into a variety of forms.

Lactic acid is an organic acid, naturally occurring which can by produced via fermentation or chemical synthesis. The process entails the hydrolysis of lacronitrile by strong acids. PLA is gotten from renewable resources due to its processing methods. Amongst the most manufactured polymer in the world is PLA. PLA poses no harm to the environment [5]. PLA, a thermoplastic has a good castability forming different shapes and is used as filament for 3D printing. Coupled with its environmentally friendly nature, PLA is biocompatible, making its absorption into the human body easy.

Parquetina nigrescens grows in secondary forest, savanna, vegetation bordering roads and gallery forest, also commonly growing on anthills. It grows on various types of soil, including marshy areas and the average 1000-seed weight is 11.2 g [6]. The plant parts needed can be harvested throughout the year. The leaves can be used fresh or dried for later use. The plant is not prone or threatened by genetic erosion [7]. *Parquetina nigrescens* is broadly utilized in conventional medication and in customary medication practice as a restorative spice [8, 9]. *Parquetina nigrescens* is mainly found flowering and fruiting during the rainy season [6].

Blending of PLA has been widely adopted to enhance PLA mechanical properties. Blending of PLA with polymers and plasticizers (biodegradable and non-biodegradable) of different sorts has been employed to achieve desired mechanical properties [6]. To improve toughness, low density poly(ethylene) (LDPE) was blended with PLA [10]. The crystallinity of PLA was observed to have a significant impact on the blend toughness. Non-crystalline PLA blends with LDPE required PLA-LDPE diblock copolymer compatibilization. And on the other hand, semi-crystalline PLA blends with LDPE exhibited toughening despite the absence of the block polymer. An approach which was implemented to enhance the mechanical properties of PLA was via the incorporation of inorganic/organic fillers. An example is a PLA-clay solvent cast blend which exhibited improved Young's modulus. A review [11] was written in 2016 which discussed the potential of PLA blends in the biomedical field, including overview of blending and mixing processing techniques and

applications of PLA blends currently in use and under development. In 2018, an author [12] presented a work which described the synthesis of high molecular weight PLA by varying the reaction time and changing the order of catalyst addition. The binary catalyst used was $SnCl_2.2H_2O$/maleic anhydride and p-toluene sulfonic acid. The molecular weight of PLA (6.503X105) was obtained in 52 hours. FTIR, 1 H and 13 C NMR determined the structure of the synthesised PLA, while GPC was used to determine the molecular weight.

Moreover, *Parquetina nigrscens* has many parts that are beneficial in treating diseases. The leaves are a typical fixing in drugs to treat madness. Antioxidant properties are present in *Parquetina nigrescens* and the antioxidants can help in protection against free radical induced ulcer as reported in [13]. The cardiotonic and catecholamine effects of *Parquetina nigrescens* extract, induced by the contractile force of the left and right atrium of the guinea pig, have been investigated in vitro, isometric contractions were recorded. *Parquetina nigrescens* extract, 5±150 μgml^{-1}, increased the contraction force by dose-dependently in the left electrically trained atria. The concentration of *Parquetina nigrescens* with 50% of the maximum effect (EC50 value) was 7.5 μgml^{-1} as disclosed in [14]. As reported in [15], the antioxidant activity of various extracts (aqueous, methanol and flavonoid) of *Parquetina nigrescens* and of butylated hydroxylanisole, as reference compound, were evaluated in terms of trapping effect, reducing capacity and inhibition of lipid peroxidation in rat liver. Extracts of P. *nigrescens* captured with 2,2diphenyllpicrylhydrazyl (DPPH) generated radicals in ascending order flavonoid> methanol > aqueous > BHA at 1000 g/ml. The reducing power followed a similar pattern to that observed in the sweeping operations. The results showed that *Parquetina nigrescens* contains antioxidants that may be helpful in reducing reactions that generate free radicals in the body.

In additions, some studies have been focusing on new materials for dental applications. For instance, conventional acrylic teeth was compared to silanized feldspar-reinforced PMMA. Upon combining of silanized feldspar, it exhibited improved properties with regards to the elastic modulus, hardness and flexural strength without comprimising the impact strength. Close results were derived while adding silica but the flexural strength diminished [16]. In 2018, a group of researchers [1] showed that the addition of nanoparticles from natural sources had a positive impact on the mechanical properties of the PMMA used. The nanoparticles were gotten from pomegranate peels and Ajwa date seeds which were embedded into the matrix (PMMA) at varying weight fraction ratio for dental applications. Nylon (polyamides) has also surfaced as suitable material for denture base materials due to its easthetics, functional characteristics and physiochemical qualities. The properties of polyamide denture base materials have been evaluated by various studies and on the basis of the results from the various studies, high impact, thermo-injectable, flexible or semi-flexible nylon is proposed to be an alternative to the popular acrylic resins [17]. Given the above, it is observed that studies have been reported and tailored to biomaterials for dental applications. However, incorporation of the PNPNP in the PLA to emerge a new biomaterial for dental application is the focus of this study. The approach is novel as PLA based composite containing PNPNP as reinforcement is scarce. The aim is to add value to the *Parquetina nigrescens* pods (wastes) through development of ecofriendly nanocomposites for biomedical application. Besides being used as reinforcement to improve mechanical properties, *Parquetina nigrescens* pods have phytochemicals which can enhance the antibacterial properties of the PLA.

2. Materials and Methods

2.1 Materials

The PLA acrylic powder was imported from China via AliExpress, and *Parquetina nigrescens* pods were obtained at Anifat's compound, Inuewe, Amuloko, Ibadan, Oyo State, Nigeria.

2.2 Equipment

Measuring cylinder, beaker, glass rod/stirrer, die mould, UNISCOPE laboratory oven, 2kg capacity tumbler ball mill (Figure 1b), precision cutting machine, ASPEX 3020 scanning electron

microscope (SEM), Philip Transmission electron microscope (TEM), Panalytical Empyrean X-ray Diffractometer (XRD), Schimadzu Fourier Transform Infrared Spectroscope, Universal Tester (Instron 3369), and Housefield Izod impact tester are the equipment used in the research work.

2.3 Procedure

2.3.1 Synthesis of Parquetina nigrescens pod nanoparticles (PNPNP) using top-down approach

Synthesis of PNPNP was achieved by grinding of the *Parquetina nigrscens* pods using a steel disc, followed by ball milling at 10 charge ratios for 40 hours intermittently at every 5 hours per guide published in [18]. The total weight of the balls in the milling machine is 414 kg. 10 percent of the total weight of the balls (41.4 kg) was the measured weight of the charge powders. This signifies the 10-charge ratio, and 10mm size steels balls were used as grinding media. The milled sample was analysed using the SEM, and TEM. The pod particle is the reinforcement/filler used in the processing of the PLA composite material to enhance its mechanical properties.

2.3.2 Specimen Preparation

Varying weights (1, 3, 5. and 7 wt%) of the PNPNP were added to acrylic powder (PLA) to develop PNPNP reinforced PLA composites. Control sample containing only PLA without PNPNP was produced to benchmark properties of the developed composites. In the composite development, a right quantity of the PNPNP at each level, mixing with 5 drops of palm kernel oil was added to the matrix (PLA) and stirred manually until the PNPNP held on to the PLA powders. The composite mixture was poured into the metallic mould cavity lined inside with aluminium foil. Open face of the mould was also covered by the aluminum foil having smooth surface, to obtain the samples with smooth surfaces area, to ensure easy removal of the composites and avoid the composites sticking to the mould. Mass of the matrix in the composite is constant throughout the experiment for all proportions, only the weight of the reinforcement was changing in the order; 1, 3, 5 and 7 percent by weight (wt%) to produce different grades of PLA based composites. The mould (containing the composite mixture, Figure 1e) was then carefully placed in the oven (Uniscope SM9053 laboratory oven), heated until the mixture melted at 200˚C, the oven was switched off and the melt was left in the oven to solidify and cool to room temperature. Then after, the composite samples were removed from the mould. The mould (Figure 1d) was designed to have cavities to produce standard specimens for tensile test, flexural and impact test. The average thickness of the specimen is 5 mm. For the Impact test, the specimen was reshaped into having a full length of 75 mm and a notch was created 48 mm from the end of the specimen. The notch was about 2 mm deep. A precision cutting machine was employed to prepare the Izod impact test specimens.

2.4 Chemical Analysis and Microstructural Characterisation

2.4.1 Transmission Electron Microscope (TEM) Analysis

Structural features and size range of the PNPNP were obtained using the TEM, model: JEM 2100F. Beam of electron passing through the samples (which was prepared by drying the PNPNP on a thin film carbon coated copper grid) were focused by an AMTXR41B 4-megapixel (2048 × 2048) bottom mount CCD camera attached to the TEM operating at an accelerating voltage of 100 keV.

2.4.2 Fourier *Transform Infrared (FTIR) Analysis*

In FTIR analysis, inspection of a material is done by measuring the quantity of light absorbed as opposed to the amount of light that has been reflected to identify unique chemical sequence and evaluate the material type by the of infrared light for the inspection. This analysis gives an effective and efficient manner to figure out unknown substances in terms of bond and (or) functional groups [19]. FTIR analysis was performed using Shimadzu Fourier Transform Infrared Spectroscopy (FT-IR).

2.4.3 X-ray Diffraction Analysis

Representative samples of PNPNP and some developed PLA materials were analysed using Malvern PanAlytical Empyrean X-ray diffractometer (XRD) with Pixcel detector possessing Bragg-Bretano geometry in continuous operating mode and automatic divergence slit type using Cu Ka radiation emitted from Cu anode material at an accelerating voltage of 45 kV and current of 40 mA to identify crystalline phases of the PNPNP reinforced PLA composites. Scanning of the samples was conducted from 0˚ to 74.9780˚ (˚2theta) at a scan step size and time of 0.0260˚ and 29.07s, respectively and the phases were detected using X'Pert High score plus software; PAB-ICSD and ICDD (2014) databases in line with [20].



Fig. 1. Materials and facilities used: (a) *Parquetina nigrescens plant having pods (b)* 2kg capacity tumbler ball mill for producing PNPNP (c) Ohaus weighing scale for quantifying proportion of PLA and PNPNP for composite developments (d) Mixture of PLA and PNPNP after stirring (e) die cavity mould for fabricating the composites (f) PLA without PNPNP additions under heating process (g) the developed polylactic acid composite's tensile samples

2.4.4 Scanning Electron Microscopic/ Energy Dispersive X-ray Spectroscopy (EDS)

ASPEX 30320 scanning electron microscope equipped with energy dispersive X-ray spectroscopy was employed to probe the structures and detect elemental constituents of the PNPNP and the particle reinforced polylactic acid nanocomposites developed. Scanning was done using electron beam accelerating at 15 kV to obtain images that give the structures of the analyzed PNPNP and the PLA composites.

2.5 Mechanical Characterisation

Mechanical characterisation of a material is a destructive technique employed to ascertain the mechanical properties of a material. These tests mostly involve the deformation and failure (fracture) of materials. It is done to know the tolerance or resistance to certain conditions involving externally applied force. Mechanical properties of a material are determined through mechanical characterisation, and these mechanical properties determine the various applications of materials. PLA was selected for this experiment because it has better stiffness compared to other polymers having similar properties with PMMA which is also used for denture replacements.

2.5.1 Tensile Test

Tensile tests were carried out under conditions where the material was exposed to a static or slowly applied external force, evaluating the mechanical properties of the materials such as the yield stress, strain, elongation, ultimate tensile strength etc. It is a mechanical test which destroys the material in the process of testing it and the method used subjects the material to a uniaxial tension until the material fails. Other critical information or details such as ductility, stiffness and strength are provided for by this test. The detailing of the tensile sample is presented in Figure 2. Analysis was carried out using the Instron 3369 of maximum capacity of 50 kN per ASTM D638-14, type I [21] at Mechanical Testing Laboratory, Department of Materials Science and Engineering, Kwara State University, Malete.

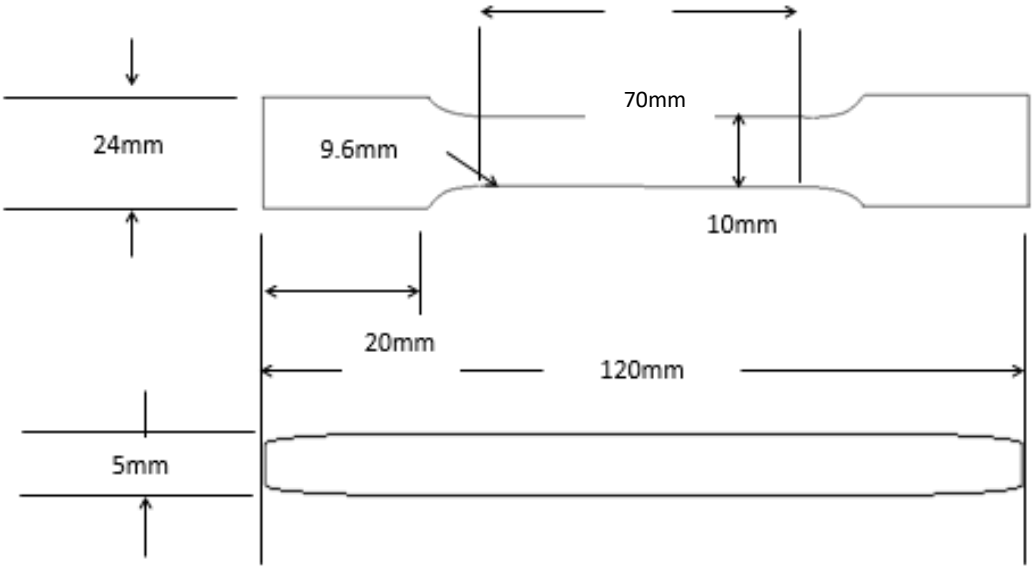


Fig. 2. Detailed diagram of the tensile specimen used

2.5.2 Impact Test

Impact test has been designed to determine the amount of energy that a material can absorb as it fractures, making it an important part in material characterisation, especially materials for artificial teeth since teeth are used for chewing. It is necessary to understand the absorption of energy properties of a material to foresee the response of the material to impact loading such as in chewing operation by the teeth (sudden application of load) which in turn becomes a determining factor of selecting a material for a desired application [22, 23]. The impact test was carried out using the Avery Denison impact tester which is capable of conducting the charpy and Izod impact test. The Izod approach was used in study which explained the reason for notching the sample at 27 mm from one end of the sample. PNPNP/PLA samples were placed on a guard and a hammer was dropped at a speed of approximated 4 ms^{-1} (12.5ft/s) to release a sudden violent blow of approximated 163 J (120ft.lb) [24] that stroke the sample against the guard. An amount of energy absorbed by the PNPNP /PLA sample before breakage was read from the foot-pound scale, which was then converted to joules. The analysis was performed per ASTM D256-10(2018) [25] with slight modifications and detailed dimensions of each sample for the impact test is presented in Figure 3.

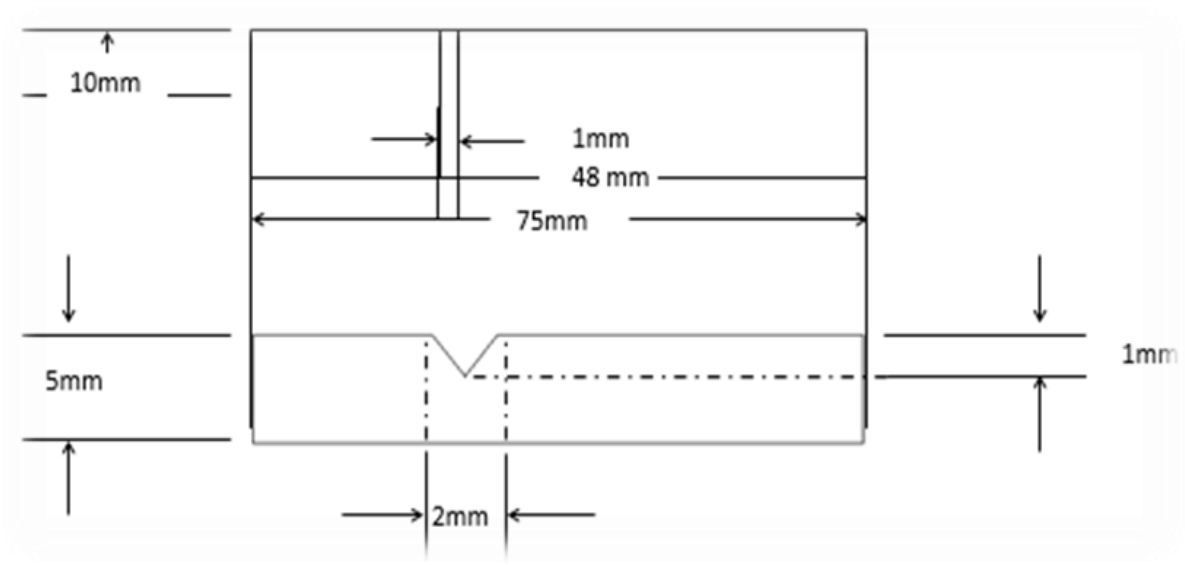


Fig. 3. Detailed diagram of the Izod impact test specimen used

3. Results and Discussion

3.1 Transmission Electron Microscopic Images of *Parquetina nigrescens* Pod Nanoparticles

Parquetina nigrescens particles have different geometries as it is evident in Figure 4 which demonstrates individual tiny particles having faint or ash colour in addition to dark particle colonies having irregular and or approximated rounded shapes. The image resolution of 50 nm establishes that size of each particle is less than 50 nm since none of the particle diameter is long as the length of the resolution line/distance. Random determination of some particle diameters indicates 12.54, 17.35, and 12.54 nm for some particle diameters. This affirms that the PLA was reinforced with the nanoparticles of an average size of 14.14 nm obtained from the *parquetina nigrescens* pods.

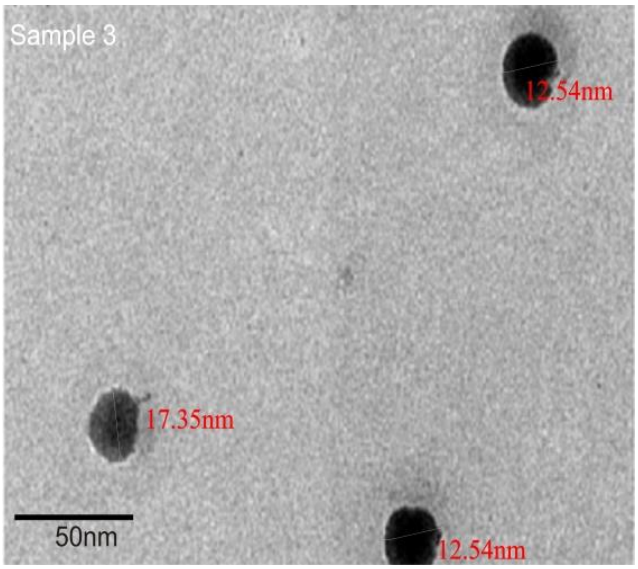


Fig.4. Transmission electron microscopic images of *Parquetina nigrescens* pod nanoparticles

Table 2 Peaks of both ordinary PLA and PLA containing 3% *Parquetina nigrecens pod nanoparticles* and their functional group

S/N	Band (CM^{-1}) PLA	Band (CM^{-1}) Composite	Functional Group (formula)	Functional Group (description)
1	512.00	512.18	C-I	Aliphatic iodo compound C-I stretch.
2	695.76	695.69	C-Br	Aliphatic bromo compound C-Br stretch.
3	756.06	756.03	C-Cl	Aliphatic chloro compound C-Cl stretch [26].
4	871.59	871.50	C-H	Vinylidiene C-H out of plane bend [26].
5	921.32	921.34	C-C	Skeletal vibration [26]
6	956.49	956.48	C-C	Skeletal vibration [26]
7	1087.85	1089.59	CN	Primary amine, CN stretch [26]
8	1183.84	1183.24	CN	Secondary amine, CN stretch [26]
9	1386.35	1385.57	$-CH_3$	gem.Dimethyl or "iso"- [26]
10	1457.16	1456.65	$-CH_3$,$-CH_2$, C-H	Methyl C-H asy/sym bend [26]
11	1758.25	1758.42	Alkyl Carbonate	Carbonyl compound [26]
12	2085.20	2085.62	-NCS	Isothiocyanate [26]
13	2398.80	2398.56	-	-
14	2946.70	2946.51	C-H	Aliphatic C-H [27]
15	2997.51	2997.15	C-H	Aliphatic C-H [27]
16	3508.99	3507.48	OH	Dimeric OH stretch [26]
17	3650.21	3647.84	OH	Non bonded hydroxyl group, OH stretch [26]

3.2 Chemical Properties of the *Parquetina nigrecens* pod nanoparticle Polylactic Acid

The FTIR analysis was done for only the control and the PLA composite containing 3wt% of PNPNP. The peaks gotten from the spectrograph were used to identify the various functional groups present in the PLA and the composite The difference was only a slight one; the peaks appeared to be very similar. The values of the peaks were very close having differences of as low as 0.18 between the PLA and the composite. It could be inferred that the addition of the reinforcement did not drastically affect the functional groups present in ordinary PLA. The result shows a decrease in transmittance of the composite (Figure 5). PLA has higher peaks transmittance indicating that an interaction between the matrix and the reinforcement triggered reaction of the PNPNP with some of the PLA molecules forming some compounds that belong to the same functional groups as the PLA constituents. Reductions in the peaks transmittances of the composite attributing to chemical reaction between the matrix and reinforcement have been reported in literature [28, 29]. The peaks are tabulated with the corresponding functional groups as shown in Table 2.

3.3 X-ray Diffractograms of the Parquetina nigrescens Pod Nanoparticle Reinforced Polylactic Acid Composite

Diffractograms in Figures 6 and 7 for the pristine PLA and PNPNP reinforced PLA, respectively show a reasonable difference upon comparison. The peaks in the XRD results signify some identified compounds. The chemical compounds/phases in the PLA and PLA based composite appear different signaling that there has been a chemical change in structure of the pristine PLA due to the addition of the PNPNP. Therefore, the reinforcement is effective in PLA altering the structure of the PLA indicating that the portion of the reinforcement present in the PLA is sufficient to cause changes in the structure due to chemical reaction established by the findings from FT-IR spectrographs in Figure 5.

3.4 Microstructural Properties of the *Parquetina nigrescens* Pod Nanoparticle Reinforced Polylactic Acid Composite

Parquetina nigrescens powders are presented as fragments of different sizes resulting from breakage due to action of various forces which the *Parquetina nigrescens* pods experienced during the disc grinding. Impacts of the force actions were felt differently by various pods leading to breakage at different rates and in varied manners which gave rise to the powders in Figure 8a.

However, after intermittent 40 hours' milling of the powders in Figure 8a, particles presented in Figure 8b were obtained. It seems the effect of ball milling is hardly seen due to agglomeration/physical fusion of the individual particles after attaining minimum sizes with increased surface areas that triggers Van der Waal's attraction [30]. This causes the particles to display as a long continuous colony having a rope shape which is surrounded by many particle debris. Each particle is seen as a hexagonal structure joining each other to skeletal framework structure. The particle agglomeration was addressed by thorough mixing with the PLA powders during the composite processing as already explained in Section .3 of this article.

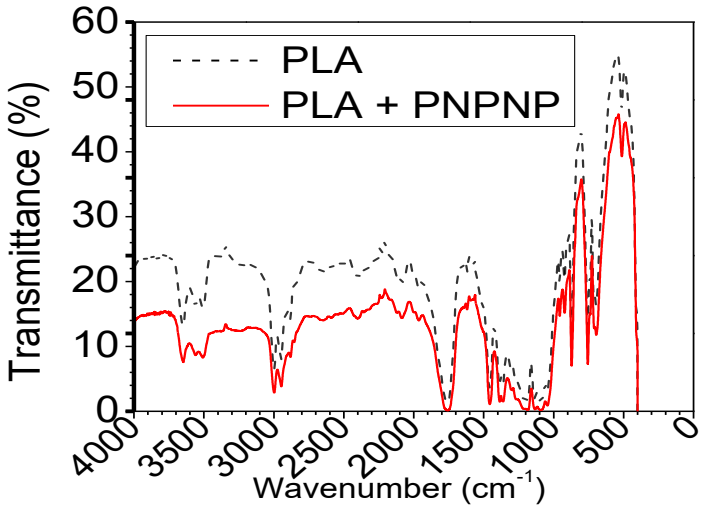


Fig. 5. Fourier Transform Infrared spectrographs of *Parquetina nigrescens* pod nanoparticle reinforced polylactic acid composite benchmarked with that of the pristine polylactic acid.

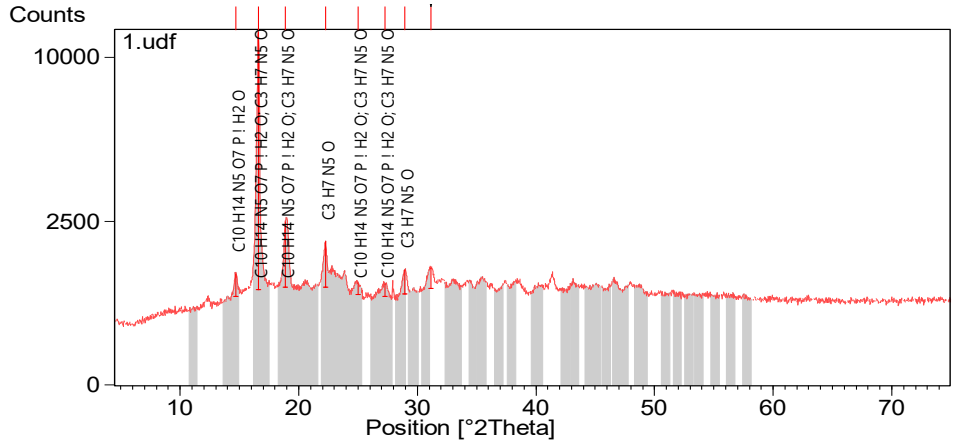


Fig. 6. X-ray diffractogram of the pristine PLA showing some identified compounds

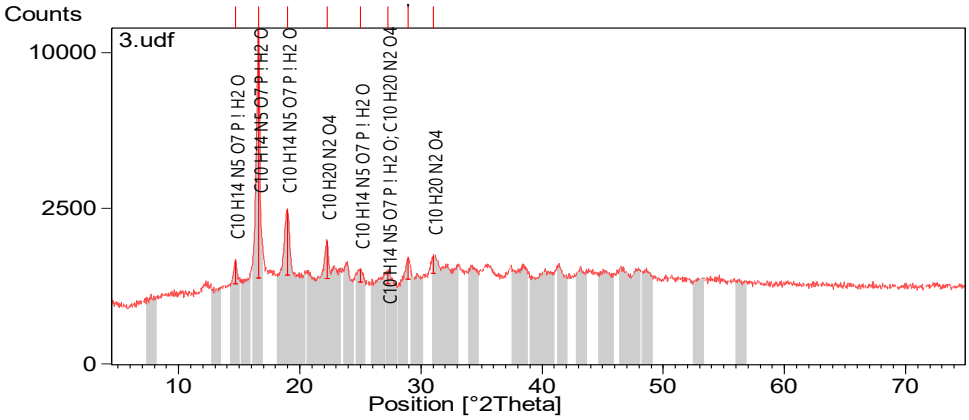


Fig. 7. X-ray diffractograms of the polylactic acid containing 3% by weight of the *Parquetina nigrescens* pod nanoparticles

Moreover, the charged powder has C as a major element. Other detected elements are O, Cl, and K (Figure 8c) but after 40 hours of milling, Mg and Cl were not detected (Figure 8d). It is proposed that both Mg and Cl particles have been covered by other particles like C and others which blocked reflection of X-ray radiation from them after incidence of the electron beam [20, 31]. Moreover, it is affirmed in Figure 9a-b that there is a difference in microstructure of the pristine PLA and that of the composite. The difference is linked with identified compounds in the pristine PLA (Figure 6) which are not the same with those detected in the PLA composites. Variations in the structures of the detected compounds are proposed to contribute to the overall microstructural differences in Figure 9a-b. Alternate peak and valley layers connected to give a continuous structure of the PNPNP/PLA composite is observed in Figure 9b while the structural configuration of the pristine PLA has a central impression surrounded by slopy layer. The observed microstructural differences imply mechanical behaviour differences between the pristine PLA and its nancomposites. The differences observed in the microstructure features of the PLA and that of the nanocomposites are in line with previous studies in literatures which also affirm that the microstructure of the polymer changes due to additions of reinforcements as observed in this study [32-34].

3.5 Tensile Properties and Impact Energies

Addition of PNPNP to the PLA matrix causes an increase in the yield strength up to 3wt% as Figure 10 demonstrates. Above 3wt%, impairment in the yield strength of the composite is noticed as the curve declines. Upon this, it can be inferred that 3wt% is the critical loading level of the PNPNP in the PLA which implies that saturation of the PLA resumes above the level. That is, above 3wt%, the binding property of the PLA is insufficient to network all PNPNP together to form a continuous single body to bear the burden of the externally applied load. The presence of the freely existing or non-binding particles within the matrix causes defect leading to structural discontinuity within the composites. Due to their weakness, externally applied stress normally concentrates on them and causes failure of the material at a stress level below the expectation. This explains the lower yield strength above 3wt%. Similar explanation is found in literature [35].

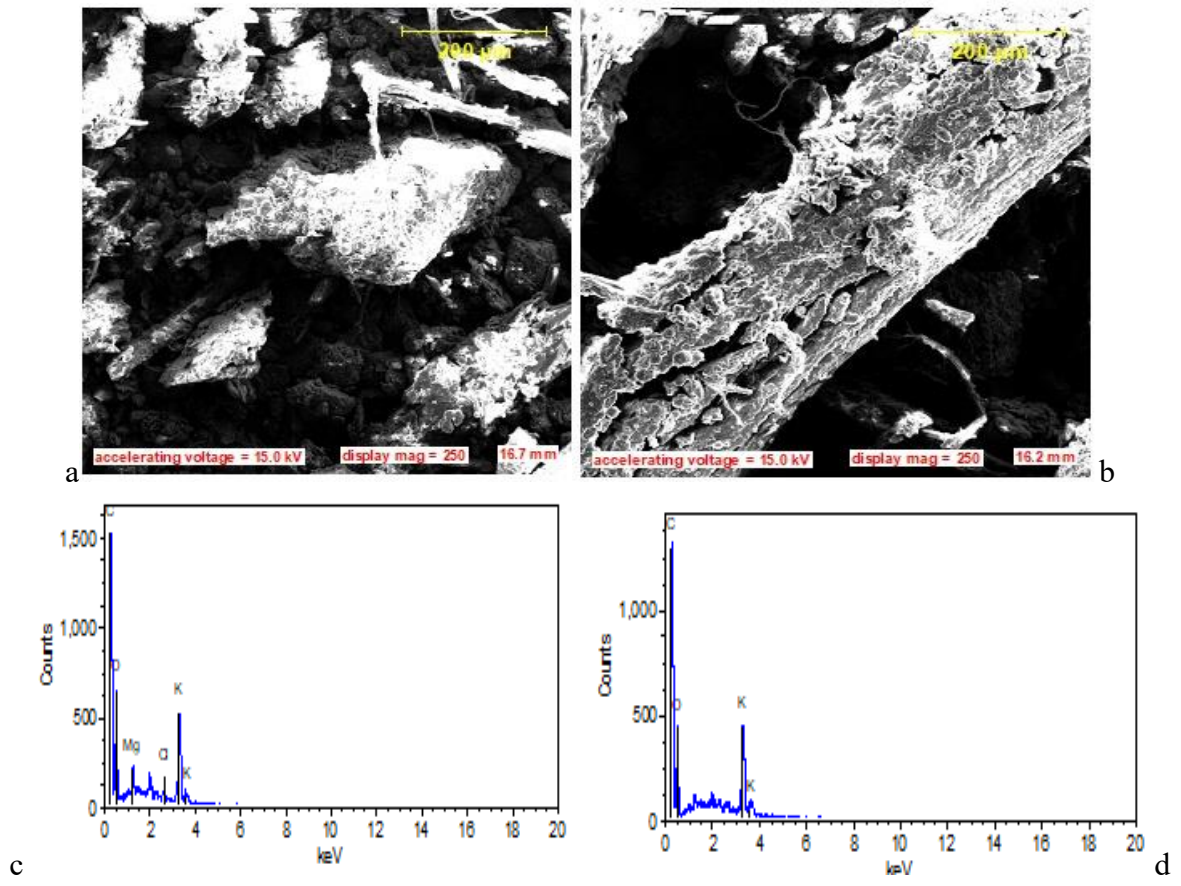
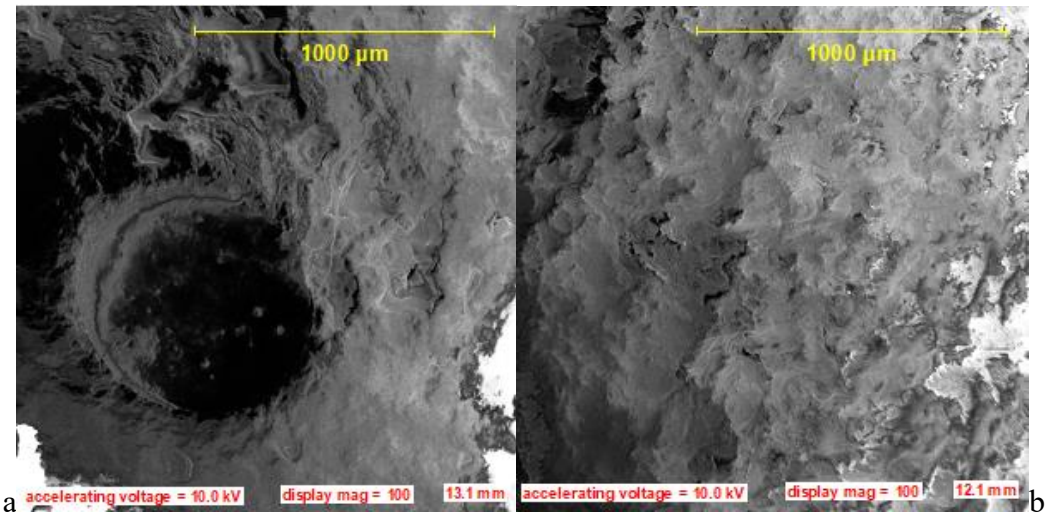


Fig. 8. SEM/EDX of *Parquetina nigrecens (a) charged* powders (b) particles obtained after milling

Moreover, similar observation is made with tensile Young's modulus in Figure 11 while Figure 12 indicates an improvement in the tensile elongation up to 5wt% of PNPNP addition to the PLA though the difference between the elongation at 3 and 5wt% is very small which implies that the matrix saturation still occurs at approximated 3wt% for the tensile properties. Moreover, enhancement in the impact energy up to 3wt% of the PNPNP (Figure 13) also buttresses the saturation of the PLA above 3wt% addition of PNPNP. Improvement in the tensile properties due to PNPNP addition in this article agrees with similar improvement in the tensile properties of the PLA reinforced with *Parquetina nigrescens* fibre reported in [36]. In the properties' comparison of PLA based composites from varied constituent of corn straw fibres reported in [36], a decrease in the tensile and bending strengths of the PLA due to corn straw fibre and corn straw fibre skin additions was noticed. Tensile strengths of different grades of PLA based composites were compared in [37], it is not clear whether addition of the combined multiwall carbon nanotubes, carbon nanofillers and graphene nanoplatelets improves or impair the tensile strength since the properties of the PLA based composites is not benchmarked with the pristine PLA polymer in the study.



a b

Fig. 9. Microstructures of (a) polylactic acid and (b) *Parquetina nigrescens* particle reinforced polylactic acid

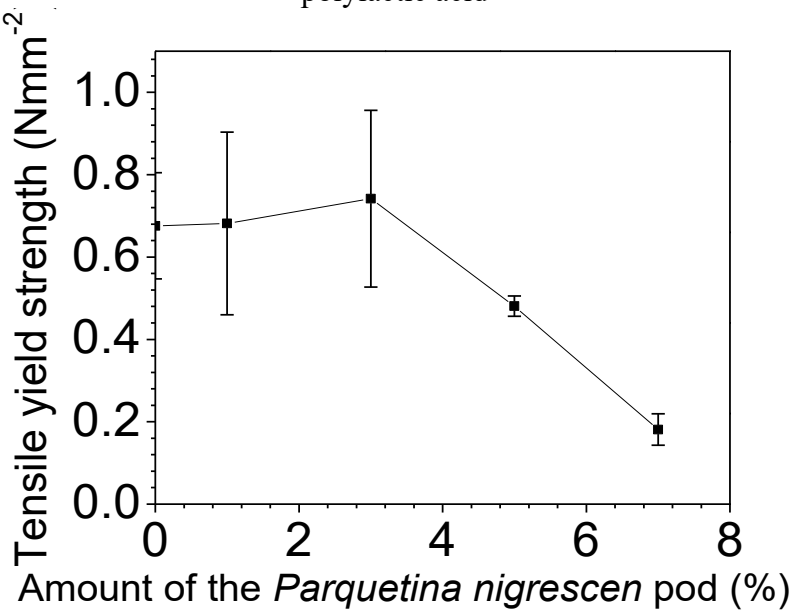


Fig. 10. Tensile yield strength of *Parquetina nigrescens* pod nanoparticle reinforced polylactic acid

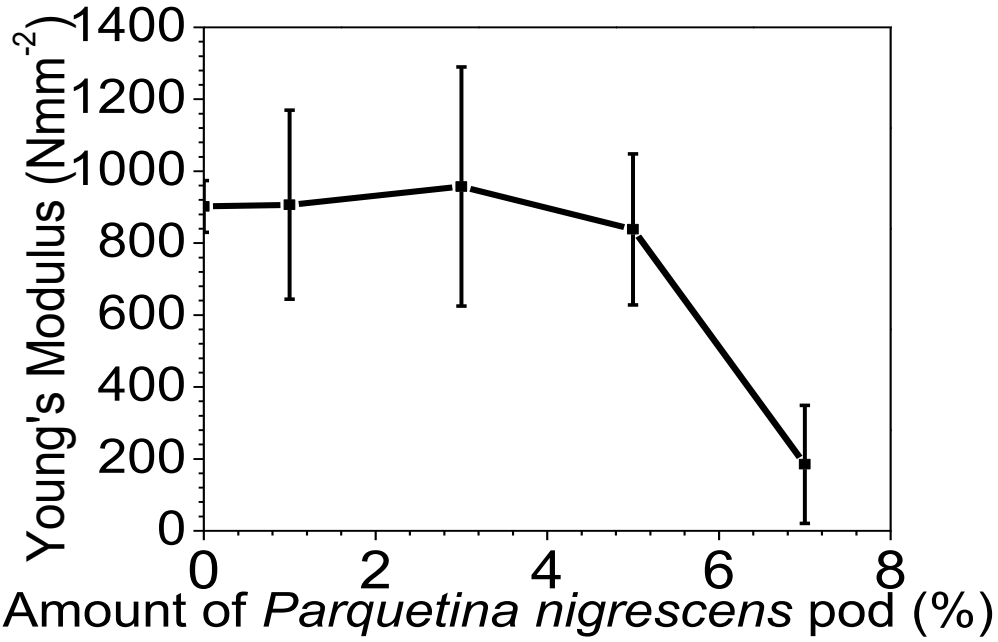


Fig. 11. Tensile modulus of elasticity of *Parquetina nigrescens* pod nanoparticle reinforced polylactic acid

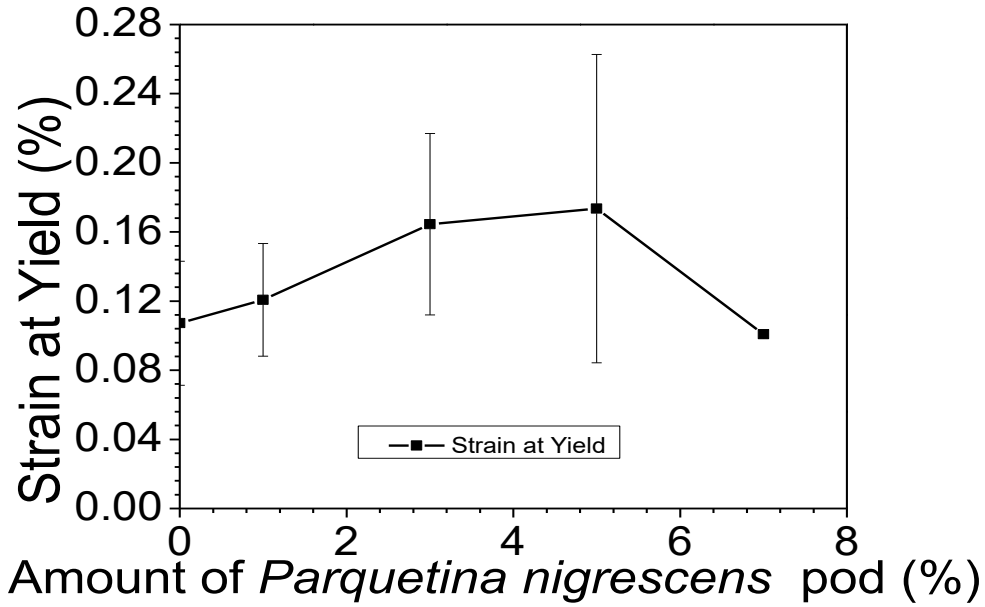


Fig. 12. Percentage elongation at yield of *Parquetina nigrescens* pod nanoparticle reinforced polylactic acid

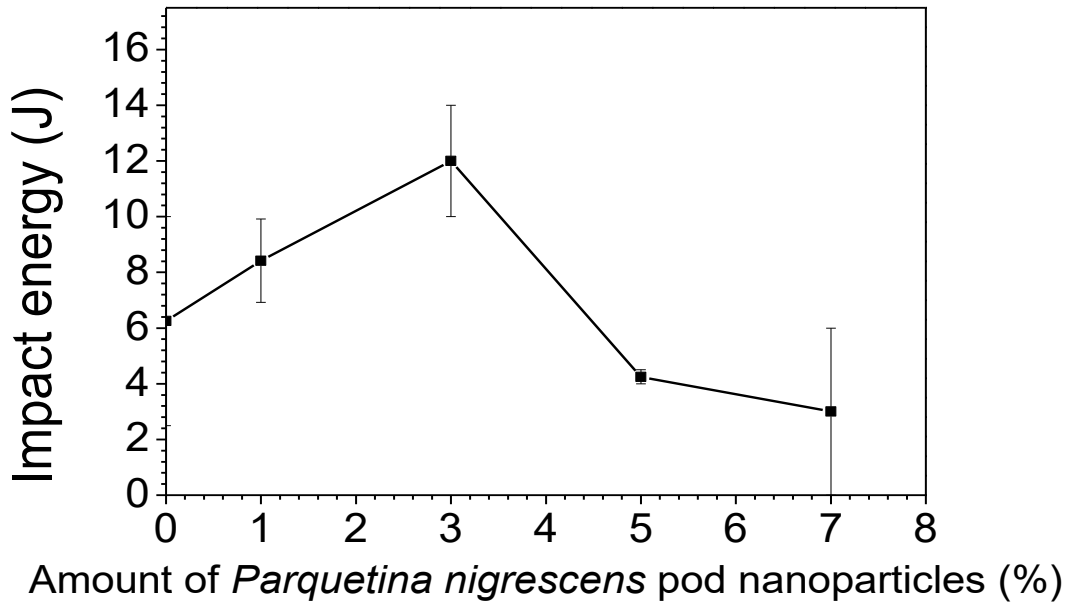


Fig. 13. Impact energy of *Parquetina nigrescens* pod nanoparticle reinforced polylactic acid

Moreover, improvement in the impact energy due to PNPNP additions is in line with some previous findings in literature [24, 38]. Improvement in the tensile properties like percentage elongation, modulus of elasticity and impact energy can be interpreted as the improvement in the ductility, rigidity, and impact toughness of the PLA due to PNPNP additions. This implies that the addition of the nanoparticles has reduced the brittleness of the PLA. The enhanced properties will aid the suitability of the PNPNP reinforced PLA for the targeted dental applications. Other required properties like compressive, flexural, and biological suitability properties will be reported in another article for publications.

4. Conclusions

From the experimental investigation of this study, the following are concluded.

i. Production of *Parquetina nigrescens* pod nanoparticles was achieved by disc grinding aided with intermittently 40 hours of ball millings with the particles obtained at 40 hours of milling have an average size of 14.14 nm determined by transmission electron microscope.

ii. Physical fusion of the *Parquetina nigrescens* pod nanoparticles was noted through scanning electron microscopy.

iii. Fourier Infrared Spectroscopic examinations established chemical reaction between the polylactic acid and *Parquetina nigrescens* pod nanoparticles, leading to formation of new compounds.

iv. X-ray diffraction study affirmed structural discrepancies between the pristine polylactic acid and its nanocomposites.

v. Decreases in tensile yield strength, tensile Young's Modulus and impact energy absorption were noted above 3% by weight of *Parquetina nigrescens* pod nanoparticles additions to PLA.

vi. Approximated 9.75% increase was noted with the maximum tensile yield strength at 3% by weight of the *Parquetina nigrescens* pod nanoparticles addition to the polylactic acid.

vii. In addition, 6.16% improvement was recorded in respect of the highest tensile modulus of elasticity at 3% by weight of the *Parquetina nigrescens* pod nanoparticles addition to the polylactic acid.

viii. Moreover, 61.75% enhancement was found with the maximum tensile elongation at 5% by weight of the reinforcement addition to the PLA.

ix. Maximum impact energy was affirmed at 3% by weight of the *Parquetina nigrescens* pod nanoparticles addition to the polylactic acid. Value of the impact energy at this level of reinforcement is 92% greater than the impact energy of the control/pristine polylactic acid.

x. Confirmed new compounds in the *Parquetina nigrescens* pod nanoparticles reinforced PLA are linked with enhanced tensile and impact energy of the nanocomposites compared with the pristine PLA.

References

[1] I.S. Sihama, K.O. Jawad, S.M. Arkan, Investigation of mechanical properties of PMMA composite reinforced with different types of natural powders, ARPN Journal of Engineering and Applied Sciences, **13** (2018) 8889-8900.

[2] S. Bose, A. Bandyopadhyay,Chapter 1- Introduction to Biomaterials, in: A. BandyopadhyayS. Bose Characterization of Biomaterials, Academic Press, Oxford, 2013, 1-9.

[3] M. Saraswathy, V. Krishnaswami, D.D. Ragini,Biomaterials for Hard Tissue Engineering: Concepts, Methods, and Applications, in: B. Bhaskar, et al. Biomaterials in Tissue Engineering and Regenerative Medicine: From Basic Concepts to State of the Art Approaches, Springer Singapore, Singapore, 2021, 347-380.

[4] X. Pang, X. Zhuang, Z. Tang, X. Chen, Polylactic acid (PLA): research, development and industrialization, Biotechnol J, 5 (2010) 1125-36.

[5] R.M. Rasal, D.E. Hirt, Toughness decrease of PLA-PHBHHx blend films upon surface-confined photopolymerization, J Biomed Mater Res A, **88** (2009) 1079-86.

[6] E. Adase, P. Ankutse, D. Kumadoh, M.A. Archer, M.O. Kyene, G.N. Yeboah, D.O. Asamoah Agyare, "A Review of Parquetina nigrescens (Afzel.) Bullock, A Plant for Traditional Medicine: Phytochemical and Pharmacological Properties", Evid Based Complement Alternat Med, 2022 (2022) 6076707.

[7] A.T. Kola-Mustapha, Y.O. Ghazali, H.T. Ayotunde, S.A. Atunwa, S.O. Usman, Evaluation of the antidiarrheal activity of the leaf extract of Parquetina nigrescens and formulation into oral suspensions, J Exp Pharmacol, **11** (2019) 65-72.

[8] S.O. Adoga, D.E. Ekle, B.A. Kyenge, T.O.-O. Aondo, C.O. Ikese, Phytochemical screening, thin-layer chromatography and antimicrobial activity study of leaf extracts, Ovidius University Annals of Chemistry, **30** (2019) 88-94.

[9] M.S. Zafar, Prosthodontic Applications of Polymethyl Methacrylate (PMMA): An Update, Polymers (Basel), 12 (2020)

[10] Y. Wang, M.A. Hillmyer, Polyethylene-poly(L-lactide) diblock copolymers: synthesis and compatibilization of poly(L-lactide)/polyethylene blends, Journal of Polymer Science Part A, **39** (2001) 2755-2766.

[11] P. Saini, M. Arora, M.N.V.R. Kumar, Poly(lactic acid) blends in biomedical applications, Advanced Drug Delivery Reviews, **107** (2016) 47-59.

[12] K.S. Sanjay, A. Prashant, C. Abhishek, High Molecular Weight Poly(Lactic Acid) Synthesized With Apposite Catalytic Combination and Longer Time, Oriental Journal of Chemistry, 34 (2018) 1984-1990.

[13] F.J. Akinrinmade, A.S. Akinrinde, O.O. Soyemi, A.A. Oyagbemi, Antioxidant Potential of the Methanol Extract of Parquetina nigrescens Mediates Protection Against Intestinal Ischemia-Reperfusion Injury in Rats, J Diet Suppl, **13** (2016) 420-32.

[14] J.Y. Datté, A. Ziegler, Pharmacological investigation on nigrescigenin-a cardenolide from Parquetina nigrescens (Afzel.) Bullock: comparative studies on cardiotonic effects of Parquetina nigrescens, g-strophanthin and noradrenaline in guinea-pig isolated atria, Journal of Pharmacy and Pharmacology, **53** (2001) 859-866.

[15] A.O. Ayoola, O. Akinloye, O.O. Oguntibeju, J.M. Oke, A.A. Odetola, Antioxidant activities of Parquetina nigrescens, **10** (2011) 4921-4925.

[16] Z. Raszewski, A. Nowakowska-Toporowska, J. Weżgowiec, D. Nowakowska, W. Więckiewicz, Influence of silanized silica and silanized feldspar addition on the mechanical behavior of polymethyl methacrylate resin denture teeth, J Prosthet Dent, 123 (2020) 647.e1-647.e7.

[17] M. Vojdani, R. Giti, Polyamide as a Denture Base Material: A Literature Review, J Dent (Shiraz), **16** (2015) 1-9.

[18] S.A. Bello, Hybrid Polymeric Nanocomposites from Agricultural Waste,1st, Published by Taylor & Francis, Boca Raton, Florida, United States, 2022.

[19] H.S. Barbara, Infrared Spectroscopy: Fundamentals and Applications, John Wiley &Son, University of Technology, Sydney, Australia, 2004.

[20] S.A. Bello, J.O. Agunsoye, S.B. Hassan, Synthesis of Coconut Shell Nanoparticles Via A Top Down Approach: Assessment of Milling Duration on The Particle Sizes and Morphologies of Coconut Shell Nanoparticles, Materials Letters, **159** (2015) 514-519.

[21] ASTM D638-14 Standard Test Method for Tensile Properties of Plastics, ASTM International, West Conshohocken, PA,, 2014.

[22] S.A. Bello, M.Y. Kolawole,Recycled Plastics and Nanoparticles for Green Production of Nano Structural Materials, in: O.V. Kharissova, L.M.T. MartínezB.I. Kharisov Handbook of Nanomaterials and Nanocomposites for Energy and Environmental Applications, Springer International Publishing, Cham, 2021, 599-630.

[23] S.A. Bello, F.O. Kolawole, S.I. Durowaye, S.W. Balogun, M.Y. Kolawole, S.A. Mohammed,Recent Developments in Techniques and Technologies for Analytical, Spectroscopic, Structural, and Morphological Characterisation of Modern Materials of Advanced Applications, in: N. KulkarniB.I. Kharissov Handbook of Emerging Materials for Sustainable Energy, Elsevier Amsterdam, 2024, 675-724.

[24] 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** (2023) 406-414.

[25] ASTM D256-10(2018), Standard Test Methods for Determining the Izod Pendulum Impact Resistance of Plastics, ASTM International, West Conshohocken, PA, 2018.

[26] A.B.D. Nandiyanto, R. Oktiani, R. Ragadhita, How to Read and Interpret FTIR Spectroscope of Organic Material, Indonesian Journal of Science & Technology, **4** (2019) 97-118.

[27] G.H. Jeffery, J. Basset, J. Mendham, R.C. Denney, VOGEL's Textbook of Quantitative Chemical Analysis,5, Longman Scientific and Technical, New York, 1989.

[28] S.A. Bello, Wear and thermal resistance properties of aluminium particulate microcomposites, Bulletin of Materials Science, **43** (2020) 1-15.

[29] S.A. Bello, J.O. Agunsoye, J.A. Adebisi, N.K. Raji, R.G. Adeyemo, A.G.F. Alabi, S.B. Hassan, Flexural Performances of Epoxy Aluminium Particulate Composites, Engineering Journal, Chulalongkorn University, **22** (2018) 97-107.

[30] S.A. Bello, J.O. Agunsoye, J.A. Adebisi, S.B. Hassan, Optimisation of charge ratios for ball milling synthesis: agglomeration and refinement of coconut shells, Engineering and Applied Science Research (EASR), **42** (2018) 262-272.

[31] S.A. Bello, S.B. Hassan, J.O. Agunsoye, M.G.Z. Kana, R.I. A, Synthesis of Uncarbonised Coconut Shell Nanoparticles: Characterisation and Particle Size Determination Tribology in Industry, **37** (2015) 257-263.

[32] P. Bazan, P. Nosal, B. Kozub, S. Kuciel, Biobased Polyethylene Hybrid Composites with Natural Fiber: Mechanical, Thermal Properties, and Micromechanics, Materials (Basel), **13** (2020)

[33] 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** (2019) e02552.

[34] S.A. Bello, M.K. Adebayo, R.G. Adeyemo, P.A. Popoola, Sustainable hybrid nanoparticle reinforced low-density polyethylene: emerging materials for engineering applications, Iranian Polymer Journal, **33** (2024) 965-980.

[35] 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** (2019) 70-77.

[36] S.A. Bello, S.I. Durowaye, W.E. Aigbona, B.O. Bolasodun, K. Audu, S.O. Abdul Ganiyu,Parquetina nigrescens–Reinforced Polylactic Acid (PLA) Composites for Engineering Applications, in: S.A. Bello Hybrid Polymeric Nanocomposites from Agricultural Waste, CRC, Taylor and Francis, USA, 2022, 279-319.

[37] X. Li, C. Guo, X. Liu, L. Liu, J. Bai, F. Xue, P. Lin, C. Chu, Impact behaviors of poly-lactic acid based biocomposite reinforced with unidirectional high-strength magnesium alloy wires, Progress in Natural Science: Materials International, **24** (2014) 472-478.

[38] S.A. Bello, O.E. Egbanubi, A.G.F. Alabi, Emerging hybrid particle-reinforced high-density polyethylene nanocomposite for bone replacement, Polymer Bulletin, **81** (2024) 1743-1766.