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DEVELOPMENT AND CHARACTERIZATION OF DATE SEED NANOPARTICLES REINFORCED POLYLACTIC ACID (PLA) NANOCOMPOSITES

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Abstract: Date seeds (DS) or wastes were converted into nanoparticles and used as reinforcement for developing polylactic acid (PLA) nanocomposites. The DS nanoparticles were synthesized using the top-down approach. The PLA having different weight fractions of the DS nanoparticles were melted in a mold using a UNISCOPE laboratory oven at 200°C. The structural and mechanical properties of the PLA nanocomposites were studied. The results revealed significant improvement when compared with the controlled specimen. The optimum values for the mechanical properties were found at 1wt% DS nanoparticles reinforced composite specimens. The SEM analysis revealed that there is a uniform particle distribution within the PLA matrix. The Fourier Transform Infrared (FTIR) spectrum affirms chemical interaction between DS nanoparticles and PLA molecules while the X-Ray Diffraction (XRD) spectrum revealed the semi crystallinity of the nanocomposite.
Keywords: Date seed, Polylactic acid, Nanoparticles, Nanocomposites

1. INTRODUCTION

The development made in the field of nanotechnology is on the increase with the aim of developing novel materials that have unique properties and improved characteristics (Zaferani, 2018). Nanomaterials, a major requirement in the field of nanotechnology to produce nano products, are materials with at least one dimension within a hundred nanometer (100 *nm*) region. Nanoparticles, an example of nanomaterials with its three external dimensions in the nanoscale region, are found in many developed products and are also used in numerous technologies (Raab et al, 2011). The top-down and the bottom-up approaches are the two synthesis strategies used to produce various nanoparticles. Although, the use of one approach over the other depends on the chemical composition and the desired features specified for the nanoparticle (Raab et al, 2011). Nanocomposite is a combination of materials, matrix, and reinforcements, with at least one component (mostly the reinforcement) in the nano-metric range (Zaferani, 2018). Current study focuses on the research and development of PLA based nanocomposites, one of the most popular areas in nanotechnology (Pielichowski et al, 2018).

In polymer nanocomposite, the polymer matrix is reinforced with nanomaterials such as nanoparticles to improve the properties of the matrix and at least one of the phases (mostly the nanoparticles) remains in the nanometer region (Karak, 2019). The properties of polymer nanocomposite depend on the reinforcement type, size, shape, chemical structure, concentration, and interaction with the polymer matrix as they can improve or slow down the dynamics of the polymer chain. Polylactic acid (PLA) is a biodegradable polymer that exhibits thermoplastic behavior. It is an aliphatic polyester (Yin et al, 2020) that is gotten from the polymerization of lactic acid or lactide (Battistella et al, 2011). It is also known as Poly lactide. The PLA has been used industrially for manufacturing textiles and packaging (Yin et al, 2020). It also has relevance in the biomedical sector (Shah et al, 2019). Poly glycolic acid (PGA) was the first biodegradable polymer to be synthesized (Mehta et al, 2005). This was followed by the synthesis of PLA and copolymers of the two (Mehta et al, 2005). These polyesters have been researched on for use as sutures, and as implant materials to repair and replace varieties of tissues (Mehta et al, 2005). PLA was discovered by the Carothers (DuPont) in the year 1932 when they developed a low molecular weight product by heating lactic acid in an enclosed space (vacuum). The inability to increase the molecular weight of the product at that time led to the suspension of further studies. Subsequently, PLA having high molecular weight was synthesized by ring opening polymerization of the lactide (Mehta et al, 2005).

PLA is naturally a biodegradable polymer; hence, they can be possibly contaminated by microbes (Suryani et al, 2018). Also, PLA exhibits mechanical properties such as brittleness, low toughness, low thermal stability, and poor dielectric properties which limit the wide use of polylactic acid in advanced applications

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(Sanusi et al, 2020). The nanoparticles of some agricultural wastes such as seeds, shells and pods are recently being used as strengthening materials to make the environment sustainable and reduce the cost of fabricating composites (Salih et al, 2018). Many studies have been reported on PLA based composites but incorporation of date seed nanoparticles in PLA is rare. The only reported study is Ajwa date seed particles added to poly methyl methacrylate (PMMA) which is reviewed as thus. In the study of the mechanical properties of PMMA composites under the influence of date Ajwa seed powder and pomegranate peel powder (Akay et al, 2019), improvement in the mechanical properties of the produced composites containing the natural powders were recorded. The value of the flexural strength, flexural modulus, shear stress, impact strength and fracture toughness rise with increasing weight fraction content for both natural powders. The properties of the produced polymer composites depend on the type, shape, size, interaction with the matrix, concentration and properties of the nanoparticles added as reported by Mohammed in 2020.

2. MATERIALS AND METHOD

The date seeds used in thlis study were gotten from the date fruits procured from Ojaf Oba market, Ilorin, Kwara State, Nigeria. The PLA powder were imported through AliExpress. The reagents used were from the Materials Charaterization Laboratory, Department of Materials Science and Engineering, Kwara State University, Kwara State, Nigeria. The equipment and apparatus used in carrying out the study are measuring cylinder, beakers, spatula, OHAUS digital weighing balance, ball mill machine, syringe, magnetic stirrer, heavy duty grinding machine, hammer, sample bowl, die mold, aluminum foil paper, UNISCOPE laboratory oven, transmission electron microscope (TEM), scanning electron microscope (SEM) with attached EDS, ultraviolet visible spectroscope (UV-Vis), X-ray diffractometer (XRD), gas chromatography - mass spectrophotometer, universal testing machine (Testometric Fs50AT UTM), impact testing machine (Avery Dennison)

This study is based on laboratory experimentation and observation. The PLA nanocomposite was developed following the steps below:

- The synthesis of the date seed nanoparticles
- The production of the PLA nanocomposite samples
- Characterization of the date seed nanoparticles and the PLA nanocomposite samples.

Date Seed Nanoparticles Synthesis

The date seed nanoparticles were synthesised using the top-down approach which involves the mechanical crushing of the date seeds to reduce the size before milling to produce the nano sized particles.

The date seeds were thoroughly cleaned with water to remove dirt and other particles that might contaminate before oven dried at 120°C for 8 hours to remove moisture.

An hammer was used to crush and reduce the size of the date seeds by breaking into smaller pieces before they were ground using an heavy duty grinding machine to produce the powder samples to be milled.

The steel balls (each with different diameter of about 5mm to 60mm) in the ball mill machine were weighed. The weight of the balls in the ball mill machine were found to be 414g using the OHAUS digital weighing balance. Employing a milling charge ratio of 10, 41.4g of the date seed powders were weighed and placed in the milling chamber with the balls. The chamber was covered and sealed tightly with screws to prevent the escape of the date seed powders from the chamber and the entrance of air into the chamber that may contaminate the date seed powders during the milling process. The date seed powders were milled for 40 hours, at approximately 7 hours per day to produce the date seed nanoparticles. Samples were taken after milling for 22 and 40 hours for analysis to determine the particle sizes.

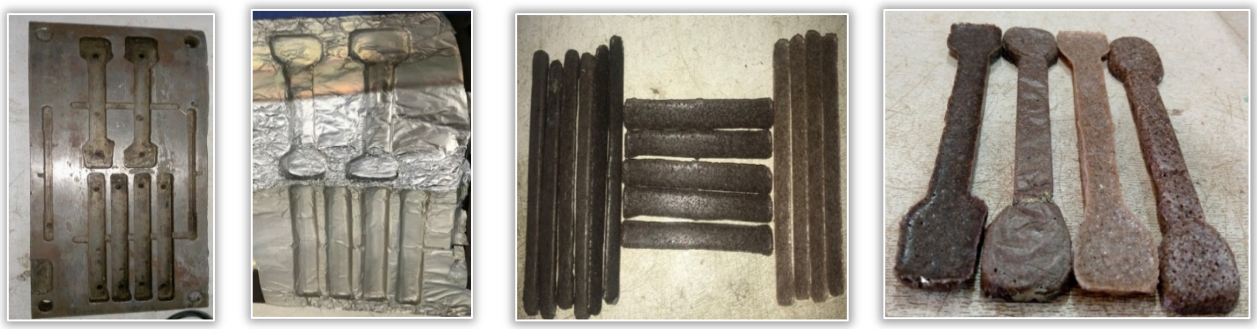

Figure 1. Nanocomposites production (a) mold (b) aluminum foil-lined mold (c, d) produced nanocomposite samples

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Polylactic Acid (PLA) Nanocomposite Production

The PLA nanocomposites were developed by incorporating the date seed nanoparticles (reinforcement) in different proportions into the polylactic acid (polymer matrix). The steel molds in Figure 1(a) were prepared by lining the inside with aluminum foil paper just like in Figure 1(b) above. This is to ensure easy removal of the PLA nanocomposite samples from the mold after processing. The produced date seed nanoparticles were weighed using OHAUS digital weighing balance (with precision of 0.0001 digits) and added to the weighed PLA powder in the sample bowl. 1, 3 and 5 wt% of the date seed particles were added to PLA (Kowalczyk et al, 2017). Thorough and continuous mixing of the date seed nanoparticles and the PLA powders was done to ensure even distribution of the reinforcement in the matrix. 5 drops of palm kernel oil were added to the mixture to stick nanoprticles to the PLA grans. After mixing, the mixture was poured in the prepared mold and placed in the oven to melt, at 200°C and allow to solidify and cool to room temperature to produce the PLA nanocomposite samples.

The control samples without reinforcement additions were also prepared. The PLA powder was weighed and the required amount of powders were poured in the prepared molds.

3. CHARACTERIZATION

Scanning Electron Microscopic Analysis

ASPEX 30320 scanning electron microscope equipped with energy dispersive X-ray spectroscopy was used to examine the structures and identify elemental constituents of the date seed nanoparticles and polylactic acid nanocomposites produced. Scanning was done with helps of electron beam accelerating at 15 *kV* to obtain images that describe the structures of the analyzed samples.

Transmission Electron Microscopic Analysis

The transmission electron microscope (TEM, model: JEM 2100F) is used to obtain structural features of the date seed nanoparticles and to measure their sizes. Beam of electron passing through the samples (which was prepared by drying the nanoparticles 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*.

X-ray Diffraction Analysis

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* was used to identify crystalline phases of the polylactic acid nanocomposites. Samples were scanned from 0° to 74.9780° (°2theta) at a scan step size and time of 0.0260° and 29.07s, respectively and the phases were identified using X'Pert High score plus software; PAB-ICSD and ICDD (2014) databases.

Fourier Transformation Infrared Spectroscopy

Bond/functional group characteristics to study interaction of the date seed nanoparticles and polylactic acid was probed using Shimadzu Fourier Transform Infrared Spectroscopy (FT-IR).

Mechanical Tests

In this study, some of mechanical tests were conducted on the PLA based nanocomposites to examine their resonses to loadings which are useful as technical requirements of the nanocomposites for their selection for an application. Figure 1(c) are the samples subjected to impact energy test while the tensile properties of the nanocomposites were determined using the samples in Figure 1(d).

Tensile Test

The tensile test was carried out on the composite samples with the Testometric Fs50AT UTM (UNIVERSAL TESTING MACHINE) per ASTM D638-14 (ASTM D638-14, 2014). The analysis was used to determine the yield strength, yield strain, Young's modulus and the energy absorbed by the composites.

Impact Energy Measurement

The impact test was carried out using the Avery Denison impact tester. The impact test was used to determine the toughness of the produced composite specimens. In this study, the Izod technique was used culled from ASTM International guidelines for testing plastics (ASTM D256-10,2018). The sample is placed on a guard and a hammer is dropped to deliver a violent blow that hits the sample against the guard. The energy absorbed by the sample prior to breakage is read from the pound scale, which is then converted to joules (where 1*ft.lb.* = 1.35581795 *J*). The sample is striked by the hammer with an energy of 120*ft.lb.*, at an impact velocity of 12.5 *ft/s* (Bello et al, 2020).

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4. RESULTS AND DISCUSSION

Microstructure and Elemental Compositions of Date Seed Nanoparticles

The micrographs and spectrograph from the SEM/EDS analysis of the date seed powder used as the feed material for the milling process are shown in Figure 2.

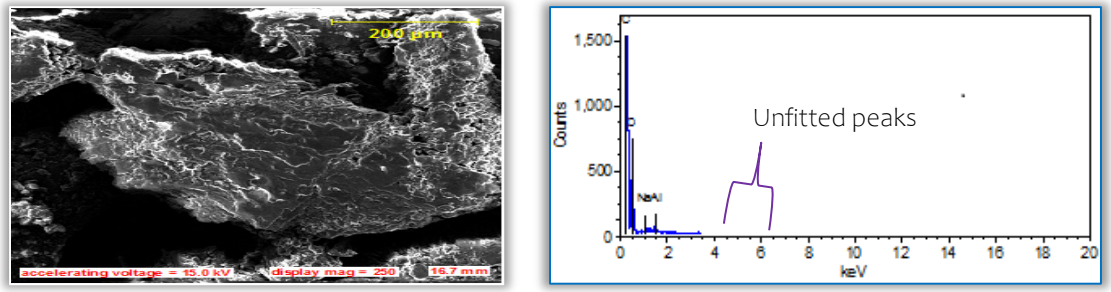

Figure 2. Microstructure and elemental constituents of date seed powder

The surface morphology of the date seed powders in Figure 2(a) reveals that the powders contain a big particle surrounded by particles of smaller sizes. Different sizes of the particles are evident that rate of breakages of the date seed fragments from the hammer crushing and subsequent grinding is not the same resulting in powder of varied sizes. Energy dispersive X ray spectrograph in Figure 2(b) reveals the presence of C, O, Na and Al having distinct peaks while other elements like W, K, Cu, Ca, Mn, Sb, S and La have count scores that are too low to have distinct peaks on the EDS spectrograph. These elements are represented by spectrum around the Al peak. The presence of C, O, S, a non-metallic element, confirms the presence of cellulose in the date seed while the metals detected confirms the mineral contents of the date seed (Bello et al, 2015).

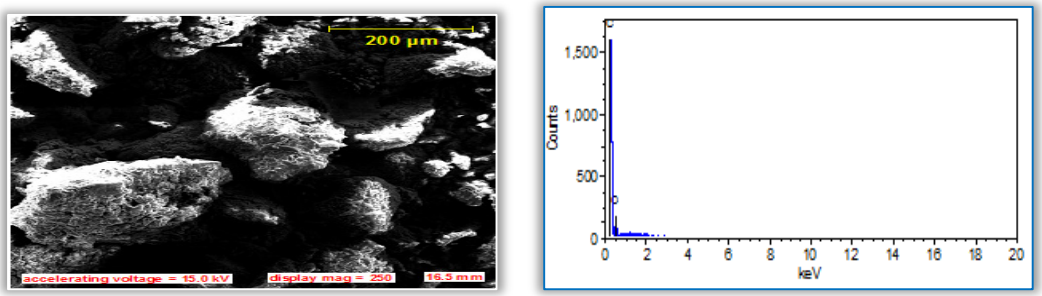

Figure 3. (a) SEM micrograph and (b) energy dispersive X-ray spectrograph of date nanoparticles

SEM micrograph of date seed nanoparticles (obtained after milling for 40 hours at 10 charge ratios) in Figure 3 shows a mass of very fine particles and few agglomerated particles. During the milling process, the date seed powder broke into smaller fragments as the steel balls and date powders collided with each other and against the wall of the mill leading to particles of smaller sizes and an increase in the surface area of the date seed particles which causes the agglomeration of the very fine particles.

Transmission Electron Microscopic Images of Date Seed Nanoparticles

Date seed nanoparticles obtained after 22 hours of milling have particles of varying sizes and deformed spherical shapes. Greater size differences are indication that the particles miniaturisation has not been accomplished at the duration, implying that further ball milling process would cause further breakage of the bigger fragments (Figure 4(a)). Moreover, at 40 hours of milling, particles appear nearly spherical in shape and equal in sizes (Figure 4(b)), affirming that ball milling above 22 hours has caused further breakage of bigger fragments and agglomeration of very fine particles. This agrees with observation in Figure 3 and findings in a research paper by Bello in 2015.

Polylactic acid is a semicrystalline polymer as it is evident from its diffractogram in Figure 5a which bears some distinct peaks fitted with identified crystalline compounds while other broad section represents the amorphous components of the polymer. Moreover, similar peaks pattern is observed with diffractogram (Figure 5b) of nanocomposite but with some different identified compounds (e.g $[C_2H_2O_2]_n$; $C_8H_6N_4O_5$) proposed to be new compounds resulted from interactions of polylactic acid molecules and date seed nanoparticles. In addition, broader peaks of the nanocomposite than those of the polylactic acid polymer proposes strengthening of the matrix by the addition of the date seed nanoparticles. Similar observation is noticed in literature (Speakman, n.d).

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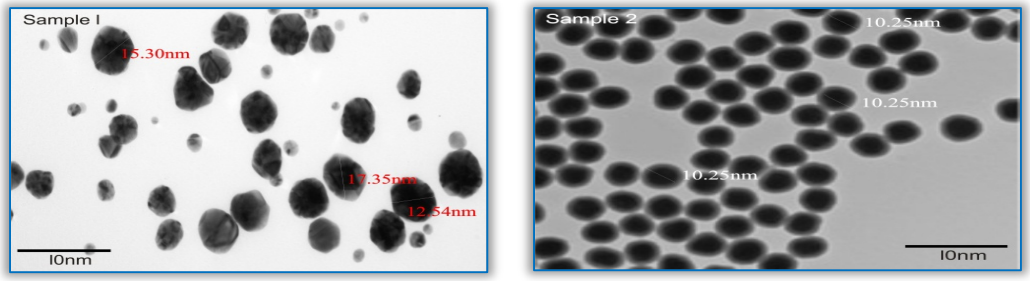

Figure 4. TEM images of date seed nanoparticles obtained after (a) 22 hours and (b) 40 hours of milling
X-Ray diffractogram of polylactic acid nanocomposites

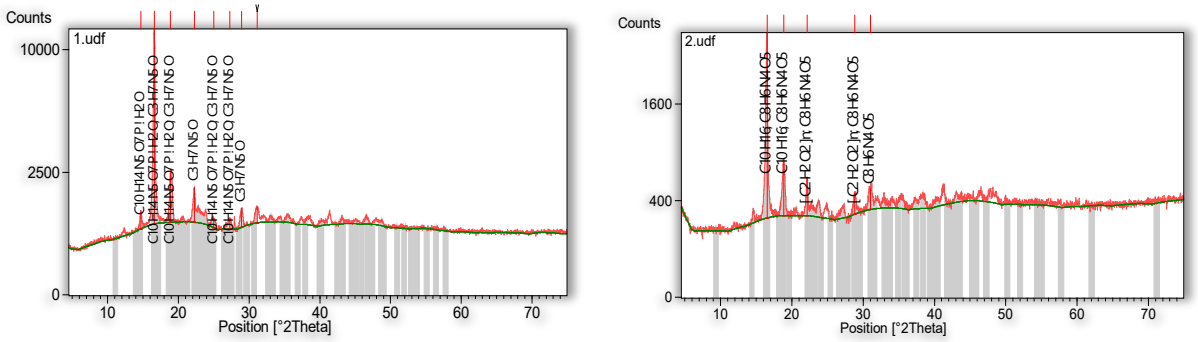

Figure 5. X-ray diffractograms of (a) polylactic acid and (b) nanocomposites

Chemical Properties of the Polylactic Acid Nanocomposites

Presence of more than five absorption band in the spectrum of the polylactic acid polymer and its nanocomposites shows that the analyzed specimens are complex molecules (Nandiyanto et al, 2019). The absorption band in the range between 3650 – 3250 cm^{-1}, reveals the presence of hydrogen bond as presented in Table 1. It is observed in Figure 6 that the bands 3647.88 and 3565.52 cm^{-1} were followed by sharp absorption intensity. This indicates the presence of an oxygen related group such as phenols, and the presence of a hydrogen bonding (Nandiyanto et al, 2019). Moreover, smaller % transmittances of the nanocomposites than those of the polylactic acid affirms that some of polylactic acid molecules have reacted with the date seed nanoparticles resulting in the new compounds that caused peak shift due to light transmittances at wavelengths different from those of some of the PLA molecules. This observation perfectly agrees with the findings in Figure 5.

Table 1. Bonds/functional group of polylactic acid nanocomposites

S/N	Band (cm^{-1})	Functional groups (Bonds)	Description and Reference(s)
1	3647.88	OH	Phenols (Nandiyanto et al, 2019)
2	3565.52	OH	Phenols (Nandiyanto et al, 2019)
3	2996.78	C-H	Aliphatic (Jeffrey, 1989)
4	2945.68	C-H	Aliphatic (Jeffrey, 1989)
5	2400.19	-	
6	2086.22	Transition metal carbonyls	(Nandiyanto et al, 2019)
7	1756.58	Alkyl carbonate	(Nandiyanto et al, 2019)
8	1616.26	C=N	(Jeffrey, 1989)
9	1575.31	Carboxylate	Carboxylic acid salt (Nandiyanto et al, 2019)
10	1456.48	CH_3-,-CH_2-	(Jeffrey, 1989)
11	1386.16	CH_3-,-CH_2-	(Jeffrey, 1989)
12	1361.07	CN stretch	Aromatic tertiary amine (Nandiyanto et al, 2019)
13	1223.62	CN stretch	Secondary amine (Nandiyanto et al, 2019)
14	1132.10	CN stretch	Secondary amine (Nandiyanto et al, 2019)
15	1088.85	CN stretch	Primary amine (Nandiyanto et al, 2019)
16	956.52	C-C	(Jeffrey, 1989)
17	921.53	C-C	(Jeffrey, 1989)
18	871.39	C-H out of plane blend	Aromatic (Nandiyanto et al, 2019)
19	756.25	C-Cl stretch	Aliphatic chloro compounds (Nandiyanto et al, 2019)
20	695.87	C-Br stretch	Alphatic bromo compounds (Nandiyanto et al, 2019)
21	512.51	C-I stretch	Aliphatic iodo compounds (Nandiyanto et al, 2019)

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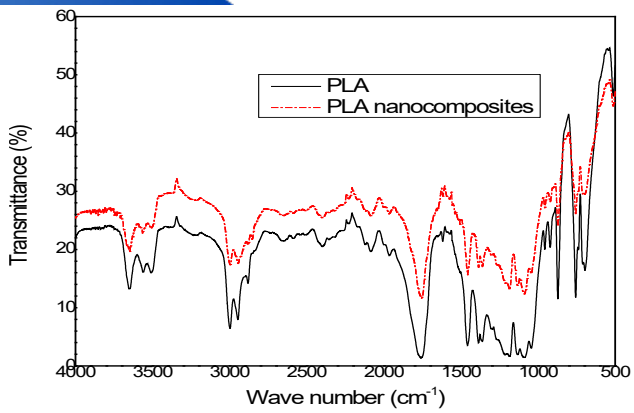

Figure 6. FTIR spectra of the polylactic acid nanocomposites stacked on that of the polylactic acid

Microstructural Properties of Polylactic Acid Nanocomposites

Microstructure of polylactic acid polymer (Figure 7) displays a continuous structure with central depression which represents portion of the PLA melt that solidifies last during processing. The continuous structure appears developed from the different polymeric grains that separated from one another by the grain boundaries which are not exactly perfect like that of the metal, affirming the polylactic acid as the semicrystalline polymer.

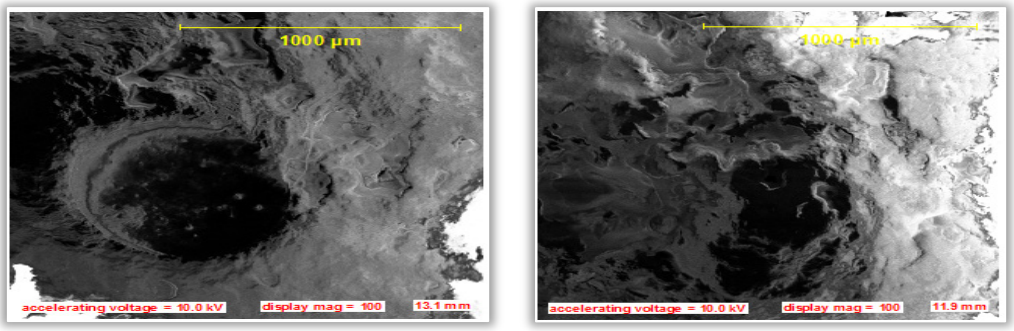

Figure 7. SEM micrographs of nanocomposite

Each of the grains could be linked with the compounds detected by the XRD (Figure 7a). Moreover, the polylactic acid nanocomposite has different structural networks as it is evident in Figure 7b. The structure appears as dendritic undulating layers that connected to assume a continuous body having fortified grain patterns due to the date seed nanoparticle additions.

Mechanical Properties

Tensile Strength

Figure 8(a) illustrates the mean values and standard deviation values of the tensile yield strength of all the produced composite specimens. It is seen that the highest mean value of tensile yield strength was exhibited by specimen 2 with 2.63467±1.12681 *MPa* while the lower mean value of tensile strength was exhibited by the specimen 4 with 0.801±0.57038 *MPa*. It is obvious that the tensile strength values increase with weight fraction of the date seed nanoparticle reinforcement. This is due to good interfacial adhesion resulting increased surface area of the date seed nanoparticles which creates amply interfaces between the matrix and the reinforcement and improve the rate at which stress is transported from the matrix to the reinforcement (Kowalczyk et al, 2017). It was observed that the control sample is weaker than the nanocomposite samples that were reinforced with date seed nanoparticles. This is because the PLA matrix alone lacks the ability to resist the tensile force it was subjected to. When a polymer matrix is reinforced with different reinforcements, the mechanical properties of the composites produced are based on the particle size, particle loading, active load transfer from the matrix to the reinforcement [15] as the improvement in the tensile strength in this study due to the particle loading has been linked with the good adhesion between the matrix molecules and the nanoparticle reinforcements.

Modulus of Elasticity

The resulting mean and standard deviation values for modulus of elasticity of the three samples examined at each nanoparticle loading level is represented in Figure 8(b). The result shows an increase in the modulus of elasticity as the weight fraction of the reinforcement in the polylactic acid matrix increases.

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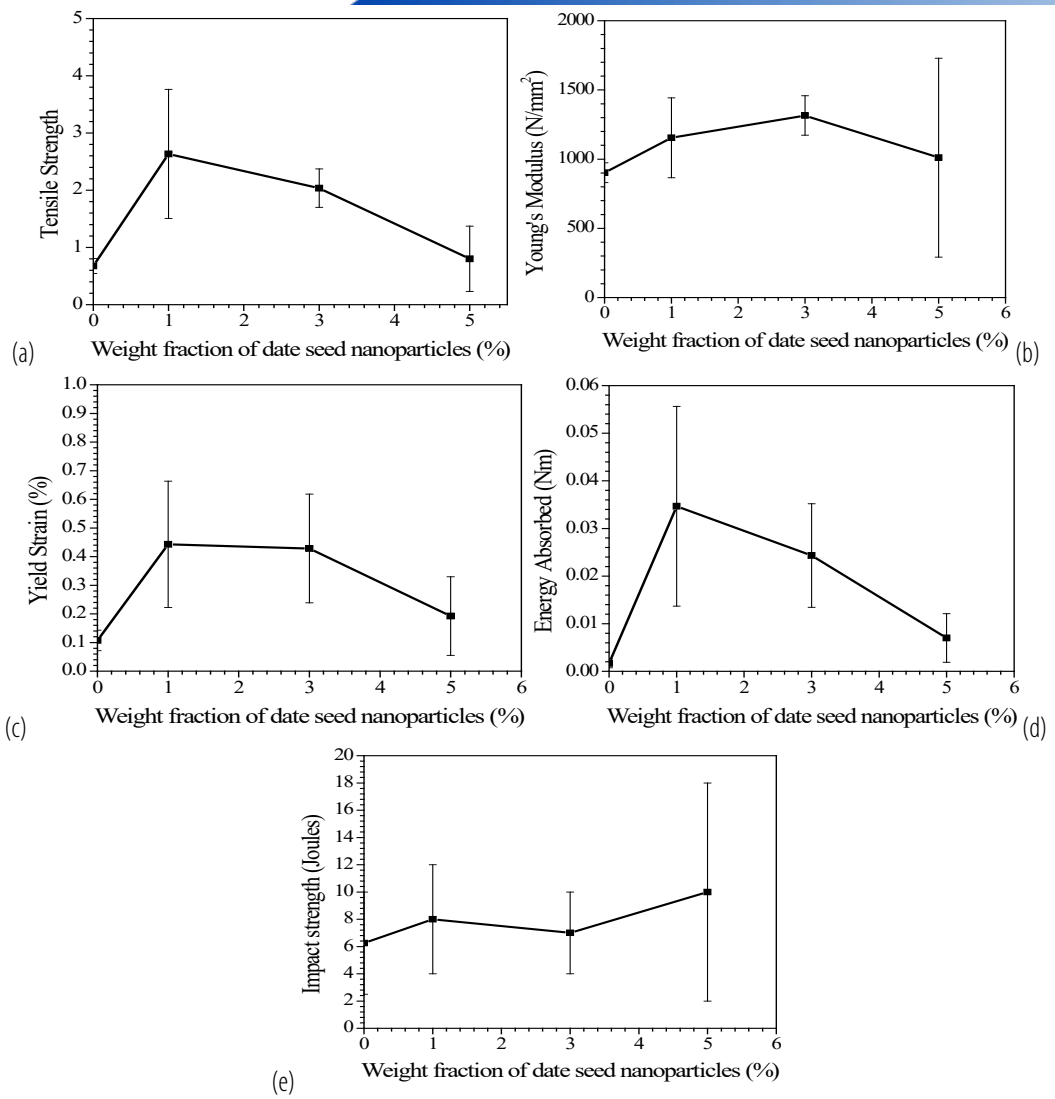

Figure 8. Mechanical properties of date seed nanoparticle reinforced polylactic acid composites (a) yield strength (b) Young's modulus (c) yield strain (d) tensile energy absorbed (e) impact energy

For sample 2 at 1% addition, the mean modulus of elasticity is 1154.17±288.1786 Nmm^{-2} but increased to 1315.409±142.0885 Nmm^{-2} at 3% date seed nanoparticle additions. The increase in the values of modulus of elasticity may be attributed to the good surface interfacial adhesion between the reinforcement and the matrix. At 4%, Young's modulus of the nanocomposite is greater than that of the polymer but lower than that of the nanocomposite at 3% by weight, implying that date seed nanoparticle saturation with the matrix has set in. The increase in the Young's modulus indicates enhancing the stiffness of the composites (Kowalczyk et al, 2017). The good surface interfacial adhesion between the reinforcement and the matrix is attributed to the nanometric size of the reinforcements, and their even distribution inside the polylactic acid matrix. The reported increases in the tensile strength and Young's modulus agree with findings by Batakliev in 2021 and Bello in 2022.

Strain at Yield

The strain at yield values for the PLA matrix reinforced with different weight fractions of date seed nanoparticles are shown in Figure 8(c). The graph indicates the mean values and standard deviation of strain at yield of all the produced specimens. The yield strain values of specimens decrease with increasing weight fractions of the date seed nanoparticles. The yield strain mean was 0.44267±0.22062 in specimen 2, 0.42833±0.18964 in specimen 3 and 0.19233±0.13746 in specimen 4. There is a decrease with the increasing weight fraction of reinforcement. Figure 8(c) shows that the control specimen 1 has a yield strain value that is lower when compared with those of the composite specimens.

Impact Energy

The results obtained after subjecting the nanocomposite specimens to impact energy test is shown in Figure 8(d). The graph reveals that the mean values of impact energy increase as the weight fraction of reinforcement in the composites increases from specimen 2 to specimen 4 but decreases slightly at

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specimen 3. Although PLA is a brittle material, addition of the date nanoparticles has improved its ability to absorb energy during sudden load impact. The enhancement could be linked with uniform distribution of the date seed nanoparticles which enable even sharing of loads transferred from the polylactic acid matrix during sudden impact loading.

5. CONCLUSION

In conclusion, the results of the various analyses carried out on the date seed nanoparticles synthesized using the top-down approach, by mechanically milling the date seed powder at a charge ratio of 10 for a maximum of 40 hours. It could be deducted that as the milling time increases, the particle size decreases. The PLA nanocomposites were produced using the date seed nanoparticles as reinforcement and characterized. The results from the analyses carried out on the nanocomposites shows that there are significant improvements in the mechanical properties of the nanocomposites linked with even dispersion of the nanoparticles within the PLA matrix.

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