Food Technology Research Journal, Vol. 1, special issue 1, 32-41, 2023

FTRJ

3D-printing of Polylactic acid/nano silica filament: Properties and Applications

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Original Article

Article information

Received 29/4/2023
Revised 13/5/2023
Accepted 20/5/2023
Published 30/5/2023
Available online 1/6/2023

Keywords:

3D printing, Polylactic acid, Nano Silica, pill organizer,d tooth brush case

ABSTRACT

The objective of this work to functionalize polylactic acid (PLA/nano silica) composite to produce environmentally friendly filament using it in Polylactic acid (PLA) and nano silica with different concentrations (1,2%) were prepared to produce PLA/nanocomposites. PLA, PLA/nano silica (1% and 2%) filaments were produced using a single screw extruder. Tensile, flexural, and thermal properties were investigated; a Scanning Electron Microscopy (SEM) test was also used to verify PLA and PLA/nano silica structure. Finally antibacterial properties of the produced nanocomposites were investigated to evaluate their performance against Staphylococcus aureus *(S. Aureus)* and Gram-negative Escherichia coli *(E. Coli)*. The results revealed that PLA/nano silica (1%) had the better mechanical and thermal properties. The PLA/nano silica (1%) filament sample was used in 3D printing (3DP) applications for producing different samples (tooth brush case and pill organizer).

1. Introduction

The process of creating a three-dimensional object from a digital 3D model is known as 3D printing. It can be used to create prototypes and, when using digital designs, can produce fine structures through layer-by-layer deposition, which can produce complex architectures and streamline fabrication procedures. Conceptually, it can be characterized as a technique for directly digital manufacturing that enables the production of a wide variety of object geometries in a wide variety of materials, including nearly anything that is obtainable as a spreadable powder, for example, ceramic, metal, metal-ceramic composite, and polymeric materials (Utela et al. 2008). That is, the various material powders (with various dimensional scales) are the factors that directly affect 3DP quality. Fused deposition modelling (FDM), the most widely used 3D printing process, uses a temperature-controlled nozzle to melt and extrude thermoplastic filament. Polylactic acid (PLA) and acrylonitrile butadiene styrene (ABS) are the two most often utilised filament materials. As previously stated (Osswald, et al., 2018). In a variety of applications, polylactic acid (PLA), a bio-based polymer, is frequently employed. Agribusiness goods like corn or starch are used to make PLA (Vidakis et al., 2021). It is now utilised as a matrix material in a variety of nanoparticle filler combinations for a larger range of applications. When employed in composites, either as a matrix or as a constituent of a polymer blend system, PLA displays excellent behaviour. Nanotechnology is the understanding and control of matter at the nanoscale, at dimensions between approximately 1 and 100 nanometers, where unique phenomena enable novel application (Clarissa et al., 2022). In industries like microelectronics, micro-electromechanical systems, and micro-photonics, silica (SiO_2), one of the most often used inorganic materials, requires production techniques with nanoscale resolution (Okamoto, 2012). Nanotechnology can be applied to 3D printing to create nanoscale structures or to include nanomaterials in the primary material.

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Many different types of materials have been discussed as fillers in a PLA matrix to provide particular qualities or improve those that already present. Silica, also known as silicon dioxide (SiO_2), can be found in crystalline and amorphous forms. Quartz is a highly crystalline material that is a mineral and a significant part of sand (Samah, et al., 2017). In the construction industry, notably in the concrete sector, crystalline SiO2 is frequently utilised as aggregates and smaller-sized fillers. Due to the fact that it is amorphous SiO2, it is used to modify 3D printing properties (Sikora et al., 2021). The purpose of this research is to functionalize a composite made of polylactic acid (PLA) and nano silica to provide an environmentally friendly filament for 3D printing and related applications. Additionally, an examination of the filament produced was performed.

Materials and Methods

Materials

Sodium Silicate, Hydrochloric acid (HCl) and sulphuric acid (H_2SO_4) were purchased from Blutruve company. The Polylactic acid, PLA (Ingeo 4043D), was imported as pellets from India that was characterized by a density 1.25g/cm^3, molecular weight 1.8*10^5 g/mol and a melt flow index (MFI) of 6 g/10 min at a temperature of 210 ◦C, according to the producer's technical data sheet.

Preparation of nano silica

According to (Thahab et al., 2020), the precipitation process was used to create nano silica. Concentrated sulfuric acid with regular addition (dropwise) was utilised to reduce the pH of the sodium silicate while being stirred magnetically. After the stirring period, A pure silica gel formed. An electric furnace at 200°C for 8 hours was used to dry the gel.

Preparation of PLA/Nano silica Composite

PLA/nano silica composite was prepared by blending PLA granules and nano silica particles with different concentrations 1, 2% (wt.) with the addition of Paraffin oil 2% of the weight of the used polylactic acid granules and nano silica powder. In addition to being water resistant, paraffin oil was employed as a plasticizer to increase the processability of PLA by lowering polymer entanglement and allowing nano silica particles to penetrate the granules during melt-mixing. (Wood and Maguire, 2011)

Filament Production

A single screw extruder (Suzhou ACC Machine, FLD-OA-made in China) was used to produce 1.75 mm-diameter filament out of PLA and PLA/nano silica (1%, 2%). The extruder chamber consists of 4 heating zones. Temperatures were set to each heating zone 170^{0}C at heat zone 4 (closer to hopper), 205ºC at heat zone 3 and 2 (middle stage), 195ºC at heat zone 1 (closer to extruder's nozzle). Screw rotational speed was set to 7.4 rpm and the built-in winder was automatically set to rotational speeds to achieve the requested diameter. Additional quality control tests were also manually conducted with random diameter measurements to the filament diameter using a caliper and optical quality control (Vidakis et al., 2021).

Figure 1. The extruder used to produce PLA/Nano silica filament

3D printing

A 3D printer (Creality 3D printer-ender 373-made in China) was used for printing some samples using PLA/nano silica filament compared with PLA filament without any additives. A method for measuring filament diameter in real time is also included in the system. In this method, the extrusion parameters are automatically modified, and the produced filament undergoes quality control during the production process for the accuracy of the diameter dimensions.

Characteristics of filament produced from PLA/nano silica composite.

- Tensile strength was determined according to the American Society for Testing and Materials (ASTM D638-3), while flexural test was measured according to ASTM D790, which is a model designed using special software according to the specified dimensions.
- Using a TGA-50 Shimadzu apparatus in Japan, thermogravimetric analysis (TGA) was performed on both the pure PLA and the PLA/SiO_2 nanocomposites at a heating rate of 10ºC to 750ºC under N_2 gas. The final sample was inserted into the instrument's open platinum pans.
- Scanning Electron Microscopy (SEM) was examined with an FEI Nano SEM 200, using an accelerated voltage of 1-2 kV.

Water Absorption

According to ASTM D-570, the moisture absorption of three samples of PLA, PLA/nano silica1%, and PLA/nano silica2% was determined. Using a precise electronic scale, samples were first weighed before being immersed in distilled water for 24 hours. The following equation (1) was used to calculate the percentage of weight gain:

$$Weight\ gained\ (W_d)\% = \frac{w_a - w_b}{w_b} \times 100 \qquad (1)$$

W_g is the weight gain percent from moisture absorption.

W_b is the weight before submerging.

W_a is the weight after certain time submerging.

Antibacterial test

The antibacterial test was determined using a screening agar-well diffusion method, and the nanocomposites' antibacterial response was evaluated. For germs like Gram-positive Staphylococcus aureus (S. Aureus) and Gram-negative Escherichia coli (E. Coli). The bacterial growth agent, which varies for each bacterium, was purchased in petri dishes (85 mm in diameter). To remove any moisture, they were first heated in a lab oven for around 30 minutes. Each bacteria was obtained using a syringe, and its solution was made by dissolving it in a natural serum. The same concentration of the bacterium was used for all tests, and it was sufficient for the procedure (growing dense bacterial colonies as seen under an optical microscope). After being homogenised, the solution was examined optically. Each number on the list of specimens represented a distinct specimen, or piece of material. Additionally, correspondingly numbered samples were put in the Petri dishes. A swab was used to collect the fluid, which was put in a test tube. The bacterium solution was evenly spread in the bacterium growth medium in the Petri dishes using the swab. On the Petri dishes, samples were arranged with the corresponding number near the middle of each dish. The Petri dishes were heated to 37 °C in a lab oven for 24 hours. The developed inhibition zones were measured afterward using optical equipment, following the same process for each specimen (Balouiri, et al., 2016).

Results and Discussions

The morphological structure of silica nano particles:

The morphological structure properties have been performed via investigation of morphological structural properties using transmission electron microscopy (TEM). As shown in Figure 1., the as-prepared silica nanoparticles show that the dominant shape of the as prepared sample is a spherical-like shape. Also, the average particle size was about ~ 35 ± 5 nm.

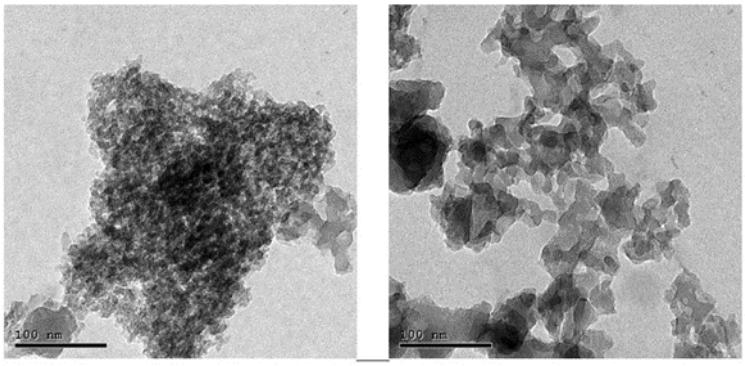


Figure 2. TEM micrograph of Hydrophilic SiO2 NPs

3D printing of the produced filament

Figure 3. depicts the 3D printing parameters utilized in the study to produce the samples in the 3D printer. According to the dimensions specified in the ASTM D638 standard, all other parameters were set to default in the software tool, and the samples were compared with PLA as a reference material in the 3D printer software tool, which was used as the slicer tool for this study.

Specifications	Value
Printing Orientation	45º
Bed temperature	60ºC
Nozzle temperature	215ºC
Infill	100%
Print speed	20 mm/sec
Print cooling	on
Fan Speed	60mm/sec

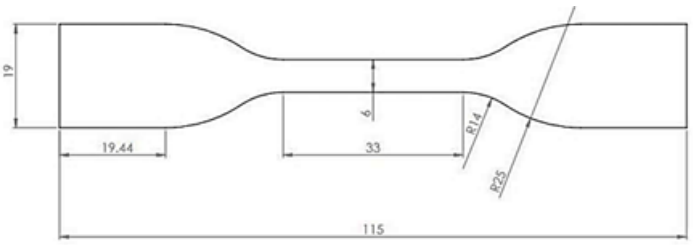


Figure 3. The 3D Printer's fundamental parameters set up to slicer software

Figure 4. illustrates the usage of Solid Works software for modelling specimen geometry in accordance with ASTM D638 standard specifications. Models are then imported into the 3D printing programme and stored in the (.stl) file format, as seen in Figure 2. (Kumar and Yeole, 2019). The samples for the tensile testing were printed using a Creality (3D-ender 372) 3D printer using PLA and PLA/ nano silica materials. Five copies of each sample were produced, as seen in figure 5.

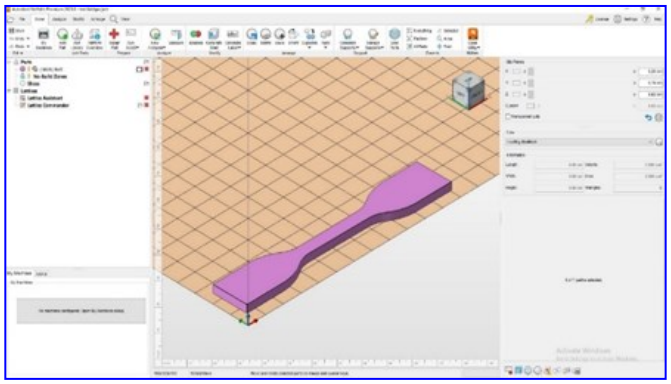


Figure 4. (.stl) file of tensile specimens imported to Netfabb

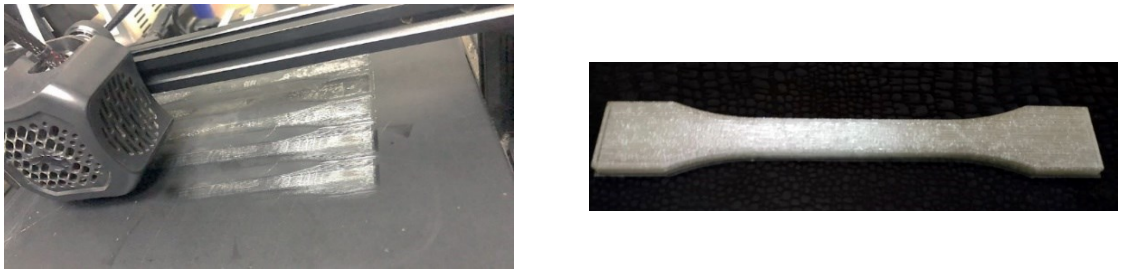


Figure 5. 3D-printed tensile specimen

Mechanical properties

Tensile strength was measured for three samples (PLA, PLA/nano silica1% and PLA/nano silica2%) according to ASTM D 638-IV. Figure 5. Represents the tensile strength for the three samples, the results observed that the highest tensile strength (54 MPa) was for PLA/nano silica1% sample, while as increasing nano silica percent to 2%, decreased the tensile strength this may be due to the bad distribution of nano silica powder in PLA pellets.

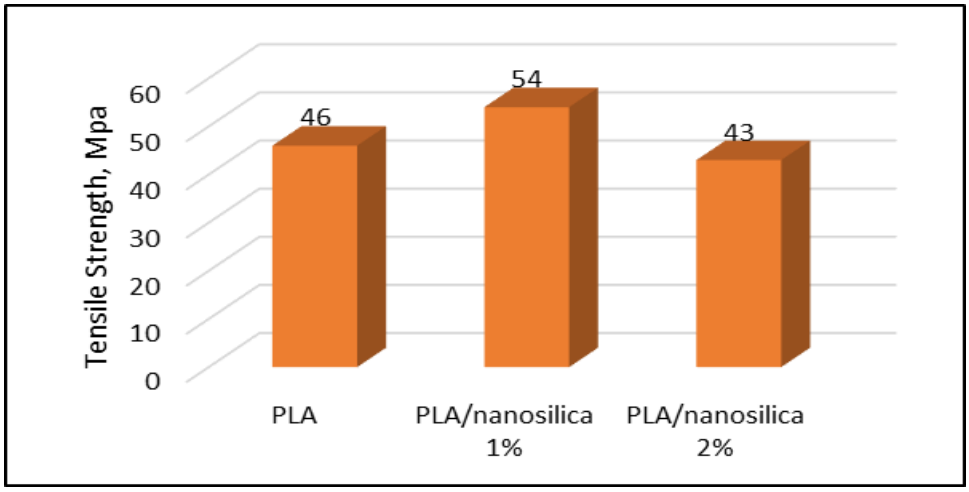


Figure 5. Tensile strength for different 3D printed samples

Flexural test

The bending test was measured according to ASTM D790, this test determines the maximum load that can be applied to the specimen. Figure 6. shows the flexural test for (PLA, PLA/nano silica1% and PLA/nano silica2%), the results observed that the highest flexural stress (81 MPa) was for PLA/nano silica1% sample. The flexural stress for sample PLA/nano silica 2% was 75MPa which is higher than Pure PLA.

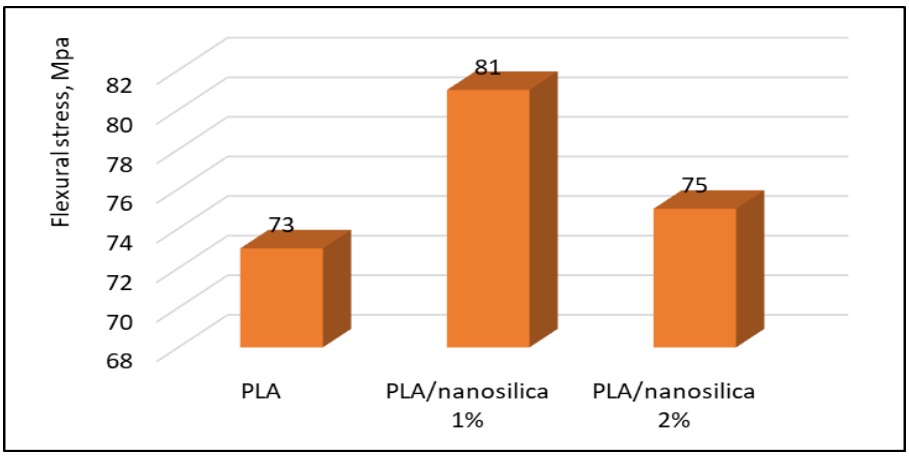


Figure 6. Flexural stress for different 3D printed samples

Thermal gravemetric analysis

It is a method for figuring out how much a sample's mass changes while it decomposes thermally. (Marazzato et al., 2007) Figure 7. demonstrates that for PLA, PLA/nano silica1%, and PLA/nano silica 2%, respectively, the sample mass loss was rapid, commencing at 345, 350, and 352C. Up to 345ºC, there is negligible sample loss in the initial stage, and most of the pyrolysis takes place in the temperature range between 350 and 420ºC.

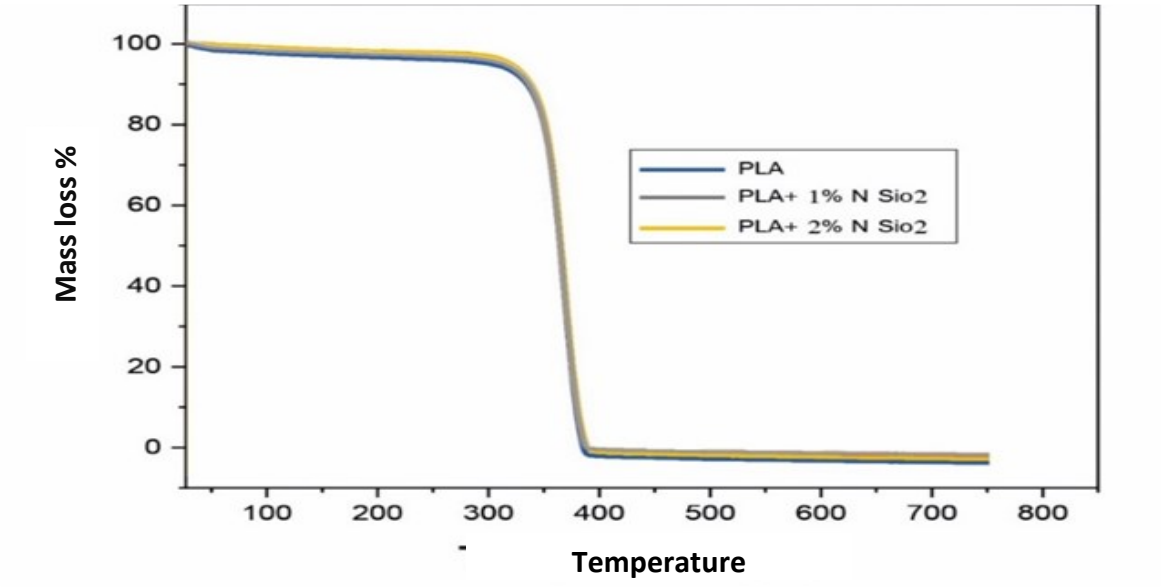
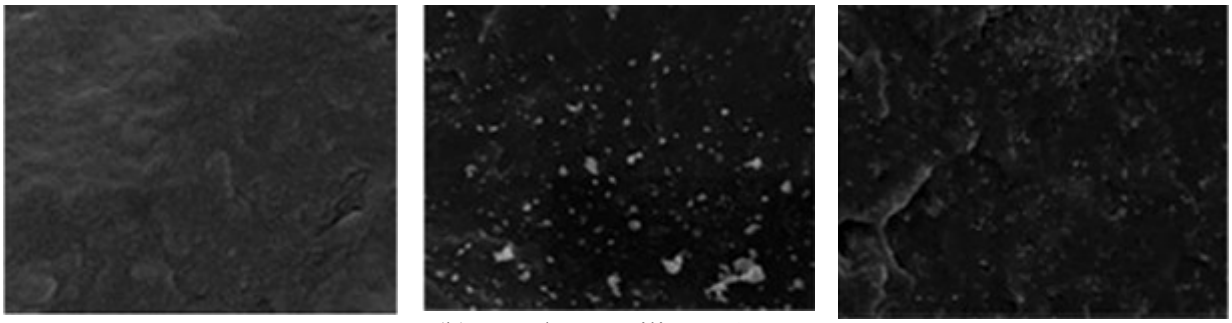


Figure 7. Thermogravimetric analysis for different 3D printed samples

SEM microstructural analysis

It is well known that the filler dispersion and adherence with the polymer matrix have a significant impact on the characteristics of nanocomposites. The smooth, featureless surface of pure PLA is depicted in Figure 8-a by the SEM image. As for the PLA/nano silica, the SiO_2 particles were detected as white dots. it is shown that PLA/ nano silica1% was uniformaly distributed in PLA matrix Figure 8-b. Because there was still a strong connection between the nanoparticles, the addition of 2% nano silica results in huge aggregates and conglomerates of the particles.



(a) PLA (b) PLA/ nano silica 1% (C) PLA/ nano silica 2%

Figure 8. SEM micrographs

Water absorption

Figure 9. displays the PLA, PLA/nano silica 1%, and PLA/nano silica 2% materials water absorption properties. This may be because the well-dispersed silicate layers with a high aspect ratio in PLA provide a barrier effect, creating a tortuous path to impede the diffusion of water molecules into nanocomposites, as opposed to PLA/nano silica1%, which had the lowest weight gain (2.17%) and PLA with the highest weight gain (4.25%) (Rhim 2013).

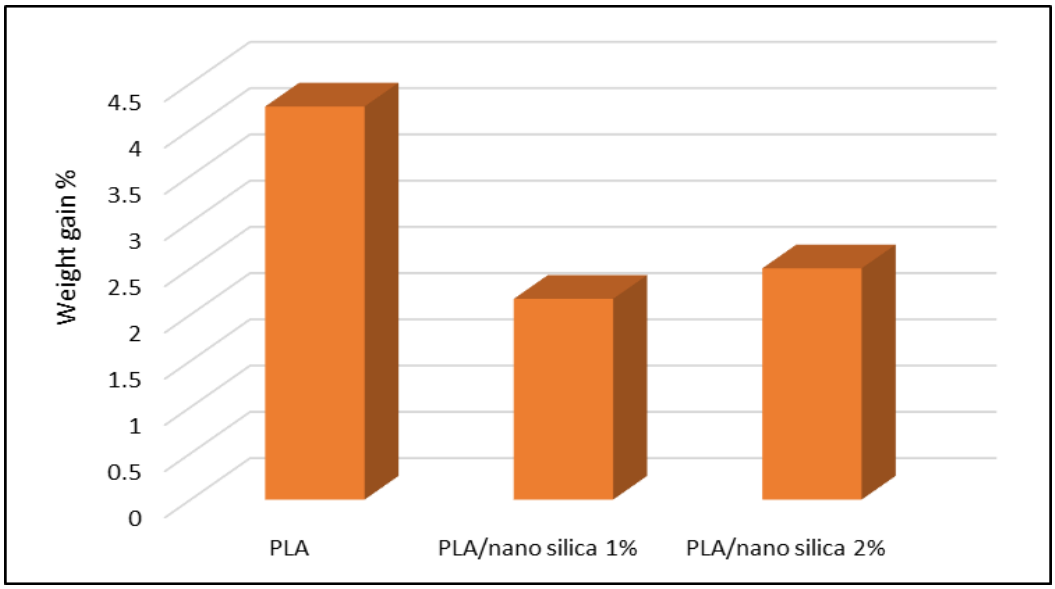


Figure 9. water absorption

Antibacterial test

An agar well diffusion screening procedure was used for comparison to assess the impact of nano silica on the antibacterial reaction. The screening process results were evaluated optically. The created nanocomposites cause a significant improvement in the materials' antibacterial properties. No inhibition zone developed with the PLA material in this test, which was expected as the PLA cannot stop bacterial growth.

Table 1. Antibacterial Activity

Sample	% Inhibition	
	Escherichia Coli	*Staphylococcus Aureus*
PLA	ND	ND
PLA/nano silica 1%	1.9	2
PLA/nano silica 2%	2	2.1

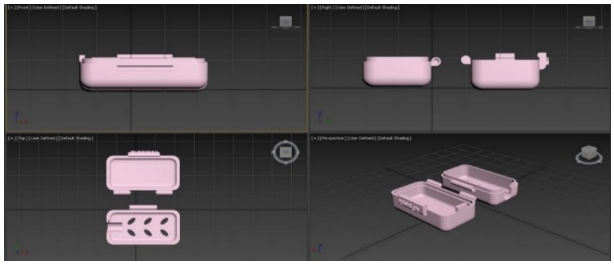
Application of 3D printing using PLA and PLA/nano silica filament

Design and print a template for a toothbrush case

Tooth brush case template was prepared using PLA/nano silica 1%.

Model description

A model used as a toothbrush holder was designed and printed with 3d printer (Kingroon kp3s, nozzle dia. 0.4mm) using Filament polylactic acid with the addition of 1% nano silica as this sample was chosen because it had better mechanical, water absorption, antibacterial properties. A model was designed to serve as a packaging and protection for a toothbrush, using 3D Max program, and then exported with the (.stl) extension as shown in Figure10.



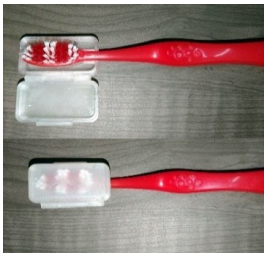


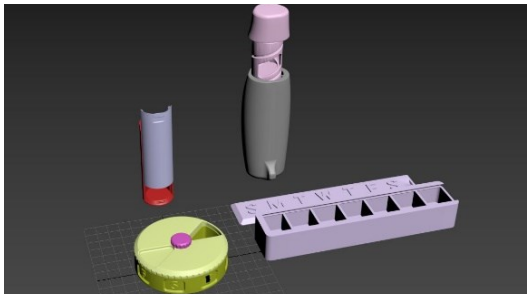
Figure 10. Design using 3D Max program and the template after printing

Table 2. Print settings for a template used as a toothbrush case

Specifications	Value
Layer thickness	0.2 mm
Printing Orientation	45º
Bed Temperature	60º
Nozzle Temperature	215ºC
Infill	20%
Print Speed	50 mm/sec
Print cooling	On
Fan speed	60 mm/sec
Support Setting	Off

Preparing and printing forms used as pill organizers

Pill organizers known as a set of models used in packaging and preserving medication tablets, and it is also used in organizing it, knowing its dates, and dividing it during the day or during the week. It was printed using a polylactic acid with the addition of 1% of nano silica. Figure 11. shows the models used as a pill organizer and the template in ultimaker cura program. The model was printed using a 3D printer (Creality 3D CR-10S pro) with a nozzle diameter of 0.4 mm, the printer setting was presented in Table 3.



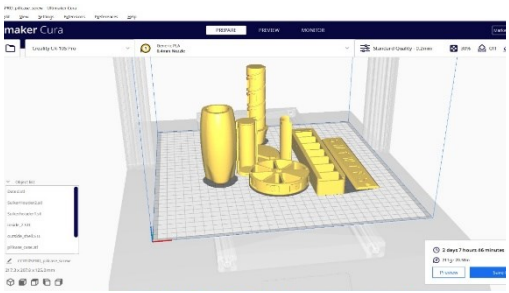


Figure 11. Pill organizer template using ultimaker cura program

Table 3. Print settings for a template used as a Pill Organizer

Specification	Value
Layer thickness	0.2 mm
Printing orientation	45^0
Bed temperature	55C
Nozzle temperature	215 C
infill	30%
Print Speed	50 mm/sec
Print Cooling	On
Fan speed	60 mm/sec
Support Setting	Off

Figure 12. Pill Organizer template after printing

4. Conclusion

Nano composite filament of PLA and nano silica was developed in two concentrations of nano silica(1, 2%) were used for the application of 3D printing technology. The results observed that the addition of nano silica(1%) to PLA increased the mechnaical strength and PLA had the higher water gain percent. The created nanocomposites cause a significant improvement in the materials' antibacterial properties. No inhibition zone developed with the PLA material in this test, which was expected as the PLA cannot stop bacterial growth.

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