Mechanical and tribological behaviour of 3D Printed Almond Shell Particles reinforced PLA (ASP/PLA) Bio-composites

Abstract:

Recently, composite filament development for 3D printing has emerged and is used for numerous applications. The present research work develops neat Polylactic acid (PLA) and Almond Shell Particles reinforced PLA (ASP/PLA) bio-composites for 3D printing and investigates the effects of printing orientation, including 0°, 45°, and 90° orientation, on the tribological and mechanical behaviours of 3D printed materials. The novel ASP/PLA filaments are extruded by the filament extrusion method with the presence of 10% Almond Shell Particles (ASPs) in the PLA matrix, and the samples are 3D printed by the Fused Filament Fabrication (FFF) technique. Mechanical characteristics such as tensile, flexural, compressive strength, and shore hardness are evaluated with respect to various 3D printing orientations. Surface quality of the 3D printed PLA composite samples is analysed with respect to length and diameter deviation. Length accuracy of the 90° oriented PLA and ASP/PLA bio-composite samples exploits a better accuracy of 99.12% and 98.81%, respectively. It is shown that adding ASPs to the PLA matrix decreases the flexural and tensile strength. Among the printing orientations, 0° flat samples result in the maximum tensile strength of 36 MPa and 28 MPa for the neat PLA and ASP/PLA composites, respectively. The lowest contact angle of 54° is observed on the ASP/PLA bio-composites 3D printed with a 90° orientation. The highest contact angle value of 94° is observed on the neat PLA 3D printed with a 0° printing orientation. A tribological study is carried out under dry conditions on the pin on disc tribometer by varying the sliding speed (1, 2, and 3 m/s) and load (10, 20, and 30 N). The result shows that the lowest coefficient of friction of 0.22 is achieved for the ASP/PLA bio-composite samples with a 0° printing orientation under a sliding load of 10 N. These kinds of newly developed compostable materials can be used for developing disposable orthotic foot appliances.

Keywords: *Almond shell; Bio-composites; 3D Printing; Tribology; Wear; Surface roughness*

1. Introduction

Additive manufacturing (AM) occupies a significant space in numerous developing areas such as automotive, aerospace, packaging, construction, and biomedical applications, etc [1]. Excellent advantages such as complex geometry in 3D printing, design freedom, low material wastage, and short manufacturing cycles lead to broad utilization of additive manufacturing technology for many applications [2]. Nowadays, all materials such as metals, polymers, and ceramic components are printed using additive manufacturing technology. Among these, polymeric materials occupy a significant space due to their low initial investment, strength-to-weight ratio, low-temperature processing, and excellent process applications. Fused Filament Fabrication (FFF) is a successful polymeric printing technology by which most engineering and commercial-grade polymeric materials such as Polypropylene (PP), Polyethylene terephthalate glycol (PETG), Polylactic Acid (PLA), and Polyether ether ketone (PEEK) are 3D printed with various profiles [3].

PLA is one of the biodegradable polymers synthesized from carbohydrate feedstock materials such as corn, wheat, and potato starch, etc [4]. It has other advantages such as being non-toxic, non-polluting, and a naturally synthesized polymeric compound compared with other polymers. PLA can be used in a wide range of applications such as electronics, packaging, automotive, and currently in prosthesis fabrication [5]. However, the drawback of PLA polymeric material is its high brittleness, low toughness, and moisture absorption.

To address these limitations, particle reinforcements like metal, wood, and ceramic particles have been added to the PLA polymer. This reduces the consumption of polymeric material and improves the thermal resistance properties of the respective polymers. Researchers have utilized wood, ceramic, and metal as reinforcements for printing PLA polymeric composites. Liu et al. studied various mechanical properties when adding various reinforcements such as wood, ceramic, carbon fibre, and metal to the PLA polymer. They 3D printed samples using the FFF technique and showed that by adding ceramic and metal powder reinforcements such as copper and aluminium, based polymer composites have better and equal mechanical properties compared to neat PLA polymer [6]. Sabarinathan et al. investigated the influence of adding crab shell particles as reinforcement to the PLA polymer composite. The addition of crab shell particles increases the flexural and compression properties compared to neat PLA polymer [7].

Waste biomass presents a significant global challenge due to the substantial volume of organic waste generated annually. The primary contributors to this waste are the forestry and agricultural sectors, with agriculture alone accounting for roughly 140 billion metric tons of waste biomass annually [8]. Currently, biomass-derived composites are widely used in eco-friendly product development in various sectors such as automobile, construction, and household work, etc. Organic reinforcements such as wood particle-reinforced composites have a higher chance of biodegradability. Various research studies are available on the usage of wood particles as reinforcement in the filament fabrication process. Kechagias et al. examined the consequence of adding coconut particles to the PLA matrix, and the process was optimized with respect to varying process parameters. The printing direction has a major impact of 80% on the tensile strength response of the developed wood-based polymer composite [9]. Table 1 shows the various agricultural wastes used as reinforcements in polymer composite preparation using 3D printing technology.

Almond shell is a bio-based waste generated after removing the seed from the fruit, and the hull is considered waste [14]. This hull portion is rich in cellulose, comprising about 31%. Every year, 1.7 metric tons of almond fruit waste are generated and considered as bio-waste [15]. This waste can be utilized in various applications such as dye absorbents, reinforcement in composites, filters, and activated carbon [16]. The utilization of this kind of bio-waste as reinforcement improves the strength of polymer composites by reducing their brittleness. The mechanical characteristics of particle-reinforced polymer composites are mostly influenced by the shape and size of the added particles [17]. The usage of organic fillers in polymer composites may hinder interface adhesion and water absorption properties. Bhagia et al. studied popular trees alongside PLA material for the formulation of polymeric composite filaments. Their research revealed that the resultant wood/PLA composites have a tensile strength ranging from 37 to 54 MPa, coupled with a Young's modulus in the approximate range of 2.9 to 4.9 MPa [18].

During the development of 3D printed components, process factors such as the number of layers, contour width, infill density, layer height, raster orientation, extrusion temperature, and printing speed have a major impact on print quality and properties [19-21]. Many studies have focused on design and optimization to obtain better mechanical properties. However, there is a limited number of reports available on the effect of printing orientation on additively manufactured polymeric samples. Hanon and Zsidai compared tribological studies on the influence of colour and printing orientation of 3D printed PLA polymer using the FFF process. The results showed that a 45° printing orientation of white PLA samples resulted in high frictional loss and maximum wear compared to other colour samples [22]. Huang et al. evaluated processing factors for the influence on the mechanical properties of ABS. The results revealed that printing orientation and layer height have a higher impact on the mechanical properties. A layer height of 0.1 mm and horizontally printed samples exhibited the highest mechanical strength compared to vertically printed samples [23].

Polymeric materials are the most promising materials for tribological applications due to their excellent properties such as vibration damping, corrosion resistance, and self-lubrication [24]. In tribological applications, friction and wear are the two intrinsic parameters when two solid surfaces move in relative motion. In numerous engineering applications, researchers have been concentrating on the development of sustainable materials with higher mechanical and tribological properties. Energy loss during tribological applications may lead to a significant loss in the economy of the concerned entity.

Addition of reinforcement may reduce friction at the contact zone and improve wear resistance in the composite [25]. Limited reports are available on tribological studies of polymeric materials reinforced with organic fibers and particles as reinforcements for the FFF process. Therefore, the current research work concentrates on tribological studies of FFF-printed organic filler reinforced PLA polymeric composites. Mohan and Saravana Kumar conducted mechanical and tribological studies on 3D printed PLA composites while varying the infill density and printing orientation. The results revealed that horizontally printed samples exhibited a lesser wear rate of 9.4 × 10–3 mm3/Nm when compared with vertically built samples [26].

Hanon et al. utilized the FFF technique to create a composite of PLA with added bronze particles. They conducted experimental research to examine the mechanical and tribological characteristics of the 3D printed components relative to their print orientation. The findings indicated that adopting the 'on edge' print orientation results in improved mechanical and tribological properties across all variations of bronze particle-infused PLA composites [27]. Fouly et al. evaluated the influence of adding various concentrations of corn cob particles to the PLA matrix and assessed mechanical and tribological properties. Addition of corn cob particles may enhance hardness by 10% and wear resistance by 150% effectively when compared with neat PLA composite [28]. From the above-mentioned studies, it is concluded that the incorporation of agricultural waste in polymeric composite filament extrusion possesses recycling ability, and the extruded filaments are very useful for the development of eco-friendly products with fully biodegradable properties. Additionally, the impact of printing orientation is an important factor to consider in the development of new novel filament for 3D printing applications.

The present study focuses on the development of Almond Shell Particles reinforced PLA (ASP/PLA) polymer bio-composite filaments for FFF 3D printing. The neat PLA and ASP/PLA composites are 3D printed with different orientations, and the outcomes of the respective orientations are comprehensively deliberated on the physical, mechanical, and tribological properties.

2. Materials and methods

2.1. Materials selection

For the polymeric filament extrusion, PLA pellets (Ingeo 3D850) were purchased from Natur Tec Private Ltd, US. The basic physical properties of the PLA pellets provided by the supplier are shown in Table 2.

Almond Shell Particles (ASPs) were collected from the food processing industry, and the shells were cleaned, dried, and crushed using a Willys mill. The physical and chemical characteristics of almond shell particles, such as density (0.40 g/cm3), and cellulose content (38.47%), hemicellulose (28.82%), and lignin (29.54%) were determined. The crushed particles were sieved using a sieve shaker with a sieve size of 300 mesh. The particles that passed through the 300 mesh size was collected and used for further processing. Particles with sizes less than 50 µm were selected and used for the filament extrusion process. The ASPs were surface treated using an alkaline medium such as sodium hydroxide solution with a concentration of 5%. Alkaline treatment was employed to eliminate surface impurities from the particle surfaces. Chemical modification alters the bonding between the matrix and the chemically treated ASPs. The selected ASP particles were used as inorganic reinforcement for the filament extrusion.

2.2. Extrusion of Almond Shell Particles reinforced PLA (ASP/PLA) polymeric filaments

Two types of filaments were extruded with and without ASPs added to PLA. In the present study, the processed ASPs and INGEO grade PLA granules were mixed uniformly using a ball mill (Make: Erweka, India) along with a suitable binding agent. After mixing, the mixture was fed into a single-screw extruder for melt blending of the ASPs with the PLA matrix. The blended polymer mixture was cut into pieces with a size of 1 cm each. The prepared and blended PLA granules containing 90% PLA and 10% ASPs were used for the further extrusion process. The extrusion process was carried out using a single-screw extruder (Make: Despar Technologies, India). The blended ASP/PLA mixture was fed into the hopper, and the extrusion process was conducted by rotating the screw rod at a speed of 30 rpm while maintaining the temperature between 155-165°C. To achieve uniform diameter, the temperature was adjusted accordingly, and the extruded filament of 1.75 mm ± 0.05 mm was maintained for the filament extrusion process. Figure 1 illustrates the filament extrusion procedure for the composite ASP/PLA filaments.

2.3. 3D printing of ASP/PLA bio polymer composite

The extruded PLA and ASP/PLA polymeric filaments, with a diameter of 1.75 ± 0.05 mm, were used for the fabrication of the bio-composite samples. They were prepared for a desktop-type 3D FFF printer (Make: Pratham 3.0, India). The printer's calibration and alignment in all axes were checked before starting the printing process.

Physical, mechanical, and tribological samples were designed in CATIAV5R20 software. In the present work, CURA 4.1 open-source slicing software was selected and used for slicing the 3D models into machine-readable G-code.

The variable process parameter such as printing orientation (0°, 45°, and 90°), and the remaining parameters like infill density (100%), printing speed (25 mm/s), bed temperature (60°C), and nozzle temperature (205°C) were considered constant for the 3D printing of the PLA and ASP/PLA bio-composites.

2.4. Characterization of 3D printed polymer sample

2.4.1. Precision and accuracy

'Accuracy' measures the precision or correctness of a product's range, which is close to the actual value. When the original CAD design is used to print multiple times, the consistency in print quality is referred to as precision. In the additive manufacturing process, temperature or heat is the main source of fabricating the component. There is a chance of distortion or bulging of the component, which may lead to changes in the accuracy and precision of the components. In this study, the accuracy and precision of the rectangular and cylindrical 3D printed sections are measured in the flexural and tribological samples. Figure 2 illustrates the line and 3D diagrams of the neat PLA and ASP/PLA bio-composite samples with several printing orientations. Dimensions such as printing width (w) and thickness (t) were measured from the flexural samples. The measurements were taken on the upper, middle, and lower portions of the 3D printed sample with respect to the width and thickness.

For measuring the length and diameter, cylindrical samples were selected, and measurements were taken at three respective places on each cylindrical sample. Accuracy measurement involves comparing the dimensions of the 3D design model with the dimensions of the final 3D printed sample. In the case of measuring the precision of the 3D printed sample, five samples were tested per each testing condition for each of the three printing orientations (0º, 45º, and 90º). The variations were considered as the standard deviation of the test condition, and they can be added as error bars in the accuracy results.

2.4.2. Physical property of the 3D printed polymeric PLA and ASP/PLA composite

The density and porosity of the 3D printed ASP/PLA composite were analyzed according to the ASTM D792-13 standard. The experimental density of the composite was measured using Archimedes' principle. The samples were weighed in distilled water and in air using a solid density measurement setup. The weight was measured using a digital weighing scale with an accuracy of 0.0001 g.

The theoretical density (ρ^{th}) of the PLA and ASP/PLA composite are evaluated based on the equation mentioned below,

$$\frac{1}{\rho^{th}} = \frac{W_p}{\rho_p} + \frac{W_m}{\rho_m} \qquad (1)$$

where W_p and W_m represent the weight fraction of ASP and PLA matrix. ρ_p and ρ_m represent the density of ASP and PLA matrix.

Void content (or) porosity(ρ_o) is the main property in which the additively manufactured composite should be studied. Void content measurement was tested as per the ASTM D 2734-94 standard. The void content is evaluated by the equation mentioned below,

$$P_o = \frac{\rho^{th} - \rho^{ex}}{\rho^{th}} X\,100 \qquad (2)$$

where ρ^{th} and ρ^{ex} are the theoretical and experimental density of the prepared PLA and ASP/PLA bio-composite.

2.5. Mechanical characterization of 3D printed sample

2.5.1. Tensile strengt

Dog bone-shaped tensile samples were 3D printed with dimensions of 165 x 19 x 3.6 mm, following the ASTM D638 standard. For each orientation, six samples were 3D printed, and the respective samples were tested using a Universal Testing Machine (Make: Tinus Olsen, UK). The tensile test experiments were conducted on the PLA and ASP/PLA composites at an experimental feed rate of 1 mm/min. To measure the strain rate of the tested samples, an extensometer was clipped on the gauge length of each sample, and the experiment was repeated six times to understand the repeatability and precision of the test results.

2.5.2. Flexural strength

Flexural test samples were 3D printed following the ASTM D 790 standard, with a cross-section dimension of 125 x 12.7 x 3.6 mm. The 3D printed samples were tested using a Universal Testing Machine (Make: Tinus Olsen, UK), with an additional bending test rig attachment coupled for the respective testing. The experiment for PLA and ASP/PLA composites with respect to various printing orientations was carried out at an experimental feed rate of 1 mm/min. Six samples were tested for each testing condition.

2.5.3. Compressive strength

Compressive testing of the 3D printed ASP/PLA composite was conducted following the ASTM D695 standard. Cylindrical samples were printed with dimensions of 12.7 mm diameter and 25.4 mm height. The experiment was repeated for six samples, and the test was conducted via the Universal Testing Machine with a cross-section head speed of 1 mm/min. Figure 3 demonstrates the tensile, flexural, and compressive tested samples with respect to various printing orientations.

2.5.4. Shore D-Hardness

The hardness of the 3D printed ASP/PLA was measured using ASTM D 2240 in shore Durometer (Make: STD-D, Gse India). The experiment was conducted using a steel needle tip with a radius of 0.1 mm. Hardness was measured at five different places, and the average value was determined as the hardness of the respective composite.

All samples were dried in a furnace at room temperature for 6 hours before commencing the mechanical testing due to the higher moisture absorption tendency of the PLA samples.

2.6. Contact angle measurement

The water absorption phenomenon, such as hydrophilicity and hydrophobicity, of the developed PLA and ASP/PLA bio-composites was measured using the contact angle measurement technique. The experiment was conducted using the sessile drop technique in an Ossila contact angle goniometer (UK). For each sample, measurements were made on the flat faces of the prepared PLA and ASP/PLA composites through the thickness of the sample. The test was performed on the polymeric surface with 5µL of water placed, and the inclination of the water angle was measured.

2.7. Wear and tribological characterization

The wear test of the 3D printed ASP/PLA composite was studied using a pin-on-disc tribometer (Make: DUCOM; Model: TR-20, India). Cylindrical samples were 3D printed with a cross-section of 10 mm in diameter and 35 mm in height. The test was conducted according to the ASTM G99-17 standard at room temperature. For the wear properties analysis, EN31 steel was selected as a counter disc for this study, which has a hardness value of 63 HRC. A cylindrical sample with different printing orientations and materials was placed in the holder while the counter EN 31 disc was rotating. This resulted in the generation of sliding frictional force and wear loss in the material. During the wear test, the sliding velocity (1, 2, and 3 m/s) and sliding load (10, 20, and 30 N) were varied, while the remaining parameters were maintained constant.

Before commencing the experiment, the 3D printed samples with different orientations were cleaned and polished with 1500 grit abrasive paper to ensure uniformity in the surfaces of the wear testing samples. This process ensures proper contact of the tribology samples with the counter disc surface. A surface roughness (Ra) value of 0.08 µm was maintained for all the samples to be tested.

Frictional force (Ff) and height loss of the samples were measured using frictional force and LVDT (Linear Variable Differential Transformer) sensors. For each test condition, three samples were tested, and their average values were considered.

The Coefficient of Friction (COF) is calculated as:

$$Coeffecient\ of\ Friction\ (\mu) = \frac{Frictional\ force\ (F_f)}{Normal\ load\ (L)} \qquad (3)$$

For measuring the specific wear rate of the tested specimen, the mass loss is considered with respect to the sliding distance. The specific wear rate is given as:

$$Specific\ Wear\ Rate = \frac{Mass\ loss}{Applied\ load\ X\ Sliding\ distance}\ (mm^3/Nm) \qquad (4)$$

2.8. Microstructure and Surface characterization analysis

Fractured 3D printed ASP/PLA composite samples with different printing orientations were studied by Scanning Electron Microscopy (SEM) analysis using a JSM-IT800 NANO SEM. The mode of fracture, layer gap, printing orientation, and ASP distribution in the matrix were examined through fractography analysis. Worn surface analysis with respect to the printed sample was detected using scanning electron microscopy. Printing orientation with respect to layer stacking was observed using a Stereo microscope.

3. Results and discussion

3.1. Accuracy of the 3D printed samples

Figure 4 (a and b) displays the length and diameter accuracy of the various orientation printed PLA and ASP/PLA composites. Length and diameter accuracy were measured using the deviation that occurred on the standard flat tensile sample and cylindrical compression sample. Considering the length accuracy of the 90° PLA and ASP/PLA composite samples, they exhibited excellent accuracy of 99.12% and

98.81%, respectively. This is because the 90° printed samples have a smaller contour compared to the 45° and 0° samples. Among the neat PLA and ASP/PLA composites, the neat PLA exhibited higher length accuracy, which is an indication of lesser shrinkage occurring on the respective samples.

For dimensional accuracy analysis, the samples with 0° and 90° orientations resulted in similar diameter accuracy, with slight variations in the standard deviation value. The print diameter accuracy of the 90° samples shows better diameter accuracy of 99.51%. This is attributed to the interfacial adhesion of each layer during 3D printing and the nozzle head's ability to move in both X and Y axes. Based on the sample dimension, the layer temperature can vary and affect the interlayer diffusion of the samples. For the 90° samples, the distance was less, and the nozzle head immediately returned to its initial position. Therefore, the interlayer diffusion was good, resulting in accuracy in the print profile. In contrast, the 45° printed samples experienced the worst diametrical accuracy of 97.81%. This is due to the influence of gravity on the printing orientation, and the samples may undergo distortion, with supports adhering to the sample surface [29].

3.2. Surface characterization of 3D printed components

Optical microscopic images of the 3D printed samples clearly show the layer adhesion, printing layers, and the gap of the neat PLA and ASP/PLA composite. Figure 5 illustrates the surface morphology and the layer gaps of neat PLA and ASP/PLA with respect to various orientations. Considering the printing orientations such as 0, 45, and 90° with respect to neat PLA and ASP/PLA, the layer gaps are higher for the ASP/PLA composite samples compared to all orientations. Specifically, in the case of the 90° orientation, the layer gaps and voids are higher when compared with all other orientations. Regarding the print strands, for all the samples of 0° and 45° for both PLA and ASP/PLA cases, they are strongly bonded with the respective shell layers. However, in the case of 90° orientation samples, the print strands are weaker, and the layers are bound together based on the adhesion bond, which fails quickly under tensile loading conditions.

3.3. Physical properties of the 3D printed PLA and ASP/PLA composite

The physical properties such as density and porosity of the 3D printed neat PLA and ASP/PLA samples were measured using the Archimedes principle, and the results are shown in Table 3. The results indicate that the addition of ASPs decreases the density of the composite. This is attributed to the lower bulk density of the added almond shell (ρ=0.35g/cm3) compared to that of the PLA polymer. Among the various combinations, the sample printed with a 90° printing orientation shows the lowest experimental density for both the neat PLA and ASP/PLA. This reduction in density may be due to an increase in the number of repeated printing layers, leading to an increase in the layer gap and a reduction in the density of the composite. A similar trend of reduction in density with the addition of wood particles has been reported by various researchers [30].

Considering the porosity of the developed composite, the addition of ASPs content may increase the porosity of the 3D printed composites. The maximum porosity of 1.529% is observed for the 90° orientation 3D printed ASP/PLA composite and 1.45% for the 90° orientation neat PLA. Apart from the particle addition, printing orientation has a major effect on the porosity of the developed composite. The lowest porosity of 0.513% is observed in the neat PLA with a 45° orientation. This is because a lesser number of layers with the internal contour of the printing lines are rigid and interlocked on 45° orientation samples. A similar observation was reported regarding the porosity of the CNT-Polyetherimide composites printed by FFF technology [31].

3.4. Mechanical property results of the 3D printed PLA and ASP/PLA composite

Figure 6 (a) depicts the tensile strength results of the neat PLA and ASP/PLA composite with respect to various printing orientations. The results reveal that the maximum tensile strength of 36 MPa and 28 MPa is observed for the neat PLA and ASP/PLA composite with a 0° printing orientation. This is attributed to the printed layers being parallel to the applied load, allowing the contours to interlock with each other effectively. In the case of the 45° orientation, samples result in a moderate number of printing contour lines interconnected with each other. However, the addition of ASP/PLA to the PLA matrix displays a decreasing trend in the tensile strength of the composite across all orientations. Adding wood particles may hinder the layer adhesion and generate micron-sized voids between the interfacial layers. The added ASPs may act as stress concentrators instead of stress distributors, thereby affecting the strength of the developed composite.

In the case of the 90° printing orientation, both the PLA and ASP/PLA samples exhibit lower tensile strength of 23 MPa and 19 MPa compared to all other printing orientations. This is attributed to the printing layers not being completely interlocked, and the printed lines being perpendicular to the applied load. As a result, the samples experience sudden catastrophic failure under tensile loading. Similar behavior was observed in a study on 3D printed ULTEM tensile samples with respect to various printing orientations [32]. The results indicated that the 0° printing orientation performed better than the 45° orientation, with a variation of 22%.

Figure 7 shows the flexural strength results of the neat PLA and ASP/PLA composite with respect to various printing orientations. A maximum flexural strength of 38 MPa and 32 MPa is observed for the neat PLA and ASP/PLA composites with respect to the 0° printing orientation. Neat PLA samples exhibit higher flexural strength compared to the ASP/PLA composites. During the flexural test, a bending load is applied to the composite material with respect to various printing orientations and material compositions. The results clearly indicate that 0° printed samples exhibit higher flexural load due to the smaller size of the contour lines and the printed layers being parallel to each other. This leads to a higher bending failure load compared to other orientations. Considering the type of samples, ASP/PLA samples experience lower flexural strength for all orientations. This is attributed to weaker interfaces of the printed lines caused by the added organic wood-based particles [33].

Figure 8 represents the compressive strength results of the neat PLA and ASP/PLA composite with respect to various printing orientations. The maximum compressive strength of 98 MPa is observed for the ASP/PLA composite with respect to the 90° printing orientation. Among the unreinforced neat PLA samples, the maximum compressive strength of 73 MPa is found for the 90° printing orientation. During the compressive test, the sample experiences the compressive load, and the printing plane is parallel with the 90° printing orientation. This results in experiencing a higher compressive load compared to other printing orientations. The ability to withstand higher compressive loads increases with increasing printing orientation until the 90° printing orientation. Dhinakaran and Sabarinathan observed similar results in 3D printed wood-based composites, showing a similar trend regarding the effect of printing orientation on composite materials. Comparing all the samples, the ASP/PLA samples exhibit higher compressive strength irrespective of all orientations. This is due to the added particles, which are able to withstand the crushing load compared to the neat PLA polymer. This resistance to free polymeric chain movement reduces the chances of buckling under compressive load in the ASP/PLA composites. Similar trends were observed by Domínguez-Rodríguez et al. in developed 3D printed composites. The least compressive strength of 43 MPa is seen for the 45° orientation printed neat PLA samples. This is because the 3D printed cylindrical compression sample may slide during compression testing, leading to layer decohesion and sliding under minimal load, causing the samples to fail before reaching their yield point [34]. Among the various mechanical testing, based on the applied load with respect to the respective alignment of the layers of the printing lines decides the sample strength.

Figure 9 shows the shore D hardness results of the neat PLA and ASP/PLA composite with respect to various printing orientations. The maximum hardness value of 78 is achieved for the 45° orientation 3D printed ASP/PLA composite samples. The highest hardness value is observed for the 45° orientation, followed by the 0° orientation, and finally the 90° orientation for all the samples. During the shore hardness test, the plunge needle was indented on the flat face for the 0° orientation 3D printed PLA and composite samples. For 0° orientation samples, the indentation was made on the filling face, which is smooth. However, in the case of 45° orientation and 90° orientation, the indentation was made on the shell, which is hard. The added wood reinforcement also influences the variation in the hardness of the composite. In this study, the ASP/PLA shows a higher hardness value when compared to all other neat PLA samples. The lowest hardness value of 72 is recorded for the neat PLA of the 90° orientation samples, and the addition of ASPs may increase the hardness value by 12% for the respective orientation. The reason for the increment in hardness for the ASP/PLA composite is the addition of ASPs, which restricts deformation under the applied load. This improvement in hardness of the ASP/PLA composite compared to neat PLA is attributed to the addition of particles that increase the hardness of the composite. For the neat PLA, the polymeric content is higher and softer in nature, and the addition of particles may increase the hardness of the composite. Similar hardness studies were conducted by Bustillos et al. on 3D printed graphene-reinforced PLA composite [35].

3.5. Contact angle results of the 3D printed PLA and ASP/PLA composite

Figure 10 shows the contact angle results of the neat PLA and ASP/PLA composite with respect to various printing orientations. The ASP/PLA composites have observed the lowest contact angle value when compared with the neat PLA sample. The lowest contact angle of 54° is seen on the ASP/PLA composite 3D printed with a 90° printing orientation, and the highest contact angle value of 94° is observed for the neat PLA 3D printed sample with a 0° printing orientation. There are two main reasons behind the variations observed in the contact angle values of the 3D printed composites. Firstly, the type of reinforcement and secondly, the printing interface layer nomenclature. For the current study, the added reinforcement, which is naturally derived ASP, readily absorbs water. Addition of ASP to the PLA polymeric composites increases the water absorption phenomenon, leading to a decrease in the sphericity of the water droplets. This reduces the contact angle value, and the composite, which is hydrophilic in nature, absorbs more water when compared with neat polymer.

Based on the printing orientation, the layer interface, number of layers, and the angle of interface may vary, reflecting on the composite end product. For the 0° printing orientation, the samples contain no additional interface compared with other 45° and 90° printing orientations. Therefore, the pathway for water intake is very limited in the 0° printed samples of both the composites. For the 90° printing orientation samples, the water droplets easily penetrate inside the layer gaps under the Fickian diffusion phenomenon, resulting in a collapse in the sphericity of the water droplets. Figure 10 clearly shows that, at higher printing orientations, there is a reduction in the sphericity of the water droplets, indicating a higher volume of water absorption by the respective composite samples. Similar results on the water absorption phenomenon on adding wood-based reinforcement in the PLA/PCL composites for the development of disposable cups were observed by Silva et al. in their studies [36].

3.6. Surface roughness results of the 3D printed PLA and ASP/PLA composite

Surface roughness is a crucial property to measure before evaluating the tribological properties of a composite. The flatness of the sample determines how uniformly the load will act on the material under sliding conditions. Figure 11 depicts the surface roughness results of the neat PLA and ASP/PLA composite with respect to various printing orientations. The surface roughness was evaluated at three different parts on the flat faces from the top, middle, and bottom, and the average value is considered for the study. Samples printed with a 0° printing orientation show the lowest surface roughness value for both the neat PLA and ASP/PLA composites. This is because of the smoother surfaces and uniform peaks and valleys compared to the other two printing orientations. For the 90° printing orientation, samples exhibit the maximum surface roughness value. This is due to the non-regulated printing layers, with contour lines stacked along the perpendicular direction, leading to an increase in the surface roughness of the respective orientation 3D printed samples. Similar studies conducted by Lee et al. on microfluidic channels printed along the 90° printing orientation reported comparable results [37]. The influence of adding ASPs to the PLA matrix on the surface roughness response is then studied. The addition of ASPs increases the surface roughness value with respect to all orientations. This is because the added ASPs result in a rougher printing surface wherever the particle is present, leading to an increase in surface roughness (Ra) value compared to neat PLA polymer.

3.7. Tribological results of the 3D printed PLA and ASP/PLA composite

Figure 12 (a) presents the specific wear rate results of varying the sliding velocity of the neat PLA and ASP/PLA samples with respect to various printing orientations. The maximum specific wear rate is detected on the neat PLA samples followed by the ASP/PLA samples with respect to an increase in the sliding velocity and applied load. Among the various printing orientations, the specific wear rate is higher for 90° printing orientation followed by 0° and 45°. From the observed results, 45° oriented samples observe a higher hardness value. The lowest specific wear rate is observed at the lowest sliding velocity due to the lesser volume of material removed from the sample surface. As the sliding velocity increases, the volume of material removed also increases, and after a certain speed, a transfer film forms on the counter surface, resulting in a steady condition in the specific wear rate [38]. This is clearly seen in the neat PLA and ASP/PLA composite of 45° printed samples at 3 m/s condition.

Figure 12 (b) displays the specific wear rate results of varying the applied load conditions of the neat PLA and ASP/PLA samples with respect to various printing orientations. The results illustrate that an increase in the sliding load has a direct impact on an increase in the specific wear rate. The maximum specific wear rate of 9.592 10^{-6} mm^3/Nm is detected on the 90° 3D printed PLA samples under a sliding load of 30 N. Considering the applied load, there is a steady increase or minimal change in the specific wear rate of all the samples with different orientations of 3D printing up to a 20 N load. Further increasing in the sliding load shows a sudden drastic increase in the specific wear rate of all the composites. This is because the sample loses its dimensional stability and gets distorted on the respective layers under repetitive axial thrust force. This is also higher for the unreinforced neat PLA samples. Adding ASPs to the PLA polymer composite reduces the specific wear rate, based on the transfer of the applied load from the reinforcement to the matrix. Furthermore, along with the various printing orientations, the samples with 45° interfacial gap along the contour are small and the interfacial adhesion is good for the respective next layers, resulting in a lower specific wear rate and improved wear resistance property compared with other orientations. Similar results were observed by Dawoud et al. on 3D printed ABS composites [39].

The maximum frictional coefficient is observed for 90° 3D printed neat PLA samples, followed by 0° samples and 45° neat PLA samples. Adding ASPs to the PLA matrix reduces the frictional coefficient. Figure 13 (a) demonstrates the coefficient of friction results of varying the sliding velocity of the neat

PLA and ASP/PLA samples with respect to various printing orientations. The maximum coefficient of friction of 0.46 is found for the neat PLA sample of 90 ° print orientation at 3 m/s sliding velocity. The minimum coefficient of friction of 0.118 is observed for the ASP/PLA sample of 0° print orientation at 1 m/s sliding velocity. Figure 13 (b) shows the coefficient of friction results of varying the sliding load of the neat PLA and ASP/PLA samples with respect to various printing orientations. The maximum coefficient of friction of 0.43 is seen for the neat PLA sample of 90 ° print orientation at 20 N sliding load. The minimum coefficient of friction of 0.22 is achieved for the ASP/PLA sample of 0° print orientation at 10 N sliding load.

Considering the orientations of the sample, the 90° 3D printed samples show the maximum frictional coefficient value. It is because of an initial condition of sliding velocity (1, and 2m/s) and sliding load (10, and 20N) and the 90° 3D printed samples exploits higher surface roughness value. After stipulated time durations the attached particles on the samples surface gets detached and the surface gets smoothened. And also, the laying phenomenon of the printed layers is vertical in the 90° 3D printed samples, and the hatching layers are angular and exhibits higher shear force under sliding [40]. This may increase the frictional force for 90° 3D printed samples. In case of increasing the sliding, speed and sliding load beyond this limit there is a sharp decrease in the frictional coefficient value. This is because of increase in the sliding speed and load that may increase the contact temperature and soften the polymeric matrix and form thin film around the counter surface [36]. It may reduce the friction in the contact zone and reduces the friction coefficient value.

3.8. Fractography and worn surface analysis of the tested composite samples

Figure 14 (a-f) presents the tensile fractography images of the various orientation printed neat PLA and ASP/PLA samples. Figures 14 (a-c) display the fractured tensile surfaces of the neat PLA samples, while figures 14 (d-f) depict the fractured surfaces of the ASP/PLA samples. Observations from the fractured images indicate that the extent of layer peel is lower in 0° 3D printed samples compared to those printed at 45° and 90° orientations. This observation aligns with the higher mechanical properties observed in the 0° 3D printed samples. Furthermore, the ASP/PLA composite exhibits a higher volume of porosity, compaction, and inter-layer gap at the fractured surface compared to the neat PLA samples. In terms of failure mode, the neat PLA 3D printed samples demonstrate a brittle mode of failure. However, the addition of ASPs tends to reduce this brittleness and results in particle pull-out in the fractured surface [41]. This phenomenon contributes to the enhancement of the modulus of the polymer composite.

Figure 15 illustrates the SEM images of the tribology tested samples of neat PLA and ASP/PLA composites. Specifically, figures 15 (a) and (b) depict the ASP/PLA samples printed at 0° and 90° orientations. Both neat PLA and ASP/PLA 3D printed samples exhibit wear scars and grooves on their surfaces. However, the 90° 3D printed samples show more severe wear marks and particle pull-outs on the contact surface compared to the 0° 3D printed samples. This observation correlates with the higher specific wear rate observed for the 90° 3D printed ASP/PLA samples. In the case of the 45° build orientation, the raster is deposited in a tilted form, resulting in gaps in the sliding surfaces. Under sliding conditions, compressive forces act along the relative motion of the samples, leading to the formation of deeper grooves on the void portion. This phenomenon results in deeper pits and cracks on the sliding surface, as depicted in figure 15 (c). For the 0° 3D printed ASP/PLA samples, a molten re-solidified debris is evident. At higher sliding loads, such as 30N (figure 15 (d)), the material melts and gets deposited as a thin film on the contact surface. This indicates that the contact surface is uniform, allowing for smoother sliding and increased contact surface area [42].

4. Conclusion

In the current study, the mechanical and tribological studies of 3D printed neat PLA and ASP/PLA composite was evaluated with respect to various printing orientations. From the observed experimental results following conclusions can be made.

1. Filament extrusion technique successfully produced composite filaments containing 10% ASP/PLA composite material.
2. Printing orientation significantly influenced the physical, mechanical, and tribological properties of the ASP/PLA composites. The 90° orientation showed the best diameter accuracy.
3. The highest tensile and flexural strengths were observed for the neat PLA samples, while the ASP/PLA composites showed slightly lower strengths, with the best performance observed for the 0° printing orientation. The maximum hardness was found in the ASP/PLA composite with a 45° orientation.
4. Contact angle measurements revealed that the ASP/PLA composites had lower contact angles compared to neat PLA, indicating higher hydrophilicity.
5. Frictional coefficients varied based on the printing orientation and sliding load, with neat PLA exhibiting higher coefficients compared to ASP/PLA composites.
6. Reinforcement with ASPs reduced the brittleness of the PLA polymer and increased the modulus of the composite, as evidenced by observed particle pull-out on fractured surfaces.

In future research, optimizing other printing parameters such as infill pattern, density, layer thickness, and raster orientation could further enhance the properties of the ASP/PLA composite. Additionally, the developed composite holds promise for applications in food packaging, orthodontic appliances, medical devices such as splints for bone fractures, and disposable orthotic foot appliances, offering potential benefits in terms of sustainability and biodegradability.

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