EFFECTS OF FUNCTIONAL FILLERS IN THE MECHANICAL PROPERTIES OF 3D-PRINTED POLYLACTIC ACID USING FUSED DEPOSITION MODELLING

A LITERATURE REVIEW

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Chapter I

Introduction

This chapter presents the background of the study, statement of the problem, objectives, significance, scope, and limitations.

1.1 Background of the Study

Additive manufacturing (AM) process with an official industry standard term ASTM F2792 [1], commonly known as 3D printing [2] or rapid prototyping [3], was first commercialized in 1980s [4]. As shown in Figure 1.1, AM involves information rendered 3D models from computer-aided design (CAD) which is converted into stereolithography or STL format which slices the model into thin layers in preparation for the layer-by-layer assembly [5, 6]. The simplicity [7], minimal waste accumulation resulting to cost-effectivity [8] while producing innovative [9] and customized complex geometrical structures [10] using various types of materials such as polymers, metals, and ceramics [5] of AM makes it attractive to various industries. Currently, AM is already widespread applied in light-weight automotive [11, 12] and aerospace structural parts [13, 14], electronics [7, 15], marine [16], and prosthetics or implants in medical industry [17, 18]. One of the most utilized additive manufacturing techniques is the material extrusion, ISO-ASTM 52900:2015 [19], which forms parts by depositing layers of solid thermoplastic material through a heated nozzle [20]. As such, this melt processing technique is trade named as fused deposition modeling [21].

![Additive Manufacturing Process](image)

*Figure 1-1 Additive Manufacturing Process [22]*
Fused Deposition Modeling (FDM) is a process where a spool of filament is pulled by a drive wheel into the heated nozzle which is set at the extrusion temperature of the material making it less viscous or in a semiliquid state. The melted filament is accurately deposited or injected in a successive manner layer-by-layer as it continues to shift locations in a horizontal X-Y plane while the build platform in z-distance is being lowered until the object is formed according to the computer-aided design (CAD) [23]. In 2009, the major patent for FDM had expired [24, 25]. As a result, it bred a newfound investment [26] of which hundreds of 3D printer startup companies emerged such as HP Inc., MakerBot Industries, LLC, Materialise NV and many more [27] [28]. Prices for FDM printers dropped by 90% [29]. With that, the FDM process has been developed to become consumer-friendly [30] to which its mechanism can be understood as analogous to a glue-gun. Shown in Figure 1-2 is the printing process of FDM. There are a wide variety of polymers that can be used for FDM applications.

![Figure 1-2 Schematic of FDM Printing Process [31]](image)

The polymer material to be 3D-printed using fused deposition modelling must be able to flow during heating and then solidify at room temperature after printing. Hence, thermoplastic filaments with low melting temperature, glass transition temperature, and thermal expansion coefficient are ideal for FDM process. These results to low
internal stresses caused during cooling. The thermoplasticity of a filament plays a vital role in this process since determines interlayer bonding. There are several thermoplastic polymer feedstocks used in FDM and one of the most widely used filament is the polylactic acid [32].

Polylactic acid (PLA) has increasingly attracted a lot of interest especially in biopolymer field due to its great biocompatibility and sustainability over other thermoplastics such as acrylonitrile butadiene styrene (ABS), polyamide (Nylon) and polyethylene terephthalate (PET) [33]. PLA is derived from lactic acid and can be hydrolytically hydrolyzed back into its monomer. Lactic acid is a naturally occurring organic acid which is a constituent of the human body and some foods. Also, lactic acid can be Lactic acid is also produced by fermenting carbohydrates from renewable resources such as corn [34]. Despite PLA being suitable in FDM processing and a sustainable substitute for petroleum-based polymers, it has its limitations with regards to its mechanical properties. Its uses are limited in applications that need plastic deformation at high stress levels due to its low strength and ductility [35]. The development of PLA filament for FDM with enhanced mechanical properties for different industrial fields are aimed to be addressed through combining reinforcements which are non-attainable by the pure filament material alone.

Several commercial polylactic acid filament composites with fillers are available in the market such as Colorfabb’s WoodFill, BronzeFill, and CopperFill PLA [36], Polymakers’s PolyMax™ and PolyTerra™ PLA [37], and Ultimaker’s Tough PLA [38]. Information regarding the filament composition is most often kept as company trade secret or a confidential formula especially to competitors. Hence, production of composite polylactic acid filament incorporated with a variety of functional fillers for 3D-printing are recently investigated by several researchers. In relation, this review article is a discussion on the effects of different types of functional fillers on mechanical properties of FDM 3D-printed polylactic acid composite parts. Limitations and a summary of the studies presented are also included.
1.2 Statement of the Problem

The main problem addressed by the studies discussed in this review article is the performance gaps of 3D-printed polylactic acid parts as polymer material in fused deposition modelling (FDM) process in terms of its mechanical properties. Although polylactic acid has been industrially produced for several decades, its applications are still limited to mostly conceptual prototypes due to its low strength and ductility [35].

1.3 Objectives

This review aims to provide analysis of experimental data available from existing studies. Specifically, this review seeks:

- To discuss the intrinsic factors affecting the mechanical properties of polylactic acid parts which are 3D-printed through Fused Deposition Modelling
- To evaluate the effects of different types of fillers incorporated to polylactic acid as a 3D-printed composite material

1.4 Significance of the Study

Fused deposition modeling (FDM) printed parts are applied in various industries. Railway, aerospace, medical business, automotive, and marine, have utilized FDM as a production technique, from prototypes to finished parts. FDM is utilized instead of other printing technologies because of the broad range of accessible thermoplastics such as polylactic acid (PLA). PLA-based technologies have emerged in recent years, stressing the ability to obtain qualities comparable to or better than conventional polymers. Effective utilization of PLA composite depends on its mechanical properties; thus, the primary purpose of this review is to have better understanding of filler addition and its properties in the mechanical performance of polylactic acid to maximize its functionality.
1.5 Scope and Limitations

This study is a review limited to published experimental studies with a discussion involving 1) intrinsic factors of polylactic acid that affect its mechanical properties and 2) the effects of different types of functional fillers and its properties through comparing the pure PLA and the filler incorporated-PLA which are 3D-printed using fused deposition modeling.
Chapter II

Polylactic Acid in Fused Deposition Modelling

Properties of polylactic acid and comparison with other filaments used fused deposition modelling will be presented. Also, the characterized mechanical properties of 3D-printed parts, factors affecting the strength, modulus, and elongation at break which are interlayer adhesion and microvoids, and post-processing methods to PLA will be discussed.

2.1 Polylactic Acid

Polylactic Acid is a polymer derived from the linking of lactic acid monomers [39] and was first synthesized in 1932. In the recent times, PLA is a versatile biodegradable thermoplastic available for FDM as its monomers are renewable. 2-hydroxy propionic acid or known as lactic acid can be polymerized through fermentation of agricultural starch sources such as sugarcane and corn which are sustainable alternative to petroleum-based polymers. Thus, aids on plastic waste accumulation [40]. Polylactic acid also requires 25–55 percent less energy as well as cost to manufacture than petroleum-derived rivals. In addition, PLA is an organic compound and has a semi-crystalline linear structure attributed from its aliphatic polyester backbone and polar carbon-oxygen linkages. Aliphatic polymers are those without aromatic rings and are more flexible and elongated before fracture. [41] It has both glass transition ($T_g$) and melt temperature ($T_m$) due to its amorphous and crystalline phases of which its temperature setting in FDM is presented in Figure 2-1. Above $T_g$ and $T_m$, primary valence bonds are distorted thus viscosity is reduced and polymer behaves as a fluid while crystallization temperature ($T_c$) is where the transition from amorphous-liquid state of the melt to the crystalline state occurs [42]. PLA has a low $T_g$ of 45-65 °C and $T_m$ of 130-200 °C [43] [44]. Characteristics of PLA such as rheological and mechanical properties, heat capacity, and density are all dependent on its $T_g$ [45]. On the other hand, degree of crystallinity and $T_m$ are dependent on the polymer’s thermal history, purity, and molar mass [46].
Figure 2-1 FDM Temperature Setting for Semicrystalline Polymers

Semi-crystalline polymers, such as polylactic acid, are distinguished from their amorphous counterparts by the formation of tightly packed and organized crystalline regions. During crystallization of this type of thermoplastics, the lamellar morphology of polymer chains is in packed and are parallel to each other in between amorphous regions lamellae. These crystalline areas contribute to strength, stiffness, toughness, and wear resistance in terms of their mechanical properties while amorphous regions provide an impact resistance [47]. The polymer chain mobility of amorphous and semicrystalline are illustrated in Figure 2-2. Amorphous polymers incrementally soften when heated above the glass transition temperature at point E in which a sudden shift in molecular mobility occurs from glassy to a rubbery state. While in semi-crystalline polymers, the crystals remain in their orderly packed lamellar structure until their melting point at point B where an increase in volume occurs until point C then flows into a liquid state at B to A [48, 49]. Moreover, semi-crystalline polymers, may be used at greater service temperatures than amorphous thermoplastics, which often lose a lot of their mechanical qualities above Tg [47]. The semi-crystalline morphology provides superior chemical resistance and biocompatibility since non-crystalline regions are known to be biodegraded or attacked by solvents and chemicals. Also, the molecular weight and density of semi-crystalline polymers is directly proportional to the degree of crystallinity due to the packing of polymer chains in these crystalline areas [48].
Nevertheless, polylactic acid is one of the most convenient, well suited, and far more thermally stable material during printing than other used filaments in FDM process [51]. The extrusion temperature in FDM is substantially higher than the melt points or glass transition because viscosity is drastically lowered at these higher temperatures, which then improves processability [52]. For PLA this ranges from 150 to 230 °C which is lower than Acrylonitrile Butadiene Styrene (ABS), Polyamide (Nylon) and Polyethylene Terephthalate (PET). [53] Moreover, its relatively low coefficient of thermal expansion (70 $\times 10^{-6}$ $^\circ$C$^{-1}$) circumvents the need of a heated print bed, enclosure, and adhesive which lowers the cost for printing while maintaining its dimensional stability. Previously mentioned properties as compared to other thermoplastics in FDM are shown in Table 2-1. Other significant advantages of PLA are that when heated, no toxic gas emission occurs. Therefore, it can be printed without ventilation system. Moreover, because lactic acid is created and released naturally by the human body, it is biocompatible and may be used in medical implants that are meant to break down and be replaced by new tissue over time due to its nontoxic breakdown via enzymes or hydrolysis [41, 51].
Table 2-1 Property Comparison of PLA, ABS, PET and Nylon [41, 54]

<table>
<thead>
<tr>
<th>Property</th>
<th>PLA</th>
<th>ABS</th>
<th>PET</th>
<th>Nylon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed Temp. °C</td>
<td>20-55</td>
<td>80-110</td>
<td>55-70</td>
<td>60-80</td>
</tr>
<tr>
<td>Heated Bed</td>
<td>Optional</td>
<td>Required</td>
<td>Required</td>
<td>Required</td>
</tr>
<tr>
<td>CTE (μm/m·°C⁻¹)</td>
<td>68-85</td>
<td>68-110</td>
<td>60-92</td>
<td>80-95</td>
</tr>
<tr>
<td>T_g</td>
<td>60-65</td>
<td>105-110</td>
<td>70-78</td>
<td>47-60</td>
</tr>
<tr>
<td>Maxim Service Temp. °C</td>
<td>52</td>
<td>98</td>
<td>73</td>
<td>95</td>
</tr>
<tr>
<td>Ultimate Strength (MPa)</td>
<td>65</td>
<td>40</td>
<td>53</td>
<td>85</td>
</tr>
<tr>
<td>Water Resistant</td>
<td>X</td>
<td>X</td>
<td>✓</td>
<td>X</td>
</tr>
<tr>
<td>Impact Resistant</td>
<td>X</td>
<td>✓</td>
<td>X</td>
<td>✓</td>
</tr>
<tr>
<td>Heat Resistant</td>
<td>X</td>
<td>✓</td>
<td>X</td>
<td>✓</td>
</tr>
<tr>
<td>Fatigue Resistant</td>
<td>X</td>
<td>X</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Stiffness (10/10)</td>
<td>7.5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Durability (10/10)</td>
<td>4</td>
<td>8</td>
<td>8</td>
<td>10</td>
</tr>
</tbody>
</table>

Despite polylactic acid being eco-friendly bioplastic is considered a suitable substitute for polymer-based petroleum with excellent biocompatibility, processibility, and less energy dependence [55], 3D printed parts with PLA has drawbacks to inherent properties such as low elongation at break, low toughness, and brittleness which restricts its use in a wide range of applications [56]. Polylactic acid has a low elongation break of less than 10% which makes it a brittle material [57]. Even though the elastic modulus and tensile strength of PLA are comparable to PET [58], it has limitations in terms of applications that require high-stress levels during plastic deformation due to its poor toughness [59]. The low crack initiation and propagation energy of PLA results to its failure by crazing [60]. Aside from the deficiency of reactive side-chain groups which makes bulk modifications challenging [61], impact toughness also depends on several intrinsic factors such as microstructure and chemistry. Accordingly, a comparison of properties with other 3D-printed thermoplastic polymers used in FDM is shown below in Figure 2-3. To overcome the drawbacks of PLA in
terms of its mechanical properties, different types of functional fillers have been studied with will be discussed in the next chapter.

Figure 2-3 a-e Ranking of 3D-printed polymers in FDM (1 being most inferior and 6 being most superior) along the different criteria [62]
2.2 Mechanical Characterization of FDM 3D-printed parts

Characterization is a process by which properties of a material is measured. As for mechanical characterization, a structure is tested according to their response to applied load or temperature. [63] Depending on the areas of application, mechanical properties can be used as guidelines to determine the effective application of FDM 3D-printed parts. As for the studies in this review, mechanical properties of 3D-printed materials are characterized mostly in terms of strength, modulus, elongation at break as well as surface analysis of which will be briefly discussed in this section. There are currently no standards yet for mechanical testing of additive manufacturing printed parts. For most studies, standard testing for thermoplastic polymers is used for 3D-printed parts [64]. These are shown in Table 2-2.

*Table 2-2 Summary of Characterization Used in 3D-printed Composites* [65, 66, 67, 68, 69, 70, 71, 72, 73, 74]

<table>
<thead>
<tr>
<th>Characterization</th>
<th>Standard Test</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile</td>
<td>ASTM D638</td>
<td>Tensile Strength and Modulus Elongation at Break</td>
</tr>
<tr>
<td>Compressive</td>
<td>ASTM D695</td>
<td>Compressive Strength and Modulus</td>
</tr>
<tr>
<td>Flexural</td>
<td>ASTM D790</td>
<td>Flexural Strength and Modulus Ductility</td>
</tr>
<tr>
<td>Impact</td>
<td>ASTM D256</td>
<td>Impact Strength or Toughness</td>
</tr>
<tr>
<td>Surface Analysis</td>
<td></td>
<td>Fracture Morphology Compositional Differences Elemental Microanalysis Particle Characterization</td>
</tr>
</tbody>
</table>
2.2.1 Strength

Strength refers to the amount of stress that a material can withstand before breaking. The amount of stress that is necessary to break the material is known as strength. Flexural (bending), compressional (shortening), tensile (stretching), and impact (hammering) are common types of strength. Some materials are strong under tensile stresses but weak under compressive stresses and vice versa. Therefore, the importance of tensile and compressive quantities depends on the application suitability [75]. However, the compressive strength data is unreliable to determine product failure during end-use for those polymers with a lower flexural modulus that are unable to rupture in compressive loadings. Whereas the impact strength is a measure of material toughness, which is defined as the amount of energy absorbed before it breaks [76].

In addition, the strength of polymers is influenced by three factors: 1) molecular weight, 2) cross-linking, and 3) tensile strength. Tensile strength increases with molecular weight. At lower molecular weights, polymer chains are weakly bound by van der Waals forces and can easily slide past each other, resulting in poor strength despite the presence of crystallinity. When a polymer has a high molecular weight, chains are larger and more intertwined, thus higher strength. Meanwhile, cross-linking restricts the motion of the chains thus increases the strength. Intermolecular bonding is important for crystallinity in the crystalline phase, as oriented chains have a higher strength [75].

2.2.2 Modulus

Modulus measures the stiffness of a material observed in the stress-to-strain ration at the linear elastic zone. Brittle polymers possess a high modulus, whereas polymers that are ductile has similar elastic modulus with higher fracture toughness. [75] Thermoplastic polymers, such as polylactic acid, have elastic deformation behavior caused by elongation of weak van der Waals bonds between neighboring
polymer molecular chains and atomic bond rather than atomic bond stretching and thus have much lower modulus values than metals and ceramics [77] [78] For 3D-printed thermoplastics, it is evident in the SEM analysis of fractured surfaces that polylactic acid has a brittle characteristic as compared to ABS and Nylon which are shown below in Figure 2-4.

![Figure 2-4 SEM of fractured surface of (a) PLA, (c) ABS, and (e) Nylon 6 using FDM](79)

### 2.2.3 Elongation at Break

Elongation at break or ultimate elongation is a measure of the ductility of a material wherein the material can undergo plastic deformation and is measured as the change in percentage of the length before it fractures. It is therefore an indication of how ‘soft’ or malleable the material is. [80] Typically, materials that are ductile are more tough compared to brittle ones and it is evident that high toughness does not only require ductility, rather it also requires considerable strength [81]. Through manipulation of the microstructure of the material, the toughness and ductility can both either increase or decrease [75].

### 2.3 Factors Affecting Mechanical Properties of 3D-Printed Parts

Mechanical properties of 3D-printed parts using FDM are different from that of the filament because of the different process parameters. This can be confirmed when comparing FDM with injection molded (IM) parts. IM is most used method when
measuring the properties of a filament. While FDM is a layer wise extrusion of melted filament until 3D part is formed, IM is a process wherein a molten thermoplastic fluid is injected or poured into the mold where it solidifies into a certain shape. [82] The difference in structure shown in Figure 2-5 constitutes to dissimilarity in the mechanical properties since FDM parts formed by solidified printed layers with inherent voids between in between. There are several process parameters in FDM some of which are infill density, infill pattern, part slicing layer thickness, gap between the build plate and print nozzle, nozzle temperature, and deposition speed. These parameters consist of numerous combinations which can be optimized and controlled to obtain a better result in the printed products [83, 84]. Optimization approaches, on the other hand, can lack critical insights into the mechanism of each particular parameter [85]. The intrinsic properties and process parameters of the manufacturing method should be taken into account these affects the mechanical properties of the parts that have been 3D-printed [86]. The poor mechanical properties of FDM-printed components are related to the intrinsic properties of the material, which are determined by interlayer adhesion and microvoids, which will be the focus of this section [87].

![Figure 2-5 Structure of PLA in (a) FDM and (b) IM](image)

2.3.1 Interlayer Adhesion

Fused deposition modelling makes 3D-printed parts through layer-by-layer deposition of melted polymer extruded through a nozzle. To form an object or a design, individual layers must adhere to each other. The property of thermoplastic material
helps in the bonding between the layers for them to stick together and it also assists in the process of solidification when the temperature gradually decreases. Due to the interaction of molecules, the bonding between the layers will be obtained when a layer remains molten and is bound to the other layer that is starting to solidify [88]. As reported in [66, 89], filament bond formation or also called as neck occurs through viscous sintering [90]. This mechanism is shown in Figure 2-6 where this inter-layer bonding formation is comprised into three subsequent steps: 1) surface contact, 2) neck growth driven by surface tension, and then 3) intermolecular diffusion of polymer chain segments across the wetted interface [91, 92]. This development of a wetted interface and the degree of intermolecular diffusion between two polymers dictate the strength of fusion bonds [93].

![Figure 2-6 Schematic of interlayer bond formation](image)

In FDM, filament is extruded at a temperature above its melting temperature onto partially cooled filament surfaces which heats up in a brief period before cooling
down again. This thermal gradient between the heated and the partially cooled filament results to the incomplete neck growth. [94]. As such, the interlayer bond formation is governed by the quantity of available residual heat that enables molecular diffusion and randomization of polymer chains at the interfacial regions. However, heat distribution is not uniform due to the low thermal conductivity of polymers [95]. Hence, this undesirable thermal gradient between successive layers results in poor interlayer adhesion and develops the form of failure points in the matrix of the printed product [96].

![Diagram of FDM printed part structure](image)

*Figure 2-7 FDM printed part structure: (left) laminae stacked in a layer-wise forming the laminate; with partial bonding in the mesostructure [92]; (right) Cross-sectional view of an FDM laminate with the neck growth (2y) [97]*

For semicrystalline materials like polylactic acid, interlayer bonding becomes more difficult [98] because the crystallization process influences neck growth, labeled as 2y in Figure 2-7, and molecule diffusion at the interface [99]. In addition, crystals besides interdiffusion length have an influence in the semicrystalline materials in terms of its bond strength [100] [101]. Neck development occurs only at temperatures above the polymer’s crystallization temperature when printing semicrystalline polymers. The start of crystallization generates a substantial rise in melt viscosity and limits neck formation as the interfacial temperature lowers, yet molecular diffusion continues until the T_g of the polymer is attained. A typical FDM on the other hand, has a relatively short bonding duration for molecular diffusion, ranging from 0.1 ms to 100 ms [102] which has a negative effect since the time to complete the coalescence or neck growth
of filaments is insufficient before it solidifies [103] [104], this produces partial neck growth in the printed parts of FDM as well as the large amount of internal voids [105].

2.3.2 Microvoids

In addition to interlayer adhesion, the impact of porous structures or voids on properties of the FDM parts are also significant. Voids may be desirable depending on the application of the FDM parts. However, when it comes to applications where optimal mechanical performance is needed, voids are undesirable since it induces stress concentrations where failure occurs [106]. Even with optimal printing parameters, these voids inside the filament and matrix, as seen in Figure 2-7, are difficult to control [106]. Thus, affecting the density, strength, and stiffness of the printed materials [107, 108, 109].

![Figure 2-8](left) Microvoids on PLA surface [110] and (right) mechanism of crack propagation [111]

There are several reasons that can cause void formation into the 3D-printed part. One can be produced during printing, and another may be already existed in the filament. During printing, air traps, uneven matrix distribution resulting to uneven filament diameters can all cause voids [110]. Moreover, most polymers are susceptible to moisture absorption [112, 113, 114]. The more polar bonds contained in the repeat
unit, the more likely a polymer will absorb water [53]. During the melting process at a specific temperature of the filament in the machine before the extrusion, this moisture boils and turns into steam bubbles, which may transform into part voids or interfere in the flow during the printing process resulting to extruder jams and affecting the operating time interval [115]. Consequently, absorbed moisture induces voids leading to initiation and propagation of microcracks as shown in Figure 2.3.2B thus limiting applications under high stress [116]. According to investigations, strength decreases with increased void sizes [87, 117, 118] of which some theoretical models also described the fracture mechanism caused by voids and specifically highlighting the hydrostatic pressure dependency of a material in terms of nucleation. However, these models are mainly applicable for materials with ductile behavior which excludes highly crystalline polymers [119]. It was discovered that components printed with the FDM technique have a high dispersion of voids at the fracture starting site, resulting in poor crack resistance and poor strength [120, 121].

The mechanical integrity of FDM printed components is significantly impacted by a lack of adhesion and microvoids that leads to structural flaws. Hence, 3D-printed parts components with a high density of defects would have poor structural mechanical properties.

### 2.4 Postprocessing Methods for Mechanical Properties

To provide enhancement in the low mechanical performance of 3D-printed polylactic acid using FDM, several postprocessing methods namely laser treatment and annealing are being investigated.

#### 2.4.1 Laser Treatment

Laser treatment is a technique used in improving the and surface quality of FDM print components. It involves surface modification and mechanical properties enhancement of 3D printed materials which includes metals and nonmetals, by utilizing the features of the laser beam which then interacts with the polymer. Studies
have shown that exposing the surface of printed part to a laser improves its surface roughness. When a laser is used to treat a printed component, the material is swiftly heated and melted. A photochemical ablation method sublimates the polymer, converting it from a solid to a gaseous state. The unwanted surface irregularities are eliminated making the surface smoother [122]. Laser treatment is a developing industrial technological method that can improve mechanical property and surface quality. It provides several advantages over traditional polishing procedures, including reduced tool or material wear, shorter processing times, and greater suitability for 3D-printed parts.

Laser treatment is a new technology for surface modification and mechanical properties enhancement of 3D printed materials which includes metals and nonmetals, by utilizing the features of the laser beam which then interacts with the polymer. Laser treatment is employed in industries such as autos, metallurgy, electronics, and aircraft as an innovative manufacturing technology. It is vital for enhancing product quality and worker productivity, automating processes, decreasing pollution, and lowering material usage. Laser polishing involves irradiating a material with a laser beam with a certain energy density and wavelength to melt or evaporate the surface layer of the material, resulting in a smooth surface and better mechanical properties [123].

Laser treatment was employed in a study conducted by Chen et al. using a fiber laser with a 200 W power and 1070 nm wavelength. Results showed that laser treatment promotes an increase in tensile strength and modulus of elasticity of polylactic acid than the untreated one. Fracture surface has been observed through using SEM to investigate the effect of laser treatment to PLA sample. Figure 2-8 shows that there are presence of air gaps, porosity, and separation of layer before laser treatment was employed to the sample. This may be due to the stacking effect during the process of printing the samples where some parts between the stacked layers of the sample remains unfilled. On the other hand, Figure 2-9 shows the enhancement of the sample after laser treatment. The improvement of its tensile strength and modulus of elasticity was because the melted surface where the laser is applied fills
the gaps of PLA, thus reduces porous regions which improves the surface quality resulting to an enhanced mechanical property. However, it was observed that the elongation break decreases. The PLA undergoes a quick heating and cooling process when the laser is applied to its surface. After laser polishing, a cold work hardening phenomena occurs, leading in a reduction in PLA ductility [124].

Another study had also investigated the effects of mechanical properties of PLA after laser polishing. The laser scanning speed was shown to have a significant influence on the tensile strength. Since the remelting zone ensured contact between the two layers, the tensile strength increased, resulting in a stronger bond. In comparison to higher laser scanning speeds, the remelting zone will be affected by greater heat under the 50 mm/s laser scanning speed per unit area and unit time. Because of the high laser energy, irregularities such as porosity, pits, and splatter will appear in the remelting zone, affecting the tensile strength of the sample. The laser energy density decreases under the 200 mm/s laser scanning speed, and the remelting part becomes smaller. The deposited lines remelted due to the laser scanning speed, and the bond strength of the deposited lines improved. Thus, tensile strength increases first, then decreases as the laser scanning speed increases [125].

Another study used a laser to treat PLA and found that the mechanical characteristics of the PLA improved. When compared to the untreated printed PLA, the PLA treated with a laser with a power of 5 W and a laser beam diameter of 200 µm enhanced its tensile strength and elastic modulus by 25.6% and 34.1 %, respectively. Because of the poor printing quality, the unpolished PLA samples have a decreased strength due to gaps and large porosities inside the sample. The porosity and bulk irregularities of PLA are decreased after laser polishing, and the interface bonding of PLA has improved [123].
Figure 2-8 Typical SEM images of fracture surface from failed FDM/PLA specimen without laser polishing: (a)-(d) different positions at same magnification [124]

Figure 2-9 Typical SEM images of fracture surface from failed FDM PLA specimen after laser polishing: (a) at low magnification; (c)-(d) at high magnification [124]

Laser polishing is a thermal procedure with rapid cooling that can cause thermally induced residual stresses or even deformation in thin components. As a result, the major problem is that the laser polishing process must be tailored to a particular material and the geometry of the component that has to be polished [126]. Another method in enhancing the mechanical properties of PLA that also involves heat is annealing.

2.4.2 Annealing

Annealing is a method in which a material is heated to a specified temperature for a period and then cooled to room temperature to alter the material properties by filling the gaps when heat is supplied which results to an enhanced mechanical property and smoother surface. The annealing process is time and temperature dependent since it requires the material to be above the recrystallization temperature for a set amount of time before cooling. The molecular surface tension is decreased at the glass transition temperature ($T_g$) resulting to the viscosity drop and enabling the substance to flow on the surface. The polymer reflows within layers, filling porous regions, staircase effect, and gaps, resulting in a smoother surface finish and improved mechanical properties [122].
A study enhanced the mechanical properties of PLA by using heat treatment by annealing with different heat exposure times and temperatures. The observed heat exposure time was 300 seconds at the temperature of 130°C. This results to the highest flexural strength of 105 MPa, which displays a 58.3% increase compared to the neat PLA. Moreover, when the temperature and time increased, the flexural strength started to decrease but still displayed a higher flexural strength compared to neat polylactic acid. It shows that PLA samples have a threshold limit temperature of 130°C, holding 300 seconds in the flexural strength test. Moreover, the highest compressive strength was recorded at 140°C temperature and 600 seconds exposure time. Fracture surface has been observed through using SEM to investigate the effect of annealing to printed PLA samples. Gaps and distinct boundaries between layers in unannealed PLA were evident. In comparison, when the printed PLA samples underwent annealing, the boundary between the layers can rarely be seen which is due to the layer bonding increased when it was subjected to a high temperature and significant exposure time [127].

Another study investigated the effects of annealing on the mechanical properties of PLA. Results show that the modulus and tensile strength increased at all temperatures, and the failure strain decreased. The decrease in failure strain demonstrates that annealing alters the behavior of the material and makes it more brittle as a result of the phase change. Maximum strength enhancement for PLA that underwent annealing compared to the unannealed PLA was 7%, which occurred at 210°C. This is because annealing causes recrystallization and the temperature enhances the bond between the layers. Moreover, the highest value of tensile modulus was 5.65 GPa for the annealed PLA while 4.9 GPa for the unannealed which shows that there is an enhancement in the tensile modulus. Increase in bonding between layers is also the reason for the increased values of tensile modulus [128].

Another study investigated the impact strength of PLA through heat treatment through annealing. The content of the PLA crystalline phase, which resulted in better
characteristics in annealed samples, is the crucial change in mechanical properties for all prepared models. The results also show that increasing the temperature has a significant positive effect, with the best results for samples at 105 °C. These samples demonstrated an 80% increase in impact strength from 35 to 63 J/m and a substantial improvement in tensile strength and modulus when compared to the neat PLA [129]. Dimensional change has been a significant drawback of annealing. PLA suffers considerable changes at low temperature such as 70 °C, while higher temperature at 110-170 °C. According to tests, this induces bending, shrinkage, and even complete melting [130].

Although the modification techniques mentioned above enhance the quality of polylactic acid in terms of its mechanical properties and surface quality for fused deposition modeling, each of them has its drawbacks. Thus, for this paper, filler addition in polylactic acid is being examined by several studies.
Chapter III

Functional Fillers in Polylactic Acid

Addition of functional fillers to form composites with improved properties has been already adopted in various types of polymers. As such, this chapter presents different types of functional fillers incorporated to polylactic acid to enhance its mechanical properties as 3D-printed parts through fused deposition modelling.

3.1 Properties of Fillers

Fillers are particulate substances [131] with usual size of less than 10 mm. It is incorporated to polymers to modify its properties [132], improve processing, and minimize the cost [133, 134]. In relation, polymer-filled composite is an admixture of a polymer matrix with particulate fillers which are chemically insoluble each other. This incorporation bridges the gaps and extending its performance to address a much broader market. Meanwhile, understanding the characteristics of fillers is essential. These includes chemical composition, surface chemistry, morphology, and thermal properties which define the suitability of fillers in polymers [135].

3.1.1 Moisture Absorptivity

One property of fillers is the the chemical composition or purity which can have both direct and indirectly significance on their application and performance. Although most fillers are nontoxic and inert, presence of impurities including moisture attributed from its hygroscopic characteristic may deteriorate the quality of the printed product [136, 137]. As mentioned previously, moisture is a relevant issue to all polymer melt processing operations especially in FDM. For instance, as wood with high moisture absorptivity is incorporated to polylactic acid at increasing content, more clogging in the nozzle occurs resulting to dimensional swelling of the 3D-printed part. [72] Also, presence of moisture in contact with PLA induce depolymerization or degradation through hydrolysis during the FDM melting process. [138]
3.1.2 Morphology

When it comes to applications in polymers, morphology or particle shape is certainly an important intrinsic property of fillers which may determine the mechanical performance of the composite. Particle shape is usually measured by a dimensionless parameter known as aspect ratio which is length (L) to a thickness (D) ratio (L/D). Most utilized of fillers are inexpensive however at the expense of having low aspect ratio. High aspect ratio fillers such as talc, mica, or layered silicates had more reinforcing effect [139] of which composites revealed higher modulus. [140] Various theoretical models can be useful to predict the reinforcing effect of fillers on modulus of the composites such as the Halpin-Tsai equation [141] [142]. From a study comparing three different nanocelluloses varying in morphology, the nanofiber (CNF) which had the largest aspect ratio demonstrated the strongest reinforcing effect on the tensile strength of the PLA composite in comparison to nanospheres (CNS) and nanocrystals (CNC). Also, PLA containing CNF exhibited lowest modulus indicating a change in fracture deformation from brittle to plastic. This is due to the longer length, network structure, and entanglements of CNF which promoted razes at multiple places. An illustration of the fracture mechanism of nanocellulose is shown in Figure 3-1. [143] However, since orientation is often undetermined, the actual effect of aspect ratio or in general is still under investigation. [144]

![Figure 3-1 Fractured mechanism of PLA/CNS, PLA/CNC and PLA/CNF](image-url)
3.1.3 Particle Size

Particle size has also a significant effect on the composite properties. Fillers dispersed in composites are usually in the size of 1–100 nanometer. In FDM polymer processing, smaller particle-size fillers may have superior effect such as better surface finish compared to larger filler, however effects in terms of the mechanical properties varies. For instance, longer fibers produce stronger printed parts in terms of modulus of elasticity and tensile strength, however, deteriorates the ductility and toughness of composites [145, 146]. Mechanical strength of polymer is predicted to decrease with the increase of particle size. This may be due to the larger particles acting as stress point concentrations and are easily debonded from the matrix which may create significant voids resulting to a higher probability of failure due to cracks and fracture propagation [139]. Meanwhile, with decreasing particle size, the possibility of chain agglomeration of fillers increases which leads to inadequate homogeneity, rigidity, and low impact strength as concentration variation of particles within the matrix act as crack initiation sites [144]. Agglomeration can be addressed chemically [139] which will be discussed in the next property.

Several studies have also examined the effects of particle size in polylactic acid. The effects of filler size on the tensile strength and modulus of 5%wt cellulose fiber [147], 30%wt calcium sulfate [148], and 10% calcium carbonates [149] are shown in Figure 3-2 and 3-3. As for calcium carbonates, increase in particle size from 32 to 63 microns increased the strength while the modulus slightly decreased or remained as compared to pure PLA composite. Meanwhile for cellulose fiber and calcium sulfate, strength and modulus increase up to a certain particle size.
As mentioned, the changes in strength and modulus can be caused by agglomeration which is defined as an assembly of smaller particles into larger sizes. The occurrence and extent of this phenomenon in polymer matrix is governed by the relative magnitude of the particle-particle forces attributed by their size and surface energy. Particulate-filled polymers are usually produced via melt mixing, as for FDM via melt extrusion of the components of which both particle-particle and
filler-polymer interaction are governed by the electrostatic and van der Waals forces. Consequently, to reduce particle-particle attraction leading to agglomeration, fillers can be treated to modify its surface charge. [151]

### 3.1.4 Surface Charge

To achieve optimal mechanical quality of the 3D-printed part, a well dispersed and optimal polymer-filler adhesion is essential. This is achieved by matching the high surface charge of fillers to that of polymers which are much lower. [139] As such, this polymer-filler adhesion can be enhanced through surface treatments of fillers with coupling agents [152]. The coupling agent diffusion at the filler surface occur in the interphase which is defined as region in contact of two phases [153]. This polymer-filler interphase is schematically represented in Figure 3-4 [154]. Interphase properties can be modified through surface treatments of fillers prior to compounding with polymer which can be achieved through chemical, ozone, and plasma treatments. [155] These treatments either eliminate the weaker layers related to the filler surface or introduce new functional groups which matches the surface charge of polymer thus enhancing filler-polymer interaction. [156]
Investigations of surface treated fillers incorporated to polylactic acid was also conducted. Silane and NaOH-treated ramie fibers at 5%wt incorporated to PLA was reported to increase the strength, elongation at break, and hardness of the composite which indicated an enhanced surface compatibility and good PLA-fiber stress transfer. This also results to improved crack propagation resistance due to better interfacial adhesion. [157] In another study, 20%wt thermally expanded vermiculite (TEV) was surface treated using isocyanate and aromatic carbodiimide. Results show that modified TEV slightly decreased the tensile strength and elongation at break while significantly increased the impact strength and modulus. This behavior indicates the presence of strong filler–filler and polymer–filler interactions. [158] Also, the effect of guineacorn husk particulates (GHP) treated with combined of alkali and silane (ALKASIL) to the mechanical properties of PLA was also studied. Compared to untreated GHP, the ALKASIL had higher strength, modulus, and elongation at break at increasing filler content. It could be inferred that lignocellulosic fillers such as GHP imparted greater stiffness on the matrix due to good dispersion of fillers which subsequently minimized voids. [159] Overall, polar functional groups on the filler surface after treatment improved the dispersion in polar solvents as surface resistance was decreased compared to untreated filler which inhibited agglomeration and formed a uniform distribution in the PLA matrix. [160] The degree of dispersion or adhesion forces in the polymer-filler interphase also depends on their contact geometry or surface area. [161]

3.1.5 Specific Surface Area

Specific surface area (SSA) is an important physical parameter which is a measure of the number of bonding points that are theoretically possible between the fillers and polymer chains and. SSA is a function of porosity, pore size distribution, shape, size, and roughness. [162] In general, most mechanical properties of filled polymer will increase as the specific surface area increases. As such it improves the interfacial adhesion and compatibility with polymer matric that are chemically dissimilar. However, up to a limit, a higher specific surface area will also result to a greater proportion of fines and an increased tendency to agglomerate which can be
difficult to disperse once they have formed while being mixed with the polymer [139]. Metals and glass spheres which are larger and non-porous particles have the lowest SSA. These are followed by minerals especially those which cleave to the smooth surfaces of crystals. Smaller fillers that are slightly porous, occupy the middle range of SSA. Lastly, very small sized fillers and minerals with high porosity has the highest specific surface areas [150].

According to investigations, higher surface area of silica resulted to an increased reinforcing effect due to strong polymer-filler while decreasing filler–filler interactions [163]. In addition, the large surface area of bamboo charcoal (BC) particles improved the stress transfer properties between PLA to BC enhanced strength and ductility index of the PLA-BC composite [164].

### 3.1.6 Conductivity

Thermal properties of fillers such as conductivity is also significant in composite processing. Polymers characteristically have thermal conductivities much lower than those for metals or ceramic materials. [165] [166] While most fillers have higher thermal conductivities, this reduces melt flow rate resulting to faster molding cycles or minimized processing time and increased thermal stability due to uniform heat dissipation to the composite material. [139] [167] Effective increase in the thermal conductivity of PLA composites was achieved by several studies. For instance, PLA-filled with 30 wt% alumina, 2 wt% carbon nanotubes, and 50 parts per hundred boron nitrides, increased the thermal conductivity of the composite by 120%, 310%, and 65% compared to pure PLA. [168] [169] [170]
Studies on PLA composites in this section are presentation of the effects to the mechanical properties of the material which are mostly as filaments or as injection molded parts. Hence, discussion in terms of interlayer adhesion and voids affected by the properties of fillers to the of 3D-printed PLA composites using FDM will be further discussed in the next sections.

<table>
<thead>
<tr>
<th>Filler</th>
<th>Moisture (%)</th>
<th>Shape</th>
<th>Aspect Ratio</th>
<th>Surface Charge (mN/m)</th>
<th>Surface Area (m^2/g)</th>
<th>Conductivity (W/Km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium</td>
<td>0.2–1.5</td>
<td>Spherical [150]</td>
<td>1.2–2.99 [150]</td>
<td>80.7 [150]</td>
<td>7–162 [150]</td>
<td>9–13 [150]</td>
</tr>
<tr>
<td>Copper</td>
<td>0.5–5 [177]</td>
<td>Spherical, Dendritic [150]</td>
<td>1.2–2.99 [150]</td>
<td>218 [150]</td>
<td>0.0637 [178]</td>
<td>400 [150]</td>
</tr>
<tr>
<td>Bronze</td>
<td>-</td>
<td>Spherical, Irregular [150]</td>
<td>1.2–2.99 [150]</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ceramic</td>
<td>5–15 [150]</td>
<td>Spherical, Irregular [182]</td>
<td>1.2–2.99</td>
<td>-</td>
<td>1.241 [150]</td>
<td>0.05–0.2 [183]</td>
</tr>
<tr>
<td>Wood</td>
<td>2–12 [150]</td>
<td>Irregular [186]</td>
<td>20–200 [187]</td>
<td>53.4 [150]</td>
<td>0.074 [150]</td>
<td>0.059–0.08 [188]</td>
</tr>
<tr>
<td>Talc</td>
<td>0.1–0.6 [150]</td>
<td>Flake [150]</td>
<td>5–20 [150]</td>
<td>130 [150]</td>
<td>2.6–35 [150]</td>
<td>2.09 [150]</td>
</tr>
<tr>
<td>CaCO3</td>
<td>0.01–0.5 [150]</td>
<td>Irregular, Spherical [150]</td>
<td>1 [192]</td>
<td>52 [150]</td>
<td>2.24 [150]</td>
<td>2.4–3 [150]</td>
</tr>
<tr>
<td>β-TCP</td>
<td>10 [193]</td>
<td>Irregular [193]</td>
<td>1.5–3 [194]</td>
<td>8.44 [194]</td>
<td>5–16 [195]</td>
<td>0.07–0.61 [195]</td>
</tr>
</tbody>
</table>
3.2 Effects of Filler

This section is a brief presentation filler effects as of nucleating and reinforcing agents.

3.2.1 Nucleating

Nucleating agents are compounds and compositions that cause polymer crystals to form through generating nucleation sites where polymer chain crystallization occurs. This is due to the reduction of the free energy caused by the surface of nuclei which is a requirement to form a new polymer nucleus. The reduction of the critical size of nuclei then takes place, and crystals start to develop more quickly. The free surface of a nucleating agent and its capacity to arrange molecules in conformation that allows fast crystallization are the most important properties of a nucleating agent. Crystallization takes place when cooling the polymer lower than its melting temperature, wherein the transformation of phase occurs. Spherulite growth rate influences the rate of crystallization [196]. Spherulites are semicrystalline regions that are spherical which are inside a non-branched linear polymer. The formation of spherulites is governed by the polymer crystallization from the melt and is influenced by various parameters, including cooling rate, polymer molecule structure, and several nucleation sites. The inclusion of nucleating agents can increase crystallinity and minimize the molding cycle time by shorter crystallization half time [197]. Spherulite diameter can range from a few millimeters to micrometers depending on the said parameters. Compared to disordered regions in a polymer, spherulites are made up of highly ordered lamellae, resulting in greater density, hardness, and brittleness. Amorphous regions link the lamellae, providing impact resistance and elasticity [198]. Figure 3-5 shows the comparison between non-nucleated polymer and nucleated polymer where it can be observed that with the addition of nucleating agent, the crystallinity of the polymer is greater than the non-nucleated one. Fillers may also have an impact on the modification of the crystal matrix. An increase in crystallinity increased the mechanical properties of the polymer such as the tensile and flexural modulus [199].
The capacity to act as nucleating agent is the most essential effect of particulate fillers [201]. A closer examination of the literature and experimental data reveals that the nucleation impact of fillers is mostly determined by physical and mechanical features. Traditional fillers, such as talc, have been employed as nucleating agents in commodity polymers for many years, and talc has the potential to enhance PLA significantly and cost-effectively. A study added 5 wt% talc to PCL and PLA. Filler addition of talc resulted in the enhancement of adhesion and miscibility of PLA domains as well as the PCL bulk phase. Moreover, mechanical properties such as tensile modulus increased up to 50% while storage modulus increased up to 58% [199]. Another study investigated the effect of talc on PLA as a nucleating agent. In the absence of talc, the crystallinity of with talc incorporated increased the crystallinity of PLA to 25%. With regards to its mechanical properties, the addition of 10 wt%, 20 wt%, and 30 wt% talc significantly increased the Youngs to 41.5%, 70.7%, and 139% respectively [202]. Precipitated calcium carbonate (PCC), as well as halloysite natural nanotubes (HNT) also exhibited a nucleating effect to polylactic acid. Both two nanofillers lowered the half crystallization time and increasing the crystal growth rate,
according to isothermal crystallization. The mechanical performance of PLA composites containing PCC and HNT improved in tensile tests, such as elongation break, young’s modulus up to 10% and 12% respectively when compared to neat PLA [203].

3.2.2 Reinforcing

Reinforcing fillers are additives that modify the mechanical properties of the polymer. These particles are usually dispersed into the polymer matrix to enhance its strength and modulus [204]. This is due to the load redistribution and crack redirection from the matrix to the filler. As a result, the characteristic of composite is highly determined with the interfacial capacity of reinforcing fillers to absorb loadings [205]. The toughening effects of reinforcing fillers are due to the breaking of intermolecular particles that releases energy which promotes a highly irregular avenue for the primary crack. The primary crack approached an orientated cluster of particles, and the energy is absorbed by the filler which in turn redirects the cracks around the cluster as can be seen in Figure 3-6 [206]. The redirection of crack to the filler enhances the mechanical property since the mechanical load is taken by the filler, and the composite strength is determined by the strength of the reinforcing filler. Moreover, the characteristic of composite is highly associated with the capacity of the interface to transfer mechanical loads from the polymer matrix to the reinforcing filler [205].

Figure 3-6 Schematic of typical crack propagation reinforced composites [206]
Polymers can be incorporated with large amounts of fillers; some even contain up to 60% of the particulate fillers. Different types of fillers have different effects on enhancing the mechanical properties of the Polymer. For instance, the addition of 30 wt% fibrous fillers such as carbon fibers to a polymer like nylon 6 can enhance the creep resistance as well as increase its stiffness to 300%. Glass filler reinforced to polymers decreases the ultimate elongation and impact strength which then is prone to warping since there is a large difference in mold shrinkage between the flow and crossflow directions. Nonfibrous fillers, such as mineral powders, have a higher stiffness than unfilled polymers, but not as high as fiber-reinforced polymers. Particulate fillers with a particle size of less than 100 μm that are reinforced to polymers are less likely to shrink and warp. When used in tight tolerance molding, particulate fillers minimize shrinkage by a percentage nearly equal to the percent volume of filler in the polymer [207]. The utilization of mussel shells to obtain calcium carbonate filler as reinforcement for polylactic acid can also be used to attain a better mechanical property. The elastic modulus of PLA increased because the modulus of the calcium carbonate filler is higher with respect to the polymer matrix, however, there was a slight decrease in strength because there is a lack of stress transfer to the filler particles from the polymer matrix [208]. Cellulose fiber can also be used as reinforcement to PLA. The mechanical properties of PLA are improved with the addition of 2 wt% cellulose fibers. The young's modulus increased up to 2000%, likewise, the strain break increased from to 20% [209]. PLA reinforced with wood flour was also investigated. It was found that with the addition of 40 wt% wood flour, the impact strength and flexural modulus increased up to 72% and 130% respectively [210].
3.3 Different Types of Functional Fillers

In this section, different types of functional fillers namely carbonaceous, metallic, ceramics and glassy, plant-based, and minerals will be introduced.

3.3.1 Carbonaceous

Carbon nanotubes (CNT) and carbon fibers are the most studied carbonaceous fillers for polymer-based composite fabrication due to their good electrical, mechanical, and thermal properties. Distinctively, CNT are ultrathin carbon fibers [211] having a honeycomb lattice structure with a planar-hexagonal arrangement of carbon atoms [212]. Polymer matrices incorporated with carbon-based was found to have a substantial improvement in the mechanical properties up to a certain filler concentration attributed from its high surface area. However, reinforcing efficiency decreases severely at higher volume fractions due to their high aspect ratio, large van der Waals interaction forces, while having poor polymer-carbon interaction which results to formation of aggregates and difficulty in dispersion of this filler in polymeric matrices [213, 214, 215].

3.3.2 Metallic

Usually, studies involving to metallic powders are mainly to improve thermal conductivity and heat resistance while maintaining or having less mechanical property deterioration [216]. The incorporation of metal fillers in polymer composites has produced new composite materials of several advantages, such as static electricity discharge and antimicrobial properties [217]. In spite of the gradual increasing interest in exploring metal-filled composites, there are only few due to the difficulty in metal dispersion and orientation in polymers. [218]

3.3.3 Ceramic and Glassy

Another category are the ceramic and glassy fillers. These are generally made of layered silicates with traces of oxides and organic matter [219] Layered silicates do not affect the microphase morphology of polymer, irrespective of the filler diameter
Also, these types of fillers have large surface area which increases the polymer-filler interaction and thus results in the reinforcement and higher solvent resistance while reducing coefficient of friction and wear rate of most composites [222]. In contrast, apart from its higher cost, ceramic and silicates also have tendency to agglomerate, have relatively low Mohs hardness, and impact resistance compared to other fillers [223].

3.3.4 Plant-based

Since there has been an increasing attention in producing biodegradable 3D-printed materials, plant-based fillers are also investigated as a substitute to conventional reinforcing fillers such as carbon and glass fibers [224]. These natural fillers provide several advantages including their low density, availability, economical, and biodegradability [225]. For instance, researchers found that beech sawdust reinforced tensile strength and flexural strength of 3D-printed composite [226]. Although compatibility between polymer and plant-based filler can be improved through thermal or chemical modification, printed polymer parts usually exhibit poor strength and high swelling due to its poor interfacial bonding between the hydrophobic polymer and hydrophilic nature of this filler type [227, 228, 229].

3.3.5 Mineral

Most common mineral fillers used in polymers are calcium carbonate, talc, and mica. From inert particulates used to reduce cost, they have now become functional additives [230]. Advantages include the increased heat-deflection temperature [231], reduced thermal expansion [232], and improved flame-retardancy of a polymer [233]. Although, this type of filler contributes significantly to the dimensional stability and molding cycle time of a polymer [234], it is usually however at the expense of tensile strength and other mechanical properties [235]. Despite its widespread utilization, surface modification or treatment is usually required to overcome weak polymer-filler interaction when used as reinforcements in plastics [236].
3.4 Studies on Different Types of Fillers Incorporated to Polylactic Acid

Presented below is a summary of the studies of various types of fillers incorporated into polylactic acid (PLA) benchmarked against pure PLA to explore its effects on mechanical properties. These are limited only to studies that are 3D-printed using fused deposition modeling and were mechanically characterized as dog bone, rectangular, or scaffold samples which is schematically shown in Figure 3-7.

3.4.1 Carbon Nanotubes and Graphene

Tensile and flexural properties of FDM-printed PLA composite containing graphene with concentrations 0.5, 1, and 2 wt% were characterized. Results show that all mechanical properties had increased at 2 wt% graphene content, indicating an enhanced stiffness. On the other hand, PLA composite with lower concentrations exhibited a decrease in strength and modulus, which can be due to the thermal degradation or printing defects such as voids, as depicted in Figure 3-8 [66].
3.4.2 Carbon Nanotubes

Mechanical properties of polylactic acid (PLA) containing carbon nanotubes (CNTs) as a function of concentration were investigated. With increasing CNT concentrations of 0.5, 2.5, and 5 wt%, both impact and tensile strength of PLA-CNT composites decrease while its modulus increases. This can be due to the CNT’s high likelihood to aggregate at high concentrations [237], where the local CNT concentration fluctuates, resulting in weaker parts and stress concentrations [238].

![Figure 3-9](image)

*Figure 3-9(a) CAD test sample, (b) Printing toolpath of extruded filaments, or “roads”, (c) 3D printed 0% CNT-PLA (left) and 5% CNT-PLA (right) [238]*

Optical micrographs of PLA and CNT-PLA composites with varied CNT loadings (0.5, 2.5, and 5%) are shown in Figure 3-10 below, indicating the presence of CNT aggregates. Since clogging ceases to occur throughout the 3D printing process, the particles must have been smaller than the nozzle diameter of 500 mm. On the other hand, these CNT aggregates will contribute to local CNT concentration...
change and have a negative impact on the printed CNT-PLA composite mechanical strength since these may act as stress concentrators leading to early failure [238].

![Figure 3-10 Optical micrographs of composite films with increasing CNT concentration [238]](image)

3.4.3 Carbon fiber, Copper, Aluminum, Ceramic, Wood

The results in this study revealed that the filler materials influence flexural and tensile properties. An analysis of fracture morphology shown in Figure 3-12 for all samples was performed which are to understand better the FDM printed parts of PLA composite in terms of its mechanical behavior. Overall, the addition of different fillers by 40 wt% decreased both flexural and tensile strength of PLA-composite except for ceramic, which slightly increased the tensile strength by 2%. Images show that aluminum, copper, and ceramic-based samples of PLA have more compact interlayer
structures that are extremely close to neat PLA compared to carbon fiber and wood-based samples of PLA. Although the modulus was decreased, indicating reduced brittleness with carbon fiber and wood, the low mechanical strength could be the effect of the defects, including adhesion between filament layers, poor compaction, and high porosity [239].

![Figure 3-11 3D printed samples of wood, ceramic, aluminum, and copper-based PLA in flat orientation: (a) tensile tests, (b) flexural tests [239]](image)

![Figure 3-12 Optical images of fracture morphology for all printed samples [239]](image)

### 3.4.4 Titanium

3D-printed polylactic acid using FDM and containing 5, 10, 15, and 20% titanium (Ti) was assessed in terms of its effect on mechanical properties. It was found
that both strength and modulus had increased compared to pure PLA, indicating an enhanced toughness and ductility, hence, was reinforced. This increase can be explained by the nucleating effect of Ti wherein content was found to be directly proportional to glass transition temperature while crystallization temperature had decreased. However, no correlation between compressive properties and Ti content was observed for loadings between 5 and 20 vol%. It was also concluded that Ti contents of ≥20 vol% adversely affect compressive properties, especially in the case of elongation, which exhibited brittle behavior as also revealed from fracture surfaces of PLA-Ti specimens shown in Figure 3-13 where severe deformation reflects toughness [240].

![Figure 3-13 Fracture surfaces of 3D printed PLA/Ti composites [240]](image)

### 3.4.5 Copper, Bronze, & Silver

Polyactic acid was incorporated with copper, bronze, and silver metallic fillers then printed through fused deposition modeling. Mechanical properties such as elastic modulus, elongation break, and tensile strength were evaluated. Due to the reinforcing effect of the metallic fillers, both elastic modulus and elongation break increased. The elastic modulus of PLA increased to 7.14%, 10.4%, and 3.25% after reinforcing with copper, bronze, and silver, respectively. Moreover, the elongation break of PLA increased to 224% for copper filler, 190% for bronze filler, and 34% for silver filler. In contrast, the tensile strength for all metal-filled PLA decreased. This may be due to the thermal degradation and printing defects such as voids, as observed from the SEM results from the fractured surface of the tensile tested samples shown in Figure 3-14 [241].
Cellulose nanofibers with a concentration of 1 wt% were incorporated into polylactic acid as filler which is then printed through fused deposition modeling, and mechanical properties of the printed part were investigated. Results showed that mechanical properties such as modulus, strength, and elongation break of the filled PLA increased. The modulus of PLA increased by 63%, its tensile strength increased by 86%, and the elongation break increased by 40%. The increase in values indicated an improvement in the mechanical properties of polylactic acid. The fracture surface was also investigated using SEM to see further the enhancement of PLA filled with CNF, as shown in Figure 3-15. The fractured part of neat PLA (a,b) revealed significant voids and poor interlayer bonding. The voids present in the neat PLA that was 3D printed are responsible for the porous structure and its lower mechanical strength. Moreover, 3D printed PLA with CNF (c,d) shows minimal voids present, and there is a good interlayer bonding which explains the improvement of the mechanical properties [242].

Figure 3-14 The micrographs of the fractured surfaces after the tensile test (a) PLA, (b) PLA-Cu, (c) PLA-Br, and (d) PLA-Ag. The magnified images of the circled portion are shown on the right side of the micrograph for each sample [241]
Figure 3-15 Scanning electron microscopy micrographs of the tensile fractured surface of, a and b, 3D-polylactic acid (PLA) (×150, ×600X) and, c and d, 3DPLA/1% cellulose nanofiber composites (×150, ×600X) [242]

3.4.7 Wood, Talc, Calcium Carbonate, Microballoon, & Silicon Dioxide

In this study, a comparison of fillers was conducted to select the optimum filler in reducing the brittle behavior of 3D printed parts of polylactic acid (PLA) composites illustrated in Figure 3-16. The PLA-talc, PLA-calcium carbonate, PLA-microballoon, and PLA-silicon dioxide composites have a smooth surface; in contrast, the PLA/wood composites had a rough surface [243].
On the other hand, the tensile strength of 3D printed composites seems lower compared with the neat PLA, except for the PLA/WF. This is probably due to the fibrous morphology of wood flour, which acted as a reinforcement, while the other fillers were irregular, plate or spherical shape. Figure 3-17 shows SEM micrographs of the filament-fractured surface of composites. The continuous phase of neat PLA was a smooth surface fracture, whereas the composites indicate a difference in adherence between the PLA matrix and fillers. The PLA matrix was wet on wood flour fiber that had good adhesion on the interfacial region between wood flour and PLA in the composites since their rough texture and porous particles. This corresponded well with the best tensile strength when compared to those of PLA composites. Although the microballoon-PLA interaction seems good, it did not have good tensile strength and PLA/WF composites due to the smooth surface and its spherical shape. The talc, calcium carbonate, and silicon dioxide agglomerated in the PLA matrix resulting from poor PLA-filler interaction. However, the rigid spherical shape of glass microballoons affected the higher Young’s modulus in PLA/MB composites compared to composites. The elongation at break of PLA composites is reduced when adding microballoon and silicon dioxide particles [243].
The flexural strength of 3D printed PLA/TC composites was greater than that of PLA composite and neat PLA. It can be explained by cracks that started on the other side of the loading and were terminated by the talc plating, which subsequently sustained the additional force. The 3D printed composites had a lower impact strength than the neat PLA except for PLA/MB. The PLA/MB composites gave the best impact strength because the spherical shape of microballoons affected a good distribution in the matrix and could be supported by an intermediate loading for a good force distribution in the composites. Another reason can be explained that the PLA/MB composites had a better bonding between layers than those of neat PLA and PLA composites. It can be investigated from SEM micrographs of the fractured surfaces of 3D printed composites after impact test, as illustrated in Figure 3-18. It was expected that the glass microballoons having spherical shape affected the easy flow of polymer melt, leading to a greater fuse between layers. While the other compounds were some voids between layers that were acted as defects in composites [243].
3.4.8 Talc

The possibilities of Talc (hydrated magnesium silicate), a common nucleating agent, for PLA 3D-printed part enhancement using fused deposition modeling was also investigated. When a first-order phase transition occurs, the heat generated may delay the cooling of the components and, as a result, improve mechanical characteristics through the process of increasing the degree of crystallization. The findings show that Talc contributed to the stiffness of printed components while simultaneously having a detrimental influence on flexural strength, which might be due to stress concentration produced by flaws such as the PLA-Talc powder incompatibility and the interfacial voids. Meanwhile, the improvement in modulus is attributed to an 11.4 % and 12.6 % increase in crystallinity for PLA/3 percent Talc and PLA/6 percent
Talc, respectively. The increase in crystallinity is direct evidence that there is in-situ melt crystallization of PLA during the FDM process, which is also attributed to the increased stiffness. The increase of modulus is significant statistically. However, flexural strength degradation and weight content of PLA/Talc are statistically insignificant [244].

![Figure 3-19 Morphology of PLA (a-c), PLA/3%Talc (d), and PLA/6%Talc (e) in SEM [244]](image)

Cross-sections of PLA specimens were typically smooth, as shown in Figure 3-18 (a-c), although some voids porosity occurred (white circles in Figure 3-18 (b)), particularly at areas far from the heated plate and adjacent to the borders. The non-uniform porosity distribution is frequent in FDM and is caused by certain thermal boundaries. [245] [246] These void pores are weak points that jeopardize the mechanical integrity of the structure. Pores were less prevalent in parts produced of PLA/3 percent Talc and PLA/6 percent Talc in FDM, as shown in Figure 3-19 (d-e). This is partly due to the effect of temperature on cold crystallization with parts made of PLA/3 percent Talc and PLA/6 percent Talc in FDM. These are evidence of improved mechanical properties as a result of Talc incorporation [244].

### 3.4.9 Calcium Carbonate and β-tricalcium Phosphate

Calcium carbonate (CaCO$_3$) and β-tricalcium phosphate (Ca$_3$(PO$_4$)$_2$, β-TCP) were investigated as fillers for polylactic acid manufactured by FDM of which mechanical characterization was carried out. Results show that compressive yield strength
decreased by 30% for both PLA-CaCO$_3$ (95 wt% - 5 wt%) and PLA-β-TCP (95 wt% - 5 wt%) and 36% also for PLA: CaCO$_3$:β-TCP 95:2.5:2.5. This decrease in strength is mainly because of the presence of microporosity. Lack of chemical interaction revealed in the FTIR analysis resulting in the agglomerate formation since there is a good dispersion of β-TCP and CaCO$_3$ in the PLA matrix and evenly distributed filler in the PLA matrix has been achieved, which can be observed in the SEM images in Figure 3-20. The nucleation effect generated by the fillers resulted in good PLA-composite fluidity, resulting in a uniform filament, as seen in the Micro-CT images in Figure 3-20 [247].

![SEM images of 3D printed samples: (a) PLA; (b) PLA:CaCO$_3$ 95:5; (c) PLA:β-TCP 95:5; (d) PLA:CaCO$_3$:β-TCP 95:2.5:2.5. Also, e and f are b and c at higher magnification [247]](image)

Flexural and compressive modulus both significantly decreased, ranging from 27% to 47%, with 5% CaCO3 and β-TCP incorporation. The presence of the particles causes a nucleation effect, which explains this phenomenon [247].
3.4.10 Calcium Carbonate

20% (M) and 50% (G) CaCO$_3$ were incorporated into polylactic acid to describe the composite by their mechanical characteristics when compared to PLA as a 3D-printed part using fused deposition modeling. It was reported that these concentrations decreased the strength of the composite, of which the effect was greater with 50%. This is probably due to the porosity and heterogeneous structure that caused a platelet-like broken surface compared to pure PLA, which had well-defined and column-like structures as observed in the SEM images shown in Figure 3-20. According to the strain and elongation data, the composites feature more rigid structures and are more resistant to deformations than neat PLA. This observation was noteworthy because fillers are known to improve hardness; however, no significant change in this parameter was observed as a function of powder granule size [248].

Figure 3-21 SEM images: Row a) discursive lines - layers and inner structure border; arrows - printing columns. Row b) arrows - individual column size: (PLA: 400 μm wide, 200 μm tall, ‘PLA-20%CaCO$_3$: 200 μm wide and tall). The circles show the holes (30–50 μm) in ‘PLA-50% CaCO$_3$’. Row c) arrows - platelet-like broken surfaces; black stars - test bar surface. N: neat PLA, G: PLA-50% CaCO$_3$, M: PLA-20%CaCO$_3$. [248]
<table>
<thead>
<tr>
<th>Type</th>
<th>Filler</th>
<th>Content by weight</th>
<th>Specifications</th>
<th>Strength</th>
<th>Properties</th>
<th>Modulus</th>
<th>Year</th>
<th>Ref</th>
</tr>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon-based</td>
<td>Graphene</td>
<td>0.5 %</td>
<td>1 %</td>
<td>2 %</td>
<td>0.010 mm</td>
<td>↓47%</td>
<td>↓17%</td>
<td>↓2%</td>
</tr>
<tr>
<td></td>
<td>CNTs</td>
<td>0.5%</td>
<td>2.5%</td>
<td>5%</td>
<td>D - 0.0001 mm</td>
<td>↓5%</td>
<td>↓10%</td>
<td>↓11%</td>
</tr>
<tr>
<td></td>
<td>Carbon Fiber</td>
<td>40%</td>
<td></td>
<td></td>
<td>D - 1.75 mm</td>
<td>↓23%</td>
<td>↓27%</td>
<td>-</td>
</tr>
<tr>
<td>Metallic</td>
<td>Titanium</td>
<td>5%</td>
<td>10%</td>
<td>15%</td>
<td>20%</td>
<td>0.0235 mm</td>
<td>↓24%</td>
<td>↓24%</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>70%</td>
<td></td>
<td></td>
<td>0.05 - 0.07 mm</td>
<td>↓74%</td>
<td>↓5%</td>
<td>↓7%</td>
</tr>
<tr>
<td></td>
<td>Bronze</td>
<td>75%</td>
<td></td>
<td></td>
<td>0.06 - 0.10 mm</td>
<td>↓76%</td>
<td>↓74%</td>
<td>↓17%</td>
</tr>
<tr>
<td></td>
<td>Silver</td>
<td>4%</td>
<td></td>
<td></td>
<td>0.005 - 0.09</td>
<td>↓3%</td>
<td>↓85%</td>
<td>↓3%</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>40%</td>
<td></td>
<td></td>
<td>D - 1.75 mm</td>
<td>↓5%</td>
<td>↓20%</td>
<td>↓42%</td>
</tr>
<tr>
<td></td>
<td>Aluminum</td>
<td>40%</td>
<td></td>
<td></td>
<td>D - 1.75 mm</td>
<td>↓5%</td>
<td>↓10%</td>
<td>↓19%</td>
</tr>
<tr>
<td></td>
<td>Ceramic</td>
<td>40%</td>
<td></td>
<td></td>
<td>D - 1.75 mm</td>
<td>↓2%</td>
<td>↓17%</td>
<td>↓47%</td>
</tr>
<tr>
<td>Glassy</td>
<td>Microballoon</td>
<td>5%</td>
<td></td>
<td></td>
<td>0.06 mm</td>
<td>↓20%</td>
<td>↓9%</td>
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<tr>
<td></td>
<td>Silicon dioxide</td>
<td>5%</td>
<td></td>
<td></td>
<td>MC - 6.3%</td>
<td>↓57%</td>
<td>↓1%</td>
<td>↓25%</td>
</tr>
<tr>
<td>Plant-based</td>
<td>Wood</td>
<td>40%</td>
<td></td>
<td></td>
<td>D - 1.75 mm</td>
<td>↓30%</td>
<td>↓42%</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Wood</td>
<td>5%</td>
<td></td>
<td></td>
<td>0.15 mm</td>
<td>↓16%</td>
<td>↓3%</td>
<td>↓17%</td>
</tr>
<tr>
<td></td>
<td>CNFs</td>
<td>1%</td>
<td></td>
<td></td>
<td>treated</td>
<td>84%</td>
<td>63%</td>
<td>14.8</td>
</tr>
<tr>
<td>Minerals</td>
<td>Talc</td>
<td>3%</td>
<td>6%</td>
<td></td>
<td>0.025 mm</td>
<td>↓3%</td>
<td>↓7%</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>CaCO3</td>
<td>5%</td>
<td></td>
<td></td>
<td>untreated</td>
<td>↓30%</td>
<td>↓7%</td>
<td>↓13%</td>
</tr>
<tr>
<td></td>
<td>CaCO3</td>
<td>5%</td>
<td></td>
<td></td>
<td>untreated</td>
<td>0.075 mm</td>
<td>↓30%</td>
<td>↓18%</td>
</tr>
<tr>
<td></td>
<td>CaCO3</td>
<td>5%</td>
<td></td>
<td></td>
<td>0.030 mm</td>
<td>↓30%</td>
<td>↓30%</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>CaCO3</td>
<td>5%</td>
<td></td>
<td></td>
<td>0.045 mm</td>
<td>↓30%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>CaCO3</td>
<td>2.5%</td>
<td>2.5%</td>
<td></td>
<td>0.03-0.045 mm</td>
<td>↓36%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>CaCO3</td>
<td>20%</td>
<td>50%</td>
<td></td>
<td>0.0015-3 mm</td>
<td>↓18%</td>
<td>↓28%</td>
<td>↓28%</td>
</tr>
</tbody>
</table>

Note: D – diameter; L – length; MC – Moisture Content
3.5 Discussion

As seen from Table 3-3, fillers are categorized according to their type, namely carbon-based, metallic, ceramic/glassy, plant-based, and minerals. Results have verified that the mechanical properties of 3D-printed PLA composites using FDM are sensitive to the filler properties most particularly to weight content and size. Under carbon-based, only graphene demonstrated an increase in strength and modulus which can be due to its low moisture absorptivity compared to CNT and carbon fiber. For metallics, only titanium increased the tensile attributed from its surface charge near to PLA while bronze decreased the impact strength which can be due to its high filler content at 75 wt%. All metal fillers increased the modulus while bronze, silver, and aluminum had decreased the elongation at break of PLA-filled composite by ↓2%, ↓7%, and ↓17% which can be explained by its intrinsic hardness and high thermal conductivity that increases crystallinity of PLA. In glassy fillers, only ceramic exhibited an increase in tensile and flexural strength and tensile modulus which may be due to its higher filler content compared to microballoon and silicon dioxide. Moreover, plant-based wood increased the tensile strength and modulus which can be attributed from its elongated shape. In mineral fillers, only talc exhibited an increase in flexural strength and modulus. The differences in mechanical properties of material indicate anisotropy. [249] and modulus which can be due to its low moisture absorptivity while having a large surface charge. Trends in changes are still unclear according to filler types as there are several properties of fillers and factors such as concentration, purity, morphology, particle size, and surface chemistry that contribute to its effects on the mechanical properties of the composite.

One of the factors that significantly contribute to the mechanical properties of composite is the concentration of the filler content. In Figures 3-21, it can be inferred that as filler content increases, the strength of 3D-printed composite mostly decreases. Usually, fillers incorporated into polymer improve its rigidity. The higher the filler content, the stronger the polymer composite, provided an optimal filler loading. However, excessive incorporation of filler may cause agglomeration in the polymer matrix. This agglomeration results to stress concentration and initial cracks, leading to
decreased particle-matrix interaction and consequent reduction in strength. [250] For instance, a study suggested incorporating calcium carbonate up to 1% increased strength by 52.4%, which thereafter decreased with respect to pure PLA. [251] Additionally, the incorporation of CNT and talc revealed a reduction in strength into the PLA matrix while the modulus increased. [252] A low CNT content is well embedded while entangled bundles are formed at high loadings [253]; while at low talc loadings, it was observed that up to 30% wt contents had significantly reinforced the modulus of 3D-printed PLA. [254] A similar result was also reported, where there was a linear relationship between the filler content and composite modulus. The increase in modulus can be attributed: 1) to the ability of stress transfer from the matrix to the filler, which enhances the material stiffness, and; 2) its ability to restrict polymer chain movement as rigid filler particles. [255]

![Figure 3-22 Strength of graphene, CNT, Ti, Talc, and CaCO₃ in increasing content](image)

T – Tensile; F – Flexural; I – Impact; C – Compressive; F – Flexural
Moreover, the decrease in modulus as shown in Figures 3-22 and 3-23 by some fillers and the marginal increase in elongation at break caused by carbon fiber and copper among all fillers indicated the change of fracture phenomenon from brittle to ductile. Since filler content and size are the same, this increase might be due to its other properties. Meanwhile, a decrease in the elongation at break suggested that composites containing higher loading of fillers became more brittle, resulting from reduced toughness than pure PLA. [256] This reduction is most likely due to crack initiations caused by agglomeration, which causes weaker structures with a lower capacity to withstand deformations [257] [258]. This is similar to a study wherein the inclusion of a 20 wt% of calcium carbonate in PLA increased its stiffness confirmed by the reduction in the elongation, both at break and maximum stress. [259]

![Figure 3-23 Modulus of graphene, CNT, Ti, and Talc in increasing content](image)

*Figure 3-23 Modulus of graphene, CNT, Ti, and Talc in increasing content*

T – Tensile; F – Flexural; E – Elasticity; C – Compressive
Figure 3-24 Elongation at break of graphene, Ti, and CaCO₃ in increasing content

Fillers with smaller dimensions provide a larger surface area, promoting better dispersion and polymer-filler interaction. This fair dispersion of fillers in the matrix could be observed from the micrographs of the PLA-talc samples in Figure 3-16 c. However, smaller particles tend to agglomerate, which explains the decrease in mechanical properties caused by the incorporation of fillers compared to 3D-printed pure PLA. Meanwhile, poor dispersion at larger filler sizes at the same loading leads to voids in the matrix, as observed in micrographs. Depicted in Figures 3-24 and 3-25 are mechanical properties in terms of various sizes of fillers with the same loading at 5 wt%. Wood and titanium with diameters 0.15 mm and 0.5 mm increased the tensile strength of PLA-filled composite by 6% and 24%. The more significant increase in flexural strength caused by talc (D0.05) than wood (D0.15) by 20% and 3% might be due to its smaller diameter. An increase in impact strength by 10% and 820% resulted from the addition of microballoon (0.06) and titanium (D0.5). An enhanced spherulization was also revealed from the micrographs due to nucleation sites induced from the incorporation of fillers. This spherulization consequently increases the ability of the composite to restrain gross deformation of the matrix, hence increasing strength and modulus. It was reported that semi-crystalline polymer such as polylactic acid with small spherulites tends to be tougher than larger spherulites. This can be attributed to larger spherulites' weak boundaries compared to small spherulites. Fillers act as stress...
concentrators and promote cavitation at the polymer-particle boundaries, resulting in the plastic deformation behavior of 3D-printed PLA.

**Figure 3-25 Strength of 5 wt% Fillers with Different Diameters**

**Figure 3-26 Modulus of 5 wt% Fillers with Different Diameters**
Dispersibility and interfacial adhesion of filler to the polymer matrix are also critical factors in determining the mechanical properties of polymer-filled composites. Among all fillers, only cellulose nanofiber (CNF) is treated with a coupling agent that alters its surface energy by diffusion due to covalent bond formation, making it compatible with the polylactic acid. Thus, even at only 1 wt% CNF content in the PLA composite, it increased its tensile strength, tensile modulus, and elongation at break by 84%, 64%, and 0.54%, indicating a favorable interaction between PLA and both CNFs. Meanwhile, according to morphological characteristics as analyzed through the SEM technique, the formation of agglomerates due to poor interfacial adhesion of fillers in the PLA matrix might cause the poor mechanical performance of 3D printed composites. Fillers are easily debonded from the matrix resulting to void formation. When specimens are stretched, the air holes grow and merge [260]. For instance, Figure with 40 wt% talc revealed multiple voids, which led to the early failure of the composite. [261] It should also be noted that incorporating titanium particles increased ultimately increased the mechanical properties of 3D-printed PLA, which can be attributed to the compatible surface energy and opposite polarity. PLA and titanium have a surface energy of 62 mN m\(^{-1}\) and 80.7 mN m\(^{-1}\), resulting in uniform filler distribution that provides a more interfacial surface for interaction. Additionally, impact fracture surface morphology of PLA composite with relatively smooth fracture mostly demonstrated a brittle fracture behavior. This can be due to the increase in of cooling threshold for melt crystallization caused by filler incorporation. As such, slower cooling rate and inter-layer duration are constructive for interlayer bonding and accumulation of crystallinity, promoting stiffness. [244] Also, in thermoplastic melting processes such as FDM, filler particles migrate from the cold regions into the melt due to a temperature gradient during cooling. This temperature gradient induces an interfacial tension at the filler-melt boundary, explaining filler-depleted surfaces in the PLA. [161] Overall, since most fillers are untreated, resulting in poor dispersion, this increases the porosity of PLA samples due to agglomeration and voids. Perhaps, if fillers were treated, it might have resulted in better mechanical properties of 3D-printed polylactic acid composites using FDM.
Each particle shape brings certain advantages, and moisture content also influences the 3D-printed part. Spherical particles such as most metallic, glassy, and mineral fillers such as most metallic, glassy, and mineral fillers contribute the highest packing density, a uniform stress distribution, lower viscosity, and increased melt flow which is favorable in FDM processing. Flake-shaped fillers such as graphene, silver, and talc have large surfaces and better orientation. Elongated fillers such as carbon, wood, and cellulose fibers provide superior reinforcement, reduce shrinkage and thermal expansion, which may also explain the increase in strength and elongation at break of 3D-printed PLA caused by these fillers. Moreover, flake-shaped and elongated fillers may suffer from flow-induced orientation and alter the shear rate of the 3D-printed composite, which may have affected the flow and diameter of the extruded filament from the FDM heated nozzle. Moreover, the higher the molecular weight (MW), the better the mechanical properties. In the incorporation of CNT, the molecular weight of PLA composite compared to pure PLA still decreased from 213.31 to 211.35 kg/mol despite the precautionary drying methods conducted. This is due to the residual moisture in CNTs, which advances to thermal degradation of PLA through hydrolysis during the FDM heating process. Although some fillers were dried before melt compounding with PLA, the residual moisture of fillers is still unclear since most studies focus on filler size and concentration. Hence, particle shape and moisture characterization should have been included for further investigations as to how these properties of fillers contributed to the mechanical performance of 3D-printed PLA.

Changes in thermal properties due to filler incorporation also contribute to the mechanical performance of 3D-printed PLA using FDM. Although the negligible effect may be observed due to the relatively fast cooling rate involved in 3D printing, fillers can still act as a nucleating agent, increasing the crystallinity of PLA. As heat conductivity increases, this may accelerate heat transfer after heated filament deposition which promotes crystal growth due the nucleation induced by fillers. Thus, this increases the overall thermal conductivity of composites, resulting in better heat distribution and interlayer adhesion. [262] This increase in the degree of crystallization provides stiffness to the polymer at the expense of its impact resistance and elasticity.
Also, the maximum crystalline content of above 38% for PLA is unpreferable in processing since crystallinity results in poor dimensional stability due to shrinkage and warpage in FDM processes [263]. In relation to these principles, it was found that graphene and CNT had decreased the glass transition temperature of PLA by 5°C characterized through differential scanning calorimetry. It was also revealed that the incorporation of titanium acted as nucleating agents, which is reflected from the decrease in cold crystallization temperature of pure PLA with 20 wt% PLA-Ti from 22.4% to 5.9%. Due to the unavailability of thermal characterizations with the incorporation filler, the effects of thermal conductivity on the mechanical properties of 3D-printed PLA composites are less understood. Hence, it should be included in future studies, especially in terms of the voids and interlayer-adhesion.
Chapter IV

Conclusion

When it comes to the applications of polylactic acid-filled products assembled through FDM technologies, it is particularly essential to understand the mechanical properties of the 3D printed material. Compared to other thermoplastics, PLA is one of the most convenient, well-suited, and far more thermally stable materials during printing than other used filaments such as ABS, Nylon, and PET. Despite PLA having excellent biocompatibility, processibility, and less energy dependence, it has drawbacks in some inherent properties. These drawbacks include low elongation at break, low toughness, and brittleness, which restricts its use in a wide range of applications, especially those requiring high-stress levels during plastic deformation.

There are two factors that affect the mechanical properties of 3D-printed parts: interlayer adhesion and microvoids. The increase in interlayer adhesion improves mechanical performance while microvoids negatively affect the 3D-printed part. Methods such as laser treatment and annealing are conducted, showing improvements in the mechanical properties. However, these postprocessing methods adversely affect dimensional accuracy as they shrink or warp the 3D-printed PLA. Thus, the incorporation of fillers to PLA is examined and characterized in terms of strength, modulus, and elongation at break since fillers have nucleating and reinforcing effects that contribute to the mechanical properties of 3D-printed PLA composite in comparison to pure PLA.

Studies involving the incorporation of fillers and their effects on the mechanical properties of 3D-printed PLA were presented and discussed. Fillers are categorized according to their types, namely: carbon-based, metallic, glassy, plant-based, and mineral. These fillers are compared according to their concentration, size, dispersibility, morphology, moisture content, and conductivity in terms of their effect
as nucleating and reinforcing agents and how it affects the microvoids and interlayer adhesion 3D-printed PLA.

All metallic fillers demonstrated an increase in tensile, flexural, and compressive modulus, which indicates an increase in stiffness. This reinforcing effect in modulus even at higher loadings and different sizes can be attributed to the high rigidity characteristic of metallic fillers. On the other hand, trends in changes in the mechanical performance according to filler types are still unclear due to the differences in other factors such as concentration, size, and surface chemistry which are usually the most investigated properties of fillers.

Fillers were known to reinforce composites at lower concentrations which was confirmed from the results that as filler content increases, the strength of 3D-printed composite primarily decreases. This decrease can be due to excessive incorporation filler that causes agglomeration in the polymer matrix leading to stress concentration and initial cracks. Thus, strength is not a linear function of concentration as there is an optimum critical concentration. Also, filler loading is directly proportional to the modulus of 3D-printed PLA composites up to a particular loading. The increase in modulus can be attributed to the stress transferability from the matrix to the filler and the polymer chain movement restrictions. Furthermore, a decrease in modulus indicates brittle to ductile behavior of the 3D-printed PLA. Also, the decrease in elongation at break implies reduced ductility having a lower capacity to withstand deformations under load.

Smaller sized fillers provide a larger surface area, promoting better dispersion and polymer-filler interaction. However, smaller sizes tend to agglomerate, which explains the decrease in mechanical properties caused by the incorporation of fillers compared to 3D-printed pure PLA. Meanwhile, poor dispersion of larger filler sizes at the same loading leads to the development of voids in the matrix, resulting in poor mechanical strength. Also, there is an increasing trend in modulus as filler size increases, indicating improved elasticity as fillers promoted cavitation at the polymer-particle interphase, resulting in the plastic deformation behavior of the 3D-printed PLA.
Although the uniform distribution of fillers in the matrix does not guarantee mechanical enhancement, two factors contribute 1) interfacial surface and 2) polymer-filler interaction. However, most fillers have a relatively broad particle size distribution, and the exact determination of the critical particle size is difficult.

Strong PLA-filler interfacial interaction results in enhanced mechanical properties of the 3D-printed PLA. PLA-filler and filler-filler interactions can be modified through surface treatment which alters its surface energy by diffusion and forming a covalent bond. This bond improves filler dispersion and distribution while preventing agglomeration even at a broader range of concentrations and sizes. However, the formation of agglomerates due to poor interfacial adhesion of filler in the PLA matrix generates points at which the fracture can propagate. This agglomeration results in microvoids formation and poor interlayer adhesion, leading to early failure of the 3D printed composites.

Although different shapes have certain advantages, morphological characterization of fillers is usually not included in most studies. Thus, the 3D-printed PLA composite analysis as a shape function is complicated since fillers can have polymorphs. Residual moisture in filler also advances the PLA into thermal degradation through hydrolysis and steam evaporation, resulting in microvoids during the FDM heating process. This degradation can be confirmed in the reduction of molecular weight and increase in porosity of 3D-printed PLA composite compared to pure PLA, which consequently decreases its strength. As for the conductivity, incorporating fillers promotes better heat distribution, increases the cooling threshold for melt crystallization, and induces nucleation sites. This increase in inter-layer duration is constructive for interlayer bonding and accumulation of crystallinity, promoting stiffness. However, an increase in the degree of crystallinity deteriorates the impact resistance, reduces elasticity, and may cause poor dimensional stability due to shrinkage or warpage.
Although polymer-filled composites such as polylactic acid already have a long application history, their property correlations are more complicated than usually assumed. As there are still limited publications on the mechanical properties of 3D-printed PLA composites using FDM, especially as functions of filler dispersibility, morphology, moisture content, and conductivity, future studies should develop a more quantitative molecular understanding of these filler properties and their synergy as nucleating and reinforcing agents.
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