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COMPARISON OF FILLER TYPES IN POLYLACTIC ACID COMPOSITES FOR 3D PRINTING APPLICATIONS

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Abstract

This research is a comparison of the addition of different fillers in polylactic acid (PLA) affecting the three-dimensional printing technique and their properties. The fillers consist of Wood flour

(WF), Talc (TC), Calcium Carbonate ($CaCO_3$), Microballoon (MB) and Silicon Dioxide (SiO_2). The 5%wt fillers were added into PLA to fabricate the filaments by single screw extruder. The specimens were fabricated by Fuse Deposition Modeling (FDM) technique. The effects of fillers on the physical, mechanical, flow, thermal and morphological properties of polymers were of interest. It was found that the 3D printed parts were completely in shape during fabrication. The 3D printed parts of PLA composites were a difference in color and texture, and exhibited a lower tensile strength than those with the neat PLA, except for the PLA/WF. The glass microballoons mixed-PLA composites gave the higher Young's modulus compared to those with composites. The 3D printed parts of PLA/TC composites had greater flexural strength than that of neat PLA and PLA composites. The impact strength and melt flow rate of PLA/MB composites were higher than that of neat PLA and PLA composites. The Vicat softening point of PLA/MB was similar to neat PLA, while PLA/$CaCO_3$, PLA/WF, PLA/TC and PLA/SiO_2 was lower compared with neat PLA.

Keywords

Polylactic Acid, Composites, Fuse Deposition Modeling, 3D Printing

1. Introduction

Nowadays, the industrial sector is growing with the rapid advancement of materials forming technology. Three-dimensional printing technique is another method that is becoming very popular. Because it can fabricate the shape complex workpieces with low production time, but it is suitable for small amounts of production. The three-dimensional printing is a virtual model creation or the fabrication of workpiece by adding material of layer-by-layer according to the desired model. Three-dimensional printing techniques have been developed to become more complex and have started to play a role in the manufacturing of parts for machine tools, engineering and medical design. However, there are also more three-dimensional printing techniques to suit the workpiece and the type of material to be created. Fused Deposition Modeling (FDM) printing technique is considered the most popular 3D printing technique. Because it is easy to use and cheap. The 3D printed parts can be polished, trimmed or drilled, and further used. This technique can be used with a variety of materials such as Polylactic acid (PLA), Acrylonitrile-butadiene-styrene (ABS), High-impact polystyrene (HIPS), Polyethylene Terephthalate (PET), Nylon, etc. (Cameron, 2015). Polylactic acid is widely used in the 3D printing industry due to easy printing and low shrinkage. PLA is a biodegradable material as naturally eco-friendly, which is brittle material and low heat distortion temperature (Sennan & Pumchusak, 2014). In addition, the various of fillers has different characteristics which affect the different of filaments in the physical and mechanical properties that make them more versatile to meet the needs of users.

In the existing literature, mostly PLA composites with the fillers were fabricated by using injection molding and casting process. Petchwattana and Covavisaruch indicated that the tensile properties of the rubber wood-filled PLA composites increased with increasing rubber wood loading, while the impact strength and the tensile elongation at break of PLA composites decreased (Petchwattana & Covavisaruch, 2014). Akbari et al. suggested that the flexural modulus of PLA composites improved while the impact strength dropped with increasing talc content (Akbari, Jawaid, Hassan, & Balakrishnan, 2013). In addition, the silica nanoparticles as reinforcing filler for PLA composites as reported by Pilić et al. (Pilićj et al., 2015). Many publications reported the more brittle behavior of PLA when adding the fillers. (Scaffaro, Maio, Gulino, & Megna, 2019; Kumar & Tumu, 2019) Likewise, the addition of fillers in other polymers displays a similar manner. (Gönenli & Yeni, 2018; Liang, 2019)

PLA composites were published in many articles but the literature of 3D printed parts of PLA composites had a few studies. Ertane et al. found that the tribological resistance of 3D printed PLA composites increased with higher 30%vol of biocarbon content (Ertane et al., 2018). The moisture content and dimensional swelling of 3D printed PLA/wood composites increased with increasing wood content while the modulus of elasticity decreased that reported by Kariz et al. (Kariz, Sernek, & Kuzman, 2018). Daver et al. reported the tensile properties and impact strength of PLA composites decreased with increasing cork content. The 3D printed composites were more ductile than that of compression moulded composites. (Daver, Lee, Brandt, & Shanks, 2018). Liu et al. found that PLA composites filled with ceramic, copper, and aluminum had similar or increased mechanical properties than that the neat PLA. In addition, the PLA composite with FDM-printed in on-edge orientation with$+45^\circ/-45^\circ$ raster angles gave the highest mechanical strength and modulus (Liu, 2019).

So, this research work aimed to compare of filler types in polylactic acid (PLA) composites and select the optimum filler types to reduce the brittle behavior of 3D printed parts of PLA composites. The PLA composites were investigated on physical, mechanical and thermal properties for several applications using 3D printing techniques. The filler types consist of wood flour (WF), talc (TC), calcium carbonate ($CaCO_3$), microballoon (MB) and silicon dioxide (SiO_2). The PLA composites were determined the flow property in term of melt flow rate (MFR). Then, the PLA composites were fabricated specimen by FDM technique to examine the physical, mechanical and thermal properties. The fracture surface of the specimen was also investigated.

2. Experimental

2.1 Raw Materials

Polylactic acid (PLA) was supplied by PTT Polymer Marketing Co., Ltd. (Thailand) in the form of pellets and using the trade name NatureWorks® PLA Polymer 4032D. Five types of filler were used in this work including wood flour (WF), talc (TC), calcium carbonate ($CaCO_3$), microballoon (MB) and silicon dioxide (SiO_2). Wood flour obtained from the wood polishing process in the teak processing factory. The average size of wood flour used in this work is less than 150 microns. The wood flour was dried in an oven at a temperature of 80°C for 24 hrs before used. Talc grade SQ-1250 was an average particle size D50 of 8±3 microns. Calcium Carbonate was untreated surface and used trade name as Q-min having an average particle size of 75 microns, supplied by Quality Minerals Co., Ltd. (Thailand). Microballoons grade K20 were hollow spherical shape of glass with an average particle size D50 of 60 microns, a density of 0.2 g/cm^3 was supplied by 3M United Co., Ltd. Silicon dioxide was precipitated silica with specific surface of m^2/g, supplied by OSG group Co., Ltd. and using the trade name Tokusil 255G. The moisture content of the precipitated silica was about 6.3%.

2.2 Filament Fabrication

The 5%wt fillers were added into polylactic acid (PLA) and fabricated as filaments with a built single screw extruder, a small laboratory mixer. The barrel temperature profiles were 190, 180 and 160°C from feed zone to die zone, and the screw speed was 40 rpm. The filaments were controlled with a diameter of 1.75±0.2 mm, then kept at 25°C at 50% humidity before further use.

2.3 3D Printed Specimen Preparation

The 3D printed specimens were prepared for testing the tensile, impact, flexural and Vicat according with ASTM D638, ASTM D256, ASTM D790 ASTM D1525, respectively. The first step, the 3D model was created in SolidWorks 2014 and converted to .STL files. Then, the .STL files were imported to Cura 2.6.2 with settings as shown in Table 1. Last step, the files were saved as .GCODE files for 3D printing in Fused Deposition Modeling (FDM) as a 3D printed tensile specimen shown in Figure 1.

Table 1: *Settings in Cura 2.6.2*

Parameters	Settings	Parameters	Settings
Nozzle extruder (mm)	0.4	Wall thickness (mm)	0.8
Layer height (mm)	0.25	Top and bottom thickness (mm)	0.8
Initial layer height (mm)	0.2	Infill density (%)	90
Layer width (mm)	0.4	Infill Pattern	Grid
Nozzle temperature (°C)	200	Base temperature (°C)	60
Printing speed (mm/s)	30	Fan speed (%)	100

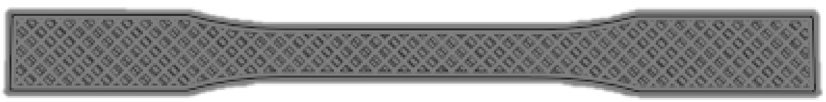

Figure 1: *Sample of 3D Printed Tensile Specimen*

2.3 Characterizations

2.3.1 Mechanical Properties

The 3D printed specimens of PLA filled with the various fillers, i.e. PLA/WF, PLA/TC, PLA/$CaCO_3$, PLA/MB and PLA/SiO_2 were tested the tensile properties presented in terms of Young's modulus, tense strength, and elongation at break according to ASTM D 638-14 with dumbbell-shaped samples. The flexural test was determined according to ASTM D 790-15 with rectangular bar-shaped samples by three-point bending method. Both the tensile and flexural properties were carried out with a universal testing machine (Model LR50K, LLOYD Instruments Co., Ltd., USA). The cross-head speed used for tensile and flexural test were 50 mm/min and 1.28 mm/min, respectively. For the impact tests, following ASTM D256-10, were tested on Izod method by Yasuda impact tester with pendulum capacity of 4 J (Yasuda Seiki Seisakusho, Ltd., Japan).

2.3.2 Flow Properties

The compounds of neat PLA, PLA/WF, PLA/TC, PLA/$CaCO_3$, PLA/MB and PLA/SiO_2 were prepared into pellet form and measured the mass of polymer melts during 10 min reported as melt flow rate (MFR). The flow test was performed by the capillary rheometer (Model 4467 – STANDARD, Instron Co., Ltd., USA) with the L/D ratio of die as 2. The test conditions were 200°C temperature with dead weight 3.2 kg.

2.3.3 Thermal Properties

The thermal properties were examined by Vicat method reported as softening point. The test was measured the temperature when the penetration of flat-end indenter through the sample with depth of 1 mm, applied force of 50 N. The initial temperature test was 30°C and the constant rate of temperature increasing was 120°C/hr.

2.3.4 Morphological Properties

The fracture surfaces of filaments and samples after impact test were investigated the dispersion of fillers and interfacial filler-polymer interaction using a scanning electron microscope (SEM) machine (Model JSM-6610, JEOL Co., Ltd., Japan) at 10kV accelerating voltage. The adhesion between the layers of 3D printed parts was also of interest.

3. Result and Discussions

3.1 Physical Properties

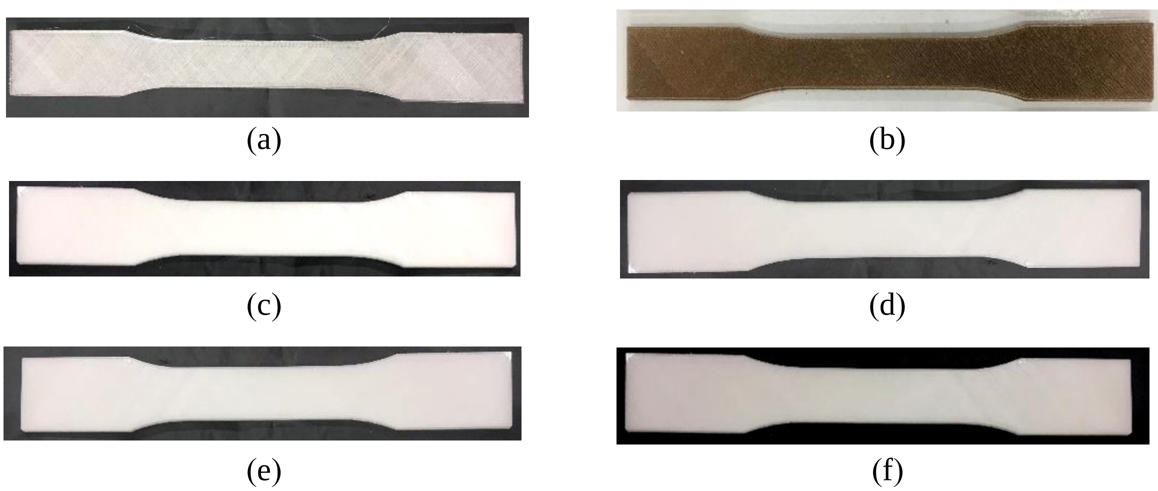

Figure 2: *The 3D printed parts of PLA composites: (a) neat PLA, (b) PLA/WF, (c) PLA/TC, (d) PLA/$CaCO_3$, (e) PLA/MB, and (f) PLA/SiO_2*

The 3D printed parts of PLA composites were illustrated in Figure 2. It was found that the 3D printed parts were completely fabricated and stable in shape during fabrication. The 3D printed composites were a difference in color and texture which were dependent on the color and physical of fillers. The PLA/TC, PLA/$CaCO_3$, PLA/MB and PLA/SiO_2 composites were a whitish, and smooth surface while the PLA/WF composites were brown and rougher surface.

3.2 Mechanical Properties

Table 2: *Tensile Properties of 3D Printed Composites*

Materials	Young's Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
Neat PLA	801.98 ± 35.12	25.47 ± 1.45	6.50 ± 1.31
PLA/WF	578.78 ± 31.07	26.91 ± 1.95	5.52 ± 0.36
PLA/TC	361.40 ± 14.45	11.00 ± 1.99	7.03 ±1.42
PLA/$CaCO_3$	466.94 ± 85.82	17.75 ± 2.28	5.94 ± 0.56
PLA/MB	768.54 ± 24.57	20.46 ± 1.22	4.96 ± 0.27
PLA/SiO_2	330.97 ± 65.55	10.95 ± 3.37	4.90 ± 1.24

Table 2 displays the tensile properties of 3D printed composites. It was found that the tensile strength of 3D printed composites seems lower compared with the neat PLA, except for the PLA/WF. The reason that the wood flour was fibrous thus it could act a reinforcement (Petchwattana & Covavisaruch, 2014), while the other fillers were irregular, platey or spherical shape. SEM micrographs of the filament-fractured surface of composites illustrate in Figure 3, it can be observed that the continuous phase of neat PLA was a smooth surface fracture while the composites show the difference of adhesion between the fillers and PLA matrix, that it was also related to tensile strength. The PLA matrix was wet on the fiber of wood flour 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 was not good tensile strength as well as PLA/WF composites due to the smooth surface and its spherical shape. The talc, calcium carbonate, and silicon dioxide were agglomerates in the PLA matrix resulting as a poor PLA-filler interaction (see Figure 3). However, the rigid spherical shape of glass microballoons affected the higher Young's modulus in PLA/MB composites compared to those of composites. The elongation at break of PLA composites reduced when adding microballoon and silicon dioxide particles.

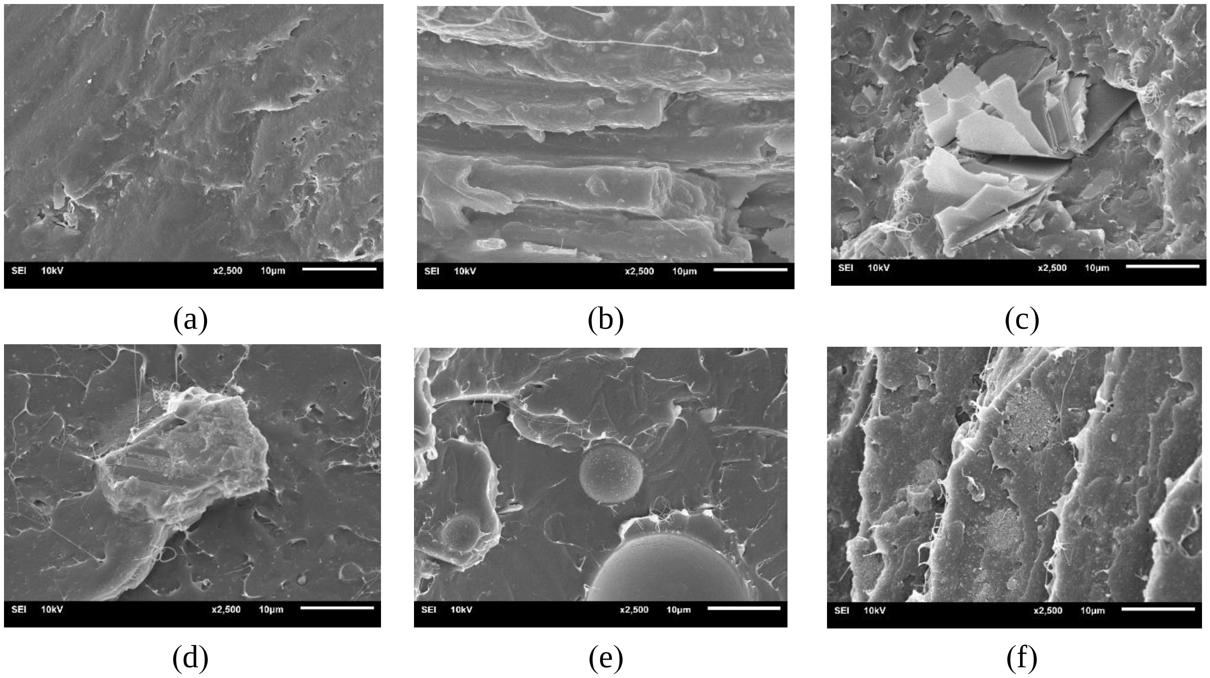

Figure 3: *SEM Micrographs of the Fractured Surface of Filament Composites: (a) neat PLA, (b) PLA/WF, (c) PLA/TC, (d) PLA/$CaCO_3$, (e) PLA/MB, and (f) PLA/SiO_2*

Figure 4 shows the flexural and impact strength of the 3D printed parts of the neat PLA and PLA composites. The flexural strength of 3D printed PLA/TC composites was greater than that of neat PLA and PLA composites. It can be explained by the cracks initiated the opposite side of loading that would be terminated by the plated of talc and then it supported the further force. The 3D printed composites had a lower impact strength than that of the neat PLA except for PLA/MB. The PLA/MB composites gave the best impact strength because the spherical shape of microballoons affected on a good distribution in the matrix, and could be supported an intermediate loading for a good force distribution in the composites (Wypych, 1999). 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 5. 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.

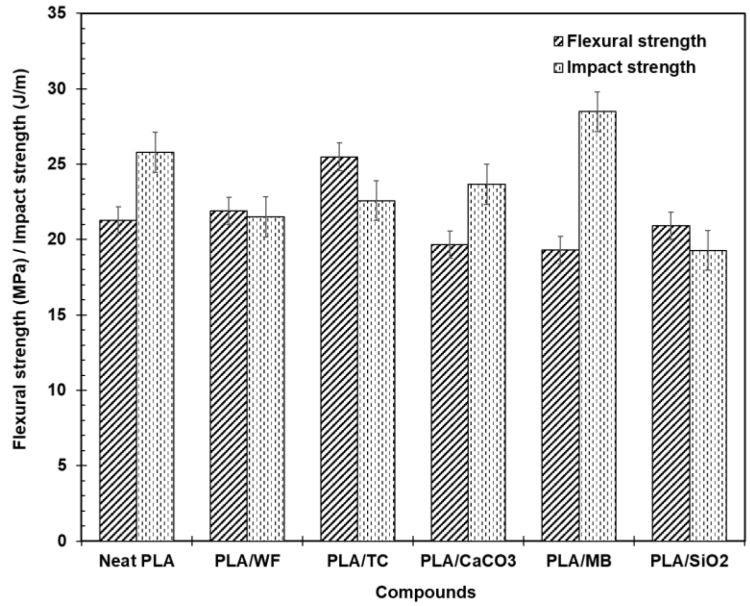

Figure 4: *Flexural and Impact Strength of Neat PLA and PLA Composites*

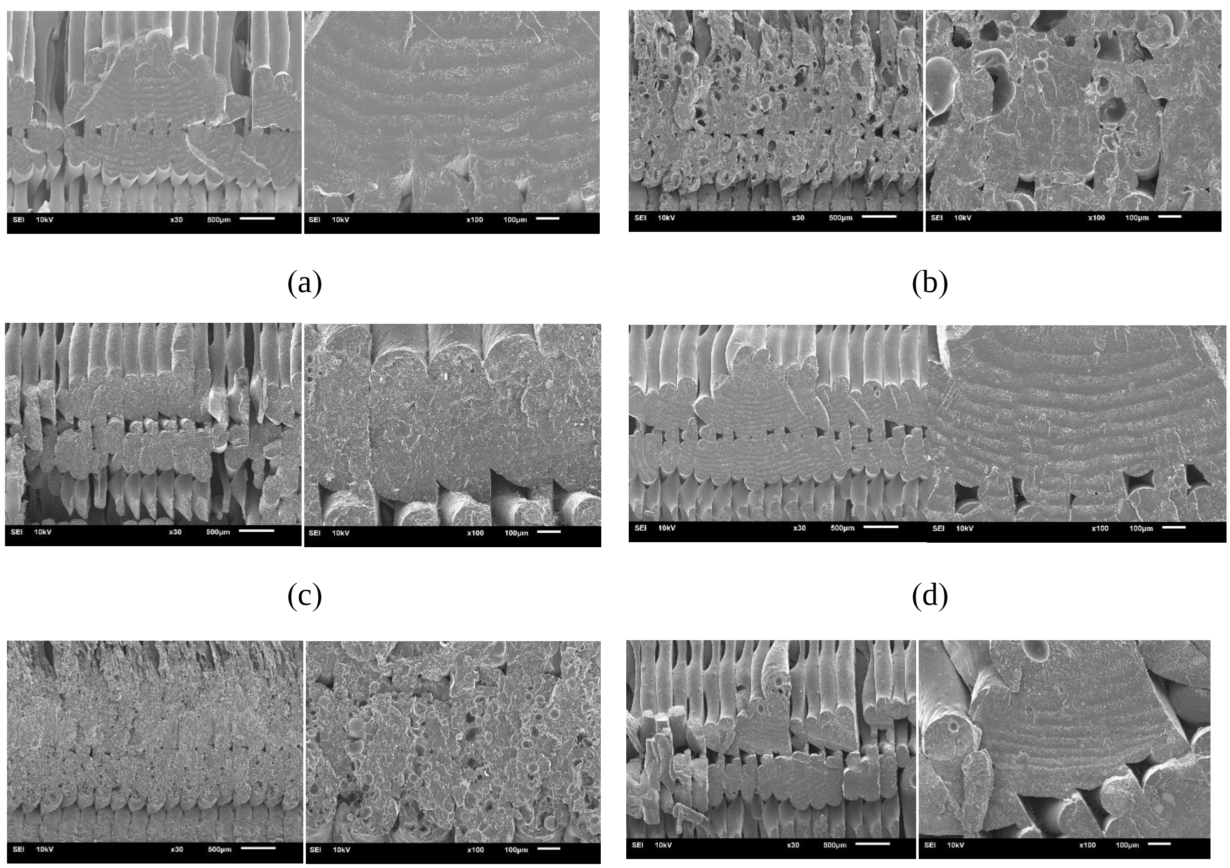

Figure 5: *SEM Micrographs of the Impact-Fractured Surface of Composites: (a) neat PLA, (b) PLA/WF, (c) PLA/TC, (d) PLA/$CaCO_3$, (e) PLA/MB, and (f) PLA/SiO_2*

3.3 Flow Properties

The melt flow rate of neat PLA and PLA composites displays in Table 3. It can be seen that the PLA/MB composites had the highest melt flow rate due to the spherical shape which could be easy to flow as reported by Liang (Liang, 2001). The result has confirmed the assumption as described earlier.

Table 3: *Melt Flow Rate of Neat PLA and PLA Composites*

Materials	Neat PLA	PLA/WF	PLA/TC	PLA/$CaCO_3$	PLA/MB	PLA/SiO_2
Melt flow rate (g/10 min)	73.7	8.4	28.8	73.2	110.24	52.8

3.4 Thermal Properties

Table 4 shows the Vicat softening point of neat PLA and PLA composites. It can be observed that the Vicat softening point of 3D printed composites was lower than that of the neat PLA except for PLA/MB. The reason was associated that the glass microballoons had the highest thermal stability as compared with those of fillers.

Table 4: *Vicat Softening Point of Neat PLA and PLA Composites*

Materials	Neat PLA	PLA/WF	PLA/TC	PLA/$CaCO_3$	PLA/MB	PLA/SiO_2
Vicat softening point (°C)	56.7	55.3	54.3	55.7	56.2	51.8

4. Conclusions

In this work, the physical, mechanical, flow, thermal and morphological properties of the 3D printed parts (i.e. neat PLA, PLA/WF, PLA/TC, PLA/$CaCO_3$, PLA/MB and PLA/SiO_2) were studied. It was found that the addition of TC and MB in PLA composites displayed the reduction of brittle behavior. The 3D printed PLA/TC composites had greater elongation and flexural strength compared to neat PLA and PLA composites because of the plated of talc that would be terminated the cracks and then it supported the further force. The PLA filled with glass microballoons gave the best impact strength, the reasons being associated with the highest melt flow rate that led to a great fusion and bonding between layers. Moreover, the TC-filled and MB-filled PLA composites were stable in shape during fabrication that was satisfied both in the manufacturing and the tough properties. For the thermal properties, the PLA slightly deteriorated

Vicat softening point when adding the fillers, except for PLA/MB. Next, we focused on the investigate the properties of PLA filled with glass microballoons for 3D printing application in the tooling holder for CNC machine. Next, we focused on investigating the friction and wear properties of 3D printed parts of PLA filled with glass microballoons for making the tool holder in the milling CNC machine.

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