Reinforcement of Polylactic acid (PLA) bio-composite with lignin from oil palm empty fruit bunches (OPEFB) for 3D printing application

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Abstract. Polylactic acid (PLA) has been used as an additive material in 3D printing due to its toxic-free and environmentally friendly property. Lignin with complex and branched chemical structures had been used as a filler to improve the mechanical strength of PLA. The availability of oil palm empty fruit bunches (OPEFB) in Malaysia had made this material a good source for lignin extraction. Thus, in this research, we aim to study the mechanical strength of PLA bio-composite material with reinforcement of lignin from OPEFB. The lignin was extracted by 1,4-dioxane with hydrochloric acid as a catalyst. The recovery of lignin from extraction solvent was done by precipitation. The lignin was successfully extracted from OPEFB with 9.04% of lignin extraction yield. The PLA/lignin bio-composite filament with 0.1% (w/w) lignin was performed by filament extruder and then used for 3D printing. The prepared sample in the form of filament and 3D printed material was characterized for mechanical strength and surface morphology. The Young’s modulus, ultimate strength and elongation at break of the PLA/lignin bio-composite sample had increased 11%, 7% and 10% respectively. After the filament was used for 3D printing, the reduction of mechanical strength had been observed. The morphology by scanning electron microscopy (SEM) confirmed the presence of lignin on the fracture surface of PLA bio-composite material. Apart from that, the interlayer adhesion had been observed in the 3D printed PLA/lignin bio-composite that caused the drop in mechanical strength of the material.

Keywords: Polylactic acid, lignin, oil palm empty fruit bunch (OPEFB), 3D printing, bio-composite material.

1. Introduction

3D printing is the construction of a physical object from additive materials with a graphical construction by using computer-aided design [1]. 3D printing, which was first invented by Charles W. Hull in 1986...
under the name stereolithography, is increasingly being used nowadays in medical applications [2]. Bone restoration, healing, and recovery are some of the medical uses of 3D printing [2]. The prototype model was constructed by the 3D printer in the manufacturing industry before going into full production [3]. Low-melting-point polymers were used as additive materials in 3D printing, including polylactic acid (PLA), polyamide (PA), acrylonitrile butadiene styrene (ABS), and polycarbonate (PC). PLA had been commonly used as an additive material because it does not caused irritation and can be used in a variety of applications [4]. Apart from that, biodegradability of PLA was also taken into consideration in material selection because of environmental concerns [4].

Liu et al. [4] had stated that PLA had a simple linear molecular chain structure microscopically. In conjunction to that, PLA had a limited mechanical strength compared to ABS, PA and PC that had a graph molecular chain [4]. This limitation could reduce the capability of using PLA as additive material in 3D printing. To improve the mechanical strength of PLA, the possible use of bio-composites materials with lignocellulose reinforcements had been studied. Furthermore, the reinforcement of complex structure lignin and cellulose from lignocellulose could modify the simple linear molecular chain of the PLA. The availability of oil palm empty fruit bunches (OPEFB) in Malaysia had triggered the selection of this raw material as a source of lignocellulose extraction [5]. In comparison to the cellulose, lignin is the best lignocellulose portion to be reinforced into PLA. The crystallinity of cellulose can help in increasing the storage modulus of the polymer and improve its mechanical strength [6]. However, owing to its hydrophobicity, PLA can mix homogeneously with lignin but not with cellulose. During the mixing and blending phase with PLA, hydrophilic cellulose appears to have poor dispersion and clump together [7].

1,4-dioxane had been selected as extraction solvent to extract the lignin from OPEFB. Different from sodium hydroxide (alkaline solvent) and ethanol, 1,4-dioxane could extract lignin with minor modification and was nearly similar towards the native structure of lignin [8][9]. This study will cover the reinforcement of dioxane lignin from OPEFB into PLA for 3D printing. Also, the comparative study of mechanical strength will be covered in the filament and 3D printed PLA/lignin bio-composite material.

2. Experimental

2.1. Material

OPEFB used in this study obtained from Tennamaram Palm Oil Mill, Batang Berjuntai. Absolute undenatured ethanol >99.8% (AR grade) purchased from Sciefex and benzene (AR grade) purchased from R&M chemical had been used for the pre-treatment of OPEFB. 1,4-dioxane (AR grade) as extraction solvent was purchased from Acros Organics with the addition of hydrochloric acid as acid catalyst purchased from Bendosen. Sodium sulfate anhydrous (AR grade) from Systerm had been used during lignin recovery. PLA granules used for PLA/lignin bio-composite preparation were supplied from NatureWorks (USA) Ingeo with grade 2003D.

2.2. Lignin extraction

The soil in OPEFB fiber was removed by washing with flowing tap water and drying in an oven at 80°C. Crushers and grinders were used to reduce the size of the dried OPEFB fiber. The water-soluble extractives were removed using cold distilled water for 8 hours, filtered, and dried overnight in an oven at 80°C. The steps were repeated by using cold ethanol-benzene mixture (1:2 (v/v)) to remove water-insoluble extractive in the OPEFB. Lignin was extracted for 90 minutes in an N2 atmosphere using a 1,4-dioxane solution as extraction solvent and 0.3M HCl concentration as an acid catalyst. The liquid fraction (filtrate) was concentrated at 40°C with reducing pressure using a rotatory vacuum evaporator. After that, 1% (w/v) Na2SO4 was added into the condensed liquid fraction in a ratio of 7:1 (v/v), followed by filtration using a Buchner funnel with water as a washing medium. The extracted lignin was dried in an oven at 40°C until it reached a constant weight. Finally, the extracted lignin was purified by washing...
and rinsing with diethyl ether and dried. The dried lignin was transformed into lignin powder by using the grinder. Equation (1) was used to measure the lignin extraction yield from OPEFB.

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\text{Lignin yield (\%) = \frac{\text{Extracted lignin (g)}}{\text{OPEFB dry weight (g)}} \times 100\%}
\] (1)

2.3. Preparation of PLA/lignin bio-composite sample

The PLA and PLA/lignin bio-composite samples were prepared in filament and 3D printed form. 100g of PLA was mixed with 0.1g of extracted lignin powder before inserted into the feeder in the Filabot FB00655 EX6 filament extruder. The temperature used was 40°C at feed, 180°C at back, 190°C at the middle, and 170°C at front of the filament extruder. The extruded filament was cooled by a cooling fan with a 75% speed and the filament diameter was adjusted to be in average of 1.75mm. The filament was 3D printed by using Creality Ender-3 Pro 3D printer at nozzle temperature of 225°C and bed temperature of 70°C. The sample was sliced by Cura software with 100% infill and line infill pattern.

2.4. Characterization

2.4.1. Universal Test Machine (UTM). Young’s modulus (MPa), ultimate tensile strength (MPa), and elongation at break (%) of the samples obtained from Universal Testing Machine (UTM) (Shimadzu, AGS-X, Japan). Filament samples were tested with crosshead speed 2.5 mm/min, load cell of 5 kN, and 25mm gauge length. 3D printed samples were prepared according to ASTM D-638 type-I with crosshead speed 50 mm/min, load cell of 5 kN, and 57mm gauge length. The samples were repeated 3 times for an average value.

2.4.2. Scanning Electron Microscope (SEM). The fracture surface of the PLA and PLA/lignin bio-composite from mechanical test was investigated using Scanning Electron Microscopy (JEOL, JSM-5600, UK). The samples were coated with palladium sputter and observed at a magnification of x50, x500, and x1500 with 7 kV accelerating voltage.

3. Result and discussion

3.1. Lignin extraction yield

1.13g of lignin was extracted from 12.5g of OPEFB by using 1,4-dioxane as extraction solvent. Based on equation (1), the lignin extraction yield of 9.04% was extracted from the OPEFB. With comparison from the study by Saha et al. [10], the extraction of lignin by using 1,4-dioxane from debarked bamboo waste achieved 15% yield. The difference in the extraction yield was due to the different type of lignocellulose biomass used for lignin extraction. Different type of biomass could extract different quality of the extracted lignin [11]. Apart from that, lignin extraction method was another factor that affect the lignin extraction yield. The lignin extraction yield from OPEFB from previous study by using sodium hydroxide (alkaline treatment) was 15% and ethanol solution (organosolv treatment) was 13% [12][13]. Each extraction method had provided different structural of lignin that could be used for their application [8]. Despite that, the mechanisms of extraction for each treatment was quite similar. β-O-4 linkage was one of the types of lignin linkage that became the critical steps in depolymerize lignin in lignocellulose biomass [14].

3.2. Universal Test Machine (UTM)

Figure 1, figure 2 and figure 3 showed the reinforcement of lignin changed the mechanical strength of the filament and 3D printed samples in terms of the Young’s modulus (MPa), ultimate tensile strength (MPa) and elongation at break (%). Overall, the filament and the 3D printed sample had shown a different value because the samples were tested in different sizes and dimensions. After the reinforcement of lignin, Young’s modulus increased from 238.58 MPa to 263.02 MPa for the filament and decreased from 1848 MPa to 1797 MPa for the 3D printed sample (figure 1). In figure 2, the ultimate
tensile strength of the PLA filament also increased with lignin reinforcement from 15.83 MPa to 16.95 MPa (figure 2(a)). However, when the filament was used for 3D printing, the ultimate tensile strength of PLA/lignin bio-composite had decreased from 68.27 MPa to 61.24 MPa (figure 2(b)). A similar finding also had been obtained from a previous study, where the reinforcement of lignin had reduced the Young’s modulus and ultimate tensile strength of the 3D printed PLA/lignin bio-composite [15]. From figure 3, a slight change with no major difference on elongation at break when the lignin was introduced into the PLA. The value increased from 7.27% to 8.00% for filament and decreased from 6.12% to 5.68% for the 3D printed sample.

The reinforcement of lignin was proved to increase the mechanical strength of the PLA. Even with 0.1% (w/w) lignin reinforcement, Young's modulus, ultimate strength, and elongation at break of the PLA/lignin bio-composite filament had all increased by 11%, 7%, and 10%. Theoretically, the lignin filler had changed the molecular structure of PLA into branched polymer and increased its mechanical strength. During the extrusion, the terminal COOH group of PLA reacts with the phenolic and aliphatic
hydroxyl (OH) group of lignin by chemical bonding [16]. The intermolecular of lignin-lignin, PLA-PLA, and PLA-lignin had influenced the tensile strength in PLA/lignin bio-composite [17]. The influence of lignin filler within PLA matrix will be explained further with SEM morphology. As the filament was used for 3D printing, the drops in mechanical strength was observed. This was due to the poor interlayer adhesion between the layer during 3D printing [15]. The relationship between viscosity, crystallize temperature and crystallization phase had played a major role for a good interlayer adhesion in 3D printing process [18].

| (a) Elongation at break of PLA and PLA/lignin filament | (b) Elongation at break of 3D printed PLA and PLA/lignin |
|---|---|
| ![Figure 3](image_url) | ![Figure 3](image_url) |

**Figure 3.** Elongation at break of PLA and PLA/lignin bio-composite in form of (a) filament and (b) 3D printed.

### 3.3. Scanning Electron Microscope (SEM)

Figure 4(a) and figure 4(b) showed the fracture surface of the PLA filament and PLA/lignin bio-composite filament from the SEM observation respectively. Results indicated that both samples had shown brittle fracture with a little plastic deformation. Figure 4(c) showed the presence of lignin that acted as rigid filler in increasing the mechanical strength of lignin [17]. Similar lignin morphology observed by [16], where the presence of cavities was also observed between the lignin and PLA in the composites. In resisting the stress during tensile test, some of the lignin had been pulled out from the sample and left a lignin pore as observed in figure 4 (d).

With little plastic deformation, the 3D printed PLA (figure 4 (e)) and 3D printed PLA/lignin bio-composite (figure 4 (f)) also had shown the brittle fracture during tensile test. However, a poor interlayer adhesion in 3D printed PLA/lignin bio-composite was observed within its structure compare to 3D printed PLA. The poor interlayer adhesion was related to the decreasing in Young’s modulus, ultimate tensile strength and elongation at break of the 3D printed PLA/lignin bio-composite. Similar observation also had been found in the previous study, where the reinforcement of lignin could cause poor interlayer adhesion for 3D printed samples [15]. Triangular void observed in the figure 4(g) in 3D printed PLA/lignin bio-composite also caused from the poor interlayer adhesion [18]. To have a better interlayer adhesion, the nozzle and bed temperature during the printing should be adjusted in the future study. Since the reinforced lignin was only 0.1% (w/w) concentration, it was hardly observed under SEM. However, similar lignin pore was observed in figure 4(h) that resulted from the pulled-out lignin.
Figure 4. SEM micrograph at fracture surface of (a) PLA filament at x100, (b) PLA/lignin bio-composite filament at x100, (c)(d) PLA/lignin bio-composite filament at x1500, (e) 3D printed PLA bio-composite at x50, (f) 3D printed PLA/lignin bio-composite x50 and (g)(h) 3D printed PLA/lignin bio-composite at x500
4. Conclusion

Lignin had been successfully extracted from OPEFB by using 1,4-dioxane with an extraction yield of 9.04%. In this study, the reinforcement of lignin was proved to increase the Young’s modulus, ultimate tensile strength and elongation at break by 11%, 7% and 10%. Although with only 0.1% of lignin reinforcement, the SEM micrograph observed the reinforced lignin supporting PLA/bio-composite filament on the fracture region. However, further studies are needed for this PLA/lignin bio-composite filament to be used in the 3D printing application. This was due to the decreasing in mechanical strength caused by the poor interlayer adhesion of the 3D printed PLA/lignin bio-composite. Also, optimized lignin composition with a perfect printing temperature was another factor that should be considered in future studies.

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