Poly(Lactic) Acid Reinforced with Alkaline Lignin Biocomposites Prepared by Thermal Extrusion for Sustainable 3D Printing Process

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Abstract. The focus of this work is the mechanical characterization of biomaterials produced by 3D printing based on fused filament fabrication (FFF) process that has been mainly used for prototype rather than functional components due to the limited mechanical properties of pure thermoplastics parts. Addition of reinforcements from natural fiber has been adopted to improve the mechanical properties of the 3D printed parts. In this study, alkaline lignin powder that has been extracted from oil palm empty fruit bunches (OPEFB) via alkaline extraction process were used as filler in the production of biocomposites with poly(lactic) acid (PLA). Poly(lactic) acid filaments filled with 1% of alkaline lignin powder and has been compared with the presence of 5% of epoxidized palm oil (EPO) by means of thermal extrusion and further proceed with 3D printing. The samples were mechanically characterized using tensile tests and the fractography were observed. Tensile test that has been done on the filaments reveal that the filament with addition of lignin and EPO shows improved mechanical properties with higher tensile strength as well as lower stiffness. The 3D printed samples of the filament compositions also exhibit similar trend where the said filament has the best mechanical properties when the EPO is incorporated in the filament.

1. Introduction

3D printing is an established technology for shape prototyping which is gaining ground in the production of functional components [1]. Fused filament fabrication (FFF) is a promising additive manufacturing (AM) technology due to its ability to build thermoplastics parts with advantages in the design and optimization of models with complex geometries, great design flexibility, recyclability and low material waste [2]. Common and not expensive printing materials are the polymers ABS (acrylonitrile butadiene styrene) and PLA (polylactic acid). Other polymers employed in FFF are the PETG (polyethylene terephthalate glycol-modified), Nylon (a kind of polyamide), PEEK (polyether ether ketone) and PEI...
(polyethylenimine), each one with particular capabilities [3]. Despite the variety of printing polymers available, their mechanical properties of stiffness and strength are naturally low. Moreover, the FFF process generates void spaces between material deposition lines, which even lowers those properties, also limiting the applicability of printed components [4]. In order to broaden the capabilities of FFF materials, research on polymer matrix reinforced composites for 3D printing has recently grown [5]. This paper to study the behavior of PLA biofilaments filled with lignin powder. The addition of lignin powder was expected to improve the mechanical and thermal properties of the PLA composite. Thus, the PLA filled with lignin powder filaments were using thermal extrusion and the mechanical properties were compared with the printed samples. Other than that, the filaments properties also were observed based on the fractography after the tensile test.

2. Methodology

2.1 Materials
Polylactic acid (PLA) 2003D in the form of pellets was supplied by NatureWorks Co. Ltd. Alkaline lignin powder was extracted from oil palm empty fruit bunches via alkaline extraction process using sodium hydroxide (NaOH) as cooling liquor and sulphuric acid (H2SO4). Thermal extrusion used in this study is FILABOT EX6 EXTRUDER. The 3D printer used for fabricating samples is RAISE 3D PRO2.

2.2 Sample Preparation
The PLA pellets that have been oven dried at 60°C for at least 3 hours were mixed with alkaline lignin powder at weight fraction of 1%. Three different filament compositions have been done (neat PLA (PLA), 1% of alkaline lignin powder with 5% EPO (PLAE1) and 1% of alkaline lignin without addition of EPO (PLAL1)). These mixtures were then proceeded to be extruded using the FILABOT EX6 EXTRUDER with fixed temperature of front, middle, back and feet of 180°C, 190°C, 180°C and 50°C respectively until a spoon of filament with diameter of 1.75mm was produced. The obtained filament was then kept in oven at 40°C to ensure the moisture removal before applied in 3D printer.

2.3 Tensile Test
Tensile test was executed in accordance to Bade et al. (2015) on the all of the filaments using a universal material testing machine, Shimadzu Autograph AGS-X series with crosshead speed of 2.5 mm/min. one set of five filament samples with 25 mm of gauge length were prepared and tested for the strength analysis. The dogbone printed samples of PLA, PLAE1 and PLAL1 were done following the standard tensile test ASTM D638 specimen type 1.

2.4 Scanning Electron Microscopy (SEM)
The fractography of the filaments after tensile test were observed using scanning electron microscope (SEM) JSM 5600. The surfaces of the samples have been sputter coated using Palladium to give conductive property. The images were taken at accelerating voltage of 6.0 kV with different magnification values.
3. Result and Discussion

3.1 Mechanical Properties of Filaments

The effect of lignin powder on the tensile strength, tensile strain and tensile modulus of PLA biocomposites at with addition of lignin powder were shown in Fig. 1 (a), (b) and (c). The results reveal that the addition of lignin at 1% increases the tensile strength from 111.08 MPa of neat PLA to 120.70 MPa and 119.80 MPa for both filaments with and without EPO respectively. This result was supposed to be related to the special chemical structure of lignin, bearing a lot of functional groups (carbonyl, phenolic or aliphatic hydroxyls, carboxyl), which intensively contributed to the interactions such as hydrogen bonding between PLA matrix and lignin powder [6]. Other than that, PLAE1 shows excellent result of tensile strain as well as tensile modulus as depicted in Fig. 1 (b) and (c). higher value of tensile strain would commonly result with the addition of EPO that give the plasticizing effect compared to the PLAL1 that has very low value of tensile strain [7] The tensile modulus of PLAE1 on the other hand, was not have significant increases showing that PLA added with lignin powder and plasticizer has good stiffness value with higher ductility compared to the PLAL1.

![Figure 1 (a). Tensile strength of PLA, PLAE1 and PLAL1.](image1)

![Figure 1 (b). Tensile strain of PLA, PLAE1 and PLAL1.](image2)
3.2 Mechanical Properties of 3D Printed Samples

Other than that, the mechanical properties of the 3D printed samples of PLA, PLAE1 and PLAL1 also were done to observe their tensile strength, tensile strain and tensile modulus as shown in Fig 2 (a), (b) and (c) respectively. It can be observed that the PLA with addition of 1% lignin powder had an increment in tensile strength from 70.36 MPa to 98.88 MPa and 50.98 MPa with addition of 5% EPO and without addition of EPO respectively in Fig. 2 (a). This trend is similar with the result of filament where addition of lignin and EPO as plasticizer give the best mechanical properties to the samples. Fig. 2 (b) and (c) reveals that PLAE1 filament obtained good mechanical properties surpassing the properties of neat PLA with absence of lignin powder. The plasticizer on the other hand helps to reduce the stiffness of the neat PLA from 4705.54 MPa to 1382.67 MPa which is crucial to ensure that the samples are not brittle hence preventing catastrophic failure.

Figure 1 (c). Tensile modulus of PLA, PLAE1 and PLAL1.

Figure 2 (a). Tensile strength of 3D printed dogbone PLA, PLAE1 and PLAL1.
3.3 Scanning Electron Microscopy (SEM)

The morphological investigations have been carried out by scanning electron microscope, examining the surface of the extruded samples. The morphologies of the neat PLA polymer and the other filaments with addition of 1% lignin powder with and without EPO have been conducted, shown in Fig. 3 (a), (b), (c), (d), (e) and (f). SEM analysis is very important to understand the miscibility and compatibility of the PLA-lignin composite and their effect on the properties of materials. At magnification of 50x, it is possible to see the round shape of filament cross section with diameter of 1.75mm. Fig.3 (a) and (b) of neat PLA filament has obvious brittle fracture with the rough surface and existence of cleavage at the cross section. Fig. 3 (c) of PLAE1 filament on the other hand show ductile characteristic with the presence smoother surface revealing the sample has fragile fracture. The lignin powder on the surface may occur while tested by tensile load applied perpendicularly to the material deposition direction. This condition had occurred not because of poor miscibility as there were no gaps or voids found surrounding the lignin powder. Other than that, Fig. 3 (d) of PLAE1 filament shows the occurrence of oily marks that is incorporated with the EPO that has been added as plasticizer that also proves the excellent mechanical properties of this filament especially on the high tensile strength and lower stiffness. Finally, Fig. 3 (d) and (e) reveal brittle behavior as the cross section show rough surface, quite similar with the neat PLA. The milky patches on the surface also mostly found on the PLA matrix.
Figure 3. SEM micrograph of (a) neat PLA filament at 50x magnification, (b) neat PLA filament at 500x magnification, (c) PLAE1 filament at 50x magnification, (d) PLAE1 filament at 500x magnification, (e) PLAL1 filament at 50x magnification and (f) PLAL1 filament at 500x magnification.

4. Conclusions
The biofilaments have been produced using PLA and reinforced with alkaline lignin powder extracted from oil palm empty fruit bunches (OPEFB) using extrusion machine. The application of 3D printing on higher strength application is getting more attention these days as it is considered as sustainable approach in manufacturing field. PLA, as commonly used thermoplastic polymer in 3D printing is highly used as filament material due to its degradability and renewability other than its ease of processing lower
temperature. The low mechanical properties of PLA especially high brittleness had limited its application hence, the addition of natural fiber as reinforcements were considered as a good solution that increase its sustainability property. This study had proven the improvement of PLA filament mechanical properties with addition of alkaline lignin powder and presence of EPO as plasticizer. PLA filament without EPO has been found to have very high stiffness which is the attribute that is not likable in higher strength applications.

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