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MECHANICAL AND THERMAL PROPERTIES OF POLYLACTIC ACID FILLED LIGNIN POWDER BIOCOMPOSITE FILAMENTS WITH EPOXIDIZED PALM OIL FOR SUSTAINABLE 3D PRINTING APPLICATION

Nurul Amirah Abd Rahman[1], Hazleen Anuar[1*], Nurfarahin Mohd. Nordin[1], Syazeven Effatin Azma Mohd Asri[1], Fathilah Ali[2], Jonghwan Suhr[3]

[1]Department of Manufacturing and Materials Engineering, Kulliyyah of Engineering, International Islamic University Malaysia, Jalan Gombak, 53100, Kuala Lumpur, Malaysia.
[2]Department of Biotechnology Engineering, Kulliyyah of Engineering, International Islamic University Malaysia, Jalan Gombak, 53100, Kuala Lumpur, Malaysia.
[3]Faculty of Mechanical Engineering, College of Engineering, Sungkyunkwan University, Natural Sciences Campus 2066, Seobu-ro, Jangan-gu, Suwon, Gyeonggi-do, 16419, Korea

* Corresponding author: hazleen@iium.edu.my

ABSTRACT

Initiative have been taken to study the effect of lignin powder and epoxidized alm oil (EPO) on polylactic acid (PLA). Since lignin is a very abundant by product with a cheap cost, using it in any value-added application would result in a significant economic benefit. EPO is a well-known plasticizer in polymer studies and the addition effect of EPO into this composite is look upon. The aim of this study is to fabricate polylactic acid (PLA) filled with lignin powder and EPO biocomposite filaments for 3D printing application based on the fused deposition modelling (FDM) process. The renewability property of the PLA has been the main consideration as sustainable approach in this work. Nonetheless, the high brittleness of PLA had limited its fitness especially in the application that requires higher strength, hence the addition of lignin as reinforcements have been implemented in this study to overcome this problem. The lignin has been extracted from the oil palm empty fruit bunches (OPEFB) fiber via alkaline extraction process and was added at different weight percent into PLA using thermal extrusion. Epoxidized palm oil (EPO) was also added at a constant weight percent for all filaments. The mechanical, thermal, and functional characterizations of the filaments have been done and compared with the neat PLA. The mechanical properties had shown the optimized properties comes from PLAE1, where addition of EPO had reduced the brittleness of PLA. Thermal studies conducted on these filaments also shows excellent thermal stability of PLAE1 with higher degradation temperature other than good miscibility of PLA and lignin.

***Keywords**: PLA, lignin, EPO, filament, 3D printing, extrusion*

1.0 INTRODUCTION

The global demand on energy, chemicals, and materials continues to increase as the world population expands. There are two major global challenges that prompt research on

renewable resources, growing sustainability and environmental-friendly, it is the depletion of petroleum- based reserves and climate change [1]. With growing concern about the negative environmental and social consequences of petrochemicals, as well as finite fossil resources, there is a growing interest in utilising natural biomass as raw materials for chemical, polymer, and material development [2], [3].

It is worth mentioning that sustainable polymers are not always biodegradable. There are two primary types of sustainable polymers: Natural polymers and synthetic bio-based polymers. Examples of naturals polymers are lignin, cellulose, hemicellulose, protein, starch and modified biopolymers, these natural polymers have been extensively used as bioplastic, composite and other applications [4]. As for synthetic bio-based polymers, such as amino acids, fatty acid, plant oils, terpenes and rosin acids, they were developed from various molecular biomass [5].

In [6] work, they highlight three areas that crucial for sustainability: (1) lignin, (2) bio-based polyolefins and (3) long chain aliphatic polycondensates. Lignin is among the highlighted area, there are enormous potentials and advantages in converting lignin into polymers. It is not only the second most abundant biomass, but also one of the most difficult to manage due to its complexities.

Lignin is considered as a waste product in several industrial processes, which make it ranking as second place in natural abundance [7]. It is predicted that around 300 billion tonnes of lignin are present in the biosphere, with around 20 billion tonnes biosynthesized globally each year. Lignin valorisation have been strived and published in large numbers of reviews and papers over the past years [8]. Lignin known as three-dimensional polymeric networking agent contribute structural support towards cell walls. Although lignin is a difficult substrate to breakdown, some microorganism, such as white-rot fungus, may digest lignin, increasing the creation of soil organic matter and therefore making lignin a biodegradable natural polymer [9].

Lignin can be used as a component in biocomposite, depending on the target application [10]. The availability, low cost, and biodegradability of lignin, as well as its high carbon content, aromaticity, and reinforcing ability, make it a good candidate as a possible component for biocomposites [11]. Lignin can be directly incorporated into the polymeric matrix without modification to inject few properties such as UV-light stabilizer, antioxidant, flame retardant and flow enhancer to reduce the production cost, reduce plastic, and potentially improve material properties [12]. Researchers have developed a polymer composites-based natural fibre in response to the question of environmental sustainability. There has been a lot of studies done on the properties of thermoplastic materials so far [13]. It is reported that the incorporation of lignin into PLA has improved PLA properties[14]. Lignin own high number of reactive functional groups, high carbon content, strong stability, and outstanding mechanical characteristics as a result of the presence of aromatic rings [15], because of their aromatic structure and the presence of phenol residues, lignin has a wide range of functions, including compatibilizers, hydrophobizing agents, flame retardants, optical modifiers, and stabilisers . Lignin was mentioned improved interfacial adhesion between COOH-lignin surface and PLA matrix through hydrogen bonding. the tensile

strength [16]. On its surface, lignin own some hydroxyl, carbonyl, carboxyl, and methyl groups, which make it a good choice for bio-based polymeric composites. These can then be used to change properties including hydrophobicity, hardness, and crystallinity in materials [17].

Additive manufacturing (AM), also known as three-dimensional (3D) printing, is an emerging technology in our world. It has recently piqued the interest of numerous industries and academic societies due to its enormous ability to change existing manufacturing processes in a cost-effective and productive manner, as well as to produce radically and conceptually new developed products [18]. A vast study has been done to produce a biodegradable 3D printing filament to fit the specific application [19]. Due to hydrolysis, lactide reformation, oxidative main chain scission, and inter- or intramolecular transesterification reactions, which may be affected by lignin surface and degraded molecules, PLA blends have been found to undergoes thermal degradation at temperatures above 200^{o}C due to mentioned occurrences [20].

As biodegradable thermoplastics make inroads into the market of filaments for fused deposition modelling (FDM) 3D printing, natural fibre fillers are becoming more popular. They have the distinct advantage of being less expensive while maintaining the filament biodegradability. Among the many benefits of FDM, there are several pitfalls that are inextricably tied to this technology, for example, the filament temperature has a significant impact on the viscosity of the molten filament [21]. This must not be too high in order to allow easy flow through the nozzle orifice, but it must also not be too low in order for the deposed filament to provide adequate structural support for the subsequent layers [22].

To overcome this, the combination of PLA/lignin/EPO as biocomposite has become an interesting idea. In this work, we are focusing on making PLA/lignin/EPO biocomposite as 3D printing filament based on the FDM process. The renewability property of the PLA has been the main consideration as sustainable approach in this work.

2.0 MATERIALS AND METHODS

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 (H_2SO_4) for precipitation. Epoxidized palm oil (EPO) (density of 0.886 g/mL with oxirane oxygen content of 2.84) was obtained from Budi Oil Enterprise Sdn Bhd, Telok Gong, Port Klang, Selangor, Malaysia.

2.2 Methods

2.2.1 Sample Preparation

The PLA pellets that have been oven dried at 60 °C for 3 h to remove the moisture prior to mixing with alkaline lignin powder at different weight fractions (1-5 phr). The composition

of PLA/lignin/EPO biocomposite filament is shown in Table 1. The mixtures were then proceeded to be extruded using the FILABOT EX6 Extruder with fixed temperature of front, middle, back and feed of 180 °C, 190 °C, 180 °C and 50 °C respectively. The extruded filaments were wounded using FILABOT spooler that passed through the FILABOT airpath as cooling mechanism until a spool of filament with diameter of 1.75 mm was produced. The obtained filaments were then placed in a desiccator with 0% relative humidity (RH) until further steps of characterization.

Table 1 Composition of the PLA/lignin/EPO biocomposite filament

Material Designation	PLA (phr)	Lignin (phr)	EPO (phr)
PLA	100	-	-
PLAL1	100	1	-
PLAE1	100	1	5
PLAE2	100	2	5
PLAE3	100	3	5
PLAE4	100	4	5
PLAE5	100	5	5

2.2.2 Sample Analysis

2.2.2.1 Tensile Test

Tensile test was executed on all of the filaments using a universal material testing machine, Shimadzu Autograph AGS-X series with a crosshead speed of 2.5 mm/min with a 5 kN load cell. A set of five filament samples with 25 mm of gauge length were prepared and tested for each filament compositions to measure the tensile strength, Young's modulus and tensile strain at break of the composites at room temperature (25 ± 2°C) and 50 ± 5% relative humidity.

2.2.2.2 Scanning Electron Microscopy (SEM)

The morphology of the filaments sample after tensile test were observed using a scanning electron microscope (SEM) JSM 5600. The tensile fracture surface was cut into smaller pieces and used as the samples. The specimens were mounted on aluminium stubs before being placed in the specimen chamber. The surfaces of the samples have been sputter coated using Palladium to give conductive property. The images were taken at accelerating voltage of 8.0 kV with different magnification values of 50x and 250x.

2.2.2.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) of all filaments were performed using a Perkin Elmer thermogravimetric analyzer (TGA4000). The temperature ranged from 30 °C to 600 °C with

a heating rate of 10° C/min under nitrogen atmosphere to examine the thermal degradation behavior. The weight loss rate was obtained from derivative thermogravimetric (DTG) data. Temperatures of maximum degradation rate (T_{max}) were also collected from maxima of DTG peaks, along with the residual weight percent measured at 600 °C.

2.2.2.4 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was carried out using a Mettler Toledo DSC equipment to obtain the glass transition (T_g), melting (T_m), and cold crystallization (T_{cc}) temperatures. Samples about 5 mg to 10 mg were analyzed under nitrogen atmosphere that consists of three steps. First, the samples were heated from 30 °C to 200 °C with a heating rate of 10 °C /min and were held at this temperature for 3 min to eliminate the thermal history of the samples as well as to remove interferences due to moisture. Next, the filaments were cooled from 200 °C to 30 °C at a cooling rate of 10 °C/min and held at 30 °C for 3 min. Finally, the samples were reheated to 200 °C at 10 °C /min.

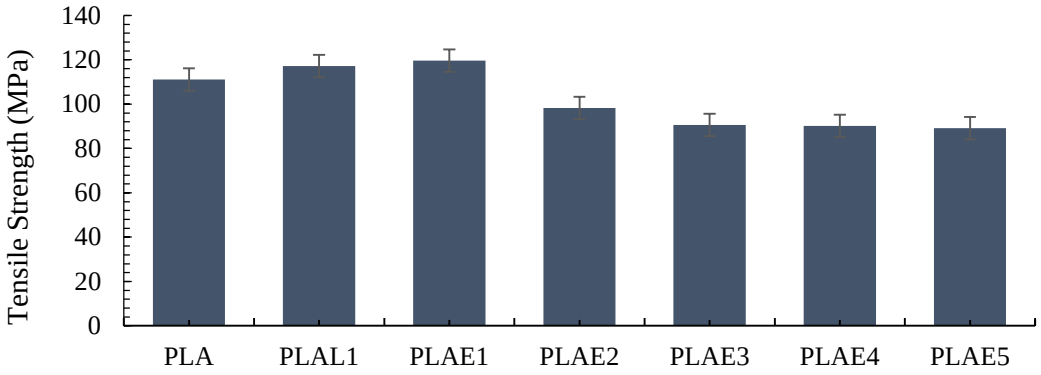
2.2.2.5 Fourier Transform Infrared Spectroscopy (FTIR)

The functional groups of the filaments were analyzed using FTIR spectroscopy under resolutions of 4 cm^{-1} with spectral range of wavenumber of 4000 cm^{-1} to 700 cm^{-1}.

3.0 RESULTS AND DISCUSSIONS

3.1. Tensile Test

The effect of lignin loading on mechanical properties of PLA filaments have been analyzed by conducting tensile test. The changes of neat PLA filament tensile strength compared to other PLA-lignin filaments were depicted as in Figure 1 (a). The addition of lignin in the PLA filament reveals improvement of the mechanical properties, where the highest tensile strength has been shown with the addition of 1% lignin (PLAL1) of 117.2 MPa. However, with addition of EPO as plasticizer, it can be observed that the tensile strength is slightly higher of around 119.7 MPa as depicted by PLAE1. This may occur due to hydrogen bonding of hydroxyl group in PLA matrix and lignin powder as well as in the epoxy group of EPO [23]. Nonetheless, the tensile strength of the PLA-lignin composite at higher lignin loading of more than 1% on the other hand, shows decrement.



Biocomposite Filament

Figure 1(a) Tensile strength of biocomposite filaments

Decrease of mechanical strength with addition of lignin as filler takes place due to agglomeration, poor dispersion of reinforcements as well as due to existence of voids between the lignin and PLA matrix [24]. The aggregation or agglomeration and poor dispersion of lignin can be observed in the Figure 3 (g), causing reduce in the mechanical properties that can be observed in the PLAE5 filament, where the composition of lignin is highest of 5%. Meanwhile, voids can be observed in the filaments with higher lignin load of more than 2% as depicted in Figure 3(d), (e) and (f) that also had reduced the tensile strength of filament with higher lignin load.

Other than that, the effect of adding lignin on the tensile strain at break of PLA filaments can be observed as in Figure 1 (b). Neat PLA has 5.58% of strain under tensile load. Generally, it can be observed that addition of different lignin load in the filament causes various effect on the tensile strain at break. The highest tensile strain at break of 5.96% was given by PLAE1 that has 1% of lignin loading and 5% of EPO. It also shall be noted that the addition the same amount of 1% lignin powder in the filament without EPO gives contradict result of decreasing tensile strain at break with only 4.93%. Other than that, there is notable decrement of tensile strain for higher lignin load of more than 1% in the filaments.

The higher tensile strain at break of PLA-lignin filament with addition of EPO as plasticizer is due to interaction of hydrogen bond between these two components, which can be explained by epoxy content in the epoxidized oil used. Hence, addition of EPO will increase the tensile strain at break as shown by PLAE1, compared to PLAL1 that was not added with EPO [25]. Even though the addition of lignin was able to improve the tensile strain at break as shown by PLAE1, there is limitation of amount of lignin that can be added in the composite. In this study, higher lignin load of more than 3% in the filaments causes decrement in tensile strain. This may highly corresponded to the aggregation of lignin in the PLA matrix, as shown in Figure 3 (g). This behavior can also be related with the large aspect ratio of the filler and the interaction between lignin and the matrix, which restricts the movement of the PLA chains [26].

Figure 1 (b) Tensile strain at break of biocomposite filaments

Finally, Figure 1 (c) shows the effect of lignin powder on the Young's modulus of the biocomposite filaments at different compositions. From Figure 1 (c), overall, it can be observed that PLA filament with addition of lignin possessed higher Young's modulus compared to neat PLA filament. This attribute is expected due to the presence of lignin that has restricted the formation of long range continuous phase of PLA that has been similarly found in the study of [27]. Other than that, it is obvious that the PLA-lignin filament with the absence of EPO (PLAL1) conveyed the highest stiffness, due to highest Young's modulus. The highest stiffness resulted with addition of 1 wt% lignin without EPO (PLAL1) at 4472.7 MPa compared to neat PLA of 3481.7 MPa

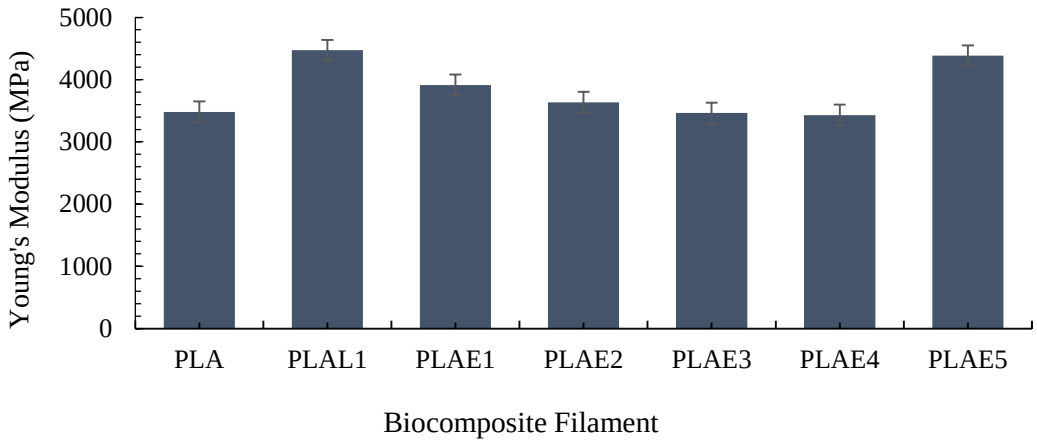


Figure 1 (c) Young's modulus of biocomposite filaments

3.2. Scanning Electron Microscopy (SEM)

Figure 2 presents the SEM micrograph at the cross-section of PLA-lignin filaments with different weight percent of lignin powder. SEM micrograph at the cross-section of the fractured filaments under tensile load was done for PLA-lignin filament at 50x magnification.

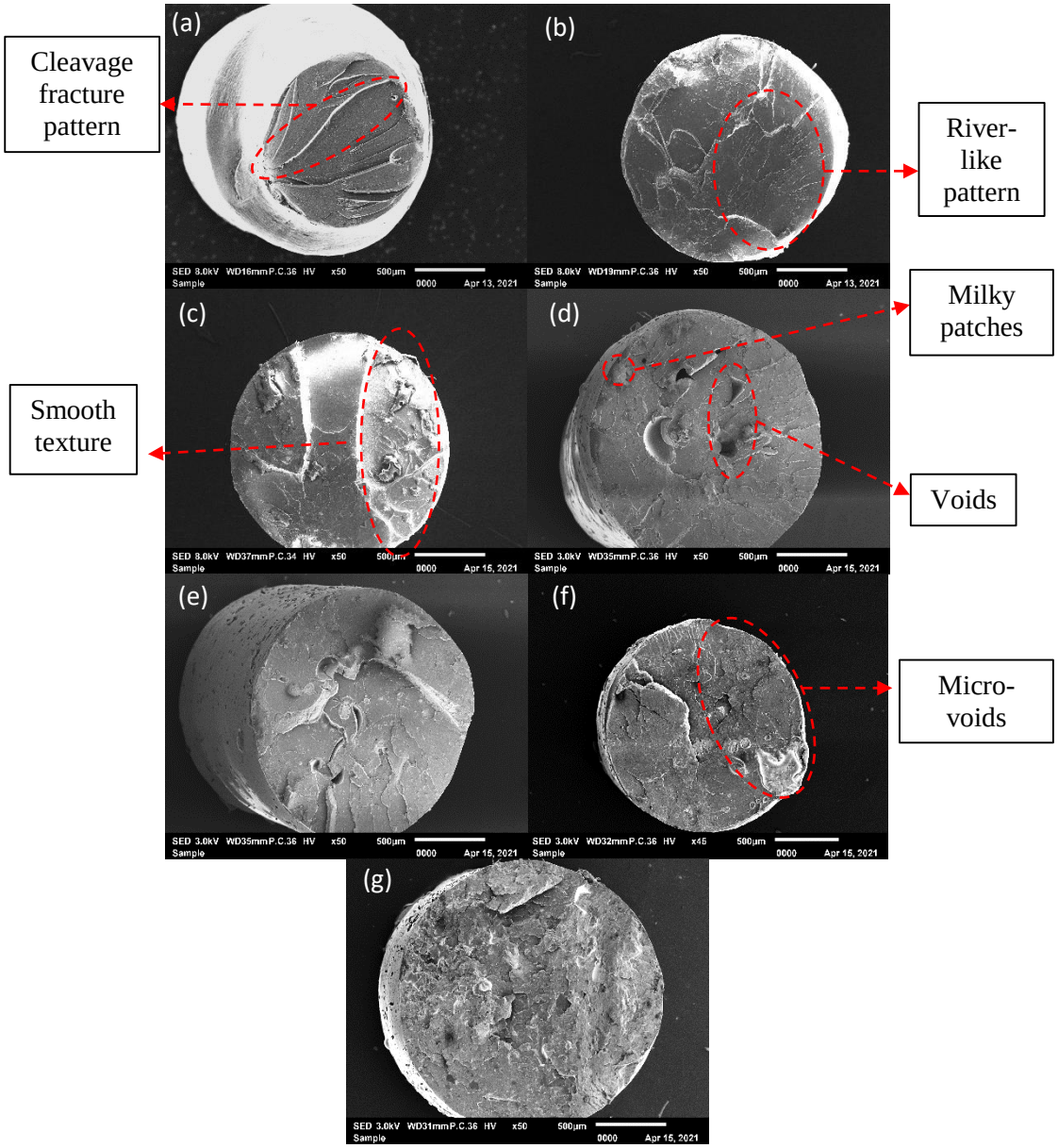


Figure 2 SEM micrograph at 50x magnification of (a) neat PLA, (b) PLAL1, (c) PLAE1, (PLAE2), (d) PLAE3, (e) PLAE4 and (5) PLAE5 filaments.

First of all, it can be observed that the morphology of neat PLA in Figure 2 (a) shows the existence of cleavage pattern at the cross section, while the cross-section of PLAL1 in Figure 2 (b) was covered with river-like pattern. PLAE1 on the other hand, illustrates different morphology with the presence of smoother surface texture as in Figure 2 (c), due to the notable existence of lignin powder on the surface that may extracted upon tensile test.

Next, there are obvious appearance of milky patches especially on the PLAE2 and PLAE3 filaments that are contributed to the EPO in Figure 2 (d) and (e) respectively. There are some obvious holes on the cross-section of PLAE2 that may be contributed to the brittleness of the PLA as there were some river-like pattern occurs surrounding the holes. This can be related with the tensile strain value of PLAE2 that is particularly low and as comparable with the strain value of neat PLA.

Meanwhile, it can be observed that the surface of the PLAE4 and PLAE5 filaments have more textured appearance compared to other filaments which may occur with higher lignin load in the filament as in Figure 2 (f) and (g) respectively. There are obvious aggregations of the lignin particles on the surface that homogenously dispersed on the entire cross-section of the fractured surface. This indicates the miscibility of the lignin in the PLA matrix, yet there is limitation on the amount lignin that may be added to work as an effective filler. Micro-voids also may be noticed on these two filaments that shows high load of lignin is not satisfactory.

3.3. Thermogravimetric Analysis (TGA)

Thermal properties of PLA-lignin filaments with EPO as plasticizer were investigated by thermogravimetry analysis (TGA), compared with pristine PLA. The TGA thermogravimetric provide information about the nature and extent of degradation of the polymeric materials as well as the improvement in thermal properties of these biocomposites with addition of lignin as filler. The TGA thermogram of PLA-lignin filaments was given in Figure 3. A detailed evaluation of the thermograms is presented in Table 2.

The TGA thermogram shows that filaments with addition of lignin as filler and EPO generally have a significant change to higher temperature for all thermal properties that include initial degradation temperature (T_o), maximum degradation temperature (T_{max}) as well as the final degradation temperature (Tf) compared to neat PLA filament. It was noticed that the T_o of neat PLA occur at around 329 °C and completely decomposed by 373 °C, with no residue remaining. Thermal decomposition of the PLAE1 on the other hand occur initially at higher temperature of 338 °C, showing good thermal stability of the filament that occur due to the formation of hydrogen bond between the carbonyl group of PLA and functional groups of lignin component [28]. The T_o of PLAL1 on the other hand not significantly change compared to neat PLA.

The reductions in the degradation temperatures were found to be more drastic with the augmentation of lignin addition of more than 1%. In Table 2, it can be observed that the addition of lignin had improved the thermal properties represented with high T_o and T_{max}. However, upon addition of higher lignin load more than 1%, the thermal properties of the

PLA-lignin had slightly changed with reduction in the initial degradation temperature as well as maximum degradation temperature. Nonetheless, it can be seen that there was increment in residue with higher addition lignin. The improvement in thermal stability of biofilaments were attributed to the addition of lignin filler itself that possessed high thermal stability [29].

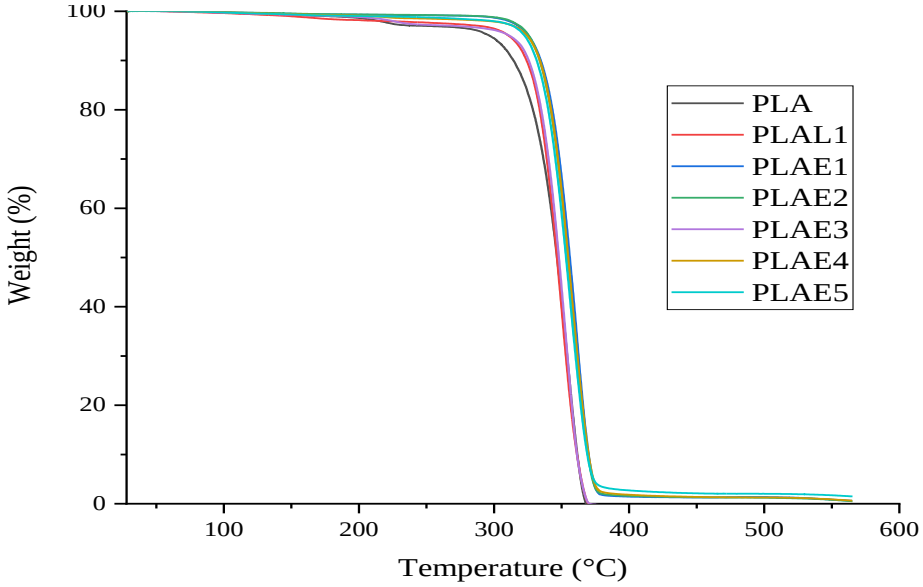


Figure 3 TGA thermogram of biocomposite filaments

Table 2 Thermal degradation temperature of biocomposite filaments obtained from TGA thermogram

Sample	T_o [a] (°C)	T_{max} [b] (°C)	T_f [c] (°C)	Residue[d] (%)	Total Weight Loss[e] (%)
PLA	329.7	353.9	373.4	0	100
PLAL1	328.9	349.6	369.7	0	100
PLAE1	338.0	360.7	380.7	0.6	99.4
PLAE2	336.8	358.3	380.5	0.5	99.5
PLAE3	332.3	353.8	370.7	0.6	99.5
PLAE4	337.8	358.6	381.0	0.6	99.4
PLAE5	335.0	356.6	380.9	1.5	98.5

[a] The initial degradation temperature, [b] The maximum degradation temperature, [c] The complete degradation temperature, [d] the amount of residue at 600 °C, [e] The total weight loss at 600 °C.

3.4. Differential Scanning Calorimetry (DSC)

DSC study has been employed to observe the influence of incorporating filler and plasticizer into the PLA matrix of the studied biocomposites. Since PLA is a semi-crystalline polymer, its thermal properties are strongly dependent on its crystallinity behavior which can be observed from the cold crystallization temperature (T_{cc}). Cold crystallization is an exothermic process that is observed due to the amorphous fraction of the PLA matrix to be partly reorganized or crystallized. T_{cc} of PLA is commonly occurred between glass transition temperature and melting temperature.

Other than that, in order to understand the processability of PLA-lignin biocomposites, it is important to know the melting temperature (Tm) as well as the glass transition temperature (T_g) of the samples. T_g is defined as the temperature below which a polymer is hard and brittle or glass state and temperature above which is soft and flexible or rubbery state, which occurs only in amorphous regions of a polymer while Tm is the temperature where the material started to melt.

Based on DSC thermogram in Figure 4, the thermal characteristics of PLA-lignin filaments have been recorded in the Table 3. The neat PLA displayed a T_g at 62.2 °C, T_{cc} at 103.6 °C and T_m at 155.9 °C. The significant changes of glass transition temperature and cold crystallization temperature can be observed in PLA filaments with addition of lignin powder as filler. First of all, there is notable shifting of cold crystallization temperature from 103.6 °C for neat PLA to higher T_{cc} at around 115 °C to 120 °C for PLA filaments with addition of lignin with different weight percent. The addition of lignin had reduced the rate of crystallization of PLA, hence the T_{cc} occurred at higher temperature. Higher T_{cc} will give the ability to the PLA to retain the microphase distribution in the amorphous region even at high thermal stress [30].

Table 3 Thermal characteristics of biocomposite filaments obtained from DSC thermogram

Sample	Glass Transition Temperature, T_g (°C)	Cold Crystallization Temperature, T_{cc} (°C)	Melting Temperature, T_m (°C)
PLA	62.2	103.6	156.0
PLAL1	61.8	116.4	157.0
PLAE1	58.7	115.7	155.0
PLAE2	58.0	114.2	156.4
PLAE3	59.1	120.8	156.7
PLAE4	53.9	113.2	156.1
PLAE5	58.5	112.6	155.2

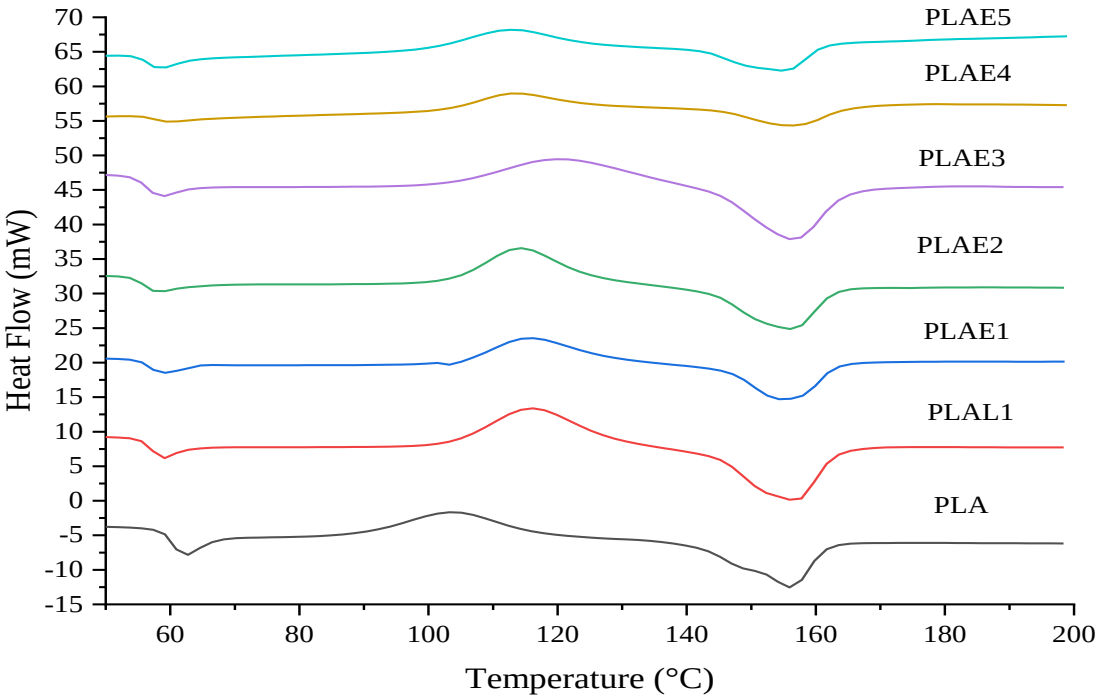


Figure 4 DSC thermogram of biocomposite filaments

Next, the DSC study also reveals the reduction of glass transition temperature from 62.2 °C for neat PLA filament to lower temperature of around 58 °C for PLA-lignin filaments with addition of EPO and different weight percent of lignin powder. This shows the effective plasticizing effect of EPO in the PLA-lignin filaments by enhancing the mobility of PLA chain that will give lower rigidity at this temperature. This is an important condition that will affect the processability of PLA. Finally, there is no significant changes of melting temperature for neat PLA filament and other filaments that has been added with lignin powder and plasticizer. Overall, it can be concluded that the PLA and lignin powder as well as EPO has good miscibility as the thermal characteristics are not mainly inherited from PLA matrix only.

3.5 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy is an indispensable technique and relatively simple method to obtain information on the functional groups of PLA-lignin biocomposites. FTIR spectra of PLA-lignin biocomposites are shown in Figure 5.

Based on the FTIR spectra, all samples showed similar absorption bands at two main absorbance regions around 1745 cm^{-1} and 2880-3000 cm^{-1} indicating that all samples have similar chemical compositions. The characteristic carbonyl stretching around 1745 cm^{-1} is attributed C=O stretching vibration [31] while peaks from 2880-3000 cm^{-1} are associated to the asymmetric and symmetric stretching vibration of CH_3 group. The peak at 1453 cm^{-1}

corresponds to CH_3 anti-symmetric bending vibration. The peaks at 1383 cm^{-1} and 1359 cm^{-1} are associated to the deformation, symmetric, and bending mode of the CH group, respectively. The peaks at 1041, 1081 and 1180 cm^{-1} are attributed to C-O stretching vibrations. Other than that, the two bands at 754 and 868 cm^{-1} could be ascribed to the crystalline and amorphous phases of PLA, respectively [32].

As for the PLAE1 and PLAL1, the samples were analyzed to see the difference in the functional groups compared with the neat PLA. The PLAL1 biocomposite exhibits some peak shifting as well as intensity changes, which may indicate the intramolecular interaction and compatibility of the PLA and lignin. The notable difference may be observed on several peaks including 2990 cm^{-1} in PLA was neutralized to 2992 cm^{-1} for PLAL1 and more intense in PLAE1. Besides, there are presence of new peaks in PLAL and PLAE1 between 1598 cm^{-1} to 1608 cm^{-1}, as well as at 1215 cm^{-1} due to the carbonyl and phenolic hydroxyl groups of lignin respectively [33].

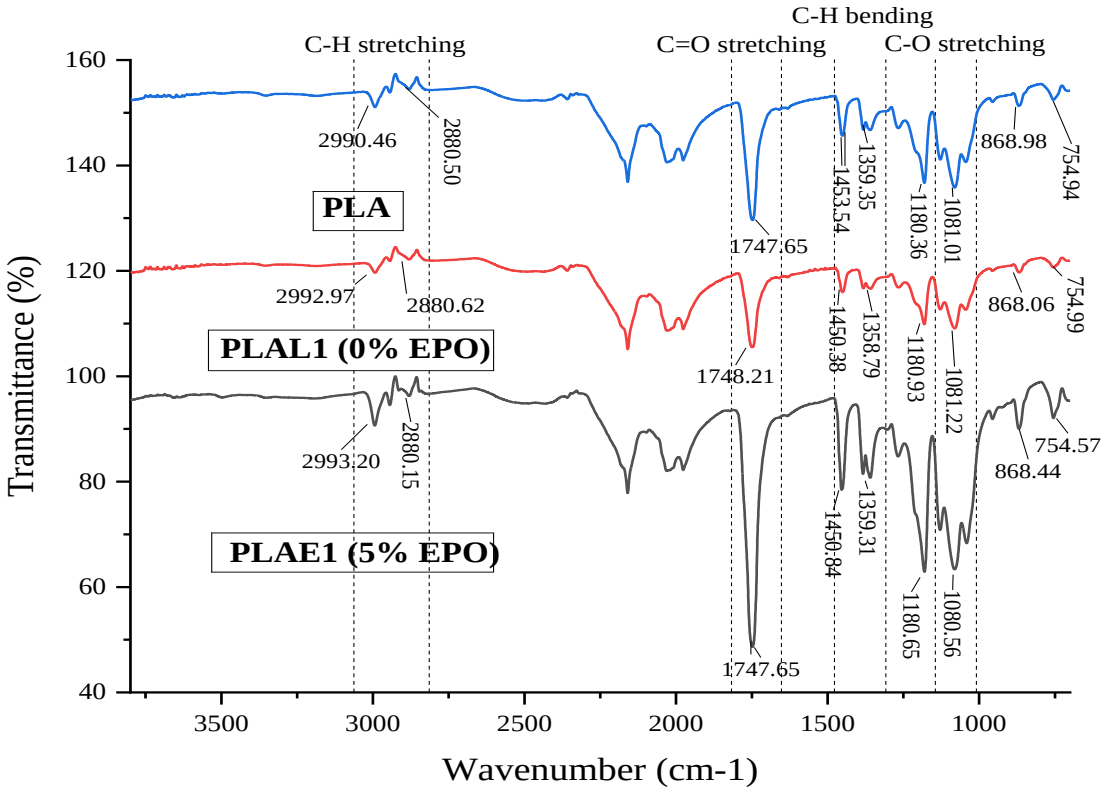


Figure 5 FTIR spectra of biocomposite filaments

Upon addition of EPO plasticizer in the PLA-lignin filaments (PLAE1), there are several changes of the spectra that can be observed as well. Notable intense peak displayed by 1747 cm^{-1} is corresponded to the aliphatic C=O stretching of esters in EPO. Other than that, the intensity of vibrations around 950 cm^{-1} to 850 cm^{-1} were indicative of C-O-C stretching of oxirane vibrations. Changes of severity for peaks around 1180 cm^{-1} and 1080 cm^{-1} were attributed to C-O-C stretching vibrations due to interactions of hydroxy groups in lignin as well as EPO through hydrogen bonding [34]. These interactions and changes of peaks indicate the miscibility of all components that mainly consists of PLA, lignin and EPO.

4.0 CONCLUSION

Improvement of mechanical and thermal properties of PLA filament are the main aim in this study for it to fit in 3D printing application for fused deposition modelling (FDM). The addition of lignin as filler and the uses of EPO as a plasticizer in the filament's fabrication was done to reduce the brittleness as well as to improve the thermal characteristics of PLA filament. PLA-lignin filaments that have been fabricated in this study had shown good mechanical properties compared to neat PLA filaments with the presence of ductile characteristics due to the addition of filler as well as a plasticizer. Other than that, it has been found that the PLA filament with lignin has better thermal properties, which is crucial as 3D printing mainly worked under variation of thermal stress. Overall, the study has shown that the uses of lignin and PLA as the main composition in the production of 3D printable filament, had allowed the development of environmentally friendly materials that give renewability and sustainability advantages.

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