

Characterization of PLA/Lignin Biocomposites for 3D Printing

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Abstract

A greater proportion of polymer-based three-dimensional (3D) printing materials are synthetic petroleum derivatives that are not biodegradable, contributing to environmental pollution and have potential adverse effects on human health. Polylactic acid (PLA) is currently the most widely used among the bio-based alternatives. This work explores alternative environmentally friendly bio-based polymers sourced from sustainable crop and forest biomass derivatives for 3D printing. Various blends of PLA/Organosolv lignin were extruded for fused filament fabrication (FFF) 3D printing process. The processing parameters and results of mechanical and thermal properties of fabricated test specimens of the biocomposite with up to 40wt% lignin concentration are presented. Results indicates that lignin, a low-cost waste product of pulping for the paper industry and bioethanol fuel production could serve as a key component of new biocomposite polymers for 3D printing applications.

Introduction

Most utility polymers are synthetic, derived from petroleum resources. Their synthesis into a great variety of desirable materials compels dependency, absent competing viable alternatives. Their collective drawbacks include processing related carbon footprint addition to the environment, non-biodegradability, and end of life disposal leading to pollution of the ocean waters. Pollution of the ocean waters presently constitute a danger to many marine animals through entanglements and ingestions that results in their deaths and in some cases, hormonal changes that potentially could affect humans that depend on them for foods [1-3].

Environmentally friendly and sustainable forest resources generating neutral carbon footprint have been considered as alternative sources of functional and engineering grade biodegradable polymers. Polylactic acid (PLA), an aliphatic polyester sourced from renewable agricultural products is the most widely used among the bio-based polymers [4]. It is biodegradable and possesses better room temperature strengths and stiffness compared to acrylonitrile butadiene styrene (ABS), the most widely used material for extrusion-based fused filament fabrication (FFF) 3D printing applications. PLA is easier to print with or without

substrate heating. It is less susceptible to warpages due to non-linear contraction of printed parts in un-enclosed print platforms. It is however brittle, has relatively low glass transition temperature and low ultraviolet light resistance, which are major drawbacks. Its good 3D printability makes it a choice candidate matrix material for natural fibers in the synthesis of biocomposites.

Several studies have been conducted on the use of bio-materials as fillers in PLA polymer matrices to achieve differing objectives. PLA has been demonstrated as a matrix material for natural fibers such as flax, cellulose, kenaf, hemp, bamboo, coir, carbon, ramie, jute, and others [5-11]. Lignin, a product of forest biomass is a subject of active research as a filler material in different synthetic [12-17] and bio-derived thermoplastic [18-21] polymer matrices. Lignin is the glue that binds cellulose fibers together and provide stiffness in plants. It is the second most abundantly available natural polymer after cellulose. As a by-product of pulping for the paper industry, it is yet to attract high value niche applications despite its perceived potentials. Depending on biomass source and processing routes, different strains of lignin are produced, such as alkaline lignin, kraft lignin, organosolv lignin, and others. Each processing route produces lignin macromolecule with peculiar functional groups and properties. Most of the earlier work on valorizing lignin through polymer composite synthesis were generic investigations for possible parts manufacturing using injection molding. Recently, different groups have focused on investigating the 3D printability of different lignin-based polymer composites.

3D printing, a group of processes in which solid objects are fabricated through layer-wise deposition of materials has provided a platform for fabricating structures for varieties of applications using different materials. The processes are particularly well-suited for fabricating composite materials, some of which may be difficult to process using traditional methods. In polymer processing, vat photopolymerization 3D printing processes have been investigated for fabricating parts using lignin-based composite materials [22-23]. FFF-based 3D printing, being the most prevalent 3D printing process because of affordability is widely used for new materials development. Although, the process is prone to porosities and anisotropic properties of fabricated parts [24]; with continuous machine and process innovations, the qualities of its fabrications would eventually match injection molded structures. FFF 3D printing of lignin-based polymer composites were recently investigated. Eleni Gkartzou *et al.* [25], investigated the printability and performance evaluation of kraft lignin-filled PLA. The work demonstrated limited success in printing PLA/kraft lignin composites because of poor rheological flow of the melts. Only 5wt% kraft lignin filled PLA was successfully printed. Higher concentrations could not be printed because of rheological challenges. Increasing concentrations of kraft lignin in PLA resulted in more brittle composite material. In another work, Ngoc A. Nguyen *et al.* [26-28] successfully produced high strength blends of up to 40wt% organosolv lignin with acrylonitrile butadiene rubber and reinforcing short carbon fibers in ABS matrix using FFF 3D printing. This synthesis of lignin in petroleum-based materials like ABS would at best be partially biodegradable and would not solve the environmental problems occasioned by process-based carbon foot print and after life polymer material disposals. Although, it provides a route for lignin valorization.

In the present work, the printability and performance of organosolv lignin filled PLA composites are explored. The aim is to develop a new utility biodegradable polymer using renewable and biodegradable biomass resources. Different organosolv lignin and PLA blends were synthesized up to 40wt% lignin and printed using FFF-based 3D printing process. Mechanical properties and thermal behaviors of printed samples were evaluated.

Experimental Procedures

Pulverized PLA made from pellets supplied by NatureWorks LLC was used as matrix for all composite synthesis in this work. The organosolv lignin used were partly sourced from American Science and Technology LLC while some were synthesized in-house. The pulverized PLA had an average diameter of 1.8 mm. The organosolv lignin were received from synthesis as dried solid blocks of materials that were later crushed and sieved to mesh size 12. All PLA and lignin materials were placed in vacuum oven at 45 °C for 24 hours before use. Composite material blends were synthesized by weight percent of constituents. For each composition, material blends were mechanically mixed thoroughly to obtain visually homogenous blends before pouring into a single screw Filabot EX2 extruder. To demonstrate the effects of composite synthesis with the aid of chemical modification of the lignin functional groups for enhanced surface bonding and miscibility with PLA, 20wt% and 30wt% lignin compositions were treated with silane compatibilizer. For these compositions, the lignin contents were pretreated with (3-aminopropyl) triethoxysilane before blending with PLA. The Filabot EX2 extruder used has a $\frac{5}{8}$ – inch outer diameter screw, length to diameter (L/D) ratio of 12, pitch of $\frac{1}{2}$ inches, and compression ratio of 2.5:1. The extrusion system setup included the extruder, a Filabot airpath that comprise of a set of six fans that provide forced air-cooling for the single filament being extruded, and a Filabot spooler. A digital measuring device mounted on the Filabot spooler was used for real-time measurement of extruded filament diameter. A 1.75 mm diameter nozzle was used for all filament extrusions. The extrusion temperatures were varied between 160 and 170 °C depending on composition. The extrusion temperature, extrusion speed, airpath cooling fan speed, and spooling speed were adjusted until stable, consistent filament diameter of 1.75 ± 0.05 mm was achieved. Spools obtained from Filabot LLC were used to collect filaments in rolls in sufficient quantities needed for test fabrications. Extruded filaments were stored in vacuumed plastic bags to prevent moisture absorption.

Creality CR-10S table top FFF-based 3D printer with Cura software was used for fabricating all tensile specimens. Tensile tests were conducted according to ASTM D638. Test specimens were fabricated with five replicates for the following weight percent of organosolv lignin in PLA: 1, 5, 10, 15, 20, 25, 30 and 40. The machine was set up for 100% density. All fabrications were made using 0.4 mm 3D printing nozzle size. The nozzle temperature was varied between 200 °C and 205 °C while the bed temperature was maintained at 60 °C. A 50 kN MTS tensile testing machine was used.

Fractographic images of representative fractured tensile samples were obtained using Hitachi SU1510 scanning electron microscope (SEM) on the secondary electron mode.

Thermal behavior was evaluated for composite material samples using differential scanning calorimetry (DSC) Q20 V24 made by TA instruments. DSC samples were subjected to three heating circles. The first was to 110 °C at 10 °C /min and then cooling to 25 °C to eliminate moisture. The second and third were to 200 °C at 10 °C /min. The tests were used to collect information on glass transition temperature (T_g), cold crystallization temperature (T_{cc}), melting temperature (T_m), enthalpy of cold crystallization (ΔH_{cc}), and enthalpy of melting (ΔH_m).

Results and Discussion

Filaments with compositions up to 40wt% unmodified organosolv lignin in PLA were extruded successfully. All the melts in the current work demonstrated good rheological properties that enabled material flow and sustained filament formation. This is in contrast to the maximum of 5wt% kraft lignin concentration previously reported [25]. Extruded filaments were used for 3D printing tensile specimens with mechanical properties shown in Fig. 1 to Fig. 3. Similar to earlier reports with any type of lignin, the tensile strengths shown in Fig. 1 decreased with increasing weight fractions of organosolv lignin. This trend is due to limited interfacial bonding between the constituents, especially because of the hydroxyl groups present in unmodified lignin macromolecules. Weight transfer between unmodified lignin and the PLA matrix material is limited. Increase in miscibility is realizable by substitution of the hydroxyl groups with other functional groups that could enhance bonding between the matrix and filler materials. Unlike kraft lignin-filled PLA that became increasingly more brittle than neat PLA at higher concentrations of the filler material, organosolv lignin filled PLA became increasingly more ductile. Strength increases due to lignin pretreatment with silane is demonstrated in Fig. 1 for 20wt% and 30wt% compositions. At 20wt% composition, strength increased from 34.4 MPa to 38.2 MPa, an 11% increase. Composites with up to 25wt% unmodified lignin had a minimum of 32.8 MPa tensile strength, which is significantly higher than the 24 MPa recorded for ABSPlus. ABSPlus is one of the common ABS materials for FFF 3D printing marketed by Stratasys, the industry leader in extrusion-based 3D printing industry. The tensile strength of ABSPlus is slightly higher than those for 30wt% and 40wt% unmodified lignin filled PLA. However, with modification using silane, the 30wt% lignin composite recorded higher strength. 40wt% lignin composition was not modified in the present work.

Figure 2 shows stiffnesses of composites with unmodified lignin ranging from 2.45 GPa for 30wt% lignin composition to 3.15 GPa for 10wt% lignin composition. Those with silane treatment were consistently high at 3.18 GPa and 3.13 GPa for 20wt% and 30wt% organosolv lignin. As can be seen, the stiffnesses of the PLA/lignin composites and neat PLA are not significantly different.

One of the limitations of PLA is its brittleness. As shown in Fig. 3, neat PLA at 4.24 percent elongation (%*EL*) is much more brittle compared to composites with higher organosolv lignin composition. Organosolv lignin addition helps to plasticize PLA. However, at higher filler material loading, higher variabilities of the percent elongation results. The higher compositions also demonstrate much higher percent elongation compared to ABSPlus at 6.85. This is an indication of superior toughness over ABS. Although chemically modified compositions

demonstrate higher tensile strengths, they tend to be more brittle compared to compositions with unmodified lignin, although not as brittle as neat PLA.

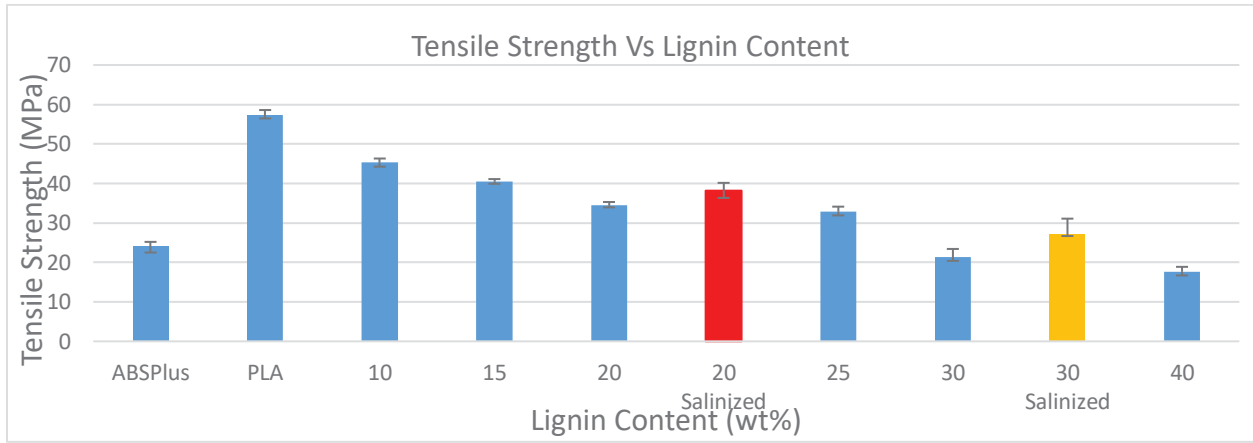


Figure 1: Tensile strengths of PLA/lignin composites in comparison with neat PLA and ABSPlus

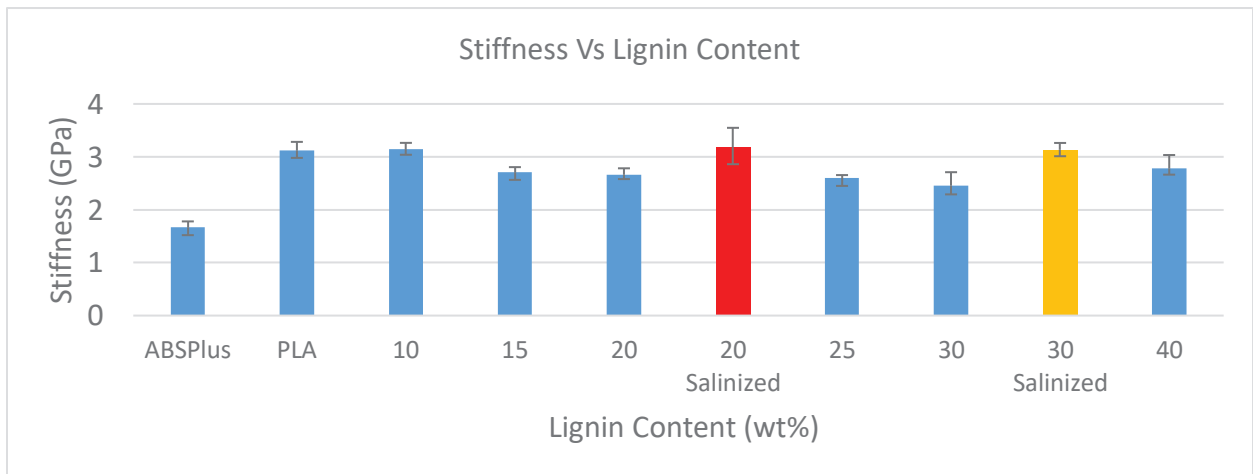


Figure 2: Stiffness values of PLA/lignin composites in comparison with neat PLA and ABSPlus

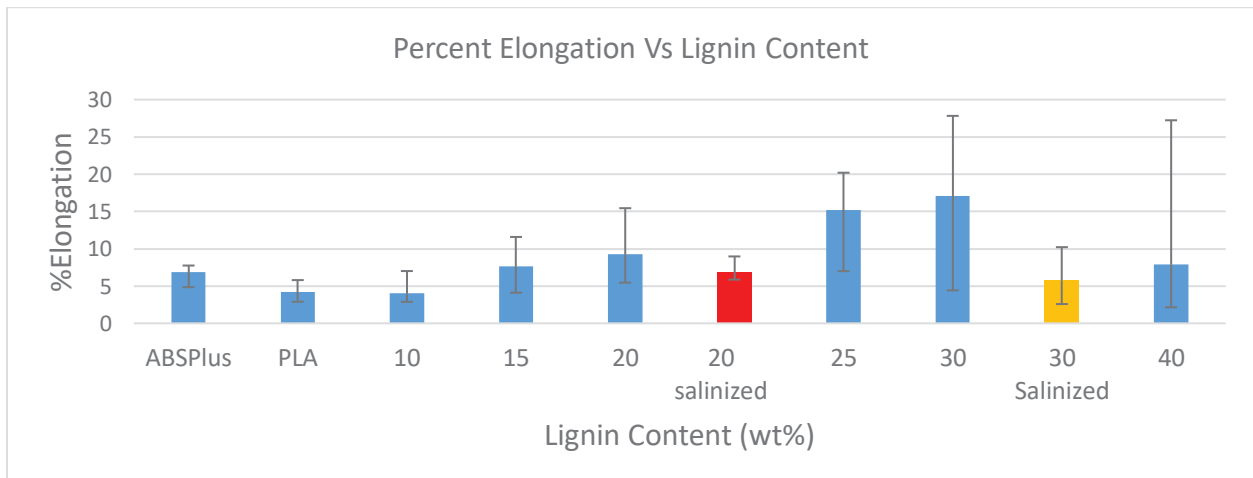


Figure 3: Percent elongation of PLA/lignin composites in comparison with neat PLA and ABSPlus

SEM Microscopy

Representative SEM fractography of tested tensile samples are shown below. The fractographs in Fig. 4a to 4c show well bonded internal structures with few incidences of small air pockets that are typical features of FFF-based 3D printed parts. Figures 4a and 4b for 10wt% and 15wt% lignin composition respectively, show more incidences of air pockets than the 20wt% lignin sample in Figure 4c. This could be because the 20wt% is a little more ductile and could have been less viscous during deposition enabling better material infill. There is no indication of lack of homogeneity in the compositions of the thermoplastic materials.

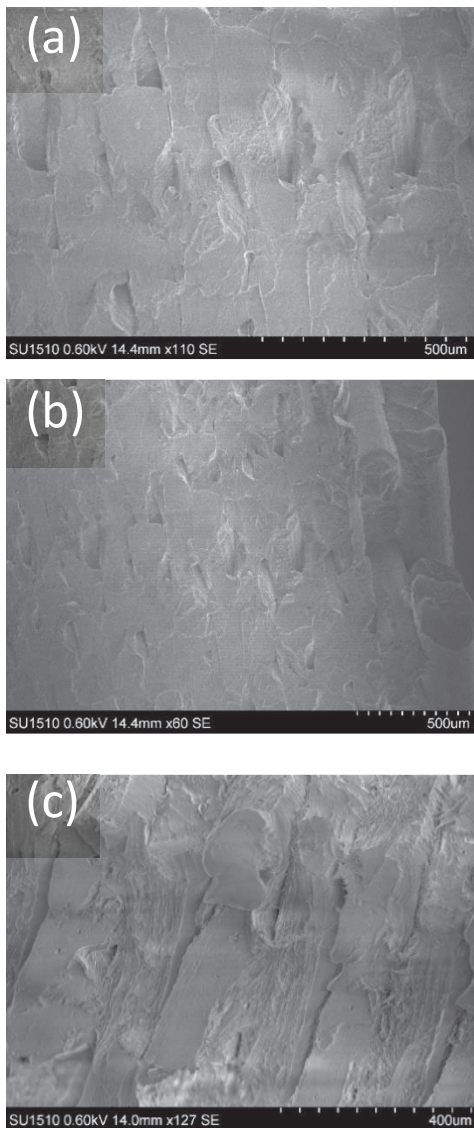


Figure 4: Representative SEM fractographs of tensile specimens for (a) 10wt%, (b) 15wt%, and (c) 20wt% lignin composition

Thermal Analysis

Figure 5 shows thermograms obtained from DSC tests of the composite samples while Table 1 shows extracted thermal parameter data. The glass transition temperatures are slightly higher at lower lignin contents. Each sample recorded a single glass transition temperature and melt temperature. Ordinarily, this could be assumed to be indicative of high miscibility of the components, but this assumption is unsupported by the decline in tensile strengths (Fig. 1) with increasing lignin content.

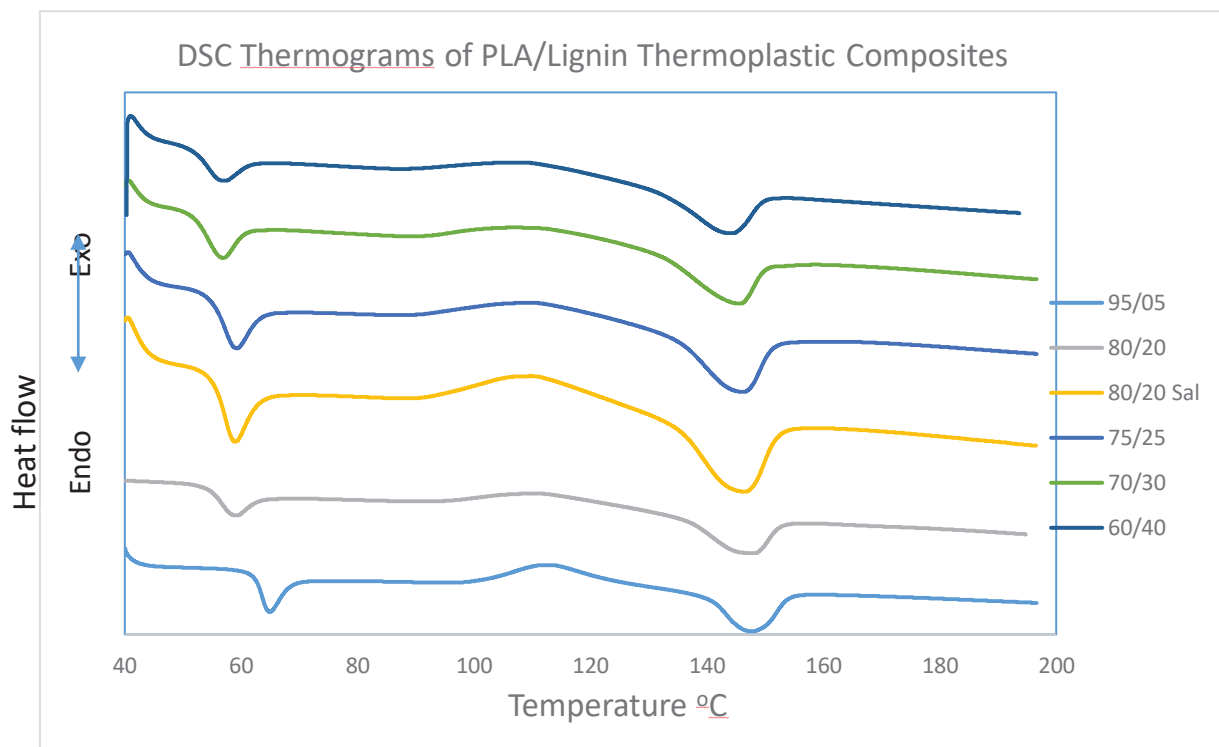


Figure 7: DSC thermograms of different PLA/lignin compositions

Table 1: Thermal property Table from DSC tests

Sample	$T_g(^{\circ}\text{C})$	$T_{cc}(^{\circ}\text{C})$	$T_m(^{\circ}\text{C})$	$\Delta H_{cc}(\text{J/g})$	$\Delta H_m(\text{J/g})$
PLA/Lig 95/05	65.133	117.02	147.21	-8.144	10.10
PLA/Lig 80/20	58.84	111.59	146.85	-6.324	9.346
PLA/Lig 80/20 Sal	58.87	110.31	146.10	-13.33	19.97
PLA/Lig 75/25	59.06	110.69	145.85	-9.358	14.58
PLA/Lig 70/25	56.68	111.51	145.28	-10.63	11.37
PLA/Lig 60/40	56.63	109.64	143.61	-7.62	11.41

Due to increased mobility of molecular chains between the glass transition and melting temperatures, some cold crystallization occurred. The single melting temperature for each of the samples could be indicative of the formation of a single type of crystal during cold crystallization. For all samples, the differences in melting temperatures are not significant. According to the DSC data, The glass transition, cold crystallization, and melting temperatures are virtually unaffected by lignin content. Although compositions with chemically modified lignin yielded higher strengths and stiffnesses, their thermal properties are similar to those with unmodified lignin.

Conclusion

This work has demonstrated the viability of organosolv lignin-filled PLA for melt extrusion at high filler material loading. This is due to favorable rheological flow of the composite melt that support sustained filament formation. The composite filament is printable for all compositions using 0.4 mm diameter 3D printing nozzle. This is possible because the composites can endure high shear rate prevalent in FFF-based 3D printing process. Although filament extrusion and 3D printing of the materials are not a challenge, the low miscibility of the constituents with unmodified lignin could limit organosolv lignin weight fractions in PLA for load bearing applications. Based on the results of mechanical tests obtained, compositions up to 25wt% organosolv lignin without modification out performs ABS material for room temperature applications. With modifications, higher weight fractions of organosolv lignin would performs better than ABS.

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