Development of a Thermoplastic Biocomposite for 3D Printing

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Abstract

Organosolv lignin, a natural cross-linked phenolic wood polymer is a by-product of the pulping process in the paper industry. It is a renewable organic natural product with potential application in many areas. It has attractive properties that make it a potential candidate for fabricating useful parts using 3D printing. Also, polylactic acid (PLA), a biodegradable thermoplastic derived from renewable sources is widely used in 3D printing polymer parts. This work seeks to study the technical viability of extruding different blends of PLA and organosolv lignin into filaments for 3D printing useful objects. Filament extrusions using different blends were evaluated. Also, the mechanical properties of printed test samples are presented. Viable blends of the biocomposite for 3D printing has the potential to provide an added-value to lignin for expanded use in many applications.

Introduction

3D printing has revolutionized how products are made and has become a benchmark technology that enables innovative materials development for a wide range of applications. Polymer-based 3D printing has mostly depended on petroleum-based materials like Acrylonitrile Butadiene Styrene (ABS), Polycarbonate (PC), Nylon and many others with significant long-term health and environmental consequences. To address these concerns, biomaterials having comparable qualities and properties are being sought as alternatives in many applications. Polylactic Acid (PLA) [1-3], a biodegradable and environmentally benign thermoplastic derived from renewable sources has been available as alternative 3D printing material for many applications. Some biocomposites made of a blend of laywood, laybrick, bamboo, straw, and carbon fiber with PLA and some other biopolymer are also commercially available for divers applications [1, 4].

Lignin is one of the most abundantly available organic polymers on earth, second only to cellulose. It is a product of the pulping process in the paper industry and biofuel production [5-6]. Although, it is used in some applications including the manufacture of vanillin, animal feed, dye dispersants, resins and cleaning chemicals, it has mostly been used as fuel for the recovery of its energy content in the paper industry. The annual production of lignin is estimated to be 50 million tons, with only 2% being used for applications other than combustion and energy production [6]. There are different types of lignin depending on processing such as kraft lignin and organosolv lignin. They are cheap materials for which high-end applications are being sought. Some earlier work have on attempted to extrude a blend of kraft lignin with PLA for 3D printing. Gkartzou, et al. [7], presented their work on the blends of kraft lignin with PLA with limited success. The blend was extruded successfully into filament at 5% kraft lignin for 3D printing experimental samples. The work highlighted challenges in achieving homogenous blends due to agglomeration of the kraft lignin in the PLA matrix that could result in nozzle clogging during printing. The clumps constitutes a limiting factor to attaining high weight fraction of lignin in the PLA matrix. The blends were found to be more brittle than the PLA matrix such that a 20 wt% composition experimental samples made by other methods could not be cut into the standard tensile specimens successfully. The present work explores the potential of organosolv lignin as filler material in PLA matrix for extrusion-based 3D printing applications.

Experimental Procedure

Pulverized PLA pellets used as the matrix material for the biocomposite polymer in this work were obtained from Filabot. They were blended in various proportions with organosolv lignin and extruded into filaments. Scanning electron micrographs of the PLA pellets and organosolv lignin particles are shown in Fig. 1. Before blending, the PLA pellets and lignin powders were dried in a Barnstead Lab-line vacuum oven for at least 48 hours at 45°C to remove moisture contents. The blends were made to obtain visually uniform dispersion of the lignin in PLA. Filabot EX2, a Filabot product was used for the filament extrusions. A spooler, obtained from the same vendor was used to wind the filaments on spools and for controlling filament tension for dimensional control. A Filabot airpath wind blowing device was placed in-between the extruder and spooler to provide cooling air flow for heat dissipation from the filament. A digital measuring machine was attached to the spooler for real-time diameter measurement to enable dimensional control. The extrusion temperature ranges from 170°C to 175°C.

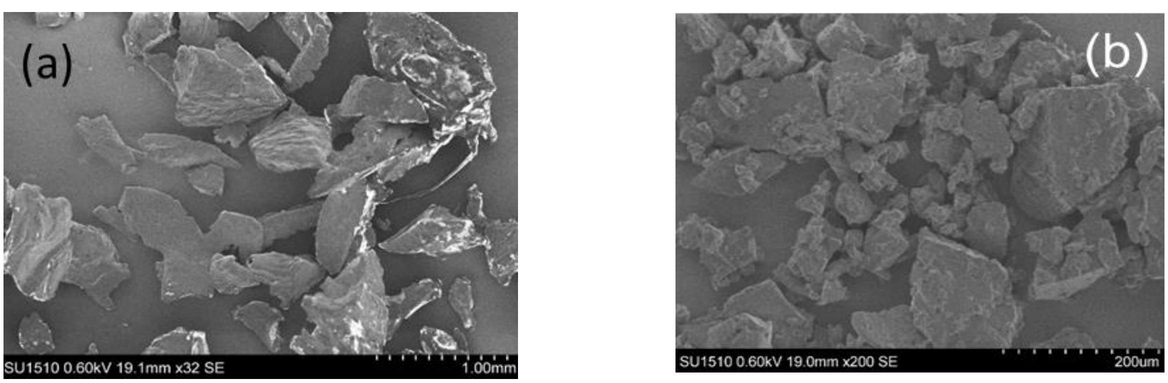

Figure 1: SEM of (a) PLA and (b) organosolv lignin

Extruded filaments were sealed in plastic bags with silica gels placed inside to prevent moisture absorption before and after use for 3D printing of test samples. Creality 10-S 3D printer was used to 3D print tensile test samples with five replicates for plain PLA, 1 wt%, 5 wt%, 10 wt%, 15 wt%, 20 wt%, and 25 wt% lignin contents in this work. Cura slicing software was used for all fabrications with zig-zag raster tool path and settings aimed to achieve 100% 3D print density. Nozzle temperatures varied from 190°C to 210°C depending on composition, while the bed temperature was maintained between 50°C and 60°C. Test samples were 3D printed and tested according to ASTM D638 standard. Microstructure of some samples were observed using scanning electron microscopy (SEM).

Results and Discussion

The filament extruded for all compositions are comparable to those that are commercially available in smoothness. Blended materials exhibited very good extrudability and flowability with no observable agglomeration of the lignin content. Dimensional consistency was achieved within 1.77±0.06 mm. The results of tensile specimens show a decrease of tensile strengths with increasing amounts of lignin content. Figure 2 shows 3D printed PLA has a tensile strength of 57.4 MPa, while those with 10%, 15%, 20%, and 25% lignin has strength values of 45.3 MPa, 40.6 MPa, 34.4 MPa and 32.9 MPa. The strengths wanes with increasing lignin content because there is no effective load transfer between the constituent materials. These strength values are however, within the range or superior to disclosed values for some 3D printed engineering grade polymers produced by Stratasys [8-9].

There's no statistical difference between stiffnesses of different sample compositions as can be seen in Fig. 3. However, Fig. 4 show a pattern of improved ductility with increase lignin content. Lignin concentrations from 15 wt% to 25 wt% yielded significantly better ductility than plain PLA. This trend is completely different from the results obtained using kraft lignin [7].

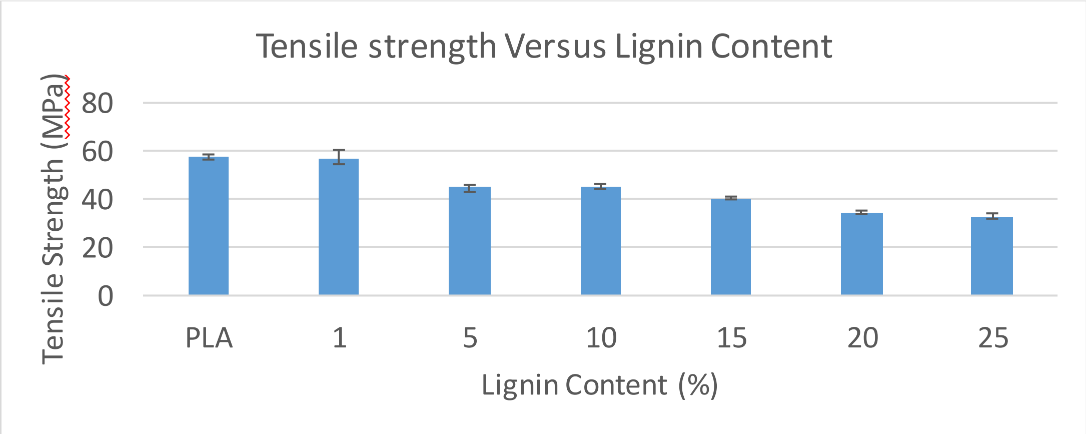

Figure 2: Tensile strength values for different lignin concentrations in 4043D PLA

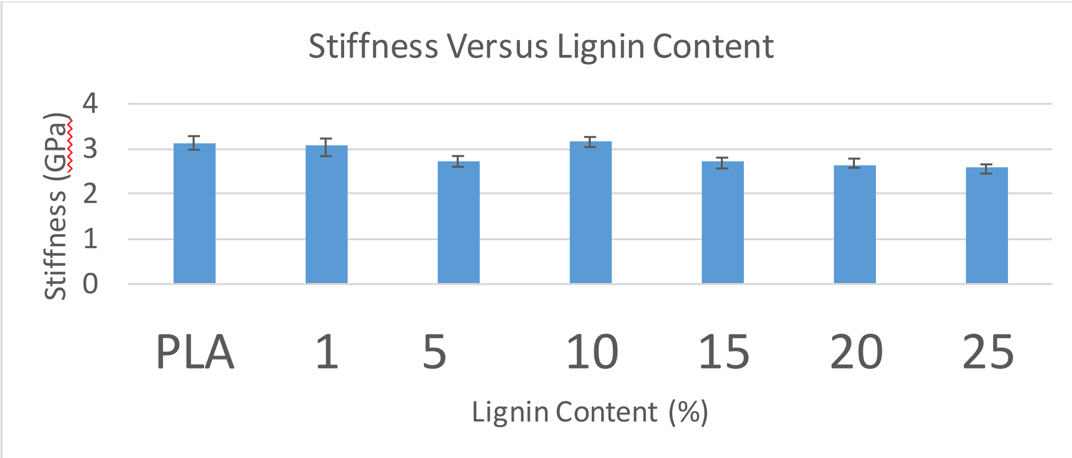

Figure 3: Stiffness of tensile samples of different lignin concentrations in 4043D PLA

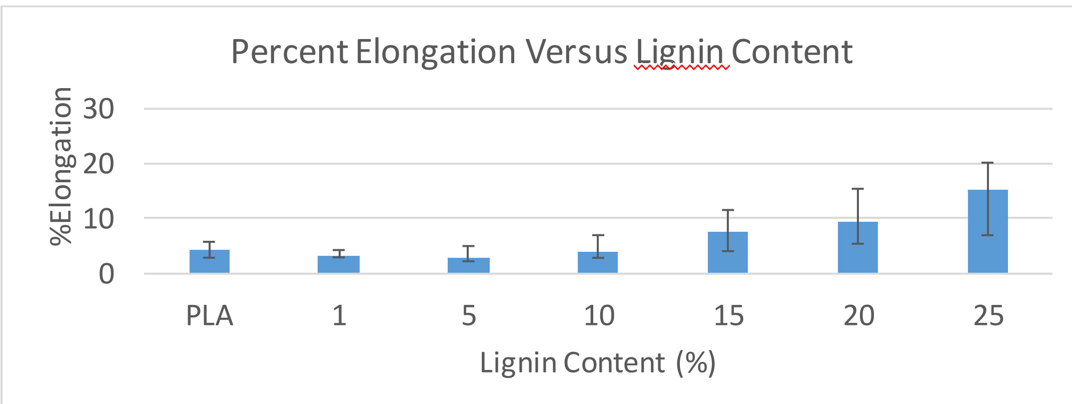

Figure 4: Percentage elongation tensile samples of different lignin concentrations in 4043D PLA

The SEM fractographs presented in Fig. 5 reveals the blend qualities of the constituent powdered materials, 3D printing qualities, and pattern of failure. Fractured surfaces show the constituent materials were well blended prior to and during the extrusion processes. There is no visual evidence of agglomeration that could have affected the extrusion qualities. Although the fabrication parameters required to obtain 100% density were selected, some incidences of porosities characteristic of extrusion-based 3D printing can be observed. The effects of these porosities on the tensile strengths of the tested samples can only be verified when higher density samples can be made using better software and/or hardware, or if a post processing step that closes the porosities is applied.

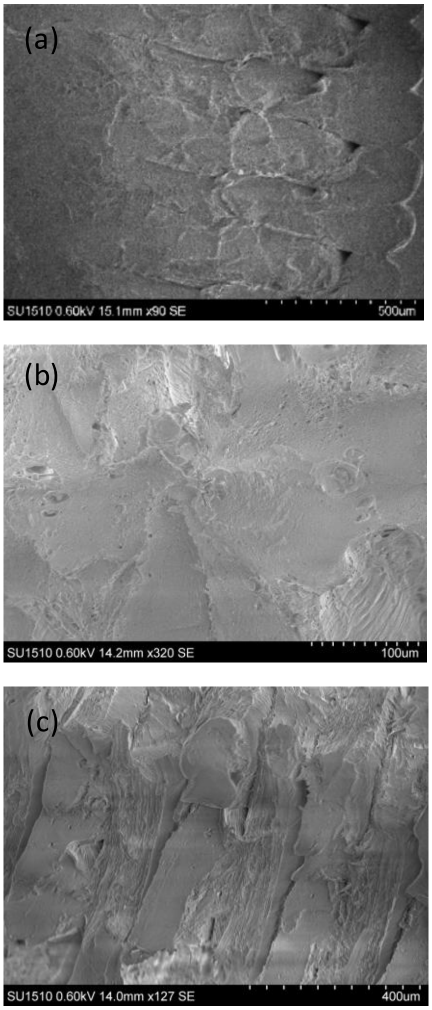

Figure 5: Representative SEM fractographs of tensile samples for (a) 10 wt% lignin, (b) 15 wt% lignin, and (c) 20 wt% lignin contents.

Conclusions

The range of the PLA/Lignin biocomposite material blends used for fabrication in this work demonstrate the viability of lignin for 3D printing applications. The results surpassed the limitations presented in earlier work using kraft lignin [7]. The blends of up to 25 wt% demonstrated good flowability during extrusion and 3D printing. The tensile strengths obtained are comparable to petroleum-based material properties under ambient temperature applications. The stiffness is virtually unaffected by increase in lignin content. There is improvement on the ductility of the biocomposite blends over plain PLA. Results for higher blend compositions of the biocomposite beyond the scope of this work will be presented elsewhere. The use of organosolv lignin for 3D printing has the potential for repurposing it for high-value niche applications that could result in lowering the cost of materials for extrusion-based 3D printing.

Acknowledgment

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