



# Comparison of the thermal, dynamic mechanical and morphological properties of PLA-Lignin & PLA-Tannin particulate green composites



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## ABSTRACT

The study of Lignin and Tannin as filler materials in PLA-based polymeric systems has been uncommon in literature. Composites of PLA-Lignin with 5, 10, 15 wt% Lignin and PLA-Tannin with 5, 10, 15 wt% Tannin were fabricated using injection moulding. SEM morphology reveals Lignin forms droplet like dispersions within the PLA matrix in contrast to Tannin. The particle size of Lignin within the matrix is also 10–150 times smaller than Tannin. Isothermal frequency sweeps on the composites show that storage modulus of PLA-Tannin composites starts to degrade at 15 wt% filler concentration and damping rises. PLA-Lignin composites do not show such degradation in storage modulus. The tensile strength of both PLA-Lignin and PLA-Tannin composites falls with increase in filler content. Lignin has a more inhibitory effect on PLA crystallization than Tannin. The onset of thermal degradation of PLA-Lignin and PLA-Tannin composites occurs at slightly lower temperatures than pure PLA.

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## 1. Introduction

Growing sustainability and environmental concerns have led to an increasing demand to replace materials obtained from non-renewable resources with bio-based materials. Green-house gas emission has now become a serious problem with disastrous consequences if left unchecked [1]. Production of petrochemicals accounts for millions of tons of CO<sub>2</sub> emissions every year [2,3]. Not only does that contribute significantly to greenhouse gases, continued usage of petrochemicals strains the waste management system and non-renewable resource reservoirs [4]. Hence, much research has been devoted to the development of bio-composites from bio-renewable sources [5–9].

However, due to limitations in chemical and/or mechanical properties, many bio-based polymers lack competitiveness with petrochemical based polymers. PLA is one bio-based polymer which has shown great promise due to good mechanical properties, low emission & energy processability, bio-degradability and

recyclability [10–14]. It is synthesized by open ring polymerization of Lactic acid which is obtained from fermentation of dextrose which in turn is obtained from corn starch [15,16]. PLA can also be easily melt processed below the degradation temperature of many natural materials opening opportunities for the development of totally bio-based composites [17]. Owing to its advantages, PLA is the first bio-based commodity plastic to be produced [18]. However, its inherent disadvantages are its high cost and low toughness which cause limitation in wide scale adoption of the polymer. One cost effective way to improve upon its limitations is the addition of filler materials to form composites.

Wood is an abundant and renewable resource in nature which has been in use long before recorded history. It is an essential component in many plant species which provides the bulk of the structural support. Many studies have shown the potential of wood based fillers as a replacement to synthetic fillers [19–23]. However, due to overutilization, the natural resources of wood are at risk of depleting at a fast rate. It has thus become a necessity to utilize wood based products more efficiently.

Lignins are aromatic polymers which constitute a large component of the cell walls of plants. They compose 15–30% of dry matter of woody plants and provide structural support and rigidity [24]. In manufacturing, Lignin is primarily produced as a by-

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product of the paper making process. More than 70 million tons of Lignin is produced annually but most of it is treated as waste or used for heat generation [25]. The structure of Lignin is a complex amorphous composition of large macromolecular entities which contains many polar groups [24]. The structural complexity makes it an interesting filler material for study. There have been studies made on the utilization of Lignin for blending with synthetic polymers and bio-based polymers. A number of studies have demonstrated that the addition of unmodified Lignin has the characteristic of imparting stiffness to polymeric matrices but may also accompanied by a reduction in failure strength [26–28]. However, this behavior was shown to vary for certain polymeric systems as shown in a study on PMMA based Lignin blends where, Lignin was shown to reduce transverse modulus & strength but improve impact resistance [29]. The structural complexity of Lignin also provides prospect for chemical modification. It was found that alkylated Lignin blended with PP to increase compatibility, improved both the impact strength and damping effect even with upto 40 wt% alkylated Lignin content [30].

A limited number of studies have been made on composites containing Lignin and PLA. It was found that increase in content of commercial Lignin and Lignin obtained from almond shells through the organosolv process results in degradation of the failure strength and somewhat the Young's Modulus. Acetylation was found to improve the mechanical properties as compared to unmodified Lignin [31]. However one study also demonstrated an increase in mechanical properties and impact strength in PLA-Lignin composites [32].

Tannins are phenolic compounds which can be extracted from the bark of many species of trees. It has been used traditionally for converting animal skins to leather with other medicinal, industrial, and agricultural uses [33]. There have been a number of studies done to explore the potential for use of tannin in adhesives and resins. It has been shown that the addition of Tannin to synthetic resin provides an opportunity for the replacement of some amount of synthetic resins with natural materials on the basis of mechanical properties. Resins with synthetic phenol-formaldehyde and Tannin based compounds were shown to maintain or improve the mechanical properties and impact strength even at high Tannin concentrations [34–37]. However, besides adhesives and resins, literature on the use of Tannin as filler material has been very limited. Two studies report that the addition of Tannin causes variable crystallization behavior in PLA and reduced mechanical properties [38,39].

So far, a comparison between Tannin and Lignin as filler materials for PLA has not been found in literature. It is thus the objective of this study to characterize the thermal, dynamic mechanical and morphological properties of PLA-Lignin and PLA-Tannin composites.

## 2. Experimental

### 2.1. Materials

The matrix used for the composites was PLA (3052D) obtained from NatureWorks LLC (MN, USA) with a crystalline melt temperature between 145 and 160 °C. Kraft Lignin used for the composites was obtained from Innventia (Stockholm, Sweden) using the LignoBoost process, which is extraction of Lignin from black liquor. Tannin was obtained from Silva Chimica (Piedmont, Italy) marketed under the brand name FINAN T and was extracted from Quebracho plant.

Composites with seven different compositions were fabricated using the above materials. Table 1 highlights the naming convention used in this work based on the composition of the composites.

**Table 1**

Composition and densities of PLA-Lignin and PLA-Tannin composites.

Designation	wt% PLA	wt% Lignin	wt% Tannin	Density (g cm <sup>-3</sup> )
Pure PLA or PLA	100	0	0	1.256 ± 0.0052
5PL	95	5	0	1.266 ± 0.0016
10PL	90	10	0	1.269 ± 0.0016
15PL	85	15	0	1.279 ± 0.0065
5PT	95	0	5	1.269 ± 0.0011
10PT	90	0	10	1.273 ± 0.0089
15PT	85	0	15	1.298 ± 0.0018

### 2.2. Fabrication

Prior to sample fabrication, the materials used for the composites were dried in a vacuum oven at 40 °C for more than 48 h using a pressure lower than 20 in.Hg below atmospheric pressure. Upon vacuum drying, the materials were dry mixed in separate batches using the desired compositions. The mixed batches were then melt mixed with PLA in a co-rotating twin screw micro-compounding system (MICRO 15, DSM, Geleen, Netherlands) at a speed of 100 rpm for 5 min keeping the chamber temperature at 185 °C.

The extrude from the micro-compounder was then injection moulded using a mini injection moulding equipment (IM5.5, DSM, Geleen Netherlands). The collecting barrel temperature of the mini-injection moulding system was kept at 185 °C and the mould was kept at room temperature. Standard dog-bone shaped (ISO 37, type 2) and rectangular specimens (60 mm × 12 mm × 1.98 mm) were fabricated for testing.

### 2.3. Thermogravimetric analysis

For each test, between 10 and 50 mg of material to be tested placed in a platinum pan was heated in the chamber of a thermogravimetric analyzer (Q50, TA Instruments). The chamber containing the sample was continuously purged with nitrogen gas at a flow rate of 10 mL/min. All samples were heated to 600 °C using a heating rate of 10 °C/min.

### 2.4. Differential scanning calorimetry

Between 10 and 15 mg of the specimen to be tested was weighed and hermetically sealed in aluminum pans. The pans were then placed in sequence in an auto sampler of a DSC analyzer (Q2000, TA Instruments) for testing. A heat-cool-heat program was used on all samples. To capture the heat flow behavior with rate of temperature change, three different heating/cooling rates were used: 5 °C/min, 10 °C/min, and 15 °C/min. For each heating/cooling rate, the samples were first heated to 185 °C, held for 5 min to erase the thermal history, then cooled to −70 °C and reheated to 185 °C.

### 2.5. Density measurements

The densities of the injection moulded samples of PLA-Lignin and PLA-Tannin composites were measured at room temperature by taking the mass and volume measurements of three rectangular samples for each composition. The density values of the composites are listed in Table 1.

### 2.6. Dynamic mechanical and tensile test

The rectangular composite samples obtained upon fabrication were tested in a dynamic mechanical analyzer (Q800, TA Instruments) using a dual cantilever setup. For obtaining the dynamic mechanical properties, a constant displacement amplitude-

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