

THERMO-MECHANICAL CHARACTERISTICS OF
POLYETHYLENE/TOBACCO LIGNIN BLENDS

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Samsul Arfin Mahmood

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SUPERVISED BY
Dr. Venkata Gireesh Menta, Ph.D.
Assistant Professor

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Samsul Arfin Mahmood

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DEDICATION

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ABSTRACT

With the expected exponential growth prospects of additive manufacturing, petroleum-based plastic products and applications are also expected to increase. For the last two decades, plastic pollution has become a concerning fact. About 25 million tons of plastics find their way into the environment annually. Traditional plastics are not biodegradable and hence they end up in landfills which is detrimental for the environment. Hence, there exists a need for renewable alternatives to traditional petroleum-derived plastics. Lignin, an abundant plant-derived feedstock, has been a perfect candidate for renewable materials.

The work in this thesis focuses on investigating the effects of mixing lignin extracted from tobacco with high-density polyethylene (HDPE) in varying concentrations. This work is performed in three stages. The first stage is the making blends of HDPE-lignin at varying concentrations (5, 10, 15 & 30 wt.%). Later all the materials were melt mixed using a single screw extruder. In the later stage for mechanical testing purposes, tensile specimens were processed via injection molding. During this process, the effect of lignin on injection molding parameters was investigated.

In the second stage, mechanical, physical and thermal tests were conducted to analyze the effects of blending on the overall performance of the lignin-HDPE blends. Tensile tests were performed to determine the ultimate tensile strength (UTS), Young's modulus and elongation at break for each blend composition. To evaluate the physical properties, hardness and density of the blends were measured. The miscibility of the blends was studied using optical microscopy. TGA tests were performed to study the thermal stability of blend materials.

In the third stage, maleic anhydride grafted polyethylene was used to compatibilize blend materials. Compatibilized HDPE-Lignin blend materials were later subjected to mechanical and physical tests to analyze and compare the effect of compatibilizer.

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CHAPTER I INTRODUCTION

1.1 Background

In recent times plastic pollution has increased than ever before. Despite growing concern about plastic pollution, increased usage of plastic products is causing more pollution than before. The world population has increased exponentially and so is the plastic production. On some beaches on the Big Island of Hawaii, as much as 15 percent of the sand is grains of microplastic [1]. At Kamilo Point, the beach is piled with laundry baskets, bottles, and containers with labels in Chinese, Japanese, Korean, English, and occasionally, Russian [2][3]. On Henderson Island, an uninhabited coral island in the South Pacific, researchers have found an astonishing volume of plastic from South America, Asia, New Zealand, and Russia [4][5]. Plastics have a valuable place in our present and future. Since we can not imagine our lives without it, attempts to make plastics safer and more sustainable are constantly being made. A process perfect enough to convert plastics back to fossil fuels (from which they are derived) can open the opportunity for reducing pollution caused by plastics. Also, plastics made from biodegradable materials can reduce the amount of overall plastics that end up in the landfill. It is true that plastics are not perfect, but they truly are an important and necessary part of our life and from here comes the motivation of this research work to dive into and investigate the property and usability of plastic made from a biopolymer named "*Lignin*".

1.2 Lignin

Lignin is generally known as a complex organic polymer. It is also known as the second most abundant terrestrial biopolymer after cellulose and is the largest renewable source of aromatic groups of nature. Lignin can be generally found in plant cell walls and is regarded as an important structural component of woody plants [6]. It is dense, amorphous, secondary cell wall polymer found in the trachea elements and sclerenchyma

of terrestrial plants. Lignin is a major component of all plants. Grass contains about 17-24 wt.%, softwood in 18-25 wt.% and hardwood in 27-33 wt.% [7].

Lignin constitutes 15-40% of the dry weight of woody plants. Based on yearly biomass growth rates, the overall production of lignin is on the order of 50 million tons/year [8]. Hence, lignin has the potential to be an important source of aromatic chemicals for the chemical industry. arising from the conversion of modern era CO₂, and its efficient utilization solves a potential puzzle in creating valuable by-products in a biorefinery scheme. To put this in perspective, it is roughly the size of the global polymer market [9]. The lignin available on the market is mainly produced from the paper industry in which it is treated as a side-product formed during the extraction of the targeted valuable product, cellulose. The isolated and commercially available amount of lignin was only 1.1 million tons in 2014. The global lignin market was valued at approximately 775 million US\$ in 2014 and is expected to reach around 900 million US\$ in 2020 corresponding to average annual growth of 2.5 % between 2015 and 2020 [11].

1.3 Structure and Extraction of Lignin

To understand lignin and its possible application, it is necessary to have some idea on its extraction and characterization. Lignin is a complex organic polymer its chemical structure knowledge is very crucial. The technology of extraction determines the structure of the product so it's very essential when it comes to blending lignin with thermoplastics.

1.3.1 Lignin Structure

Lignin is a natural polyphenol and as already mentioned it is formed from monolignols. Lignin can only be described by an average empirical formula which shows the molar ratio of 9 carbon atoms to other elements or functional groups of lignin. The C₉ formula is the most frequently applied average empirical formula which shows the molar ratio of 9 carbon atoms to other elements or functional groups of lignin; the formula represents an average repeat unit formed by the constituting monolignols. The C₉ formula

of spruce (softwood) lignin is $C_9H_{7.92}O_{2.40}(OCH_3)_{0.92}$, on the contrary, C_9 formula of hardwood lignin is $C_9H_{7.49}O_{2.53}(OCH_3)_{1.39}$ [12].

The model structures for spruce lignin were created first by Freudenberg[13], Adler [14], Brunow [15]. A simplified structure model based on the results of Adler was given below. Gellerstedt et al. [16] mentioned in their findings that lignin has two types namely, type 1 Figure 2.2 (a) and type 2 Figure 2.2 (b) form in plants. Type 1 lignin is found 48 w/w% in softwood while 40 w/w% is type 2 [16].

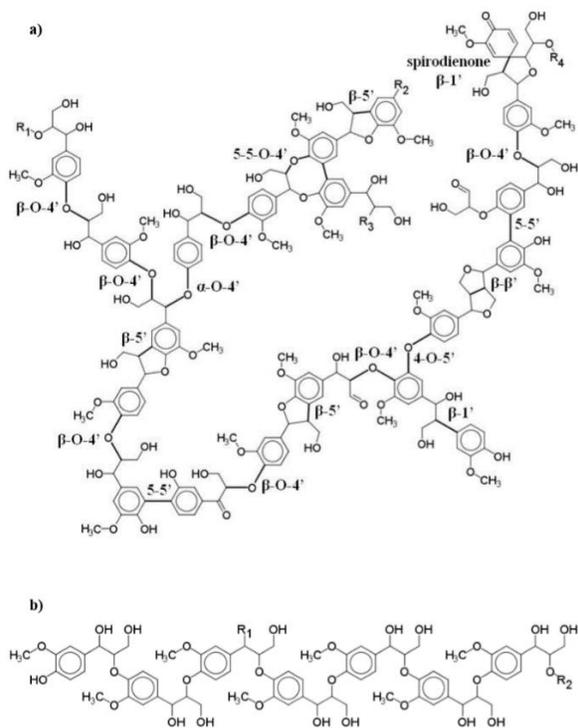


Figure 1.1 Model structure of spruce lignin based on [14] & [16]. (a) Type 1 lignin (b) Type 2 lignin

Gellerstedt mentioned that type 1 lignin is found in a glucomannan-lignin-xylan complex which forms a bond to the cellulose fibrils via hydrogen bridges. The different linkages formed with the repeating unit can be seen from the figure above. The type 2 lignin is found in a xylan-lignin-glucomannan complex which is located around the cellulose fibrils entrapped into type 1 lignin. In type 2 lignin mostly β -O-4' ether bonds form between the repeat units. This bond makes β -O-4' ether bond the most frequent linkage not only in softwood but also in hardwood lignin. These linkages combine up to 50% of the bonds in softwood and 60% in hardwood [17].

1.3.2 Lignin Extraction

Kraft process is the most popular pulping method. The Kraft process is considered as a developed method of the soda process. In the Kraft process, wood chips are cooked in an alkaline aqueous medium. Similarly, to the soda process, most of the α -O-4-ether and β -O-4-ether bonds of lignin are cleaved by the end of the cooking procedure. The weight average molecular weight of softwood and hardwood Kraft lignin is 19800 and 3700-3900 g/mol respectively [18]. The structure model of softwood Kraft lignin is presented in Fig 2.3. In the Kraft process, most of the Kraft lignin is burnt. The amount of commercially available Kraft lignin was 100 thousand tons in 2014 [19].

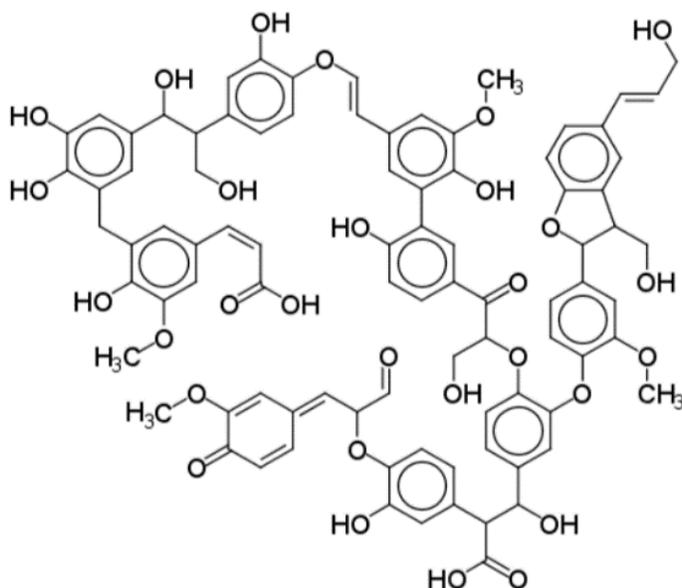


Figure 1. 2 The model structure of softwood Kraft lignin based on the structural model of Adler[14] and the reaction taking place during pulping [20]

The organosolv process [21] is a widespread technology that is based on the extraction of lignin by polar organic solvents like methanol, ethanol, formic acid, and acetic acid. The property and structure of organosolv lignin solely dependent on the choice of solvent during extraction. The Alcell® procedure appears most often in scientific papers. This method consists of the extraction of lignin with 40-60 wt.% aqueous ethanol [22].

In recent times, the Sulphate process [18] has become the main source of commercially available lignin. This amount is approximately 1.0 million tons in 2014 [19]. The pH of the reaction medium dictates the amount of sulfite, bisulfite and dissolved sulfur dioxide used. In the industry, the sulfite process is carried out mainly under acidic conditions. The weight average molecular weight of softwood and hardwood lignin is 36000-61000 g/mol and 5700-12000 g/mol, respectively. Lignosulfonates are soluble in water, ethylene glycol and dimethyl sulfoxide [23].

1.4 Motivation

With the expected exponential growth prospects of additive manufacturing, usage of plastic products and applications are also expected to increase. Hence there exists a need for renewable alternatives to traditional petroleum-derived plastics. Also keeping in consideration, the amount of plastic that goes into landfills and does not decompose, there is an utter need for bioplastics and finding alternative solutions to traditional thermoplastics such as Polyethylene, Polypropylene, Poly Vinyl Chloride, etc. With many future possibilities, this research focuses on the investigation of thermal and mechanical properties of High-Density Polyethylene (HDPE) blended with lignin-derived from tobacco stalks. Thermoplastics are not biodegradable, and lignin is a biopolymer found abundantly in nature and is biodegradable. Lignin degradation is basically done by microorganisms like fungi and bacteria. It's complex atomic chains open the opportunity for blending with available petroleum-based thermoplastics. Lignin used in this work is drawn from tobacco stalks. Tobacco stalks are mostly wastage and some of them are used for burning but the process includes environmental pollution and tobacco consumption via cigarette lead to lung cancer and several other health issues. In this work, lignin was added to the thermoplastic by a certain percentage and their mechanical and thermal behavior of the blend material was observed. The blend material reduces the concentration of traditional plastics and at the same time utilizes the tobacco stalks which paves the way towards sustainability.

1.5 Scope

The methods applied in this research aims to process and investigate the properties of tobacco lignin blended with a thermoplastic HDPE (High-density polyethylene). Single screw extruder was used to blend materials and an injection molding machine was used to produce test samples. All the coupons were tested for their mechanical properties such as ultimate tensile strength, Young's modulus, and strain at the break. Thermal properties were also investigated to understand the stability of blend materials. This works also demonstrates the processability of lignin when blended with thermoplastics.

The thesis is arranged as follows: Chapter II covers a literature review on thermoplastic and lignin and some related research works performed on polymer blend; Chapter III describes the methodology and the whole blending and injection molding processes which includes stage I: *Extrusion process of the blend materials* , Stage II: *Mold design and injection molding of the blend materials* and followed by Stage III: *Effect of injection molding parameters on processing lignin*, which describes the effect of increasing lignin content in blend on injection molding parameters and also the processing challenges faced with lignin and their solutions. All the test sample preparation described in Chapter III are subjected to mechanical and thermal tests. All test procedures are presented in Chapter IV. All the results obtained from the tests described in Chapter IV are presented in Chapter V. Conclusions are reached and future recommendations of this research are offered in Chapter VI.

CHAPTER II REVIEW OF LITERATURE

The purpose of this chapter is to provide a basis for this study by reviewing literature that is pertinent to the goals and objectives of this research. The topics of literature reviews are the blend composition, mechanical and thermal properties of the thermoplastic-Lignin blend.

2.1 Thermoplastic-Lignin Blends

In recent times lignin has been added to several polymers which will be discussed in detail later in this section. The intriguing fact is the definition of the resulting material. Is it a blend or composite? So, understanding the conceptual clarification of the definition is necessary. Later comes the discussion on the various classes of materials prepared. Interaction is a very important part of material property.

2.1.1 Blend/Composite

There is a considerable amount of confusion within the literature about the definition of polymer/lignin combinations. Blend and composite are completely two different concepts. A blend is a mixture of at least two polymers interacting with each other through interdiffusion, while in a composite the polymer and the filler interact through adsorption at a definite surface. The nature of interdiffusion is determined by the interaction of the polymers, by their mutual miscibility. Weak interaction results in thin interphase and a heterogeneous blend with large dispersed particles. While strong interaction leads to homogenous blend with no observable particles. Some of the research works have been done on the miscibility and particle distribution in the blend material [24][25][26]. In a composite, a polymer with mobile chains adsorbs on the solid, well-defined surface of a filler. Generally, mineral fillers are dispersed in the matrix as the second component, but polymers such as lignin can also act as a filler. Thermosetting polymers do not melt, retain their size and possess the necessary well-defined surface, but

the powder of a glassy homogenized below its glass transition temperature (T_g) can also meet this condition.

Although the definition above clarifies how blends differ from composite, it is not confirmed whether lignin acts as a filler or forms a blend with the second polymer. Most of the commercial lignin as mentioned before comes from pulping and their molecular weight gets reduced. Most of these lignins are soluble in some solvent. T_g of lignin is lower than the processing temperature of typical thermoplastic polymers. Some commonly known lignin and their T_g is given in Table 2.1 [11]. The hominization of lignin with thermoplastic results in a blend. This statement is generally supported by the SEM or optical microscopy analysis. The size of the lignin particles distributed across the surface of the thermoplastic polymer is considered one of the determining factors in case of blends. If the lignin particle breaks up and mixed with polymer homogeneously then the process is considered as a blend.

Table 2. 1 *Glass transition temperature of different lignin determined by DSC tests* [11]

Type of Lignin	Glass transition temperature ($^{\circ}\text{C}$)
Softwood Kraft lignin	162
	141
	153
Hardwood Kraft lignin	108
Kraft lignin	165
Alcell® (organosolv) lignin	97
Hardwood organosolv lignin	95
Rice straw soda lignin	155
Wheat straw soda lignin	150
Softwood sodium-lignosulfonate	138
Hardwood sodium-lignosulfonate	127

2.1.2 Thermoplastic Polymer Blend with Lignin

Lignin as a component for the blend is being studied for a long time. Lignin blend with thermoplastic polymer has been studied for more than a decade now. Kubo et al. discussed the analysis of intermolecular interaction in lignin-synthetic polymer blends while Pucciariello et al. investigated the physical properties of straw-based lignin blends [2][3]. Canetti et al. observed the good dispersion of lignin particles in polyethylene terephthalate (PET) while Kadla and Kubo found two components immiscible and explained immiscibility with the lack of hydrogen bonding compared to polyethylene oxide [2][27]. On the contrary, Jeong et al. found PET and lignin to be completely miscible [28]. These results were based upon the mechanical testing including tensile testing of blend materials. Miscibility was also claimed for polymers with aromatic rings such as poly(4-vinyl-pyridine) and polyaniline [29][30]. It has also been found that PET forms H bonds with lignin. Polyolefin/lignin combination has also been studied by and reported by authors [31] but they found weaker bond formation than that of LDPE, PS, PP, PET which will be discussed in a later section. However, miscibility and compatibility properties are highly dependent on the source and processing of lignin followed by the choice of polymer it gets blended with.

The claim for strong H bond happening in blend material was clarified using FTIR spectra and composition dependence of the T_g of the blend which possessed a single T_g [32]. Some other authors performed investigations on poly(vinylpyrrolidone)-Lignin blends [30] as well as about polyaniline/ Lignin blends [33]. Both investigations lead to a conclusion being the respective polymers being fully miscible thus creating a strong bond with lignin. Although Rodrigues et al. tested blends with FTIR spectroscopy and cyclic voltammetry, the SEM micrographs recorded on their samples indicated the presence of lignin particles [30]. This proves that lignin particles are not distributed properly and did not create homogeneous particle distribution with the polymer. The effect of FTIR and cyclic voltammetry was unable to answer these questions. The contradiction in the role of H- bonds in the interaction of the polymer with lignin is mentioned extensively by polyvinyl alcohol (PVOH)/ Lignin blends. There are not many studies done on this kind of blend but all of them converge to a specific solution saying they do not form a homogeneous blend [34][35]. This led to contradiction because PVOH has a significant amount of active

OH group. Optical microscopy even can lead to the wrong conclusion due to unpredictable noise existence and incorrect magnification. Hydrogen bonds seemed to influence the biopolymer/lignin blend as well. PLA for example, when blended with lignin, showed the weak bond and was immiscible [36]. However, SEM micrograph analysis performed by Ouyang et al. showed that PLA does create a homogenous blend structure [37]. In addition to that, polyhydroxy butyrate (PHB) was claimed to have miscibility when lignin is added up to 40%. With the increase of percentage, the separation of lignin from the polymer was observed. The conclusion was drawn from the SEM and DSC tests and which confirms the phase separation and the reason was claimed to be intermolecular adhesion of lignin particles in the blend [38][39]. Despite all the claims made on the lignin/polymer blend by the researchers, complete miscibility failed to take strong footing. All the blends in most cases shown heterogeneity in structure and their properties did not turn out to be very good. This leads to a search for alternate available sources of lignin and investigates if this holds any reasonable value. Tobacco turned out to be one such potential candidate.

2.1.3 Tobacco as a Source of Lignin

Tobacco has been one of the most important industries to at least three states (North Carolina, Georgia and Kentucky) in the USA and accounts for over 185,000 jobs [40]. The tobacco plant is widely known and cultivated mainly nicotine, as we know that nicotine is present everywhere in the plant except for the seeds. Every year a large amount of tobacco stalks is produced, although most of them are disposed of as waste or used as fuels. This leads to a huge waste of resources and causes environmental pollution. Cellulose and hemicelluloses have higher percentages (30-40%) wherein tobacco stalks lignin content is around 5%.

Some researchers have investigated the extraction process of lignin from the tobacco plant and the characterization of lignin. Effects of beating on tobacco stalks as mechanical pulps and utilizing it for producing energetic briquettes [41][42]. Faix et al. isolated milled wood lignin from tobacco leaves. MWLs were characterized by quantitative pyrolysis-gas chromatography using a resistant heating instrument. Curie-point pyrolysis-gas chromatography/mass spectrometry and pyrolysis-mass spectrometry were used for

characterization and it was found that tobacco lignin contains approximately 10% 4-hydroxyphenylpropane, 78-82% guaiacyl-propane and 10-13% syringylpropane moieties [43]. Curie point pyrolysis mass spectrometry and Curie point pyrolysis high-resolution gas chromatography was applied by Scheijen et al. [44], The conclusion was that mentioned extraction processes are not suitable for getting a pure form of lignin fraction from tobacco plant rather the acid-treated fractions are highly dependent on the origin of the material to be extracted and the selection of acid used for extraction

Despite all these works, lignin from the tobacco plant has not been studied to a full extent. Lignin has been blended with some common polymers. The next two sections involve some basic known attributes of PE as polymers and summarize some work related to lignin blended with polyethylene and the outcome of those investigations.

2.1.4 PE as a thermoplastic polymer

Worldwide plastics consumption is of the order of 170 million tons annually in round figures, with a turnover of US\$560 billion. Over the past five years, global plastics consumption has grown consistently by an average annual rate of 4%, comparable with steel and aluminum rates [45]. PE covers most of the market share of thermoplastic polymers. So, it is an obvious thing to investigate the effect of lignin as a filler in polyethylene which covers a good portion of the plastic industry.

Polyethylene, commonly known as PE $-(CH_2-CH_2)_n-$ is a broad family with versatile properties that is depended on the polymerization process used. Based on the process, PE is divided into LDPE (Low-density PE), HDPE (High-density PE), LLDPE (Linear low density) and UHMWPE (Ultra-high molecular weight PE). The density of PE ranges from .890 to .960. The molecular weight of PE ranges from a few thousand to 3000000 and higher. The general advantages are low price with good property, easily transformable, low absorption of water, low coefficient of friction and good machinability. All molten state processing methods are usable for PE such as extrusion, injection, compression, blow molding, thermoforming, foam, coating, powdering, co-extrusion, fluidized bed, etc. [45]. Neat thermoplastic polyethylene has low moduli that involve high strain for moderate loading. PE has very weak loss factors and does not heat up under high-

frequency currents. Which is why they cannot be welded by high-frequency technique. Polyethylene has a very good insulating property, but its fire-resistant capability is not great.

High-Density Polyethylene (HDPE) is one of the most commonly used plastics around the world for a wide range of applications ranging from milk bottles to plastic pipes used in the construction industry. 86% of all PE goods are made of HDPE. HDPE compared to LDPE is more rigid with better thermal and creep behavior, lower coefficient of friction and high-pressure strength and more transparent. The continuous use of temperature in an unstressed state for HDPE is considered at 110-120⁰C while the service temperature is lower 50-120⁰C due to loading caused in service initiate modulus of decay, strain, creep, relaxation.

2.1.5 HDPE Blend with Lignin

In recent times, many investigations have been performed and reported on biocomposites/ blends made from lignin and polymer (thermoplastic/ thermosets) [3][2][28][29][30][38]. Effect of blending lignin with low-density polyethylene (LDPE) shows that long term heat exposure degrades the blend characteristics and effects on the mechanical properties [46]. Esterified lignin and polyethylene when compatibilized and blended together show very little changes in mechanical properties whereas blend shows thermal stability up to 40% lignin concentration [47]. Some main challenges lie in blending lignin with polyethylene is that lignin has weak bonding capability. Recent works have shown that chemically modified lignin when blended improves mechanical properties as well as water absorption capability of the blend material [48][49]. Soda based lignin showed higher mechanical properties when blended with HDPE. However, the melting temperature and degradation temperature was reportedly decreased [50]. In another study showed that lignin-derived from straw through steam explosion shows a drop in tensile strength but an increase in stiffness when blended with low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE) and atactic polystyrene (PS) [3]. Kharade et al. [51] investigated lignin blended with both HDPE and LDPE and compared how lignin polymer blend reacted to mechanical tests when lignin is

added up to 30% (wt.). They claimed that the blend property reduced with the increase of lignin and then compared the properties by adding ethylene acrylic acid copolymer. Also thermal stability improvement by adding lignosulphonate with PE was reported [52]. Sulfur-free lignin as a composite of PE has been investigated by Košíková et al. [53]. Processing stabilization and lignin's impact on the processing of PE has been studied by Gregorová et al. [54]. The reason for choosing PE as a component was its ever-growing market and easy manufacturability and good thermal and mechanical properties.

In all these cases some were carried out by using non compatibilized lignin while others used compatibilizer. Some authors reported the effects of PE/PP to blend with esterified or alkylated lignin. These open a new direction to investigate which is the effect of plasticizer or plasticizing element in PE-lignin blend.

2.1.6 Plasticizer/Compatibilizer

Oils and plasticizers, which are solvents, are commonly added to polymer compounds to improve the material's processing ability and softness. The addition of a plasticizer into a compound reduces its melt viscosity and reduces elastic modulus. If the plasticizer is properly miscible, the glass transition temperature will also tend to decrease [55]. Plasticizers are typically used for obtaining better flexibility at ambient and low temperatures. In addition, in most cases, the addition of plasticizers leads to cost savings.

The effect of plasticizers has been studied on multiple occasions. Multiple authors have investigated the effect of plasticizer/ compatibilizer in the PE-lignin blend. Effect of PEG, Ethyl carbonate as plasticizers has been studied by Bouajila et al. [56]. They recorded a drop of T_g after specific sorption site saturation point. Depending on whether the site is saturated or not plasticizer selection may vary. Using glycerin as a plasticizer in PVA/Lignin blend brought some success. With the increase of glycerin content, the elongation at break increased and tensile strength dropped initially and stabilized later [57]. Mechanical and thermal properties of compatibilized composites made from LDPE and esterified lignin was studied by Sailaja et al. [47]. They found that with the addition of MA (Maleic anhydride) as a compatibilizer, esterified lignin can really improve the mechanical and thermal properties of lignin. Also, EVA (ethylene- vinyl acetate) copolymer can

increase the property of the blend with the lignin content up to 30% (wt.) [53]. The effect of compatibilizer on the properties of LDPE/PP blend was also studied by Luo et al. [58]. The results showed that for non-compatibilized blends, the tensile strength reduces slightly as the content of lignin changes from 10 wt.% to 30 wt.% but it shows a little increased by the presence of 40 wt.% lignin. Non compatibilized lignin blend had a loss of tensile strength due to weak interfacial adhesion which was improved upon the application of maleic anhydride. The compatibilizer increased toughness of the material making it more flexible. Both tensile strength and tensile modulus of blends increases with the addition of 20 wt.% PE-g-MA due to its good compatibilization effect according to the literature. For this problem maleic anhydride was selected as a compatibilizer for two reasons. First, it has been put to the application by researchers and from literature, it can be understood that it can increase the interfacial adhesion between the filler and matrix. Secondly, due to the processability, cost, and availability of PE-Mag, it was a suitable candidate as a compatibilizer.

2.2 Problem Outline

As creating innovative products requires the sustainability of processes followed by eco-friendliness in material development, current endeavors are towards making use of new materials (biocomposites). But along with this comes new challenges such as variability of the properties, resource-saving, functionality and low cost in all stages of the product life cycle [57]. This is why the current work aims to use the byproducts of tobacco production (on which, the economies of three states depend) to reduce the harmful environmental effects of HDPE.

In this research work, HDPE was blended with lignin extracted from tobacco. To investigate the blend material properties lignin was added to these two above mentioned polymers in a varying concentration up to 20% (wt.). Processing parameters for all blend combination was investigated and reported. All blend materials were subjected to mechanical tests for comparison with other reports. Optical microscopy was also done to investigate the miscibility and particle dispersion. Thermal analysis was also performed to analyze the thermal degradation behavior of the blend materials. The effect of plasticizer

is a very intriguing phenomenon, and which is why the plasticizer effect on tobacco lignin blended with PE was also investigated and all the results have been reported for future recommendations.

CHAPTER III METHODOLOGY: BLENDING, EXTRUSION, MOLD
DESIGN, INJECTION MOLDING

3.1 Material Selection

For this research work, HDPE (High-density polyethylene) was used with a melt flow index (MFI) of .9g/10 min and a density of .954g/cm³. Lignin was extracted from tobacco stalk using a proprietary process. HDPE pellets were vacuum dried at 60 °C for 6-9 hours to get rid of unnecessary moisture content during processing. Both materials were stored in a controlled environment in a sealed container to ensure quality.

To investigate the effect of compatibilizer on the HDPE-Lignin blend, maleic anhydride grafted polyethylene was used. The PE-MAg was purchased from Sigma Aldrich.

3.1.1 Blend Preparation

Thermoplastic pellets were blended with tobacco lignin in varying concentrations. Tobacco lignin was crushed into granulated form and then manually mixed with PE pellets. Table 3.1 indicates blend composition and lignin percentage in it.

Lignin was added to HDPE at 5%, 10%, 15% and 30% of the total weight. In the case of compatibilizer, maleic anhydride grafted polyethylene was added with 50 wt.% HDPE and 30 wt.% lignin. Lignin was added to HDPE and manually mixed with a stick for a few minutes. Then these blends are kept in a sealed container. Figure 3.1 shows a sample blend material after manual mixing at the initial phase. At higher temperatures with the presence of shear force, the materials break their chain and make new bonds and upon solidification, a homogenous blend of new material is achieved.

Table 3. 1 *Blend composition*

Blend samples	HDPE (wt.%)	Lignin (wt.%)	PE-Mag (wt.%)
1.	100	0	0
2.	95	5	0
3.	90	10	0
4.	85	15	0
5.	70	30	0
6.	50	30	20



Figure 3. 1 Sample blend material after manual mixing

3.2 Mixing Processes

The process of making blends involves mixing which is basically achieved by distribution or dispersion of a minor component within a major component serving as a matrix. In our case which goes without saying that, lignin is the secondary component and

PE is the matrix. The major component can be considered as the continuous phase and the minor component as distributed or dispersed phases in the form of droplets, filaments or agglomerates.

3.3 Extrusion

Extrusion is a very vital step in material processing. During extrusion, a polymer melt is pumped through a shaping die and formed into a profile. This profile can be a plate, a film, a tube or having any cross-sectional shape. In today's polymer industry, the most commonly used extruder is the single screw extruder. The single screw extruder can have either a smooth inside barrel surface, then it is called a conventional single screw extruder. Figure 3.3 demonstrates the pin mixing section on the screw of a single screw extruder.

For lower viscosity fluids, such as thermoplastic polymer melts, the mixing action caused by the cross-flow are not enough to re-orient, distribute and disperse the mixture. Re-orientation of the interfaces between primary and secondary elements and some distributive mixing can be introduced by any disruption in the flow channel [58].

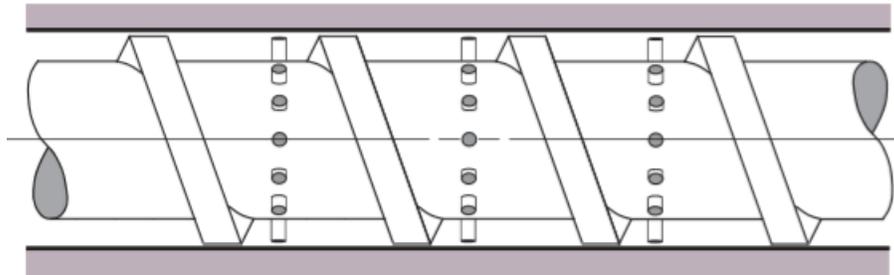


Figure 3. 2 Pin mixing section on the screw of a single screw extruder [58]

In this experiment, a Filabot EX2 single screw extruder has been used. Figure 3.4 shows the single screw extruder used for processing. The extruder generates filaments which were later pelletized and kept in a sealed container before injection molding. It has an extrusion rate of over 0.91 kg per hour. For PE/Lignin blends extrusion parameters used are as follows:

Extruder diameter 2.85 mm

Material input size 3.18 mm pellets

L/D ratio 12

Compression ratio of 2:5:1

Drive force 9.6 Nm

Feed screw and drive 35 RPM



Figure 3. 3 Processing blend filaments with Filabot EX2 single screw extruder

3.4 Injection Molding

Injection molding is the most important process used to manufacture plastic products. Today, more than one-third of all thermoplastic materials are injection molded and more than half of all-polymer processing equipment used is injection molding. The major components of the injection molding machine are the plasticating unit, clamping unit, and the mold. Injection molding machines are classified by international convention.

The cycle begins when the mold closes and then the injection of the polymer into the mold cavity is initiated. Once the cavity is filled, a holding pressure is maintained to

compensate for the shrinkage. Once the part is sufficiently cooled, the mold opens, and the part is ejected. Below, Figure 3.5 presents the molding diagram with all limiting conditions. The melt temperature is bound by a low temperature that results in the unfilled cavity and high temperature that leads to degraded material. The hold pressure is bound by a low pressure that leads to excessive shrinkage or low part weight and high pressure that causes flash.

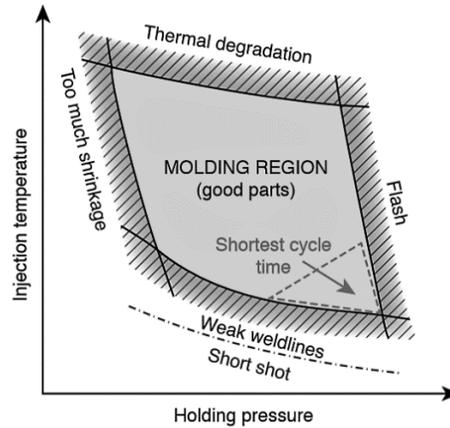


Figure 3. 4 The molding diagram

Another vital part of processing is the mold design as the improper way of designing may lead to errors and resulting in a badly processed part. Which is why the next section covers the mold design for this research work.

3.4.1 Mold Design

Mold material selection and mold design is a very important part of any polymer processing. Mold material has an impact on polymer properties which is investigated by Ozcelick et al. [59]. The main challenge of designing mold is to design gate and runner. For a single cavity mold sprue gate is generally used. In this experiment, the ASTM D638 specimen was required as the output of the injection molding. As this does not have a negative section a single sprue gate is more than enough. In this type of gate, sprue feeds material directly into the cavity rapidly with the minimum pressure drop. Typically, the part shrinkage near the sprue gate will be low; shrinkage in the sprue gate will be high.

This generally results in high tensile stresses near the gate. The traditional design approach is to set the sprue diameter about 1.0 mm larger than the nozzle exit diameter.

The initial difficulties faced with PE/Lignin blend was the lignin’s tendency of adhesion. Due to its adhesive nature, it seemed difficult to eject the sample out from a traditional mold without warping the sample as it clings onto the aluminum surface of the mold. For this processing, a three-piece mold was designed and put into application. The middle piece has the cavity and it’s a plate with the same thickness as that of a D638 tensile testing specimen. Adequate draft angle was provided so the specimen can easily come out after the cooling phase.

3.4.2 Challenges with processing lignin

Processing lignin was very challenging due to its complex structure and behavior at different temperature range. Lignin was first blended with PLA 4043D and it was used as a control unit to identify processing parameters and processing issues associated with it. For the first attempt, 5% lignin was added with 95% PLA and test coupons were injection molded. Table 3.2 shows the processing parameters used for the blends.

Table 3. 2 Injection parameters of PLA-Lignin blends

Test Runs	Injection pressure (psi)	Barrel Temp (F)	Nozzle Temp (F)	Injection Time (s)	Clamping Pressure (Psi)	Hold Time (min)	Cooling Time (min)	Plate Temp (F)
1	1500	370	355	8.7	5000	4.1	1	200
2	3000	370	355	8.6	5000	4.1	1	200
3	4000	370	355	4.5	5000	5.2	1	200

4	3700	385	400	2.5	5000	10.2	1	200
5	1500	385	400	2.5	5000	10.2	1	200

Initially, injection parameters were set for that of raw PLA. The nozzle temperature was kept lower than the barrel temperature, so the material does not degrade during the injection. Clamping pressure was fixed at 5000. Several injections were made at this temperature which resulted in incomplete injection as shown in Figure 3.5



Figure 3. 5 Incomplete injection with lignin

On later attempts, the injection pressure was increased to 3000 psi to compensate for the incomplete injection. This resulted in slightly better injection but still, the sample was not testable, so the injection pressure was changed to 1500 psi. Barrel and nozzle temperatures were increased to 385⁰F and 400⁰F respectively so the material can melt properly in the barrel. The injection pressure was reduced because the molten plastic act as high viscosity liquid and resist the flow if pushed at a higher pressure. The plate temperature was fixed at 200⁰F. This parameter combination solved the under injection problem but the sample had sink marks as shown in Figure 3.6.



Figure 3. 6 Sink mark in injected sample

Sink mark is generally caused when there is uneven heat distribution between the top and bottom pieces of mold and shorter hold time. Increased hold time allows material to flow through the nozzle when the injection is closed, and it fills the rest of the cavity. In this case, proper time was allowed for the entire mold to heat up, so they have the same temperature distribution. Then hold time was increased from 5 minutes to 10 minutes. This resulted in a sample without sink marks or brittleness. These samples were later subjected to tensile testing to investigate the blend properties. The processing of PLA/Lignin had higher processing time and a low success rate. The average processing time for injection of tensile testing sample was approximately 40-45 minutes. As blend material adhered to mold surface, heat gun was used to melt residue lignin stuck at mold and then wiped. Moreover, success rate of getting a testable sample was 40% which is also very low.

The processing PLA/lignin blend was difficult. Also, tests conducted on the sample showed inconsistent properties due to the presence of air bubbles in the samples. Some approaches were taken during processing to reduce the void amounts. All materials were heated in a vacuum oven and stored in a sealed container to reduce moisture accumulation on materials. Also, the lignin may degrade over time if kept at high temperature for a long time. This causes increased fumes when injected. So, as mentioned in the processing

section the material was introduced in the hopper at smaller quantity to reduce degradation. Despite these solutions the samples were not completely free of voids. This is why PLA/Lignin blend was not satisfactory from the point of processing and testing. Detail discussion on the behavior of PLA/lignin blend sample is provided later in the results section. Hence, HDPE was used to blend with lignin. The knowledge acquired from PLA/Lignin processing was used in the injection molding of HDPE lignin blends.

3.4.3 Injection Molding Parameters

Injection parameters influence the part finish and part's property. Changing the parameters leads to sometimes desirable and sometime non-desirable outputs. PE has optimum injection parameters on which the desired output can be found. In this investigation, the molding parameters were set by testing out different parameters by design of the experiment and keeping all parameters fixed and then gradually changing one parameter and so on. Blend materials are injection molded using a Morgan Press G-125T injection molding machine. Figure 3.6 shows the injection molding used for processing tensile coupons.

The influence of lignin addition to HDPE on the injection molding parameters was studied at concentrations of 5, 10, 15 and 30 wt.% of tobacco lignin. The parameters were then compared to those used in producing the neat HDPE samples.



Figure 3. 7 Morgan injection molding machine

Table 3. 3 HDPE/Lignin injection molding parameters

Injection Runs	Injection pressure (psi)	Barrel Temp (F)	Nozzle Temp (F)	Injection Time (s)	Clamping Pressure (Psi)	Hold Time (sec)	Cooling Time (min)	Plate Temp (F)
Neat PE	3000	390	400	8.7	7000	2	1	200
5% PE Lignin	3500	390	400	8.6	7000	2	1	200
10 % PE Lignin	4000	390	400	8.9	7000	2	1	200
15% PE Lignin	4500	390	400	8.6	7000	2	1	200
30% PE Lignin	5000	395	420	8.6	7000	2	1	200

Table 3.2 shows the processing parameters for different blends. Except for an increase in injection pressure, no changes to the injection molding parameters of HDPE was needed. The parameters remained almost constant for all lignin concentrations. It was found that higher injection pressure was needed as the lignin content was increased. This is related to the rheological properties of the material. The specific gravity tests discussed in section 5.3 demonstrates that the density of the blend increases with the increase of lignin. During processing higher injection pressure was required for blend materials with the increase of lignin percentage. The higher the pressure and resultant pressure gradient at the mold gate, the faster the material flows. Which is why, increased flow length required increased entrance pressure, to generate the same pressure gradient to maintain the polymer

melt speed. Apart from this, all the parameters remained constant and this implies that the addition of lignin does not affect injection molding parameters for products made from HDPE, which can be useful while analyzing the processing costs of such products.

The addition of lignin does not have a significant influence on the injection molding parameters. In conclusion, it can be said that tobacco lignin when blended with thermoplastic such as HDPE, does not obstruct the processability of the polymer blend.

In this section, the test procedure and test setups are discussed. There are many material constants to describe the material's mechanical properties. For an isotropic and homogeneous elastic material, these constants could be bulk modulus (K), Young's modulus (E), shear modulus (G), Poisson's ratio (ν), etc. To understand the effect of lignin in thermoplastic the tensile specimens were subjected to tensile tests. To evaluate the physical properties, density and hardness tests were performed. This chapter also includes the optical microscopy of the test samples in order to understand how the lignin particles distributed in the thermoplastic matrix. The thermal degradation of the blend material is another important feature of this investigation. TGA analysis was performed and thermal stability of the blend material is also reported.

4.1 Tensile Testing

All the test samples were subjected to a tensile test in an MTS INSTRON 5585 H tester. For testing, wedge-shaped clamps were used. From test data, ultimate tensile strength was measured. Also, Young's modulus and strain at break were also measured. For testing at least five tensile testing specimens were used to find the variation of all blend compositions. All test was performed according to the ASTM standards.

In a tensile test, the tensile specimen is pulled at negative z-direction at a constant velocity and displacement was measured. The next few sections will explain the testing procedure and setup and data fitting and forming the stress-strain curves.

4.1.1 Specimen Preparation

At least six tensile specimens were processed for each blend composition and five of them were tested using the MTS INSTRON 5585 H tester.



Figure 4. 1 HDPE-lignin ASTM D638 Type IV tensile test coupons

4.1.2 Tensile Testing

All the samples were pulled towards the negative Z direction while keeping the one end fixed in the clamps. The samples were stretched until they reach rupture points. The tensile tester provided raw data for load in Newtons and displacements in mm.

4.1.3 Data Analysis

All the raw data were collected, and MATLAB was used for calculating stress-strain. Due to the small load cell, the vibration from the hydraulics of the MTS machine was observed in the raw data. The noise was filtered out using a Savitzky-Golay filter. Later, filtered data were used to form a stress-strain curve for blend materials. Ultimate tensile strength, modulus of elasticity and elongation at break were also calculated and analyzed.



Figure 4. 2 Tensile testing of the sample specimen

4.2 Hardness Testing

To investigate the physical properties of blend material, Rockwell hardness testing was performed. For Rockwell hardness test a Wilson 4JR hardness tester (B Scale) with 100 kg loading and 1/16-inch steel ball was used. Five runs for individual blend were done to ensure the validity of tests. Standard deviation and average were calculated and compared with neat HDPE hardness data.

4.3 Density Testing

Archimedes' principle states that the buoyant force experienced by a submerged object is equal to the weight of the liquid displaced by the object. Experimentally this appears in the fact that the submerged object apparently weighs less by an amount equal to the weight of the liquid displaced. The buoyant force can be expressed as

$$F_b = W_{air} - W_{liquid} = dgv \quad (4.1)$$

Where d is the density of the liquid, g is the acceleration of gravity and V is the volume of the immersed object. Since we know that $W=mg$. The apparent change in mass when submerged is

$$m - m_{\text{apparent}} = d_{\text{liquid}}v \quad (4.2)$$

From this equation, the density of the material can be easily calculated. For this research work, the specific gravity of the blend materials was calculated. The density and specific gravity of the test coupons were measured using a Mettler Toledo precision balance in accordance with ASTM D792. Five coupons from each blend compositions were tested.

4.4 Optical Microscopy

The cross-section of test coupons was investigated under optical microscopy to study the miscibility of lignin particles in HDPE. Leica DVM6 optical microscope was used to capture the lignin grain distribution on the test specimen and LAS X version 3.0.8.19082 was used to analyze the images. Comparisons between the different PE-lignin composition micrographs were performed to have a better understanding of the blend morphology. For testing, broken specimen resulted from tensile testing were taken and cut to get rid of the deformed section caused due to tensile testing. The cross-section of the test coupons was then polished using a BUEHLER Ecomet 4000 variable speed polisher. The polishing speed was 120 rpm. Figure 4.6 shows the optical microscope used for this test purpose.



Figure 4. 3 Optical Microscope

4.5 Thermogravimetric Analysis

Thermogravimetric analysis was performed into all blend materials to investigate the thermal stability induced due to the addition of lignin. Thermogravimetric analysis (TGA) testing was performed on a TA Instruments Discovery TGA 550 equipment. Tests were conducted as per ASTM E1131 standard. Samples of 15-20 mg of neat HDPE and HDPE/lignin blends were tested under Nitrogen atmosphere at a heating rate of 10 °C/min from 25°C to 600°C. Once the mass loss plateau was established, the environment in the furnace was switched from inert to reactive oxygen environment. Both TGA and DTGA data were plotted and analyzed. Findings from TGA experiments are included in the next chapter which is the result section.

CHAPTER V RESULTS AND DISCUSSION

This chapter presents an analysis of the data obtained from the tests performed in the previous chapter. The discussions on the effect of lignin in thermoplastic are made based on the test results which include both mechanical, physical and thermal testing. The change of property imparted by lignin was also enclosed in this chapter along with a possible explanation of the phenomenon noticed during test and test results.

5.1 Tensile Testing of PLA/Lignin

Test coupons obtained from injection molding were subjected to tensile tests. Figures 5.1, 5.2 and 5.3 show the stress-strain curves for PLA/Lignin blend of 5 %, 15%, and 25% respectively. It can be seen from the figure that; sample data are not consistent when lignin content goes beyond 5% wt.

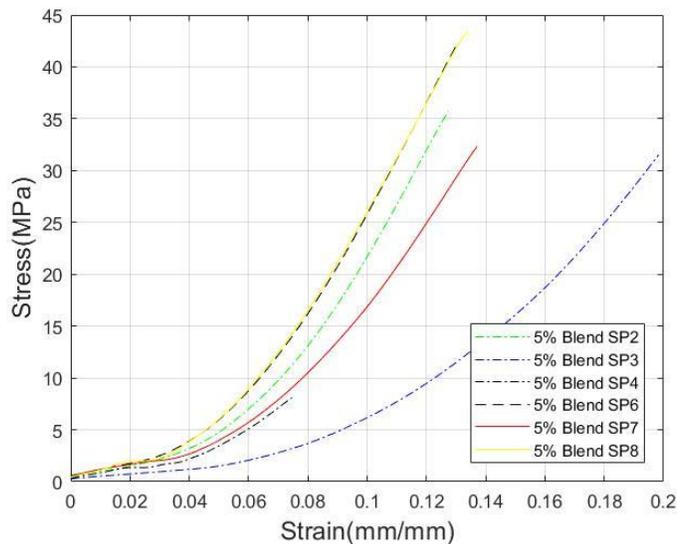


Figure 5. 1 Stress-strain curve of PLA/ Lignin 5% blends

It can also be seen that all the test sample from a batch does not behave consistently when the tensile test is performed. Figure 5.2 and Figure 5.3 shows that some of the samples broke prematurely when a tension load is applied. The reason was that blend was not homogenous. Tobacco lignin did not bond with PLA matrix properly. This resulted in

high accumulation of lignin in PLA than other regions in the matrix. As a result, some samples behaved brittle while some samples demonstrated comparatively higher flexibility. To further investigate this discontinuity of blend materials, the tensile samples were put under the optical microscope.

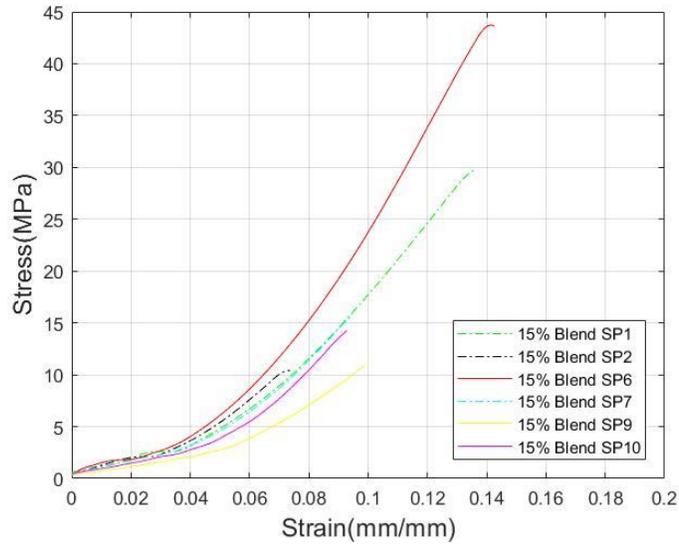


Figure 5. 2 Stress-strain curve of PLA/ Lignin 15% blends

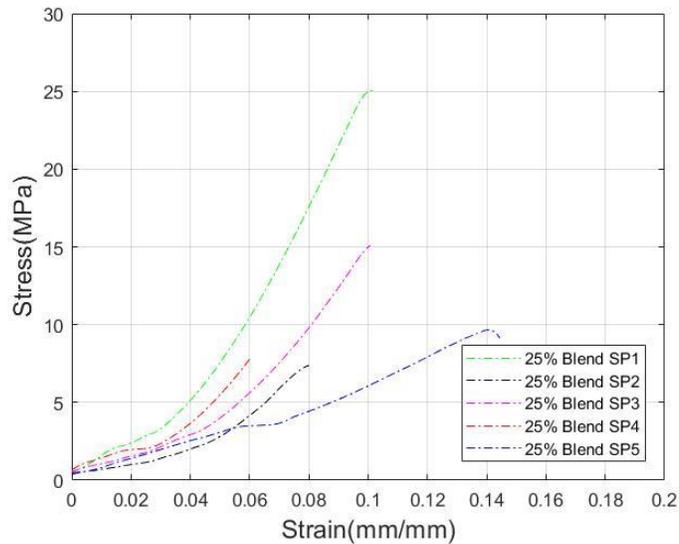


Figure 5. 3 Stress-strain curve of PLA/Lignin 25% blends

5.2 Optical Micrographs of PLA/Lignin

Optical micrographs of 0% 5% 15% and 25% were shown in figure 5.4. It can be seen from the optical micrographs that, raw PLA shows typical semi-crystalline microstructure while in the case of a 5% blend, a clear sign of lignin traces was visible in the matrix. The blackish region confirms the tobacco traces in PLA. Figure 5.4 (c) shows a 15% PLA/Lignin blend. It is clearly visible in the image that increase of lignin percentage introduces voids in the matrix. The increased amount of black region can justify the increase of lignin. In case of 25% blends, larger voids/bubbles were also noticed.

To further understand the effect of bubbles in PLA/Lignin blend material, bubble size was calculated for all the samples. The frequency distribution of bubble size for all compositions of the blend was calculated. Figure 5.5 shows bubble size distribution for 5%, 15% and 25% blend materials. The higher amount of bubbles is visible when the lignin percentage is increased. Although it can be misleading as the 15% blend seemed to have the greatest number of bubbles but 25% blend had fewer bubbles but those were of higher sizes. As a result, the total amount of area covered by bubbles was higher when lignin was added at 15% and 25%. 5% PLA/Lignin blend had comparatively a smaller number of bubbles which resulted in comparatively better consistency and tensile property.

This increased amount of void justifies the reason for the premature failure of test samples when lignin is added at a higher percentage. As a result, samples which had comparatively less bubble had comparatively good tensile properties while samples with voids had low mechanical properties.



(a)



(b)



(c)



(d)

Figure 5. 4 Optical micrographs of PLA/lignin (a) 0% (b) 5% (c) 15% & (d) 25% blends

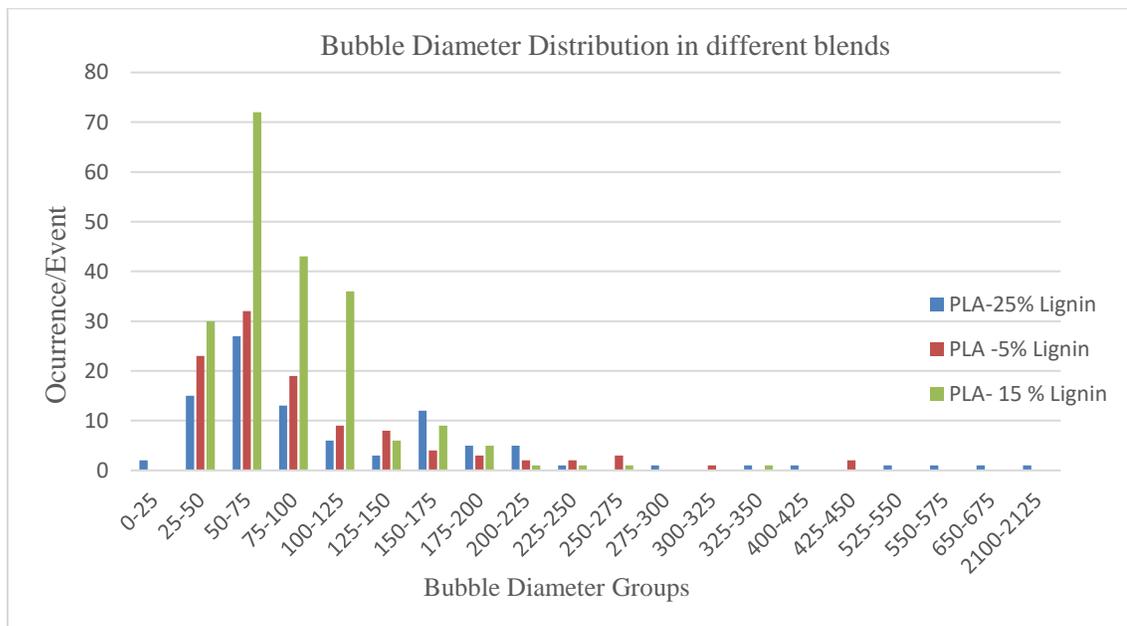


Figure 5. 5 Bubble size distribution for different PLA/Lignin blend composition

These test results show the variation in properties and the presence of bubbles in blend material. Tobacco lignin seemed to be incompatible to make blends with PLA due to weak interfacial bonding. On the other hand, HDPE is a standard material for injection molding and is more flexible than PLA. Blending lignin with HDPE instead of PLA

reduces the difficulties caused by PLA. This is why lignin was blended with thermoplastic which is HDPE and the results obtained from the tests were discussed in the following sections.

5.3 Tensile Test of HDPE/Lignin

Figure 5.6 shows the tensile stress-strain curves of HDPE/Lignin blends. Figure 5.7 and 5.8 compares the tensile strength and modulus of the blends. With an addition of 5 wt.% of lignin, the tensile strength dropped slightly by 2.6%. However, the decrease is within the margin of error. Similar results were observed for 10 wt.% and 15 wt.% as shown in Figure 5.7. Statistically, the tensile strength remained unaffected by the addition of lignin up to 15 wt.%. However, when lignin content was increased to 30 wt.% of lignin, tensile strength dropped by 19%.

Overall, the tensile modulus improved with the increase of lignin content. Tensile modulus increased by 4%, 29%, 25% and 8% with the addition of 5, 10, 15 and 30 wt.% of tobacco lignin to the HDPE. Elongation at break decreased by 22%, 39%, 47% and 62% when the lignin content was increased by 5, 10, 15 and 30 wt. %. Table 5.1 combines all ultimate tensile strength, Young's modulus and elongation at break for all blend compositions. From this, it can be observed how the addition of tobacco lignin affects the mechanical properties of HDPE.

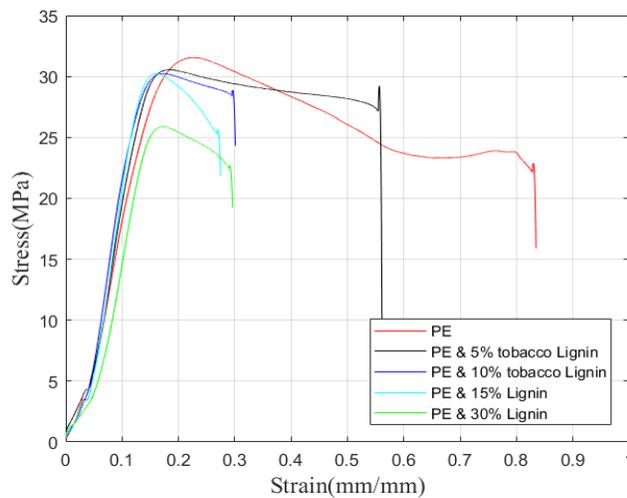


Figure 5. 6 Stress-strain curve of HDPE/Lignin blends

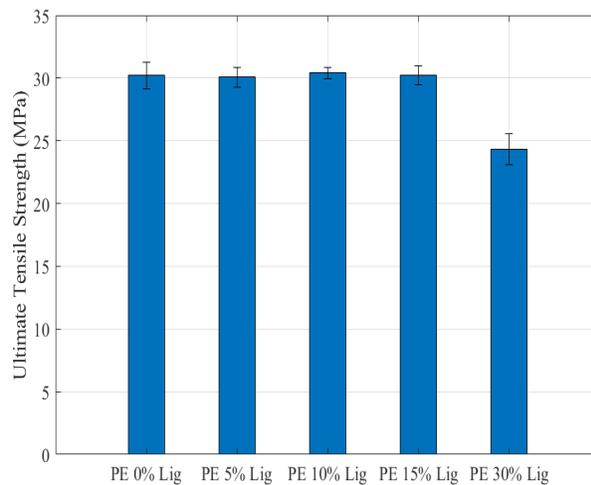


Figure 5. 7 Bar chart comparing UTS of HDPE/Lignin blends

Table 5. 1 Comparison of tensile properties of HDPE/Lignin blend

Blend composition	Ultimate tensile strength (MPa)	Young's modulus (GPa)	Strain at break (mm/mm)
Neat PE	30.20 ± 1.05	0.24 ± .02	0.61 ±.13
5% PE Lignin	29.42 ±0.76	0.25 ±.02	0.47 ±.11
10% PE Lignin	30.41 ±0.44	0.31 ±.02	0.37 ±.03
15% PE Lignin	30.22 ±0.74	0.301±.03	0.32 ±.03
30% PE Lignin	24.34 ±1.23	0.2676 ±.02	0.23 ±.04

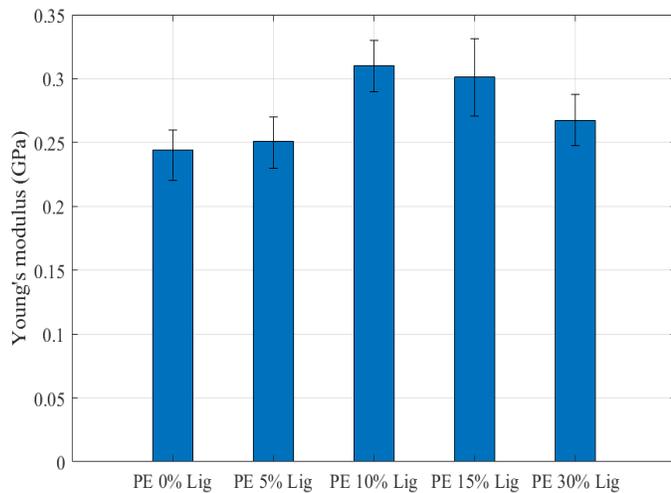


Figure 5. 8 Bar chart comparing Young's modulus of HDPE/Lignin blends

Table 5.2 compares the results obtained in this study with those from the literature. As seen in the table, most of the literature showed a reduction in tensile strength as high as 48% and as low as 3.7% with the addition of 10 wt.% of lignin. Unmodified tobacco lignin of the current study showed superior performance compared to the more expensive acetylated and butyrate lignin at 30 wt.% addition of tobacco lignin, the decrease in strength observed is comparable or better than other modified lignin materials.

Table 5. 2 Comparison of UTS of HDPE/Lignin blend in related works

	Materials	Change in UTS % with the increase of lignin content in the blend	
		10 wt.% PE Lignin	30% PE Lignin
Present work	HDPE-tobacco lignin	0.69% increase	19.40% decrease
Earlier works			
<i>P. Alexy et al.</i> [46]	LDPE -Lignin	3.70% decrease	55.55% decrease

<i>R. Sailaja et al.</i> [47]	LDPE – esterified lignin with phthalic anhydride	-	16.66% decrease
<i>Laura Dehne et al</i> [48]	Acetylated Lignin Propionate LigninButyrate Lignin	17.3% decrease 10.86% decrease 4.34% decrease	39.13% decrease 13.04% decrease 13.04% decrease
<i>R. Pucciariello et al.</i> [3]	LLDPE LDPE HDPE	73.47% decrease 75% decrease 47.82% decrease	-
<i>J. Samani et al.</i> [60]	Non-wood soda lignin 5% MAPE added	2.85 % increase 5.40% increase	8.1% increase 12.5% increase
<i>F. Luo et al.</i> [58]	Non compatibilized Lignin	4.76% decrease	-
<i>Kharade et al.</i> [51]	HDPE-Lignin	37.76% decrease	52.63% decrease

5.4 Hardness Test

To characterize the physical properties of the blends, Rockwell hardness tests were Performed. The Rockwell hardness numbers for different blend specimens are shown in Figure 5.9. As seen in the Figure, the hardness number decreased with an increase in lignin content. The hardness number remained almost the same at 5 wt.% concentration. However, with the addition of 10, 15 and 30 wt.% of tobacco lignin, a decrease of 3%, 13%, and 21% respectively was observed. Comparisons with earlier works could not be made as no published literature has reported the hardness of HDPE-lignin or any kind of polymer and lignin blends.

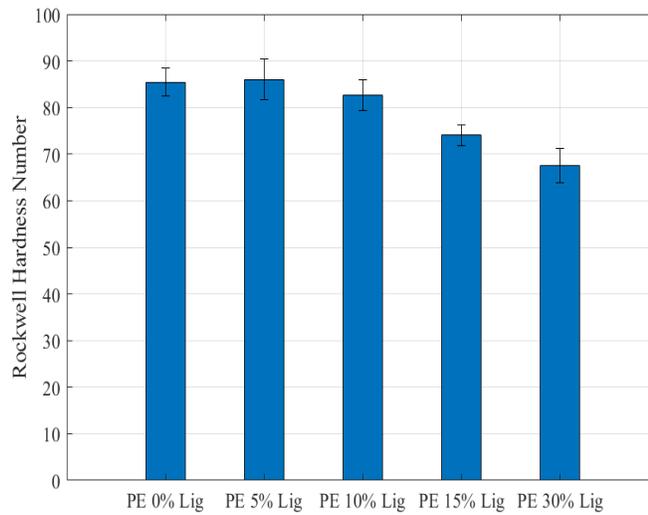


Figure 5. 9 Rockwell hardness number comparison for all HDPE/Lignin blends

5.5 Density Test

Below given in Figure 5.10 where it compares the specific gravity of all the blend materials. Density constantly increased with the addition of lignin. Neat HDPE showed a density of .84 g/cm³. Density increased by 2.3%, 5.9%, 7.1% and 23% with the increase of lignin by 5,10,15 and 30 wt.% respectively.

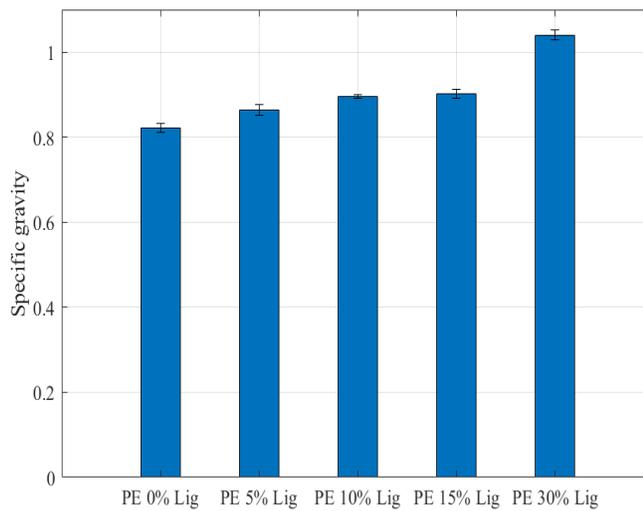


Figure 5. 10 Specific gravity comparison for all HDPE/Lignin blends

5.6 Optical Micrographs

All tensile testing specimens were cut and polished in the polisher. The samples were then placed under the optical microscope to better understand the distribution of lignin particles in the HDPE. As shown in Figure 5.11 (a) optical micrograph of the neat HDPE sample shows a semi-crystalline structure. Furthermore, from the observed images it can be seen that HDPE is compact and elastic material which shows no visible cracks at the cross-section due to the tensile test. Figure 5.11 (b) shows optical micrographs of 5% blend material. It can be observed how lignin particles are distributed in the HDPE matrix. Lignin particles are widely dispersed, and varying sizes of particles were seen. There were some white segments that were identified as HDPE. These are the sections where lignin failed to have a homogenous distribution and interfacial adhesion.



(a)



(b)



(c)



Figure 5.11 Optical micrograph of (a) Neat HDPE (b) 5% (c) 10% (d) 15% & (e) 30% blends

Similar cases were observed in 10, 15 and 30% however, there were some differences. In the case of 15% and 30% blends, there were some big agglomerates of lignin in the matrix. The particle distribution was similar to that of 5% and 10% blends. However, from the visual inspection, the lignin particle sizes seemed comparatively higher in 15% and 30% blends. In the case of 15% and 30% blends, lignin was found covering some portion of the matrix surface turning it black and there were some white segments of polyethylene. A higher concentration of lignin (blackish regions in PE matrix) suggests that there may not be a homogenous distribution of lignin across the matrix. The reasons are lignin's tendency of adhesion to itself rather than thermoplastic.

From Figure 5.11, it can be observed that lignin is homogeneously distributed in some sections of the interface but not in all regions and some regions have higher concentrations. This discoloration of brown and black regions was observed to different degrees which can be attributed to the tobacco's inherent staining behavior. To have a deeper understanding of the mixing process of HDPE pellets with tobacco lignin, grain distribution across the surface of the specimen was studied. For this, all the grains were quantified by measuring the grain diameter and the data was then analyzed to form a probability density function for the grain sizes by using equation 1.

$$f(x, \mu, \sigma) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[\frac{-(x-\mu)^2}{2\sigma^2}\right] \quad (5.1)$$

Where,

mean μ

standard deviation σ

variance σ^2

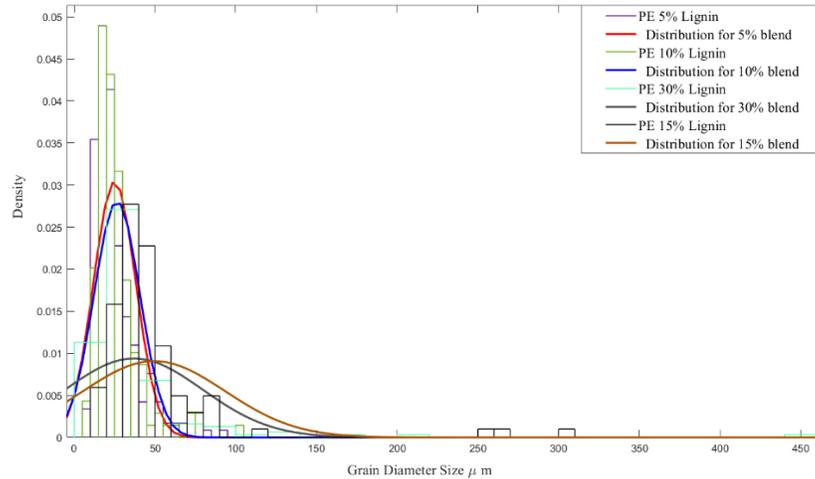


Figure 5. 12 Frequency distribution of lignin particles for various blend compositions

A histogram created from the sample data has been shown in Figure 5.12 which represents overall lignin grain sizes in diameter (μm) and their frequency in the specimen for all blend compositions. All blend compositions showed grain size ranging from $10\mu\text{m}$ to all the way up to $150\mu\text{m}$. There was also some agglomeration of $450\mu\text{m}$ in the matrix. The normal distribution shows that, for 5% and 10% blends, the average grain size is $25\mu\text{m}$. However, for 15% and 30%, grain size has wider ranges and average been between $25\text{-}75\mu\text{m}$. Related research works show that; particle distribution is significantly dependent on the esterification of lignin. It was reported that acetylated lignin has around $55\mu\text{m}$ of grain diameter and butyrate lignin implied better grain distribution and sizing of $14\mu\text{m}$ [48]. Current research work involves tobacco lignin which is not esterified, and it shows an average grain size of $25\mu\text{m}$ for 5% and 10% blends and $50\mu\text{m}$ for 15% and 30% blends which is better than the acetylated lignin. Butyrate lignin has better grain sizing and distribution than tobacco lignin but this adds a significant cost to esterify lignin [48].

Furthermore, Tobacco lignin does not present any large agglomeration in PE lignin matrix. From the above comparison, it can be easily perceived that tobacco lignin has comparatively better compatibility than other unmodified lignin.

5.7 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was performed to evaluate thermal degradation as well as the compositional properties of the blends. Figure 5.13 and 5.14 shows the TGA and DTGA curves of the lignin blends. Table 5.3 shows the decomposition onset temperature, end temperature, and peak temperature. Decomposition onset temperature is defined as the temperature at which 5 % weight loss occurs. The temperature at which maximum weight loss observed is the peak temperature of the derivative curve.

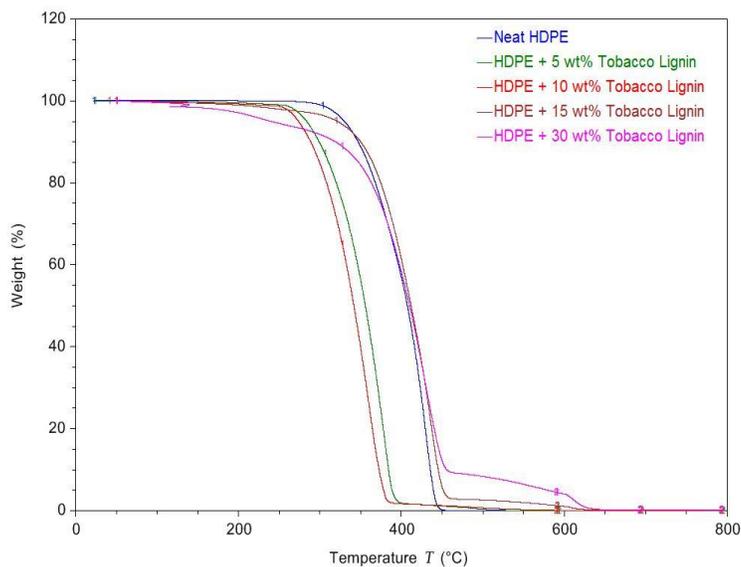


Figure 5. 13 TGA curves for different blend compositions of HDPE and tobacco lignin

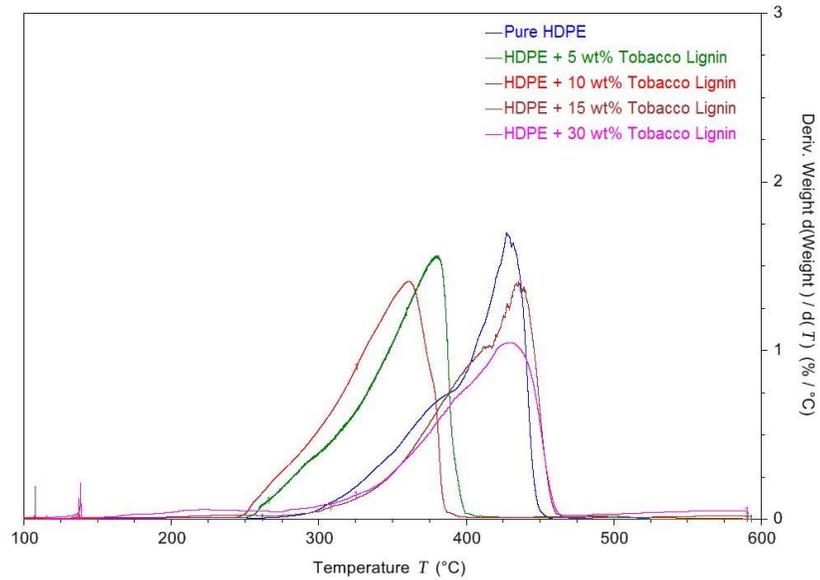


Figure 5. 14 DTGA curves for different blend compositions of HDPE and tobacco lignin

From Figure 5.13, the degradation temperature of HDPE starts at 330.19 °C and continues to degrade until 441.61 °C. Initially, at lower concentrations of 5 wt.% and 10 wt.% of lignin, the decomposition appears to be initiated at lower temperatures than the neat HDPE. With 5 wt.% and 10 wt.% increase of lignin, the onset decomposition temperature dropped by 14% and 17% respectively. The degradation peak temperature also dropped by 11% and 15% respectively. However, at higher concentrations of 15 wt.% and 30 wt.%, the onset and peak temperatures were almost similar to that of neat HDPE. The residual mass content at 600 °C steadily increased to as high as 1.21 mg. At lower concentrations, lignin accelerates the thermal degradation but at higher concentrations, tobacco lignin is acting as a thermal stabilizer.

Table 5. 3 TGA test results comparison for all blend compositions

Blend Composition	T _{onset} (°C)	T _{End} (°C)	Decomposition Peak Temp (°C)	Residual Mass at 600 °C (mg)
Neat PE	330.19	441.61	427.26	0.01
5% PE Lignin	283.68	390.70	380.04	0.02
10% PE Lignin	273.74	377.93	360.96	0.09
15% PE Lignin	321.51	449.38	430.26	1.21
30% PE Lignin	320.97	448.66	429.35	4.48

5.8 Effect of Compatibilizer on PE-Lignin blends

As already mentioned in the previous chapter, to investigate the effect of compatibilizer, the effect of PE-MAg (Maleic anhydride grafted polyethylene) was added to 30 wt.% HDPE-Lignin blend. ASTM D638 Type IV specimens were processed and subjected to mechanical tests and optical microscopy tests. The result was then compared with non-compatibilized blend materials.

5.6.1 Tensile Testing

Tensile properties of five blend samples prepared through an extrusion and injection molding processes were evaluated. Figure 5.15 shows the comparative stress-strain curve when 20 wt.% PE-MAg is added with 30 wt.% lignin and 50 wt.% HDPE. It can be seen from the figure that the addition of PE-MAg did not improve the tensile property. Ultimate tensile strength remains the same as that without compatibilizer. A comparative bar chart showing Young's modulus has been provided later in this section for clarity.

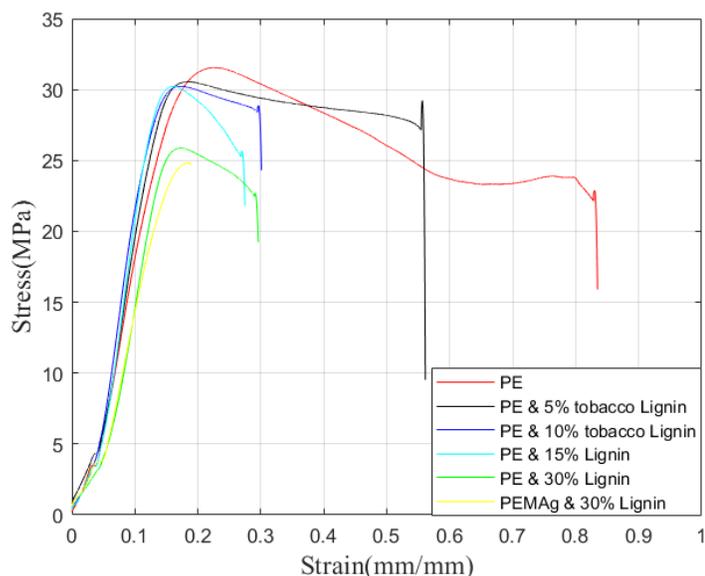


Figure 5. 15 Stress-Strain curve comparing PEMAg-30 wt.% lignin with other blend compositions

Figure 5.16 shows a comparative bar chart to compare the effect of compatibilizer on Young's modulus. Young's modulus was decreased by 22%. Also, the elongation at break was reduced by 18%. It was found that the addition of the compatibilizer made the blend material more brittle causing it to fail at the comparatively lower strain. However, Luo et al. blended esterified lignin with EVA and PE-MAG and found improved properties. The reason behind this incompatibility with tobacco lignin can be justified by deeper observation of blend specimens by optical micrographs [61].

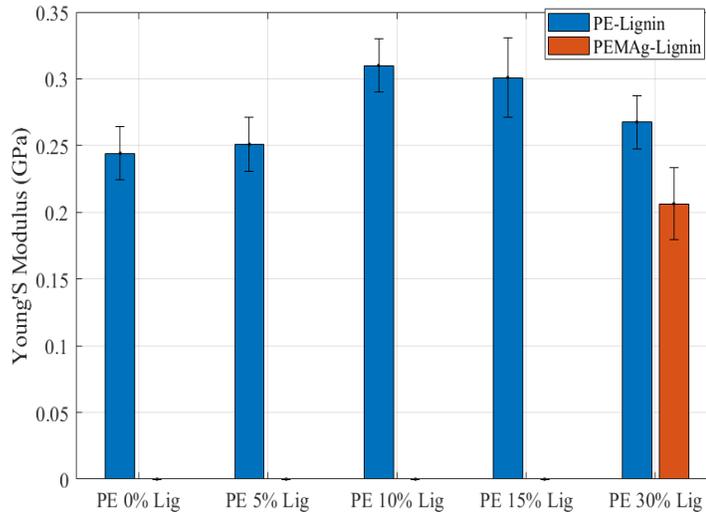


Figure 5. 16 Comparative bar chart showing Young's modulus

5.6.2 Hardness Testing

A hardness test was performed to evaluate the resistance of the compatibilized blend material upon indentation. Similar test procedures were followed, and a quantitative comparison was made with all blend materials. Figure 5.17 shows the comparison of the Rockwell hardness test results. Rockwell hardness number increased by 10% which means that the material has become more harder and which justifies the reason for material having lower strain at break. The effect of compatibilizer is not visible in ultimate tensile strength where it remains almost the same as that of non-compatibilized lignin, but hardness test reveals materials brittle property.

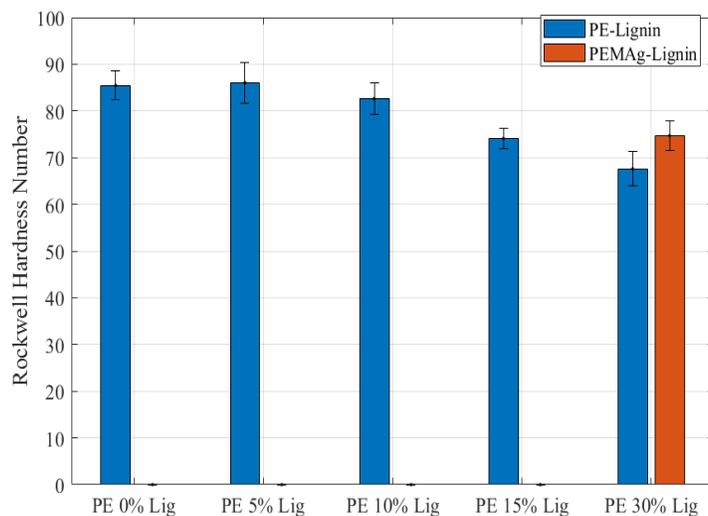


Figure 5. 17 Effect of compatibilizer on Rockwell hardness number

5.6.3 Density Testing

Figure 5.18 shows another comparative bar chart showing the change in specific gravity in 30 wt.% lignin blends with the addition of PE-MAg. It can be seen from the bar chart that specific gravity has little to no effect whether the blend material is compatibilized or not. As the amount of lignin remains the same in the blend, the overall specific gravity of the blend material remains constant throughout the process.

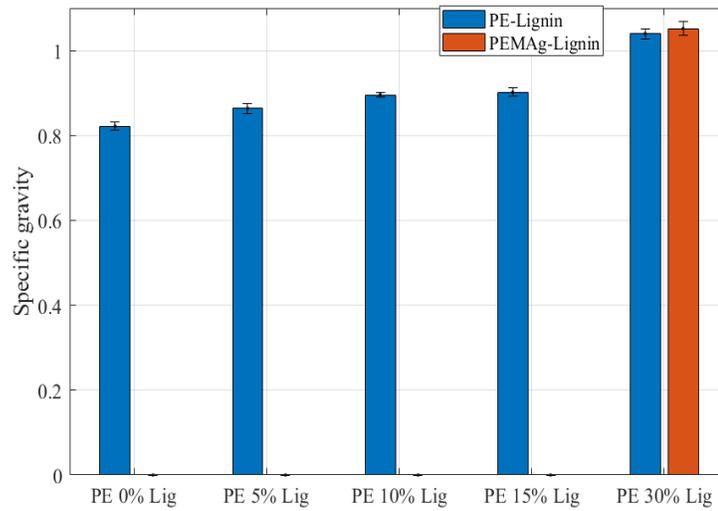


Figure 5. 18 Effect of compatibilizer on the specific gravity of blend material

5.6.4 Optical Microscopy Test

Optical microscopy was also performed on the blend sample where PE-MAg was added as a compatibilizer. The samples were cut in the small sections and a similar polishing technique was used before subjecting under the optical microscope. Figure 5.19 shows some sample pictures obtained from optical microscopy. The picture shows that lignin has covered all the interface of the matrix. The blackish region suggests the dispersion of lignin in the matrix. In the case of un-compatibilized blend specimen, optical micrograph revealed white thermoplastic sections where lignin was not distributed properly. But unlike that scenario compatibilizer managed to increase the interfacial adhesion between lignin and HDPE thus creating a good bond between two polymers. Due to this reason particle size analysis was not performed in case of compatibilized blend material. Despite having a good spread of lignin particles in the matrix, the tensile property did not increase as it has mentioned before. The possible reason could be the comparative lower tensile property of PE-MAg than HDPE used in this investigation which resulted in cumulative drop of young's modulus and strain at break making the material brittle. The addition of lignin increases the brittle nature of the material. Luo et al. reported to have better young's modulus and elongation after the addition of compatibilizer [62]. However,

in that case, esterified lignin was used instead of raw lignin. Esterification has been previously mentioned to have increased property of the blend. In this case, it seemed that compatibilizer does not affect the raw tobacco lignin as it does to esterified lignin.

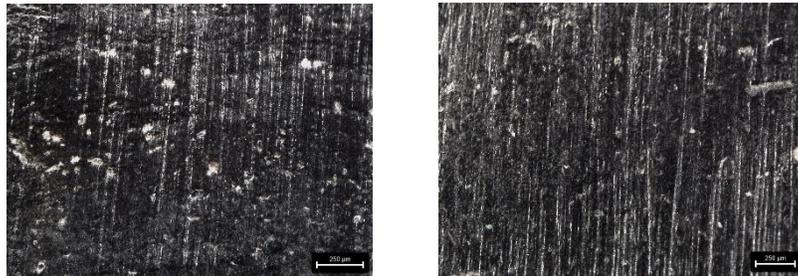


Figure 5. 19 Optical micrographs of 30 wt.% lignin blend after adding compatibilizer

6.1 Conclusions

In this study, the effect of blending tobacco lignin with HDPE was successfully investigated. Lignin was added to HDPE at 5%, 10%, 15% & 30% by wt. and the materials were processed via melt mixing, extrusion, and injection molding to prepare test specimens. Coupons were then tested for their physical, mechanical and thermal properties. Test results show that the addition of tobacco lignin did not have any effect on the injection molding processing parameters implying that it does not add any cost to the processing. Tensile strength remained almost unaffected with the addition of lignin up to 15 wt.% but showed a sudden drop of 19% at 30 wt.% lignin concentration. These values are comparable or in most cases superior to expensive acetylated or butylated lignin reported in the literature. Overall, tensile modulus increased with an increase in lignin. The density and specific gravity also increased but the material became softer with the increase in lignin. Optical microscopy revealed that HDPE-lignin blends have an uneven distribution of lignin particles for all the blend composition, but the overall grain size was found to be better than other research works performed on esterified lignin. Thus, making the tobacco lignin comparatively better. TGA results showed that while the thermal decomposition accelerated at lower concentrations, higher percentiles of lignin stabilized the decomposition onset and degradation temperature.

To address the drop in mechanical properties at 30% by wt. addition of lignin, maleic anhydride grafted polyethylene was added as a compatibilizer to increase the interfacial adhesion between tobacco lignin and thermoplastic. The addition of compatibilizer in blend material demonstrated that PE-MAg has little difference in the ultimate tensile strength of un-compatibilized blend material. However, tensile modulus and elongation at break decreased by a good amount. Also, optical microscopy revealed that compatibilization helped the dispersion of lignin throughout the interface of polymer but making the material brittle in the process. The reason behind this is the application of 20% PE-Mag reduced the overall quantity of HDPE in the blend. As the tensile property

of PE-Mag is not as same as HDPE the overall tensile property was reduced. Overall, blending unmodified tobacco lignin with HDPE shows great promise as a potential replacement to commercial HDPE.

6.2 Future Work

Throughout this investigation, all the standards were followed, and all the tests were performed according. Processing and storing of materials were closely observed for any unwanted mistakes. Yet, this research work does have some limitations, and thus many improvements can be done to make this work more accurate and reliable.

Firstly, the processing was done in a single screw extruder and then a ram-type injection molding machine. Nowadays most of the industry uses a double screw extruder and screw-type injection molding machine which allows equivalent heat distribution and proper mixing of the blend constituents. Higher quality of mixing can be ensured and by utilizing these processing systems and parameters. Also, the miscibility study has been performed by several researchers as the polymer properties depend on their miscibility. Miscibility studies can be performed to introduce more clarity to this work. Tensile specimens studied in this experiment had some tolerances which if reduced can impart more accurate mechanical test result on blend characteristics. Flexure and Izod impact testing of the blend material can also be investigated to have more information on the properties of HDPE-lignin blend. Melt flow index is a very important parameter of polymer rheology which was not performed in this research work. MFI data will introduce deeper knowledge related to the viscosity of the blend material and its characteristics during processing.

Secondly, the SEM test can be performed in the future to have information on the miscibility and bonding of lignin chains with polyethylene chains and how lignin is distributed and acts in a thermoplastic matrix.

Finally, the effect of compatibilizer was investigated in this research work. However, there are other available compatibilizers and plasticizers which can improve the tensile strength, tensile modulus, and elongation at break if applied properly. Even there

are some biodegradable polymers such as PLA (polylactic acid) and biodegradable compatibilizer is available which if applied with lignin can reduce the usage of petroleum-based plastics. This might reduce the environmental pollution caused by regular plastic products. Not all of these areas are investigated to a large extent. As a result, there remains ample room to investigate the effect of tobacco lignin blended with other biopolymers.

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