

CHEMICALLY MODIFIED LIGNIN – A POTENTIAL RESOURCE MATERIAL FOR COMPOSITES WITH BETTER STABILITY

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Abstract: In this study, Kraft softwood lignin was treated with acetic and propionic anhydride to produce esterified lignin. Reactions were performed at 85°C. The product was characterized using IR, DSC and different parameters required to index the ease of process-operation. The chemically modified as well as esterified lignin was then blended with bio-renewable polymer such as polylactide (PLA) and extruded into composite films. The films were then subjected to routine analysis like FTIR and TGA. In addition to that mechanical properties were also verified by standard tensile testing protocols. Preliminary results gave a positive indication to go for further studies. This will confirm the results and establish the range of properties achievable.

Keywords: Bio-degradable Composite, Lignin, Modification, Synthesis, Characterization.

1. Introduction

Lignin is a naturally occurring polymer that acts as a binder for cellulose and hemicellulose in the plant structure. Lignin is also generated in large quantities by industrial pulping processes (mainly Kraft pulping). Nearly 80 million tons of lignin are produced annually from the paper industry alone. Currently, a major amount of the lignin produced is used as an alternative source of boiler fuel, although its energy-production efficiency is less than that of coal. Due to its huge natural abundance lignin may be considered as a potential candidate to be utilized as low cost filler for bio-degradable composites, possibly even adding to material properties.¹

In spite of having many advantages, naturally occurring lignins are rarely used in polymer industry due to their brittleness and difficulty to process. To address this limitation, functionalgroup modification as well as structural modification of natural lignins is one of the major thrust areas of concern for lignin-research. Based on this modification concept, new opportunities are gradually becoming more visible for creating sustainable materials using lignin. Although, low compatibility of lignin with polylactide (PLA) is one of the major

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drawback for using lignin, functional group modification may be an effective to overcome this drawback. With an attempt to use the lignin as a tailoring material into a usable thermoplastic for making composites we modified lignin polymer by esterification. This will not only help to reduce the volumes of petroleum based plastics used today, but also would help developing new composites.

2. Material and Methods

In our present study esterified lignin was generated by the treatment of acetic and propionic anhydride on kraft softwood lignin. Initially we tried with smaller batches using 15g of kraft lignin, 160 mmol of acetic anhydride and 460 mmol of propionic anhydride. To check any temperature effect on the efficiency of this synthetic process we performed the experiments at two different temperatures – 85⁰C and 110⁰C. Later on the reaction was scaled up to 150gm of kraft lignin maintaining experimental temperature at around 85⁰C. The product was subjected to routine characterization analysis as well as to the analysis of processability parameters. The esterified lignin was then blended with PLA under different processing temperatures. The main reasons for blending are: To reduce high-cost of some polymers with low-cost one, to Improve mechanical and physical properties, to control the rate of biodegradation, to decrease proceeding temperature etc. In all the cases the average weight ratio of the esterified dry kraft lignin was kept constant at 10%. The first three composite samples were prepared at three different temperatures 155, 165 and 175⁰C keeping screw speed constant at 70 rpm. During the preparation of such samples three common steps were followed – dry blending, compounding and extruding films. During the preparation of the fourth sample a little modification was performed at the process level by pre-compounding a 10g, 60/40 mix of modified lignin and PLA with a screw speed of 140 rpm and 155⁰C. The compound was then subjected to dry blending with PLA to get a blend with 10% esterified lignin followed by compounding and film extruding at the same screw speed at a temperature of 155⁰C. As a reference, pure PLA was extruded at 165⁰C.

3. Physicochemical Characterization

During characterization ATR-FTIR was used and all measurements were performed in air at room temperature. The equipment used was a Thermo Scientific Nicolet iS5 FT-IR Spectrometer. The iD3 ATR is available with **single reflection Zinc Selenide (ZnSe)** 7mm crystal. Thermogravimetric analysis (TGA) was used to study the thermal properties of the films. All samples were heated from 25 to 600⁰C in air. Differential Scanning Calorimetry (DSC) was used to analyze the thermal properties of the films. DSC was carried out with the

following temperature program: heating from 25 to 165°C at 55°C/min, followed by cooling from 165°C to -20°C at -50°C/min and then a final heating to 190°C. The samples were kept isothermally for 10 and 5 minutes respectively before and after cooling. For the optical microscopic images the samples were pressed together by glass microscope slides. Tensile tests were performed on all the extruded films at a pulling speed of 12 mm/minute. The width of all samples was 0.3325 mm with a thickness ranging from approximately 0.14 to 0.50 mm. SEM was utilized to examine the interaction between lignin and the polymer matrix. While performing tensile-test and impact studies, samples were prepared by sputtering gold particles for sensing better electron conductivity on the surface of the sample. As it is already known that PLA is sensitive to heat, so the electron beam was shot at an intensity of 10 kV to reduce the deformation on the sample surface.

4. Results and Discussion

Going through the visual appearance of the films processed at different temperatures it was concluded that the process temperature has a noticeable effect over the final film formation (**Fig. 1**). In fact at 155°C the texture of brown colored film indicated that esterified lignin was well-distributed in the PLA, and an increase in temperature to 175°C resulted in a highly separated film, with scattered patches of aggregated lignin (esterified) in the PLA matrix. However, we noted an appreciable improvement of the produced films on decrease in temperature and pre-blending of the two components. The variation of composition was visualized by taking microscopic images at respective temperatures (**Fig. 2**). The surfaces of composite-blends are usually smooth, which consists of a high proportion of the polymer matrix.

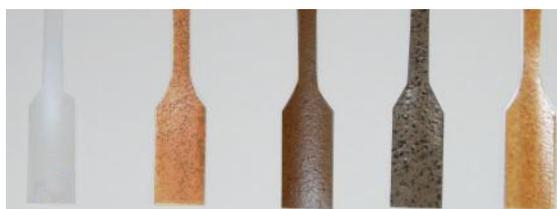


Fig. 1 Composite Films Produced at Different Temp: *From left:* Pure PLA, Composite (EL-PLA) 155°C, Composite (EL-PLA) 165°C, Composite (EL-PLA) 175°C and EL-PLA 150°C pre-blend. [EL= Esterified Lignin]

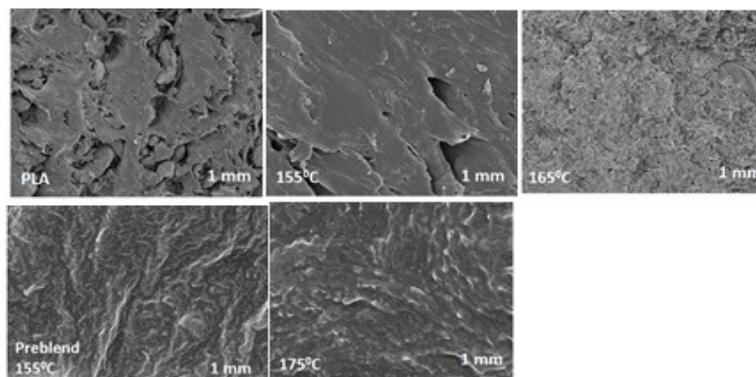


Fig. 2 Microscopic Images of the Composite Films

Confirmation in favour of the existence of intermolecular interactions between PLA and lignin (modified as well as unmodified) came from DSC and FTIR studies. Comparing the respective IR data (**Fig. 3**), it is very much possible to estimate the large difference between the spectra of the unmodified and the esterified lignin and therefore it could be concluded that the reactions had occurred. Switching from unmodified kraft lignin to its modified version (esterified) the most prominent difference what could be noted with their IR spectra was the major decrease in the peak-intensity in the spectral region $3000\text{--}3500\text{ cm}^{-1}$. This region is typified by the presence of phenolic and aliphatic hydroxyl groups. On the other hand, the formation of ester functionality by the reaction between anhydrides and lignin-hydroxyl groups is confirmed by large increase of the carbonyl peak appearing at 1730 cm^{-1} (**Fig3**). The previous studies also indicated the same type of observation.²

In the composite blend the peak due to hydroxyl groups in lignin as well as modified lignin is shifted to higher wavenumber region higher concentration of aliphatic hydroxyl groups as opposed to phenolic hydroxyl groups. Higher concentration of aliphatic hydroxyl is accordance with the idea that upon reaction with PLA, both existing aliphatic and phenolic hydroxyl groups on lignin, turns into aliphatic nature due to the linear nature of PLA. Another indication in favor of increase in aliphatic nature of PLA groups is the appearance of peaks at $\sim 3000\text{ cm}^{-1}$ and at $\sim 2950\text{ cm}^{-1}$ due to C-H stretching of methyl group and methylene groups respectively. While for lignin and esterified lignin the methyl group is almost nonexistent, a minor but prominent shoulder-like peak appearance is visible for PLA-lignin composite. The relative band intensity of methylene group is enhanced with the addition of PLA chains. On going from lignin counterpart (modified as well unmodified) to lignin-PLA composite blend the most remarkable and noticeable change in IR spectra occurs in the range

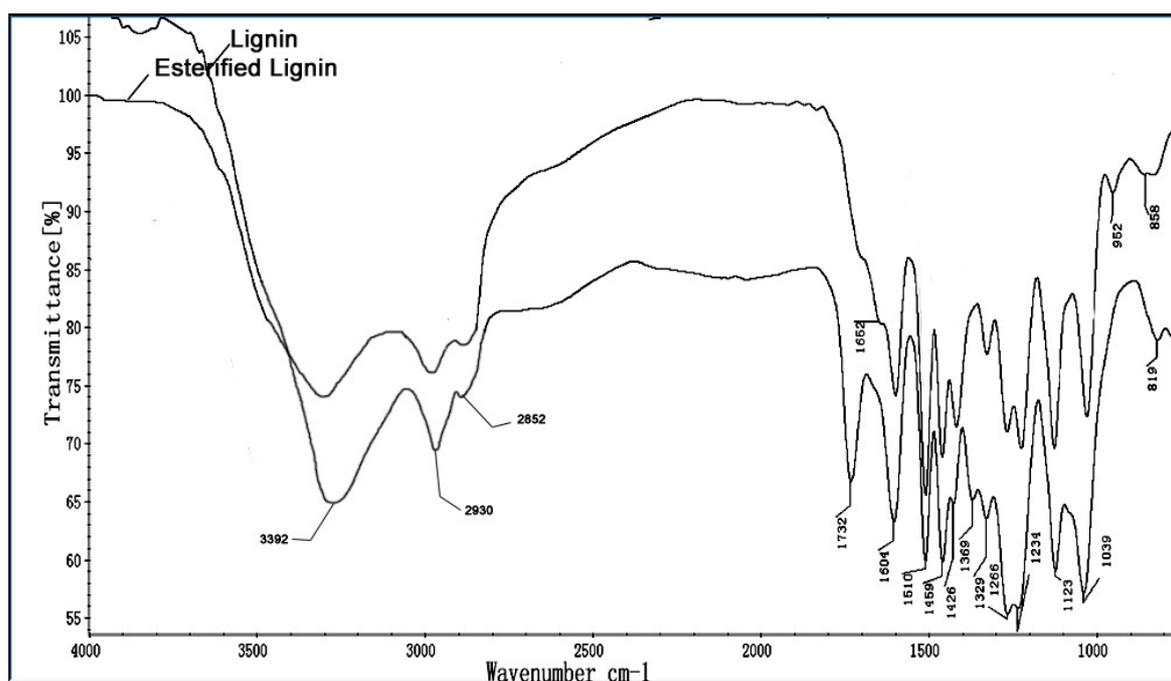


Fig. 3 FTIR Spectra of Lignin and Esterified Lignin

of $1650 - 1750 \text{ cm}^{-1}$. This is due to keto-group $\text{C}=\text{O}$ functionality. Initially, the IR band due to carbonyl group of esterified lignin and unmodified lignin appear at $\sim 1740 \text{ cm}^{-1}$ and 1650 cm^{-1} respectively. In the composite blend, the carbonyl group of esterified lignin is shadowed by the peak at $\sim 1735 \text{ cm}^{-1}$, while for unmodified lignin this peak at $\sim 1735 \text{ cm}^{-1}$ appears as an additional peak. Aromatic skeletal vibrations of lignin benzene rings are confirmed by the appearance of the peaks at ~ 1590 , ~ 1510 , and $\sim 1420 \text{ cm}^{-1}$, which remain totally unaffected due to blending process. Two more additional peaks at $\sim 1450 \text{ cm}^{-1}$ and 1360 cm^{-1} are due to C-H deformation of methyl and methylene and symmetric C-H bending of the PLA residues respectively.⁵

As indicated from DSC study, pure PLA has the melting point (T_m) at $122\text{-}127^\circ\text{C}$ and the effect of lignin on this T_m is very low (**Fig 4**). In the event, DSC curves indicated high degree of crystallinity due to low miscibility of lignin and PLA. To estimate the material's stability TGA measurements were performed (**Fig 5**). Here also the comparative study between the thermograms of lignin and modified lignin indicated that esterification invokes noticeable effect on thermal stability. Degradation temperature of the raw lignin became much improved when esterified with anhydrides. In the PLA blended composite lignin acts as anti-oxidizing agent during degradation which is the key factor for better thermal stability.

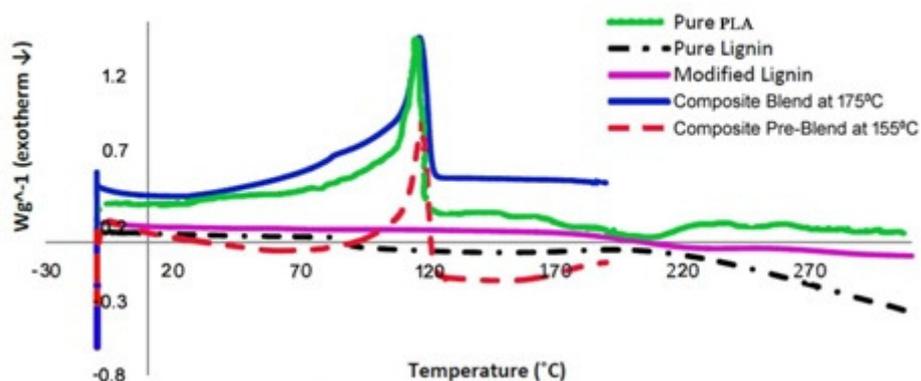


Fig. 4 DSC Thermogram for PLA, Lignin and Different Composite Blends

In comparison to pure PLA, common mechanical properties like tensile strength, elongation, and modulus - all were reduced with increasing lignin content in the lignin-PLA composite blends. This fall in mechanical properties is mainly due to two factors: interference of PLA continuous phase and accelerated thermal degradation due to increasing lignin contents.⁴ The sample blended at 175⁰C show lower stress at break-point due to large aggregates of esterified lignin in the composite matrix. Stiffness becomes less prominent for the composite samples blended at lower temperatures 155⁰C and 165⁰C and also for the pre-blended sample at 150⁰C (**Fig 6**). The composite blends loose great amount strength and stiffness due to moisture-induced movements of the lignin component and not due to biological decay.

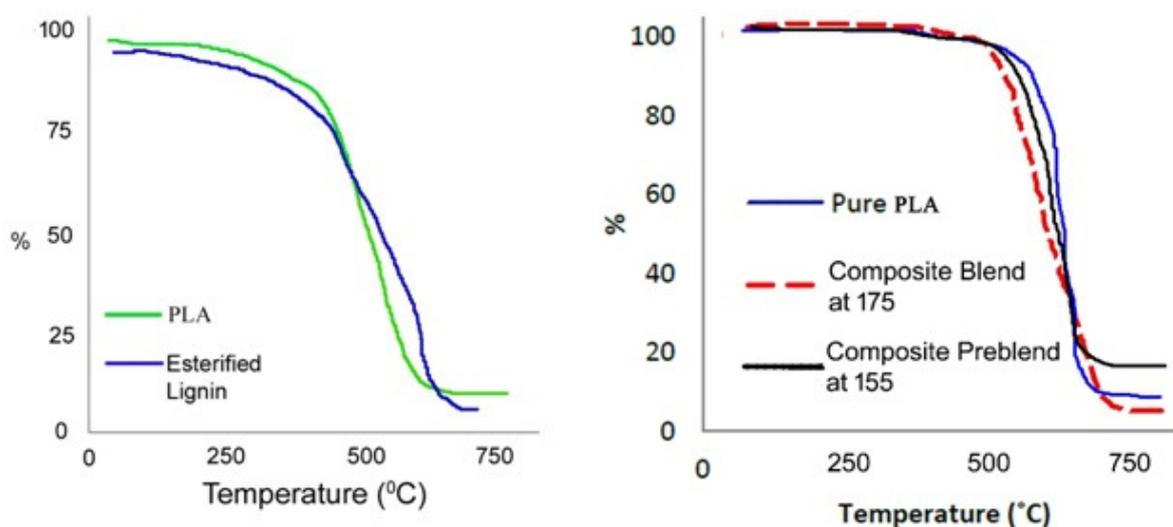


Fig. 5 TGA Thermogram for PLA, Lignin and Different Composite Blends

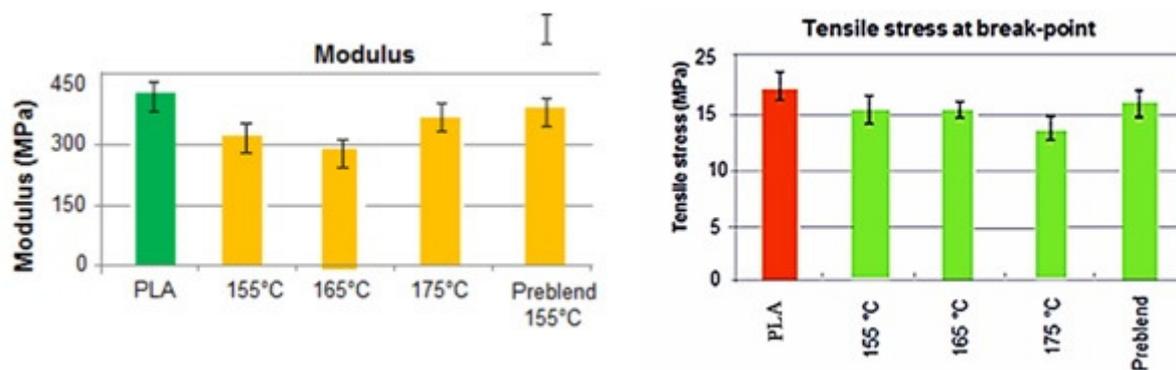


Fig. 6 Tensile Strength and Stiffness Studies for PLA, Lignin and Different Composite Blends

5. Conclusion

This work indicates that lignin can be esterified when reacted with anhydrides. At 170⁰C the esterified lignin is not well blended with PLA in the composite matrix, however lowering the temperature and pre-blending the components result in formation of much improved composite film. The resulting composite blend exhibits a higher dimensional stability, a reduced hygroscopicity and improved resistance to microbial decay, but has reduced mechanical properties. However, the esterified lignin is a better choice for composite blending in comparison to raw lignin, which in turn offers increased thermal stability. Lignin itself acts as anti-oxidizing component in composite blend.

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