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Fast pyrolysis allows converting of up to 75% of biomass into a crude bio-oil, which can be separated into a phenolic rich fraction (PRF) via ethyl acetate extraction while a sugar rich fraction preferentially concentrates in the aqueous phase. Rheological and thermal characterization of heat treated PRF from pyrolysis of Douglas Fir is performed using cone and plate rheology set up, dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). The results show that this material demonstrates a unique thermoplastic behavior with low $T_g$ and softening point that can be systematically manipulated through changes in thermal history. As these materials are good candidates for development of hot melt adhesives, lap shear tests were also performed using wood stripes to evaluate their mechanical properties as an adhesive.

Optimization of properties of the PRF is sought in this study through polymer blending with other bio-degradable thermoplastic poly($\varepsilon$-caprolactone) (PCL) and poly(lactic acid) (PLA). Blends of PRF/PCL and PRF/PLA of different ratios are prepared by solvent casting and melt blending and thermally and thermomechanically characterized for their miscibility and phase behavior. Presence of molecular interactions are further investigated using Fourier transform infrared spectoscopy (FTIR). The blends show complete miscibility based on their $T_g$ and
melting points and significant improvement in shear strength is observed. Mechanisms leading to changes in properties are described and a physical model is proposed. The blend systems have good potential to be used as a thermoplastic bio degradable adhesives with satisfactory properties.
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Dedication

To my mother

And the memory of my father.
CHAPTER 1. Introduction

1.1. Research summary

Crude bio-oil is a complex mixture of a large number of compounds that can be separated into a sugar rich and an organic fraction using solvent fractionation by ethyl acetate. It is economically essential to find useful application routes for these phases. Concentrated in the ethyl acetate soluble phase of the oil are the phenolic compounds which are originated from thermal cracking of lignin during pyrolysis and make up about 25-30% of the oil.\(^1\) They comprise both monomeric and oligomeric phenolic compounds. The organic phenolic rich phase (PRF) of the pyrolysis bio oil has been assessed for adhesive and resin applications in recent years mostly as a phenolic feedstock for preparation of phenol formaldehyde resins.\(^2\)–\(^4\) Nevertheless utilization of this phase in its original uncombined form has been small and limited to applications such as replacements for CCA and/or creosote as a wood preservative due to the difficulties in characterization and utilization arising from instability.\(^5\) The main objective of the present work is to investigate in detail the thermal, rheological and mechanical properties of a heat treated stabilized phenol rich fraction (PRF) of a crude bio-oil obtained from hybrid poplar wood through a fast pyrolysis process. The focus will be to evaluate this fraction for potential value adding applications such as adhesives and sealants. Preliminary experiments reveal interesting thermoplastic-like properties suggesting the potential of this fraction of crude bio-oils as a melt process-able material or hot-melt adhesive. In particular, as pre heat treatment has an obvious effect on some of this fraction’s properties the effect of thermal history on the rheological behavior of PRFs will be assessed through dynamic mechanical analysis and rheological experiments. In addition blends of PRFs
and other thermoplastic natural polymers might lead to applications as a hot melt adhesive system. The lignin rich nature of this fraction also makes it a good candidate for other applications in which lignin is currently being used as primary material such as carbon fiber production. On the other hand while there have been several studies concerning the whole bio oil, rheological and thermal properties of this phase have not been adequately studied and many interesting properties of this phase such as the reversible thermoplasticity have been overlooked. Moreover modification of this phase to achieve optimized mechanical properties which are the main weakness of this material would open doors to utilizing this phase in many applications. Our preliminary observations revealed that the PRF fraction suffers from brittleness and lack of deformability. Our approach to address this issue would be using polymer blending. Blending is an inexpensive and effective method to improve processing and product quality. There are a number of biodegradable thermoplastics currently considered for application as hot melt adhesives including poly(e-caprolactone) (PCL) and poly(lactic acid) PLA. The carbonyl functional group in PCL and PLA has the potential ability to form intermolecular bonds with the hydroxyphenyl groups present in the PRF. PCL has a low T_g of -60°C and a melting point of 60 degrees and might act as a plasticizer. These polymers could be blended with the PRFs and may enhance the strength and deformability of the final system. The accomplishment of this proposed research is expected to contribute an in-depth understanding of thermal and rheological properties, structure, stabilization and processing of PRFs. The proposed research is significant because it may launch new applications routs for this fraction of bio oil. The reversible thermoplastic behavior is of particular interest, as one might process the PRF bio-oils with traditional melt processing technologies, such as extrusion or injection molding. This is
particularly important in applications like fiber spinning used recently in carbon fiber production from pyrolytic lignin.

1.2. Literature review

1.2.1. Pyrolysis bio-oil and its properties

Ligno-cellulosic biomass being the world most abundant renewable resource has attracted much attention in recent years and efforts have been made to optimize processes like pyrolysis for commercial competitiveness. Concern over fossil fuels has triggered more efforts in the previous decades towards processes to convert biomass into liquid fuels which can mainly be grouped into two: high-pressure liquefaction and fast pyrolysis. Assessments have shown that fast pyrolysis is the most promising process. Common upon all types of fast pyrolysis processes is a high rate of heat transfer, moderate temperatures (450-600°C) and a short residence time of product vapors in the reactor. These conditions result in a high yield of conversion of biomass (50-75%) to a liquid product. 12

Although the bio refinery concept is mainly derived by the demand in the transportation sector for biomass-derived fuel, the feasibility of the process depends on the production of value added products and chemicals besides fuel. Developing adhesive resins that are based on biomass pyrolysis oil has been in focus.13 A very important step in the way to use bio oils as a source for chemicals and materials is effective separation of different compounds into fractions of different groups of materials. Bio oil is a complex mixture of large number of compounds which cannot be separated using distillation like petroleum.12 Although there are a number of different
classifications, bio oil compounds may be classified into five categories: (1) hydroxyaldehydes, (2) hydroxyketones, (3) sugars and dehydrsugars, (4) carboxylic acids, and (5) phenolic compounds.\textsuperscript{14}

1.2.1.1 Phenolics from lignin

The phenolic compounds are the products of degradation of lignin during pyrolysis. Lignin is the essential structural polymer of wood and second only to cellulose as the most abundant organic substance in plants. Lignin splits to smaller mono and polyphenols during the process of pyrolysis. There are differences between the building blocks of softwood and hardwood lignin. Softwood lignin is also called guaiacyl alcohol or coniferos lignin because it is made up of coniferyl alcohol units. Hardwood lignin is made up of sinapyl alcohol and coniferyl alcohol. The structure of guaiacol and syringol is represented in Figure 1-1. Phenols are extremely interesting as building blocks of new synthetic bioplastics, phenol-formaldehyde resins or epoxy-or polyurethane materials, as just a few options.\textsuperscript{15,16}
Pyrolysis operating conditions and feedstock parameters can influence the yield of phenols. For example, higher heating rate with a thinner bed thickness favors the production of primary phenols. Water treatment seems to have different effects on softwoods and hardwood barks.

The pyrolysis of lignin in the presence of formic acid and an alcohol results in the complete conversion of the original macromolecular phenylpropane structure with the formation of a complex mixture of low-molecular-mass compounds. The majority of these seem to be aliphatic hydrocarbons, although a substantial number of phenolic structures are also present. A minor portion of the latter has been converted to oxygenated benzoic acid structures.

1.2.1.2 Aging

Pyrolytic bio oil is known to age over time. Changes often happen in a number of physical properties such as viscosity and homogeneity during storage and handling of these oils.
aging of bio oil is not only a concern with handling and storage but also with utilization. Diesel engines fueled by bio fuel injection reportedly stopped working after a short time due to clogged pores in their injection system. Preheated bio oil tended to seal the passageways to the engine. Evidently this is a big problem in the application of these oils as fuel and there have been efforts to hinder or delay the process of aging by using additives.

The storage stability and the thermal behavior of the whole bio-oil, the upper layer, and the bottom layer of bio-oils obtained by vacuum pyrolysis of softwood bark have been evaluated in a study by Ba et al. Samples were stored at different temperatures (40, 50, and 80 °C) for up to 168 h and at room temperature. Aging at room temperature of the raw bio-oil resulted in increase of the viscosity during the first 65 days, after which a plateau was reached. The addition of methanol to the bio-oil improved its properties and increased its stability and that of its mixtures. Aging and thermal stability of bio-oils obtained by vacuum pyrolysis of softwood bark is also mentioned in another study where it was found that the aging effect is more pronounced for the bottom layer than for the upper layer and that the upper layer contributes to lowering the aging rate of the bio-oil. Increase in viscosity was mainly caused by polymerization of the bottom-layer contained compounds.

Most studies concerning aging of pyrolysis oils are looking into changes happening over time to oil stored in closed and sealed containers. Accelerated aging test conducted at elevated temperatures are done making sure no volatiles are leaving the system. But from the adhesive and sealant development point of view, the physical and chemical changes associated with aging may be potentially desirable. Changes in physical and mechanical properties in an adhesive resin are essential. Almost all adhesives undergo a change in properties from the point of application to the time of service. For example curing of a thermosetting resin results in dramatic change of
properties through a cross linking reaction of monomers and transforms a liquid resin into a rigid high strength solid structure while some other adhesives may achieve a solid state by evaporation or removal of solvent or may be hardened by cooling down as in hot melts.

1.2.1.3 Nano-structures in bio-oil

A study of microstructure of bio-oils suggested through using small angle neutron scattering that BCOs are nano-structured fluids constituted by a complex continuous phase and nanoparticles mainly formed by the association of units of pyrolytic lignins. Lignin oligomers are nanoparticles that aggregate and form clusters of branched structures as a result of aging. Values obtained for fractal dimension in this modeling indicated a quite open structure as opposed to an expected packed globular structure. Several studies confirm that lignin oligomers can form particles of nanometer dimensions which in turn can aggregate and form clusters of branched structures. Micic et al divided self association of lignin into four structural levels from nanometer on the scale range to a fraction of a millimeter, suggesting that the forces of association are of different nature in each level. While at the first two levels where monomers are coming together and forming globules, covalent bonding is responsible, later when clusters and super structures are formed, H bonding and Van der Waals interactions are believed to be at play.

1.2.2. Rheological and morphological characterization of bio-oil

Garcia-Perez et al. studied two pyrolysis bio oils prepared from bark. The bio oils from softwood and hardwood species contained waxy material and were able to separate into a top and
bottom layer, the top layer rich in waxy material and extractives and the bottom contained more of the heavier compounds. Microscopic imaging at different temperatures demonstrated that the oils have a multiphase structure comprising of the waxy materials, aqueous droplets, heavy compounds and char in a matrix of hollocellulose derived compound (Figure 1-2). Their microscopic study also revealed that the waxy and aqueous droplets dissolve in the matrix at higher temperatures and waxes crystallize when cooled.

Figure 1-2 Softwood bark residue-derived oils (25°C) (a) Phase contrast; (b) polarized light by Garcia-Perez et al. 28

Strain and frequency sweeps were conducted at several different temperatures. Microstructures (e.g., waxy materials) in the bio-oil matrix were in part, responsible for the high viscosity and non-Newtonian behavior that is observed at <50 °C. The upper layer was described as a Bingham liquid at temperatures lower than 45°C and this behavior has been attributed to the melting of waxy materials in the oil and their condensation in smaller crystals when rapidly cooled. They also suggested based on their rheological results that a structural network is present in the material between the oligomers that are believed to be in micelle form and can impart gel
behavior to the mixture. The structure was supposed to be broken at higher temperatures or higher frequencies of applied stress (Figure 1-3).

![Diagram of Tan δ as a function of strain at different temperatures](image)

**Figure 1-3** Tan δ as a function of strain at different temperatures by Garcia-Perez et al.²⁸

The effect of temperature and the addition of methanol on the viscosity of the bio-oil obtained from the fast pyrolysis of wood chips, alone and mixed with char at different concentration, versus the shear rate, have been studied and the results obtained showed that these bio-oils are pseudoplastic fluids which can be described using the Ostwald de Waele model.⁹ Rheological studies have been carried out on bio-oil resembling materials such as Eucaliptus tar pitches.⁸ The apparent viscosity was measured in the static mode as a function of the temperature at a constant shear rate and as a function of the shear rate at constant temperature as shown in Figure 1-4. In the transient mode the apparent viscosity was measured as a function of the shear time at constant temperature and shear rate.
Dependence of the apparent viscosity on the temperature in the range studied follows an Arrhenius type law. And activation energy and constants of the relationship for each pitch sample were calculated by Williams–Landel–Ferry (WLF) Equation. The WLF equation describes the reduced variables shift factor of polymers for two given temperatures (a reference temperature $T_r$ and another temperature $T$) in terms of empirical parameters. Parameters of WLF equation were calculated for several temperatures and the results show that the free volume increases with increasing temperature. Therefore, the viscosity of pitches can be associated with the presence of free space in the material, in accordance with the free volume theory.
1.2.3. Methods of fractionating the bio-oil

A number of fractionation techniques have been developed over the years to generate fractions of similar polarity and to concentrate the un-distillable compounds. Early attempts to separate the phenolics from the oil were made by Elder using solvent separation methods such as ether solubility proposed by Shriner et al.\textsuperscript{29,30} This method involves washing with water and extraction with ether (Figure 1-5). It was concluded that single components present in this pyrolytic oil are present in such low concentrations as to preclude the isolation of any one particular chemical species and although the phenolic fraction is a mixture, all compounds are derivatives of phenol and would have the same type of chemical properties. He analyzed the fraction using gas chromatography and mass spectroscopy. His results indicates that the phenols account for an average of 13.34\% of the gravimetrically but he could only identify 3\% of them using chromatography and concluded that the rest is nonvolatile polymeric phenols.
Pure mixture of phenols such as syringol and guicol have been recovered from Eucalyptus wood derived tar using vacuum distillation and liquid-liquid extraction using alkaline and organic solvents.\textsuperscript{31}

Another solvent fractionation technique known generally as the national renewable energy lab (NREL) method involves dissolving the oil in ethyl acetate which separates the oil into two
distinct phases: An organic-rich, ethylacetate-soluble phase and an aqueous phase. This process is illustrated in Figure 1-6. The ethyl acetate-soluble phase was then extracted with aqueous NaHCO₃ (5% w/w) and the basic aqueous layer was saved for isolation of the acidic organic fraction, which contained the phenolic and neutral (P/N) fractions.³²

Figure 1-6 NREL method of extraction of phenolics.¹²

1.2.4. Characterization of bio-oil fractions

1.2.4.1 Characterization of water insoluble fraction pyrolytic lignin

Bio-oils are easily separated into an aqueous fraction and an organic fraction by adding water to bio-oil. Upon adding water viscous oligomeric lignin-containing fraction settles at the bottom,
whereas a water-soluble fraction rich in carbohydrate derived compounds form a top layer. However, much overlap of compound types exists in both fractions. Ba et al. fractionated bio oil from pyrolysis of bark residues into water soluble and insoluble fractions according to the method that was described by Scholze et al.\textsuperscript{7,33}

![Diagram of the water insoluble fraction extraction.](image)

**Figure 1-7 Diagram of the water insoluble fraction extraction.**\textsuperscript{7}

They compared the chemical composition of the volatile materials that can be detected by GC and thermal decomposition using TGA. GC-MS analysis indicated that the major portion of the polar compounds contained in the whole bio-oil is concentrated in the water-soluble fraction (WSF). Thermal decomposition of the bio-oil and its fractions seemed to be a gradual process with no clear steps according to TG curves. The DTG curve indicated that the bio-oil consisted of three groups of molecules with different thermal resistance. The first group, consists of light compounds. The second group contains high-molecular-weight compounds that are involved with a high cracking energy. The third group is composed of high-molecular-weight water-
insoluble compounds. TGA indicated that the water-soluble compounds decompose at a relatively higher temperature than the whole bio-oil and the WSF.

Scholtze et al. prepared the water insoluble fraction of the bio oil (the pyrolytic lignin) with a similar method and characterized it using GC/MS, FTIR and functional group analysis and compared it with milled wood lignin (MWL). Results showed that the basic units of pyrolytic lignins have similarities with MWL. For example the content of hydroxyl groups (10.7%-13.6%) in pyrolytic lignin is similar to that of milled wood Lignins. Splitting of methoxyl groups and cutting of the propyl side chain was observed by Py–GC/MS. They suggested based on their results that oligomeric molecules in pyrolysis oils are desorbed from the feedstock by thermal ejection.

Chaala et al 2004 used several mass spectroscopy techniques on the water-insoluble fraction from fast pyrolysis liquids (pyrolytic lignin) for molar mass characterization and used the data to partially identify the monomeric and dimeric structures. The detected monomers correspond to known lignin derived compounds in bio-oil, the detected dimers have some similarities to phenylcoumaran structures.

1.2.4.2 Characterization of ethyl acetate extracted PRF

Chum et al. used Gas chromatography/Mass spectrometry to detect low molecular weight, volatile components. They identified 21 compounds which accounted for about 15% of the total mass. Size exclusion chromatography showed that the phenolic /neutral (P/N) products have approximately 42% of components in the range of 0-250 apparent molecular weight, 25% in the 250-450 range, and 25% from 450 to several thousand. These results suggests that the P/N
product has a higher amount of low molecular weight materials compared to those that elute from the gas chromatographic set up. They conclude that this is because not all these materials are volatile; they contain more polar groups than simple phenolic compounds, and are, therefore, more difficult to chromatograph under the conditions employed. Other characterizations revealed that the phenolic/neutrals compositions include a high phenolic, hydroxyl and aldehyde content. Pyrolysis/fractionation/solvent evaporation increases substantially (by factors of 3 to 5) the free phenolic content and decreases by a factor of two the methoxyl content of the P/N product, compared to the original starting milled wood lignin.

Table 1-1 Quantities of volatile monomeric compounds in the phenolic/neutral phase of bio-oils from various feedstocks obtained from GC/MS.32

<table>
<thead>
<tr>
<th>Compound name</th>
<th>RT (min)</th>
<th>ASPEN</th>
<th>REDWOOD</th>
<th>SO PINE</th>
<th>CO PINE</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Hydroxy-3-Methoxy-Benzene</td>
<td>46.63</td>
<td>0.14</td>
<td>0.36</td>
<td>0.21</td>
<td>0.30</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methoxy phenol</td>
<td>47.05</td>
<td>0.08</td>
<td>0.10</td>
<td>0.15</td>
<td>0.19</td>
</tr>
<tr>
<td>MW178</td>
<td>48.33</td>
<td>0.33</td>
<td>0.74</td>
<td>0.49</td>
<td>0.83</td>
</tr>
<tr>
<td>Total Wt%</td>
<td></td>
<td>1.3</td>
<td>2.3</td>
<td>2.4</td>
<td>2.6</td>
</tr>
<tr>
<td>UNIDENTIFIED</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOTAL</td>
<td>9.2</td>
<td>14.2</td>
<td>14</td>
<td>14</td>
<td>14.2</td>
</tr>
</tbody>
</table>
They also measured the viscosity of several samples of P/N fraction. Increasing the moisture level to 5% drops the viscosity by a factor of ten. Addition of 25 and 50 wt % of phenol decreases the viscosity to 680 and 80 cP, respectively, at 30° C., or to 150 and 30 cP at 45° C. The P/N product viscosity can thus be controlled and maintained at a desired practical level by addition of small or large levels of low-molecular weight compounds, such as water or phenol, or by an increase in operating temperature, or a combination of both.

1.2.5. Upgrading and applications of fractions

Sugars from the aqueous phase of the oil have been considered for conversion into ethanol for many years and the feasibility of a bio refinery concept in which sugars are effectively detoxified and fermented into ethanol and lipids has been more recently demonstrated.34,35 To further improve the cost effectiveness of the process, proper use of the organic phase should also be made. Concentrated in this ethyl acetate soluble phase of the oil are the phenolic compounds which are originated from cracking of lignin during pyrolysis and make up about 25-30% of the oil.1 It contains both monomeric and oligomeric phenolic compounds.

This fraction has been proposed for use as a wood preservative either alone or in combination with other preservatives, to replace CCA and or creosote but the more commercially successful application of this fraction so far has been in production of resin adhesives.5 Chum, et al., 1989 reported that this fraction exhibited good performance as an adhesive or adhesive extender for waterproof plywood.2 PF resoles with 50% or more of the phenol substituted with the phenolic
fraction of bio oil have shown comparable or better performances in making wood products.\textsuperscript{3,36} There is also evidence of better water resistance and bond quality.\textsuperscript{4} Phenol formaldehyde resins made by direct incorporation of lignin from various sources such as Bagasse and bark have shown improved shear strength and thermal stability.\textsuperscript{37} Bio oils have been also studied for use as bio binders in pavement materials.\textsuperscript{38} Adding bio oils to asphalt binders has resulted in improved high temperature performance of the asphalt and better rutting resistance due to their antioxidant characteristics.\textsuperscript{39}

Another interesting and relatively new application for this phenolic rich phase is in production of carbon fibers. Pyrolitic lignin has been successfully used in production of carbon fiber (Qin 2010) and its desirable because of higher carbon content than other industrial lignins.\textsuperscript{6,40} Rheological properties are important in the process of fusion spinning of these fibers and can affect the costs significantly.\textsuperscript{41}

1.2.6. Bio-oil and polymer blending

\textbf{1.2.6.1 Blends of bio-oil with adhesive resins}

Several researches have attempted blending the bio-oil with adhesive resins to achieve desired properties. In a study by Mourant the rheological properties of a phenol– formaldehyde resin containing various ratios of softwood pyrolytic oil resins of various compositions were obtained by mixing the PF-resin with pyrolytic oil at different ratios 50, 75, and 85\% on a weight basis.\textsuperscript{42} Rheological properties were investigated using the simple Bingham rheological model for viscoplastic fluids. Flow activation energy was determined for the various resin blends and the pyrolytic oil between room temperature and 508\textdegree C and correlations relating the flow activation
energy to the weight fraction of pyrolytic oil in the resin were proposed. It was shown that addition of softwood bark pyrolytic oil to a PF-resin increased its viscosity. The addition of pyrolytic oil increased gel times to values significantly higher than those obtained with the neat PF resin.

Other resins such as isocyanates have also been used in blends with the bio-oil. Mixtures of polymethylene diphenyl diisocyanate (pMDI) with pyrolysis bio-oils was studied by DSC and rheology. The viscosity increased with time for all mixtures. In addition, viscosity of the hybrid mixtures seemed to increase with bio-oil content. The mixtures tested had bio-oil contents of 0, 20, 30, 35, 40, 50, 60, 70, 80, 90, and 100%. Rheological and chemical analysis results confirmed that chemical reactions occur between pMDI and bio-oil at room temperature.

1.2.6.2 Lignin/phenolics and biodegradable polymer blending

Polymer blending is a common inexpensive way to improve properties. Thermoplastic blends of several biodegradable polymers with lignin and lignin esters have been analyzed in terms of thermal and mechanical properties. Lignin-starch, lignin-gelatin and starch-gelatin-lignin polymer films have been studied for tensile properties and water absorption. Blends of poly L-lactic acid (PLLA) (Figure 1-8) and lignin prepared by manual mixing have been investigated for their thermal and mechanical properties. DSC and FTIR spectral analyses indicated the existence of intermolecular interaction between PLLA and lignin. FTIR results confirm hydrogen bonding between the carbonyl groups of PLA and hydroxyl group of lignin. The $T_g$ and $T_m$ of PLLA decreased as the content of lignin in the blends increased. The mechanical properties of the blends were measured by tensile test. With the addition of lignin to
PLLA, the $\sigma_{\text{max}}$ and $\epsilon_{\text{max}}$ of the material decrease, but the E remains almost constant over the lignin content up to 20%.

![Structure of PLLA](image)

**Figure 1-8 Structure of PLLA.**

Poly(ε-caprolactone) (PCL) is a highly crystalline polymer that is miscible with several amorphous polymers through specific interactions. Furthermore, the fraction of carbonyl groups of PCL that hydrogen bonded with hydroxyl groups of a hydrogen bond donating polymer can be calculated by FTIR analysis. Phenolic compounds are well-known hydrogen bond donating materials. Therefore blend of PCL and PRFs are expected to have some miscibility involving hydrogen bonding. The hydrogen-bonding strength of PCL blends with three different well-known hydrogen-bonding donor polymers i.e. phenolic, poly(vinylphenol) (PVPh), and phenoxy was investigated with differential scanning calorimetry and FTIR. The chemical structures of PCL and donor polymers are represented in Figure 1-9.
Figure 1-9 Structures of PCL, phenolic, PVP, and phenoxy used for the study of blends.47

Figure 1-10 Experimental and theoretical predictions of Tg vs. blend compositions.47
Figure 1-11 Relation of the hydrogen bonded fraction of the carbonyl group within various PCL blend systems Phenolics (square), PVPh (circle) and phenoxy (rectangle).47

All these blends exhibit a single $T_g$ over the entire blend compositions, indicating that these blends are fully miscible in the amorphous region. The dependence of $T_g$ on the composition of these blends is shown in Figure 1-10.

The hydrogen-bonded fraction of the carbonyl group fractions of the molten state of blend systems were calculated by FTIR spectroscopy. The hydrogen-bonded fraction increases with the increasing content of these hydrogen-bonding donor polymers. Figure 1-11 shows the hydrogen-bonded fraction of the carbonyl group versus the PCL content with phenolic, PVPh, and phenoxy, indicating that the phenolic/PCL blends have a greater fraction of hydrogen-bonding formation.
Thermal and mechanical properties of lignin/PCL blends were studied by Li et al.\textsuperscript{48} It was found that these two polymers were partially miscible. They also traced intermolecular hydrogen binding by FTIR at higher lignin contents. Higher lignin content also meant higher young’s modulus but lower elongations at break (more brittle).

1.3. Intellectual merit

Phenolic rich fraction of the pyrolysis bio oil has found applications in production of thermosetting adhesives in combination with formaldehyde and recently has been studied for carbon fiber production. However due to instability and poor mechanical properties the applications have been very limited. The structure and properties of this phase has yet to be further studied. The overall objective of this proposal is to investigate the structure and properties of phenolic rich fraction of pyrolysis bio oil in order to improve the understanding of thermal and rheological behavior and enhancement and adjustment of properties for adhesive applications. The central hypothesis is that thermal treatment and blending with other components influence the structure and properties of the PRFs. The rationale of this proposed research is that understanding how the treatment influences the rheological and thermal properties of the PRF will allow tunable thermoplastic materials with pre designed softening points and proper mechanical properties to be developed and put to application.

Three specific aims will be pursued to test the central hypothesis and accomplish the overall objective of this proposed research. Aim #1: Characterization and Identification of mechanisms leading to thermo sensitive effect: The approach to be applied is thermal and mechanical analysis and property assessment combined with microscopy and spectroscopy techniques. Aim #2: Enhancement of properties through polymer blending and development of a bio-based hot
melt adhesive system: The approach to be applied is blend preparation and morphological, thermal and mechanical analysis and physical property assessment. Aim #3: Assessing and modeling kinetics of thermal degradation of PRF and blends.

1.4. Research objectives

- Preparation of a stabilized thermoplastic phenol rich fraction by extracting the crude bio-oil with ethyl acetate and by removing the volatiles through heat treatment at different temperatures

- Characterize and determine the chemical, thermal and rheological properties of the stabilized phenolic rich phase, study the effect of heat treatment regimen on molecular weight distribution, $T_g$, softening point and dynamic mechanical behavior to better adjust its thermoplastic behavior.

- Enhancement and adjustment of mechanical and thermal properties through plasticization of the PRF and blending with other thermoplastic polymers, more favorably common biodegradable polymers and evaluation of morphology, miscibility and characterization of rheological and thermal properties of the blends system as a potential bio-based hot melt adhesive system.

- Study the kinetics of thermal degradation of the PRF and comparison of parameters and kinetics of thermal degradation with blends of PRF with biodegradable polymers.
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CHAPTER 2. Rheological properties and tunable thermoplasticity of phenolic rich fraction of pyrolysis bio-oil

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Abstract

In this work we report on the preparation, characterization and properties of a thermally treated lignin-derived phenolic rich fraction (PRF) of wood pyrolysis bio-oil obtained by ethyl acetate extraction. The PRF was characterized for viscoelastic and rheological behavior using dynamic mechanical analysis (DMA) and cone and plate rheology. A unique thermoplastic behavior was evidenced. Heat-treated PRFs acquire high modulus but show low temperatures of thermal flow which can be systematically manipulated through the thermal pretreatment. Loss of volatiles, changes in molecular weight and glass transition temperature ($T_g$) were investigated using thermogravimetric analysis (TGA), mass spectrometry (MS) and differential scanning calorimetry (DSC), respectively. Underlying mechanisms for the thermal and rheological behavior are discussed with regard to interactions between pyrolytic lignin nano particles present in the system and the role of volatile materials on determining the properties of the material resembling in several aspects to colloidal suspension systems. Low thermal flow temperatures and reversible thermal effects can be attributed to association of pyrolytic lignin particles due to intermolecular interactions that are easily ruptured at higher temperatures. The thermoplastic behavior of PRF and its low $T_g$ is of particular interest, as it gives opportunities for application of this fraction in several melt processing and adhesive technologies.

2.1. Introduction

Among the possible processes for biomass conversion, fast pyrolysis is of particular interest as it can process a vast array of lignocellulosic materials, resulting in a liquid product known as pyrolysis bio-oil. Crude bio-oil is a complex mixture of a large number of compounds that can be broadly classified into: volatile organic compounds (hydroxyacetaldehyde, formic acid, acetic
acid, acetol), water, monophenols, furanic compounds, sugars (fermentable and cross-linked), and lignin oligomers. \(^1,2\) Partitioning the crude bio-oil with ethyl acetate results in the production of an organic-soluble phase containing phenolic compounds and neutral fractions and an aqueous phase containing carbohydrate and carbohydrate derived products. \(^3\) Concentrated in the organic phase are the mono and oligomeric phenolic compounds (the heavier oligomeric phenolic compounds are often called pyrolytic lignin) resulting from the thermal cracking of lignin and make up to 25-30% of the crude oil. \(^4\) In this study this phase is referred to as the phenolic rich fraction (PRF). While the aqueous fraction has shown good promise for production of ethanol and lipids through fermentation, \(^5,6\) valorization of the organic phase is still limited despite the efforts to use this fraction as a phenolic feedstock for the preparation of phenol-formaldehyde resins. \(^7-9\) Also utilization of this phase in its original uncombined form has been small and limited to applications such as replacements for creosote as a wood preservative. \(^10\)

Heat induced physical changes in bio-oils are mostly attributed to the reactions going on in the organic phase and are often investigated in studies using carefully sealed samples to simulate the aging process during storage. \(^11-13\) The process often results in some increase in viscosity and molecular weight, but does not reflect the bigger changes that occur when the oil is heated openly and the volatiles are able to leave the system. There is evidence of such changes for example in small combustion engines fueled by bio-oil where the formation of tar causes plugging of holes and passageways when the oil is pre heated before being fed into the injector for better fluidity \(^14\) and solidification of the bio-oil when heated under vacuum \(^15\). These heat induced transformations are of course setbacks in fuel and energy applications but could be used to advantage in applications such as adhesives and sealants and deserve more attention regarding the its mechanism and controlling parameters.
While there are similarities, pyrolytic lignin has a peculiar structure compared to native and industrial lignins in its much lower molecular weight and unsaturated structures\textsuperscript{16,17} which often leads to apparent differences in properties. In a recent attempt to produce carbon fiber through spinning of pyrolytic lignins\textsuperscript{18} it was reported that the heating conditions used for stabilization of other technical lignins could not be used for the pyrolytic lignins as the individual fibers in contact with each other fused together, even at very low thermostabilization heating rates. Pyrolytic lignin oligomers are highly concentrated in the PRF along with neutral fractions and light volatile materials\textsuperscript{3} and previous small angle neutron scattering (SANS) analysis of bio-oils suggests that association of pyrolytic lignin oligomers results in the formation of nano structures in the form of particles\textsuperscript{19} which makes the PRF an interesting system to be analyzed in regard to its physical properties. Identification of the role of different components and parameters governing the transformations would help us with control and adjustment of properties in the system and opens the way to possible new applications.

In this study we investigate in detail the thermo-mechanical and rheological properties of unheated and openly heat treated samples of ethyl acetate extracted PRF using dynamic mechanical analysis and rotational rheology and propose that this material is able to exhibit a pseudo-thermoplastic behavior, in which thermoplasticity is thermally tunable. The underlying mechanisms for this tunable thermoplasticity and the role of volatile materials and lignin particle interactions are further investigated and discussed through thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), molecular weight analysis and optical microscopy.
2.2. **Materials and methods**

2.2.1. **Preparation and heat treatment of the PRF**

Pyrolytic bio-oils were prepared by the pyrolysis of Douglas-fir meal (< 2 mm) at 500°C in an Auger reactor as described elsewhere. The PRF was extracted from the bio-oils, using a 1:1 ratio of ethyl acetate/bio-oil according to a modified procedure of Chum. The mixture was shaken for 5 min at 30°C and left to equilibrate for 6 h forming distinctive aqueous and ethyl acetate phases. While the phenols are preferentially extracted into the organic phase, the anhydro-sugars concentrate in the aqueous phase. The organic phase was separated by decantation from the aqueous phase. Excess ethyl acetate was removed from the organic phase by using a rotary evaporator.

Heat-treated PRF samples were prepared by heating portions (of known weight) in open aluminum pans for 10 h at 60, 80 and 100°C. The samples were then allowed to cool to room temperature, re-weighed and stored at 5°C until testing. These samples are referred to as P60, P80 and P100, respectively, in relation to the temperature of the pre-treatment.

2.2.2. **Thermogravimetric analysis (TGA)**

TGA was performed on a TA instruments SDT Q600 under nitrogen atmosphere (100 ml/min). Unheated PRFs (10 mg) were analyzed by isothermal runs at 60, 80 and 100°C for 10 h. Dynamic ramps were performed on both heat treated and unheated samples at a rate of 5°C/min.
from room temperature to 550°C. Three replicates of each sample was used to ensure consistency.

2.2.3. Electrospray Ionization - MS

Average molecular weight of the PRF samples were determined by positive ion electrospray ionization (ESI-MS) performed on a LCQ-Deca instrument (Thermo Finnigan). PRF samples were dissolved in methanol (1 mg/ml) containing 1% acetic acid and introduced into the ESI source at a flow rate of 10 µl/min. The ion source and capillary voltages were 4.48 kV and 47 V, respectively at a temperature of 275°C. The MS were scanned between m/z (mass to charge ratio) 50 and 2000. The number average molecular weight ($M_n$) was calculated as $M_n = \Sigma M_i N_i / \Sigma N_i$ and weight average molecular weight ($M_w$) as $M_w = \Sigma M_i^2 N_i / \Sigma M_i N_i$, where $M_i$ and $N_i$ are the m/z and intensity of the ions, respectively.

2.2.4. Differential Scanning Calorimetry (DSC)

DSC measurements were collected for the heat treated samples with a TA DSC Q800 instrument. 10 mg of each material was placed in an aluminum pan and ramps of 15°C/min were performed from -40°C to 120°C under nitrogen atmosphere. Glass transition temperature ($T_g$) was calculated as the midpoint temperatures of the step changes in heat capacity on the heat-flow curve of the heating run. A conditioning pre run was avoided due to the heat sensitive nature of our material.
2.2.5. Dynamic Mechanical Analysis (DMA)

DMA was conducted on a TA instruments DMA model Q800 in dual cantilever mode (span 50 mm). In this study, basswood veneers 60 mm × 13 mm × 1 mm, were used to make 2-ply laminate DMA specimens according to methods previously established in our laboratory. The veneers were lightly hand sanded along the grain with 220-grit sandpaper and cleaned with a paper towel immediately prior to resin application. Two types of samples were made to represent the unheated and heat-treated PRFs. For the first group of samples unheated PRF was uniformly applied with a brush to each wood surface in coverage of 70 g/cm² and the coated plies were then hand pressed into a sandwich. To observe step by step changes in the thermo-mechanical properties of the material as a function of heat treatment, DMA tests were carried out in a cyclic fashion. That is, 5 successive temperature scans were conducted on one sample from room temperature to 120°C with thermal ramps of 2°C/min, 1Hz frequency. After each run, the sample was allowed to cool down in the DMA before another scan was conducted. Thermomechanical properties were recorded during heating and cooling in these 5 successive cycles.

A second group of bonded sandwich samples were heated in a Carver hydraulic hot-press for 10 h using a light pressure of ca. 190 KPa (minimum that can be applied and measured by the instrument gauge) at 60, 80 and 100°C to mimic the P60, P80 and P100, samples, respectively. For these preheated samples, DMA temperature scans were conducted at 1Hz from room temperature to 120°C with a heating rate of 2°C/min. 5 replicates of each sample were used.
2.2.6. Microscopic Analysis

The visualization of the PRFs microstructure was carried out with an Olympus BX51 optical microscope using cross-polarized light in order to detect the presence of crystals. Imaging the material at higher temperatures was carried out by use of a Linkam hot stage coupled to a Linkam TMS 94 control unit.

2.2.7. Cone and plate rheology

Rheology measurements were performed using a Scientific Rheometric® RDA III with a cone and plate set up, 25 mm in diameter, and a cone having a 0.2 radian angle. For the control samples, a small amount of liquid PRF sample was placed on the plate, after which the cone was slowly brought down until a gap of 0.5 mm was set. The pre-heated samples were either in a paste or brittle solid form and thus hard to place in between the cone and plate. Therefore they were first heated for a very short time at the corresponding pretreatment temperature (60, 80 and 100°C) and the resulting low viscosity melt was placed on the plate, in a similar fashion as described for the unheated PRF. Excess material bulging from the sides was trimmed after setting the gap. Strain sweep experiments were performed at a frequency of 3 rad/s on untreated and preheated samples at room temperature to determine the linear viscoelastic limits. Frequency sweep tests (0.1-70 rad/s) were conducted at room temperature at a strain of 1%. Temperature sweeps were also conducted from 30 to 120°C with an angular velocity of 3 rad/s and a strain of 1%. Each experiment was repeated at least 3 times to ensure reproducibility.
2.3. Results and discussion

The PRFs showed temperature dependant changes in their state after heat treatment. Upon removing the samples from the oven they were all in liquid form, but their state started to change as soon as they began to cool down to room temperature. While P60 turned into a thick viscous paste, P80 and P100 turned into a solid, with P80 appearing more deformable than the brittle and glassy P100 (Figure 2-1). Upon reheating above the pre-treatment temperature, all samples started to fuse and flow, similar to the behavior of thermoplastics in that it is thermally reversible. The low temperature flow of the PRF is in contrast to the behavior of technical and isolated lignins that do not show thermal flow unless they are chemically modified.\textsuperscript{24–26} The reversible thermal flow of the PRF suggests a form of molecular organization/disorganization undergoing as a result of temperature change.

![Figure 2-1 Visual state of PRFs without heat pretreatment and after isothermal heat pretreatment](image)

(a) unheated (b) P60 and (c) P100.

2.3.1. Dynamic Mechanical Analysis (DMA)

To observe the thermal transition and flow of PRFs and gain an accurate insight on the rate and quality of changes to properties such as the storage (\(E'\)) and loss modulus (\(E''\)) during the heating of the PRF, DMA was used. DMA is an excellent tool to monitor the instantaneous changes that
occur in mechanical properties of materials as a function of temperature. Tests were conducted on wood-bonded assemblies of the unheated as well as preheated PRF bio-oils. The purpose of testing the unheated samples was specifically to observe the step by step transformation of the fresh PRF from its original state towards the harder stronger material that develops upon heating. Changes in property occur after each step as the same sample goes through several runs of DMA (as explained in the methods) with a heating cycle from ambient to 120°C. The results are shown in Figure 2-2a where curves corresponding to successive runs are numbered from 1 to 5. Increase in ambient temperature modulus starts from the second run and the trend continues on with the following runs. Development of higher E’ and the thermoplastic character in the unheated PRF sample can be observed. During each run, an increase in temperature induces a decrease in the storage modulus of the assembly. This is accompanied by appearance of a peak on the tan δ (E”/E’) curve which could potentially be assigned to the beginning of fusion and flow of the PRF. A subsequent shifting of position of the peak to higher temperatures can be seen (Figure 2-2b) indicating that each temperature ramp induces partial change which causes the flow temperature to increase.
To assess the final stable material, heat-treated assemblies were evaluated. The data from these samples (Figure 2-3) are highly reproducible indicating that the material has in fact reached a stable state. The E’ curves each exhibit a distinct deflection point for the different heat-treatment schedules. This observation is more pronounced when evaluating the tan δ curves (Figure 2-3b).
Since this softening of the bonded assembly corresponds to a molecular relaxation the peaks can be assigned to the thermal flow temperatures of the PRFs. The values of thermal flow temperature are in agreement with our earlier visual inspections. The transition point also shifts to a higher temperature as the pretreatment temperature of the PRF bonded assemblies is increased.

While presence of various microstructures (e.g., waxy materials forming crystals) are shown to influence thermal and rheological properties\textsuperscript{2,13} of whole bio-oil the PRF appeared mostly uniform in our microscopy observations with small presence of aqueous phase droplets still remaining in the system after fractionation. Cross-polarized light revealed very small amounts of crystalline waxy material in the PRF composition which was not considered likely to influence the physical properties. The heat-treated samples are free of aqueous droplets as they have either dissolved into the matrix or evaporated as a result of heating and they do no reappear upon cooling indicating the homogeneity of the heat-treated PRFs. No distinct difference can be observed in the appearance of the high temperature fused sample and the cooled sample therefore the structural changes leading to the PRF thermal flow are happening in a smaller scale not visible with optical microscopy.

2.3.2. Rheology analysis

Rotational rheological properties of the PRF were also investigated using a cone and plate set up. Strain sweeps were carried out to determine the linear viscoelastic (LVE) region of the PRFs. A strain value of 1\% was found to fall within the LVE and was chosen to ensure all tests were
carried out in the linear region. The behavior of the shear storage modulus (\(G'\)) and shear loss modulus (\(G''\)) in frequency sweep tests at 30°C for heat treated PRF oils are presented in Figure 2-4. Once again a systematic increase in \(G'\) and \(G''\) is observed with increasing pretreatment temperature. Both \(G'\) and \(G''\) for all samples appear linear on the graph for almost the whole range of frequencies. As the graphs are plotted on a logarithmic scale, this suggests that the behavior of \(G'\) and \(G''\) are described by a power law:

\[
G', G'' \sim \omega^n \quad (2-1)
\]

Where \(\omega\) is frequency and \(n\) is the index. The wedge mark in Figure 2-4 indicates that the \(n\) value is close to 1 for both \(G'\) and \(G''\) for the entire frequency range. In that regard \(G'\) is not following the classical Maxwell terminal behavior since it is not proportional to \(\omega^{2.27}\). \(G'\) and \(G''\) forming curves in the form of parallel straight lines is most often seen within stable dispersions and gels.28 The difference here though is that the values of \(G''\) are higher than \(G'\) which is indicative of a dominant viscous behavior. Therefore, although the heat-treated samples appear in a solid form, their behavior is more viscous than elastic which indicates that a strong structure or a chemical network does not exist.28 The unheated sample’s modulus vs. frequency plotted in Figure 2-5 shows a reduced dependence on the frequency having lower \(n\) values than samples that have been heat treated. Additionally, it is obvious that heat-treated samples demonstrated significantly higher values of \(G'\) and \(G''\). More importantly, a transition from viscous to elastic can be seen. While \(G''\) is higher at low frequencies, \(G'\) and \(G''\) crossover at frequency close to 1. Hence at \(\omega > 1\) the material behaves like a gel with \(G' > G''\) and parallel straight lines with a slight slope. In that regard the unheated PRF is the only sample that shows characteristics of a gel at higher frequencies.
Figure 2-4 Storage ($G'$) and loss shear modulus ($G''$) of heat-treated PRFs as a function of shear rate at a testing. (Strain and temperature of 1% and 30°C respectively)
Figure 2-5 Storage ($G'$) and loss shear modulus ($G''$) of unheated PRF. Power law values of $n$ are shown and a crossover can be seen. (Strain and temperature of 1% and 30°C respectively)

Previous work has suggested through SANS analysis that bio-oils are nano structured fluids constituted by a complex continuous phase and the nano particles are primarily formed by the association of units of pyrolytic lignin.\textsuperscript{19} Pyrolytic lignin oligomers are present in the oil mostly in tetrameric units as particles of nanometer in dimension and can aggregate and form clusters of branched structures. In thermoplastic polymers increase in temperature causes the polymeric chains to start sliding past each other and the materials softens.\textsuperscript{29} The mechanism of softening for the PRF may be different as it is not consisted of long chains but small oligomers in particle form. Moreover the pyrolytic lignin is present in the PRF along with neutrals and volatiles due to our method of extraction. As such one may think of the PRF as a colloidal suspension system, and expect some of its behavior to follow the well studied physics of colloids. The term colloid describes a wide range of multiphasic substances composed of particles roughly 10 nm–10$\mu$m in size dispersed in a continuous phase.\textsuperscript{30} Inter-particle interactions are among important controlling factors governing physical and rheological properties in colloidal suspensions.\textsuperscript{31}

Due to similarities in the chemistry and structure between the pyrolytic lignin and other technical lignins\textsuperscript{17,32} the intermolecular forces involved in the PRF’s hardening and flow reversibly are probably similar to forces that are known to cause lignins to self-associate in both aqueous and organic solvents.\textsuperscript{33,34} Such associations and dissociations are reversible and therefore do not rise from covalent chemical changes.\textsuperscript{33} Furthermore, Guerra et al observed that the self association can be thermally interrupted.\textsuperscript{35} A number of driving forces are deemed possible for lignin association. Sarkanen\textsuperscript{36} underlines non-bonded orbital interactions between
the aromatic moieties as a driving force where aromatic rings can be attracted to one another through π orbitals when arranged face to face. Micic et al. divided self association of lignin into different structural levels from nanometer on the scale range to a fraction of a millimeter, suggesting that the forces of association are of different nature in each level. While at the first two levels where monomers are coming together and forming globules, covalent bonding is responsible, later when clusters and super structures are formed, hydrogen bonding, Van der Waals interactions and electronic π orbital interactions are believed to be involved. In that regard several forms of interactions can also be present for the case of the PRF. Due to high content of phenolic hydroxyl groups in the PRF formation of hydrogen bonds are expected between the oligomeric pyrolytic lignin particles. Hydrogen bonds are thermally reversible and the strength of hydrogen bonded complexes can be tuned easily by several factors including changing solvent or temperature.

Data collected from temperature sweeps with the cone and plate set up allows us to further examine the thermal transition witnessed with the wood-sandwiched samples in the DMA testing. These sweeps are performed to monitor the behavior of the samples at a fixed frequency through a temperature ramp. In Figure 2-6, the shear G’ and G’’ of PRF samples during a temperature scan at a frequency of 3 rad/s are presented. A systematic temperature effect is observed. Namely a decrease in both G’ and G’’ for all the samples is evidenced as the temperature increases. More interestingly is however the shape of these curves. G’ curves clearly reveal 3 stages in the temperature dependence. In the case of P60 sample for example, a rapid loss in G’ is observed from room temperature up to ca. 40°C at which point a plateau region is observed, where there is minimal temperature dependency. This plateau region is rather short (5 to 10°C) and is followed with another steep temperature dependent region. The
same behavior is observed other heat-treated samples, with the plateau region extending to higher temperatures as the pretreatment temperature increases. The 2 regions of steep decrease in modulus can be attributed to different types of bonds being broken. Thermal fluidity is brought about by accelerated molecular motion and by suppression of interactions, such as hydrogen bonds between molecules.\textsuperscript{39} The first stage likely corresponds to the weaker π orbital interactions which are broken at lower temperatures, and the second represents the rupture of hydrogen bonds at higher temperatures. Strong hydrogen bonding is shown to be the cause of suppression of thermal mobility and infusibility in a model lignin molecule while a similar lignin type with weak hydrogen bonding could be thermally brought to a flow.\textsuperscript{40} Low temperatures of thermal flow in PRFs may suggest low strength of hydrogen bonding but due to differences between lignin and PRF in size of molecules and complexity of the structure no definite conclusion can be made.

**Figure 2-6** Thermograms of shear storage modulus and loss modulus. (Strain=1\%, Frequency = 3 rad/s)
2.3.3. DSC analysis

As evidenced by the DSC thermograms (Figure 2-7) the value of $T_g$ of the PRFs are very low, in the -7 to 15°C range, depending on the thermal pretreatment and significantly lower than the $T_g$ reported for isolated and technical lignins in the literature (150-260°C). No other thermal events such as melting are detected in the DSC thermogram. This indicates that the materials as expected are primarily amorphous. There are no indicators of transition on the DSC curves at the temperatures formerly marked by the DMA and rheology suggesting that these transitions are similar to the softening points of polymers. These transformations cannot be detected by DSC because they are not a clear phase transition but can be measured using thermomechanical measurements used in this study. The temperatures of the beginning of the second steep decrease in modulus from the cone and plate method are in good agreement with the DMA tan δ peaks as shown in Figure 2-8 and represent the beginning of thermal flow that occur in these materials.

Figure 2-7 DSC thermograms showing the $T_g$ of different heat-treated PRFs.
Since PRF contains the products of cracking of lignin during pyrolysis, lower values of T_g are expected. T_g is directly related to the molecular weight of lignins as shown on a study of thermal behavior of fractionated kraft lignins by DSC. Table 2-1 shows the number average (M_n) and the weight average (M_w) molecular weight of the PRFs obtained by ESI mass spectroscopy. Since during heat treatment low weight volatiles are leaving the system, polydispersity (M_w/M_n) was expected to decrease, but it remains mostly constant which might be due to the fact that most volatiles that are believed to be nonpolar hydrocarbons such as aromatics are largely not ionized by positive ion ESI-MS and hence not detected. Heating can result in crosslinking and polymerization reactions of lignin oligomers that lead to the increase in average molar masses in bio-oils. Pyrolysis-gas-phase chromatography has shown that in softwood pyrolysis oils, coniferyl alcohol (180 g/mol) makes up for more than 90% of pyrolytic lignins therfore M_n...
value of the unheated control PRF (729 g/mol) estimates a mainly tetrameric structure for the pyrolytic lignin in the PRF. Although the main building block unit and some structures remain intact during pyrolysis, study of chemical structure of pyrolytic lignin reveals that majority of aryl ether bonds that are shown to hinder thermal flow and influence thermal fusability and $T_g$ of lignins do not survive the pyrolysis process and therefore the pyrolytic lignin’s structure is free of these linkages.

Table 2-1 Average $M_n$ and $M_w$ of heat-treated and unheated PRF obtained by ESI-MS

<table>
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<th>Control</th>
<th>P60</th>
<th>P80</th>
<th>P100</th>
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<td>$M_n$ (g/mol)</td>
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<td>766</td>
<td>783</td>
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<tr>
<td>$M_w$ (g/mol)</td>
<td>877</td>
<td>894</td>
<td>933</td>
<td>949</td>
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</table>

2.3.4. TGA analysis

Although increase in $T_g$ due to heating is in part due to the increase in molecular weight, it seems that other factors are also involved. The extent of the increase in the $T_g$ does not depend linearly to the changes in molecular weight as reported by Kubo and are not proportional to the slight change in molecular weight (especially between P80 and P100). We should here shift our attention to the volatile low molecular weight content of the PRF. These volatile low molecular
weight portions facilitate the mobility of lignin particles and may act as a plasticizer as suggested in an earlier study of lignins. The isothermal TGA curves of

Figure 2-9 show the extent and rate of weight loss of PRF at the temperatures previously used for heat treatment. Clearly the PRF contains considerable amounts of volatile materials which are partially evaporating during the different heat treatment procedures. Although there is a sudden weight loss at the first hours showing rapid loss of volatiles the curve plateaus suggesting the possibility to stabilize PRF at least inside a certain temperature range. Figure 2-10 shows the TGA and differential thermogravimetric (DTG) curves of the heat-treated PRF samples. Increased thermal stability of the heat treated samples can be seen in the TGA ramps with a rightward shift of the broad peak that represents the range with the highest rate of weight loss. The peak of DTG curve for unheated PRF ranges between 80 – 120°C and represents the loss of moisture, residual ethyl acetate and volatile compounds (volatile acids and alcohols).
Figure 2-9 Isothermal TGA thermograms at three different temperatures on unheated PRF sample.

Figure 2-10 TG and DTG thermograms for different heat-treated samples.
Volume fraction or the fraction of volume occupied by solid particles, is an important parameter in controlling the properties of colloidal suspensions.\textsuperscript{44} Since the amount of pyrolytic lignin is fixed, its volume fraction can be altered through changing the volatiles content. The volatile compounds act as a continuous phase filling in between the particles. It can be proposed that heat treatment increases the volume fraction of pyrolytic lignin particles by removal of volatiles and lights and may facilitate the formation of bonds and interactions as particles become closer to each other. As a result mobility becomes more difficult and the softening and flow point shifts to higher temperatures. Furthermore the increase in modulus observed in our study as a result of heat treatment also resembles the trend well known for colloidal suspensions in which both $G'$ and $G''$ are shown to increase largely depending on the volume fraction of solid particles with dominance of viscous behavior at lower values of volume fraction.\textsuperscript{45} suspensions with a larger volume fraction will also have a larger viscosity, and this viscosity grows when volume fraction increases.\textsuperscript{30} Increase in dynamic viscosity for heat treated samples is evident in Figure 2-11 showing dynamic viscosity vs. frequency for unheated and heat-treated samples measured by cone and plate set up. The unheated oil shows a shear thinning behavior with viscosity decreasing at higher frequencies. The heat-treated specimens show characteristics reminiscent of a Newtonian fluid with viscosities more independent of frequency. Effect of volatiles in viscosity is also reported by the early work of Chum et al \textsuperscript{3} where addition of low molecular weight compounds such as phenol is reported to decrease the viscosity of phenolic fraction.
2.4. Conclusions

High modulus and viscosity structures from the PRF of pyrolysis bio-oils can be achieved when openly heat-treated. Upon reheating, PRFs undergo a reversible softening and flow resembling the behavior of thermoplastics, and the heat-treatment temperature governs the thermal flow or softening temperature. DMA results demonstrate that the thermal flow of the PRF can be systematically manipulated through changes in thermal history. The PRFs also show very low values of $T_g$ that increases with thermal treatment. The structure of the PRF can be envisioned as
a colloidal system based on the presence of pyrolytic lignin nano particles in a continuous phase of neutral and volatile material. Evaporation of volatiles increases the volume fraction of particles which leads to higher viscosity and modulus, to a point that the material turns into a glassy solid. Dominant viscous behavior of the heat-treated PRFs suggests that a chemical network is not present. Several types of inter-particle interactions can be imagined for the lignin particles in the PRF. Presumably the breakage of these bonds as a result of heating leads to increased mobility of particles and brings about material flow. Two stages of softening suggest that the bonds are ruptured at different temperatures based on their strength. The reversible thermoplastic behavior is of particular interest, as one might process the PRF with traditional melt processing technologies, such as extrusion or injection molding or with optimization of properties considered for hot melt adhesive applications. Control over flow temperature and manipulation of modulus through heat treatment can be used for tailoring materials with pre-designed properties.

Acknowledgment

Authors would like to thank Shuai Zhou for preparation of the oil and operation of the pyrolysis reactor. We would also like to thank the Sun Grant Initiative – Western Regional Center for their financial support of this research. The LCQ-Deca mass spectrometer was a gift from Thermoscientific.

Supporting Information Available: Optical microscopy images of whole bio-oil and the PRF samples showing the microstructures present. This material is available free of charge via the Internet at http://pubs.acs.org.
2.5. References


CHAPTER 3. Micibility and thermomechanical characterization of blends of phenolic rich fraction of pyrolysis bio oil and poly(ε-caprolactone)

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Abstract

Our previous work reported on unique thermoplastic properties of the heat treated phenolic rich fraction (PRF) of bio-oil obtained through fast pyrolysis of wood. Successful application of this phase as an adhesive or in melt processing technologies requires optimization and improvement of its properties. Blends of PRF with poly(ε-caprolactone) (PCL) are prepared and their properties are assessed. Mechanical strength of the blends is measured through lap shear tests and their miscibility is studied using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and optical microscopy. Presence of molecular interactions are further investigated using Fourier transform infrared spectroscopy (FTIR). Significant increase in shear strength of the blends is observed and a single composition dependent $T_g$ indicate that miscible blends are formed. FTIR data also confirms the existence of interaction between the PRF and PCL. The blend system has good potential to be used as a thermoplastic bio-degradable polymer with satisfactory properties.

3.1. Introduction

The current need for renewable energy sources has driven processes such as pyrolysis of biomass as a source of energy and fuel, and a variety of by-products. Although fuel production generally attracts the most attention, value-added by-products such as resins and adhesives hold much promise in legitimizing and making a biorefinery economically viable. In addition limited availability of bio based polymers which can address the demands of the industry such as low
cost and high performance has led to high volume of scientific research towards modification
and enhancement of properties of these materials.

We have previously reported on the rheological and thermomechanical properties of the phenolic
rich fraction (PRF) of bio-oil obtained through fast pyrolysis of wood.\textsuperscript{1} Fast pyrolysis is a unique
process that can convert a vast array of lignocellulosic raw materials into an oil, which is a
complex mixture of compounds resulting from break down of lignin and cellulose.\textsuperscript{2,3} Solvent
fractionation is a potential process for separation of different compounds in crude bio-oil. One
common solvent fractionation technique involves dissolving the crude oil in ethyl acetate, which
separates the oil into two distinct phases\textsuperscript{4}: PRF which is an organic, ethyl acetate-soluble phase
rich in mono and poly phenolic compounds originated from lignin degradation and an aqueous
phase rich in anhydro-sugars originated from cellulose and hemicellulose. While the sugars can
be converted to transportation fuels and chemicals, the PRF still requires a viable market. Our
previous study demonstrated that solid glass-like structures can be obtained via heat treatment of
the PRF which upon reheating, undergo a reversible softening and flow resembling the behavior
of thermoplastics.\textsuperscript{1} Moreover the thermal flow or softening point temperature of the PRF can be
systematically manipulated through changes in thermal history. The thermoplastic behavior of
PRF and its low $T_g$ is of particular interest, as it gives opportunities for application of this
fraction in several melt processing and adhesive technologies. Nevertheless for this material to
be successfully used in such applications it should acquire a number of properties. Mainly the
PRF’s mechanical properties should be assessed and optimized.

Among the various approaches, blending is a convenient way to adjust the properties of
polymers and effectively improve the processing characteristics of a thermoplastic polymer. One
common biodegradable polymer used to improve mechanical properties in blends is poly(e-caprolactone) PCL, a polyester which possesses high ductility and deformability.\textsuperscript{5} As a polyester, PCL is an electron acceptor polymer capable of forming strong hydrogen bonds with molecules with hydroxyl groups such as phenolics, poly(vinylphenol) (PVPh), and phenoxy.\textsuperscript{6–8} PCL has also been reported to form biodegradable miscible blends with electron donor natural polymers such as chitin, chitosan, and catechin that contain hydroxyl groups through the formation of hydrogen bonds.\textsuperscript{9,10}

Improvement in properties is largely dependent upon the miscibility of the two components. Low levels of miscibility can cause blends to suffer from inferior mechanical properties.\textsuperscript{11} Miscibility of two polymers is related to the amount and strength of intermolecular interactions between the two components.\textsuperscript{12} Lignin is a polyphenolic natural polymer and is the origin from which the PRF is derived. Biodegradable blends of lignin and PCL have been studied for their thermal and mechanical properties by Li et al.\textsuperscript{13} Their research concluded that the melt blend of the two components was not miscible, which was contributed to the small number of phenol groups and as a result smaller hydroxyl content in the lignin. The PRF is the result of lignin degradation and therefore PRF and lignin have similarities in structure and chemistry, yet according to our experiments PRF is different in a number of physical and thermal properties. For example, PRF has much lower molecular weight and unlike lignin demonstrates a softening point and can be brought to flow at higher temperatures. PRF has also been shown to have a higher phenolic hydroxyl content\textsuperscript{4} and therefore seems to be a suitable compound for forming a miscible blend with PCL. Such a blend is expected to show improvements in mechanical properties compared to the pure PRF.
In this paper we study in detail PRF/PCL blends of varying compositions and investigate the miscibility in regard to changes in thermal transitions and crystallinity by differential scanning calorimetry (DSC) measurements and polarized optical microscopy. Thermomechanical behavior of the blends are also investigated using dynamic mechanical analysis (DMA) and shear strength of the materials are evaluated using lap shear test. Fourier transform infrared spectoscopy (FTIR) is used to monitor the interactions and formation of possible bonds in the blends.

3.2. Materials and methods

3.2.1. Preparation and purification of the PRF

Pyrolytic bio-oils were prepared by the pyrolysis of Douglas-fir meal (< 2 mm) at 500°C in an Auger reactor as described elsewhere. The PRF was extracted from the bio-oils, using a 1:1 ratio of ethyl acetate/bio-oil according to a modified procedure of Chum. The mixture was shaken for 5 min at 30°C and left to equilibrate for 6 h forming distinctive aqueous and ethyl acetate phases. While the phenols are preferentially extracted into the organic phase, the anhydro-sugars concentrate in the aqueous phase. The organic phase was separated by decantation from the aqueous phase. Excess ethyl acetate was removed from the organic phase by using a rotary evaporator.

The pyrolysis bio oil contains several acidic compounds which bring the pH usually to a range of 2-4. Further purification was carried out to remove the organic acids and highly polar compounds similar to the method proposed by Chum et al. First a water wash is performed to remove the remaining water soluble materials. In our case the PRF was mixed with 1:1 ratio of
water to oil and upon standing in a separator funnel the water portion standing at the bottom was
drained off. The PRF was then mixed with an aqueous sodium bicarbonate solution of 5% weight at a ratio of 1:1. After sitting for ca. 5 h the PRF was again extracted from the separator funnel. This step results in a PRF with a pH ranging 5.5 –6.5. The remaining moisture and ethyl acetate will then be evaporated from the PRF.

PRF was then heat-treated by placing portions of known weight in open aluminum pans in an oven for 10 h at 100°C. The samples were then allowed to cool to room temperature, re-weighed and stored at 5°C until testing.

3.2.2. Blend preparation

The PCL (Tone™ Polymer P757) was obtained from a commercial supplier in pellet-form. Solvent casting was used to prepare samples for DSC and FTIR measurements. 10% (weight) solutions of PCL and PRF in dichloromethane were prepared and blended to achieve mixtures of 10, 20, 50, 75% PCL content. The mixtures along with solutions were then transferred into aluminum pans in small amounts (10 – 15 g) and left at room temperature for the solvent to evaporate. Samples were then kept at 40°C in the oven for 48 hours for removal of the remainder of the solvent and completion of crystallization process. Blends with the same ratios were also prepared by melt mixing of the components in aluminum pans heated on a hot surface at 100°C manually for 5 min to achieve well dispersed mixtures.
3.2.3. DSC

Heat flow measurements were made with a TA DSC Q800 instrument. 10 mg of each blend prepared from solvent casting was placed and sealed in an aluminum pan and put through two scans. On the first scan the material was heated from 0 to 100 at a rate of 15°C/min to collect the heat of fusion in melting of PCL and then rapidly cooled. A second scan was performed from -80 to 40°C to observe the T_g.

3.2.4. Optical microscopy

To investigate the spherulitic morphology of the crystallized samples an Olympus BX51 polarizing microscope equipped with a CCD digital camera was used. The specimen temperature was controlled by a Linkam heating stage coupled with a TMS-94 temperature programmer. Materials and blends were cast on a glass slide and melted at 100°C for 10 min then brought to 45°C and held for 2h for isothermal crystallization to take place. Picture data was stored and processed using Image software.

3.2.5. DMA

Thermo-mechanical properties of the blend samples were studied using a TA instruments DMA model Q800 in dual cantilever mode (span 50mm). Two types of samples were made, first group of samples were to observe the melting and softening point of the resins and hence were made using a sandwich type 2 ply form to contain the material after softening according to methods
previously established.\textsuperscript{17} Basswood veneers 60 mm × 13 mm × 1 mm were used. The veneers were lightly hand sanded along the grain with 220-grit sandpaper and cleaned with a paper towel immediately prior to resin application. PRF and PRF/PCL melt blended samples were brought to flow by briefly heating at 100°C and then uniformly applied to each wood surface in coverage of 70 g/cm\textsuperscript{2} and the coated plies were then lightly pressed into a sandwich.

Second group of samples were made to observe the effect of \( T_g \) on the thermo-mechanical properties and were made by thermally casting the PRF/PCL blend material into a mold prepared according to the dimensions of a standard DMA sample of 60 mm × 13.8 mm × 3.2 mm. The inner surface of the mold was covered with aluminum foil for ease of release. DMA temperature scans were conducted at 1Hz from room temperature to 100°C with a heating rate of 5°C/min. 5 replicates of each sample were used.

3.2.6. FTIR

Infrared spectra were recorded on a Thermo Nicolet Nexus 670 spectrometer (Nicolet, Thermo Scientific) spectrometer using an attenuated total reflectance (ATR) set up. 32 scans at a resolution of 4 cm\textsuperscript{-1} were used to obtain the signal. The sheets of neat PRF and its blends with PCL were prepared by melting and then quickly quenching to room temperature. A pointed pressure tip was used to hold the samples on a crystal plate of the Ge crystal.
3.2.7. Lap shear testing

Basswood veneers of thickness 0.8 mm were used to prepare the lap shear samples. 22.8 cm × 12.5 cm stripes were cut out of the sheets. Approximately 0.15g PRF, PCL or blends were heated to flow and spread over each sheet on the designated bonding area of 6.45 cm². The two sheets were then placed on heated platens of a Carver press at 100°C for 10 min. Test samples were kept pressed after removing from the press using clamps until cooled to ambient temperature. Samples were kept at a conditioning room for 1 week prior to the tests. The shear strengths of the adhesive joints were determined on an Instron 22kip frame at a speed of moving clamps of 50 mm/min. Two spacers were placed at the clamping area on each side to make sure that the bond line is in line with the pulling direction. The loading was carried out up to the beginning of failure or shearing along the interface of the joint. The value of shear strength was calculated by dividing the maximum shear force by the bound area and the value were presented as the average of five measurements.

3.3. Results and discussion

3.3.1. Lap shear

The PRF has shown interesting thermal behavior and has the potential to be utilized in various applications including adhesive and melt processing technologies. Particularly the thermoplastic character and its ease of flow at higher temperatures make it a candidate for use as a hot melt adhesive. For PRF to be successfully used as an adhesive it is important that it possesses
adequate mechanical strength. A common testing method for evaluating strength of adhesives including hot melts is the lap shear test. Figure 3-1 shows the average shear strength of PCL:PRF blends measured by the lap shear tests. The values are the average of 5 tests per sample and variation is also shown as error bars of standard deviation. It is worthy to note that the reported values for lap shear of formulated hot melt adhesives ranges between 0.35 and 4.8 MPa\textsuperscript{18}. It is apparent that the PRF’s strength is relatively low but addition of even a small amount (10\%) of PCL has a significant impact on the strength of PRF and increases the strength by almost 400\%. A 5\% PCL was tested to fill the gap due to big difference in the results between PRF and PCL\textsuperscript{10}. The strength of the 5\% PCL is almost half of that of 10\% and a great improvement over the neat PRF. Nevertheless adding more PCL (20\%) does not bring much improvement in shear strength. Also for the blends containing 50\% or more PCL all specimens break with 100\% wood failure as the adhesive becomes stronger than the wood strip. That is the reason why the strengths are the same for these specimens as it is actually the maximum strength of the wood strip. The significant increase in strength is very interesting and suggests that the blends of PRF:PCL may be benefiting from strong interactions between the two components that results in noticeable improvement in properties.
Figure 3-1 Average shear strength of blends of PCL:PRF and standard deviation measured by lap shear test of bonded wood stripes.

A well-known and extensively used method for investigation of miscibility of polymer blends is by measuring the heat flow during temperature scans of the DSC. A single $T_g$ for each blend composition is observed and the calculated value of the $T_g$ is labeled close to each curve. A single glass transition indicates that each blend is miscible over the entire blend composition. The broadness of the transition, or the section between the onset of the transition to the end is narrower for the PCL and blends with higher content of PCL and it becomes wider for the blends with higher PRF content.
According to the Fox equation for a miscible polymer blend system \(^{20}\):

\[
\frac{1}{T_g} = \frac{x_1}{T_{g1}} + \frac{x_2}{T_{g2}} \tag{3-1}
\]

where \(T_g\) is the glass transition temperature of blend, \(T_{g1}\) and \(T_{g2}\) are those of the components.

Figure 3-3 depicts the experimental data points on a graph along with Fox equation plotted as a solid line. Although the Fox equation is successful in describing many blend system, other equations are more suitably used to describe \(T_g\) of miscible polymer blends with specific interactions (such as hydrogen bonding). The most prominent of such equations is proposed by Kwei \(^{21}\):
\[ T_g = \frac{W_1 T_{g1} + kW_2 T_{g2}}{W_1 + kW_2} + qW_1 W_2 \]  \hspace{1cm} (3-2)

Where \( W_1 \) and \( W_2 \) are the weight fractions of the components and \( k \) and \( q \) are adjustable parameters. \( k \) describes the intermolecular interactions and \( q \) describes the strength of interactions such as hydrogen bonding. \( q \) is also the representative of the balance between breaking of intra molecular hydrogen bonding and forming the intermolecular hydrogen bonding. A positive \( q \) indicates that the intermolecular interactions are stronger than intra molecular interactions and otherwise the value of \( q \) will be negative. In Figure 3-3 values from the Kwei equation with \( k=1 \) and \( q=1 \) appear to fit the experimental data with good accuracy. The positive deviation from the Fox equation is commonly attributed to the existence of strong interactions between the two components. In our blend system, a \( q \) value of 1 can be an indication of a balance between the disruption of intra-molecular PRF hydrogen bonding and forming of intermolecular hydrogen bond between PRF and PCL.
Figure 3-3 Experimental T<sub>g</sub> values from DSC measurements, and model predictions vs. composition.

In Figure 3-4 the first scan DSC heat flow curves of the different blend compositions show the change of the melting behavior of the PCL with the addition of PRF. PRF is previously shown to be completely amorphous<sup>1</sup> and hence does not exhibit a melting point (T<sub>m</sub>), whereas neat PCL shows a T<sub>m</sub> of approximately 65°C. Note that melting temperatures of the blends are obviously changing in a range of more than 20°C wide with the variation in composition. Depression of equilibrium melting temperatures are often representative of presence of specific interactions (including hydrogen bonding) between the two components<sup>24</sup>. Such a conclusion cannot be made as the measured T<sub>m</sub>’s are not equilibrium melting points but the shift can be held as indicative of a change in the crystalline phase or the interfaces of the two phases.
Figure 3-4 DSC Thermograms from first scan for PCL:PRF blends of different compositions from solution casting.

Specific interactions can effectively influence the crystallinity in a blend system. From the heat of fusion $\Delta H$ measured by the DSC, the degree of crystallinity ($X_c$) was calculated based on PCL weight assuming a value of 136 J/g for 100% crystalline PCL$^{21}$. Table 1 shows $T_m$, heat of fusion of the blend $\Delta H$, heat of fusion per PCL weight and $X_c$ of the PCL portion of the blend. Degree of crystallinity noticeably decreases for blends with less amount of PCL, nevertheless crystallinity does not change significantly for the blends containing 50% and more PCL. The depression of crystallinity is expected in miscible crystalline/amorphous polymer blends due to
decreased segmental mobility of the crystalline polymer and as a result of the depressed melting point.\textsuperscript{25}

**Table 3-1 Melting temperature (Tm) and heat of fusion (∆H) and crystallinity (Xc) of PCL/PRF blends.**

<table>
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<tr>
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<th>Tm</th>
<th>∆H (J/g blend)</th>
<th>∆H(J/g PCL)</th>
<th>Xc (PCL) %</th>
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</tbody>
</table>

Figure 3-5 depicts the polarized optical micrographs of PCL and PRF/PCL blends. The PCL 50 blend shows less ordered and partially disrupted spherulite structures compared to the neat PCL nevertheless the size of the spherical grains appear to be similar. The size decreases for the PCL20 and PCL10 blends and the structure of the spherulites become more irregular. The smaller size and increased number of spherulites shows that the nucleation density has been increased but the crystals could not form perfectly and the degree of crystallization decreases as calculated by the heat of fusion of the blends. The amorphous PRF phase constitutes to the disorder in spherulite form and may provide more sites for heterogeneous nucleation. Thinner less perfect lamellas might contribute to lower melting points observed on the DSC.
3.3.2. DMA

Thermal analysis results discussed so far suggests the miscibility of the blends due to existence of single $T_g$s and suppression of $T_m$s. The phase behavior can also be studied through thermomechanical analysis to further validate the results for PRF/PCL blends. DMA measures the rate and quality of changes to properties such as the storage ($E'$) and loss modulus ($E''$). For observation of melting and softening point temperatures, tests were conducted on wood-bonded assemblies of the blends so that the sandwich form restrains the material shape during the melt transition. $E'$ of PCL/PRF blends vs. temperature during DMA temperature ramp is shown in Figure 3-6a. Noticeably the PRF has the greatest modulus and retains its stiffness until passing 70°C where softening reduces the composite modulus. As the ratio of PCL increases in the blends, the modulus decreases. Also with the blends having higher amount of PCL a transition can be observed as a sudden drop on the modulus curve indicated in Figure 3-6a by the arrows between 40 to 65°C.
As noted with the DSC analysis the higher PRF content blends exhibited a lower $T_m$, this holds true as the observed $T_m$ in the DMA data shows the same behavior. The transition is more pronounced on the PCL curve itself and gets smaller on the other blends within which the amount of PCL is lower. This melting step can also be observed on the tan $\delta$ plot of the blends (Figure 3-6b). A sharp tall peak is apparent on the tan $\delta$ of pure PCL and it becomes less distinct as it also shifts to lower temperatures as the PCL content lowers. Smaller melting traces on the DMA can be associated with melting peaks on the DSC results which is due to less amount of crystalline PCL and reduced degree of crystallinity in blends of high PRF content as discussed earlier. Moreover the observed composition dependent shift in position of this melting transition is further evidence of existence of specific interaction between the two components of these blends namely the formation of hydrogen bonds in accordance to the DSC results and demonstrating the behavior of a miscible blend system.

The melting step is followed by another stage of decrease in modulus for the blend systems in accordance to the softening behavior of the PRF. This second softening transition is represented by large broad peaks occurring at higher temperatures on the tan $\delta$ curves. We have previously reported on and discussed the softening of the PRF and its temperature dependence.\textsuperscript{1} Since the PRF portion of all compositions has gone through the same heat treatment they are expected to have the same softening point. Therefore any change in softening point of the compositions can be attributed to the added PCL. Interestingly the tan $\delta$ plots demonstrate that the onset of this second transition does not seem to be influenced by the composition of the blends as the tan $\delta$ peaks are all located at the same temperature for all blends. PCL75 does not show this second softening and follows the behavior of pure PCL due to high PCL content.
Figure 3-6 (a) Storage modulus E’ of blends of PCL:PRF from DMA temperature ramp. (b) Tan δ curves of DMA samples.

As DSC results indicated T_g’s of the blends are located at sub ambient temperatures. In order to view the transition on the DMA liquid nitrogen was used to run the temperature ramps starting from -80°C. Since all blends are solid and rigid at low temperature ranges sandwich type specimens were not needed. The results are shown in Figure 3-7, where only PCL and 2 other
blend systems with higher portion of PCL are presented. Other blends and PRF are not shown because they proved to be too brittle to be tested at these sub ambient temperatures and failed before the thermal limits could be reached. Nevertheless by observation of the results from the 3 blends a clear trend can be seen with the position of tan δ peak in regard to composition. The tan δ peak can be held as a representative of the T_g of these materials and is obviously moving towards higher temperatures as the amount of PRF in the blend is increased. This is again in accordance to our previous results from the DSC.

Figure 3-8 summarizes the results from the DSC and DMA and provides a comparative visual of changes in thermal transition points of all blends. The results for T_g from DMA and DSC follow the same trend and are closely matching but there is more mismatch with higher PCL content. The melting point is following an almost linear path as it is increasing with PCL content. The softening point of the blend systems remains unchanged with composition.
Figure 3-7 Storage modulus and Tan δ of PCL:PRF blends at sub-ambient temperatures.

Figure 3-8 Relationship of melting temperature and T_g calculated from DMA and DSC with PCL content.
3.3.3. FTIR

From the analysis of the $T_g$ and $T_m$ obtained from the DSC results which were also validated by the thermomechanical DMA results, it may be reasonably assumed that the miscibility of the two components is due to specific interactions formed in a molecular level. The most highly expected source of such interactions according to the functional groups in the system is formation of hydrogen bonds between the carbonyl group of PCL and hydroxyl group of PRF. FTIR measurements enable one to obtain an accurate measure of the interactions in most polymer blends. It should be noted though that the interactions between the components in biopolymer blends are usually not strong enough to detect any shift in the absorption band of characteristic groups\textsuperscript{26}. Hydrogen bonds are exempt because of their strength. Figure 3-9b shows the FTIR spectra of the carbonyl stretching region of PCL, PRF and their blends. Spectra of the neat PRF exhibits a broad peak at 1710 cm$^{-1}$. This absorption band is commonly seen in the spectra of the pyrolytic lignin and is assigned to the carbonyl groups that are present in small amounts.\textsuperscript{27} An absorbance peak of 1728 cm$^{-1}$ can be seen for the neat PCL. Carbonyl groups of crystalline and amorphous conformation of PCL are known to exhibit peaks at 1724 and 1736 respectively. The peak at 1728 might be the result of overlapping of the two peaks with the crystalline portion dominating. There is almost no change in the position of $C=O$ peaks of blends with high content of PCL but with the 50% and less PCL blends a clear shift of the carbonyl peak to lower wave numbers can be seen. It is important to note that in PCL blends with polymers containing OH groups specially phenolics, an absorption band near 1706 is often assigned to hydrogen bonded carbonyl group.\textsuperscript{28} In our case the carbonyl group of neat PRF is close to 1706, which is possibly due to intermolecular interactions of its own carbonyl and
hydroxyl groups. Therefore it can be proposed that the observed shift in the peak position towards lower wave numbers as the PRF portion increases may be due to the greater contribution of hydrogen bonded carbonyl groups as new bonds form between PRF and PCL.
Figure 3-9 FTIR spectra of blends of PCL:PRF. Inset showing the entire range a) the OH stretching region b) C=O stretching region.

Figure 3-10 Relationship of absorbance of C=O and O-H with PCL ratio.
Figure 3-9a shows the FTIR spectra of the hydroxyl stretching region of PCL, PRF and their blends. A very weak absorption peak at 3450 cm⁻¹ is visible on the PCL spectra corresponding to the vibration of the hydroxyl groups at the chain end terminal. A broad intense band centered at 3392cm⁻¹ in the spectrum of pure PRF is observed and mainly assigned to the hydrogen bonded and free hydroxyl groups. The center of the peak obviously moves toward higher wavenumbers as PCL is added and its ratio is increased. Since the peak on the pure PCL at 3450 is too small its contribution to the peak position shift can be neglected and we may conclude with more certainty that the position shift is a clear sign of formation of hydrogen bonds between the OH groups of PRF and C=O groups of PCL. The relationship between the absorbance bands of carbonyl and hydroxyl spectra and content of PCL is shown in Figure 3-10. This plot suggests that the shifts on both C=O and O-H absorbance bands are more significant at lower PCL content blends and plateaus as the PCL content goes above 50% indicating very little difference in the spectra of PCL50, PCL75 and PCL.

3.4. Conclusion

Shear block tests demonstrate that addition of PCL to the PRF improves the shear strength significantly even at small amounts. The improvement in mechanical properties suggests the miscibility of the blends and formation of specific interactions. Existence of a single composition dependant $T_g$ in the blend systems of PCL and PRF is evidence of miscibility and existance of specific interactions between the components. These interactions also influence the crystallinity of the PCL at higher contents of PRF. DMA results also confirms a composition dependant $T_g$ and reduction in $T_m$ of the blends. Nevertheless softening point of the PRF is independant of
PCL content. FTIR analysis further validates that miscibility of the blends are due to formation of hydrogen bonds between the hydroxyl and carbonyl groups of the PRF and PCL. The adjusted and improved properties combined with the other interesting thermosensitive characteristics of PRF will facilitate the utilization of this new phase as biodegradable plastic or as an adhesive in several application where hotmelts are conventionally used.
3.5. References

(1) Sahaf, A.; Laborie, M.-P. G.; Englund, K.; Garcia-Perez, M.; McDonald, A. G. 


CHAPTER 4. Thermal stability and kinetics of degradation of blends of phenolic rich fraction of bio-oil and poly(ε-caprolactone)

4.1. Introduction

Ligno-cellulosic biomass being the world most abundant renewable resource has attracted much attention in recent years and efforts have been made to optimize processes like pyrolysis for commercial competitiveness. One common solvent fractionation technique involves dissolving the oil in ethyl acetate which separates the oil into two distinct phases: An organic-rich, EA-soluble phase and an aqueous phase rich in anhydrosugars.¹ The organic phase is rich in phenolic compounds originated from lignin degradation. Our previous study demonstrated that solid glass-like structures can be obtained via heat treatment of the Phenolic rich phase (PRF) which upon reheating, undergo a reversible softening and flow resembling the behavior of thermoplastics.² Moreover the thermal flow or softening point temperature of the PRF can be systematically manipulated through changes in thermal history. The thermoplastic behavior of PRF and its low \( T_g \) is of particular interest, as it gives opportunities for application of this fraction in several melt processing and adhesive technologies.

Processing of the PRF at temperatures above its softening point is of interest. Such a process is only successful if this phase acquires good resistance to thermal degradation that allows acceptable residence times in the processing equipment at high temperatures. Blending with other polymers may offer opportunities to improve thermal degradation of PRF. A biodegradable polymer is of course preferred for blending with PRF. One common biodegradeble polymer used in blends is poly(e-caprolactone) PCL, a polyester which possesses high ductility and
deformability. We have used PCL to improve the mechanical properties of the PRF. Thermal degradation of PCL has been studied and acceptable thermal stability is observed. Composites of polycaprolactone (PCL) and vital wheat gluten (VG) have been studied and the degradation activation energy (Ea) of the composites has increased at higher VG levels.

In this study thermal degradation of PRF and blends of PRF/PCL is studied by thermogravimetric analysis (TGA) and three common non-isothermal methods are used in order to determine the apparent activation energies.

4.2. Materials and methods

4.2.1. Materials

Pyrolytic bio-oils were prepared by the pyrolysis of Douglas-fir meal (< 2 mm) at 500°C in an Auger reactor as described elsewhere. The PRF was extracted from the bio-oils, using a 1:1 ratio of ethyl acetate/bio-oil according to a modified procedure of Chum. The mixture was shaken for 5 min at 30°C and left to equilibrate for 6 h forming distinctive aqueous and ethyl acetate phases. While the phenols are preferentially extracted into the organic phase, the anhydro-sugars concentrate in the aqueous phase. The organic phase was separated by decantation from the aqueous phase. Excess ethyl acetate was removed from the organic phase by using a rotary evaporator.

The pyrolysis bio oil contains several acidic compounds which bring the pH usually to a range of 2-4. Further purification was carried out to remove the organic acids and highly polar compounds similar to the method proposed by Chum et al. First a water wash is performed to
remove the remaining water soluble materials. In our case the PRF was mixed with 1:1 ratio of water to oil and upon standing in a separator funnel the water portion standing at the bottom was drained off. The PRF was then mixed with an aqueous sodium bicarbonate solution of 5% weight at a ratio of 1:1. After sitting for ca. 5 h the PRF was again extracted from the separator funnel. This step results in a PRF with a pH ranging 5.5 -6.5. The remaining moisture and ethyl acetate will then be evaporated from the PRF.

PRF was then heat-treated by placing portions of known weight in open aluminum pans in an oven for 10 h at 100°C. The samples were then allowed to cool to room temperature, re-weighed and stored at 5°C until testing.

The PCL (Tone ™ Polymer P757) was obtained from a commercial supplier in pellet-form. Blends were prepared and blended to achieve mixtures of 20, 30 and 50% PCL content by melt mixing of the components in aluminum pans heated on a hot surface at 100°C manually for 5 min to achieve well dispersed mixtures.

4.2.2. TGA procedure

TGA measurements were taken using a Q600 thermogravimetric analyzer (TA Instruments) in an inert atmosphere. Thermogravimetric curves were obtained at four different heating rates of 2, 10, 20 and 50 °C/min between room temperature and 500°C. Nitrogen gas was used as an inert purge gas at a flow rate of 100 ml/min to avoid oxidation of the sample. Samples of approximately 15 mg were placed in an open aluminum pan and records of sample temperature, weight and its first derivative were taken.
4.2.3. Kinetic analysis

The kinetic behavior of the thermal degradation of polymer is generally described by rate equations. It is assumed that the rates of conversion are proportional to the concentration of reacted material. The rate of conversion can be expressed by the following the basic rate equation

\[
\frac{dx}{dt} = \beta \frac{dx}{dT} = K(T)f(x) \tag{4-1}
\]

where \( x \) is the degree of advance or conversion defined by

\[
x = \frac{w_0 - w}{w - w_f} \tag{4-2}
\]

where \( w \) is the weight of the sample at a given time \( t \), \( w_0 \) and \( w_f \) refer to values at the beginning and the end of the weight loss event of interest. \( f(x) \) and \( K(T) \) are functions of conversion and temperature, respectively. \( K(T) \) the temperature dependence of the rate of weight loss can be substituted by the Arrhenius equation:

\[
K(T) = A \exp\left(-\frac{E}{RT}\right) \tag{4-3}
\]

where \( E \) is the activation energy, \( A \) the pre-exponential factor and \( R \) the gas constant.

By combining the Eqs. (4-1) and (4-3), the equation can be transformed into non-isothermal rate expression.

\[
\beta \frac{dx}{dt} = A \exp\left(-\frac{E}{RT}\right)f(x) \tag{4-4}
\]
In eq. 4-4, f(x) depends on the mechanism of the decomposition reaction. Various methods can be used to calculate activation energy E. The first one used in this study is the isoconversional Friedman method. This method is based on the logarithm of eq. 4-4. If you apply the logarithm of the conversion rate $\frac{dx}{dt}$ as a function of temperature from eq. 4-4 one will get:

$$\ln \left( \frac{dx}{dt} \right) = \ln \left( \beta \frac{dx}{dT} \right) = \ln(f(x)) - \frac{E}{RT} \quad (4-5)$$

From this equation values of E for a given value of x can be calculated by plotting $\ln \left( \beta \frac{dx}{dT} \right)$ against $\frac{1}{T}$ over a wide range of x.

The activation energy can also be determined by Kissinger method using the equation

$$\ln \left( \frac{\beta}{T^2} \right) = \ln \left( \frac{AR}{Eg(x)} \right) = \ln \left( \frac{AE}{RG(x)} \right) - \frac{E}{RT} \quad (4-6)$$

Which is derived from eq. 4-4 by integration assuming A, f(x) and E are independent of T.

The third method is also an isoconversional method which assumes that f(x) is not changing with the heating rate for all x values. Using Doyle’s approximation

$$\ln \left( \frac{AR}{Eg(x)} \right) \approx 5.331 - 1.052 \frac{E}{RT} \quad (4-7)$$

we will have

$$\ln \beta = \ln \left( \frac{AE}{RG(x)} \right) - 5.331 - 1.052 \frac{E}{RT} \quad (4-8)$$

For a constant x, one can plot $\ln \beta$ obtained from thermograms recorded at several heating rates vs. $\frac{1}{T}$ and generate straight line whose slope can be used to evaluate the activation energy.
4.3. **Results and discussion**

Figure 4-1 shows thermal degradation curves of neat PRF corresponding to dynamic experiments carried out at different heating rates. The corresponding derivative thermogravimetric curves are also shown. It is evident from these curves that thermal degradation of PRF does not occur in a one step process in a narrow temperature range but the weight loss is gradual over a wide range of temperatures. The slow constant weight loss is a result of PRF being a mixture of numerous compounds degrading at different temperatures. This is also evident in the DTG curves where many peaks can be observed instead of a usual one or two degradation peaks. Nevertheless a broader outline of a peak made from all these smaller peaks can still be seen with the highs point regarded as the temperatures with maximum rate of degradation. With increasing the heating rate the degradation of PRF starts at a higher temperature and the temperature of maximum degradation also shifts to the right.
Figure 4-1 Curves of TG for PRF at different heating rates and their first derivative DTG
Figure 4-2 shows the TG and DTG curves of thermal decomposition of neat PCL at different values of $\beta$. In contrast with PRF thermal degradation of PCL occurs through one sharp step between 380 and 450°C depending on the heating rate. Again the onset of degradation and the
position of the peak on DTG which represents the maximum degradation temperature shows a shift that depends on $\beta$.

TG and DTG curves of blends of PRF/PCL of different blend ratios conducted at 10$^\circ$C/min rate are demonstrated in Figure 4-3. From the curves it is apparent that both PRF and PCL degradation are affecting the shape of the TG curves and the gradual weight loss is still visible though with a smaller slope. DTG curves also reveal two distinct areas of decomposition with a broad peak area of decomposition for PRF stretched in 100 – 300$^\circ$C region and a narrow sharp peak representative of PCL decomposition.

A more detailed analysis of the curves reveals interesting changes in the degradation of these blends. The PCL degradation peak originally positioned at 408$^\circ$C shifts to lower temperatures for the blends. However a trend cannot be observed in regard to composition of the blends. Since processing of these materials are in the focus of this research, we shift our attention to the temperature range of 150 – 250$^\circ$C which is mostly used for melt processing of such compounds. Table 4-1 shows the ratio of remaining material by weight during the TGA runs for the PRF and blends at a series of temperatures between 150 and 250$^\circ$C. PCL shows no degradation at this temperature range so all weight loss can be attributed to the PRF degradation. Therefore the remaining weigh ratio is also calculated based on the PRF portion of the blends, making possible assessment of the effect of PCL blend formation on the degradation of the blends. The remaining PRF weight ratio obviously increases in the blends as more PCL is blended. Formation of a miscible blends and hydrogen bonds are believed to affect the degradation temperature of the PRF as changes in thermal stability and degradation has been reported in miscible blends.\textsuperscript{11}
Figure 4-3 Curves of TG for PRF/PCL blends at different heating rates and their first derivative DTG
Table 4-1 Ratio of remaining material by weight during the TGA runs for the PRF and blends between 150 and 250°C. Ratios calculated based on the PRF portion of the blends shown in parentheses.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>PRF</th>
<th>PCL20</th>
<th>PCL30</th>
<th>PCL50</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0.96</td>
<td>0.98 (0.97)</td>
<td>0.98 (0.97)</td>
<td>0.99 (0.98)</td>
</tr>
<tr>
<td>175</td>
<td>0.91</td>
<td>0.96 (0.95)</td>
<td>0.97 (0.96)</td>
<td>0.98 (0.96)</td>
</tr>
<tr>
<td>200</td>
<td>0.82</td>
<td>0.91 (0.89)</td>
<td>0.92 (0.89)</td>
<td>0.97 (0.94)</td>
</tr>
<tr>
<td>220</td>
<td>0.76</td>
<td>0.85 (0.81)</td>
<td>0.87 (0.81)</td>
<td>0.96 (0.92)</td>
</tr>
<tr>
<td>250</td>
<td>0.67</td>
<td>0.75 (0.69)</td>
<td>0.8 (0.71)</td>
<td>0.94 (0.88)</td>
</tr>
</tbody>
</table>

4.3.1. Kinetic analysis

Data from all heating rates was used to calculate the activation energies by three methods for the reason of comparison. To calculate the activation energy using the Friedman method, \( \ln \left( \frac{dx}{dT} \right) \) was plotted against \( \frac{1}{T} \) for a constant x value. The results for PRF, PCL20 and PCL50 are shown in Tables 4-2 to 4-4. The mean values of activation energy were 106.2, 135.6 and 143.5 kJ/mol for PRF, PCL20 and PCL50, respectively.

Secondly Kissinger-Akahira-Sunose was used to calculate the activation energy for different conversion values by plotting \( \ln \left( \frac{\beta}{T^2} \right) \) against \( \frac{1}{T} \). The calculated activation energies for PRF, PCL20 and PCL50 are shown in Tables 4-2 to 4-4.
Table 4-2 Activation energies of PRF by FR, KAS and FWO methods.

<table>
<thead>
<tr>
<th>Conversion x</th>
<th>FR</th>
<th>KAS</th>
<th>FWO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>87.8</td>
<td>88.9</td>
<td>91.4</td>
</tr>
<tr>
<td>0.2</td>
<td>88.2</td>
<td>89.4</td>
<td>92.2</td>
</tr>
<tr>
<td>0.3</td>
<td>97.9</td>
<td>89</td>
<td>92</td>
</tr>
<tr>
<td>0.4</td>
<td>102.5</td>
<td>92.4</td>
<td>95.4</td>
</tr>
<tr>
<td>0.5</td>
<td>107.7</td>
<td>97.9</td>
<td>100.9</td>
</tr>
<tr>
<td>0.6</td>
<td>107.2</td>
<td>100.3</td>
<td>103.3</td>
</tr>
<tr>
<td>0.7</td>
<td>113</td>
<td>102.5</td>
<td>105.5</td>
</tr>
<tr>
<td>0.8</td>
<td>118.3</td>
<td>106.9</td>
<td>109.8</td>
</tr>
<tr>
<td>0.9</td>
<td>117</td>
<td>109.3</td>
<td>112.2</td>
</tr>
<tr>
<td>1</td>
<td>122.7</td>
<td>112.3</td>
<td>115.2</td>
</tr>
<tr>
<td>Mean</td>
<td>106.2</td>
<td>98.9</td>
<td>101.8</td>
</tr>
<tr>
<td>St Dev</td>
<td>12.2</td>
<td>8.8</td>
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</tbody>
</table>

Table 4-3 Activation energies of PCL20 blend obtained by FR, KAS and FWO methods

<table>
<thead>
<tr>
<th>Conversion x</th>
<th>FR</th>
<th>KAS</th>
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<tr>
<td>0.1</td>
<td>86.59</td>
<td>85.53</td>
<td>88.81</td>
</tr>
<tr>
<td>0.2</td>
<td>87.34</td>
<td>86.84</td>
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</tr>
<tr>
<td>0.3</td>
<td>108.8</td>
<td>94.62</td>
<td>98.2</td>
</tr>
<tr>
<td>0.4</td>
<td>125</td>
<td>107.4</td>
<td>110.7</td>
</tr>
<tr>
<td>0.5</td>
<td>146.1</td>
<td>129.1</td>
<td>131.7</td>
</tr>
<tr>
<td>0.6</td>
<td>152.3</td>
<td>144.9</td>
<td>147</td>
</tr>
<tr>
<td>0.7</td>
<td>158</td>
<td>150.8</td>
<td>152.9</td>
</tr>
<tr>
<td>0.8</td>
<td>162</td>
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<td>158.2</td>
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<tr>
<td>0.9</td>
<td>163.9</td>
<td>158.6</td>
<td>160.6</td>
</tr>
<tr>
<td>1</td>
<td>166.2</td>
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<td>162</td>
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<tr>
<td>Mean</td>
<td>135.6</td>
<td>127.4</td>
<td>130.1</td>
</tr>
<tr>
<td>St Dev</td>
<td>31.42</td>
<td>30.88</td>
<td>30.23</td>
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</table>
Table 4-4 Activation energies of PCL50 blend obtained by FR, KAS and FWO methods.

<table>
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<tr>
<th>Conversion x</th>
<th>FR</th>
<th>KAS</th>
<th>FWO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>92.52</td>
<td>91.79</td>
<td>95.31</td>
</tr>
<tr>
<td>0.2</td>
<td>126.6</td>
<td>117.5</td>
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<tr>
<td>0.3</td>
<td>128.4</td>
<td>125.1</td>
<td>128.3</td>
</tr>
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<td>0.4</td>
<td>138.7</td>
<td>129.8</td>
<td>133.2</td>
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<tr>
<td>0.5</td>
<td>147</td>
<td>134.8</td>
<td>138.1</td>
</tr>
<tr>
<td>0.6</td>
<td>155.5</td>
<td>139.6</td>
<td>142.8</td>
</tr>
<tr>
<td>0.7</td>
<td>158.8</td>
<td>143.9</td>
<td>146.9</td>
</tr>
<tr>
<td>0.8</td>
<td>161.3</td>
<td>147.4</td>
<td>150.4</td>
</tr>
<tr>
<td>0.9</td>
<td>162.7</td>
<td>148.9</td>
<td>151.9</td>
</tr>
<tr>
<td>1</td>
<td>163</td>
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<td>153.4</td>
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<tr>
<td>Mean</td>
<td>143.5</td>
<td>132.9</td>
<td>136.1</td>
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<tr>
<td>St Dev</td>
<td>22.59</td>
<td>18.09</td>
<td>17.94</td>
</tr>
</tbody>
</table>

Lastly the method of Flynn- Wall-Ozawa was used from plotting of \( \ln \beta \) against \( \frac{1}{T} \) at a fixed conversion. The linearly fitted data plotted for PRF is shown in Figure 4-4 as an example. The plot shows that the data is linear and parallel. The mean values of activation energy were 101.8, 130.1 and 136.1 kJ/mol for PRF, PCL20 and PCL50, respectively.
Figure 4-4 The FWO method applied to calculate the activation energy of thermal degradation for PRF.

Figure 4-5 Dependence of activation energy on the conversion for thermal degradation of PCL according to FR, KAS and FWO methods.
The dependence of values of activation energy calculated from the three methods on the conversion for the neat PCL is shown in Figure 4-5. From the calculated data it is evident that approximately equal values of E are obtained for the whole conversion range by using any of the three methods for all the compositions. In order to provide means for comparison based on composition Figure 4-6 presents the activation energies for all materials and blends calculated from the FWO method on a single plot. Neat PRF has the lowest values and the E increases as PCL is added in the blend. While for neat PCL and neat PRF values of E are almost constant in the conversion range, these values increase for the blends with higher conversion. This means that the degradation mechanism can be regarded as unchanged for the neat materials but is more complex in the blends.¹²
Figure 4-6 Activation energies of PRF, PCL and blends thermal degradation vs. conversion according to FWO method.

4.4. Conclusions

Thermal stability and kinetics of the thermal degradation of PRF, PCL and their blends was determined from a series of experiments at four heating rates (2, 10, 20 and 50 oC/min). Based on the weight loss data during the TGA runs and the calculated ratio of PRF in the blends in the processing temperature range of 150-250°C it is evident that addition of PCL increases the thermal stability of PRF in this temperature range. Friedman, Flynne-Walle-Ozawa and Kissinger-Akahira-Sunose methods were used in order to determine kinetic parameters. Results obtained from all three methods are approximately equal. The activation energies was found to
be approximately constant in the 0.1–0.9 conversion range for the neat materials, but rising in the
blends with advancement of the reaction suggesting that the degradation mechanism is
unchanged for the neat materials but might be more complex and include more steps for the
blends.
4.5. References


CHAPTER 5. Miscibility and thermomechanical properties of bio-mass based blends of phenolic rich fraction of pyrolysis bio-oil and poly (lactic acid) PLA

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Abstract

Phenolic rich fraction (PRF) of pyrolysis bio-oil has been shown to possess the ability to be heat treated into a glassy solid, resulting in a thermo-responsive resin. In that regard PRF can be considered as a potential valuable by-product that can be utilized in a variety of applications including adhesives and support the economics of the pyrolysis process that is mainly driven by energy and fuel needs. Optimization of properties of the PRF is sought in this study through polymer blending with another bio-mass derived thermoplastic poly(lactide acid) (PLA). Blends of PRF/PLA of different ratios were prepared by solvent casting and thermally and thermomechanically characterized for their miscibility and phase behavior using differential scanning calorimetry DSC and dynamic mechanical analysis DMA. Adhesive performance was evaluated using a lap shear test and Fourier transform infrared FTIR spectroscopy was used to investigate the existence of specific interactions such as hydrogen bonds in the blends. Signs of phase separation were observed on the DSC and FTIR for solvent casted blends, however all blends showed complete miscibility after melting. A single composition dependent glass transition (T_g) was also observed in the DMA data that supported the DSC results. Shear strength was improved significantly and the PRF/PLA 50/50 and 75/25 blend ratios showed a good balance of cohesion and adhesion to the surface, resulting in higher values of shear strength.

5.1. Introduction

Pyrolysis of many types of biomass is a promising route to producing energy and fuel and is under extensive study because of the current need for renewable energy sources. The process is also important because the bio-oil produced can be a source for a variety of by-products and chemicals such as resins and adhesives. In addition limited availability of bio based polymers
which can address the demands of the industry such as low cost and high performance has led to high volume of scientific research towards modification and enhancement of properties of these materials.

We have previously reported on the rheological and thermomechanical properties of the phenolic rich fraction (PRF) of bio-oil obtained through fast pyrolysis of wood. Fast pyrolysis is a unique process that can convert a vast array of lignocellulosic raw materials into an oil, which is a complex mixture of compounds resulting from break down of lignin and cellulose. Solvent fractionation is a potential process for separation of different compounds in crude bio-oil. One common solvent fractionation technique involves dissolving the crude oil in ethyl acetate, which separates the oil into two distinct phases: PRF which is an organic, ethyl acetate-soluble phase rich in mono and poly phenolic compounds originated from lignin degradation and an aqueous phase rich in anhydro-sugars originated from cellulose and hemicellulose. While the sugars can be converted to transportation fuels and chemicals, the PRF still requires a viable market. Our previous study demonstrated that solid glass-like structures can be obtained via heat treatment of the PRF which upon reheating, undergo a reversible softening and flow resembling the behavior of thermoplastics. Moreover the thermal flow or softening point temperature of the PRF can be systematically manipulated through changes in thermal history. The thermoplastic behavior of PRF and its low $T_g$ is of particular interest, as it gives opportunities for application of this fraction in several melt processing and adhesive technologies. Nevertheless for this material to be successfully used in such applications it should acquire a number of properties. Mainly the PRF’s mechanical properties should be assessed and optimized.
As a biomass-based aliphatic polyester, poly(lactic acid) PLA has attracted increasing attention in recent years due to its excellent mechanical properties, biodegradability and potential renewability and its annual supply is expected to increase rapidly. It is also one of the most widely studied biopolymers in blending technology. Blends of polymers are made to modify and tailor properties. Compatibility and miscibility of the binary blends is mostly dependent upon the interactions among two components (Flory Higgins) and is an important factor in determining the resulting properties. There are numerous studies regarding blends of PLA with various counterparts, i.e.: poly(butylene succinate) (PBS), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), poly (vinyl alcohol) (PVA), poly (ethylene glycol) (PEG), poly(epichlorohydrin-co-ethylene oxide) (PEEO), poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) PVAc. Research has shown that PMMA and PHB, and PVAc are able to form miscible blends with PLA. The likelihood of two polymers forming a miscible blend becomes higher if there are specific interactions, particularly hydrogen bonding among the components. It is expected that when functional groups able to form hydrogen bonds are present in the system a miscible blend is formed. Nevertheless this does not always prove to be true in practice, for example no indications of hydrogen bonding were found by FTIR analysis with blends of lignin and PLA despite the presence of hydroxyl functional groups in chemical structure of lignin and carbonyl groups in PLA. Also there has been mixed reports on miscibility of PLA and phenolic compounds. Zhang et al. reported phase separation and no specific interactions in the blends of PLA/poly(vinylphenol) (PVPh). Meanwhile Meaurio et al. argued that the blend of the two polymers are completely miscible in all compositions given proper conditions.
PRF is primarily the result of lignin thermal decomposition and is rich in mono and oligomeric phenolic compounds\textsuperscript{17}. The PRF is reported to have a higher phenolic hydroxyl content \textsuperscript{4} compared to lignin. Therefore based on their structure and chemistry, PLA and PRF can potentially form a miscible blend. Such a blend is expected to show improvements in mechanical properties compared to the pure PRF. Several analytical and characterization methods including thermal and mechanical analysis are used in this study to determine the existence and conditions of miscibility between the two components and the influences on the properties of the blends.

### 5.2. Materials and methods

5.2.1. Preparation and purification of the PRF

Bio-oils were prepared by the pyrolysis of Douglas-fir meal (\(< 2 \text{ mm}\)) at 500\(^\circ\text{C}\) in an Auger reactor as described elsewhere.\textsuperscript{18} The PRF was extracted from the bio-oils, using a 1:1 ratio of ethyl acetate/bio-oil according to a modified procedure of Chum.\textsuperscript{4} The mixture was shaken for 5 min at 30\(^\circ\text{C}\) and left to equilibrate for 6 h forming distinctive aqueous and ethyl acetate phases. While the phenols are preferentially extracted into the organic phase, the anhydro-sugars concentrate in the aqueous phase.\textsuperscript{4,19} The organic phase was separated by decantation from the aqueous phase. Excess ethyl acetate was removed from the organic phase by using a rotary evaporator.

The pyrolysis bio oil contains several acidic compounds which bring the pH usually to a range of 2-4.\textsuperscript{17} Further purification was carried out to remove the organic acids and highly polar
compounds similar to the method proposed by Chum et al. First a water wash is performed to remove the remaining water soluble materials. In our case the PRF was mixed with 1:1 ratio of water to oil and upon standing in a separator funnel the water portion standing at the bottom was drained off. The PRF was then mixed with an aqueous sodium bicarbonate solution of 5% weight at a ratio of 1:1. After sitting for ca. 5 h the PRF was again extracted from the separator funnel. This step results in a PRF with a pH ranging 5.5 -6.5. The remaining moisture and ethyl acetate was then evaporated from the PRF.

PRF was then heat-treated by placing portions of known weight in open aluminum pans in an oven for 10 h at 100°C. The samples were then allowed to cool to room temperature, re-weighed and stored at 5°C until testing.

5.2.2. Blend preparation

PLA was obtained from a commercial supplier in pellet-form. Solvent casting was used to prepare samples for DSC and FTIR measurements. 10% (weight) solutions of PLA and PRF in dioxane were prepared and blended to achieve mixtures of 10, 30, 50, 75% PLA content. The mixtures along with solutions were then transferred into aluminum pans in small amounts (10 – 15 g) and left at room temperature for the solvent to evaporate. Samples were then kept at 50°C in the oven for 48 hours for removal of the remainder of the solvent and completion of crystallization process. Material from each composition was also hot pressed into a sheet of 0.8mm thickness using a Carver press. A sufficient amount of material was placed between release paper and spacers were used to achieve the desired thickness. The material was then
pressed at 180°C for 5 min under an initial pressure of 50 Kg/cm². The sheets were then removed and allowed to cool to room temperature before cutting into test specimens.

5.2.3. DSC

Heat flow measurements were made with a TA DSC Q800 instrument. 10 mg of each blend prepared from solvent casting was placed and sealed in an aluminum pan and put through two scans. On the first scan the material was heated from 0 to 100°C at a rate of 15°C/min to collect the heat of fusion in melting of PLA and then rapidly cooled. A second scan was performed from -80 to 40°C to observe the T_g.

5.2.4. DMA

Thermo-mechanical properties of the blend samples were studied using a TA instruments DMA model Q800 using single cantilever mode (span 17.5 mm). Liquid nitrogen was used to run temperature scans from sub-ambient temperatures to study the influence blending exhibited on the specimen. Samples were prepared by cutting them to 8mm ×13 mm according to recommended test sample dimensions for single cantilever from the hot pressed sheets described earlier. Temperature ramps at a rate of 5°C/min were performed with a single frequency of 1Hz and a displacement of 10μm for all samples.
5.2.5. FTIR

Infrared spectra were recorded on a Thermo Nicolet Nexus 670 spectrometer (Nicolet, Thermo Scientific) spectrometer using an attenuated total reflectance (ATR) set up. 32 scans at a resolution of 4 cm\(^{-1}\) were used to obtain the signal. The sheets of neat PRF and its blends with PLA were prepared by melting and then quickly quenching to room temperature. A pointed pressure tip was used to hold the samples on a crystal plate of the Ge crystal.

5.2.6. Lap shear testing

Basswood (\textit{Tilia Americana}) veneers of thickness 0.8 mm were used to prepare the lap shear specimens which were cut to 22.8 cm \(\times\) 12.5 cm. Approximately 0.3g of each blend composition was placed on the designated bonding area of 6.45 cm\(^2\) of each sheet. The two sheets were then overlapped at the bonding area and placed in between two metal slabs covered with non stick paper and then pressed by heated platens of a Carver press at 180\(^\circ\)C for 3 min. Test samples were removed from the hot press and let cool to ambient temperature. Samples were kept at a conditioning room for 1 week prior to the tests. The shear strengths of the adhesive joints were determined by an Instron 22kip frame at a speed of moving clamps of 50 mm/min. Two spacers were placed at the clamping area on each side to make sure that the bond line is in line with the pulling direction. The loading was carried out up to of failure of the joint. The value of shear strength was calculated by dividing the maximum shear force by the bound area and the value were presented as the average of five measurements.
5.3. **Results and discussion**

5.3.1. **DSC**

Study of miscibility of binary blends of polymers is often carried out by the well known DSC method of analyzing the $T_g$ of the blends. If a blend shows a single $T_g$ intermediate between the two $T_g$s of the blend components the assumption is that the two blends are miscible. Two successive scans were recorded for the blends of this study in order to study both the amorphous and crystalline phases of the blend. The DSC heat flow curves of different PRF/PLA blend compositions obtained by solvent casting from the first scan are shown in Figure 5-1. DSC trace of pure PLA shows two major features. A heat jump representing a $T_g$ at 60°C and a melting peak at 153°C. Other compositions also show melting peaks that move towards lower temperatures as the ratio of PRF in the blend increases. PRF is previously shown to be completely amorphous\(^1\) and does not exhibit a $T_m$. Therefore the melting peak corresponds solely to the crystalline part of PLA. The shoulder appearing on the melting peak of the 25/75 blend can be indicative of a melt-recrystallization process that often is observed with semi-crystalline polymer materials and is attributed to the unstable crystalline region.\(^{21}\) While the double melting peak is not seen with the melting of pure PLA, its appearance once PFR is added demonstrates the effect of PRF addition to the behavior of PLA melt-crystallization. Such an effect is also reported by Jamshidian et al.\(^{22}\) where addition of synthetic antioxidant phenolics to PLLA caused the material’s double melting peak to become more pronounced.

Another feature observed on the heat flow traces of the blends is a heat jump that occurs at temperatures close to $T_g$ of pure PLA. The jump is more pronounced for the 70, 50 and 25 and
more subtle for the 90 PRF blends. The presence of this transition point in the blends suggests that phase separation is occurring to some extent and miscibility of the blends obtained from solvent casting is not complete. The traces from the second DSC run on the other hand reveal some important changes. As seen in Figure 5-2 the transition does not occur at the same temperature for the blends as before. Instead the blends show a single composition dependent Tg that shifts to lower temperatures as the PRF ratio increases. The change in thermal behavior indicates that the phase separation does not happen once the material is melted during the heating scan and the system becomes miscible. Similar behavior has been reported for blends of PLA with poly methylmethacrylate and polyvinylphenol and is attributed to the favorable solvent – polymer interactions that tend to exclude one phase from the growing domains during solvent evaporation and leave behind macroscopic phase separated domains. These domains are removes during the heating and melting of PLA.

The position of the peak of the melting curve also changes with composition. Tm of the crystalline component in a polymer blend depends on both morphological and thermodynamic factors. Since miscibility is not perfect before melting the Tm changes of the components should be attributed to the morphological aspects and dimensions of the crystalline lamellas rather than specific interactions between the components.
Figure 5-1 First scan DSC traces for PRF, PLA and their blends obtained by solvent casting

Figure 5-2 Heat flow curves showing the $T_g$s of PRF, PLA and PRF/PLA blends of different compositions obtained from second scan of DSC.
According to the Fox equation for a miscible polymer blend system\textsuperscript{23}:

\[
\frac{1}{T_g} = \frac{x_1}{T_{g1}} + \frac{x_2}{T_{g2}} \quad (4-1)
\]

where $T_g$ is the glass transition temperature of blend, $T_{g1}$ and $T_{g2}$ are those of the components.

Figure 5-3 depicts the experimental data points on a graph along with Fox equation plotted as a solid line.

\[
\%	ext{crystallinity} = 100 \times \frac{H_m}{H_fW} \quad (4-2)
\]
where $H_f$ is the enthalpy of fusion (as measured by integrating the melting peak area from DSC thermograms) and $H_m$ is the enthalpy of fusion per gram of a %100 crystalline PLA which is assumed 93.6 J/g. $W$ is the weight fraction of PLA due to amorphous nature of PRF. As represented by Table 5-1 PRF/PCL blends have different degrees of crystallinity depending on composition. In addition to $T_m$ and heat of fusion of the blend $H_f$, table shows the heat of fusion per PLA weight and $X_c$ of the PLA portion of the blend. The degree of crystallinity is lower for blend systems having higher PRF content. The depression of crystallinity is expected in miscible crystalline/amorphous polymer blends due to decreased segmental mobility of the crystalline polymer and as a result of the depressed melting point.25

<table>
<thead>
<tr>
<th>Blend</th>
<th>$T_m$</th>
<th>$H_f$ (J/g blend)</th>
<th>$H_f$ (J/g PLA)</th>
<th>$X_c$ (PLA)%</th>
</tr>
</thead>
<tbody>
<tr>
<td>90/10</td>
<td>153</td>
<td>2.4</td>
<td>24</td>
<td>25</td>
</tr>
<tr>
<td>70/30</td>
<td>138</td>
<td>8.1</td>
<td>27</td>
<td>29</td>
</tr>
<tr>
<td>50/50</td>
<td>135</td>
<td>15.5</td>
<td>31</td>
<td>33</td>
</tr>
<tr>
<td>25/75</td>
<td>133</td>
<td>23.4</td>
<td>31.2</td>
<td>33</td>
</tr>
<tr>
<td>0/100</td>
<td>130</td>
<td>35.7</td>
<td>35.7</td>
<td>38</td>
</tr>
</tbody>
</table>
5.3.2. DMA

Some thermal transitions can also be traced from the changes in mechanical properties of materials. The evaluation of the thermomechanical properties of the blend compositions are of interest due to their potential application as adhesives. Also such an analysis provides further validation for the results obtained earlier for PRF/PLA blends. Thermal analysis results discussed so far suggest the miscibility of the blends, due to the existence of a single \( T_g \) once the materials goes through a heating stage that results in the melting of PLA. DMA measures the rate and quality of changes to properties such as the storage \( (E') \) and loss modulus \( (E'') \). Figure 5-4 depicts how \( E' \) of different PRF/PLA blend compositions change during a temperature ramp from 0\( ^\circ \)C to 80\( ^\circ \)C. The heating range was chosen to observe changes in \( E' \) as the material goes through it \( T_g \). Results from a PRF sample could not be obtained as the sample would fail at sub ambient temperatures due to extreme brittleness. However it is obvious from the data recordings of Figure 5-4 that blends with higher percentage of PRF acquire higher \( E' \) at lower temperatures. The trend suggests that the PRF contributes to this higher \( E' \). Yet the higher modulus of PRF rich blends comes with loss of strength at lower temperatures. The higher modulus of PRF rich blends however comes with loss of strength at lower temperatures. The sharp decrease in \( E' \) can be associated with \( T_g \) of the blends. Dependence of the position of this transition on composition of the blends is in agreement with the results obtained from the DSC and hints toward miscibility of the blends and presence of interactions between PRF and PLA. Pure PLA demonstrates a constant value of \( E' \) throughout the ramp up to around 50\( ^\circ \)C when it starts to fall. The distinction of the \( T_g \) is more evident in the tan \( \delta \) curve in Figure 4b. The pure PLA curve has a peak at 58\( ^\circ \)C which is identical to the \( T_g \) recorded from the DSC. The other blends however exhibited peaks at...
temperatures higher than the previously recorded $T_g$'s of their corresponding DSC interpretation.

Nevertheless the trend of increase in $T_g$ with PLA content stays the same.
Figure 5-4 (a) Storage modulus $E'$ vs. temperature of blends of PRF/PCL from DMA temperature ramp. (b) Tan δ curves of DMA samples.
5.3.3. Shear strength

Mechanical strength is an important factor with performance of industrial polymers and adhesive materials. Application as a processible thermoplastic or as a hot melt adhesive would be very limited due to its poor mechanical strength. However, the use of blended PRF/PLA systems show a significant improvement in bonding performance. Lap shear testing is a very common method in evaluating the strength of adhesive materials. The average shear strength of PRF, PLA and their different blend compositions recorded from lap shear tests are presented in Figure 5-5. An interesting trend can be seen here. Adding PLA to PRF improves its strength at all blend compositions. Since the lap shear test is conducted using basswood as substrate, the results of the test are not only representative of the materials strength or internal cohesion but also reflect the quality of adhesion of the blends with the wood. Pure PLA samples show lower strength than some of the blend compositions. Inspection of the bonding area of shear specimens after the test reveals that the pure PLA specimens show minimum wood failure. In other words de-bonding happens at the interface due to poor adhesion between PLA and wood. PRF seems to have good adhesion with the substrate but its own poor mechanical strength causes fracture through the centerline. The 50/50 PRF/PLA blend seems to provide the optimum balance between adhesive to substrate bonding and cohesion of the resin adhesive. Miscibility and interactions present between PRF and PLA improves its mechanical strength and provides cohesion and PRF provides good bonding with wood. At this level adhesive becomes stronger than the substrate and we witness 100% wood failure.
5.3.4. FTIR spectroscopy

The results obtained so far from thermal and mechanical properties of the blends of PRF/PLA are all indicative of miscibility of the two components which is a result of existence of interactions among them. However more evidence should be obtained to support such a claim. FTIR spectroscopy is a powerful tool to investigate chemical structures and has been widely used for studying specific interactions in polymers. The chemical structure of the PRF and PLA supports the possibility of formation of specific interactions, namely hydrogen bonding. The chemical groups involved in hydrogen bonding of these blends are the hydroxyl group of the
PRF and the carbonyl group of the PLA. As a result their two absorption band regions are of more importance in this study. It was noticed during collection of DSC results that the PRF/PLA blends obtained from solvent casting demonstrated signs of phase separation during the first heating scan. To investigate films of different blend ratios of PRF/PLA from solvent casting were analyzed through FTIR. Figure 5-6 shows the carbonyl spectral region of our blend systems. The absorption band at 1754 cm$^{-1}$ corresponds to the strong C=O stretching of PLA.$^{26}$ Spectra of the neat PRF exhibits a broad peak at 1710 cm$^{-1}$. This absorption band is commonly seen in the spectra of the pyrolytic lignin and is assigned to the carbonyl groups that are present in small amounts.$^{27}$ The same broad peak can also be observed at the same wavelength in the spectra of 90/10 and 75/25 blends. On the other hand the 25/75 blend sample shares the 1754 cm$^{-1}$ band with the pure PLA and the 50/50 sample demonstrates both peaks, one at 1754 cm$^{-1}$ and the 1710 cm$^{-1}$. Notice that position of these two peaks remains constant for all compositions and is marked in Figure 5-6 with two straight lines. No appreciable change in the position of these peak in the IR spectrum indicates that the interactions between the two components are negligible. Therefore immiscibility of these blends are once again demonstrated as previously discussed with the DSC results. The FTIR peaks stem from separate PRF and PLA phase domains left behind after solvent evaporation.
We now shift our attention to the hydroxyl spectral region of these solvent casted blends shown in Figure 5-7. Broad bands in the region between 3200 to 3600 cm\(^{-1}\) are characteristic of strong hydrogen bonded hydroxyl groups.\(^28\) Free hydroxyl groups have sharp peaks at higher frequencies. The band centered at 3390 cm\(^{-1}\) in the spectrum of pure PRF can mainly be assigned to the hydrogen bonded and free hydroxyl groups as both groups are deemed to be present in the PRF but distinct peaks associated to each one cannot be observed. Pure PLA does not show any features in this region. Yet again the position of the hydroxyl band peak does not change in different compositions indicating lack of interactions among the two components.

**Figure 5-6 Carbonyl stretching region of PRF/PLA blends of different compositions obtained from solvent casting**
Figure 5-7 Hydroxyl stretching region for PRF/PLA blends of different compositions obtained from solvent casting

FTIR spectra changes completely at the carbonyl stretching region for the blends undergone melting shown in Figure 5-8. It can be seen that PLA and PRF still acquire their respective absorption band peaks at 1754 cm\(^{-1}\) and 1710 cm\(^{-1}\). However there is a big shift on the position of the peaks for 75/25 and the 50/50 blend both to 1725 cm\(^{-1}\). Two broad peaks can be located on the spectra of 90/10 and 70/30 possibly corresponding to contributions from carbonyl stretching of PLA and PRF. The change in spectra after the heat treatment of the blends indicates that interactions are now present in the system.
Figure 5-8 Carbonyl stretching region of melt quenched PRF/PLA blends of different compositions

Figure 5-9 shows the hydroxyl spectral region of PRF/PLA blends that went through a melting step and there appears to be a shifting toward higher of the peaks associated to hydroxyl groups. As the position of the free hydroxyl band is not apparent, one can assume that the shift is due to the change in association of hydrogen bonded hydroxyls. This may indicate that the inter-association or hydroxyl-hydroxyl band is being replaced by hydroxyl-carbonyl band that is generated from the newly formed hydrogen bands between the two components.
Figure 5-9 Hydroxyl stretching region for melt quenched PRF/PLA blends of different compositions

Figure 5-10 better depicts the relationship between the position of the peak on the carbonyl stretching region and hydroxyl stretching region with composition of the blends that were heated to melt. As PLA portion increases the position of both peaks move to higher frequencies and the trend is somewhat similar between the O-H and the C=O.
Figure 5-10 Relationship of PRF/PLA composition with position of stretching bands from melt quenched samples

5.4. Conclusions

Binary blends of PRF and PLA were obtained by casting from dioxane solvent. Signs of phase separation were observed during the first DSC run as all the blends still demonstrated a transition around $T_g$ of PLA. Nevertheless all blends showed complete miscibility after going through melting step. The miscibility was determined by a single composition dependent $T_g$ recorded on DSC. Crystallinity of the blends also is influenced by composition as more PRF portions reduced the crystallinity of the PLA. This cannot be attributed to interactions between the components as the casted films are immiscible, and morphological aspects should be responsible. Thermomechanical analysis also demonstrates the change in $T_g$ of the blends depending on their
composition. Properties of the blends obtained by DMA of hot pressed samples, shows that high PRF content blends acquire increased storage moduli at lower temperatures but they rapidly lose their stiffness as temperature rises due to their lower T_g s. Addition of PLA increases the T_g and extends the strength regions of the blends to higher temperatures. Lap shear test reveals significant improvement in PRF strength due to PLA addition. PRF provided adequate adhesion to wooden surface while PLA’s adhesion to the surface was poor. However, improved shear strength values were recorded for 50/50 and 75/25 blends that provided optimum balance of cohesion and adhesion. FTIR spectroscopy confirmed the immiscibility of the cast films as no considerable interactions were detected due to unchanged spectra. In contrast the melted samples showed signs of hydrogen bonding between the PRF hydroxyl and PLA carbonyl groups.

Miscibility of the two components provided after heating is well desired and suitable for applications such as hot melt adhesion that bio based thermoplastics such as PLA are considered for and the compatibility of PRF with surfaces such as wood serves as an improvement to adhesion properties.
5.5. References


CHAPTER 6. Conclusions and further research

6.1. Conclusions

6.1.1. Thermoplasticity and rheology of PRF

Heat treatment was shown in this study to have a systematic effect on the physical properties of the PRF. The initially liquid PRF was transformed into an apparent paste or a solid based on the temperature of the heat treatment. TGA shows that different fractions of volatile materials evaporate at each treatment temperature and the materials weight becomes constant after approximately 10h of heat treatment. Storage modulus increases by each heating cycle as shown by DMA results and there is a softening transition point which is dependent on the temperature of the heat treatment which is also verified by cone and plate rheology. T_g of the PRF is also shifting to higher values as a result of the heat treatment. All heat treated PRFs show a dominant viscous behavior. The unheated PRF goes through a transition from viscous to elastic at higher frequencies.

It was proposed that this thermo sensitive behavior result from the colloidal structure of the PRF with the lignin oligomers present as nano particles in a continuous phase of lights and volatiles. When heat treated lignin nano particles associate with hydrogen bonds forming in between while the volatiles leave the system. These hydrogen bonds are thermally reversible so at higher temperatures the bonds break and the particles or the lignin oligomers can move more freely and the material flows.
The thermo sensitive characteristic and ease of flow of PRF paired with low viscosity at higher temperatures makes it a good candidate for use in melt processing and manufacturing techniques that involve processes such as extrusion or injection molding in its neat form or with addition of fillers for improved properties. The softening point and other physical properties can be controlled and adjusted by applying the appropriate heat treatment regimen.

6.1.2. Properties of blends of PRF and biodegradable polyesters

6.1.2.1. PFR/PCL blends

Investigation of properties of blends of PRF and PCL prepared from solution casting and melt blending showed that these two components are capable of forming blends with high levels of miscibility. The miscibility is evident from existence of a single composition dependent \( T_g \) that is measured from DSC traces and DMA data. There is also changes to melting temperature and crystallinity of the PCL which is present in the blends with different compositions. The PRF retains its softening temperature and it is shown that PCL content does not affect the temperature at which this transition occurs. The miscibility of the blends results in improvement in the mechanical properties of the blends as measured by standard lap shear tests. Neat PRF proves to be weak and brittle but blending with PCL even in small amounts improves the shear strength significantly. Miscibility of the two components is believed to be the result of existence of specific interactions in the form of hydrogen bonds between the carbonyl group of the PCL and hydroxyl group of PRF. FTIR spectroscopy provided further evidence of such interactions with clear shifting of the peaks on the spectra in the carbonyl and hydroxyl stretching regions.
6.1.2.2. **PRF/PLA blends**

Blends of PLA and PRF where prepared by method of solution casting. The same analytical techniques used before was also used for investigation of miscibility and properties of the PLA blends, including DSC and DMA. First DSC scan hints toward possible phase separation and immiscibility of the blends. Second scan shows a single composition dependant Tg showing that the blends have become miscible after melting. The phase separation in solution casted samples can be attributed to the solvent effect when it is evaporated leaving behind domains of PLA and PRF, which will then move and mix at melting. FTIR spectroscopy further proved the solution casted samples to be immiscible as no interactions could be traced from the spectra. However the melted samples demonstrated shifts in the position of peaks on both hydroxyl and carbonyl stretching regions.

The shear strength results of PRF/PLA blends were not following the same trend as for the PRF/PCL blends. The difference stems from surface compatibility and adhesion of these two polymers with wood. PCL demonstrated good bonding with the wooden substrate while PLA adhesion was weak. The dissimilarity was reflected in shear results with PRF/PLA blends reaching optimum strengths at the 50:50 ratio while in the case of PCL there was a constant improvement towards higher ratio of PCL in the blend.

6.1.2.3. **PRF/Polyester blends (physical model)**

The observed properties and thermal transformations of blends investigated in this study can be summarized in a physical model based on the structure of the PRF and the biodegradable polyesters PLA and PCL. PLA and PCL are long chain polymers with high molecular weights while PRF is comprised of oligomers of lignin in particle form. The particles are able to form
reversible hydrogen bonds with the carbonyl sites on the polymer chains. This model is represented schematically in Figure 6-1. These bonds are then broken when heated and the material is brought to flow.

Figure 6-1 Schematic representation of a physical model illustrating the PRF and polyester blend structure.

6.2. Future research

6.2.1. Investigation of rheological properties at low strains

The results from cone and plate rheology in this study showed a dominant viscous behavior for all heat treated PRFs. The formation of hydrogen bonds among lignin particles in PRF is
expected to result in a material that behaves like a gel. The gel properties cannot be observed with rheometer under higher strain rates as it causes breakage of the bonds. Performing very low strain measurements of rheological properties for the PRF and blends with PLA and PCL and comparison of the results will help verify the proposed model and the role of intermolecular hydrogen bonding.

6.2.2. Modeling the viscosity

Preliminary results show that there is a systematic decrease in the viscosity of PRFs vs. temperature. To describe the effect of temperature on viscosity of polymer melts, several models can be used. The dynamic viscosity of PRF will be measured in a range of temperatures above the glass transition by the means of temperature controlled rheometer. The experimental results would be discussed in terms of the classical WLF (Williams-Landel-Ferry) and Arrhenius models. The model which provides the best data fit will be identified.

6.2.3. Using scattering techniques to verify the role of lignin nano particles

X-ray scattering is a technique widely used to study the structure of crystalline solids. Non crystalline solids and materials with no long range order can also be studied with this technique using methods of elastic scattering of monochromatic x-rays. Among these methods is the small angle Neutron scattering. Small-angle scattering (SAS) is a powerful technique for investigating large-scale structures from 10 Å up to thousands and even several tens of thousands of angstroms. The most important feature of the SAS method is its potential for analyzing the inner structure of disordered systems. SANS will help with the task of determination of structure and
presence of any possible short/long rang order in the structure of the PRFs in the solid and liquid state and will possibly clarify the role of nano lignin particles in the solidification and flow of the PRFs.

6.2.4. Further study of mechanical properties

In this study limited investigation of mechanical properties was performed through lap shear testing. Lap shear test is a commonly used method for characterization of strength of hot melt adhesives. Other mechanical properties are of interest if the PRF blends are to be considered for applications such as melt processed materials. PRF and its blends are to be tested for tensile and bending strength. The tensile test allows the measurement of percentage elongation and strain at break and provides a quantitative assessment of brittleness and deformability of the materials.