Mississippi State University

Scholars Junction

5-2-2009

An investigation of using pyrolysis bio-oil as part of the binder system for wood-based composites

An Mao

Follow this and additional works at: https://scholarsjunction.msstate.edu/td

Recommended Citation

Mao, An, "An investigation of using pyrolysis bio-oil as part of the binder system for wood-based composites" (2009). *Theses and Dissertations*. 604.
https://scholarsjunction.msstate.edu/td/604

AN INVESTIGATION OF USING PYROLYSIS BIO-OIL AS PART OF THE BINDER

SYSTEM FOR WOOD-BASED COMPOSITES

By

An Mao

AN INVESTIGATION OF USING PYROLYSIS BIO-OIL AS PART OF THE BINDER

SYSTEM FOR WOOD-BASED COMPOSITES

By

An Mao

Approved:

_____   _____
Sheldon Q. Shi   Moon G. Kim
Assistant professor of Forest Products   Professor of Forest Products
(Major Advisor)   (Co-advisor)

_____   _____
Philip H. Steele   Leonard L. Ingram Jr.
Professor of Forest Products   Professor of Forest Products
(Committee Member)   (Committee Member)

_____   _____
Rubin Shmulsky   George M. Hopper
Professor of Forest Products   Dean of the College of Forest Resources
Graduate Coordinator of the Department
of Forest Products

Name: An Mao

Date of Degree: May 2, 2009

Institution: Mississippi State University

Major Field: Forest Products

Major Professor: Dr. Sheldon Q. Shi, Dr. Moon Kim

Title of Study: AN INVESTIGATION OF USING PYROLYSIS BIO-OIL AS PART OF THE BINDER SYSTEM FOR WOOD-BASED COMPOSITES

Pages in Study: 59

Candidate for Degree of Master of Science

The objective of this research was to investigate the feasibility of using the pyrolysis bio-oil as part of a binder system for wood-based composites. Liquid products obtained from pyrolysis process of pine wood were mixed with reactants, such as isocyanate. The adhesive binder system was blended with flakes to fabricate flakeboard. The effect of the resin content and the mix ratio of the adhesive on the physical and mechanical properties of the flakeboard were examined. Dynamic mechanical analysis (DMA) was also employed to investigate the thermal properties of the adhesives. The results indicated that a bio-oil content of 25% showed comparable properties to those produced by pure pMDI adhesive. A good correlation between the DMA results and the mechanical properties of the flakeboard was also obtained. The increase of bio-oil content in the adhesive system improved the curing speed but reduced the adhesive stiffness.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

Historically, wood was only used in its solid form as lumber or timber. As the availability of large-diameter trees decreased and their prices increased, the wood industry began to look for new products which led to the invention of wood composite products. Adhesive is a critical component of any wood composite product and it is always the most expensive component. Therefore, research on the wood adhesives has been very active since the composite products were first introduced.

Flake/strand-based wood composites

Flake/strand-based wood composites, such as oriented strand board (OSB) are made from thin, rectangular-shaped wood flakes/strands bonded with fully waterproof adhesives. In this thesis, the term "flakeboard" is used to describe the product made from wood flakes randomly oriented in the board. In the flakeboard fabrication, a small amount of wax is added to help prevent the moisture absorption into the board during brief periods of wetting. Flake/strand-based product was introduced to the construction industry in the later 1950s in the United States and Canada (Laufenberg 1984). The OSB was first produced in Canada in 1960s. It was not until 1982 that the first true OSB mill was constructed (Green and Hernandez 1998). OSB's superior performance

1

has allowed it to become popular in a wide range of applications such as wall sheathing, floor underlayment, roof sheathing, and I-joist web in both commercial and residential building construction. OSB is also used in furniture, reels, trailer liners, and recreational vehicle floors. The number of flakeboard mills increased by more than 50% from 1990 to 1997. Currently the total OSB production in North America is approximately 706 million ft^3 and there are approximately 20 companies who manufacture OSB in the United States, Canada, and Europe (Hiziroglu 2007). Because of the limited supply of large-diameter logs resulting in a decline in plywood production, the production of OSB should continue to increase in the future.

Phenol Formaldehyde (PF)

PF resin is one of the most popular adhesives in the manufacture of flakeboard. It is also the earliest commercial synthetic resin (Baekeland 1909). PF is able to form hydrogen bonds and mechanical inter-locking with wood (Schmidt 1998) and thus provide good bonding with wood components. PF is a thermoset polymer, which can be formed from an elimination reaction of phenol with formaldehyde. Phenol is reactive with formaldehyde at the ortho and para sites which allow up to 3 units of formaldehyde to attach to the phenol ring. This forms a hydroxymethyl phenol. The hydroxymethyl group is capable of reacting with either another free ortho or para site, or with another hydroxymethyl group. The first reaction forms a methylene bridge, and the second forms an ether bridge. The liquid PF is an alkaline water-based solution of low molecular weight PF chains. During the blending operations, it is sprayed onto dried flakes. When heated, the cross linked structure is formed by a step-growth

polymerization reaction in the presence of acid or base catalysts.   PF resin can also be applied in a powder form, which may allow a better control of the mat moisture content. Compared with powdered PF, the liquid PF is lower cost, greater ease of handling and application, and better flake coverage at normal loadings.   Although there are many advantages for PF adhesives, they are known to need prolonged press time and have higher thickness swelling compared with isocyanate adhesives (Miller 2002).

Polymeric diphenylmethane diisocyanate (pMDI)

PMDI is also a popular adhesive for flakeboard/OSB.   It is a cross-linking and nonpolar thermoset.   PMDI resins were developed during World War II and quickly became known as adhesives that can bond ''anything to anything'' (Marra 1992).   Since they were first introduced to the German particleboard market in early 1970s, the use of isocyanate binders in composite boards has grown significantly.   With worldwide production in excess of 1,500,000 tons annually, pMDI binders are now used in over 20 percent of the OSB industry worldwide and are in routine production in medium density fiberboard (MDF) mills in Europe and North America (Papadopoulos et al. 2002).   MDI is a complex mixture of the isomers of di-, tri-isocyanates and higher polymeric aromatic species derived from side reactions and are generally sold as pMDI (polymeric MDI) and EMDI, an emulsion of pMDI in water.

The pMDI adhesive exhibits some enhanced performance characteristics compared to PF resin, such as higher bonding strength, increased water repellency, and no formaldehyde emission.   However, it is more expensive than PF (Gagnon et al. 2003).

3

In addition, the high reactivity pMDI may lead to some problems such as adhesion to press platens.

Adhesive binder systems

Blending pMDI with a low cost material such as amine-based resin or other polymers is attractive from an economic standpoint.   This is even more attractive if reasonable adhesive properties of the so-obtained adhesive can be obtained.   PMDI has been blended with PF, UF and MF resins to form pMDI binder systems (Pizzi 1995; Enomoto et al. 2000; Weihong et al. 2004).   The isocyanate group (-NCO) can react rapidly with the methylol group (-CH$_2$OH) presented in PF, MF and UF resins (Pizzi 1995).   Some studies were conducted on PF/bio-oil binder systems (Himmelblau and Grozdits 1998; Roy et al. 1999; Chan et al. 2002; Amen-Chen et al. 2002), based on the fact that the phenolic groups contained in the bio-oil are able to replace a portion of the phenol in the phenol-formaldehyde co-reaction.   It was also reported that tannins (Pizzi et al. 1995), lignin (Newman and Glasser 1985), and furfural (Leitheiser and Johns 1983) could be mixed with pMDI resin to form a binder system.   However, these studies did not give satisfactory adhesive properties and resulted in increased difficulties of handling and application.

Pyrolysis bio-oil

The liquid product from biomass pyrolysis is known as fast pyrolysis oil or bio-oil. Pyrolysis is the degradation of biomass by heat in the absence of oxygen, which results in the production of charcoal, liquid, and gaseous products.   For the wood materials, the

hemicelluloses break down first at temperatures of 470 to 530 K.   The cellulose follows in the temperature from 510 to 620 K.   Lignin is the last component to pyrolyze at temperatures of 550 to 770 K (Demirbas and Arin 2002).   Bio-oil is produced with short reaction times and rapid cooling or quenching from the pyrolysis temperatures, which produces a condensate that is not at thermodynamic equilibrium during storage.

Bio-oils are multi-component mixtures of different size molecules derived from depolymerization and fragmentation of cellulose, hemicellulose and lignin, which are not related to the elemental composition of bio-oil and petroleum derived products.   The 99.7% of bio-oil, a complex mixture containing carbon, hydrogen and oxygen, is composed of water, acids, alcohols, aldehydes, esters, ketones, sugars, phenols, guaiacols, syringols, furans, lignin derived phenols and extractible terpene with the multi-functional groups (Guo et al. 2001).   Depending on the biomass feedstock and pyrolytic processes, the viscosities of bio-oils vary in a large range.

Bio-oil has a water content of as high as 15-30 wt% derived from the original moisture in the feedstock and the product of dehydration during the pyrolysis reaction and storage.   The oxygen content of bio-oils is usually 35-40% (Oasmaa and Czernik 1999; Scholze and Meier 2001), distributed in more than 300 compounds depending on the biomass feedstock type and severity of the pyrolytic processes (temperature, residence time and heating rate).   The high oxygen content leads to a lower energy density than the conventional fuel by 50%.   Bio-oil is also immiscible with hydrocarbon fuels.

Gagnon et al. (2004) conducted research mixing the pMDI with bio-oil to produce a new adhesive binder system.   This binder system is expected to improve the adhesive

properties and the hydrocarbons from the bio-oil may act as a self-releasing agent which may reduce the platen adhesion problems.

Dynamic mechanical analysis (DMA)

Dynamic mechanical properties of a material refer to the response of a material when it is subjected to a periodic force. These properties may be expressed in three terms: dynamic storage modulus, dynamic loss modulus, and the mechanical damping term.

The applied mechanical load elicits a corresponding strain (deformation) whose amplitude and phase shift can be determined. The mode of deformation governs whether the complex modulus is E*. The complex modulus E* is the ratio of the stress amplitude to the strain amplitude representing the stiffness of the material. The magnitude of the complex modulus is:

$$|E^*| = \frac{\sigma A}{\varepsilon A}$$

The complex modulus is composed of the storage modulus E' and the loss modulus E'', as shown in Table 1.1. They are dynamic elastic characteristics and are material-specific; their magnitude depends critically on the frequency, the measuring conditions and history of the specimen.

In the linear-viscoelastic range, the stress response has the same frequency ($\omega=2\pi f$) as the deformation input excitation. The analytical parameters in dynamic tests are: amplitudes of the deformation and the stress, time displacement δ/ω between the deformation and stress.

Table 1.1   Formulas for calculating the complex modulus E*, storage modulus E', loss
            modulus E'' and loss factor tanδ

$$|E^*| = \sigma_A/\epsilon_A$$
$$E'(\omega) = |E^*| \cdot \cos\delta$$
$$E''(\omega) = |E^*| \cdot \sin\delta$$
$$\tan\delta = E''(\omega)/E'(\omega)$$

The storage modulus E' represents the stiffness of a viscoelastic material.   It is proportional to the energy stored during a loading cycle.   It is roughly equal to the elastic modulus for a single, rapid stress at low load and reversible deformation.

Loss modulus E'' is defined as being proportional to the energy dissipated during one loading cycle.   It represents the energy lost as heat, and is a measure of vibration energy that has been converted during the vibration which cannot be recovered.

Phase angle δ is the phase difference between the dynamic stress and the dynamic strain in a viscoelastic material subjected to a sinusoidal oscillation.   The phase angle is expressed in radians (rad).

Loss factor tanδ is the ratio of loss modulus to storage modulus.   A high tanδ indicates a material with high nonelastic strain component.   While a low value indicates one that is more elastic.   Thus, the dynamic properties provide information at the molecular level leading to an understanding of the polymer mechanical behavior.

Investigation on dynamic mechanical properties of resins by DMA

DMA has been widely used for studying thermosetting wood-adhesive cure (Steiner and Warren 1981; Myers et al. 1991; Christiansen et al. 1993; Follensbee et al. 1993; Kuzak and Shanmugam 1999). Because it can directly reveal the mechanical response of adhesives under the controlled cure conditions, DMA has been extensively utilized to compare wood adhesive curing rates, to study the effects of additives on the resin cure behavior and thermal stability, and to help find optimal hot pressing parameters. Kim et al. (1991, 1996) used DMA to study the cure behavior of PF resins formed from various synthesis parameters and under several conditions to investigate the effect of proportion of urea on cure behavior of PF resin. Geimer and Christiansen (1991) applied DMA to investigate the curing behavior of PF resin in special environments, such as steam injection pressing (SIP).

In some studies, DMA was combined with other analysis methods to investigate the relationship between microscopic molecular structure and macroscopic mechanical properties of a material. These methods include solid-state nuclear magnetic resonance spectroscopy (NMR) (Marcinko et al. 1998), inversion recovery cross polarization measurement (IRCP) (Marcinko et al. 1999), and fourier transform infrared spectroscopy (FT-IR) (Ling et al. 2008).

DMA analysis was also used for investigating the thermal stability of cured adhesives. In a study on thermal behavior of wood adhesives (Umemura et al. 1996), four types of wood adhesive (UF, MF, PF, and isocyanate) were heated under high stream pressure and conventional hot-platen environment, followed by the DMA test. The two heating methods were compared and the characteristics of each type of adhesive were

8

found.   Umemura et al. (1998, 1999) employed DMA to study the thermal stability of isocyanate resin cured with water and with several kinds of polyols.   It was found that the emulsion-type pMDI cured with water exhibited a lower thermal stability than the PF resole.   The pMDI resin when cured with only water showed a dramatic decrease in storage modulus near 200°C (Umemura et al. 1998).   However, its thermal stability was shown to be dramatically improved by the addition of dipropylene glycol-type polyols with molecular weights between 400 and 1000 (Umemura et al. 1999).

Objectives

(1). To investigate the physical and mechanical properties of flakeboard with pyrolysis bio-oil as part of a pMDI binder system.

(2). To analyze the effects of pyrolysis bio-oil on the curing behavior of a pMDI binder system.

CHAPTER II

MECHANICAL PROPERTIES OF FLAKEBOARD BONDED WITH PMDI/BIO-OIL

ADHESIVE SYSTEMS

Introduction

Flakeboard is an engineered, mat-formed panel product made of wood strands or flakes and bonded with waterproof adhesives under heat and pressure conditions. Over the last two decades, wood-based panel market has experienced a tremendous growth (Zhu et al. 1998). Polymeric diphenylmethane diisocyanate (pMDI) is one of the primary adhesives used to make flakeboard. Some advantages associated with pMDI adhesive include greater tolerance for higher moisture content wood, lower press temperatures, shorter press cycles, energy savings, lower resin application ratio, and higher productivity. Potential disadvantages mainly include: the adhesion to press platen problem and high cost.

To address these issues, efforts have been made to mix pMDI with other adhesives such as urea formaldehyde adhesive (UF), melamine formaldehyde (MF), and phenol formaldehyde adhesive (PF) (Deppe 1977; Tinkelenberg et al. 1982; Pizzi and Walton 1992; Hao and Liu 1993a 1993b; Pizzi 1995; Grigoriou 2000; Frick and Motter 2001; Simon et al. 2002).

UF resin is one of the most commonly used adhesives for indoor applications. It is inexpensive and has high bonding strength with wood. However, it is not resistant to water and has the concern of formaldehyde emission (Myers 1984). It has been found that to have copolymerization with pMDI in water in the absence of UF hardeners with a long curing time, the predominant reaction is the UF methylol group ($-CH_2OH$) with the isocyanate group to form urethane bridges (Despres et al. 2006; S. Wieland et al. 2006), other reactions can only be observed in the absence of water (Shadurka et al. 2003). When the resin is cured, urethane bridges, methylene bridges, as well as the polyureas are all covalently linked in the same network (Despres et al. 2006; Wieland et al. 2006). Moreover, in the presence of water and a UF hardener, co-reaction still occurs between the isocyanate groups and UF resins methylol groups to form a urethane crosslink, which are thought to improve the bonding strength between UF and pMDI (Wieland et al. 2006).

In the 1980s, Pizzi (1983) found that when pMDI and amino-resin were sprayed on flakes separately, the internal bond (IB) of both dry and wet boards were similar to its original strength. However, when the two adhesives were mixed first and then sprayed, the board's IB was reduced to only 30%–50% of its original strength. Pizzi (1993) also developed a UF-pMDI binder system for plywood by adding pMDI to UF resin, followed by mixing and adding other components, such as NH_4Cl, a commonly used UF hardener. Hao and Liu (1993) found that spraying the emulsified (EMDI)-UF mixture without adding NH_4Cl gave a better result than that with adding a hardener.

Simon et al. (2002) investigated the copolymerization between the UF and pMDI, and found that the co-reaction between the UF and pMDI can improve the bonding

11

strength by forming methylene cross-links instead of the urethane bridges which are a small proportion of the crosslinking reactions. This reaction occurred in the presence of water and hardener. If the hardener was not used, less co-reaction occurred. The water introduced into the UF-pMDI mixture by addition of UF resin showed no reaction with the pMDI.

Research work on PF-pMDI binder systems has also been conducted for wood composites. PF can form hydrogen bonds and mechanical interlocking with wood (Schmidt 1998). Some studies (Rosthauser and Schmelzer 2001; Rosthauser and Detlefsen 2001; Preechatiwong et al. 2007) focused on the physical combination of the two adhesives. However, because of the much difference in polarity and incompatible chemical functional groups between the two adhesives, the mixture was not uniform. Some researchers replaced pMDI with an emulsified pMDI (Wang 2004). However, this replacement did not provide a combination of suitable storage life and performance (Miller et al. 2002). Miller et al. (2002) conducted a study to acylate the PF resin. The esterfication of the phenolic oxygen greatly reduced the reactivity of the PF portion in the mixture when combined with the pMDI to form a single phase liquid material with a storage life of more than 2 weeks at the room temperature. A patent was issued on a solid PF and pMDI binder system (Rosthauser and Detlefsen 2001). Solid PF powders were directly added into the pMDI to form a suspension system which has a relatively high viscosity. The solid PF-pMDI system was reported to be much more stable than the liquid resole-pMDI binder system (Lim and Chiu 1993). It also provided much higher IB for the particleboard than the sequentially applied solid resole and pMDI binder systems.

Tannins (Pizzi et al. 1995), lignin (Newman and Glasser 1985), natural oils and furfural (Leitheiser and Johns 1983) have also been mixed with pMDI resin to form a binder system.

Pyrolysis bio-oil comes from the renewable biomass sources. Currently, it is used both as an energy source and a feedstock for chemical production (Mohan 2006). Bio-oil can possibly be a suitable component in pMDI/bio-oil binder system for OSB or particleboard because at least 80% of the chemicals in the bio-oil (sugars, carboxylic acids, phenols, alcohols, water, tannin/lignin derivatives) are expected to react with pMDI (Gagnon et al. 2003). Bio-oil is a multi-component mixture of different size molecules derived from depolymerization and fragmentation of cellulose, hemicellulose and lignin. Over 99% of bio-oil is composed of water, acids, alcohols, aldehydes, esters, ketones, sugars, phenols, guaiacols, syringols, furans, lignin derived phenols and extractible terpene with multi-functional groups. Studies have been conducted replacing part of phenol with bio-oil to produce bio-oil/PF adhesive (Chum et al. 1989; Himmelblau and Grozdits 1998; Roy et al. 1999; Chan et al. 2002; Amen-Chen et al. 2002). Results showed that the bio-oil was able to participate in the phenol/formaldehyde reaction. However, the properties of these adhesives were not satisfactory. Recently, research on a pMDI /bio-oil binder system was reported (Gagnon et al. 2004). The binder system was derived from softwood bark bio-oil and pMDI. The bio-oil produced by the pyrolysis process was to replace about 30-40% by weight of the pMDI in a 4% adhesive-containing particleboard. Results showed that mechanical properties and thickness swelling of homogeneous boards exceeded the minimum requirements in ANSI A208.1-1993 and ASTM 1037-96a standards. The study indicated that the bio-oil could

be mixed at a percentage of as high as 40% with pMDI and gave acceptable interior grade particleboard properties. It was also shown that bio-oil can effectively solve the issue of bonding to press platen.

The objective of this research is to investigate the feasibility of using the pyrolysis bio-oil as part of the pMDI/bio-oil binder system for wood-based composites.

Experimental

Materials

Wood flakes were obtained from Norbord (Guntown, MS). The original moisture content of the flakes was 15%-18%. Flakes were dried in an oven (BLUE M Electrical Company, Blue Island, IL, USA) to obtain a moisture content of 4%. The moisture content was measured by a moisture balance (CSC Scientific Company, Fairfax, VA, USA).

Bio-oil was produced from the pyrolysis of pine wood in the Mississippi State University (MSU) auger reactor. Pine wood particles were pyrolyzed at 450 ^{o}C with a retention time of approximately 2 seconds. The crude bio-oil was filtered to remove biomass residuals including charcoal, and stored at 4 ^{o}C in a refrigerator. Water content of the bio-oil was 18%, and viscosity was 368 mPa·s at 25 ^{o}C.

PMDI (LUPRANATE M20FB) was provided by BASF The Chemical Company (Wyandotte, MI). It was a dark yellow liquid with viscosity of 226 mPa·s at 25 ^{o}C. The pMDI resin was stored at 25 ± 3 °C in a sealed container under a relative humidity 60 ± 5%.

14

Pyrolysis bio-oil was mixed with pMDI at various mixing ratios (Table 2.1). Bio-oil was first weighed and then poured into a beaker. Acetone was added into the bio-oil, and the mixture was stirred by hand to make it uniform. The purpose of adding acetone was to decrease the viscosity of the adhesive system. The bio-oil-acetone mixture was poured into another beaker which contained pMDI. After about 8 minutes, the mixed adhesives began to generate bubbles and thick foam appeared on top of the resin. The bubbles were attributed to the generation of CO_2, which resulted from isocyanate-water or isocyanate-carboxylic acid reaction. Foam seemed to rapidly appear in the presence of air. If the mixture was performed at a lower temperature, the reaction was slower and the foaming reaction was delayed. For quick reaction between pMDI and bio-oil, after it was formed, the adhesive binder system was blended and sprayed on the wood flakes within 8 minutes.

Methods

Flakes were first placed into a blender. Wax and the mixed adhesives were pumped through plastic tubes separately and sprayed onto the flakes with an atomizer. After about 5 minutes for the blending, flakes were removed from the blender and weighed. Before the flakes were randomly placed on the platen by hand to form a 60 cm × 60 cm mat, a "No Stick Cooking Spray" obtained from a local store was sprayed onto the platen to prevent adhesion of the panel to platen.

The mat was loaded into a 90 cm × 90 cm Dieffenbacher hot press, pressed for 5 minutes at a pressure of 10 MPa at 200°C. The press closing time was 0.5 minute for all the boards. The manufactured boards were then cooled, cut into small samples and

conditioned prior to testing.   The design of experimental boards is shown in Table 2.1.

A total of 15 board types were fabricated (two replicates for each board type) including

the 4 control boards.   There were a total of 26 boards.

Table 2.1   Experiment design and board manufacture parameters

MDI/ bio-oil/ acetone ratio	100/0/0, 100/0/2.5, 75/25/2.5, 50/50/5, 25/75/7.5
Resin content	3%, 5%, 7% (based on oven-dry flake weight)
Board construction	One uniform layer, random orientation
Board dimension	60 (L)×60 (W)×1.1 (T) cm
MC of flakes	4%
Water content of bio-oil	18%
Water content of wax	50%
Wax content	1% (based on oven-dry flake weight)
Solvent	Acetone
Solvent content	10% (based on bio-oil solid weight)
Replicates	2
Total boards	30

The IB, modulus of rupture (MOR), modulus of elasticity (MOE), density, and

thickness swell (TS) of the flakeboard were evaluated according to the American

Standard Test Methods (ASTM) D1037-06a.   The boards were conditioned at 20±3 $^{\circ}$C

and 65±5% relative humidity (RH) for 7 days before testing.

Three-point bending tests were conducted on the flakeboard.   Three samples

(33.0 cm × 7.6 cm ×1.1 cm) were cut from each board to produce a total of six samples

for each board type.   Before testing, the length, width, thickness, and weight of each

specimen were measured.   For the three-point bending test, an INSTRON testing

machine was used with a center point load applied to the top surface of the samples.

The MOE and MOR values of each sample were calculated from the load and displacement data.

For the IB test, six samples (5.1 cm × 5.1 cm ×1.1 cm) were cut from each board to produce a total of 12 samples for each board type.   The length, width, thickness, and weight were measured before testing.   Each sample was bonded with hot melt glue to the aluminum blocks which were attached to an INSTRON testing machine to apply tension load.   The IB of each sample was obtained from the peak load over the sample cross-section area.

Viscosity of the adhesives was measured in accordance with the procedure described in ASTM D445.   For each mixture, two kinematic viscosities (determined value) were obtained from measuring the flow time and the calibration constant of the viscometer.   The kinematic viscosity result was calculated as an average of the two acceptable determined values.   The dynamic viscosity was determined by the kinematic viscosity and the density of the mixture.

For the density measurement, six samples (5.1 cm × 5.1 cm ×1.1 cm) were cut from each board.   For each resin composition, there were a total of 12 samples.   The final density of flakeboard for each resin composition was the average of the densities of 12 samples.

For TS and WA tests, two samples (15.2 cm × 15.2 cm ×1.1 cm) were cut from each board so that a total of four samples were obtained for each board type.   The length, width, thickness, and weight were measured before the TS and WA measurements.   The thickness of each specimen was an average of four measurements of four points located at the corner one inch from the edge of the specimens.   The samples were then

submerged in water at the room temperature for 24 hours.   Samples were then measured again.   TS value was obtained from the thickness changes before and after the 24-hour water immersion.   WA value was obtained from the weight changes before and after the 24-hour water immersion.

Results and Discussion

Viscosity

In the flakeboard fabrication, the spraying method applied the resin.   Because of the high viscosity of pyrolysis bio-oil, the viscosity of the pMDI/bio-oil mixture is too high to be sprayed uniformly.   Therefore, as previously described mixed bio-oil with acetone, a polar solvent, to reduce the viscosity.   Table 2.2 shows the viscosity of the adhesive systems with and without adding acetone.   The viscosity of bio-oil decreased from 368 mPa·s (before adding acetone) to 121 mPa·s (after adding acetone) and the viscosity of the adhesives decreased with an increase of bio-oil content.   Adding acetone resulted in less effect of the pMDI/bio-oil composition ratio on system viscosity.   In addition to reducing viscosity, it was reported that the acetone also contributed to stabilizing, homogenizing the adhesive binder systems (Roy et al. 1999).

Table 2.2　　Viscosity of the adhesive systems with acetone added in and without acetone

Resin code	Resin composition			Viscosity
	PMDI (%)	Bio-oil (%)	Acetone (%)	(mPa·s)
M[a]	100	0	0	226
MA[b]	100	0	2.5[a]	151
75M25BA	75	25	10[b]	188
50M50BA	50	50	10[b]	146
25M75BA	25	75	10[b]	127
BA	0	100	10[b]	121
B	0	100	0	368

[a] Based on pMDI weight
[b] Based on bio-oil solid weight

Table 2.3　　Mechanical and physical properties of flakeboard bonded with adhesive binder systems

Resin application rate (%)	Resin code	Board Density (g/cm³)	IB (MPa)	MOR (MPa)	MOE (MPa)	TS (%)	WA (%)
3	M	0.79	0.65	46.0	9,182	20.0	25.1
5	M	0.84	1.21	56.4	9,737	14.9	19.0
7	M	0.88	1.44	63.1	10,536	13.1	14.2
3	MA	0.81	0.81	54.1	8,711	22.0	27.9
5	MA	0.85	1.34	58.4	8,713	16.6	21.4
7	MA	0.87	1.83	64.8	10,507	13.2	15.6
3	75M25BA	0.85	0.58	43.6	7,908	26.5	26.4
5	75M25BA	0.85	1.01	49.5	8,523	20.5	22.6
7	75M25BA	0.85	1.4	51.8	9,005	14.5	13.0
3	50M50BA	0.79	0.5	43.9	6,721	27.1	28.8
5	50M50BA	0.81	0.69	46.5	6,826	21.9	24.4
7	50M50BA	0.80	0.74	48.4	8,525	18.9	18.5
3	25M75BA	0.76	0.25	33.6	6,399	45.7	40.7
5	25M75BA	0.84	0.52	35.7	6,585	34.7	34.1
7	25M75BA	0.81	0.55	46.7	8,177	29.8	32.6

Internal bond

As shown in Table 2.3 and Figure 2.2, when the resin content is 7%, flakeboard bonded with the pMDI-acetone has the highest IB value.　For all of the five resin mixes, as the resin content increased, the IB increased.　At 7% resin content, the IB for the

specimen made from 25% bio-oil and 75% pMDI is equivalent to that made from 100% pMDI.   When bio-oil content is higher than 25%, IB of the flakeboard was significantly reduced.

In the hot-pressing of wood composite boards, many factors can affect the mechanical properties.   These factors include mat moisture content, pressing schedule, resin type and board thickness.

As shown in Table 2.1, the bio-oil for the adhesive binder system had a moisture content of 18%, which increased the mat moisture content. This moisture interfered with the adhesive bonding, which reduced the IB property.

Bio-oil contains some large molecules such as tannin/lignin derivatives.   These molecules may need more time to diffuse and penetrate into the wood surface, which may require increased hot pressing time.

Bending properties

Table 2.3, Figure 2.3, and Figure 2.4 give bending properties (MOR and MOE) of flakeboard made from adhesive binder systems.   For each of the three resin contents, flakeboard bonded with pMDI and acetone mixture had the highest MOR.   As the pMDI/bio-oil ratio increased, the MOR value of the flakeboard decreased.   At a pMDI/bio-oil ratio of 25/75, the MOR showed the lowest value.

The results for MOE are similar to those of the MOR results described above. For each of the three resin contents, the highest flakeboard MOE is obtained when bonded by pMDI and acetone.   As the pMDI/bio-oil ratio increased, the MOE value for the flakeboard decreased.

MOR and MOE showed a decreasing trend, but not as significant as IB. IB mainly tests the adhesive bonding in the flakeboard. However, the bending properties may not only reflect to the adhesive bonding, but also to many other factors, such as material lay-up and press cycle.

The properties of the cured adhesive may also affect the bending properties of flakeboards. DMA results (Figure 3.3) showed that the storage modulus (E') of all adhesives as a function of temperature. It can be clearly seen that at a temperature of 200 ^{o}C (the same temperature as the platen temperature of the hot press), a highest storage modulus of the adhesive is obtained when it is formed by mixing pMDI and acetone. As the pMDI/bio-oil ratio increased, the storage modulus for the adhesives decreased. The storage modulus results correlate well (R^2=0.9446 for correlation between the MOR and the storage modulus, R^2=0.8914 for correlation between the MOE and the storage modulus) with bending test results (Figure 2.5, Figure 2.6).

Thickness swelling and water absorption

From the results of the 24-hour immersion test in water (Table 2.3, Figure 2.7, Figure 2.8), for each of the three resin contents, as the pMDI/bio-oil ratio decreased, the TS and WA increased. Flakeboard bonded with pure pMDI has the lowest TS and WA while flakeboard bonded with pMDI/bio-oil of 25/75 gives the highest TA and WA.

Thickness swelling can be affected by different parameters and materials, such as wood species, flake dimension, resin type, resin content, blending efficiency, board density, and press condition (Halligan 1970). PMDI can easily penetrate into wood cell wall and cause bulking action. The bulked wood cell wall is kept in a swollen state.

21

At this swollen condition, wood cannot expand further in response to contact with water (Rowell and Ellis 1981). In this study, as the bio-oil content in the binder system increased, the amount of large molecules, such as tannin/lignin derivatives increased, leading to less diffusion and penetration of adhesive into the flakes. Therefore, wood components with less resin penetration tended to absorb more water and swell more. In addition, at a high bio-oil content, most of the isocyanate groups in pMDI react with hydroxyl groups from bio-oil, and the isocyanate groups are less available to interact with the flake hydroxyl groups, which may affect the TS and WA. Moreover, hydrophilic chemicals in bio-oil, such as carboxylic acids and alcohols, tend to attract water when the specimens were immersed in water (Gagnon et al. 2004).

Conclusions

An investigation of pyrolysis bio-oil as part of the binder system was conducted in this research. Liquid products obtained from the fast pyrolysis process of pine wood were mixed with pMDI resin to form an adhesive binder system. The adhesive binder system was blended with flakes to make flakeboard. The effect of the resin content and the mix ratio of the binder system on the physical and mechanical properties, such as IB, MOR, MOE, TS, and WA of the flake-based composites were examined.

As the bio-oil content in adhesive binder systems increased, the IB, MOE and MOR values of the flakeboard decreased, while the TS and WA values increased. Adding acetone into binder systems reduced the viscosity, which helped the resin application process.

From the results obtained from this research, a bio-oil content of 25% showed comparable properties to those produced by pure pMDI.

Literature cited

Amen-Chen C. B. Riedl, W. Xiangming and C. Roy. 2002. Softwood bark pyrolysis oil-PF resols part 1. Resin synthesis and OSB mechanical properties. Holzforschung 56: 167-175.

Chan F., B. Riedl, X. M. Wang, X. Lu, C. Amen-chen and C. Roy. 2002. Performance of pyrolysis oil-based wood adhesives in OSB. Forest Products Journal 52 (4): 31-38.

Chum H., J. Diebold, J. Scahill, D. Johnson and S. Black. 1989. Biomass pyrolysis oil feedstocks for phenolic adhesives. Adhesives From Renewable resources. American Chemical Society p135-149.

Deppe H. J. 1977. Technical progress in gluing particleboard with isocyanates. Holz Rohund Werkstoff 35: 295-299.

Despres A., A. Pizzi and L. Delmotte. 2006. ^{13}C NMR investigation of the reaction in water of UF resins with blocked emulsifiable isocyanates. Journal of Applied Polymer Science 99 (2) 589-596.

Frick T. and B. Motter. 2001. PMDI as an additive to UF- and MUF-resins for particleboard production. In: Proc. 35th Inter. Particleboard Composite Materials Symposium. Washington State University, Pullman, WA.

Gagnon M., C. Roy and B. Riedl. 2004. Adhesives made from isocyanate and pyrolysis oils for wood composites. Holzforschung 58: 400-407.

Gagnon M., C. Roy, D. Rodrigue, and B. Riedl. 2003. Calorimetric and rheological study of isocyanate-pyrolysis oil blends. Journal of Applied Polymer Science 89: 1362-1370.

Grigoriou A. H. 2000. Straw-wood composites bonded with various adhesive systems. Wood Science and Technology 34: 355-365.

Halligan A. F. 1970. A review of thickness swelling in particleboard. Wood Science and Technology 4 (4): 301-312.

Hao B. Y. and Z. T. Liu. 1993a. The study on the curing process of urea formaldehyde and isocyanate mixture adhesive by DSC. Wood Industry 7 (2): 2-6.

Hao B. Y. and Z. T. Liu. 1993b. The primary study on straw particleboard. Wood Industry 7 (3): 2-7.

24

Himmelblau D. A. and G. A. Grozdits. 1998. Production of wood composite adhesives with air-blown, fluidized-bed pyrolysis oil. International Contributions to Wood Adhesion Research 137-148.

Leitheiser R. H. and W. E. Johns. 1983. Isocyanate/furfural blends binders for wood composites. In: 17th Particleboard/Composite Meterials Series Proceedings. Pullman, Washington. pp: 249-258.

Lim J. T. C. and C. Shui-tung. 1993. Phenol formaldehyde steam pressing of waferboard. U.S. Patent 5217665.

Miller T. R., J. W. Rosthauser. 2002. Aqueous mixed pMDI/phenolic resin binders for the production of wood composite products. U. S. Patent 6,416,696.

Mohan D., C. U. Pittman and P. H. Steele. 2006. Pyrolysis of wood/biomass for bio-oil: a critical review. Energy & Fuels 20: 848-889.

Myers G. E. 1984. How mole ratio of UF resin affects formaldehyde emission and other properties: a literature critique. Forest Products Journal 34 (5): 35-41.

Newman W. H. and W. G. Glasser. 1985. Engineering plastics from lignin. Xll: Synthesis and performance of lignin adhesives with isocyanate and melamine. Holzforschung 39 (66): 345-353.

Pizzi A. 1983. Wood Adhesives Chemistry and Technology. Dekker, New York.

Pizzi A. 1993. Advanced Wood Adhesive Technology. Dekker, New York. pp 48.

Pizzi A. and T. Walton. 1992. Non-emulsifiable, water-based diisocyanate adhesives for exterior plywood. Part1. Novel reaction mechanisms and their chemical evidence. Holzforschung 46 (6): 541-547.

Pizzi A., V. Leyser and C. Westermeyer. 1995. Adhesive compostion comprising isocyanate phenol-formaldehyde and tannin, useful for manufacturing plywoods for exterior application. U.S. Patent 5407980.

Preechatiwong W., W. Yingprasert, B. Kyokong. 2007. Effects of phenol-formaldehyde/isocyanate hybrid adhesives on properties of oriented strand lumber (OSL) from rubberwood waste. Songklanakarin Journal of Science and Technology 29 (5): 1367-1375.

Rosthauser J. W. and H. G. Schmelzer. 2001. Mixed pMDI/solid novolac resin binders for the production of wood composite products. U.S. Patent 9,794,976

Rosthauser J. W. and W. D. Detlefsen. 2001. Mixed pMDI/resole resin binders for the production of wood composite products. U. S. Patent 9,773,796.

Rowell R. M. and W. D. Ellis. 1981. Bonding of isocyanate to wood. In: Urethane Chemistry and Applications. K. N. Edwards, ed. American Chemical Society, Washington, DC. pp. 263-284.

Roy C., L. Calve, X. Lu, H. Pakdel and C. Amen-chen. 1999. Wood composite adhesives from softwood bark-derived vacuum pyrolysis oils. Biomass, a growth opportunity in green energy and value-added products; proceedings of the 4th Biomass Conference of the Americas p521-526.

Shadurka V., W. G. Binder, M. Dunky and W. kantner. 2003. Blocked isocyanates in UF resins: reaction pathways and cross-linking. In Proceedings of the 7th Panel Products Symposium, Llandudno, UK. p57.

Simon C., B. George and A. Pizzi. 2002. UF/pMDI wood adhesives: Network blend versus copolymerization. Holzforschung 56 (3): 327-334.

Tinkelenberg A., H. W. Vaessen, K. W. Suen and P. G. J. Leusink. 1982. Combinations of low formaldehyde-aminoplast glues and pMDI. The Journal of Adhesion 14 (3&4): 219-231.

Wang W., Z. Xianquan and L. Renshu. 2004. Low formaldehyde emission particleboard bonded by UF-pMDI mixture adhesive. Forest Products Journal 54 (9): 36-39.

Wieland S., A. Pizzi, W. Grigsby, J. Warnes and F. Pichelin. 2006. Microcrystallinity and colloidal peculiarities of UF/isocyanate hybrid resins. Journal of Applied Polymer Science 104: 2633-2636.

Zhu S., D. Tomberlin and J. Buongiorno. 1998. Global forest products consumption, production, trade and prices: global forest products model projections to 2010. Global Forest Products Outlook Study Working Paper GFPOS/WP/01, Food and Agriculture Organization of the United Nations, Rome
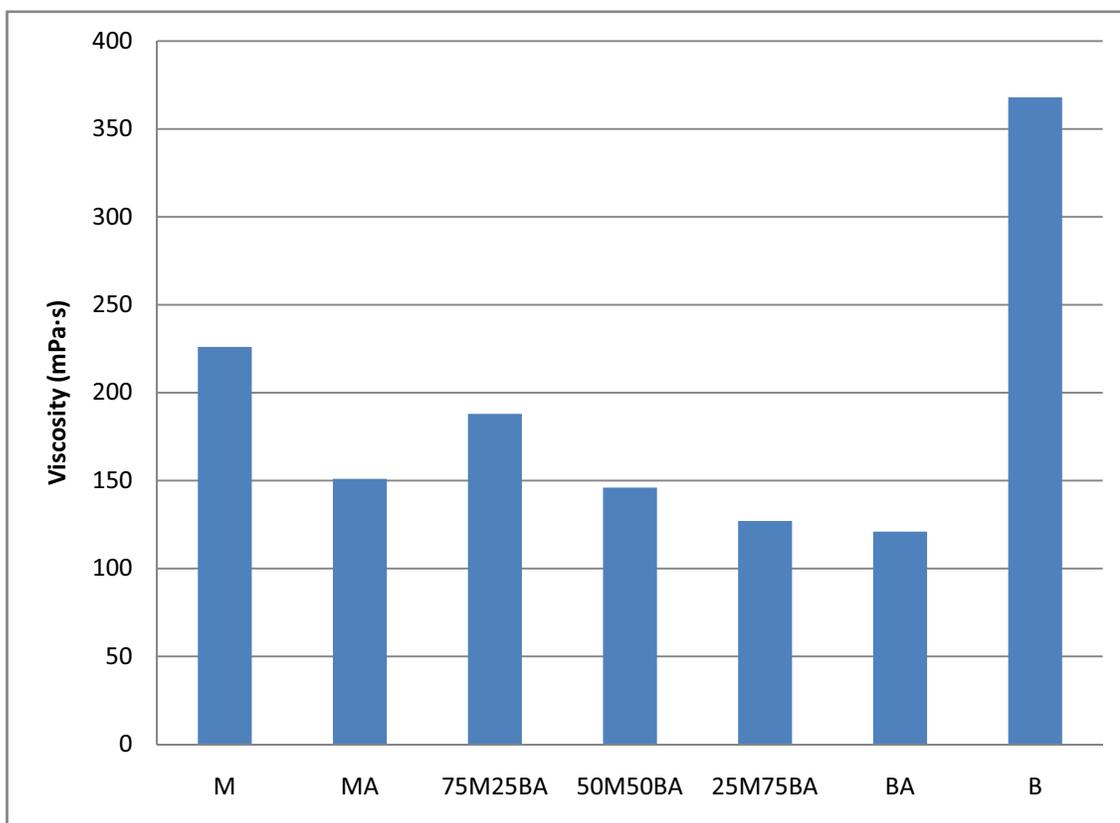
Figure 2.1

Viscosities of pMDI/bio-oil adhesives.

M: pMDI; MA: adhesive composed of pMDI and acetone; 75M25BA: adhesive composed of 75% pMDI, 25% bio-oil and acetone; 50M50BA: adhesive composed of 50% pMDI, 50% bio-oil and acetone; 25M75BA: adhesive composed of 25% pMDI, 75% bio-oil and acetone; BA: mixture of bio-oil and acetone; B: bio-oil

Figure 2.2

IB of flakeboards bonded with the pMDI/bio-oil adhesives with different bio-oil contents.

M: pMDI; MA: adhesive composed of pMDI and acetone; 75M25BA: adhesive composed of 75% pMDI, 25% bio-oil and acetone; 50M50BA: adhesive composed of 50% pMDI, 50% bio-oil and acetone; 25M75BA: adhesive composed of 25% pMDI, 75% bio-oil and acetone

Figure 2.3

MOE of flakeboards bonded with the pMDI/Bio-oil adhesives with different bio-oil contents.

M: pMDI; MA: adhesive composed of pMDI and acetone; 75M25BA: adhesive composed of 75% pMDI, 25% bio-oil and acetone; 50M50BA: adhesive composed of 50% pMDI, 50% bio-oil and acetone; 25M75BA: adhesive composed of 25% pMDI, 75% bio-oil and acetone
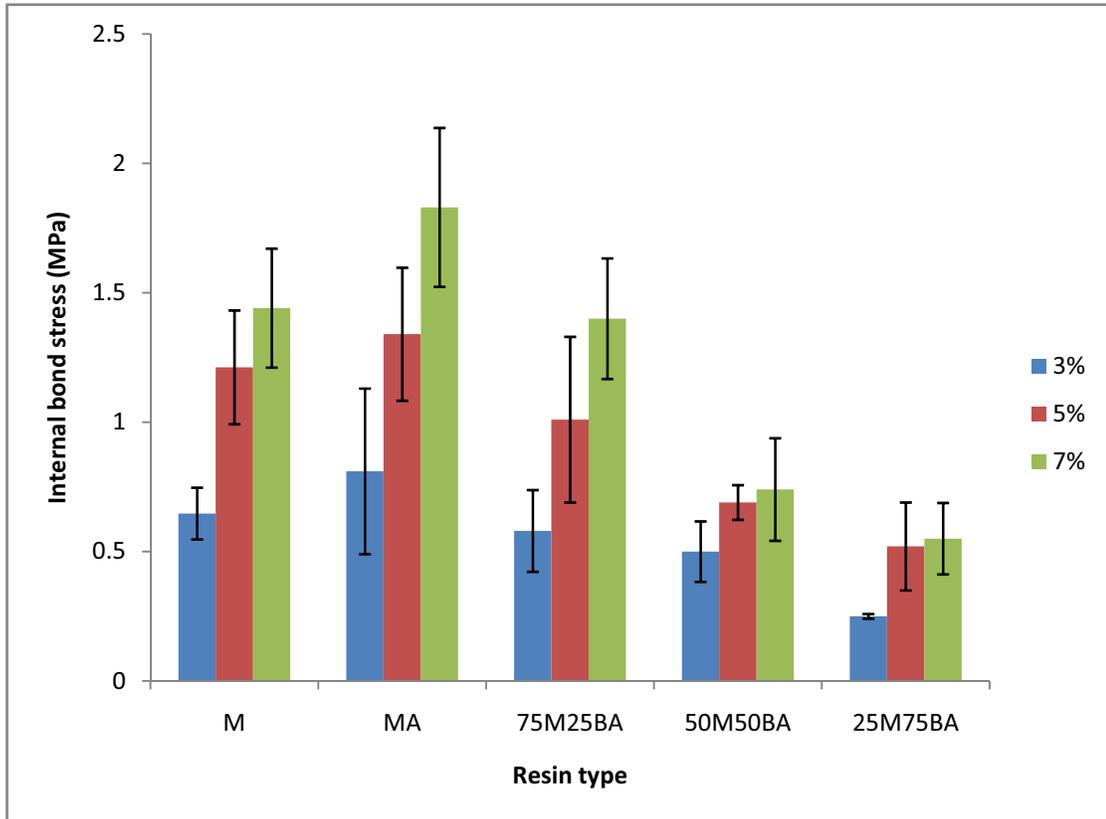
Figure 2.4

MOR of flakeboards bonded with the pMDI/Bio-oil adhesives with different bio-oil contents.

M: pMDI; MA: adhesive composed of pMDI and acetone; 75M25BA: adhesive composed of 75% pMDI, 25% bio-oil and acetone; 50M50BA: adhesive composed of 50% pMDI, 50% bio-oil and acetone; 25M75BA: adhesive composed of 25% pMDI, 75% bio-oil and acetone
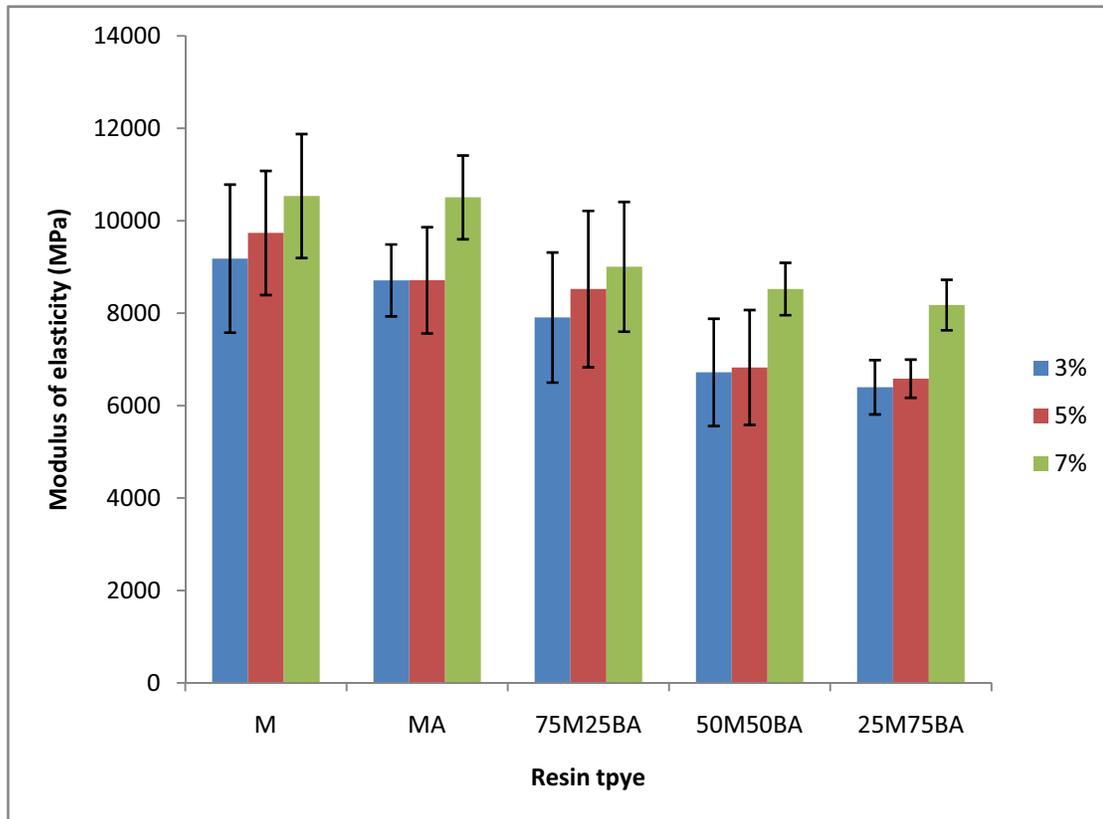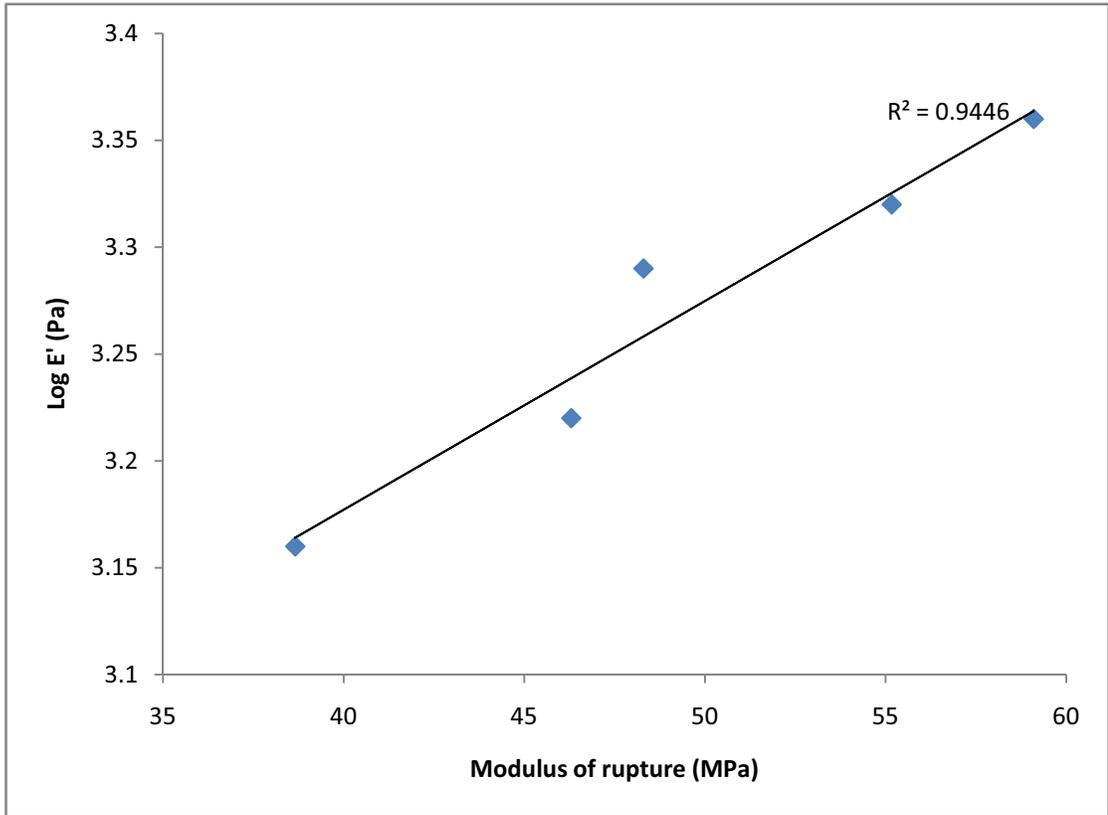
Figure 2.5

Correlation between the mean MOR of the flakeboards for each adhesive type and the
storage modulus of the adhesives at the temperature of 200 ^{o}C
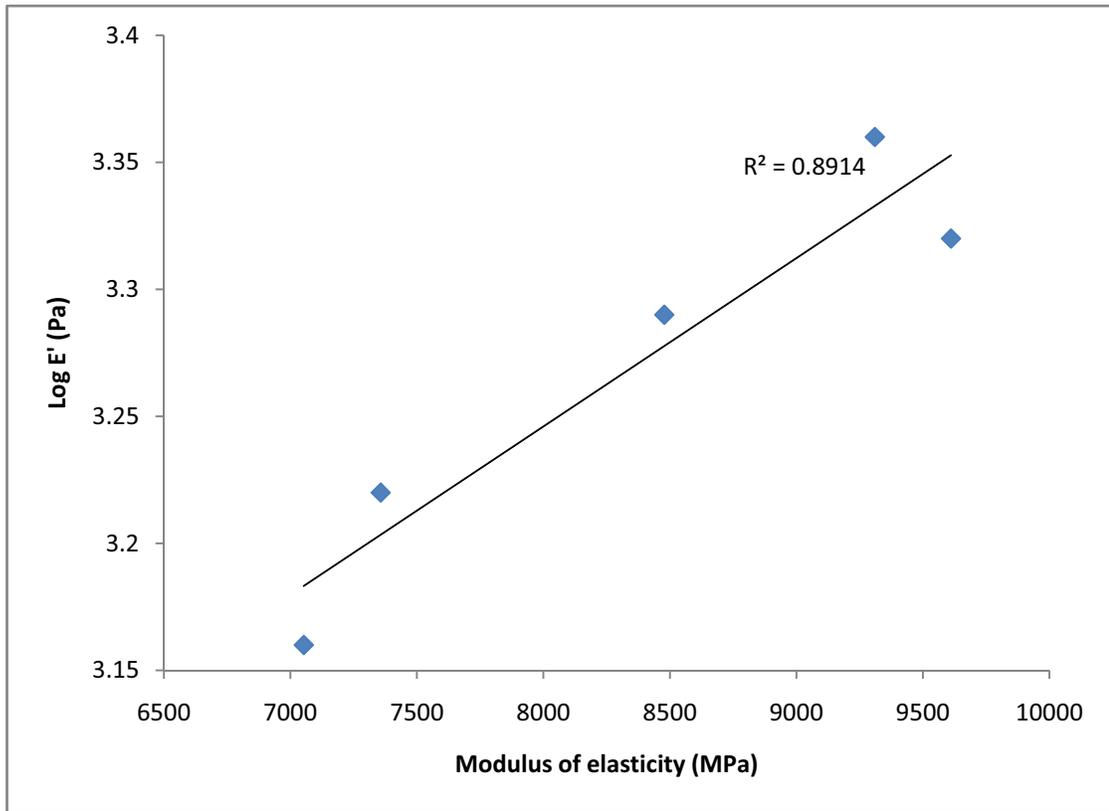
Figure 2.6

Correlation between the mean MOE of the flakeboards for each adhesive type and the
storage modulus of the adhesives at the temperature of 200 ^{o}C
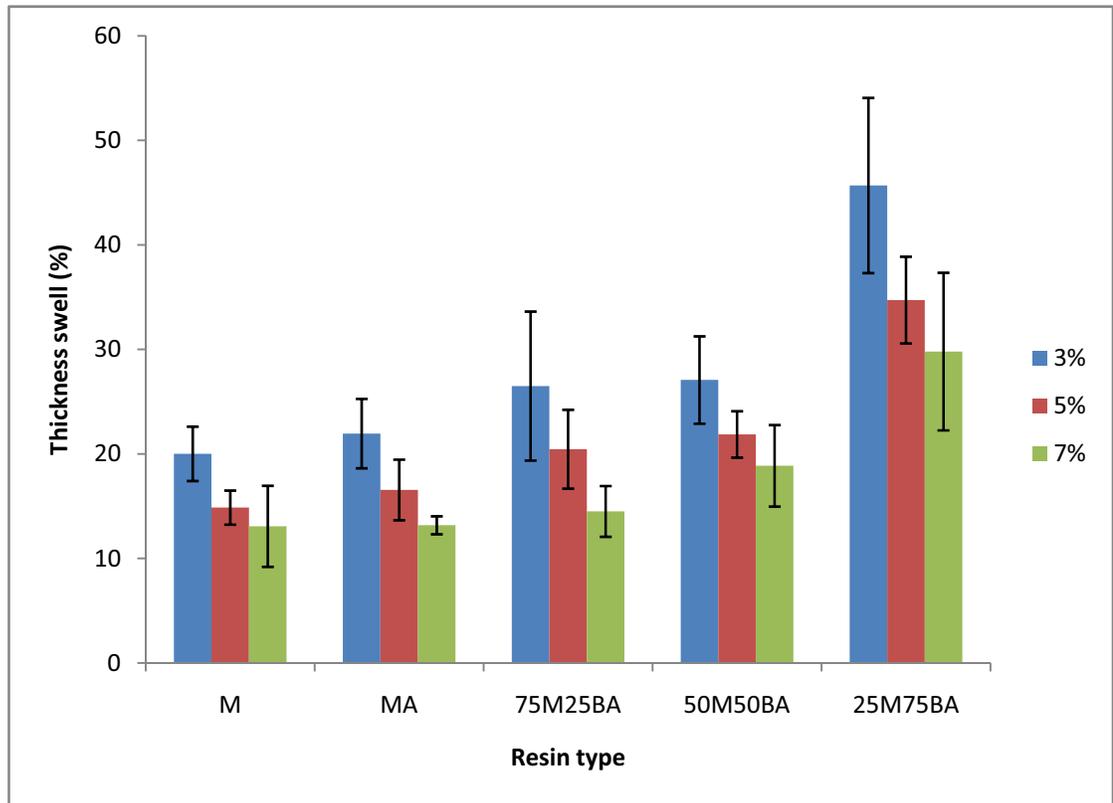
Figure 2.7

TS of flakeboards bonded with the pMDI/Bio-oil adhesives with different bio-oil.

M: pMDI; MA: adhesive composed of pMDI and acetone; 75M25BA: adhesive composed of 75% adhesives pMDI, 25% bio-oil and acetone; 50M50BA: adhesive composed of 50% pMDI, 50% bio-oil and acetone; 25M75BA: adhesive composed of 25% pMDI, 75% bio-oil and acetone
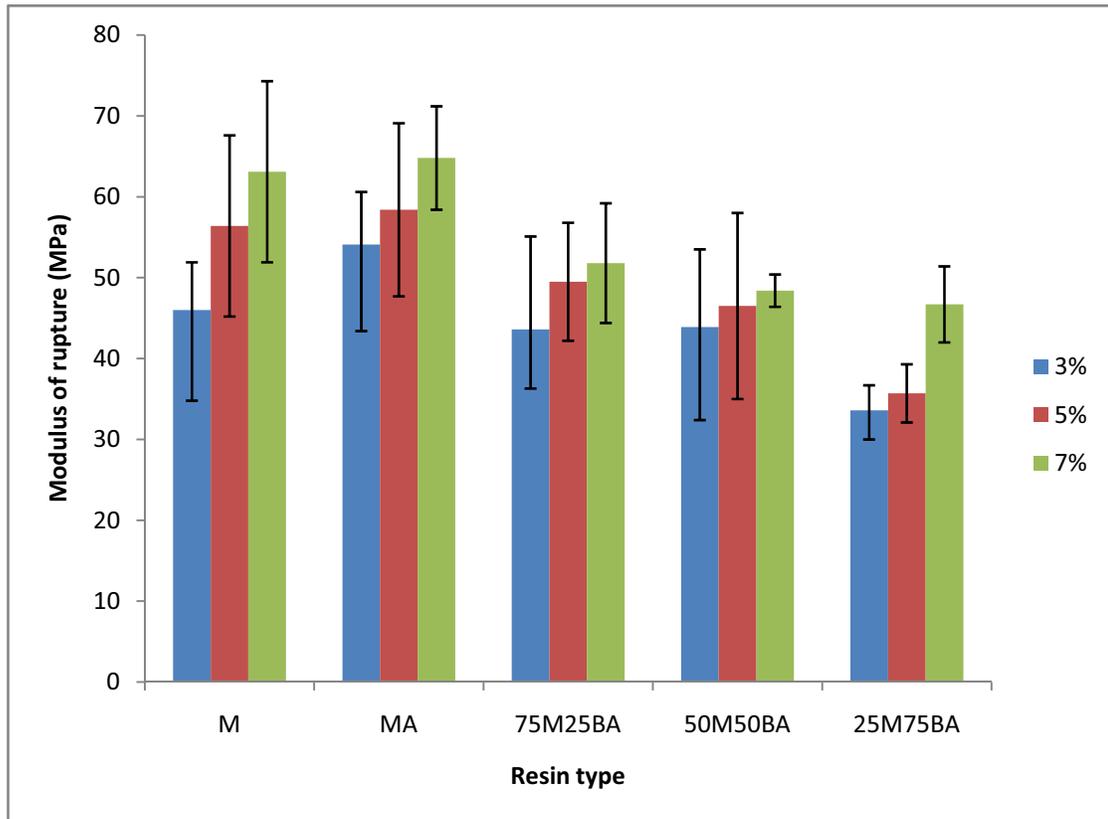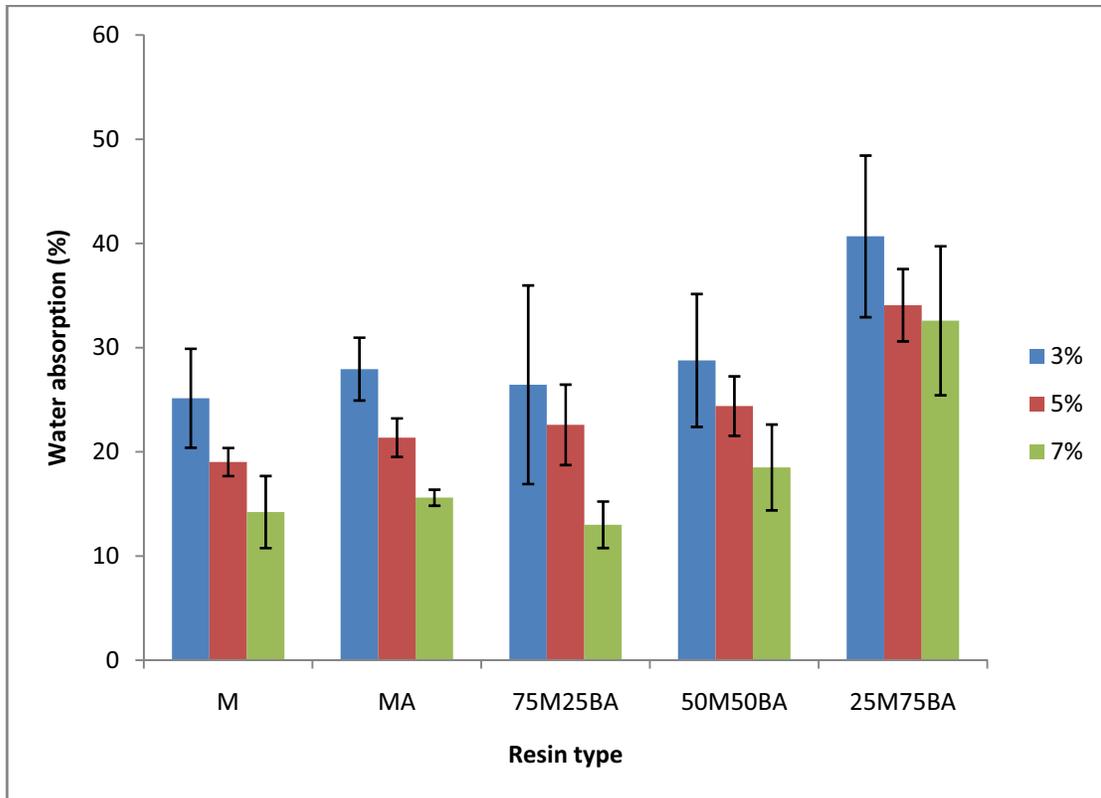
Figure 2.8

WA of flakeboards bonded with the pMDI/Bio-oil adhesives with different bio-oil contents.

M: pMDI; MA: adhesive composed of pMDI and acetone; 75M25BA: adhesive composed of 75% adhesives pMDI, 25% bio-oil and acetone; 50M50BA: adhesive composed of 50% pMDI, 50% bio-oil and acetone; 25M75BA: adhesive composed of 25% pMDI, 75% bio-oil and acetone

CHAPTER III

DYNAMIC MECHANICAL PROPERTIES OF PMDI/BIO-OIL ADHESIVE SYSTEMS

Introduction

Liquid pMDI can easily wet the wood surface and penetrate into the wood material (Scoville 2002). The surface of wood is rich in chemical functional groups called hydroxyl groups (-OH). PMDI resins are terminated in isocyanate groups (-N=C=O), which readily react with the wood hydroxyl groups, forming urethane linkages. Moreover, pMDI resin cures by reacting with the water in the wood and creating urea linkages, which creates a rigid, polar network (Wittman 1976; Rowell and Ellis 1981). This is an important contributor to the adhesion properties of pMDI. This hydrolytic stability allows the use of higher moisture content wood. Some pMDI-bonded wood composite products with larger cross-sections use steam injection hot-pressing to transfer heat uniformly throughout the cross-section. PMDI resins are not as thermally stable as PF, but they are faster curing. pMDI resins may be difficulty in processing due to their high reactivity, adhesion to platens, lack of cold tack, high cost and the need for special storage (Rosthauser et al. 2003). In general, the wood composite industry uses pMDI in the core only (Gagnon et al. 2004).

The blending of pMDI with a low cost material such as amine-based resin or other polymers is attractive for the potential cost savings in a commodity product. This is

even more attractive if a reaction mechanism exits between the pMDI and the substituted polymer other than a simple physical blending, and the adhesive properties of the blended mixture are improved. In some studies, pMDI has been blended with PF, UF and MF resins for the wood composites applications (Pizzi 1995; Enomoto et al. 2000; Weihong et al. 2004). In these adhesive systems the isocyanate group (-NCO) reacts rapidly with the methylol group (-CH$_2$OH) present in PF, MF and UF resins (Pizzi 1995). However, Adcock et al. (1999) claimed that co-reaction between UF and pMDI is not a preferred reaction and may be insignificant. Thermal analysis, such as thermomechanical analysis (TMA), dynamic mechanical analysis (DMA), and differential scanning calorimetric (DSC) was employed to further elucidate such co-reactions. Simon et al. (2002) applied TMA and ^{13}C NMR to study the reactivity between the UF and pMDI. It was demonstrated that in the presence of water and under the acidic hardening conditions, the bond strength between the UF and pMDI was improved by co-reaction between pMDI and UF resin methylol groups forming methylene cross-links. It was shown that the water in the UF resin did not react with pMDI isocyanate groups, but rather contributed much to increase the strength of the cured adhesive. Wang (2006) conducted mechanical tests and DSC analysis showing that the acidic hardener NH$_4$Cl inhibited the EMDI-UF curing and also sensitive to the adhesive application method. If the NH$_4$Cl hardener was added after mixing EMDI and UF, the mechanical properties of particleboard were improved. The DSC results also showed that UF could react well with the pMDI in the presence of acidic hardener.

Bio-oil from pyrolysis process consists of many different oxygenated organic compounds, some of which contain phenolic hydroxyl groups. Studies have been

conducted on the bio-oil and PF adhesive systems (Chum et al. 1989; Himmelblau and Grozdits 1998; Roy et al. 1999; Chan et al. 2002; Amen-Chen et al. 2002A). Phenolic-rich bio-oil was used to substitute a part of phenol in PF resin formulations to produce bio-oil-PF adhesives for wood-based composites. Amen-Chen et al. (2002B) used DSC with varied scan speeds and isoconversional kinetics to study the curing of a bio-oil-PF resin with 25% of phenol being replaced by bio-oil. It was showed that the curing mechanism of bio-oil-PF resin and pure PF resin were similar. Increasing the bio-oil content would reduce the thermal resistance of the adhesive. Athanassiadou et al. (2001) investigated the molecular weight distribution of three PF resin formulations: 1) PF resin with 40% phenol substituted by bio-oil (40% PF resin), 2) PF resin with 50% phenol substituted by bio-oil (50% PF resin), and 3) pure PF resin. He found that the gel permeation chromatography (GPC) graph of 40% PF resin was similar to that of the pure PF resin. However, the GPC graph of 50% PF resin had a broader peak at higher molecular weights. DCS analysis was employed showing that the phenol-substituted PF resin cured faster than the pure PF resin and also had a higher heat of reaction. The phenol-substituted PF resin obtained higher crosslinking density than the pure resin.

It was reported (Gagnon et al. 2003) that at least 80% of the chemicals in the bio-oil (sugars, carboxylic acids, phenols, alcohols, water, and tannin/lignin derivatives) are expected to react with pMDI. Thus, bio-oil has the possibility to be a suitable component in pMDI/bio-oil binder system for OSB or particleboard. Gagnon et al. (2003) studied the reaction of pMDI and bio-oil by DSC. The bio-oil content in the adhesive binder systems were 0, 20, 30, 35, 40, 50, 60, 70, 80, 90, and 100%. It was found that the chemical reaction between the pMDI and bio-oil occurred below $100\,^{\circ}C$,

even as low as at room temperature (20 $^\mathrm{o}$C). The DSC analysis showed that the peak temperature of the reaction decreased as the bio-oil content in pMDI/bio-oil binder systems increased. When the bio-oil content was around 30 - 40%, the heat of reaction reached its maximum. The rheological study of various pMDI/bio-oil ratios was also performed to evaluate the evolution of viscosity as a function of time for different pMDI/bio-oil mixtures. The initial viscosity of the blends was proportional to the bio-oil content. An exponential increase of viscosity was demonstrated for all pMDI/bio-oil mixtures.DMA has been widely utilized to compare the adhesive cure rates, to study the effects of additives on resin cure behavior and thermal stability, and to help optimize hot-pressing conditions (Zheng 2002).

The object of this study was to use the DMA to elucidate the thermal properties and cure behaviors of the pMDI/bio-oil binder systems.

Experimental

Materials

The pMDI (LUPRANATE M20FB) used in this adhesive binder system was provided by BASF The Chemical Company (Elorham Park, NJ, USA). It is a dark yellow liquid with the viscosity of 226 mPa·s at 25 $^\mathrm{o}$C. Before the experiment, pMDI resin was stored in a sealed container under a condition of 60 ± 5% relative humidity and 25 ± 3 °C.

The pyrolysis bio-oil was mixed with the pMDI to produce adhesive binder system. The bio-oil was produced from pyrolysis of pine wood in the Mississippi State

University auger reactor. The pine wood particle was pyrolyzed at 450 $^{\circ}$C with a retention time of 2 seconds. The crude bio-oil was filtered to remove the biomass residuals including charcoal, and stored at 4 $^{\circ}$C in a refrigerator. The water content of the bio-oil was 18%.

Wood flakes with a thickness of 0.05 cm were cut from water-soaked pine wood blocks with a disk flaker and were conditioned to equilibrium moisture content (EMC) of approximately 10% in an environmental chamber at $20 \pm 3^{\circ}$C and $65 \pm 5\%$ relative humidity. These flakes were sealed in plastic bags to maintain constant moisture content before testing. The adhesive binder systems used in the DMA testing were formed with different mixing ratios of pMDI and bio-oil (Table 3.1). Bio-oil was first weighed and then poured into a beaker. Acetone was added into the bio-oil, and the mixture was stirred by hand to make it uniform. The bio-oil-acetone mixture was poured into another beaker which contained pMDI.

Table 3.1 Composition of the adhesive binder systems in DMA analysis

Resin code	Resin composition		
	PMDI (%)	Bio-oil (%)	Acetone (%)
M	100	0	0
MA	100	0	2.5 [a]
75M25BA	75	25	10 [b]
50M50BA	50	50	10 [b]
25M75BA	25	75	10 [b]

[a] Based on pMDI weight
[b] Based on bio-oil solid weight

Double layers of wood flakes (6.0 cm × 1.0 cm × 0.05 cm) were used as the curing substrate. The adhesives were brushed onto the wood flakes uniformly by a

disposable brush and the excess adhesive was then removed with a glass rod. The blends ratio was based on resin solids.

Methods

TA Instruments Model Q 800 was used for the DMA testing. Elastic modulus (stiffness) and a mechanical damping (toughness) for materials were obtained. DMA fixed frequency mode was used for the testing.

A dual cantilever holder was devised to test the specimens in a bending mode. A torque wrench was used to tighten the clamp locking screws at a torque of 1.1 N-m. The wood samples were clamped on the tangential surfaces so that the bending occurred in the radial direction in order to produce a shear deformation perpendicular to the grain.

DMA temperature scans were performed in a temperature range of 50-200 ^{o}C. A heating rate of 10 ^{o}C min^{-1} with a 1 Hz frequency and strain amplitude of 15 μm were applied for all the DMA testing. A minimum of three replicates were tested. An effort was made to keep the curing conditions of the replicates consistent. The variation was observed, but the general trends of the DMA response among the replicates were similar to each other.

Results and Discussion

During the curing of thermoset resins, peaks in tanδ can often be assigned to gelation and vitrification. The gelation results from a transition between the liquid and rubbery states to form resin network. Vitrification happens when resin converts to the glass state. Zheng (2002) investigated the effect of thermal behavior of wood flakes on

the curing behavior of pMDI binder system.   Results showed that there was little change on the storage and loss modulus of wood flakes during the thermal scan indicating that the wood flakes did not obscure the cure analysis.

A thermal scan of pure pMDI on a pine flake is shown in Figure 3.1.   No sharp increase for the storage modulus and tanδ peak was observed.   Ni (1996) and Zheng (2002) also reported the same result with similar adhesive systems.   After the peak, the storage modulus decreased slightly until a temperature of 200 ^{o}C was reached.   However, gelation and vitrification peaks could not be observed from the tanδ curve.

Figure 3.2 shows the thermal scan of the pMDI-acetone binder system on the wood flake.   Similar to the neat pMDI curves, neither a sharp increase of storage modulus nor tanδ peak was observed.   The storage modulus increased at the initial stage, reached its peak at 112 ^{o}C, and followed by a slight decrease.   For the storage modulus, the peak temperature for the pure pMDI was lower than that for the pMDI-acetone system, which means the pure pMDI cured faster than the pMDI-acetone system.   The addition of acetone reduced the reactivity of pMDI.   The peak storage modulus of pMDI-acetone system was higher than that of the pure pMDI.   It may be because of the deeper penetration of adhesive into the wood component as a result of lower viscosity of the adhesive with the addition of acetone.

Figure 3.3 compares the storage modulus of the pure pMDI and the four adhesive binder systems.   Generally, the higher the bio-oil content, the shorter the curing rate, as indicated by the time to reach the maximum storage modulus.   The wood surface has abundant chemical functional groups such as hydroxyl groups (-OH) (Wittman 1976; Rowell and Ellis 1981).   Isocyanate groups (-N=C=O) in pMDI resin can react readily

41

with the hydroxyl groups on wood, forming urethane linkages. Moreover, the resin can cure by reacting with the water in the wood and the urea linkages are formed to create a rigid and polar network. The reaction between the pMDI and the water is quicker than that with any other hydroxyl-containing compounds. When water is present, the water-pMDI reaction dominates all other reactions (Veaver and Owen 1995). Therefore, as the bio-oil content in adhesive systems increased, more water was introduced. Isocyanate groups reacted with water first to form urea linkages. The more the water introduced, the faster was the reaction.

From the storage modulus curve, it can also be seen that at the storage modulus peaks, pMDI-acetone curve has the highest modulus value among all the adhesive systems, while the pMDI/bio-oil ratio of 25/75 has the lowest storage modulus. For the five different adhesive systems tested in the experiment, different water content, viscosity, and isocyanate group contents were combined. The pMDI-acetone adhesive had the lowest water content and lowest viscosity. Isocyanate groups can readily penetrate into wood flakes and react with hydroxyl groups on wood to form chemical bonds directly with wood. The isocyanate also reacts with the moisture within the wood cell walls, so that the adhesion through the physical interactions is enhanced. The pure pMDI adhesive can bond wood chemically and mechanically, but most bonds formed on the surface of wood with less penetration into wood cell walls compared with the pMDI-acetone system.

Adhesive with a pMDI/bio-oil composition ratio of 75/25 has a comparable curing speed and a peak storage modulus to those of the pure pMDI. This may be attributed to the appropriate amount of isocyanate groups and water. Some studies

(Steiner 1986) indicated that the maximum adhesive strength of the isocyanate-wood bond occurred at about 8-12% moisture content.   Moreover, bio-oil contains significant amounts of compounds such as sugars, carboxylic acids, phenols, alcohols, water, and tannin/lignin derivatives (Melany et al. 2003).   The hydroxyl compounds of especially large molecules with at least two hydroxyl groups such as tannin/lignin derivatives can form networks with pMDI which may be important to the adhesion of the isocyanates.

With an increase of the bio-oil content, more water was introduced into the adhesive system.   The excess water apparently consumes most of the isocyanate groups in pMDI.   This water reaction reduces the urethane linkages between pMDI and wood which may affect the strength and durability of the composites.

Chemicals from bio-oil with at least two function groups which can react with isocyanate groups formed the polymer structures during the curing process.   However, those small molecules, such as phenols, alcohols and aldehydes which contain only one functional group can only form chains without much extension.   With the increase of the temperature, the short chains will decompose resulting in a slight decline of the storage modulus curves after they reach the peaks.   It was reported that urethane linkages from phenols cleaved at the temperature above $120\,^{\circ}C$ (Charles and Ni. 1998).   Moreover, it can be clearly seen that with the bio-oil content in adhesive binder systems increases, the decline of modulus curves is more obvious.   This is because more small molecules are introduced to the adhesive systems with the increase of bio-oil content.

From the storage modulus curves, for the same temperature from 100 to $200\,^{\circ}C$, the modulus of five adhesives increased with pMDI/bio-oil ratio.   The higher the storage modulus of adhesive, the higher the mechanical property should be obtained.   In the hot

pressing process of this study, the platen temperature was 200 °C, while the actual core temperature should be less than 200 °C depending on board thickness and moisture content.   Therefore the modulus of the adhesives at the core temperature of the flakeboard mat during the hot pressing (up to 200 °C) may be important to the mechanical properties of flakeboard.   DMA analysis results (Figure 3.4) showed a good correlation (R^2=0.9907) with the internal bond test results (Figure 2.2).

Figure 3.5 shows the tanδ of the five adhesive binder systems as a function of temperature.   The lower the tanδ, the lower the loss modulus, and the higher the storage modulus obtained.   A good correlation (R^2=0.8846) was shown between DMA tanδ trace and mechanical properties of flakeboard (Figure 3.6).

Conclusions

From the three basic dynamic mechanical parameters obtained from the DMA tests, storage modulus, loss modulus, and tanδ value, the material dynamic performance was interpreted.   In this study, five different types of adhesives were tested via DMA and their curing behavior was analyzed.   Temperature scans were performed in a temperature range of 50-200 °C with a heating rate of 10 °C minnute^{-1}, frequency of 1Hz, and strain amplitude of 15 μm.   With an increase of bio-oil content in the adhesive binder system, less time was needed to reach the maximum storage modulus.   The adhesive with the pMDI/bio-oil ratio of 75/25 had the fastest curing speed but the lowest modulus value at a temperature as high as 200 °C.   PMDI/acetone adhesive showed the best thermal mechanical properties among the five adhesive systems.   A good

correlation was observed between the DMA results (storage modulus and tanδ) and the mechanical properties of the composites.

Literature cited

Adcock T., M. P. Wolcott and S. M. Peyer. 1999. Urea formaldehyde/diphenylmethane diisocyanate copolymer adhesives: possible use as an adhesive system for straw based particleboard. Proc. of the third European panel products symposium, Llandudno, UK, pp 67–76.

Amen-Chen C. B. Riedl, W. Xiangming and C. Roy. 2002. Softwood bark pyrolysis oil-PF resols part 1. Resin synthesis and OSB mechanical properties. Holzforschung 56: 167-175.

Amen-Chen C. B. Riedl, W. Xiangming and C. Roy. 2002. Softwood bark pyrolysis oil-PF resols part 2. Thermal analysis by DSC and TG. Holzforschung 56: 273-280.

Athanassiadou E., S. Tsiantzi, P. Nakos. 2001. Wood adhesives made with pyrolysis oils. A. C. M. Wood Chemicals plc.

Bergland L. and R. M. Rowell. 2005. Handbook of Wood Chemistry and Wood Composites. CRC Press.

Chan F., B. Riedl, X. M. Wang, X. Lu, C. Amen-chen and C. Roy. 2002. Performance of pyrolysis oil-based wood adhesives in OSB. Forest Products Journal 52 (4): 31-38.

Chum H., J. Diebold, J. Scahill, D. Johnson and S. Black. 1989. Biomass pyrolysis oil feedstocks for phenolic adhesives. Adhesives From Renewable resources. American Chemical Society p135-149.

Enomoto. 2000. Preparation and bonding properties of isocyanate/phenolic glue mixes. Wood Adhesives 2000. Extended Abstracts. Forest Products Society. Nevada.2000.80.

Frazier C. A. and J. Ni. 1998. On the occurrence of network interpenetion in the wood-isocyanate adhesive interphase. Adhesion & Adhesives 18: 81-87.

Himmelblau D. A. and G. A. Grozdits. 1998. Production of wood composite adhesives with air-blown, fluidized-bed pyrolysis oil. International Contributions to Wood Adhesion Research 137-148.

Gagnon M., C. Roy and B. Riedl. 2004. Adhesives made from isocyanate and pyrolysis oils for wood composites. Holzforschung 58: 400-407.

Gagnon M., C. Roy, D. Rodrigue, and B. Riedl. 2003. Calorimetric and rheological study of isocyanate-pyrolysis oil blends. Journal of Applied Polymer Science 89: 1362-1370.

Ni J. 1996. Molecular investigation of the wood/pMDI adhesive bondline. Virginia Polytechnic Institute & State University. Blacksburg, VA

Pizzi A., V. Leyser and C. Westermeyer. 1995. Adhesive compostion comprising isocyanate phenol-formaldehyde and tannin, useful for manufacturing plywoods for exterior application. U.S. Patent 5407980.

Rosthauser J. W., G. H. Schmelzer. 2003. Process for production of production of wood composites using a mixed pMDI/solid novolac resin binder. EP Patent 1159326.

Rowell, R.M. and W.D Ellis. 1981. Bonding of isocyanates to wood. Urethane Chemistry and Applications Symposium Series 172. American Chemical Society Washington D.C. 263-284.

Roy C., L. Calve, X. Lu, H. Pakdel and C. Amen-chen. 1999. Wood composite adhesives from softwood bark-derived vacuum pyrolysis oils. Biomass, a growth opportunity in green energy and value-added products; proceedings of the 4th Biomass Conference of the Americas p521-526.

Scoville C. R. 2002. Characterizing the Durability of PF and pMDI Adhesive Wood Composites Through Fracture Testing. Master Thesis. Virginia Polytechnic Institute & State University. Blacksburg, VA. 77pp.

Simon C., B. George and A. Pizzi. 2002. UF/pMDI wood adhesives: Network blend versus copolymerization. Holzforschung 56 (3): 327-334.

Steiner P. R. 1986. Bonding wood composites with isocyanate. In Canadian Forestry Service. Cat. No. Fo 42-91.

Weaver F. W. and N. L. Owen. 1995. Isocyanate-wood adhesive bond. Applied Spectroscopy 49 (2): 171-176.

Wang W., Z. Xianquan and L. Renshu. 2004. Low formaldehyde emission particleboard bonded by UF-pMDI mixture adhesive. Forest Products Journal 54 (9): 36-39.

Wittman. 1976. Die Holzverklebung mit Isocyanat. Holz als Roh-und Werkstoff 34 (11): 427-421.

Zheng J. 2002. Studies of PF resole/isocyanate hybrid adhesives. Ph.D. dissertation.

Virginia Polytechnic Institute & State University. Blacksburg, VA. 198pp.

Adcock T., M. P. Wolcott and S. M. Peyer. Urea formaldehyde/di- phenylmethane diisocyanate copolymer adhesives: possible use as an adhesive system for straw based particleboard. Proc. of the third European panel products symposium, Llandudno, UK, pp 67–76.
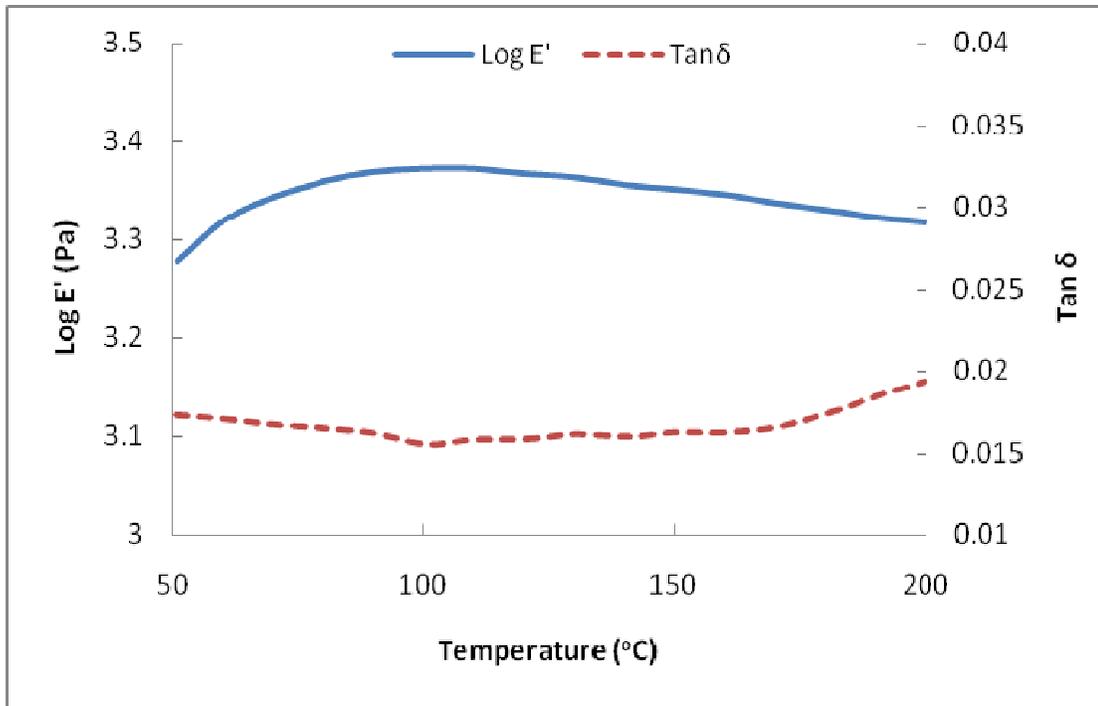
Figure 3.1

Dynamic mechanical response curves showing storage modulus (E') and damping term (tanδ) for pure pMDI as a function of temperature (T)
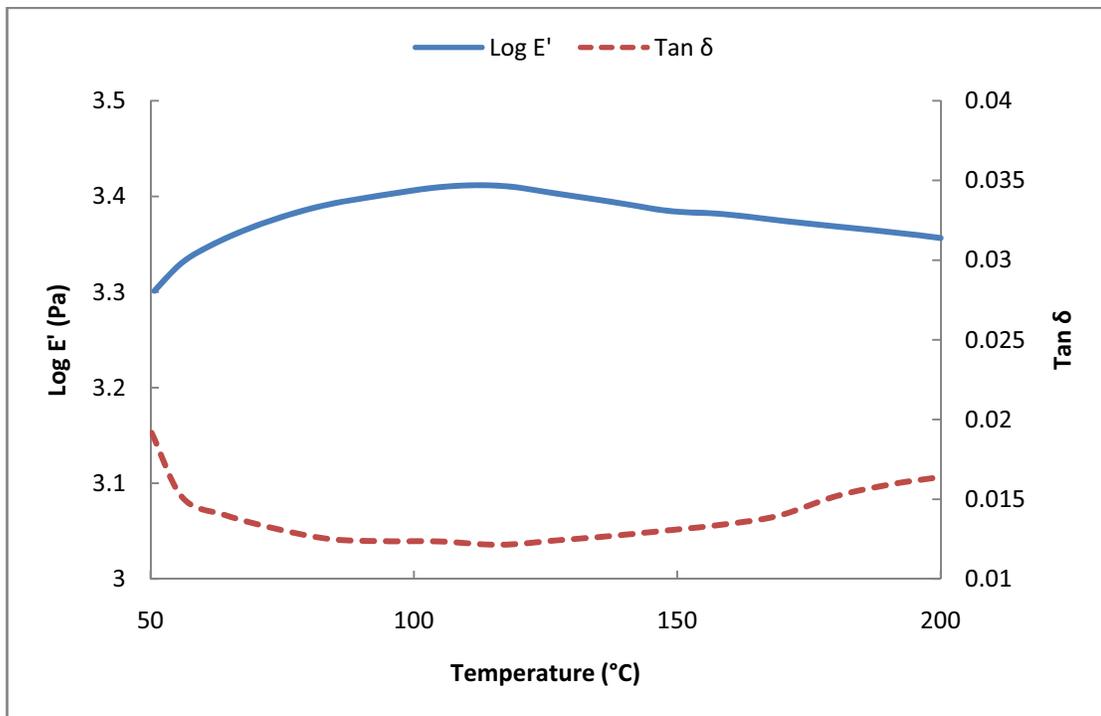
Figure 3.2

Dynamic mechanical response curves showing storage modulus (E') and damping term (tanδ) for pMDI-acetone adhesive as a function of temperature (T)
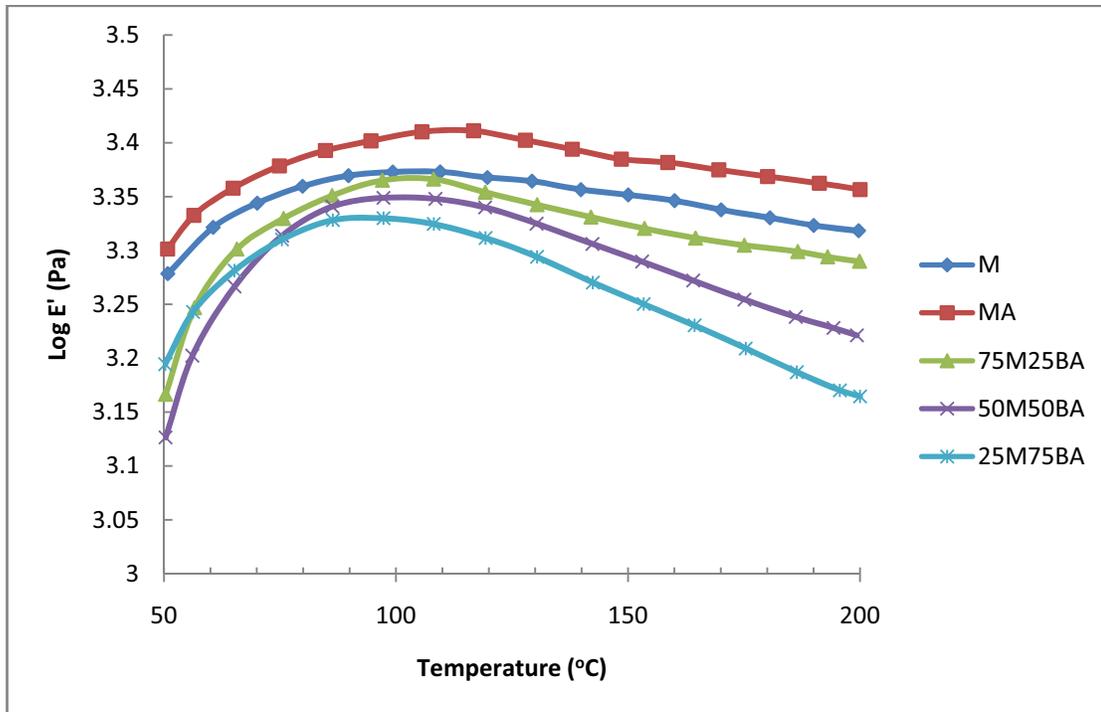
Figure 3.3

Dynamic mechanical response curves showing storage modulus (E') for all adhesives as a function of temperature (T).

M: pMDI; MA: adhesive composed of pMDI and acetone; 75M25BA: adhesive composed of 75% pMDI, 25% bio-oil and acetone; 50M50BA: adhesive composed of 50% pMDI, 50% bio-oil and acetone; 25M75BA: adhesive composed of 25% pMDI, 75% bio-oil and acetone
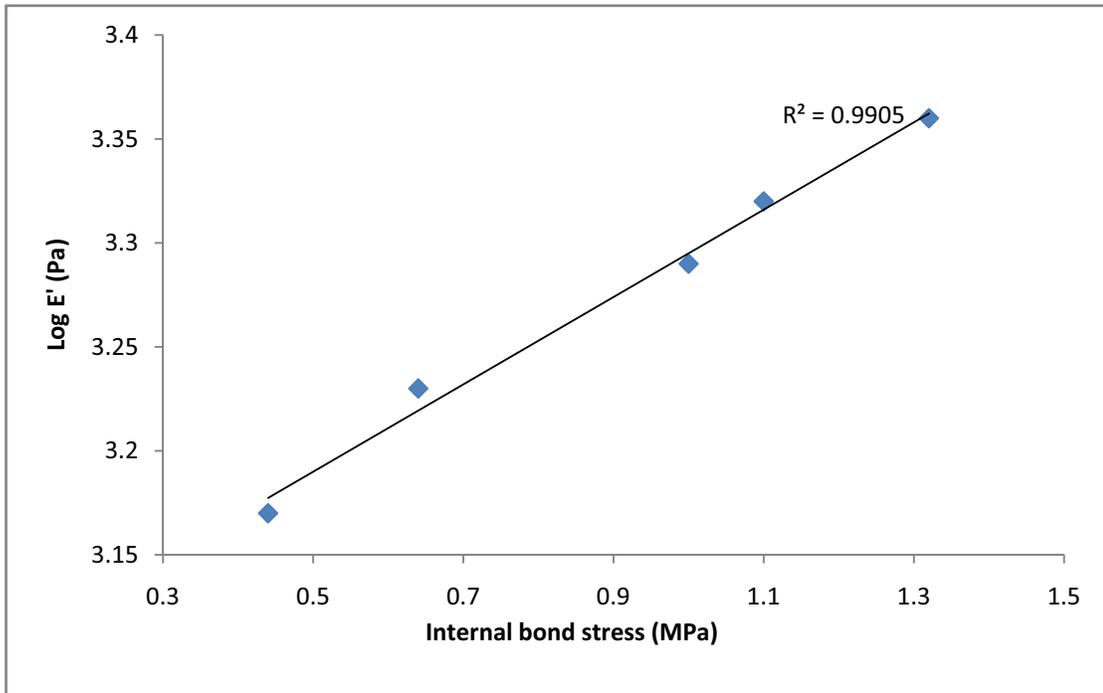
Figure 3.4

Correlation between the mean IB of the flakeboards for each adhesive type and the mean storage modulus of the adhesives at the temperature range from 180 to 200 $^{\circ}$C (from the core temperature to the face temperature)
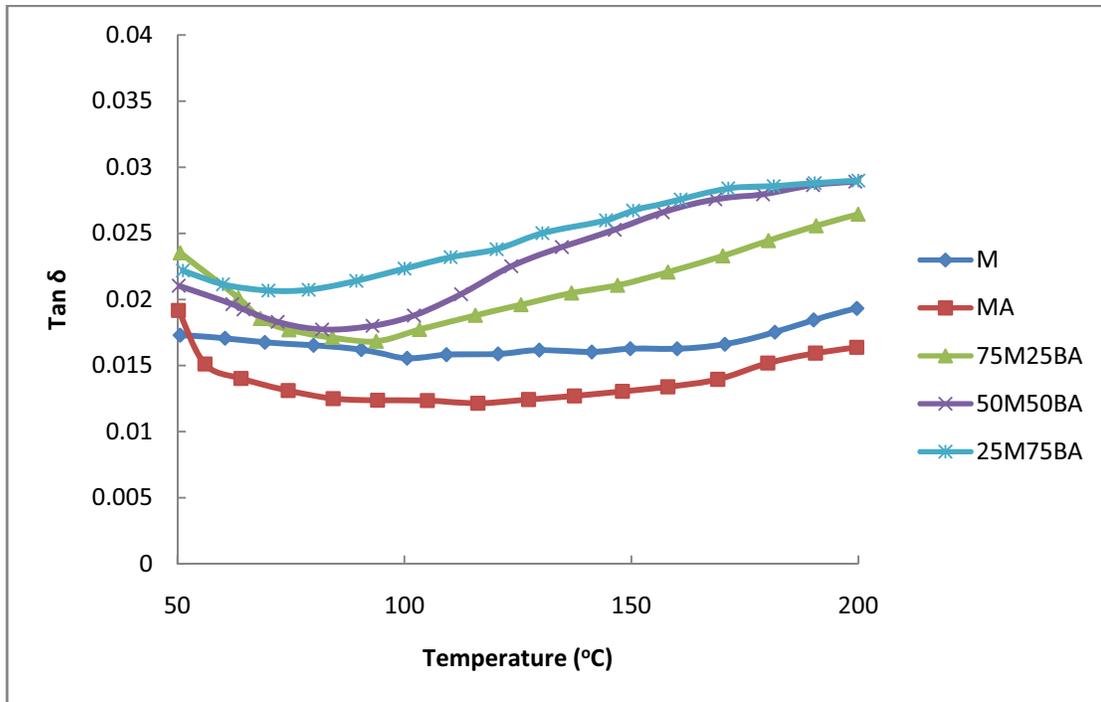
Figure 3.5

Dynamic mechanical response curves showing damping term (tanδ) for all adhesives as a function of temperature (T).

M: pMDI; MA: adhesive composed of pMDI and acetone; 75M25BA: adhesive composed of 75% pMDI, 25% bio-oil and acetone; 50M50BA: adhesive composed of 50% pMDI, 50% bio-oil and acetone; 25M75BA: adhesive composed of 25% pMDI, 75% bio-oil and acetone
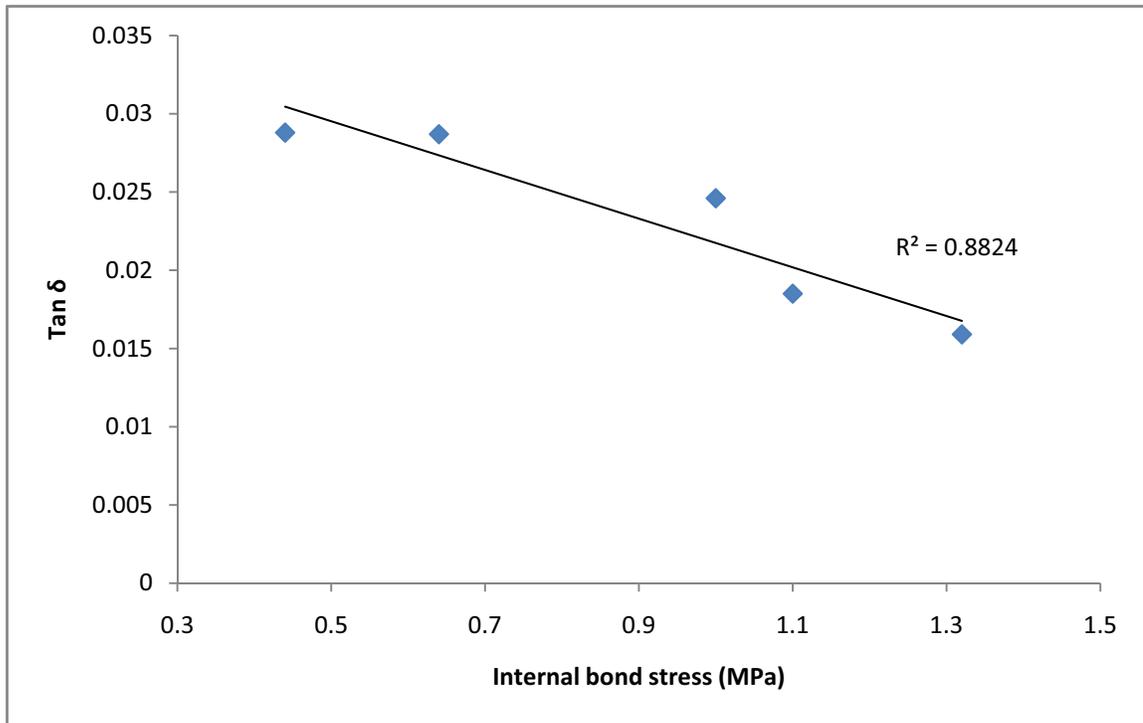
Figure 3.6

Correlation between the mean IB of the flakeboards for each adhesive type and the mean tanδ of the adhesives at the temperature range from 180 to 200 °C (from the core temperature to the face temperature)

CHAPTER IV

CONCLUSIONS

In this study, an investigation of pyrolysis bio-oil as part of a pMDI binder system was conducted.   Pyrolysis bio-oil obtained from the fast pyrolysis process of pine wood was mixed with pMDI resin to form three adhesive binder systems.   The adhesive was blended with flakes to fabricate flakeboard.   The effects of the resin content and the bio-oil content on the physical and mechanical properties were examined. These properties included IB, MOR, MOE, TS, and WA.   DMA was also employed to investigate the thermal curing behavior of the adhesives.   DMA tests were performed on these samples at a temperature range of 50 to 200 $^{\circ}$C.   A heating rate of 10 $^{\circ}$C min^{-1} with a 1 Hz frequency and strain amplitude of 15 μm were used for the DMA testing.

The addition of acetone into the adhesive system successfully reduced the viscosity of adhesive for the easiness of the spraying application.   As the bio-oil content in adhesives increased, the mechanical and physical properties of the composites (IB, MOE, MOR, TS and WA) decreased.   Even though adding the bio-oil tended to lower the mechanical strength of the flakeboard, the flakeboard with 25% bio-oil content showed comparable properties to those produced with pure pMDI.

The DMA results showed a good correlation with the mechanical properties of the composites.   The increase of bio-oil content in the adhesive binder system improved

curing speed but reduced adhesive strength. PMDI/acetone adhesive showed the best thermal mechanical properties among the five adhesive systems investigated. The bio-oil content of 25% had a similar curing behavior and bonding strength compared with the pure pMDI.

LITERATURE CITED

Baekeland L. H. 1909. Method of making insoluble products of phenol and formaldehyde. U.S. Patent 942,699.

Chelak W. and W. H. Newman. 1991. MDI high moisture content bonding mechanism, parameters, and benefits using MDI in composite wood products. Proceeding of the Washington State University International Particleboard/Composite Materials Series Symposium (USA) 25: 205-229.

Christiansen A. W., R. A. Follendbee, R. L. Geome, J.A. Koutsky and G. E. Myers. 1993. Phenol-formaldehyde resin curing and bonding in steam-injection pressing. Holzforschung 47: 76-82.

Demirbas A. and G. Arin. 2002. A overview of biomass pyrolysis. Energy Sources 24: 471-482.

Follensbee, R. A., J. A. Koutsky, A. W. Christiansen, G. E. Meyers and R. L. Geimer. 1993. Development of dynamic mechanical methods to characterize the cure state of phenolic resole resins. Journal of Applied Polymer Science 47: 1481-1486.

Gagnon M., C. Roy and B. Riedl. 2004. Adhesives made from isocyanate and pyrolysis oils for wood composites. Holzforschung 58: 400-407.

Gagnon M., C. Roy, D. Rodrigue, and B. Riedl. 2003. Calorimetric and rheological study of isocyanate-pyrolysis oil blends. Journal of Applied Polymer Science 89: 1362-1370.

Galbraith C. J. and J. L. Well. 1990. MDI binder: A profit-making alternative for OSB/waferboard. Wood adhesives 1990 Proceedings. Forest Products Society, Madison, WI, pp: 20-25.

Geimer R. L. and A. W. Christiansen. 1991. Adhesive curing and bonding: response to real time conditions. In: H. Chung-Yun, T. Bunichiro, B. Susan J., eds. Adhesives and bonded wood products: Proceedings of symposium. November 19-21.

Green D. W. and R. Hernandez. 1998. Codes and standards for structural wood products and their use in the United States. In: Proceedings of the Forest Products Study Group Workshop. 1998 June.

Guo Y., Y. Wang and F. Wei, 2001. Research progress in biomass flash pyrolysis technology for liquids production. Chemical Industry Engineering Progress 8: 13-17

Hiziroglu S. 2007. Oriented strand board as a building material. Food Technology Fact Sheet. FAPC 145: 1-4

Kim, M. G., W. L-S Nieh and R. M. Meacham. 1991. Study on the curing of phenol-formaldehyde resol resins by dynamic mechanical analysis. Industrial & Engineering Chemistry Res 30(4): 798-803.

Kim, M. G. and C. Watt. 1996. Effects of urea addition to phenol formaldehyde resin binders for oriented strandboard. Journal of Wood Chemistry and Technology 16(1): 21-34.

Kuzak, S. G. and A. Shanmugam. 1999. Dynamic mechanical analysis of fiber-reinforced phenolics. Journal of Applied Polymer Science 73: 649-658.

Laufenberg T. L. 1984. Flakeboard fracture surface observations and correlation with orthotropic failure criteria. 1984. Journal of the Institute of Wood Science. 10 (56): 57-65.

Marcinko J. J., S. Devathala, P. L. Rinaldi and S. Bao. 1998. Investigating the molecular and bulk dynamics of pMDI/wood and UF/wood composites. Forest Products Journal 48 (6): 81-84.

Marcinko J. J., P. L. Rinaldi and S. Bao. 1999. Exploring the physicochemical nature of pMDI/wood structural composite adhesion. Forest Products Journal 49 (5): 75-78.

Marra A. 1992. Technology of wood bonding: Principles in practice. New York. Van Nostrand Reinhold.

Miller T. R. and J. W. Rosthauser. 2002. Aqueous mixed pMDI/phenolic resin binders for the production of wood composite products. U.S. Patent 6,416,696.

Myers G. E., A. W. Christiansen, R. L.Geimer, R. A. Follensbee and J.A. Koutsky. 1991. Phenol-formaldehyde resin curing and bonding in steam-injection pressing. I resin synthesis, characterization, and cure behavior. Journal of Applied Polymer Science 43(2): 237-250.

Oasmaa A. and Czernik S. 1999. Fuel oil quality of biomass pyrolysis oils-state of the art for the end-users. Energy Fuels 13: 914-921.

Papadopoulos A. N., C. A. S. Hill, E. Traboulay and J. R. B. Hague. 2002. Isocyanate resins for particleboard: PMDI vs EMDI. Holz als Toh- und Werkstoff 60: 81-83.

Schmidt R. G. 1998. Aspects of wood adhesion: Application of ^{13}C CP/MAS NMR and fracture testing. Dissertation for doctor of philosophy. Virginia Polytechnic Institute and State University.

Scholze B. and Meier D. 2001. Characterization of the water-insoluble fraction from pyrolysis oil (pyrolytic lignin) Part I. PY-GC/MS, FTIR, and functional groups. Journal of Analytical and Applied Pyrolysis 60:41-54.

Steiner P. R. and S. R. Warren. 1981. Rheology of wood-adhesive cure by torsional braid analysis. Holzforschung 35 (6): 273-278.

Umemura K., A. Takahashi and S. Kawai. 1998. Durability of isocyanate resin adhesives for wood I: thermal properties of isocyanate resin cured with water. Journal of Wood Science. 44: 204-210.

Umemura K., A. Takahashi and S. Kawai. 1999. Durability of isocyanate resin adhesives for woodII: effect of the addition of several polyols on the thermal properties. Journal of Applied Polymer Science 74: 1807-1814.

Umemura K., S. Kawai and H. Sasaki. 1996. Curing behavior of wood adhesives under high steam pressure. The Journal of Adhesion 59: 87-100.