Flakeboard Bonded with Polymeric Diphenylmethane Diisocyanate/ Bio-Oil Adhesive Systems

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Abstract

The objective of this study was to investigate the feasibility of using the bio-oil generated from the Mississippi State University's (MSU's) fast pyrolysis process as part of a polymeric diphenylmethane diisocyanate (pMDI) binder system for flakeboard production. The bio-oil was obtained from the pyrolysis process of pine wood (*Pinus* spp.) at the MSU bio-oil laboratory. The effect of the resin content and the pMDI to bio-oil ratio on the physical and mechanical properties of the flakeboards was examined. The properties include internal bond, modulus of rupture, modulus of elasticity, thickness swelling, and water absorption. The effect of adding acetone into the pMDI/bio-oil resin on the properties of flakeboards was also investigated. The results showed that the incorporation of acetone reduced the viscosity of the adhesive by up to 67 percent, from which the efficiency for resin spraying on the flakes was improved. The higher the bio-oil content, the lower the mechanical strength of flakeboard obtained. However, the pMDI resin with a bio-oil content of 25 percent showed comparable bonding properties to those of pure pMDI resin.

Under high temperature and pressure conditions, flakeboards are made of wood strands and/or flakes with waterproof adhesives. Over the last two decades, there has been a tremendous growth in the wood-based panel market (Zhu et al. 1998). Polymeric diphenylmethane diisocyanate (pMDI) is one of the primary adhesives used in flakeboards. Although there are advantages associated with pMDI adhesives, such as a greater tolerance for higher moisture content wood, lower press temperatures, shorter press cycles, less energy consumption, and lower resin application ratio, the issues of adhesion to press platen and high costs may limit its industrial application. Efforts have been made to mix pMDI with other adhesives, such as urea formaldehyde adhesive (UF), melamine formaldehyde adhesive, and phenol formaldehyde adhesive (PF; Deppe 1977; Tinkelenberg et al. 1982; Pizzi and Walton 1992; Hao and Liu 1993a, 1993b; Pizzi et al. 1995; Grigoriou 2000; Frick and Motter 2001; Simon et al. 2002).

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 that bonded purely with pMDI resin. Pizzi (1993) also developed a UF-pMDI binder system for plywood by adding pMDI to the UF resin, followed by mixing and adding other components, such as NH_4Cl, a commonly used UF hardener. Hao and Liu (1993a, 1993b) found that spraying the emulsified pMDI (EMDI)–UF mixture without adding NH_4Cl gave a better result than when a hardener was added.

Simon et al. (2002) explored the copolymerization between the UF and pMDI and found that the co-reaction between the UF and pMDI could improve the bonding strength by forming methylene cross-links instead of the urethane bridges (a small proportion of the cross-linking reactions). This reaction occurred in the presence of water and hardener. Without the hardener, less co-reaction occurred. No reaction with the pMDI was observed when water was introduced into the UF-pMDI mixture by the addition of UF resin.

Research on PF-pMDI binder systems has also been reported for wood composites (Rosthauser and Detlefsen 2001, Rosthauser and Schmelzer 2001, Preechatiwong et al. 2007). Because of the great difference in polarity and incompatible chemical functional groups between the two adhesives, which causes inconsistent mixing, Wang et al.

(2004) replaced the pMDI with an EMDI. However, the resulting adhesive did not present a combination of appropriate storage life and binding performance (Miller and Rosthauser 2002). By acylating PF resin, Miller and Rosthauser (2002) found that the esterification of phenolic oxygen greatly reduced the reactivity of the PF portion in the resin mix when combining the pMDI to form a single-phase liquid material with a storage life of more than 2 weeks at room temperature. As described in a patent on the solid PF and pMDI binder system (Rosthauser and Detlefsen 2001), solid PF powders were directly added into the pMDI to form a suspension system that 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 Shui-Tung 1993), and a much higher IB for particleboards could be achieved from the solid PF-pMDI system than that from 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) were also researched to mix with pMDI resin to form a binder system for wood-based composites.

Fast pyrolysis of biomass is conducted at a high heating rate under high temperature in the absence of oxygen. Biomass decomposes to generate liquids, vapors, and solid chars. Generally, fast pyrolysis of biomass produces 60 to 75 percent by weight of liquid pyrolysis bio-oil, 15 to 25 percent by weight of chars, and 10 to 20 percent by weight of vapors (Mohan et al. 2006). Because liquid pyrolysis bio-oil is a multicomponent mixture of different size molecules derived from depolymerization and fragmentation of cellulose, hemicellulose, and lignin, over 99 percent of pyrolysis bio-oil is composed of water, acids, alcohols, aldehydes, esters, ketones, sugars, phenols, guaiacols, syringols, furans, lignin-derived phenols, and extractible terpene with multifunctional groups. As a renewable biomass source, bio-oil is currently used as an energy source and a feedstock for chemical production (Mohan et al. 2006). Bio-oil could be used as a proper component in pMDI/bio-oil binder system for oriented strand board or particleboard because at least 80 percent 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), although many of them do not serve as cross-linking agents and adhesion promoters. Studies to replace part of the phenol with bio-oil to produce bio-oil/PF adhesives (Chum et al. 1989, Himmelblau and Grozdits 1998, Roy et al. 1999, Amen-Chen et al. 2002, Chan et al. 2002) showed that the bio-oil could participate in the phenol/formaldehyde reaction, but the bonding performance of these adhesives was not satisfactory. Recently, the research (Gagnon et al. 2004) on a pMDI/bio-oil binder system that was derived from softwood bark bio-oil and pMDI indicated that the bio-oil produced by the pyrolysis process could replace about 30 to 40 percent (by weight) of the pMDI in a 4 percent adhesive-containing particleboard. By applying the adhesive, the mechanical properties and thickness swelling of homogeneous boards exceeded the minimum requirements in ANSI A208.1-1993 (American National Standards Institute 1993) and ASTM 1037-96a (ASTM International 1996) standards. It was suggested that the bio-oil could be mixed at a percentage as high as 40 percent with pMDI and obtained acceptable interior grade particleboard properties. In addition, the issue of bonding to

the press platen was also effectively resolved by using the bio-oil.

The objective of this research was to investigate the feasibility of using the bio-oil generated from Mississippi State University fast pyrolysis process as part of the pMDI/bio-oil binder system for flakeboard.

Materials and Methods

Wood flakes were obtained from Norbord Inc. in Guntown, Mississippi. The moisture content (MC) of the flakes was 15 to 18 percent. The flakes were further dried in an oven at the laboratory to an MC of 4 percent. The MC was determined by a moisture balance (CSC Scientific Company, Fairfax, Virginia). The bio-oil used in this study was made from the fast pyrolysis process of pine wood (*Pinus* spp.) in the auger reactor at Mississippi State University. Pine wood particles were pyrolyzed at 450°C with a retention time of approximately 2 seconds. After biomass residuals were removed by a charcoal filter, the bio-oil obtained, which had a water content of 18 percent and a viscosity of 368 mPa·s at 25°C, was placed in a refrigerator with a constant temperature of 4°C.

The pMDI resin (Lupranate M20FB) was supplied by the BASF Chemical Company in Wyandotte, Michigan. It was a dark yellow liquid with a viscosity of 226 mPa·s at 25°C. The resin was stored at 25°C ± 3°C in a sealed container under a relative humidity of 60 ± 5 percent.

After being weighed, the pyrolysis bio-oil was poured into a beaker and mixed with pMDI at various mixing ratios (Table 1). To reduce the viscosity of the adhesive system, acetone was added into the bio-oil. The bio-oil–acetone mixture was stirred by hand to make it uniform and then poured into another beaker containing pMDI. The mixed adhesives began to produce bubbles, and thick foam appeared on the top of the resin after about 8 minutes. The bubbles were attributed to the generation of CO_2, which resulted from an isocyanate–water or isocyanate–carboxylic acid reaction. When the mixture was prepared at a lower temperature, the reaction was slower. Under a quick reaction between the pMDI and the bio-oil, the adhesive binder system was blended and sprayed onto the wood flakes within 8 minutes. During blending, the flakes were placed in the blender first and then the wax and the mixed adhesives were pumped through plastic tubes separately and

Table 1.—Experiment design and board manufacture parameters.[a]

Parameter	Amount
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 ovendry flake weight)
Board construction	One uniform layer, random orientation
Board dimension (cm)	60 (L) by 60 (W) by 1.1 (T)
MC of flakes (%)	4
Water content of bio-oil (%)	18
Water content of wax (%)	50
Wax content (%)	1 (based on ovendry flake weight)
Solvent	Acetone
Solvent content (%)	10 (based on bio-oil solid weight)
No. of replicates	2
Total no. of boards	30

[a] MDI = diphenylmethane diisocyanate; L = length; W = width; T = thickness; MC = moisture content.

sprayed onto the flakes with an atomizer. After about 5 minutes of blending, the flakes were removed from the blender and weighed. Before the flakes were randomly placed on the platen by hand to form a 60 by 60-cm mat, a no stick cooking spray obtained from a local store was sprayed onto the platen to prevent the bonding between the formed mat and the platen.

A Dieffenbacher hot press with a platen dimension of 90 by 90 cm (3 by 3 ft) was used for the flakeboard pressing. Each mat was loaded into the hot press and pressed for 5 minutes at a pressure of 10 MPa at 200°C and a press closing time of 0.5 minute. After the boards were cooled, they were cut into small test samples using the same cutting pattern and then placed into a conditional chamber with a temperature of 20°C ± 3°C and a relative humidity of 65 ± 5 percent until equilibrium. A total of 30 boards with 15 board types (two replicates for each board type), including the four control boards, were fabricated (Table 1).

IB, modulus of rupture (MOR), modulus of elasticity (MOE), density, and thickness swell (TS) of the flakeboards were tested based on the procedure described in ASTM D1037-06a (ASTM International 2006).

For the static bending testing, the three-point bending method was followed using the INSTRON testing machine. The MOE and MOR properties, averaged from six replicates (from two boards with three samples cut from each board), were obtained. The dimensions of each test sample were 33.0 by 7.6 by 1.1 cm. For the IB testing, 12 samples (six samples of each of two boards), each sized 5.1 by 5.1 by 1.1 cm, were used. The IB specimens were bonded with hot melt adhesive to the aluminum blocks, which were attached to the fixture for the Instron testing machine. The length, width, thickness, and weight of each sample were measured prior to the mechanical testing.

The viscosity of the adhesives was measured in accordance with the procedure described in ASTM D445 (ASTM International 2004). For each adhesive mix, two kinematic viscosities (determined value) were obtained from measuring the flow time and the calibration constant of the viscometer. The dynamic viscosity was determined by the density of the resin, while the kinematic viscosity was the average of the two acceptable determined values. The density of the boards for each resin composition was an average of 12 samples (six samples of each of two boards), each sized 5.1 by 5.1 by 1.1 cm.

Four samples (two samples of each of two boards), each sized 15.2 by 15.2 by 1.1 cm, were used to determine the TS and WA. Before testing, the length, width, thickness (the average of four measurements located at the four corners 1 in. from the edge), and weight of each sample were measured. After the samples were submerged in water at room temperature for 24 hours, the dimensions and weight were measured again, and TS and WA were calculated based on the procedure described in ASTM D1037-06a (ASTM International 2006).

Results and Discussion

Viscosity

Acetone (a polar solvent) was reported to reduce the viscosity of pyrolysis bio-oil (Roy et al. 1999). In order to use the spraying method efficiently, the acetone was added into the bio-oil to reduce the viscosity of the adhesive system. Table 2 shows the viscosities of the adhesive

Table 2.—*Viscosity of the resins with different mixing formulations.*

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

[a] The resin codes represent the indicated resin compositions.
[b] pMDI = polymeric diphenylmethane diisocyanate.
[c] Based on pMDI weight.
[d] Based on bio-oil solid weight.

systems with and without the acetone. The viscosity of the bio-oil decreased from 368 to 121 mPa·s as a result of the incorporation of acetone. The effect of the pMDI/bio-oil composition ratio on the viscosity was also reduced. Roy et al. (1999) also reported that adding acetone could not only reduce the viscosity, but also stabilize and homogenize the adhesive binder systems.

Although the viscosity of the adhesive was reduced up to 67 percent by adding acetone into the binder system, acetone may behave as a volatile organic compound due to its relatively high volatility. From an environmental standpoint, alternative solvents with less volatility, such as methyl ethyl ketone, would be a preferable replacement for acetone.

Internal bond

As shown in Table 3 and Figure 1, for all the five resin mixes, IB increased as the resin content increased and reached the highest value when the resin content was 7 percent. At 7 percent resin content, the IB for the samples made from 25 percent bio-oil and 75 percent pMDI (1.4 MPa) is comparable to those made from 100 percent pMDI (1.44 MPa). The IB of the flakeboards significantly reduced when the bio-oil content was higher than 25 percent.

As the bio-oil content in the adhesive binder systems increased from 0 to 75 percent, at 3, 5, and 7 percent resin content, the IB values of the flakeboards decreased by 62, 57, and 62 percent, respectively.

Adding acetone into pMDI resulted in higher IB values for the flakeboards compared with those bonded with the pure pMDI. Adding acetone improved uniformity of the bond lines between the flakes.

Furthermore, some factors, such as mat moisture content, pressing schedule, resin type, and board thickness, could affect the mechanical property during the hot pressing. As shown in Table 1, the 18 percent MC in the bio-oil would increase the overall mat moisture content, which could interfere with the adhesive bonding and reduce the IB property. Some large molecules, such as tannin/lignin derivatives, in the bio-oil may need a longer time to spread to the wood surface, which may require a longer hot-pressing time.

Bending properties

Table 3 and Figures 2 and 3 illustrate the bending properties (MOR and MOE) of flakeboards made from the adhesive binder systems. The flakeboards that bonded with

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Table 3.—Mechanical and physical properties of flakeboard bonded with different resin formulations.[a]

Panel no.	Resin application rate (%)	Resin code[b]	Board density (g/cm^3)	IB (MPa)	MOR (MPa)	MOE (MPa)	TS (%)	WA (%)
1	3	M	0.79	0.65	46.0	9,182	20.0	25.1
2	5	M	0.84	1.21	56.4	9,737	14.9	19.0
3	7	M	0.88	1.44	63.1	10,536	13.1	14.2
4	3	MA	0.81	0.81	54.1	8,711	22.0	27.9
5	5	MA	0.85	1.34	58.4	8,713	16.6	21.4
6	7	MA	0.87	1.83	64.8	10,507	13.2	15.6
7	3	75M25BA	0.85	0.58	43.6	7,908	26.5	26.4
8	5	75M25BA	0.85	1.01	49.5	8,523	20.5	22.6
9	7	75M25BA	0.85	1.4	51.8	9,005	14.5	13.0
10	3	50M50BA	0.79	0.5	43.9	6,721	27.1	28.8
11	5	50M50BA	0.81	0.69	46.5	6,826	21.9	24.4
12	7	50M50BA	0.80	0.74	48.4	8,525	18.9	18.5
13	3	25M75BA	0.76	0.25	33.6	6,399	45.7	40.7
14	5	25M75BA	0.84	0.52	35.7	6,585	34.7	34.1
15	7	25M75BA	0.81	0.55	46.7	8,177	29.8	32.6

[a] IB = internal bond; MOR = modulus of rupture; MOE = modulus of elasticity; TS = thickness swelling; WA = water absorption.
[b] Resin codes are defined in Table 2.

pMDI and acetone mixture showed the highest MOR among the three resin contents while demonstrating the lowest value at the pMDI/bio-oil ratio of 25/75. The MOR of flakeboards decreased as the pMDI/bio-oil ratio decreased. As the bio-oil content in the adhesive binder systems increased from 0 to 75 percent, at 3, 5, and 7 percent resin content, the MOR values of the flakeboards decreased by 30, 32, and 22 percent, respectively.

As with the MOR results, at each of the three resin contents, the highest MOE was obtained when the flake-board was bonded with pMDI/acetone mix. The MOE of the flakeboards decreased as the pMDI/bio-oil ratio was decreased. As the bio-oil content in the adhesive binder systems increased from 0 to 75 percent, at 3, 5, and 7 percent resin content, the MOE values of the flakeboards decreased by 27, 37, and 26 percent, respectively.

However, the rates of decrease in MOR and MOE as the pMDI/bio-oil ratio decreased were slower than that of IB, indicating that the IB property is more affected by the incorporation of bio-oil into the binding system than that for the bending properties. The bending properties may not only reflect adhesive bonding, but also many other factors, such as material lay-up and press cycles.
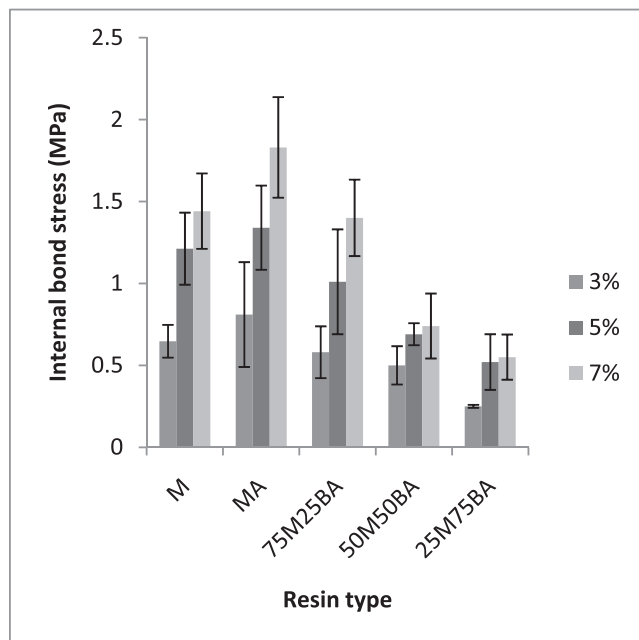

Figure 1.—Internal bond of flakeboards bonded with the polymeric diphenylmethane diisocyanate (pMDI)/bio-oil adhesives with different bio-oil contents. M = pMDI; MA = adhesive composed of pMDI and acetone; 75M25BA = adhesive composed of 75 percent pMDI, 25 percent bio-oil, and acetone; 50M50BA = adhesive composed of 50 percent pMDI, 50 percent bio-oil, and acetone; 25M75BA = adhesive composed of 25 percent pMDI, 75 percent bio-oil, and acetone.
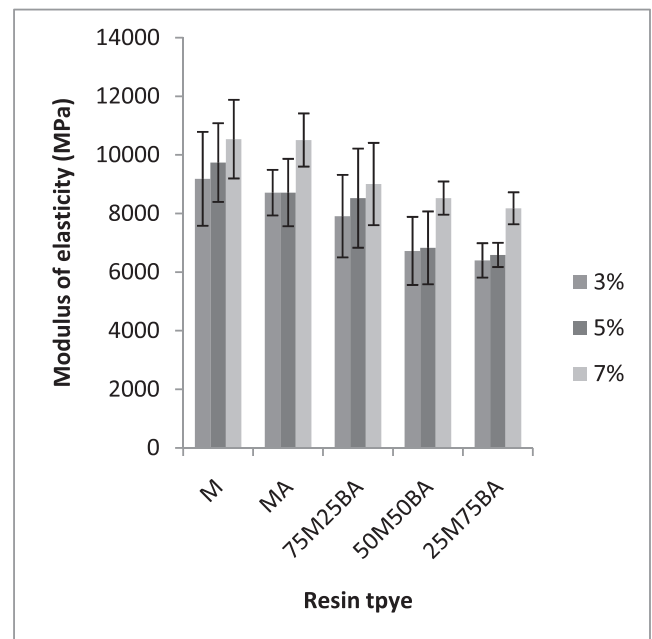

Figure 2.—Modulus of elasticity of flakeboards bonded with the polymeric diphenylmethane diisocyanate (pMDI)/bio-oil adhesives with different bio-oil contents. Resin types are defined in Figure 1 legend.
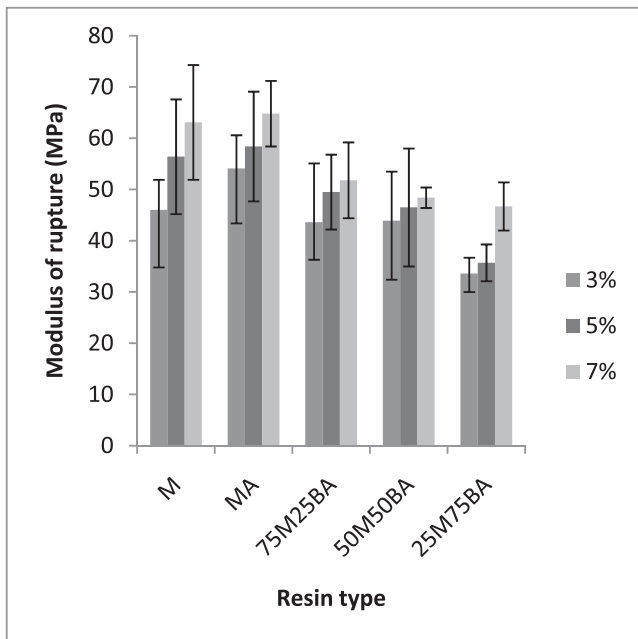
Figure 3.—Modulus of rupture of flakeboards bonded with the polymeric diphenylmethane diisocyanate (pMDI)/bio-oil adhesives with different bio-oil contents. Resin types are defined in Figure 1 legend.
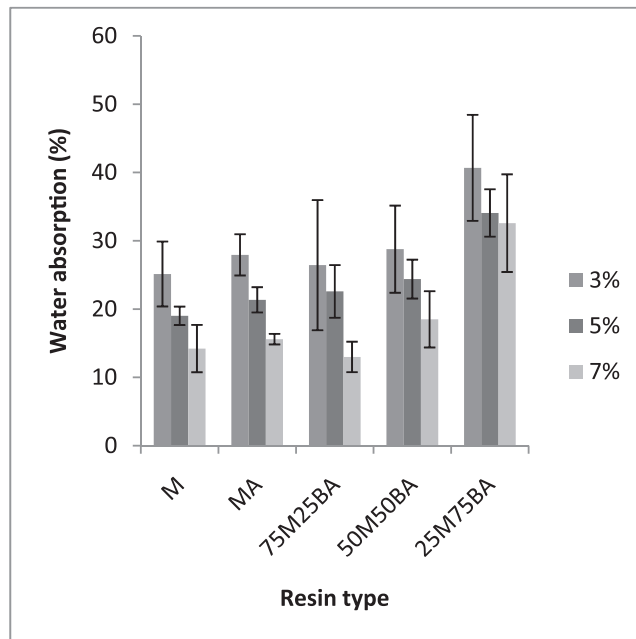

Figure 5.—Water absorption of flakeboards bonded with the polymeric diphenylmethane diisocyanate (pMDI)/bio-oil adhesives with different bio-oil contents. Resin types are defined in Figure 1 legend.

Thickness swelling and water absorption

The results of the 24-hour immersion test in water are shown in Table 3 and Figures 4 and 5. TS and WA increased as the pMDI/bio-oil ratio decreased for each of the three resin contents. As the bio-oil content in the adhesive binder systems increased from 0 to 75 percent, at 3 percent resin
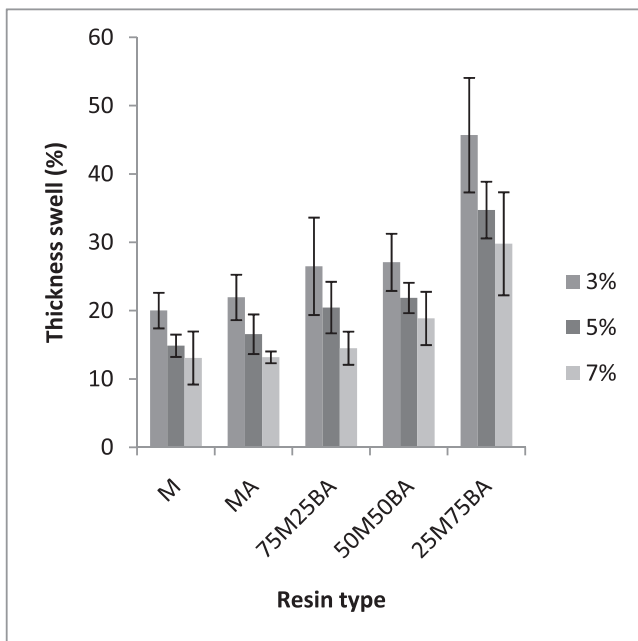

Figure 4.—Thickness swelling of flakeboards bonded with the polymeric diphenylmethane diisocyanate (pMDI)/bio-oil adhesives with different bio-oil contents. Resin types are defined in Figure 1 legend.

content, the TS and WA values increased by 129 and 62 percent, respectively; at 5 percent resin content, the TS and WA values increased by 133 and 79 percent, respectively; and at 7 percent resin content, the TS and WA values increased by 127 and 130 percent, respectively. Flakeboards that bonded with the pure pMDI showed the lowest TS and WA, while the flakeboards that bonded with the pMDI/bio-oil of 25/75 gave the highest TA and WA.

TS can be affected by various parameters, 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 walls (Marcinko et al. 1998), which causes bulking action, and the bulked wood cell wall is kept in a swollen state. In this swollen condition, wood cannot expand further in response to water (Rowell and Ellis 1981). In this study, since the bio-oil in the binder system increased the amount of large molecules (such as tannin/lignin derivatives), the higher the bio-oil content, the less diffusion and penetration of adhesive into the flakes. As a result, the wood components with less resin penetration tended to absorb more water and swell more. Moreover, the hydrophilic chemicals in the bio-oil, such as carboxylic acids and alcohols, tended to attract water when the samples were immersed in water (Gagnon et al. 2004).

Conclusions

Flakeboards were fabricated from wood flakes with the adhesive binder system formed by mixing the liquid products obtained from the fast pyrolysis process of pine wood and the commercial pMDI resin. The effect of the resin content and the mixture ratio of the binder system on the physical and mechanical properties including IB, MOR, MOE, TS, and WA of the flake-based composites were examined.

As the bio-oil content in the adhesive binder systems increased from 0 to 75 percent, at 7 percent resin content, the IB, MOE, and MOR values of the flakeboards decreased by 62, 26, and 22 percent, respectively, while the TS and WA values increased by 127 and 130 percent, respectively. The effect of adding bio-oil is greater on the IB property than on the bending properties of the flakeboard. The viscosity of the adhesive was reduced up to 67 percent by adding acetone into binder systems, which helped the resin application process. At 7 percent resin content, the bonding property of the flakeboards made using the adhesive with the bio-oil content of 25 percent was comparable to that with pure pMDI.

Acknowledgments

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