

# Dynamic Mechanical Properties of Polymeric Diphenylmethane Diisocyanate/Bio-Oil Adhesive System

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## Abstract

Bio-oil obtained from the pyrolysis of pine wood was mixed with polymeric diphenylmethane diisocyanate (pMDI) to form an adhesive binder system for flakeboard. Acetone was added for reducing the viscosity of the adhesive system. The thermal properties and curing behavior of five different adhesive mixes were examined using dynamic mechanical analysis (DMA). Temperature scans were performed in a range of 50°C to 200°C with a heating rate of 10°C/min, frequency of 1 Hz, and strain amplitude of 15  $\mu\text{m}$ . Results indicated that less time was needed to reach the maximum storage modulus of the adhesive mix with an increase in bio-oil content. The adhesive with the pMDI/bio-oil ratio of 25/75 presented the fastest curing speed but the lowest modulus value at temperatures of approximately 100°C. The pMDI-acetone adhesive showed the best thermal mechanical properties among the five adhesive binder systems.

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Liquid polymeric diphenylmethane diisocyanate (pMDI) can easily wet the wood surface and penetrate into the wood substrate (Scoville 2002) due to the rich hydroxyl groups ( $-\text{OH}$ ) in wood. pMDI resins are terminated in isocyanate groups ( $-\text{N}=\text{C}=\text{O}$ ), which readily react with wood hydroxyl groups to form urethane linkages. Moreover, the pMDI resin cures by reacting with water in wood and creating urea linkages to construct a rigid polar network (Wittman 1976, Rowell and Ellis 1981), which plays an important role contributing to the adhesion properties of pMDI. This hydrolytic stability of pMDI allows the use of wood flakes with higher moisture content compared with phenol-formaldehyde (PF) resin. However, the pMDI resin may cause difficulties in the composite processing due to its high reactivity, adhesion to platens, lack of cold tack, high cost, and special storage requirements (Rosthauser and Schmelzer 2003). In general, the pMDI resin has been used only for the cores of the mat-forming wood composites (Gagnon et al. 2004).

Interest has arisen in blending pMDI with low-cost materials such as amine-based resins or other polymers for the commodity products (Pizzi et al. 1995, Adcock et al. 1999, Simon et al. 2002, Rosthauser and Schmelzer 2003, Preechatiwong et al. 2007). It would be even more attractive if a reaction occurred between the pMDI resin and the substituted polymers other than a simple physical blending. pMDI has been blended with PF, urea-formaldehyde (UF), and melamine-formaldehyde (MF) resins (Pizzi et al. 1995, Enomoto et al. 2000, Weihong et al. 2004), in which the isocyanate group ( $-\text{NCO}$ ) reacted rapidly with the methylol

group ( $-\text{CH}_2\text{OH}$ ) in PF, MF, and UF resins (Pizzi et al. 1995). Adcock et al. (1999) claimed that co-reaction between UF and pMDI was not a preferred reaction and may be insignificant. Thermal analysis, such as thermomechanical analysis, dynamic mechanical analysis (DMA), and differential scanning calorimetry (DSC), was used to further elucidate such co-reactions. Simon et al. (2002) applied thermomechanical analysis and  $^{13}\text{C}$  nuclear magnetic resonance to study the reactivity between UF and pMDI. It was demonstrated that in the presence of water and under acidic hardening conditions, the bond strength between UF and pMDI was improved by the co-reaction between the pMDI and UF resin methylol groups to form methylene crosslinks. It was shown that the water in the UF resin did not react with pMDI isocyanate groups, but rather contributed considerably to the strength increase of the cured adhesive. Weihong et al. (2004) did the DSC analysis of the pMDI-UF resin and found that the acidic hardener

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NH<sub>4</sub>Cl inhibited the curing of emulsified pMDI (EMDI)–UF. They also found that the acidic hardener NH<sub>4</sub>Cl was sensitive to the adhesive application methods. It would be beneficial to the mechanical properties of the particleboard if the NH<sub>4</sub>Cl hardener was added after mixing EMDI and UF. The DSC results also showed that UF could react well with pMDI in the presence of acidic hardener.

Studies on the bio-oil and PF adhesive systems (Chum et al. 1989, Himmelblau and Grozdits 1999, Roy et al. 1999, Amen-Chen et al. 2002a, Chan et al. 2002) revealed that the bio-oil from the pyrolysis process consists of many different oxygenated organic compounds, some of which contain phenolic hydroxyl groups. The phenolic-rich bio-oil was used to substitute part of phenol in the PF resin formulations to produce bio-oil/PF adhesives for wood-based composites (Himmelblau and Grozdits 1999, Roy et al. 1999, Chan et al. 2002). Using DSC with varied scan speeds and isoconversional kinetics, Amen-Chen et al. (2002b) investigated the curing process of a PF resin with 25 percent of the phenol being replaced by bio-oil. It was shown that the curing mechanism of the 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) examined the molecular weight distribution for three PF resin formulations: (1) PF resin with 40 percent phenol substituted by bio-oil (40% PF resin), (2) PF resin with 50 percent phenol substituted by bio-oil (50% PF resin), and (3) pure PF resin. It was found that the performance of the 40 percent PF resin in a gel permeation chromatography graph was similar to that of the pure PF resin. However, the graph of the 50 percent PF resin had a broader peak at higher molecular weights. The DSC analysis showed that the phenol-substituted PF resin cured faster than the pure PF resin and also released more heat during the reaction. The bio-oil/PF resin had a higher crosslinking density than the pure resin.

It was reported by Gagnon et al. (2003) that at least 80 percent of the chemicals (sugars, carboxylic acids, phenols, alcohols, water, and tannin/lignin derivatives) in bio-oil were expected to react with pMDI, although many of them did not serve as crosslinking agents and adhesion promoters. Thus, the bio-oil could possibly be a suitable component in pMDI/bio-oil binder system for oriented strand boards or particleboards. Using DSC, Gagnon et al. (2003) investigated the reaction of pMDI and bio-oil at the bio-oil contents of 0, 20, 30, 35, 40, 50, 60, 70, 80, 90, and 100 percent in the adhesive binder systems. It was found that the chemical reaction between the pMDI and bio-oil occurred at a temperature below 100°C, even at room temperature (20°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. The heat of reaction reached its maximum when the bio-oil content was approximately 30 to 40 percent. Gagnon et al. (2003) also evaluated the evolution of viscosity as a function of time for different pMDI/bio-oil mixtures. The rheological study of various pMDI/bio-oil ratios indicated that the initial viscosity of the blends was proportional to the bio-oil content and the viscosity increased exponentially for all pMDI/bio-oil mixtures.

A recent study (Mao et al. 2011) investigated the effect of the resin content and the mixture ratio of the pMDI/bio-oil adhesive binder system on the physical and mechanical properties of flakeboards including internal bond, modulus

of rupture, modulus of elasticity, thickness swelling, and water absorption. The results showed that the pMDI resin with a bio-oil content of 25 percent showed comparable bonding properties to those of pure pMDI resin. However, the thermal properties and cure behaviors of the pMDI/bio-oil binder systems associated with wood flakes still remain to be investigated.

DMA has been widely used to compare the adhesive cure rates, examine the effects of additives on resin cure behavior and thermal stability, and help optimize hot-pressing conditions (Zheng 2002). DMA measures the dynamic mechanical properties of a material under a periodic force. These properties are generally expressed in three terms: storage modulus, loss modulus, and tan delta ( $\tan \delta$ ). The storage modulus ( $E'$ ) represents the stiffness of a viscoelastic material, loss modulus ( $E''$ ) represents the energy dissipated as heat, and  $\tan \delta$  is expressed as the ratio of loss modulus to storage modulus. A  $\tan \delta$  peak usually indicates a point at which a material is undergoing a transition (Christiansen et al. 1993). Thus, the dynamic properties provide information of the polymer mechanical behaviors. The objective of this study was to use the DMA to elucidate the thermal properties and cure behaviors of the pMDI/bio-oil binder systems.

## Materials and Methods

The pMDI (Lupranate M20FB) was provided 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.

The bio-oil produced from the fast pyrolysis process of pine wood in the Mississippi State University auger reactor (Mohan et al. 2006) was mixed with pMDI. Pine wood particles were pyrolyzed at a temperature of 450°C with a retention time of 2 seconds. The bio-oil was obtained after the biomass residuals were removed by a charcoal filter. The obtained bio-oil had a water content of 18 percent and a viscosity of 368 mPa·s at 25°C. The bio-oil was stored in a refrigerator with a constant temperature of 4°C before use.

Wood flakes with a target thickness of 0.05 cm were chopped from water-soaked pine wood blocks with a disk flaker and conditioned to equilibrium moisture content of approximately 10 percent in an environmental chamber at 20°C ± 3°C and 65 ± 5 percent relative humidity. These flakes were sealed in plastic bags to maintain a constant moisture content before testing. The adhesive used in the DMA testing were formed with different ratios of pMDI and bio-oil (Table 1). The bio-oil was weighed and then poured into a beaker. After adding the acetone, the bio-oil was stirred by hand to make it uniform. The bio-oil–acetone mixture was poured into the pMDI resin.

Wood flakes were cut to a dimension of 6.0 by 1.0 by 0.05 cm. The adhesive blend was brushed onto the wood flakes uniformly by a disposable brush, and the excess adhesive was then removed with a glass rod. The calculation of the resin spread was based on resin solids.

DMA tests were conducted using TA Instruments Model Q 800 with a fixed frequency mode, to examine the elastic modulus (stiffness) and mechanical damping (toughness) for the composites. A dual cantilever holder was devised to test the specimens in a bending mode. With a torque of 1.1 N·m, a wrench was used to tighten the clamp locking screws. For each test, two flakes were clamped together with a glue line

Table 1.—Composition of the adhesive binder systems in dynamic mechanical analysis.

Resin code <sup>a</sup>	Resin composition (%)		
	pMDI	Bio-oil	Acetone
M	100	0	0
MA	100	0	2.5 <sup>b</sup>
75M25BA	75	25	10 <sup>c</sup>
50M50BA	50	50	10 <sup>c</sup>
25M75BA	25	75	10 <sup>c</sup>

<sup>a</sup> The resin codes represent the indicated resin compositions.

<sup>b</sup> Based on pMDI weight.

<sup>c</sup> Based on bio-oil solid weight.

between the flakes. In order to produce a shear deformation perpendicular to the grain, the wood samples were clamped on the tangential surfaces so that the bending occurred in the radial direction (Fig. 1).

DMA temperature scans were performed in a temperature range of 50°C to 200°C. A heating rate of 10°C/min with a frequency of 1 Hz and strain amplitude of 15 μm were applied for all the DMA testing. For each condition, at least three replicates were used. Although slight variations were observed, the general trends of the DMA response among the replicates were similar to each other.

## Results and Discussion

During the curing of thermoset resins,  $\tan \delta$  peaks can often be assigned to gelation, a transition between the liquid and rubbery states to form resin networks, and to vitrification, which happens when resin converts to the glass state. Zheng (2002) investigated the effect of thermal behavior of wood flakes on the curing behavior of the pMDI binder system and found 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.

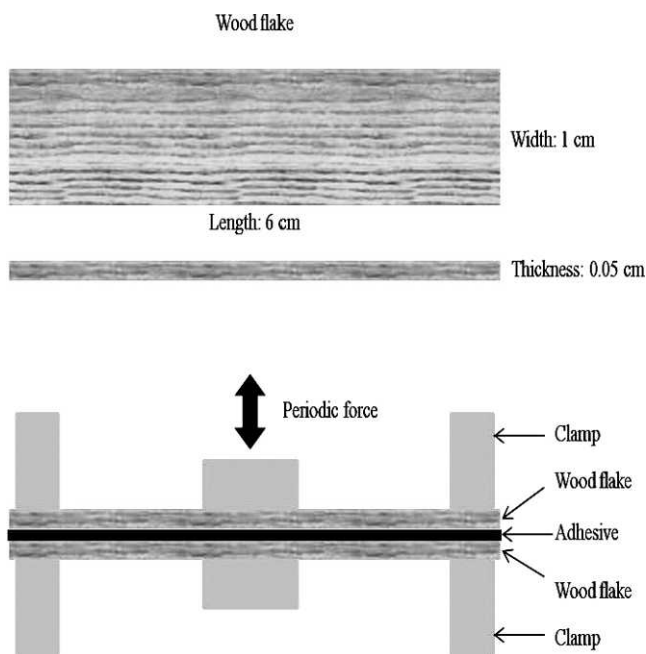


Figure 1.—Dynamic mechanical analysis sample sketch and test mode.

A thermal scan of pure pMDI on a pine flake is shown in Figure 2. No sharp increase in storage modulus or  $\tan \delta$  peak was observed, which was consistent with the results reported by Ni (1996) and Zheng (2002). After reaching the maximum value at around 100°C, the storage modulus decreased slightly until a temperature of 200°C was reached. However, gelation and vitrification peaks could not be observed from the  $\tan \delta$  curve.

Figure 3 shows the thermal scan of the pMDI-acetone binder system on wood flakes. Similar to the neat pMDI curves, neither a sharp increase in the storage modulus nor in the  $\tan \delta$  peak was observed. The storage modulus increased at the initial stage, reached its peak at 112°C, and decreased slightly. In regard to the storage modulus, the peak temperature for the pure pMDI was lower than that for the pMDI-acetone system, indicating that the pure pMDI cured faster than the pMDI-acetone system. This was because 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, which could probably be explained by the addition of acetone helping the adhesive penetrate the wood much deeper because of the lower viscosity.

A comparison of the storage modulus between the pure pMDI and the four adhesive binder systems is presented in Figure 4. As seen in Figure 4, the higher the bio-oil content used, the faster the curing speed and the shorter amount of time needed to reach the maximum storage modulus. Abundant chemical functional groups such as hydroxyl groups (–OH) are present on wood surface (Wittman 1976, Rowell and Ellis 1981). Isocyanate groups (–N=C=O) in pMDI resin can react readily with the hydroxyl groups on wood surface and form the urethane linkages. Moreover, the resin can cure by reacting with water in wood, and the urea linkages are formed to create a rigid and polar network. The reaction between pMDI and water is faster than with any

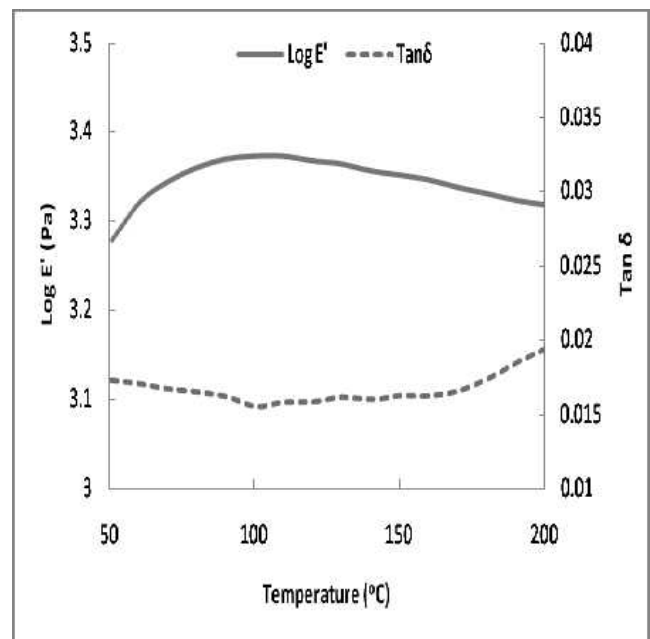


Figure 2.—Dynamic mechanical response curves showing storage modulus ( $E'$ ) and damping term ( $\tan \delta$ ) for pure polymeric diphenylmethane diisocyanate as a function of temperature.

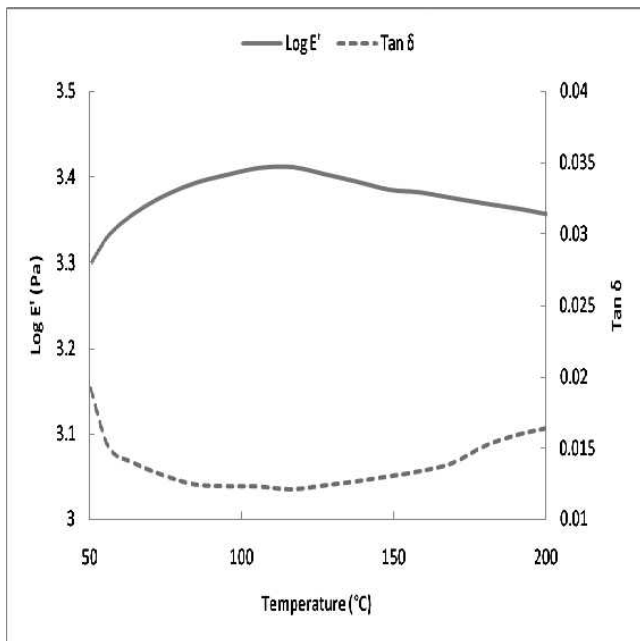


Figure 3.—Dynamic mechanical response curves showing storage modulus ( $E'$ ) and damping term ( $\tan \delta$ ) for polymeric diphenylmethane diisocyanate-acetone adhesive as a function of temperature.

other hydroxyl-containing compounds. When water is present, the water-pMDI reaction dominates all other reactions (Weaver and Owen 1995). As the bio-oil content in adhesive systems increases, more water is introduced. Since isocyanate groups react with water first to form urea linkages, the more water that is introduced, the faster the reactions are completed.

As seen from the storage moduli curves in Figure 4, at the storage modulus peaks, the 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. Among the five different adhesive systems tested in the experiments with different combinations of water content, viscosity, and isocyanate group content, the pMDI-acetone adhesive had the lowest water content and lowest viscosity. Isocyanate groups can readily penetrate into the wood flakes and react with hydroxyl groups on wood to form chemical bonds directly with wood (Weaver and Owen 1995). The adhesion through the physical interactions is enhanced due to the reaction between the isocyanate and the moisture within the wood cell walls (Rowell and Ellis 1981). The pure pMDI adhesive can bond wood chemically and mechanically (Weaver and Owen 1995).

The adhesive with a pMDI/bio-oil ratio of 75/25 had a comparable peak storage modulus to that of the pure pMDI (Fig. 4). Steiner (1986) indicated that the maximum adhesive strength of the isocyanate-wood bond could be achieved at approximately 8 to 12 percent moisture content. Since the wood flakes used had a moisture content of 10 percent, the water in the adhesive with a pMDI/bio-oil ratio of 75/25 should have resulted in a higher moisture content of wood flakes than that of the pure pMDI, resulting in lower isocyanate-wood bond strength. However, bio-oil contains significant amounts of sugars, carboxylic acids, phenols, alcohols, water, and tannin and lignin derivatives, which may contribute to the adhesive bonding (Gagnon et

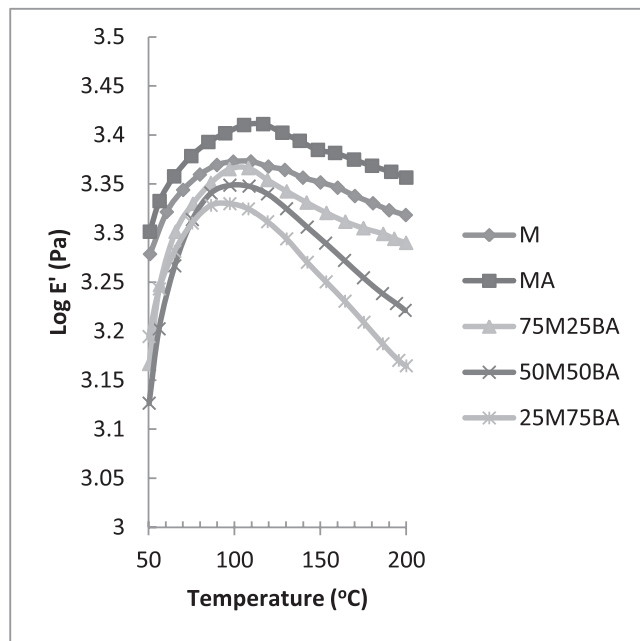


Figure 4.—Dynamic mechanical response curves showing storage modulus ( $E'$ ) for all adhesives as a function of temperature. M = polymeric diphenylmethane diisocyanate (pMDI); MA = adhesive composed of pMDI and acetone; 75M25BA = adhesive composed of 75 percent pMDI, 25 percent bio-oil, and acetone; 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.

al. 2003). The hydroxyl compounds of especially large molecules with at least two hydroxyl groups such as tannin and lignin derivatives can form networks with pMDI, which could be important to the adhesion of isocyanates.

With an increase in the bio-oil content, more water was introduced into the adhesive system. The water consumed most of the isocyanate groups in pMDI through reactions that reduced the urethane linkages between pMDI and wood. Therefore, excess water would affect the strength and durability of the pMDI bonded composites.

Chemicals from bio-oil with at least two functional groups that 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 one single functional group, can only form chains without much extension. With an increase in temperature, the short chains will decompose, resulting in a slight decline in the storage modulus curves after reaching the peaks. It was reported that urethane linkages from phenols cleaved at the temperatures above 120°C (Frazier and Ni 1998). Moreover, as shown in Figure 4, as the bio-oil content in adhesive binder systems increases, a decline in modulus curves is more obviously observed, indicating that more small molecules have been introduced to the adhesive systems with the increase in bio-oil content.

Based on the storage modulus curves in Figure 4, the modulus of all five adhesive mixes increased with pMDI/bio-oil ratio at the temperatures ranging from 100°C to 200°C. The higher the storage modulus of adhesive observed, the greater the mechanical property that could be obtained. In the previous study (Mao et al. 2011), a

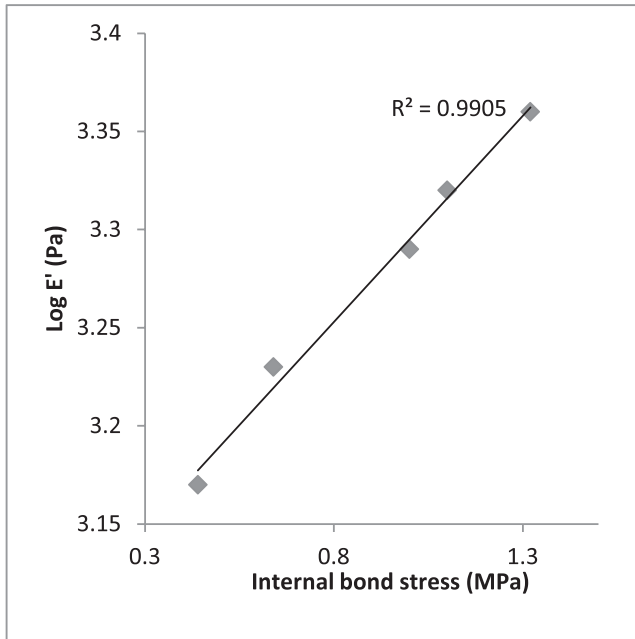


Figure 5.—Correlation between the mean internal bond of the flakeboards for each adhesive type and the mean storage modulus of the adhesives at the temperature range from 180°C to 200°C (from the core temperature to the face temperature).

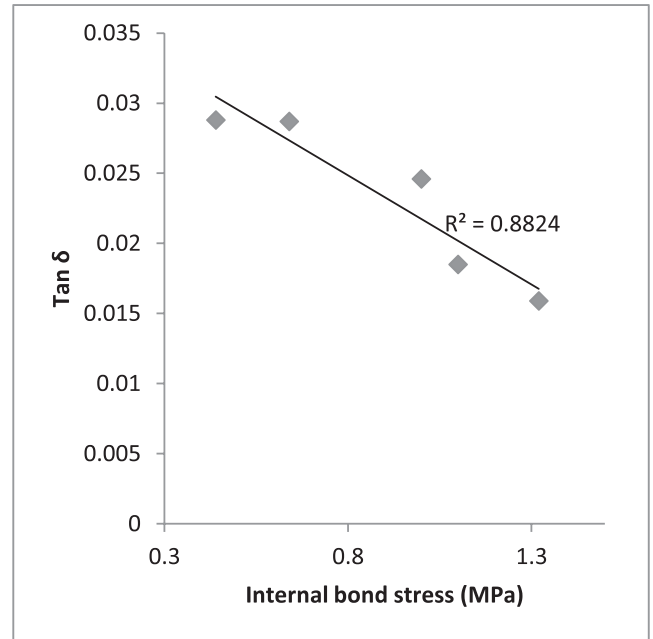


Figure 7.—Correlation between the mean internal bond of the flakeboards for each adhesive type and the mean tan  $\delta$  of the adhesives at the temperature range from 180°C to 200°C (from the core temperature to the face temperature).

platen temperature of 200°C was used during the hot pressing process to make flakeboards bonded by these adhesives. The actual core layer temperatures of the flakeboards would be less than 200°C. Therefore, the modulus of the adhesives at the core layer temperatures in the flakeboard mats during the hot pressing (up to 200°C) could be important to the mechanical properties of flake-

boards. DMA results (Fig. 5) showed a good correlation ( $R^2 = 0.9907$ ) between the storage modulus of these adhesives and the internal bond of flakeboards bonded by these adhesives (internal bond data were reported previously; Mao et al. 2011).

Figure 6 shows the tan  $\delta$  of the five adhesive binder systems as a function of temperature. The lower the tan  $\delta$  and loss modulus observed, the higher the storage moduli obtained. A good correlation ( $R^2 = 0.8846$ ; Fig. 7) is shown between the DMA tan  $\delta$  traces of these adhesives and the internal bond data of the flakeboards in Mao et al. (2011).

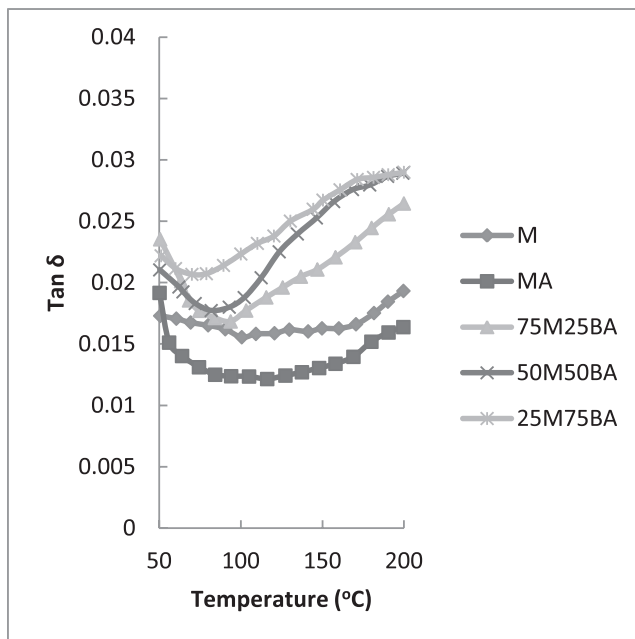


Figure 6.—Dynamic mechanical response curves showing damping term (tan  $\delta$ ) for all adhesives as a function of temperature. Resin types are defined in Figure 4 legend.

## Conclusions

The curing behaviors of five different types of adhesives were investigated using DMA. Temperature scans were performed in a temperature range of 50°C to 200°C with a heating rate of 10°C/min, frequency of 1 Hz, and strain amplitude of 15  $\mu\text{m}$ . With an increase in bio-oil content in the adhesive binder system, less time was needed to reach the maximum storage modulus, indicating that the adhesive binder system had a faster curing speed. 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. The pMDI-acetone adhesive presented the best thermal mechanical properties among the five adhesive systems. A good correlation was observed between the DMA results (storage modulus and tan  $\delta$ ) and the mechanical properties (internal bond) of the composites.

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