EFFECTS OF ISOMER RATIO ON PMDI RESIN REACTIVITY AND ORIENTED STRANDBOARD PROPERTIES

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Abstract. The effect of varying 2,4′-MDI to 4,4′-MDI isomer ratio in diphenylmethane diisocyanate (pMDI) adhesives was investigated. In addition to probing resin cure kinetics, oriented strandboard panels were produced to investigate the effect of isomer ratio on panel properties. With one exception, differential scanning calorimetry results showed a trend of increasing activation energy with increasing 4,4′-MDI content—the opposite of what was predicted. Results of internal bond testing indicate that increasing 4,4′-MDI content gave higher internal bond strength, but no correlation was evident between resin and panel density, MOR, MOE, or 24-h thickness swell. It is important to note that isomer ratio was not the only variable within the resin series; oligomer content and hence viscosity increased as 4,4′-MDI content increased, which complicated the analysis.

Keywords: pMDI, 2,4′-MDI, 4,4′-MDI, differential scanning calorimetry, activation energy, internal bond strength, isomer ratio.

INTRODUCTION

Polymeric diphenylmethane diisocyanate (pMDI) binders are commonly used to produce structural wood composites when superior strength and moisture resistance of the finished product is desired. The unique properties of pMDI binders permit wood composite manufacturers to utilize higher MC furnish, reduce press time, and produce composite products with no added formaldehyde.

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The preparation of commercial pMDI wood binders is a complex process and industry patents cover many details of the synthesis process; therefore, only a brief overview of the pMDI synthesis process is provided here. A more detailed description of the pMDI synthesis process can be found in Twitchett (1974) and Zheng (2002). Of the methods available for making isocyanates, phosgenation of primary amines is the most practical and widely used commercial method (Twitchett 1974). In this process, aniline is treated with defined amounts of formaldehyde and hydrochloric acid in an agitated reactor; the reaction mixture is then heated to 100°C to convert intermediate products into primary amines (Twitchett 1974). The primary amines are then treated with phosgene gas to complete the conversion to isocyanates (Zheng 2002).

Because of the variety of side reactions that can occur during the pMDI synthesis process, commercial pMDI wood binders exist as a mixture of MDI monomers and oligomers with an average functionality of approximately 2.8 and contain 30 – 32% isocyanate (Twitchett 1974; Lay and Cranley 1994). The most common MDI monomers in commercial pMDI are: 2,4′-MDI (5 – 10%), 4,4′-MDI (>90%), and trace amounts of 2,2′-MDI (Zheng 2002). Chemical structures for the 2,4′- and 4,4′-MDI monomers are presented in Fig 1. The isocyanate group at the second carbon is more sterically hindered than the isocyanate groups attached to the fourth carbon (Fig 1); therefore, it is hypothesized that pMDI binders with higher 4,4′-MDI content will be more reactive and develop higher physical properties in finished oriented strandboards (OSBs) compared with pMDI binders with higher 2,4′-MDI content.

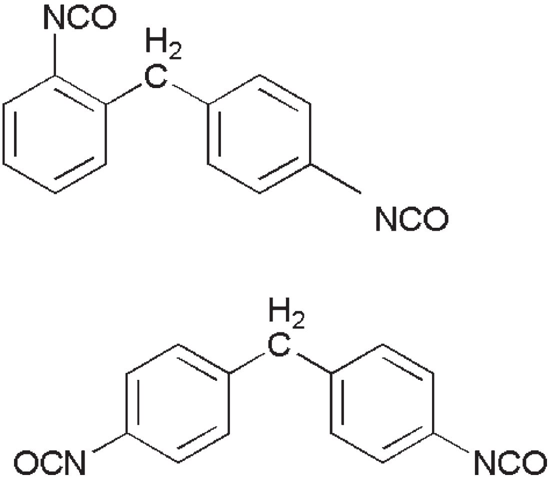

Figure 1. 2,4′-MDI monomer (top); 4,4′-MDI monomer (bottom).

Several authors have used differential scanning calorimetry (DSC) methods to evaluate the cure of pMDI with wood (Steiner et al 1980; Harper et al 2001; He and Yan 2005, 2007). Steiner et al (1980) used DSC to investigate wood/pMDI and water/pMDI reactions when pMDI binders were first introduced to the wood binder market. Results indicated that the wood/pMDI reaction involves a two-stage process with the second stage having higher activation energy. Findings also showed that water plays an important role in the wood/pMDI reaction, particularly at higher temperatures, and that different reaction products appear to be formed in the presence of water (Steiner et al 1980). More recently, Harper (1998) and Harper et al (2001) used DSC techniques to evaluate the pMDI/wood reaction in saturated steam environments. He and Yan (2005) used DSC to investigate the effect of MC on the cure kinetics of pMDI/wood mixtures. Results showed that MC had a significant influence on the curing kinetics of the pMDI/wood reaction (He and Yan 2005). Both reaction rate and reaction enthalpy increased with increasing MC and activation energy decreased with further increase in MC above 6% (He and Yan 2005). Other work by He and Yan (2007) studied the effect of wood species on the cure kinetics of the wood/pMDI reaction by combining aspen, white birch, maple, or southern yellow pine wood flour with pMDI resin on a 50/50 or 25/75 weight basis. Wood species affected the activation energy, reaction enthalpy, and reaction rate of the wood/pMDI reaction (He and Yan 2007). Reaction kinetics were also affected by the pMDI/wood ratios for oven-dry systems, but not for systems containing moisture, confirming that hydroxyls in wood were restricted as reactants under oven-dry conditions (He and Yan 2007).

The primary focus of this study is to determine the effects of varying the 2-4′- to 4-4′-MDI isomer ratio on the relative strength and durability of pMDI bonded oriented strandboards. In addition to the investigation of isomer ratio effects on panel properties, differential scanning calorimetry was utilized to determine any differences in cure kinetics relative to isomer ratio.

EXPERIMENT

Resin Preparation and Characterization

Five resin samples were prepared. A standard product (product names omitted to protect proprietary resin formulation data) with a low 2,4′-MDI content was blended with a high 2,4′-MDI content product to create a "master blend" with a relatively high 2,4′-MDI content. The master blend was then mixed with increasing proportions of a standard product having a relatively high 4,4′-MDI content to create a series of five resin samples with a pattern of increasing 4,4′-MDI content (Table 1). The samples were prepared with resins having similar total isocyanate content so that the effects of isomer ratio would be evident (Table 1). Materials used to create the five resin blends were supplied by Bayer MaterialScience LLC.

Resin samples were characterized according to standard industry methods for polyurethane raw materials. Resin viscosity and isocyanate content were determined according to the methods described in ASTM D 4889-04 (ASTM 2004) and ASTM D 2572-97 (ASTM 2003), respectively. Sample monomer content, 2,4′-MDI content, and 4,4′-MDI content were determined by high-performance liquid chromatography analysis according to the methods described in ASTM D 7252-06 (ASTM 2006a).

Differential Scanning Calorimetry

Sample preparation and DSC setup were similar to the method used by He and Yan (2005). Yellow poplar (*Liriodendron tulipifera*) flakes were ground into flour using a Wiley mill and then screened using an 80-mesh screen (Tyler mesh series). The flour was conditioned to a MC of 7.5 ± 0.5% for consistency with the board study. The DSC samples were prepared by combining the flour with each of the resin blends at a 50/50 mass ratio under a nitrogen blanket.

All DSC measurements and curve analyses were made using a Q100 DSC and the Universal Analysis 2000 software from TA instruments. High-volume, stainless steel DSC pans were used to prevent components of the test samples from evaporating at temperatures up to 250°C. Dynamic scans were made at heating rates of 2.5, 5, and 10°C/min and samples were scanned at 35 – 250°C. Samples were then cooled to –50°C and reheated to 250°C. No residual cure was evident. A minimum of three samples were analyzed for each of the five resin blends at each heating rate, and average values for peak temperature and reaction enthalpy were calculated.

The activation energy (E_a) was obtained by the isoconversional method using peak temperatures of the DSC scans at the three different heating rates. An expression relating heating rate and

Table 1. *Resin analysis results.*

Resin no.	1	2	3	4	5
NCO (%)	31.4	31.2	31.5	31.2	31.5
Viscosity (mPa/s)	101	142	134	170	225
Monomer content (%)	59.6	56.0	52.4	48.3	44.5
2,4′-MDI (%)	24.4	19.3	14.1	8.8	3.6
4,4′-MDI (%)	34.4	36.1	37.8	39.2	40.9
4,4′-MDI/total monomer (%)	57.7	64.5	72.1	81.2	91.9
Ratio 2,4′- to 4,4′-MDI	1:1.4	1:1.9	1:2.7	1:4.5	1:11.4

temperature for the nth-order reaction developed by Kissinger (1957) was used to calculate activation energy.

$$\ln\left(\frac{\Phi}{T^2}\right) = \frac{E_a}{RT} + \ln\left(\frac{RA}{E_a}\right)$$

where Φ is the heating rate, E_a is the activation energy in kJ/mol, T is the peak temperature in K, and R is the gas constant.

A plot of $\ln(\Phi/T^2)$ vs 1/T yields a straight line from which the activation energy can be obtained. Although the isocyanate reaction has shown signs of autocatalysis (Harper et al 2001), He and Yan (2005) compared the Kissinger equation with an autocatalyzed equation introduced by Prime (1997) and found minimal differences in calculated activation energies for wood/pMDI mixtures at moisture contents greater than zero. Therefore, the isoconversional method was selected here as a result of its simplicity. Degree of cure (α) was obtained by taking the partial integral of the exotherm curve at the desired temperature using the DSC software.

Board Fabrication

Mixed hardwood flakes composed primarily of yellow-poplar (*Liriodendron tulipifera*), maple (*Acer* spp.), and aspen (*Populus* spp.) were used. Flakes were donated by a Weyerhaeuser OSB mill located in Sutton, WV. The flakes, as received, contained approximately 35% fines by volume and were 9% initial MC. All flakes were passed over a wire screen with openings of 25.4 × 12.7 mm to remove fines. Screened flakes were then dried in an oven until the desired MC of 7.5 ± 0.5% was reached.

One percent slack wax and 4% resin were applied to the dry flakes using a 0.914 × 1.83 m lab blender (Blender Systems by Coil Mfg Ltd, Vancouver, Canada). Resin was applied using spinning disk atomizer with 30 9.5-mm-dia orifices. The blender rotated at a speed of 20 rpm with an atomizer disk speed of 9700 rpm. Each blender load provided furnish for three boards and consisted of 8 kg of flakes, 508 g of resin, and 77 g of slack wax. The resin was applied in 120 s and total blend time was approximately 5 min. The resinated flakes were hand-formed (random orientation) into a 0.83- × 0.83-m mat before pressing. Each board contained 3 kg of resinated flakes to achieve a target density of 641 kg/m^3.

A Dieffenbacher 400-t laboratory press was used to consolidate the mats into finished boards. The press cycle consisted of 40-s closing time with 120-s pressure and 20-s degas time. The press platen temperature was 204°C. The platen temperature and press cycle were chosen to ensure full cure of the resin within the core; the conditions represent common press cycles for isocyanate-bonded panels. Pressing data confirmed that final core temperature reached the target of 135°C. The finished boards were stored at ambient conditions until the boards were cut into samples for physical testing.

Board Testing

Physical testing samples were prepared from each of the 30 test panels according to ASTM D 1037-06a (ASTM 2006b). Boards were tested to determine the effect of isomer ratio on panel density, internal bond strength, MOE, MOR, and thickness swell. Ten internal bond, two soak, and two flexural samples were prepared from each of the test panels. All samples were conditioned at 50% RH and 20°C (24 h minimum) before testing.

RESULTS AND DISCUSSION

The five resin blends were fully characterized and key resin parameters appear in Table 1. A significant change in the ratio of 2,4′- to 4,4′-MDI occurs between resins 1 (1:1.4) and 5 (1:11.4). This decrease in 2,4′-MDI content from resin 1 to 5 was designed to test the hypothesis that resins high in 2,4′-MDI would have a higher cure activation energy (E_a) as a result of steric effects; therefore, it was hypothesized that resin 1 would have the highest E_a with a decreasing trend in E_a values for resins 2 – 5. Note that isocyanate content was intentionally held constant to not impact the results of the study. However, the blend strategy led to several other important resin parameters changing. In particular, as 4,4′-MDI content increased, oligomer content and hence viscosity increased. This suggests that the 2,4′-MDI resin is less reactive than its 4,4′-MDI counterpart; the 2,4′-MDI resin has lower oligomer content and hence viscosity than the 4,4′-MDI-rich system.

Resin Properties

Typical DSC scanning curves for resins 1, 3, and 5 are shown in Fig 2. All curves displayed a single peak around the same temperature; however, the shape of the curves varied by resin and by ramp rate within a given resin. No patterns in curve shape were observed for any of the heating rates.

Table 2 lists peak temperature (T_p), degree of conversion at peak (α_p), and activation energy (E_a) for each of the five resins. Overall, activation energies presented here are slightly lower than the published values of 65 – 68 kJ/mol for wood/pMDI mixtures under similar conditions (He and Yan 2005).

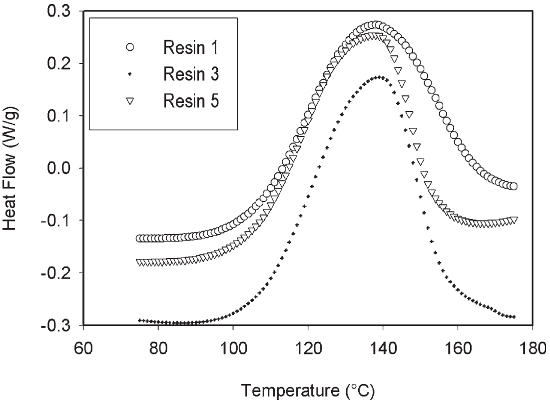

Figure 2. Typical differential scanning calorimetry curves at 5°C/min.

The activation energy data follow an interesting pattern (Table 2). Resin 1 exhibits a relatively high E_a, but E_a drops substantially for resin 2. For resins 2 – 5, there is a pattern of increasing activation energy. This pattern in E_a values does not agree with our hypothesis that increasing 4,4′-MDI content would decrease activation energy. However, two confounding variables—percentage monomer content and resin viscosity—may be responsible for masking trends associated with isomer ratio. Decreasing monomer content (Table 1) indicates an increase in concentration of oligomers in these resins that scales with the corresponding increases in viscosity. These larger constituents are less reactive than smaller monomer components simply from collision theory; therefore, the decrease in monomer content from resin 1 to 5 may have caused a trend of decreasing reactivity, obfuscating the hypothesized increase in reactivity with increasing 4,4′-MDI content. Hence, the effect of isomer ratio on activation energy cannot be determined conclusively in these samples. Note that statistical comparisons are not possible for the E_a data (each E_a value is computed from the slope of the regression line, which includes multiple data points). High R^2 values are observed for the regressions (Table 2).

Isomer ratio appears to have a negligible effect on peak temperature and degree of cure at peak with no significant trend observed for any of the three heating rates (Table 2). The maximum variability for peak temperature was 4.83°C. Peak temperature results presented here are approximately 8 – 18°C higher than peak temperatures

Table 2. *Peak temperature, peak conversion, and activation energy.*

	2.5°C/min		5°C/min		10°C/min			
Resin no.	T_P (°C)	α_P (%)	T_P (°C)	α_P (%)	T_P (°C)	α_P (%)	E_a (kJ/mol)	R^2
1	125.0	51.40	138.7	51.62	154.3	62.43	60.14	0.9995
2	123.2	58.62	137.1	61.31	157.6	50.12	50.00	0.9900
3	123.9	59.84	137.6	63.71	155.2	63.27	55.61	0.9967
4	123.9	59.02	139.3	59.02	153.3	61.28	59.42	0.9974
5	125.7	62.45	137.1	65.09	153.9	61.10	62.29	0.9895

reported by He and Yan (2005) for wood/pMDI mixtures at similar moisture contents; however, a different resin was used in that work. The results for degree of conversion at peak (Table 2) are quite variable and no significant trend is evident for any of the heating rates. No statistically significant trends were found in the reaction enthalpy and rate constant data (not shown).

Panel Properties

Results for panel internal bond as tested by ASTM D-1037 (ASTM 2006b) appear in Fig 3. A clear trend of increasing internal bond strength from resin 1 – 5 is evident with resins 4 and 5 having significantly higher (α = 0.10) internal bond (IB) strength compared with resins 1 and 2 (Fig 3). These results appear to support the hypothesis that increasing 4,4′-MDI content improves panel properties; however, the confounding variables of monomer content and viscosity make it difficult to draw conclusions specific to the effect of isomer ratio. In particular, the increase in resin viscosity from resin 1 to 5 (Table 1) could have influenced IB performance. It is known that changes in viscosity can effect resin atomization, penetration, and distribution on the flakes during blending, causing significant changes in panel properties (Kamke and Lee 2007). However, based on the authors' experience, the relatively small change in viscosity (0.101 – 0.225 Pa/s) should not have significantly affected resin distribution at 4% resin loading. Therefore, changes in resin penetration characteristics as a result of the increase in viscosity from resin 1 – 5 most likely had the greater effect on panel properties relative to the other potential effects of viscosity. An investigation into the penetration characteristics of the five sample resins was not conducted.

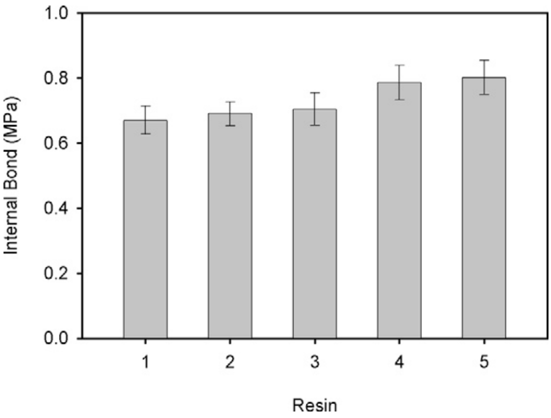

Figure 3. Panel internal bond strength as tested by ASTM D-1037 (ASTM 2006).

Table 3. *Mean panel properties as tested by ASTM D-1037 (*ASTM 2006*).*

Resin no.	Panel density (kg/m^3)	MOE (MPa)	MOR (MPa)	24-h thickness swell (%)
1	668.3	3813	25.98	11.61
2	665.9	3342	21.36	10.78
3	672.8	3346	22.49	11.67
4	679.7	3386	23.00	12.46
5	661.8	3536	23.66	11.21

Mean results for panel density, MOR, MOE, and 24-h thickness swell as tested by ASTM D-1037 (ASTM 2006b) appear in Table 3. Results of analysis of variance (α = 0.10) showed no statistically significant differences among the five resins. As stated previously, the confounding effects of resin viscosity and monomer content may have masked any effect of isomer ratio on these panel properties.

CONCLUSIONS

Results of DSC analysis showed a general pattern of increasing E_a with increasing 4,4′-MDI content, disagreeing with the hypothesis that increasing 4,4′-MDI content would decrease activation energy. Isomer ratio appeared to have a negligible effect on peak temperature and degree of cure at peak with no significant trend for any of the heating rates. Generally, results here were similar to those reported by He and Yan (2005). Panels bonded with the resins showed a pattern of increasing IB with increasing 4,4′-MDI content. The resins did not have a significant effect on panel density, MOR, MOE, or 24-h thickness swell. A trend of increasing viscosity and decreasing monomer content within the resin samples may have masked the effects of isomer ratio, making it difficult to draw conclusions regarding the general effect of isomer ratio on resin reactivity and panel properties. Future work on this subject should investigate the effect of isomer ratio while continuing to hold isocyanate content constant and controlling monomer content and resin viscosity more carefully. This type of synthetic control may be difficult to attain for isocyanate resins.

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