

# Calorimetric and Rheological Study of Isocyanate–Pyrolysis Oil Blends

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**ABSTRACT:** The reaction of polymethylene diphenyl diisocyanate (pMDI) with pyrolysis oils (PO) was studied by differential scanning calorimetry (DSC) and rheology. Chemical reactions between pMDI and PO occur under 100°C, as shown in DSC scans. DSC analysis showed that the peak temperature of the reaction decreased as the PO content of the PO–pMDI blends increased. The heat of reaction is at its maximum around 30–40% PO content. A rheological study of various PO–pMDI blends was done to evaluate the evolution of viscosity with time for different PO–pMDI hy-

brid mixtures. The initial viscosity of the blends is directly proportional to the PO content. An exponential increase of viscosity was demonstrated for all PO–pMDI mixtures. Rheological and chemical analysis results confirmed that chemical reactions occur between pMDI and PO at room temperature. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1362–1370, 2003

**Key words:** isocyanates; pyrolysis oils, differential scanning calorimetry; rheology; curing of polymers

## INTRODUCTION

The composite wood panel market depends on supply and demand, but also on cost of the materials used. The cost of the adhesive in a wood composite panel can be as high as 22% of the total cost of the panel.<sup>1</sup> Therefore, continuous search for low-cost adhesives is needed. In addition, industry is coping with the problems associated with formaldehyde and other hazardous emissions from wood composite panels. It must also dispose of large volumes of bark residues.

The main objective of this study was to evaluate the reactivity of a low emission wood panel adhesive that has the potential to decrease the cost of wood panels. This adhesive, which is under development, is made of an isocyanate called polymethylene diphenyl diisocyanate (pMDI) blended with a softwood bark-derived pyrolysis oil (PO), known under the trademark of Biophen™.<sup>2</sup>

pMDI is a light brown liquid, with a viscosity of between 150 and 250 mPa · s. Isocyanates are used to make polyurethane foam and plastics among other goods. More than 25 years ago, it was discovered that this reactive product could be used as a wood adhe-

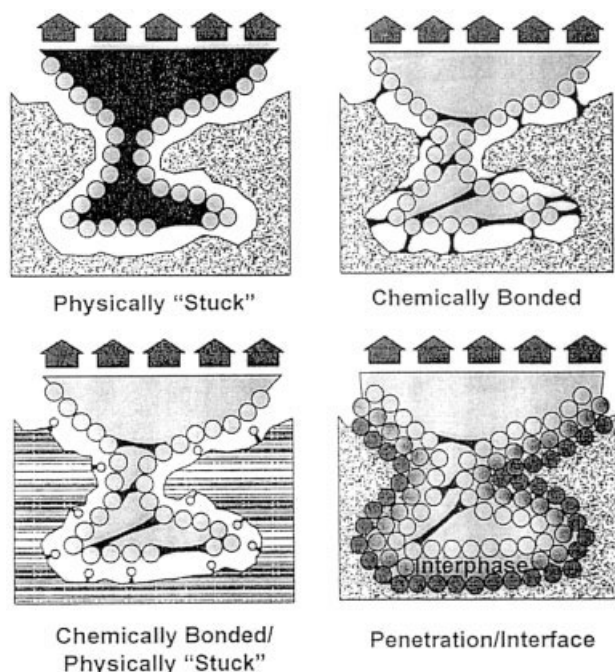
sive without the disadvantage associated with formaldehyde-based adhesives. Isocyanates do not emit formaldehyde, take less time to cure, and use lower press temperatures. It can also be used with high moisture content wood compared to phenol–formaldehyde (PF) and urea–formaldehyde (UF) resins.<sup>3</sup> Due to its unique performance properties, pMDI has been recognized as an adhesive for laminated strand lumber (LSL) and for bonding agricultural fibres into panels.<sup>4</sup> The most popular adhesive area for pMDI is for bonding oriented strandboard (OSB).<sup>5</sup> One of the disadvantages, however, of isocyanates is cost. The price of most isocyanates is approximately twice that of PF, though they are used at a lower application rate.<sup>1</sup> Sellers<sup>5</sup> reported that cost adhesive contribution can range from a few percent and can reach up to 32% of the total cost of the manufactured product. Also, the price of pMDI affects its popularity in the user sector, even though the quantity of pMDI used is third that of the PF required to obtain similar panel properties. Second, this adhesive is so reactive that it may cause sticking of the panel to caul platens. Using a release agent like wax on the cauls, or using paper laminations, can reduce this problem, at the expense of a higher production cost. In Europe, the wood panel industry uses pMDI in the core only, with PF binder on surface, to avoid such a problem.

Isocyanates react with all nucleophilic chemicals (acids, alkalines, alcohols, amines, etc.). They react with most of the —OH reactive moieties that can form urethane linkages, while with water, carboxylic acids,

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**Figure 1** Chemical bonds of pMDI with wood compared with PF resins.<sup>28</sup>

and amines, urea linkages are formed. Also, pMDI bonds with wood chemically and mechanically (Fig. 1). This provides greater strength as bonds are formed between wood particles during hot pressing.<sup>3</sup> Isocyanates do not react in a phenol-like condensation reaction, as conventional PF resins do, but must first react directly with moisture in the wood to ensure a good bond by producing polyureas. However, when pMDI reacts with water or carboxylic acid, it also produces CO<sub>2</sub>, which contributes to foaming of the mixture. Urethane linkages are produced by pMDI-wood hydroxyl reaction. Both urethane and urea linkages contribute toward increasing the dimensional and moisture stability of wood panels.

Renewable energy resources, like wood bark residues and industrial wastes such as scrap tires, can be used as energy source. One of the processes used to produce energy and recycle organic wastes is pyrolysis. By definition, pyrolysis is a thermal decomposition process in the absence of oxygen. Pyrolysis of biomass yields wood charcoal, pyrolysis oils (PO), water, and gaseous products. The proportion of these products depends on the process conditions used. Fast pyrolysis of biomass produces 75% liquids, 12% char, and 13% gas.<sup>6</sup>

The principle of fast pyrolysis is that biomass is rapidly heated at a temperature between 450 and 600°C in the absence of air or oxygen. By condensing the organic vapors formed, a dark reddish liquid is obtained. This liquid is called pyrolysis oil or bio-oil. It has a heating value equivalent to about half that of conventional fuel oil.<sup>6</sup> It also contains many reactive

chemicals that are liable to react with isocyanate (sugars, carboxylic acids, phenols, alcohols, water, tannin/lignin derivatives, etc., see Table I). If wood is used as a pyrolysis feedstock, complex PO arises from the degradation of lignin, cellulose, hemicellulose, and other organics, giving a broad spectrum of phenolics and other complex oxygenated molecules that evolve from the thermal decomposition process. PO can be actually considered like a micro-emulsion in which the continuous phase is an aqueous solution of holo-cellulose decomposition products that stabilizes a discontinuous phase of pyrolytic lignin macromolecules through a variety of mechanisms such as hydrogen bonding.<sup>6</sup> Vacuum pyrolysis is a special case of a fast pyrolysis process in which a low reaction pressure is used.

In general, the moisture content of the oil is between 15 and 30% and the pH is about 2.5–3.0. The viscosity depends on the kind of feedstock used, on the water content of the oil, on the kind of chemicals present in the oil, and on the oil ageing process. Typically, the viscosity lies between 25 and 1000 mPa · s at 40°C. Elemental analysis reveals that these oils are highly oxygenated and contain little nitrogen.<sup>6</sup> The density is approximately 1.2 g/mL. Polar solvents, like methanol, can be used to stabilize, homogenize, or reduce the viscosity of PO, but esterification or acetalization can occur between the added solvents and PO chemicals.<sup>7</sup>

The blending of pMDI with a low cost material such as PO is attractive from an economic standpoint. This is even more attractive if the adhesive properties of the so-obtained blend are improved, due to the presence of chain extenders and acid-catalyzed agents in PO. The sticking to platens might also be lessened or inhibited due to the presence of the hydrocarbons in PO, which may act like a self-releasing agent in the binder. The presence of water in PO creates a three-component reactive system, which could help the polymerization process by forming polyureas and by autocatalyzing the PO-pMDI reaction. Isocyanates and biomass-derived pyrolysis oils when combined have the potential to end up in a new kind of hybrid adhesive,

**TABLE I**  
Chemical Groups Present in Biophen™

Component	%
Hydrocarbons	3.0
Sugars	9.0
High and low weight carboxylic acids	11.5
Phenols	10.0
Alcohols and esters	3.5
Steroids and triterpenoids	4.0
Ketones and hydroxyketones	3.0
Water	10.0
Tannin/lignin derivatives	46.0

Reproduced from ref. 7.

which would increase the competitiveness of isocyanate adhesives and provide new opportunities to the wood composite board industry.

Studies of the reactivity of mixtures of pMDI and PO are not reported in the literature. Most of the studies linked to pMDI mixtures have been performed on different types of mixtures. Examples include tannins, natural oils, PF and UF resins.<sup>8,9</sup> Enomoto et al.<sup>10</sup> found that the presence of phenolic resins in PF-pMDI blends increased the reaction rate. As PF resins contain about 50% water, the reaction between PF and pMDI produces a large quantity of urea linkages together with CO<sub>2</sub>. Isocyanates react very rapidly with methylol groups of PF resins, but the reaction of pMDI and water is also rapid, and can autocatalyze cure of the adhesive by forming an amine, which is quite reactive to pMDI.<sup>9</sup> Enomoto et al.<sup>10</sup> also observed that as the PF content was increased, the exothermal peaks due to PF and pMDI moved toward the lower temperatures. According to these studies, it was speculated that the polymer matrix prepared by the polymerization of the pMDI disturbed the cure reaction of PF. However, no evidence of copolymerization of PF and pMDI was obtained by the authors.<sup>10</sup>

Zhuang and Steiner<sup>11</sup> investigated pMDI-phenol mixtures. They observed that the presence of an electron-withdrawing group in the phenol molecule retarded the thermal reaction and slowed it down. Their results demonstrated the effect of substitution on the thermal diisocyanate-phenolic hydroxyl reactions. The addition of a phenolic OH group to the NCO moiety of pMDI is likely dependent on the oxygen atom electron density of the phenolic OH group, which is directly related to the effect of substituents on the benzene ring. In addition, intramolecular hydrogen bonding and steric effects could affect the reaction between the phenolic hydroxyl group and pMDI. Since PO contains several phenolic and polyphenolic compounds, this study is highly relevant in the context of the work herein presented.

Pizzi and Owens<sup>12</sup> studied the pMDI adhesion mechanism in wood with differential scanning calorimetry (DSC). They found that the pMDI-water reaction is catalyzed by the presence of lignocellulosic compounds. They also discussed the proportion of urea linkages in a particleboard bonded with pMDI. In fact, their study showed that during hot pressing, it appears that panel surfaces, at a temperature of 180–200°C, exhibit evidence of covalent bonding at the interface. In the board core, where the maximum temperature reaches 115–120°C, the dominant bonding reaction is attributed to polyureas formed by the pMDI-water reaction. Some interfacial wood-adhesive covalent bonding still occurs in the panel core, but at a lesser degree.

Fabris et al.<sup>13</sup> found that the addition of reactive hydrogen labile compounds to pMDI, before blending

with wood, contributed to the formation of long chain polymers. These polymers facilitate the cure and the reaction of the adhesive with wood during pressing. The authors observed that the modulus of elasticity of wood panels was improved with this kind of adhesive. However, no information about the water resistance of wood panel made with this adhesive is mentioned.

Sleeter and Roos<sup>14</sup> worked on hybrid adhesives for biological residue panels. The authors prepared mixtures of pMDI with different kinds of polyunsaturated natural oils (soybean, linseed, safflower, etc.). The presence of polyunsaturated linkages seemed to increase the reactivity of the mixture. The best results were obtained with linseed oil, due to the high unsaturated linkages content of this oil. The cost of the adhesive was lowered and the sticking to the platens was eliminated, due to the self-releasing agent contained in natural oils. Isocyanates mixed with 40% of natural oil seemed to perform as well or better than pure pMDI as a wood binder.

Adcock et al.<sup>15</sup> tried to mix emulsifiable pMDI with UF resins to prepare a low-cost adhesive for strawboard. Unfortunately, they did not achieve success with the mixture, because both water sorption and thickness swelling increased with increasing UF levels. Although the UF resin reached some degree of polymerization, it did not adhere well to the strawboard substrate and this resin was unable to reinforce the panel. Other authors investigated pMDI-furfural<sup>16</sup> and pMDI-tannins blends<sup>17</sup> for particleboard and other types of panels.

Research has been conducted on pyrolysis oils by Chan et al.<sup>18</sup> and Amen-Chen et al.<sup>19</sup> used for the partial substitution of phenol in PF resins by softwood bark-derived pyrolysis oil commercialized under the trademark of Biophen™. This oil has a high phenolic and polyphenolic content due to its bark origin. Chan et al.<sup>18</sup> were able to substitute up to 45% of phenol by Biophen™ and OSB boards made with such adhesives displayed excellent OSB panel mechanical properties and dimensional stability that were comparable to the commercial control products.

## CALORIMETRIC EVALUATION

One of the methods used to characterize the reactivity of adhesives is DSC. Resin cure analysis by DSC may be carried out under isothermal or dynamic conditions where a predetermined heating rate is applied. Kinetic parameters can be obtained by at least four different methods: the Borchart-Daniels technique, the ASTM-698 method (isoconversional), the isothermal method, and the Vyazovkin method, also known as the "Model-Free" method.<sup>20–23</sup>

Due to the complexity of the series of reactions taking place when a pMDI-PO mixture cures under

the application of heat, cure kinetics characterization for this type of resin is based on a phenomenological approach rather than a mechanistic one.

When studying kinetics of resin cure by DSC, the chemical conversion or extent of reaction  $\alpha$  is defined as the fraction of the area under the DSC curve at a given time,  $\Delta H_0$ , divided by the total area of such a surface  $\Delta H_T$ :

$$\alpha = \Delta H_0 / \Delta H_T \quad (1)$$

where the reaction rate is a function of  $\alpha$ :

$$d\alpha/dt = kf(\alpha) \quad (2)$$

Here  $k$  is the rate constant, and  $f(\alpha)$  is to be determined and is assumed to be independent of temperature. It is also assumed that the heat of reaction ( $dH/dt$ ) is proportional to the rate of conversion  $d\alpha/dt$ .

In this study, the Borchart–Daniels and the so-called Model-Free methods were used.

These two methods are conceptually different. For Borchart–Daniels and  $n$ th order kinetics,

$$d\alpha/dt = k(1 - \alpha)^n \quad (3)$$

Using the Arrhenius relationship,

$$k(T) = Z \exp(-E/RT) \quad (4)$$

where  $Z$  is the pre-exponential factor,  $E$  the activation energy,  $R$  the gas constant, and  $T$  the absolute temperature.

Combining eqs. (2) and (3) gives

$$d\alpha/dt = Z \exp(-E/RT)(1 - \alpha)^n \quad (5)$$

Taking logarithms of eq. (5),

$$\ln(d\alpha/dt) = \ln(Z) - E/RT + n \ln(1 - \alpha) \quad (6)$$

Equation (6) is solved with a multiple linear regression in the form of  $z = ax + by + cz$ . The advantage of this approach is that useful kinetic parameters are obtained with only one DSC scan at a given heating rate. This approach saves time for the quick understanding of how a thermoset cures. However, kinetic parameters are scan-rate dependent and the results must be carefully evaluated.<sup>19</sup>

The Model-Free method is based on the concept that the energy of activation is a function of conversion  $\alpha$  but is constant at a given conversion and is independent of the heating rate applied to the sample. This method requires at least three dynamic curves with different heating rates:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (7)$$

Using heating rate as  $\beta = dT/dt$ , eq. (7) becomes

$$\frac{d\alpha}{dT} = \frac{kf(\alpha)}{\beta} \quad (8)$$

Substituting  $k$  by the Arrhenius expression  $k = Z \exp(-E/RT)$  into eq. (8) gives

$$\frac{d\alpha}{f(\alpha)} = \frac{Z}{\beta} \exp(-E/RT)dT \quad (9)$$

By integrating conversion  $\alpha$  at a given temperature  $T$ ,

$$\int_0^\alpha d\alpha/f(\alpha) = g(\alpha) = Z/\beta \int_{T_0}^T \exp(-E/RT)dT \quad (10)$$

Since  $E/2RT \gg 1$ , the temperature integral can be approximated by

$$\int_{T_0}^T \exp(-E/RT)dT \approx (R/E)T^2 \exp(-E/RT) \quad (11)$$

Substituting the temperature integral and using the logarithms on both sides of the equation,

$$\ln \frac{\beta}{T_\alpha^2} = \ln \left[ \frac{RZ}{Eg(\alpha)} \right] - \frac{E}{RT_\alpha} \quad (12)$$

For each conversion  $\alpha$ ,  $\ln(\beta/T_\alpha^2)$  is plotted against  $1/T_\alpha$ .

This provides a straight line with slope  $-E/R$  for each conversion.<sup>21–23</sup>

## EXPERIMENTAL

### Materials

The pMDI isocyanate resin used in this study was provided by Dow Chemical and is commercialized under the trademark of Isobind 1088<sup>TM</sup>. It is a light brown liquid with a viscosity of 219 mPa · s (room temperature) and an isocyanate group (NCO) content of 31.2%. The pMDI behaves like a Newtonian fluid. The sample was kept at room temperature to avoid any precipitation of dimers and oligomers at low temperature.

The PO, which was combined with pMDI to form a hybrid adhesive, is known as Biophen<sup>TM</sup> and is commercialized by Pyrovac (Québec, Canada). This pyrolysis oil is rich in phenolics and tannin/lignin derivatives (see Table I).<sup>7</sup> The Pyrocycling<sup>TM</sup> process, which

was used to produce the Biophen™, has been recently demonstrated at the industrial scale.<sup>24</sup> The process involves the vacuum pyrolysis of softwood bark residues. The process converts bark residues into 30.7% phenolic-rich oil (Biophen™), 29.2% charcoal, 20.5% gas, and 19.6% water (wt %, anhydrous feed basis).

The Biophen™ material used in this set of experiments originated from a mixture of spruce bark 66% (v/v) and fir bark 33% (v/v); there was approximately 1% of hardwood bark. The feedstock was pyrolyzed at 530°C under a total pressure of 26 kPa in a Pyro-cycling™ Process Development Unit (PDU) at a feed rate of 27 kg/h. The initial bark moisture content was 10%. The volume of bark treated for this experiment (run H64ABC) amounted to 622.5 kg. The duration of the pyrolysis run was 23 h.

The crude PO from the PDU was vacuum filtered, to remove fine charcoal particles greater than 6 μm. The PO sample contained 14.8% of water. It was stored in a cooler at 4°C. This special batch of PO was prepared under the specific conditions described above, so as to have the right viscosity and water content.

### Calorimetric method

A calorimetric study of the PO–pMDI blend was performed. The Isobind 1088™ sample was weighed first; PO was then added to get a 1 g blend. Immediately after 3 min of vigorous stirring, approximately 5 mg was taken with a Pasteur pipette and put inside the DSC reusable stainless steel high pressure capsule (Mettler no. 51140404). More than 12 different ratios of PO–pMDI were scanned and analyzed (0, 5, 10, 15, 20, 30, 35, 40, 50, 60, 80, and 100% of PO content), at 10°C/min, in the range of 25–250 °C.

The calorimeter used for the DSC scanning was a Mettler DSC 20 equipped with a Mettler Toledo Star<sup>e</sup> System software. To investigate the calorimetric parameters, a preliminary test was conducted using the simple single-scan Borchart–Daniels method. A second test using Vyazovkin's Model-Free technique was performed with the most promising mixtures, so as to allow a prediction of the pot life of the most reactive pMDI–PO combinations and to obtain the activation energy ( $E$ ) as a function of degree of conversion ( $\alpha$ ). Three different scan rates were used for this part of the study: 5, 10, and 15°C/min. Samples were scanned from room temperature to 250°C. The software allows a Model-Free simulation to be made to determine the evolution of the thermochemical behavior with time. The Model-Free DSC results were then compared with the results from the rheological study by observing the viscosity of the mixtures as a function of time.

### Rheological method

The rheological study enables the evolution of the viscosity of different thermoset mixtures to be ob-

served as a function of time. This part of the project used an ARES rheometer from Rheometric Scientific. A predetermined amount of the sample was placed between two aluminium disposable plates of 25 mm diameter. The gap (distance between the plates) chosen was 0.85 mm. The dynamic measurement mode was chosen in order to study the sample under “no flow” conditions. The frequency of the oscillation was chosen as 1 rad/s and the deformation strain amplitude was at 0.3 in order to remain within the linear deformation domain. All measurements were recorded after 5 min of mixing between the two-part adhesive, at room temperature. This time corresponds to the preparation of the mixture and the rheometer setting. At least 3 replicates were used for each mixture. The mixtures tested had PO contents of 0, 20, 30, 35, 40, 50, 60, 70, 80, 90, and 100%.

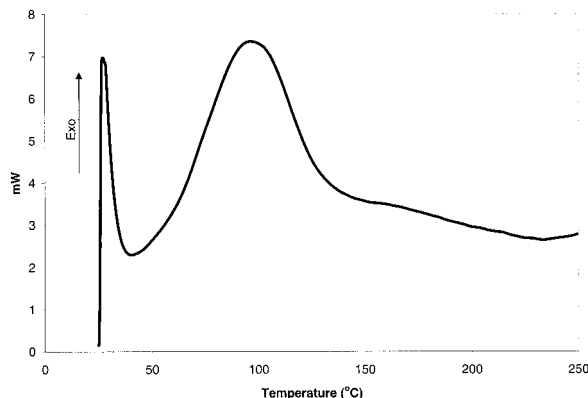
## RESULTS AND DISCUSSION

When the mixture of Biophen™ and pMDI is prepared, reaction immediately begins. After less than 10 min, CO<sub>2</sub> evolved and the hybrid adhesives began to foam. Thick foam appears on top of the resin, but if promptly removed, the liquid generally remained less viscous underneath. Foam seems to rapidly appear in presence of air. If the mixture is performed at a lower temperature, the reaction is slower and foaming starts later. CO<sub>2</sub> production is attributed to isocyanate–water or isocyanate–carboxylic acid reaction.

The mixture of pMDI and PO seemed to be heterogeneous. In fact, in the final rigid foam, a certain amount of PO still appeared as droplets in the foam. When both the initial and final mixtures are observed with a microscope, two phases are observed. This behavior can be confirmed by a rheological study (below), since if an emulsion is formed between pMDI and PO, a maximum should be observed in the curve of viscosity as a function of Biophen™ content.

### DSC scanning of mixtures

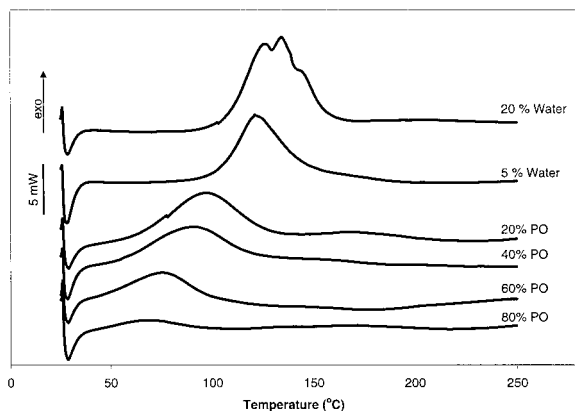
Figure 2 shows a typical DSC thermogram of the hybrid adhesives. The first peak near 25°C is simply the settling of the DSC signal. The reaction rate seems to be at a maximum near 100°C and has a high heat of reaction evolution when compared with results of PF. This peak indicates that a reaction occurs between pMDI and PO. Water reacts as well at a higher temperature. It can be seen that the exothermic peak seems to be asymmetric, possibly due to an overlapping endothermic response from both unreacted phenol compounds and the reaction products, i.e., boiling and melting phenomena.<sup>11</sup> Pizzi et al.<sup>9</sup> showed that pMDI–water reaction occurs between 87 and 117°C, while this study revealed pMDI–water peaks at 121–136°C (Fig. 3). This difference might be explained by



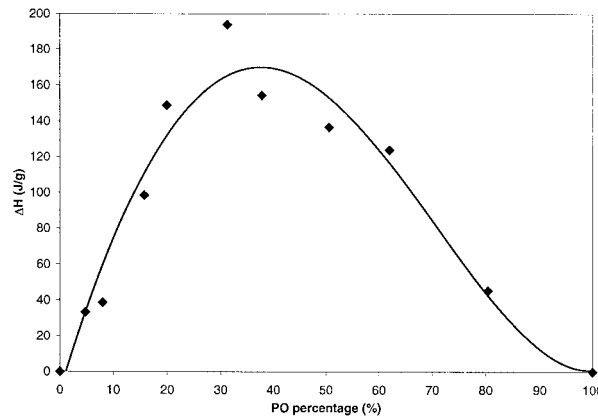
**Figure 2** DSC scan at 10°C/min for the 30% PO-pMDI blend.

the use of a different kind of pMDI as well as scan speed. All phenolic-based components in the PO presumably reacts to produce urethane linkages. Water reacts with pMDI to produce carbonic gas and amines, which immediately reacts with isocyanate to form urea linkages. Carboxylic acids contained in oil will react and produce CO<sub>2</sub> as well. At least 80% of the chemicals in the oil (sugars, carboxylic acids, phenols, alcohols, water, tannin/lignin derivatives, etc., see Table I) are expected to react with pMDI.

Figure 3 exhibits DSC scans for different PO content mixtures. It is interesting to see that the reaction temperature decreases with increasing pyrolysis oil content. Enomoto et al.<sup>10</sup> made the same observation for PF resins-pMDI mixtures: the higher the PF content, the lower the peak temperature. This phenomenon could be attributed to a lowering of the energy of activation. Isocyanates and PO alone do not react between 25 and 300°C. This observation on pMDI is confirmed by Pizzi et al.<sup>9</sup> From all scans, the most reactive mixtures, as determined by heat of reaction (integrated DSC curves), appear to lie between 20 and 40% of Biophen<sup>TM</sup> content (Fig. 3). The higher the area



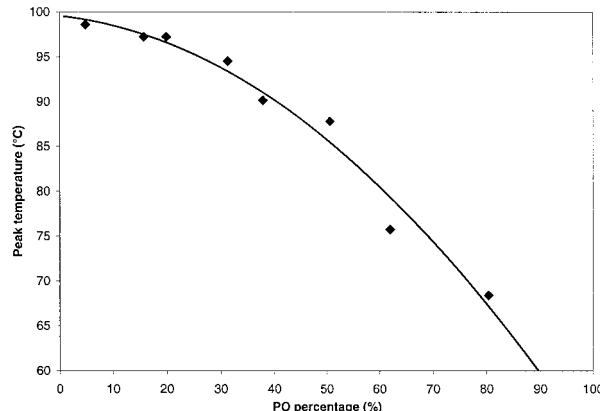
**Figure 3** DSC curves for various PO-pMDI and water-pMDI mixtures.



**Figure 4** Heat of reaction of different mixtures of PO with pMDI (main peak).

under the curve, the higher the heat of reaction and the higher the reactivity and crosslinking potential of the adhesive. A high peak at low temperature, where the surface under the curve is at a maximum, leads to optimal polymer formation. In this study, peaks of the mixtures seemed to exhibit the expected shape with a higher reactivity of the adhesive mixtures at 20–40% Biophen<sup>TM</sup> content. This is comparable to the PF reactivity, but at a much lower temperature.<sup>20</sup>

Figure 3 also illustrates the reaction peak of 5 and 20% water-pMDI reaction, near 120°C. Pizzi et al.<sup>9</sup> found that the pMDI-water reaction occurs near 87–117°C; they also found multiple peaks in this region (like in Fig. 3), which they attribute to multiple, simultaneous reactions. Only one peak was observed for the water-pMDI reaction in most cases. Differences between both behaviors can be attributed to scan rates and pMDI differences. From the water-pMDI reaction peak, it is possible to observe that the above reaction occurs at a higher temperature than the PO-pMDI reaction. In fact, water reacts with pMDI at a temperature higher than other organic oil components in the PO. Since water does not react at the same tempera-



**Figure 5** Maximum peak temperature of the calorimetric reaction for different concentrations of PO in pMDI.

**TABLE II**  
**Pot Life Time (min) of Different Hybrid Mixture for**  
**Specific Temperature, Mixture, and % of Cure as**  
**Predicted from "Model-Free" Results**

Temperature (°C)	Mixture (% of PO)	% of cure				
		10	30	50	75	95
0	30	278	606	815	1116	1429
	35	79	268	735	2529	N/A
	40	703	780	885	886	887
25	30	46	89	121	168	225
	35	25	57	120	311	673
	40	68	92	116	140	167
100	30	0.9	1.3	1.8	3.5	3.9
	35	2.5	2.5	2.5	3.1	5.7
	40	0.4	0.8	1.3	2.0	4.4
150	30	0.2	0.2	0.3	0.4	0.6
	35	<1	<1	<1	<1	<1
	40	0.04	0.09	0.2	0.3	0.8

ture as PO, it is easier to segregate both reactions. A few scans were made strictly with different amounts of water in pMDI to confirm this observation. Pure water reacts with pMDI at a higher temperature than PO-pMDI (between 10 and 55°C higher) and the polyurea formed has a heat of reaction similar to that of PO-isocyanate. PO, however, contains about 15% water and the water-pMDI peak could not be observed in DSC analysis of the PO-pMDI mixtures. Two explanations are possible: (1) some pMDI has already reacted with PO and less pMDI is available to react with water, or (2) it is possible that the water-pMDI peak is hidden by the PO-pMDI reaction peak.

Another smaller peak, near 160°C, seems to occur very often in the thermograms. This deformation of the baseline could possibly be attributed to the glass transition ( $T_g$ ) of the product formed. However, DSC scans were recorded a second time after complete cure of some PO-pMDI mixtures to observe evidence of a  $T_g$ , while no evidence of such a  $T_g$  near 160°C was observed for PO-pMDI mixtures. Nevertheless, this peak does not appear in all mixtures. It could be possible that this unexplained peak is due to a recombination of organic chemicals or another chemical reaction between PO compounds.

Figure 3 also shows that at high PO content, the curve becomes increasingly exothermic at high temperatures. This phenomenon could be explained by the thermal degradation/reaction of cellulosic derivatives at high temperatures. In fact, after 200°C, the cellulosic derivatives contained in PO become unstable and tend to decompose. High PO content mixtures exhibit this behavior when probed by DSC.

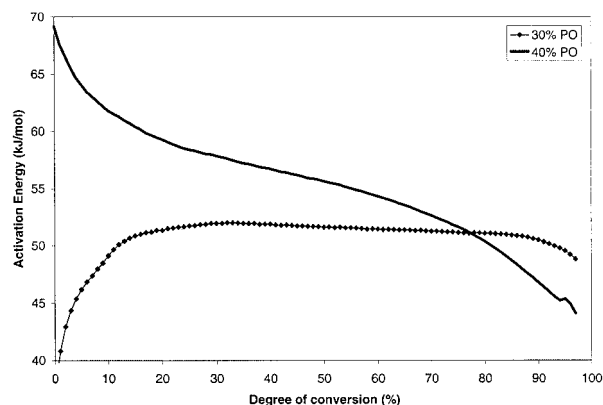
Figures 4 and 5 present the heat of reaction and the peak temperature vs PO content, respectively. The curve in Figure 4 clearly reveals that a maximum of heat of reaction is reached between 30 and 40% of PO content mixture. This could be a sign that such mix-

tures have the best stoichiometric ratio. The correlation coefficient for the curve on Figure 4 is high ( $R^2 = 0.9448$ ) and the curve can be fitted to a polynomial ( $y = 0.001x^3 - 0.209x^2 + 11.35x - 15.875$ ).

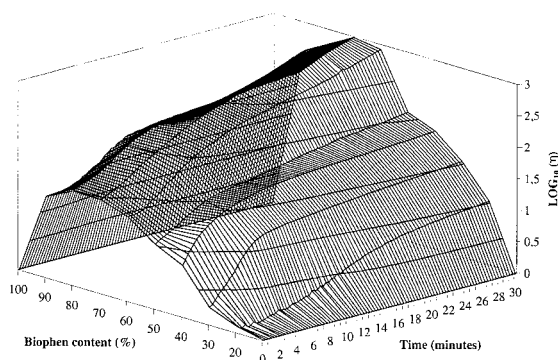
Figure 5 shows that higher PO contents produce lower peak reaction heating temperatures ( $y = -0.0042x^2 - 0.0659x + 99.549$ ,  $R^2 = 0.9735$ ). At PO concentrations up to 20%, the peak temperature does not seem to change. A rapid decrease of peak temperature occurs at concentrations higher than 30% of Biophen™ content. This is due to a lowering of the energy of activation. The peak reaction temperature varies with activation energy. As the energy of activation decreases, the peak temperature also decreases. If activation energy is high, it will be more difficult for molecules to overcome the energetic barrier to allow the reaction to take place. These molecules need higher temperatures to facilitate the chemical reaction between pMDI and PO. The excess of unreacted components in the PO also plays an important role. These unreacted molecules absorb exothermic energy from the main reaction and contribute to decrease the reaction peak.

#### Evaluation of the reaction using the DSC model free

A study of the projected stability of the 30, 35, and 40% Biophen™/pMDI blends was made using the DSC Model Free (Table II). This study required 3 scans at different temperature rates. As shown in Figure 6, the activation energy as a function of the degree of cure for the 30% PO content sample was rather constant at approximately 51 kJ/mol. The sharp decrease near the 100% cure point may be due to the diffusion-kinetics-driven cure process. For the 40% PO content sample, the activation energy decreased from 68 kJ/mol toward a value of approximately 44 kJ/mol. This suggests that there are either two competing reactions or



**Figure 6** Activation energy evolution curve as a function of the degree of conversion ( $\alpha$ ) for various pMDI-PO mixtures.



**Figure 7** Evolution of viscosity as a function of time and PO content.

overlapping reactions, as the percentage of PO is increased.

As described above, Model-Free kinetics allows modelization of isothermal cure of adhesives. Table II shows that hybrid adhesives are cured after less than 3 h at room temperature. If the temperature is lowered, the pot life of the adhesive becomes longer. This evaluation is very useful to determine the pot life of the adhesive and the increase of viscosity with time.

Since the Model-Free method requires at least three scans at three different scan rates, it is more precise than the Borchart–Daniels method, which uses only one scan rate. The Model-Free method points out toward a rapid increase of the viscosity for all mixtures at room temperature. In addition, the higher the temperature, the lower the curing time for a specific cure.

### Rheological behavior of the mixture

Figure 7 illustrates the evolution of viscosity with time and PO content. The viscosity increased with time for all mixtures. In addition, viscosity of the hybrid mixtures seemed to increase with PO content. This means that the higher the PO content, the higher the difficulty to blend the adhesive with wood strands for OSB. The best compromise seems to be between 20 and 50% of PO content. Such mixtures, however, seem to be relatively stable for 30 min after which time the viscosity increases too rapidly to use this product with a conventional blending system for OSB. Initial viscosity of the 20–50% Biophen™ blends do not allow a fine and homogenous spray to be achieved on the wood strands. However, all the “zero time” measurements correspond, in fact, to 5-min-old measurements, because all the viscosity measurements were performed after 5 min to allow for the same reactivity preparation time.

The high initial viscosity observed for the 70–80% PO freshly prepared blends can probably be attributed to the pre-cure of the components in the emulsion mixture.<sup>25</sup> In fact, it is probable that both pMDI and

PO are only partially mutually soluble, and react with themselves, as visually observed on the rigid cured foam. Boucher et al.<sup>26</sup> observed an emulsion in PO, meaning that oil is an emulsion of aqueous and organics compounds. The rheological study shows that the mixture is a multiphase heterogeneous system. The presence of a maximum in the viscosity curve indicates the presence of an interface between nonmiscible components in the mixture. If components were miscible, a smooth and monotonic curve would be observed for a mixture of components and with both pure components. Here, a positive curve is observed above this “ideal perfect mixture deviation.” PO and pMDI both have a lower viscosity than the mixture viscosity. Viscosity values are then increased by the shear strength formed between the liquid droplets (pMDI) and the continuous phase (PO), until 80% PO content. This strength is related to interfacial forces in the emulsion.

A greater variation of viscosity was observed between replicates at the beginning and at the end of the measurements, for all mixtures investigated. Standard deviations of 10–60% were calculated, depending on the PO content. Generally, the higher the PO content, the higher the standard deviation between all replicates (at least 3 replicates per blend). At more than 40% PO content, the precision of the results was reduced.

Isocyanates behave like a Newtonian fluid while PO has a different behavior at room temperature. An evolution of viscosity with time was also observed for the pure PO kept at room temperature. The viscosity was shown to increase from 600 to 750 mPa · s in less than 15 min. Boucher et al.<sup>27</sup> also reported this behavior. This could be explained by the fact that PO is a polydispersed system at 30°C. It is known that the behavior of PO at room temperature is not Newtonian. Under 30°C, PO has a very high dynamic viscosity, because of the structured state of the three-dimensional molecules present in the PO. This structured state is caused by waxy substances that agglomerate (lignin derivatives, fatty acids, high molecular weight esters, etc.). It is known that a large portion of these substances are soluble in alcohols, ketones, and low molecular weight aldehydes. However, fatty acids, which could represent more than 5% by weight of PO, are less soluble in methanol. The presence of water in PO might promote the agglomeration of these substances. Above 50°C, PO starts to behave like a Newtonian fluid because of the destruction of the three-dimensional structures.<sup>25</sup> A viscosity analysis made at 50°C showed that the viscosity is more homogenous between replicates. A balance exists between solvent strength and agglomeration tendency strength, at different temperatures.



## CONCLUSIONS

Using viscosity and DSC data, it was possible to hybrid pMDI-PO adhesive for OSB applications. DSC indicated that the best reactivity and chemical linkages are obtained between 30 and 40% of PO content in the hybrid adhesive. A rheological study indicated that the viscosity of the pMDI-PO mixture might be too high from an application standpoint. Combination of the above two techniques showed that the best mixture with the lowest viscosity seemed to be for the 30–40% PO blends. Adequate spraying equipment are needed to allow a uniform blending for OSB manufacture or other kinds of wood composites. However, this kind of blending system for viscous adhesives is not available to our knowledge. More research is also necessary to better understand the reactivity of these hybrid adhesives. Lowering the reactivity of the mixtures by adding an inhibitor or a solvent, or working with a special emulsified pMDI with a reduced degree of reactivity, might be worth being investigated in the future.

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