Assessment of pMDI Cure in Saturated Steam Environments

David P. Harper  
*Graduate Research Assistant*

Michael P. Wolcott  
*Associate Professor, Dept. of Civil & Environmental Engineering, Washington State Univ., Pullman, WA*

Timothy G. Rials  
*Project Leader, Southern Research Station, USDA Forest Service, Pineville, LA*

**Abstract**

The ability of an autocatalyzed kinetic model to describe the cure of polymeric diphenylmethane diisocyanate (pMDI) in a saturated steam environment was evaluated. A standardized differential scanning calorimetric (DSC) method was modified to fit a first order autocatalyzed kinetic model. Kinetic parameters were also determined *in situ* by micro-dielectric analysis (μDEA). Model results revealed agreement between DSC models and partial cure experiments. Models derived from μDEA data predicted cure times that were longer than those models generated by DSC. The difference in the models derived from μDEA and DSC was attributed to the sensitivity of the techniques to network formation and isocyanate consumption, respectively.

**Introduction**

Complex environments of steam, mechanical pressure, and heat are often encountered in wood-composite manufacture. The evaporation of water within the wood cells or the use of steam injection pressing often produces localized regions of saturated steam within a composite during pressing (12,13). Cure evaluation is difficult in such harsh environments. Several mechanical techniques have been developed to assess the rate of bond strength development under realistic manufacturing conditions (8,10). The advent of micro-dielectric analysis (μDEA) allows for the monitoring of cure during composite manufacture by placing a dielectric sensor in the wood-adhesive bondline. The cure is then monitored by changes in conductivity of the adhesive system. The conductivity is a measure of the movement of ions and dipoles (induced or permanent) within the electric field of the sensor. As the temperature of the adhesive increases, viscosity decreases and the ions within the system move more freely. Thus, the adhesive system is more conductive. At the onset of cure a maximum in conductivity is reached when the adhesive starts to build molecular weight and inhibit ion flow and dipole alignment. At vitrification a stable three-dimensional network is formed, relating to a minimum in ion viscosity, that flattens into a constant conductivity.

The use of μDEA has been found compatible with many thermoset polymer systems (4, 5). More recently, μDEA has been used *in situ* to monitor the cure of polymeric diphenylmethane diisocyanate (pMDI) during particleboard manufacture (21). The signal of pMDI cure proved to dominate the dielectric response. In other resin systems, the movement of moisture through the panel can be problematic (22). The implementation of μDEA by itself lends little insight into the nature of the makeup of the pMDI-wood adhesive bondline. However, coupled with mechanical and calorimetric techniques it becomes a powerful tool in monitoring the evolution of bondline morphology (9).

Controversy exists over the composition of cured pMDI in the presence of wood (7,11,18,19). Possible reaction products are polyurea, biuret/polyuret, allophanate, and urethane bonds. The mixture of possible reaction products makes the formulation of mechanistic models difficult. However, by considering the reaction as a whole, a phenomenological approach to modeling cure can be taken. Care must be taken to reproduce realistic processing environments when evaluating cure.
The results obtained from a phenomenological model will only be valid for the derived testing conditions. There is little literature available on the attempts to model pMDI cure in a realistic processing environment. Chelak and Newman (2) used the technique outlined in ASTM E698-79 (1) by differential scanning calorimetry (DSC) to evaluate the kinetics of the pMDI-wood system at varying fiber moisture contents. To increase the exothermic heat output, pMDI was added directly in the DSC sample pan at the 50 percent level relative to the actual mass of the wood present. The DSC pans were hermetically sealed under 500-psi pressure. No compensation was made for the mass of the water present. Care was taken to ensure that the kinetics followed an Arrhenius relation. The results indicated that the moisture present changed the kinetics of the system. The higher moisture content fibers increased the rate of cure and decreased the temperature at which cure occurs.

A problem with the use of DSC for kinetic analysis is the ability for the instrument to detect small change in exothermic heat generation for the low levels of pMDI typically used during manufacture. Typically, elevated amounts of resin are used to produce larger exotherms. A shift in reaction products may occur if the ratio of reactive materials has changed. This may lead to erroneous kinetic parameters. However, the use of too small amount of resin will also produce erroneous results when the limits of the DSC's sensitivity have been reached in the later stages of cure. Therefore, a compromise must be reached between resin levels and sensitivity or a new technique must be incorporated.

The kinetics assumed by the ASTM E698-79 follows an nth order relationship. Typically nth order kinetics are catalyzed reactions where the greatest rates of conversion of the starting material into reaction products occurs at the onset. Considering any of the possible reaction paths that have been proposed for the cure of pMDI, an nth order equation cannot describe the entire cure process (23). The cure process is complicated by the many simultaneously occurring events that makes modeling difficult. Without the extraction of the cure rate from cure data the kinetic behavior of the pMDI-wood system cannot be determined.

Objectives

The overall objective of this research is to determine an accurate model for the cure of a pMDI-wood system. In order to accomplish this goal a new technique for acquiring cure information and finding kinetic parameters must be developed. The specific goals of this research are:

1. To monitor the cure of the pMDI-wood system with μDEA in a saturated steam environment.

2. Utilize a kinetic model that accurately represents the cure of the pMDI-wood system under the processing conditions presented.

3. Compare μDEA to DSC techniques for developing kinetic models.

4. Relate the kinetics to physical phenomena during the cure process.

Methods and Materials

Quaking aspen (Populus tremuloides) flakes were used for this study. Aspen logs were locally obtained and quartered to produce a radial face. The blocks were cut from the quartered logs and placed in distilled water and a vacuum for 2 hours. A sliding microtome was used to slice strands to a 0.66-mm thickness. The strands were then dried between glass plates in a 103°C oven. The flakes were then conditioned at ambient.

Three, 5, and 7 percent oven dry mass Mondur Bayer 541 pMDI was applied to one face of the aspen strands with an atomized spraying technique. μDEA was conducted in situ by placing a sensor directly in the bondline between opposing pMDI-coated flakes to obtain the change in conductivity of the curing adhesive. The degree of cure and rate of cure were calculated from the conductivity data for flake pairs pressed in an enclosed steam producing press.

Dielectric Analysis

μDEA was performed for isothermal temperatures of 110°, 120°, 130°, and 140°C inside a closed steam generating press. A Micromet Eumetric System III dielectric analyzer with mid-conductivity signal conditioner and integrated digitated electrode (IDEX) sensor controlled by Mmssoft software were employed for data acquisition. Data was collected at 10 sec. intervals over four frequencies, 1, 10, 100, and 1,000 Hz, for 20 minutes. Resin amounts of 0, 3, 5, and 7 percent were applied to 88.9 by 25.4 mm aspen strands. An IDEX sensor and a thermocouple were placed between two sprayed flakes.

A maximum in the conductivity of specimens coated with resin was taken to be the onset of dielectric cure. The maximum in conductivity also corresponds to a minimum in ion viscosity and the point at where network formation begins to inhibit flow of the adhesive. At the point where the adhesive network has been formed, a constant minimum should occur. However, in actuality this minimum resembles an asymptote. Therefore, a criterion must be established for the completion of cure. In epoxy systems the slope of the conductivity near the completion of cure has been related to crosslink density, i.e., a flatter slope correlates to a higher crosslink density and more complete cure (5). As a criteria for complete cure in this system:

Wood Adhesives 2000
\[
\frac{d \log \sigma(t)}{dt} = 0.01 \log(\text{siemens})/\text{sec.}
\]  

A degree of cure (\(\alpha\)) was then calculated by:

\[
\alpha = \frac{\log \sigma_{\text{max}} - \log \sigma(t)}{\log \Delta \sigma}
\]  

where:

- \(\sigma(t)\) = the conductivity at any time,
- \(\sigma_{\text{max}}\) = the maximum conductivity,
- \(\Delta \sigma\) = the difference between the maximum and the minimum conductivity, where the completion criteria was met.

### Differential Scanning Calorimetry

A series of DSC ramped-temperature experiments were performed. Seven percent pMDI was applied to aspen strands. The flake pairs were placed together, and 25 mg was punched out with a small hole punch and placed in stainless steel DSC pan. Two \(\mu\)l of distilled water was added to provide enough moisture for a saturated steam environment. The DSC pan was hermetically sealed to contain volatile gasses. Ramps were then performed from 30° to 200°C for heating rates of 1, 5, 10, 15, and 20°C/min. Degrees of cure were calculated.

\[
\alpha = \frac{Q(t)}{Q_0}
\]

where:

- \(\alpha\) = was the degree of cure,
- \(Q(t)\) = the residual heat at time, \(t\), and
- \(Q_0\) = the total heat of reaction.

\(Q_0\) was calculated by numerically integrating the power \((P(t))\) with respect to time by the trapezoidal method. To obtain the rate of cure:

\[
\frac{d\alpha}{dt} = \frac{P(t)}{Q_0}
\]

Partial cure isothermal DSC experiments were carried out, to be used for comparison with DSC ramped-temperature experiments. Assembled flake pairs with 7 percent pMDI were pressed at isotherms in the presence of saturated steam at 110°, 120°, 130°, and 140°C. The flake pair was pressed to 0, 25, 50, 75, and 100 percent of \(\mu\)DEA cure then removed and immediately quenched to stop the progression of cure. A 25-mg specimen was removed and 2 \(\mu\)L of distilled water was added to a hermetically sealed DSC pan. A temperature ramp was then performed on each specimen from 30° to 200°C at a rate of 20°C/min.

### Results and Discussion of Cure Modeling

The influence of moisture has been problematic for \(\mu\)DEA by shorting out the electrodes etched on the sensor surface. The sensor has proven to be effective when monitoring pMDI in high moisture environments (9). The movement of moisture has little influence on the conductive response during cure. Further, the dielectric response of the wood substrate bares little influence over the changes occurring in the dielectric cure spectrum of pMDI.

### Kinetic Characterization of Cure

The kinetics of cure need be characterized as either nth order or autocatalyzed. The degree of cure was calculated for the \(\mu\)DEA results according to Equation 2. The numerical derivative of the cure was taken with respect to time. The cure rate was then plotted vs. the degree of cure (Fig. 1). The maximum rate of cure does not occur at the onset of cure such as is indicative of nth order kinetics. Instead the \(\alpha\) at the maximum cure rate occurs at greater than 50 percent cure. Autocatalyzed kinetics most commonly has a maximum cure rate at 30 to 40 percent cure (16). A general model for autocatalyzed kinetics introduced by Lam (15) with one rate constant \((k)\) is:

\[
\frac{d\alpha}{dt} = k \alpha^m (1-\alpha)^n
\]

where:

- \(m\) and \(n\) = reaction orders.

The ultimate conversion in this model is assumed to be 1. The overall order of the reaction is \(m + n\). To check the overall reaction order a series of plots where made for differing \(m + n\) over integer steps. The overall order of the reaction was taken to be the plot with the most linear behavior, highest coefficient of determination \((R^2)\) from a least squares linear regression. Although first and second order kinetics exhibit high \(R^2\), the second order kinetic models display a slightly quadratic shape. Further the later stages of cure (left portion of the plot) displays a divergence from first order kinetics. The
divergence is believed to be a diffusion event where the rate is being limited by the proximity of the reactants [9]. This diffusion event occurs late in the development of a three-dimensional adhesive network as determined by μDEA. For the purpose of finding kinetic parameters, the region where the data diverges from linear will not be considered within this study. The kinetics of diffusion has been discussed elsewhere (3,14). The kinetics of the system then followed the Arrhenius relation (Eq. 6).

\[ \ln k = \ln A - \frac{E}{RT} \]  

where:

- \( A \) = the Arrhenius frequency factor,
- \( E \) = the activation energy,
- \( R \) = the ideal gas constant, and
- \( T \) = the absolute temperature.

Plotting \( \ln k \) vs. \( 1,000/T \) can check the assumption for the Arrhenius relation (Fig. 2).

The autocatalyzed kinetic model was fit to the μDEA data through a linear interpolation of Equation 7. Equation 7 assumes that the kinetics is first order. The Arrhenius parameters can then be found by linear interpolation of the Arrhenius plot (Fig. 2).

\[ \ln \left( \frac{d\alpha}{d\tau} \right) = \ln k + n \ln \left( \frac{1 - \alpha}{\alpha} \right) \]  

**Multiple DSC Ramps Technique**

Kinetic parameters can be accurately estimated by the use of multiple DSC ramps (16). These ramps require the use of different heating rates to observe the shift in the temperature at the exothermic peak, \( \alpha_{\text{max}} \). This procedure has been standardized for the determination of first-order catalyzed kinetic parameters (1). The standardized ASTM E698 method requires that nth order kinetics is followed and \( \alpha_{\text{max}} \) is constant. The procedure must be modified in order to meet the assumptions of autocatalyzed kinetics (15). The modification of the method can be taken from two different approaches by

1. evaluating at Equation 5 at \( \alpha_{\text{max}} \) or
2. following the ASTM E698 technique and modifying \( A \). The later method would assume that the \( E \) is accurately calculated from the nth order kinetic model by neglecting the dependence \( \alpha_{\text{max}} \) on temperature (16).

The solution for the modification of ASTM E698 to fit autocatalyzed kinetics (now referred to a DSC method 1) can be obtained from Equation 8. The right side is dependent on the temperature, \( T \), when considering a constant heating rate \( \beta \) and, \( T_p \) is the temperature at \( \alpha_{\text{max}} \).

\[ \ln \beta + f(\alpha_{\text{max}}) = \ln \left( \frac{AE}{R} \right) - 5.33 - \frac{105E}{RT_p} \]  

The second method using multiple DSC ramps requires the modification of \( A \) only to fit autocatalyzed kinetics (15). \( B \) is a stoichiometric ratio of reactants. \( B \) is considered to be 1 when the quantities of reactants are mixed. In the case of the pMDI cure, multiple reactions are occurring simultaneously with an unknown mixture of reaction products. Thus, the assumption of \( B = 1 \) is used.

\[ A \approx \frac{\beta E e^{\frac{E}{RT_p}}}{RT_p^2 \left[ 2\alpha_{\text{max}} + 2\beta\alpha_{\text{max}} - 3\alpha_{\text{max}}^2 - B \right]} \]

**Single Ramp DSC Technique**

Proctor and others have developed a technique for the determination of kinetic parameters from a single DSC ramp (17). Parameters can be calculated from a non-linear least squares method to fit Equation 11. The non-linear regression was performed for up to 80 percent of cure. Cure beyond 80 percent was very dependent upon diffusion control. The method is suspected to be sensitive to the amount of adhesive placed in the DSC pan. Lack of a
Table 1.—Kinetic parameters obtained from isothermal μDEA and DSC ramp methods.

<table>
<thead>
<tr>
<th>Method/β</th>
<th>E (kJ/mol)</th>
<th>A × 10^5 (s^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>μDEA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3% pMDI</td>
<td>75.1</td>
<td>1,500</td>
</tr>
<tr>
<td>5% pMDI</td>
<td>65.5</td>
<td>73</td>
</tr>
<tr>
<td>7% pMDI</td>
<td>82.6</td>
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<td>Multiple ramp DSC</td>
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</tr>
<tr>
<td>Method 2</td>
<td>60.1</td>
<td>23.2</td>
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<tr>
<td>Single ramp DSC</td>
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</tr>
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<td>20</td>
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Figure 3.—Comparison of DSC and μDEA results for pMDI cure. μDEA was used as a basis for partial DSC cure experiments at the four isothermal temperatures. μDEA predicts residual beyond the sensitivity of the DSC.

Comparison of Modeling Methods

The determined kinetic parameters show some discrepancy between DSC and μDEA techniques for modeling cure (Table 1). DSC and μDEA are sensitive to different parts of pMDI cure (Fig. 3). The cure prior to the exothermic peak in the DSC data is likely the consumption of isocyanate. In contrast, μDEA is sensitive to the formation of a three-dimensional network during vitrification. The mechanisms that drive the consumption of isocyanate and network formation are different. μDEA is a more sensitive method for measuring the bond development during the latter stages of cure and may be related to bond strength development through mechanical testing. The relationship between the structure and μDEA has been confirmed by using dynamic mechanical analysis as a means of measuring the crosslink density (5).

μDEA models accurately reflect the degree of cure calculated from the data (Fig. 4). No attempt was made to model the possible diffusion events occurring late in cure. As expected, the kinetic models fall short of predicting the later stages of cure. Remarkably, though, the differences are not great and differ only at very high degrees of cure. In a manufacture situation, boards are often hotstacked so that the elevated temperatures are maintained within the panel for a period long enough to complete cure. Thus, increased cure times brought on by diffusion will be compensated for by the hotstacking.

DSC method 1 calculates activation energies that are close to those calculated by ASTM E698 (Table 1). The activation energies for the DSC methods are close, but the frequency factors differ by a factor of 6-10 from
Figure 5.—Comparison of model cure predictions and partial cure DSC results for 110°C to 140°C isotherms (the modified ASTM and modified A curves overlap).

DSC ramp methods 1 and 2. The frequency factor used by the ASTM E698 method depicts cure that progresses much more slowly than the partial cure experiments.

The use of one DSC ramp to calculate kinetic parameters proves consistent over-heating rates used in this study. However, the single ramp method predicts much longer cure time than the multiple ramp methods and partial cure studies (Fig. 5). Prime (16) states that for the majority of reactions the single ramp method overestimates $E$ and $A$ when compared to isothermal experiments. The single ramp method is not routinely consistent (16). Prime does further state that the discrepancy between techniques may be that the model does not accurately describe the system. The point is reiterated by Yourefi et al. that differences between isothermal and dynamic experiments have been attributed to a weak kinetic model (23). The simplicity of the kinetic model may explain the differences observed between the single ramp method and the partial cure study. However, multiple ramp methods do show good agreement with the partial cure experiments.

Conclusions

Large differences were observed between the μDEA and DSC modeling techniques. DSC techniques have a higher sensitivity to the early stages of cure. The higher activation energies observed for the μDEA models are likely from the different cure reactions occurring during vitrification. The sensitivity of μDEA to network formation makes this technique a more credible link than DSC for relating cure to bond strength (9). However, the use of any cure model must accompany mechanical study and careful control of adhesion parameters to be used successfully as a predictor of end properties.

The ASTM E698 did not successfully model the cure behavior observed in this system. The partial cure studies revealed that the ASTM E698 method predicts cure time that are much longer than those observed. The cure followed first order autocatalyzed kinetics. The modifications made to the ASTM E698 for autocatalyzed kinetics produced two models that were very close in their cure predictions. The two DSC ramp
methods agreed with the partial isothermal cure studies at 120°, 130°, and 140°C. From this study, using one technique over the other does not afford a particular advantage.

The area under exothermic peaks late in cure may have been limited by the small amount of adhesive used in the study. The use of excessive amounts of pMDI may change the molar ratios of reaction products and thus change the kinetics of the cure. The lack of a complete exothermic peak was more detrimental to the single ramp DSC studies and may explain the discrepancies observed between single ramp and multiple ramp techniques. The loss of the heat because of sample size is likely not to change the location of the exothermic peak. Since the shift in exothermic peak temperature is the only information in determining kinetic parameters, the multiple ramp methods are likely more accurate than single ramp methods.

References