THE EVALUATION OF 4-4’ DIPHENYLMETHANE DIISOCYANATE CURE IN A SATURATED STEAM ENVIRONMENT

By

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The members of the Committee appointed to examine the thesis of DAVID PAUL HARPER find it satisfactory and recommend that it be accepted.

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Chair
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THE EVALUATION OF 4-4’ DIPHENYLMETHANE DIISOCYANATE
CURE IN A SATURATED STEAM ENVIRONMENT

Abstract

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The cure of polymeric 4-4’ diphenylmethane diisocyanate, PMDI, in wood composite
manufacturing has been the subject of much research. The exact contribution of
polyurethane, polyurea, and polyurete formation with PMDI/wood bonding is still
debated. This study foregoes the mechanism controversy and studies the cure as a whole.
Micro-Dielectric Analysis, μDEA, was utilized to monitor the cure of PMDI in controlled
heat, steam, and pressure representing those encountered during wood composite
manufacturing. A small steam-generating chamber was mounted to a universal testing
machine producing saturated steam environments between 110° and 140°C. The degree
of conversion calculated from μDEA was a basis for further spectroscopic, calorimetric,
and lap-shear analysis. Differential Scanning Calorimeter (DSC) and Fourier Transform
Infrared spectroscopy (FTIR) techniques revealed a large consumption of isocyanate
early in cure. However, mechanical strength as revealed by lap-shear analysis developed
late in cure. Low lap-shear strengths and a plateau in conversion rates were detected for
110° and 120°C may indicate a diffusion-controlled reaction and crystallization effect. A
phenomenological approach to kinetics was utilized to model the reaction. Isothermal
μDEA and dynamic DSC data were fit to a first order autocatalyzed model. ASTM E698-
79 was modified to fit an autocatalyzed model. The modifications were compared to a
method of performing a single dynamic temperature ramp to obtain kinetic parameters. Higher activation energies were obtained for μDEA than DSC methods. In addition, ASTM methods for DSC produced higher activation energies than single dynamic ramps and compared favorably with data obtained from the previous DSC study. The observed differences in activation energy relate to differing mechanisms in chemical and physical cure.
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Dedication

For Wyatt
CHAPTER 1

INTRODUCTION

Abstract

The cure of 4-4’ diphenylmethane diisocyanate, PMDI, is the subject of controversy. The interest in its use as a wood adhesive has grown with the growing need for structural composites. An overview of the significance the use of PMDI in wood composites and in processing these materials is presented. The specific research objectives of monitoring and modeling cure are discussed in relation to process optimization. Isocyanate research, analytical techniques in evaluating thermoset cure and kinetics are reviewed. This chapter and the following chapters are to be read as a complete or separate document. The first chapter is a review of relevant research, the second chapter compares analytical techniques of monitoring cure, the third chapter discusses kinetic modeling of the PMDI system, and the fourth chapter discusses the conclusion.

Introduction

The Use of PMDI in Wood-based Composites

In the past two decades polymeric 4-4’ diphenylmethane diisocyanate, PMDI, has become an important binder in the wood composites industries. Although PMDI has been around since the 1930’s, only until the past fifteen years has it become economically feasible to use it as a binder in wood. The cost of PMDI as a binder for wood is substantially greater than other readily available wood binders such as urea-
formaldehyde, phenol-formaldehyde, and melamine-formaldehyde based on weight (Steiner 1986). However, recent advances in manufacturing and changes in the availability of saw timber for exterior applications have made a market for PMDI as a wood adhesive.

**The Manufacturing Process**

PMDI is now widely used in manufacturing particle and strand composites such as TimberStrand®. These products show dimensional stability due strong adhesive bond and moisture resistance. These properties are achieved with the use of less resin on a weight-percent basis than other liquid resins. Some water that can cause panel blows or a reduction in properties is taken out of the system through a reaction that produces the adhesive bond. Thus, an advantage over other resin systems that cross-link through condensation reactions and introduce more water into the system is achieved. This leads to the utilizing of higher moisture content wood in composite manufacture and reduces drying costs.

The isocyanates are extremely reactive (Steiner 1986). This very attractive feature was also one of its greatest pitfalls, it would bond to metal. This made it difficult to produce a 100 percent PMDI bound panel. Until the introduction of cull release agents or self-releasing PMDI, it was impossible. Today self-releasing resins are common place (Prather et. al 1995).

PMDI binds at lower temperatures and shorter pressing cycles. These characteristics give rise to additional savings in the manufacturing process. However, controlling these parameters is not well understood. Isocyanates are very reactive which
may lead to a variety of outcomes. The reaction outcomes are dependent upon the amount of moisture in the panel, temperature, and the catalyst, though rarely used, or other impurities. The outcomes of these reactions have a profound effect on end properties, such as strength, stiffness, moisture resistance, and bond strength.

**Characterization of Cure to Control Manufacturing Parameters**

Several process parameters need to be identified and evaluated for process control: influence of heat and moisture, time to cure, degree of cure, and the rate of cure. To this date the manufacturing parameters effecting cure have not been linked to the different chemical reactions. The characteristics of the final panel properties have led to many suppositions for possible reactions (Frisch, et. al 1983, Johns 1980, Frink and Sachs 1981). There exists the likelihood of a distribution of reaction products. The distribution of these products and their morphology depends highly on the manufacturing conditions. The need exists for cure models to manufacturing parameters.

**Objectives**

The overall objective in cure characterization is to produce an adhesive bond that will meet the prescribed specifications in the shortest period. Many unknowns exist relating to the cure of PMDI under normal processing conditions. Investigating these unknowns requires the use of *In-situ* methods of monitoring cure. Most commonly available techniques used for the analysis of cure use methods that do not occur under conditions encountered during pressing. It is the objective of this research to monitor and model the cure of PMDI under conditions of steam, pressure, and temperature encountered during wood composite manufacture by the use of micro-dielectric analysis.
Techniques more commonly used in the analysis of thermosets are employed for comparison and to provide insight into the dielectric response of cure. Models derived by calorimic techniques are also employed.

Literature Review

PMDI

Isocyanate-Wood Adhesive Bond

Much work has been done in trying to predict the wood-isocyanate bond in a wood composite. The exact nature of the reactions that take place in a press is still unknown. Possible bonding reactions have been presented by Deppe (1977), Johns (1980), Frink and Sachs (1981), and Frisch et. al (1983). The reaction of free hydroxyl groups, possibly from wood components, and isocyanates yield a urethane Johns (1980). Isocyanate can further react with an amine in the urethane to form urea. The urea then reacts further with isocyanate to form a biuret, which is trifunctional. Another possibility for cross-linking is a urethane-isocyanate reaction to form allophanate. An isocyanate cyclic structure, isocyanurate, can also form during pressing. Frink and Sachs (1981) pointed out that many of these reactions are dependent on internal conditions of the composite during pressing and this may be too simplified of a representation. A water-isocyanate reaction to form primary amines may be dominant as opposed to urethane formation.

Work has been done in investigating the products of these reactions. Wittman (1976) used CO$_2$ emission formed from the water-isocyanate reaction to calculate the percentage of isocyanate consumed in this reaction. On a laboratory scale press that was
enclosed to capture the gas, he predicted that 1/4 to 1/3 of the isocyanate groups were involved in this reaction. The amount was dependent on moisture content and resin level.

Several groups have tried to isolate the individual wood components and whole wood to compare the isocyanate reactions. Rowell and Ellis (1981) investigated whole wood and methyl-isocyanate modified holocelulous and lignin. The infrared spectra of several weight percentage gains were investigated and compared to unmodified dry wood. Urethane, primary, and secondary amines were observed in the reacted spectra, however, there was no isocyanate present, all was consumed in the reaction.

It has been presented that the use of low molecular weight isocyanate bonds chemically to ligno-cellulosic material (Johns 1983). Under the typical manufacturing of wood composites, urethane structures have not been found. However, large amounts of polyureas are normally observed. This is probably do to the quick reaction of high molecular weight isocyanate with water. The high molecular weight polymeric isocyanate does not have the mobility to bond to the hydroxyl sights on the cellulose. In an investigation of the high moisture content of wood and PMDI, it was found that the rate of cure increased with moisture content (Chelak and Newman 1991). This investigation was performed using first order kinetics according to ASTM E698-79 on DSC.

Galbraith and Newman (1992) used lignin, hemicellulose, cellulose, and whole wood in isolated reactions with PMDI. These reactions were investigated utilizing DSC and FTIR. The DSC results show that there was a reaction between the PMDI and lignin, hemicellulose, and dry wood. The lignin reaction started as soon as 100°C and the hemicellulose at 105°C. The whole wood component was cured by 120°C. The
interaction between cellulose and PMDI was negligible in comparison to the other two wood components. The behavior of this system could be attributed to the crystalline structure of cellulose not freeing hydroxyl groups. The lignin-PMDI reaction shows strong traces of urea and urethane along with an absence of the lignin reactive site.

Weaver and Owen (1992) used phenyl isocyanate in a reaction with glucose, cellulose, lignin, and wood at different moisture contents (MC). By employing FTIR all components were found to react with the phenyl isocyanate, however, the rates of the reactions differed greatly. Lignin reacted much faster then did cellulose, yet water reacted faster than both. It is suggested that there may be an ideal wood MC to achieve a degree of wood isocyanate interaction. Steiner (1986) alluded to the ideal bonding of wood with isocyanates being in the range of 8-12 percent MC.

Wendler et. al (1996) found adhesive chemistry to change as a function of MC, temperature, and time. Nuclear magnetic resonance, NMR, was used to observe PMDI and wood interactions. Biuret and urea was detected in all samples. Biurets appeared more abundantly at low MC and high temperature, up to 160°C and decomposes at 185°C. Urea dominates above 4.5 percent MC and lower temperatures. Urethane linkages are believed to form at extended times at temperature above 185°C. However, urethane and urea formations are not cleanly resolved by the $^{15}$N labeling method used in this study.

Rasthauser et. al (1997) utilized extraction, FTIR, and phenyl isocyanate treatments to determine the chemistry of isocyanate binders in the manufacture of particle board. Extracted wood samples treated with phenyl isocyanate were found to be the same as those of untreated wood when infrared spectroscopy was performed. This
process shows that 90 percent of the phenyl isocyanate was recovered and not chemically bonded to wood. Solution NMR showed a significant amount of diphenyl urea and only trace amounts of other compounds that were not identified. FTIR was then conducted In-situ during the pressing of a particleboard panel using PMDI as the binder. The results of experiment showed an initial increase in the formation of urea with a rapid decline in the second half of cure. The late decrease in urea indicates the formation of biuret. This formation could be masked by dimer formation associated with polyurets. To discover the effects of the chemical bond on board properties, wood was treated with phenyl isocyanate to cap the free hydroxyls. The treated wood and untreated wood were then sprayed with PMDI and pressed under similar conditions. The resulting internal bond and 24-hour thickness swell showed no significant differences.

**Isocyanate in Wood Composites**

Several studies have been conducted comparing traditional formaldehyde based adhesives and isocyanates. Deppe (1977) investigated the utilization of isocyanates in wood composites. He proposed that a urethane bridge would form between the hydroxyl groups in the cellulose and that polyurea would form to bind wood components. These bonding characteristics presented certain advantages over phenol-formaldehyde PF bonded composite: increased dimensional stability, shorter press cycles, water not a product of cure, decreased density without a loss in strength properties, and less need to sort particle geometry. Some of the drawbacks were also presented: adhesion to metal, high relative cost, and hygroscopic. Frink and Sachs (1981) compared mixed hardwood flakeboard using PF and PMDI. By utilizing PMDI in manufacturing reduced press time
and temperature, flake MC, resin level, and panel density achieve similar strength properties as PF resins.

Ball (1981) addressed many problems associated with isocyanate adhesives. He reported on self-releasing adhesives, water emulsified isocyanate, and low formaldehyde emissions of isocyanate bonded composites. Ball reported on the use of multiple layer composites in production. These composites utilize outer layers bonded with traditional formaldehyde based resins or a veneer layer pressed on top of the composite. The result is a composite that utilizes already available isocyanates and it does not stick to the culls. Steiner (1986) expanded on the possibilities of isocyanate adhesives by utilizing catalysts (Frisch et. al 1983), steam injection pressing, co-reaction with formaldehyde and other polymers, and blocked isocyanates (Zhuang and Steiner 1993).

Hawke et. al (1992) investigated the effect of mat MC on strength properties of polyisocyanate bonded hardboard. The results showed no difference in strength properties for mats with MC between 8-22 percent. The polyisocyanate level of 3 percent had greater strength properties than those bonded with PF resin at the 10 percent level and 7 percent mat MC. Hawke et. al (1993) compared the physical properties of hard board bonded with the same characteristics as above. Thickness swell, linear expansion, and accelerated aging tests were performed on the hardboards. The PMDI bonded boards out performed the PF bonded board in the physical tests.

Sun et. al (1994a) evaluated the use of elevated PMDI levels in producing a wood fiber composite with superior strength properties. It was found that the 20 percent PMDI level were the most efficient in improving strength properties. 3 and 10 percent PMDI levels proved to very similar to 20 and 30 percent PF levels. Sun et. al (1994b) compared
the physical properties of these boards in similar study. The physical properties of PMDI panels improved significantly with increasing resin levels with the exception of water absorption. PMDI was found to be more effective in minimizing the water absorption and thickness swell. However, lower PMDI levels were statistically similar to PF levels of 20 and 30 percent. For linear expansion, PMDI and PF resins were similar.

**Internal Mat Conditions**

PMDI has been found more suitable for use in steam injection pressing over PF resin. They have been found to have higher internal bonds, lower thickness swell and water absorption (Galbraith and Newman 1992), and greatly reduced press times (Steiner 1986). Geimer (1982) found that steam injection pressing takes advantage of rapid heat transfer to the core to lower press times. The steam acts to plasticize the wood and allows for lower pressure, for press closure and creates a low-density face that eliminates sanding. Walter (1992) found improvement in dimensional stability and thickness swell with steam injection pressing. Hua (1997) showed that flakes pressed in steam environments showed less creep than those pressed in without steam.

Kamke and Casey (1988) investigated the role of platen temperature and press closing time on internal panel properties. Thermocouples and hypodermic pressure probes located in the face and core regions of a flakeboard panel monitored these properties. Faster press closing times and higher platen temperatures resulted in the faster heat transfer to the core and high steam buildup in the face and core. Density gradients develop after press closure. This gradient could be the result of stress relaxation leading to strain recovery in another panel layer by observing gas pressure fluctuations.
Humphrey (1990) found it important to understand the interdependence of gas flow, temperature, and bond formation to optimize the manufacturing process. PF resins offer an impenetrable barrier to vapor flow after water has been evaporated from the glue line. Trapped moisture leads to the development of internal stresses in the pressed composite and delamination.

\textbf{µDEA}

Day et. al (1990a) related the endpoint of an epoxy cure reaction to Ion Viscosity. A linear relationship was found between the $T_g$, glass transition temperature, and the Log Ion Viscosity. The employment of Thermal Mechanical Analysis (TMA) and Dynamic Mechanical Analysis (DMA) determined $T_g$ and end of cure. It was observed that processing conditions could affect the time to cure. It was suggested that the Ion Viscosity provide a more accurate indication of cure than observation of time in an environment with varying conditions.

In cured samples of polyetheretherketone, PEEK, Day et. al (1990b) monitored the diffusion of water by employing µDEA. As the concentration of water in a polymer changes, the mobility of dipoles change. Thus, there is a change in dielectric constant. PEEK was evaluated in both crystalline and amorphous phases and compared to a polyimide and a epoxy system. All systems showed agreement with the employed Fickian diffusion model in varying moisture conditions. Differences were observed between amorphous, higher rate of diffusion, and crystalline, slower diffusion rate. The sensors were sensitive to changes in structure and diffusion.
Four phenol-formaldehyde, PF, resin formulations and a tannin-modified-resorcinol-formaldehyde resin were compared by Rials (1992) by µDEA. By mapping the Log Ion Viscosity, discernible differences were detected among the different PF resin formulations. It is suggested that the slope of the Log Ion Viscosity vs. Time plot is directly related to the rate of cure. It is further suggested that the higher ion viscosity is related to a higher cross-link density.

The cure of PMDI was monitored in-situ during pressing of particleboard (Wolcott and Rials, 1995a). The influence of moisture movement in a composite panel was observed by pressing with furnish only. However, in comparing pressed panels containing PMDI and resin cured in a controlled oven, the latter stages of cure are similar. This would suggest that PMDI dominates the dielectric signal late in pressing. The onset or completion of cure was not determined; this is attributed to the difficulties in identifying the contributions of each component to the signal.

The conductivity measured by µDEA is independent of frequency and can be averaged over a range of frequencies (Wolcott and Rials, 1995b). This technique was employed to investigate the potential for monitoring UF and PMDI resin cure in-situ. The two resin systems show vast contrasts, which can be attributed to the condensation reaction of the UF resin and the polyurea reaction of isocyanate and water. µDEA did discern between three different UF resin formulations. A resin formulation not expected to cure showed a higher end conductivity than did the standard UF face and core resins. However, it is not clear if this is an artifact of moisture movement or the resin cure itself. The PMDI panels utilized the same resin formulation at the core, mid, and face regions in the panel. The core had peak conductivity at a lower temperature than did the mid
region. However, the face region had two peaks. It is unclear whether or not the peaks are due to a two-stage cure reaction, moisture movement, or both; this is left open for investigation.

**Resin Cure and Bond Formation**

Bolton and Humphrey (1977) developed a device to determine the degree of cure by the bond strength development in a tensile test. Wood discs were sprayed with UF resin. The wood was then bonded to aluminum discs with epoxy and then screwed onto a heated platen. The samples are heated for a period of time and then tested in tension with a delay of only six seconds. Strength development was the charted over time. Humphrey and Bolton (1979) proposed using this device to test varying resin and wood moisture levels. Further, they proposed this device could test bond development in a known panel temperature regime. Humphrey and Ren (1989) made modifications to the earlier design described above in order to keep a constant MC within the sample. This was accomplished by the addition of steam ports in a sealed environmental chamber. Thermocouples and a RH probe exchanged information with a steam supply in order to achieve the proper MC of the wood at elevated temperatures. The sample was adhered and tested as in the above method.

Humphrey and Zavala (1989) developed a lap-shear-testing device in order to test bond formation. Two wood strands are sprayed with adhesive and held in a universal-testing machine by pneumatic grips. Horizontally mounted platens provide heat and pressure for bonding. After the scheduled cure period, bonding pressure is released slightly and tested in shear. The platens do not completely retract to provide support for the moment placed on the specimen.
Geimer et. al (1990) utilized DMA, DSC, and lap-shear evaluation to determine bond development and resin cure. Resin samples were impregnated on glass cloth and then allowed to precure in a humidity chamber at room temperature, and then placed in a controlled temperature and humidity environment. This sample was then conditioned for 0% and 91% RH conditions over saturated salt solutions. An enhancement in differences in precure conditioning was observed with the 91% RH pre-DMA conditioning. A portion of the DMA sample was trimmed for DSC analysis to insure that the sample was subjected to the same conditioning. A constant rate of heating of 10°С/min was maintained to observe the exothermic reactions. The chemical and mechanical responses were plotted. The response is a percentage of cure taken from the uncured and a partially cured area under the residual heat and 
\[\tan \delta\] curves respectively. The response demonstrated that a small change in chemical response correlated into a large change in mechanical response. These responses do not directly correlate to bonding properties.

Bond development was evaluated by a lap-shear test (Geimer et. al 1990). The bonds in this study were tested in a cooled condition unlike a similar test discussed earlier by Humphrey and Zavala (1989). Further, the test did not provide horizontal support to reduce the moment on the shear specimens. Two opposing air operated cylinders in an environmental chamber bonded the specimens. Openings in the face of the platens provided the steam or conditioned air.

Lap-shear bond strength development was compared to DSC kinetics for phenol-formaldehyde wood systems (Wang et. al 1995). A bond rate was determined from the linear slope of the bond strength before reaching a maximum. This rate was then used to calculate Arrhenius parameters by plotting rate versus the inverse of temperature. Cure
kinetics was also performed on resin only and resin-wood systems in the DSC. It was found that the resin-wood system resulted in higher activation energies than resin only systems.

**Comparison of Techniques**

Many techniques are readily available in evaluating bond formation within a composite panel. However, it is difficult to evaluate bonds between small wood samples. Bolton and Humphrey (1977) and later Humphrey and Ren (1988) pulled tension samples immediately after pressing to evaluate the rate of bond formation. This technique is dependent upon the penetration of the epoxy into the wood, and if the glueline, wood, or epoxy strength is being tested.

Humphrey and Zavala (1989) evaluated bond strength development by a lap-shear test. This test was conducted hot or immediately after pressing. The heated platens continued to apply a small amount of pressure on the sample after pressing to reduce the moment in the sample. Geimer et. al (1990) utilized a lap-shear test on cooled samples. The test conducted did not provide horizontal support. The lap-shear test imparts a non-uniform stress on the bondline and leads to three-dimensional strains in the adherent. This questions whether the bond strength is actually being tested.

DMA, DSC, and µDEA are readily available to evaluate resin cure. However, cure characteristics are important only if they produce an adequate bond (Geimer et. al 1990). It is essential to mechanically test gluelines to destruction to see bond strength formation. This mechanical evaluation can eventually be related back to µ-DEA to achieve the idealized situation, continuously and non-destructively evaluate bond strength development (Bolton and Humphrey 1977).
Kinetic Models

Many models and methods are available for investigating kinetic parameters (Prime 1981, Kiran and Iyer 1994). Few methods have been investigated in the study of wood adhesive interaction. The greatest difficulty in analyzing these systems is in quantitative analysis of these systems in realistic pressing environments. Humphrey and Ren (1989) developed a method for evaluating adhesive bond by pulling round wood flakes in tension perpendicular to the grain. The bond strength was then evaluated in a controlled humidity and temperature environment. The bond strengths were then fit to a first order kinetic model by a linear regression to strength development. Lap-shear tests have also been performed to obtain kinetic parameters using a first order model (Humphrey and Zaval 1989, Wang et. al 1995). The lap-shear experiments also tried to mimic conditions within a pressing environment.

DSC analysis has been a common tool used in the determination of kinetic parameters. One reliable method has been to run dynamic ramps at multiple heating rates (ASTM E698 1979). An increase in temperature at the maximum rate of heat generation, $T_p$, is a function of heating rate. In cases where $T_p$ occurs at a constant degree of cure, $\alpha$, kinetic parameters can be found. This method has been shown to be reliable for catalyzed and autocatalyzed reactions that meet the assumptions of the model (Prime 1981). However, when the reaction does not follow first order kinetics and $T_p$ occurs at varying $\alpha$, a modification to the method must be made to fit other kinetic models (Lam 1987). Lam proposed that the ASTM method did not fit his autocatalyzed kinetic model.
Summary

The possibility for increasing physical and mechanical wood-composite properties by the use of PMDI in high moisture pressing exists. The mechanisms that govern the cure of PMDI in hot pressing have not been evaluated with great success. A system composed of a distribution of reaction products that lead to the unique properties of the PMDI adhesive bond is likely. Slight changes to processing conditions could swing to favor one polymer reaction or another. A shift in the distribution of reaction products can potentially have a large effect on the final product. The need exist for reliable methods of predicting cure in a complex processing environment.

The difficulty remains that there exists no single method that predicts all important panel properties. Lap-shear techniques have been shown to be reliable and inexpensive in the monitoring of thermoset cure. The values obtained from the experiments do not relate to a specific property of the adhesive or adherent, but the results provide a good comparison mapping their interaction. μDEA has been proven to be compatible with the PMDI/wood system. μDEA is related to lap-shear techniques by both being sensitive to crosslink density. However, μDEA not necessarily related to the development of mechanical strength but rather to the viscosity of the adhesive.

DSC and FTIR can monitor the progression of chemical including the consumption of free isocyanate. Both DSC and FTIR are not related to mechanical strength development, however. The determination of reaction products has proven to be difficult with FTIR, but FTIR has been used successfully for in-process monitoring of isocyanate consumption. DSC cannot be used in conditions where a large amount of mechanical pressure is placed on a specimen during cure. DSC creates its own highly
controlled environment where small changes in heat are measured. Reactions occurring early in cure generally produce more heat than those occurring late in cure where crosslinks are formed. Thus, $\mu$DEA and lap-shear results thus would become effective for monitoring changes late cure and DSC and FTIR are effective early in cure.

Methodologies have been established for modeling thermoset cure. Phenomenological approaches have been implemented to model complex systems. In addition, complex systems have been fit to both nth order and autocatalyzed kinetics. The kinetic models have the potential for modeling complex processing environments. These models could then implemented for the optimization of processing parameters and control of the end product.
Literature Cited


CHAPTER 2

THE EVALUATION OF 4-4’ DIPHENYLMETHANE DIISOCYANATE CURING IN A SATURATED STEAM ENVIRONMENT:

A COMPARISON OF TECHNIQUES

Abstract

The cure of polymeric 4-4’ diphenylmethane diisocyanate, PMDI, in wood composite manufacturing has been the subject of much research. The exact contribution of polyurethane, polyurea, and polyurete formation with PMDI/wood bonding is still debated. This study foregoes the mechanism controversy and studies the cure as a whole. Micro-Dielectric Analysis (µDEA) was utilized to monitor the cure of PMDI in a controlled heat, steam, and pressure environment representing those encountered during wood composite manufacturing. A small steam-generating chamber was mounted onto a universal testing machine producing saturated steam environments between 110° and 140°C. The degree of cure calculated from µDEA was a basis for further spectroscopic, calorimetric, and lap-shear analysis. Differential Scanning Calorimeter (DSC) and Fourier Transform Infrared spectroscopy (FTIR) techniques revealed a large consumption of isocyanate early in cure. However, mechanical strength, as revealed by lap-shear analysis, developed late in cure. Low lap-shear strengths and a plateau in conversion rates were detected for 110° and 120°C and may indicate a diffusion-controlled reaction and crystallization effect.
**Introduction**

Polymeric 4-4’ diphenylmethane diisocyanate (PMDI) has proven to be an effective binder in wood composites (Deppe 1977, Johns et. al 1981, Frink and Sachs 1981). Even at elevated moisture contents, PMDI achieves physical and mechanical properties comparable or superior to those of phenol-formaldehyde binders (Deppe 1977, Frink and Sachs 1981, Chelak and Newman 1991, Hawke et. al 1992, and Hawke et. al 1993). Pressing wood composites at high moisture contents can produce improved composite properties while decreasing energy consumption and VOC emissions from dryers (Chelak and Newman 1991). In addition, steam injection pressing has been shown to capitalize on the unique behavior of PMDI cure under high moisture conditions (Johnson et. al 1993). The injection of saturated steam into a mat produces a rapid rise in core temperature, decreasing press times, and softens the wood component for decreased mat pressures (Geimer 1982).

Because the complex nature of wood composite manufacturing complicates the study of adhesive cure, much controversy exists over the actual reactions leading to the PMDI adhesive bond. The possible bonding mechanisms of PMDI have been extensively discussed and investigated (Johns 1980, Weaver and Owen 1992, Galbraith and Newman 1992, Wendler et. al 1996, Rosthauser et. al 1997). Isocyanate reacts readily with water to form an amine (Equation 1). The amine is highly reactive and quickly combines with PMDI to form ureas (Equation 2). The difunctional ureas are known to form long chain polymers that can crystallize (Yadev et. al 1996). Polyureas may react with the remaining PMDI to form a biuret (Equation 3) or polyuret. These trifunctional or higher molecules form crosslinked networks, but are thermally reversible.
A potential for chemically bonding wood exists by the reacting isocyanate and wood hydroxyl groups to form a urethane bond (Equation 4). The urethane can further react with isocyanate to form an allophanate (Equation 5), which provides sites for crosslinking. Allophanate and biuret formations are thermally reversible at temperatures as low as 106°C but generally occur between 120° and 150°C (Saunders and Frisch 1962). There has been little solid evidence of the urethane reaction occurring in substantial quantities within realistic pressing conditions and with high molecular weight isocyanates (Johns 1983, Wendler et al 1996, Rosthauser 1997). Finally, isocyanate can
react with itself to form difunctional uretdiones (Equation 6) or isocyanurates (Equation 7) for another possible crosslinking reaction (Saunders and Frisch 1962).

\[
\text{Equation 4} \\
R-N=C=O + R'-OH \rightarrow \begin{array}{c}
\text{R} \\
\text{N} \\
\text{C} \\
\text{O} \\
\text{R}'
\end{array}
\]

\[
\text{Equation 5} \\
R-N=C=O + R''\text{N-C=O}R'' \rightarrow \begin{array}{c}
\text{R} \\
\text{N} \\
\text{C} \\
\text{O} \\
\text{R}' \\
\text{O} \\
\text{R}''
\end{array}
\]

\[
\text{Equation 6} \\
2R-N=C=O \rightarrow \begin{array}{c}
\text{H} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{N}
\end{array}
\]

\[
\text{Equation 7} \\
3R-N=C=O \rightarrow \begin{array}{c}
\text{H} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{N} \\
\text{O} \\
\text{C} \\
\text{O}
\end{array}
\]

Although much of the recent research concerning PMDI bonding of wood addresses the mechanism of bonding, a need exists for an effective method of monitoring the rate at which PMDI is converted into a network polymer. An effective method of monitoring cure must consider: 1) the point at which the bond strength can resist delamination 2) reduction of free isocyanate levels for safe storage and handling and
optimization of resin usage. Therefore, accurate analysis of cure and its relation to mechanical properties would lead to process models that optimize press-times and resin usage.

Methods exist for evaluating the progression of the cure reaction regardless of pathway. Most available techniques measure properties resulting from cure, not changes in molar concentrations of the reactants. However, many of these techniques cannot evaluate cure in realistic conditions of heat, steam, and pressure.

Secondary methods of evaluating physical changes occurring during cure can be correlated to bond strength between adherents. Lap-shear tests succeed in characterizing cure of thermoset adhesives with wood substrates (Humphrey and Zavala 1989, Geimer et. al 1990). Lap-shear specimens can be pressed under controlled conditions for evaluation. Shear strength obtained from lap-shear tests relates directly to the crosslink density of the adhesive.

Micro-dielectric analysis (μDEA) is used to monitor ion flow and dipole orientation with an applied alternating electric field. The change in conductivity of a thermoset resin during cure relates directly to viscosity (Day 1988). In addition the viscosity of a curing thermoset is affected by the morphology. The effects of diffusion, crystallinity, and crosslink density have been detected by μDEA (Day et. al 1990a and Day et. al 1990b). Because of its sensitivity, μDEA is susceptible to moisture movement inside of a panel encountered during manufacturing (Wolcott and Rials 1995a). The cure of PMDI, however, dominates the dielectric response during the pressing of a particleboard panel (Wolcott and Rials 1995b).
Primary measures of cure may also be approached by calorimetric and spectroscopic techniques. Calorimetric methods measure the heat generated by the cure reaction. The heat generated corresponds directly to the conversion of the reactants. However, no direct correlation exists between measured heats and bond strength development (Geimer et. al 1990). Spectroscopic techniques, such Fourier Transform Infrared spectroscopy (FTIR) and nuclear magnetic resonance, can measure quantities of reactants and products present. These methods have the capability of also determining the identity of the reactants. In the study of PMDI cure, overlapping signals mask urethane, biruret, and polyurea formation, but the amount of isocyanate still present can be reliably detected (Wendler et. al 1996, Rosthauser et. al 1997).

**Objectives**

The overall goal of this research is to characterize the cure of PMDI by developing an in-situ technique to monitor PMDI resins while pressing wood composites. The development of an effective technique will aid in efficient process modeling to optimize press-times and resin usage. The monitoring technique should be sensitive to both the chemical and physical measures of cure. The cure of PMDI should be mechanically sufficient as to prevent panel blows and chemically stable to minimize free isocyanate exposure. The three specific objectives of this research are:

1. Monitor PMDI cure in a saturated steam environment by the use of μ-DEA,

2. Validate the use of μ-DEA by calorimetric, mechanical, and spectroscopic techniques, and

3. Relate μ-DEA cure to chemical and physical cure phenomenon.
Methods and Materials

Flake Preparation

Quaking aspen (Populus tremuloides) was chosen for its uniformity, availability, and popularity in the composites industry. Aspen logs were locally obtained and quartered, producing a radial face. To minimize differences due to early and late wood structure, blocks cut from the quarters were submerged in distilled water under vacuum for two hours. A microtome was used to slice strands to 0.60-mm thickness. The strands were dried between plate glass in a 103°C oven. The strands were then sorted for defects and allowed to equilibrate at room temperature for a minimum of two days before testing.

A commercial PMDI (Mondur Bayer 541) was applied to the strands using a small handheld airbrush. The mass of the specimen was sequentially inspected until the target resin level was met (+/- 1%, oven-dried mass basis).

Steam Pressing

The coated strands were cured using a 127-mm diameter chamber attached to a screw driven, universal testing machine. The press was composed of an internal reservoir for steam generation and two heated aluminum platens enclosed with a polyurethane sleeve (Figure 1). Upon heating, liquid water was evaporated in the integrated reservoir. The steam passed through a baffle system and holes in the bottom platen to reach the pressing area. Samples were pressed to 0.90-mm stops. The deformation corresponded to a 25 percent compaction ratio while ensuring good contact between the two strands. Four cartridge heaters embedded into each platen provided heat, while on/off controllers
maintained the temperature. To prevent oscillations in temperature at the set-point, two heating rates were utilized, 6.5°C/min for 110°C and 16°C/min for 120°, 130°, and 140°C. The saturated steam environment was monitored with an attached pressure sensor and maintained at each of the set-point temperatures.

**Figure 1:** Environmental chamber mounted to a universal-testing machine. An integrated reservoir supplies steam to maintain a saturated steam environment.

**Dielectric Analysis**

Isothermal dielectric scans were performed at 110°, 120°, 130°, and 140°C inside the steam-press. A Micromet Eumetric System III dielectric analyzer with a mid-conductivity signal conditioner and integrated digitated electrode (IDEX) sensor was used. Using a personal computer, data was acquired at 10 second intervals over four dielectric frequencies (1, 10, 100, and 1000 Hz), for 20 minutes. Resin levels of 0, 3, 5, and 7 percent were applied to 88.9 x 25.4-mm aspen strands. An IDEX sensor and a
thermocouple were placed between two sprayed flakes and secured by masking tape applied to both ends of the flake pair.

For resin-coated specimens, the maximum conductivity was taken as the onset of cure. Previous research with epoxy resins has shown this conductivity maximum corresponds to a minimum in viscosity and the beginning of network formation (Day et al. 1990a). The cessation of cure is marked by a minimum constant in conductivity that resembles an asymptote. Therefore, a slope criterion must be established to mark complete cure. In epoxy systems, the conductivity slope has been related to crosslink density, i.e. a low slope correlates to a high crosslink density (Day et. al 1990a). As a criterion for complete cure in this system:

$$\frac{d \log \sigma(t)}{dt} = 0.01 \log (\text{siemens}) s^{-1}$$

Equation 8

The degree of conversion ($\alpha$) is calculated by:

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

Equation 9

Where $\sigma(t)$ was the conductivity at any time, $\sigma_{\text{max}}$ was the maximum conductivity, and $\Delta \sigma$ was the difference between the maximum and the minimum conductivity.

The degree of cure determined from the $\mu$DEA experiments was used as a baseline for the subsequent DSC, lap-shear, and FTIR experiments. The cure process was evaluated at 0 (onset of cure), 25, 50, 75, and 100 percent as defined by dielectric data. Specimens were pressed to the prescribed level of dielectric cure and then removed for evaluation by other techniques for comparison. The specimen was removed from the press and quenched gently between two steel plates at room temperature. The time
required for removal and quenching did not exceeding 30 seconds. This process created an inherent time difference between µDEA and partial cure tests.

**DSC**

Seven percent PMDI was applied to 12mm x 55mm x 60-mm flakes on a single side. The 7 percent resin load was to increase the observed heat of reaction that was very small for 3 percent PMDI. A 25-mg sample was removed from the partially cured flakes and placed in a stainless steel DSC pan sealed with a rubber O-ring. To maintain a saturated steam environment within the DSC pan, 2µl of distilled water was added. Dynamic temperature scans were then performed with a 20°C/minute heating rate from 30° to 200°C.

To determine the degree cure from the DSC scans, the residual heat of cure was calculated by numerically integrating the power and time relationship for each ramp using the trapezoidal method. The degree of cure was then defined by:

$$\alpha = \frac{Q(t)}{Q_0}$$

Equation 10

where, $\alpha$ is the degree of conversion, $Q(t)$ is the residual heat at time, $t$, and $Q_0$ was the total heat as determined from an un-pressed sample.

**Lap-shear**

A PMDI dosage consistent with a 3 percent resin level was applied to the bonded tip area only (Figure 2). A resin level of 3 percent was selected experimentally to reduce the bonding efficiency observed in higher resin loads. Wood strands the lengths equal to
that from the grip to bond area were coated with silicon based release agent and placed on the specimen. These strands were used to ensure that the specimens were pressed evenly, while excluding discontinuities and preventing adhesion to the flakes. Tabs adhered to the specimens were applied prior to pressing with a hot melt adhesive. With the exception of being evaluated at times corresponding to the 3 percent PMDI level of dielectric cure, 6 specimens were pressed for the same isotherms as described in the DSC methods.

A screw-driven universal testing machine equipped with urethane coated tension grips was used for mechanical evaluation. The tension grips were mechanically tightened to secure both tabbed ends of the sample. The test speed was set at 1.27mm/min. Specimens were tested to ultimate strength noting wood or adhesive failures.

![Figure 2: Skematic of a lap-shear specimen. The lap-length represents the bonded portion of the strand where the resin is applied. Tabs were applied to align the sample in the testing apparatus.](image)

**FTIR**

FTIR was performed on partially cured aspen flake pairs coated with 7 percent PMDI. Impermeable Teflon® cloth was placed between the flake pairs to prevent bonding. A 7 percent PMDI resin load helped to increase the isocyanate signal over 3 or
5 percent levels. Attenuated Total Reflectance spectroscopy (ATR) was performed by placing a flake on either side of the ATR crystal in contact with the PMDI coated face. The isocyanate peak at 2275-2263 cm\(^{-1}\) was very pronounced despite the noise in other regions of the spectrum. A small peak observed in the isocyanate region (wave number 2260 cm\(^{-1}\)) of the ATR spectrum for aspen was subtracted from the absorption of the specimens coated with PMDI.

**Results and Discussion**

**Dielectric Cure**

Moisture changes have proven problematic in the dielectric monitoring of wood composites (Wolcott and Rials 1995a). However, using a controlled isothermal saturated steam environment minimizes these difficulties. The dielectric response of wood in this environment differs substantially from that of a wood/PMDI system (Figure 3). This result is consistent with those achieved by Wolcott and Rials (1995a) where the dielectric response of the wood/water component is discussed in greater detail.
**Figure 3:** µDEA conductive response for wood and wood/PMDI at a 120°C platen temperature for resin levels of 0, 3, 5, and 7 percent.

**Influence of Resin Level**

The influence of resin levels on conversion is shown in (Figure 4). Higher levels of conversion are reached in less time for a 3 percent resin level when compared to the larger resin loads. After longer times in the press cycle strands coated with 3 and 5 percent resin completed cure significantly faster than the 7 percent level. Longer cure times may indicate a more diffusion-controlled reaction at higher resin levels. Differences in conductivity can be generally observed where the 5 and 7 percent levels show a larger conductivity change than the 3 percent level. The large conductivity change indicates a morphologic difference impeding the ion flow. Possible sources for differences in morphology could be attributed to an increase in crosslink density, crystallinity, or both. As in epoxy resins, these morphological differences can control diffusion of moisture, thereby regulating reaction rate, at higher resin levels.
Figure 4: Degree of cure for a 130°C platen temperature for varying resin levels. Degree of cure was calculated by a ratio of the change of conductivity at a given time to the total change in conductivity from the onset to cessation of cure.

Influence of Cure Temperature

Cure rate is highly dependent on temperature. The maximum rate increases with an increase in temperature (Figure 5 and Figure 6). A shift to a maximum in cure rate at higher degrees of conversion accompanies an increase in temperature. Late in cure, a shoulder occurs in the reaction rates for a period at 110° and 120°C and to a small extent at 130°C. The shoulder represents a large amount of cure time even though it occurs above 80 percent of cure (Figure 6). Two possible explanations for the shoulder event are a diffusion-controlled event or dissociation of biruet or alophanate.

Allophanate and biruet dissociation is reported to occur in the temperature range from 120° to 150°C (Saunder and Frisch 1962). However, biuret formation was
prevalent in wood-isocyanate cured systems at low moisture contents (below 4.5%) and temperatures above 160°C (Wendler et. al 1996). Biuret formation was not reported to breakdown until 185°C. At lower temperatures and high moisture content polyurea formation dominated cure, but biuret linkages were still present. The polyurea network appeared to be stable for long cure times at 120°C.

Diffusion occurs when a reactant is being limited and not held within close proximity to other reactants during cure. Differences in morphology of a system control diffusion. However, more amorphous polyurea network shows greater rates of diffusion than more crystalline networks (Yadev et. al 1996). The formation of polyurea crystals was found to be rate dependent and thus, temperature dependent (Figure 5). In addition, increasing crosslink density provides spatial separation between polymer chains and reduces intermolecular forces (Saunders and Frisch 1962). The spatial separation gives rise to the higher diffusion rates in amorphous polymers. µDEA has been shown to be sensitive to changes in crosslink density and crystallization in thermoset polymers (Day et. al 1990a and Day et. al 1990b).
Figure 5: Cure rate for degree of cure at 5 percent PMDI. A shoulder exists in the cure rate at 0.85 cure for 110° and 120°C.

Figure 6: Rates of cure for vary platen temperatures at 5 percent PMDI. A shoulder in the cure rate exists at 350 seconds for 110°C platen and 175 seconds for 120°C.
The reaction of isocyanates and water to form polyureas is well documented (Saunders and Fisch 1962). Due to the long chain structure of polyureas, there are many sites available for hydrogen bonding and are known to be highly crystalline in structure. Differences in conductivity can again be observed between PMDI cured at low and high temperatures. A large drop and lower final conductivity at 110°C indicates a difference in morphology between the low and high temperature cured adhesive bonds. The differences in conductivity become less apparent above 120°C. This drop in conductivity can be attributed to the crystallization of urea at lower temperatures impeding ion flow.

**Comparison of Techniques**

A rapid drop in the isocyanate was observed using FTIR prior to the onset of dielectric cure (Figure 7). This large decrease in isocyanate was consistent with the high degree of cure measured by DSC for 130° and 140°C (Figure 8). Cure measured by DSC at low temperatures did not develop as rapidly as that evaluated by FTIR. ATR is a surface technique and is unclear how far into a specimen it investigates. Pressed specimens may have allowed for more absorption of PMDI by reducing viscosity during heating. This absorbed PMDI may reduce the amount isocyanate available.

The depth of PMDI penetration in wood is measured to be 1.0 to 1.5 mm (Marcinko et. al 1995). The cure products are masked by the strong wood signal in the ATR spectrum (Rasthauser et. al 1997). Reaction products present on the surface may hide free isocyanate, but DSC results indicate isocyanate is consumed before the cessation of dielectric cure. Reaction products and depth of resin penetration may limit the movement of free isocyanate not consumed early in cure. In addition the evidence of
diffusion would suggest a highly crystalline polyurea structure being formed at lower temperatures. However, polyuret or biurret formation is more likely to occur at higher temperatures where there is an increase in crosslink density.

Lap-shear results show little gain towards shear strength of the bond with the progression of chemical cure (Figure 9). The lap-shear results agree closely with the µDEA, which shows that cure develops at a much slower rate than spectroscopic and calorimetric techniques indicate. Both viscosity and bond strength depend on crosslink density. Thus, mechanical methods of evaluation are sensitive to chain building and possible crosslinking that contribute to the strength of the adhesive bond.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Resin (%)</th>
<th>Peak Conductivity (log ohm⁻¹)</th>
<th>Minimum Conductivity (log ohm⁻¹)</th>
<th>Difference (log ohm⁻¹)</th>
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<tr>
<td>110</td>
<td>3</td>
<td>-8.24</td>
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<td>0.96</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>-7.64</td>
<td>-8.73</td>
<td>1.09</td>
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<td></td>
<td>7</td>
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</tr>
<tr>
<td>120</td>
<td>3</td>
<td>-7.62</td>
<td>-8.28</td>
<td>0.66</td>
</tr>
<tr>
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</tr>
<tr>
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<td>7</td>
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</table>

Table 1: Differences among µDEA conductivities for varying resin levels and platen temperatures. The difference represents the loss of conductivity from the onset to the cessation of cure.

The measure of viscosity by µDEA is more sensitive in the later stages of cure than that of the lap-shear test. However, actual mechanical strength of the bond cannot be directly evaluated by µ-DEA. Where lap-shear analysis revealed strength differences
between adhesive bonds cured at low and high temperatures there was a larger drop in conductivity at 110°C than at the higher temperatures (Table 1). At 110° and 120°C lap-shear analysis, according to the established criteria for degree of conversion, shows only 80 percent of conversion where the higher temperatures are reaching complete cure at 75 percent dielectric cure. The large drop in conductivity that was attributed to crystallization may also reduce the shear strength of the bond. Crystal formation reduces crosslink density and the ability to transfer stress.

Figure 7: FTIR results for the reduction in the isocyanate peak. µDEA used as the basis for FTIR analysis with the exception of an uncured PMDI coated strand reported at 0 dielectric conversion.
Figure 8: Comparison of DSC and μDEA results for PMDI cure. μDEA was used as a basis for partial DSC cure experiments at different platen temperatures.

Figure 9: Average lap-shear results using μDEA cure as a basis at different platen temperatures. The average wood failures are presented as an upper limit to the test.
Conclusions

µDEA has shown to be an effective tool in the monitoring of PMDI cure in a saturated steam environment. The change in conductivity associated with PMDI cure can be readily discerned from the dielectric response of wood under controlled pressing conditions. The measure of ion flow through the system is very sensitive to slight changes in the formation of the adhesive network during cure. Although µDEA is closely related to mechanical evaluation, it cannot directly predict strength changes resulting from different cure parameters. However, the potential of modeling process parameters still exists. In comparison to analytical methods that monitor the chemical advancement of cure, µDEA is not sensitive to the earlier stages of cure. Of relevance to the manufacturing of wood composites with PMDI adhesives, the amount of free isocyanate remaining in a product is a health concern that must be considered. FTIR has shown that free isocyanate is consumed rapidly, well before dielectric cure is complete. However due to the strength of the wood ATR signal, no evidence was presented as to the nature of the reaction resulting from cure.

A shoulder in the cure rate during the late stages of cure for 110° and 120°C is not evident at higher temperatures. A diffusion-controlled reaction could be one possibility for the decrease in rate of conversion, or a strong case for crystallization could also be made. Due to the structure of polyurea chains that are believed to form during PMDI cure, crystallinity is higher for lower reaction rates. Crystallization has been associated with increases in mechanical strength for polymeric materials; however, the morphology will determine the performance of the system. In temperature regions where
crystallization is more likely to occur, lap-shear values are lower and a large drop in conductivity was observed. The potential for the reduction of stress transfer exists with the presence of more crystalline structures and fewer crosslinks.


CHAPTER 3

THE EVALUATION OF 4-4’ DIPHENYLMETHANE DIISOCYANATE CURE IN A SATURATED STEAM ENVIRONMENT:

KINETIC STUDY

Abstract

Many commonly used techniques to model adhesive cure in wood composites do not consider realistic pressing conditions. Micro-dielectric analysis (µDEA) was performed inside a saturated steam environment to monitor the adhesive cure of 4-4’ diphenylmethane diisocyanate (PMDI) with wood strands. A first order autocatalyzed kinetic model was employed for analysis to determine kinetic parameters. The kinetic parameters followed an Arrhenius relation. More common dynamic calorimetric techniques were performed to compare kinetic results. A single dynamic ramp technique and µDEA produced models that predicted similar results at higher temperatures, but µDEA predicts a longer cure time at low temperatures. A modified ASTM method predicted an earlier completion of cure. The modified ASTM methods are in agreement with results previously obtained by partial cure experiments (Harper 1998). The isothermal µDEA method predicts higher activation energies and Arrhenius frequency factors than single dynamic ramps. The differences among the activation energies and frequency factors suggest the modeling of different cure phenomenon by calorimetric and
dielectric techniques. Calorimetric and µDEA methods model different reactions that occur simultaneously at higher temperatures and independently at lower temperatures.

**Introduction**

A primary manufacturing objective is to minimize processing time to maximize production capacity and profits. The cure of 4-4’ diphenylmethane diisocyanate, PMDI, must consume free isocyanate during the manufacture of wood composites and have enough mechanical strength to resist delaminating upon opening the press. Kinetic modeling can provide an effective means of optimizing process parameters. During the manufacture of wood composites, the wood/adhesive system is exposed to rapidly changing conditions of pressure, steam, and heat. Controversy abounds over the nature of the wood/PMDI adhesive bond produced under realistic processing environments (Johns 1983, Weaver and Owen 1992, Galbraith and Newman 1992, Wendler et. al 1995, Rosthauser et. al 1997). The complex nature of the reaction makes mechanistic approaches to modeling extremely difficult. It has been shown that the cure of PMDI in a saturated steam environment can be monitored *In-situ* (Harper 1998). Micro-dielectric analysis (µDEA) can be applied to a phenomenological model of cure.

Few methods used to evaluate cure can be applied in realistic processing environments (Humphrey and Zavala 1989, Geimer et. al 1990, Humphrey 1990). Differential Scanning Calorimeter, DSC, is one such method where volatile gases can be contained during evaluation. A saturated environment can be created inside the DSC pan, but mechanical pressure cannot be applied to the sample as in manufacturing. However, numerous studies have been conducted using calorimetric techniques to

A basic rate equation (Equation 11) relates the rate of cure at a constant temperature to a function \( f(\alpha) \) of cure by a constant \( k \), where \( \alpha \) is the degree of cure.

\[
\frac{d\alpha}{dt} = kf(\alpha) \quad \text{Equation 11}
\]

The rate constant follows the Arrhenius equation,

\[
k = Ae^{\frac{E}{RT}} \quad \text{Equation 12}
\]

or

\[
\ln k = \ln A - \frac{E}{RT} \quad \text{Equation 13}
\]

where \( E \) is the activation energy, \( A \) is the Arrhenius frequency factor, \( R \) is the ideal gas constant, and \( T \) is temperature. The Arrhenius frequency factor relates the amount of collisions that need to occur in a unit time to carry out the reaction, and the activation energy describes the amount of energy needed to propagate cure.

Two types of phenomenological kinetic models are available for the modeling thermosetting adhesives, nth order and autocatalyzed (Prime 1981). The thermoset models are related to the rate equation by \( f(\alpha) \). Reactions that have their greatest rate of cure at the onset of the reaction are characterized as nth order. For \( f(\alpha) \) an nth order reaction is described by Equation 14, where \( n \) is the order of the reaction.

\[
f(\alpha) = (1 - \alpha)^n \quad \text{Equation 14}
\]

In contrast, autocatalyzed kinetics is characterized by \( d\alpha/dt \) reaching a maximum at 30-40 percent cure (Prime 1981). In general autocatalyzed reactions take the following form:
\[ f(\alpha) = a^m(1 - \alpha)^n \]  

Equation 15

where \( m \) and \( n \) are reaction orders whose sum is equal to the overall reaction order. From previous research, the cure of PMDI would most closely fit the autocatalyzed model (Harper 1998). Most commonly, a maximum rate of cure is reached at 45-55 percent of cure. Although this behavior does not strictly follow the specified criteria, it certainly is more accurate than an \( n \)th order kinetics approach. Standardized methods do exist for evaluating kinetic parameters of \( n \)th order reactions (ASTM E698-79 1979). However, these methods must be modified for autocatalyzed models (Prime 1981, Provder et. al 1983, Lam 1987).

**Objectives**

The overall objective for kinetic modeling the cure of PMDI is to optimize processing parameters to shorten pressing cycles. To optimize a process where PMDI is used as the adhesive, two events must be considered in the model: 1) the point at which the bond strength can resist panel blows and 2) reduction of free isocyanate levels for safe storage. The importance associated between the chemical and mechanical properties in modeling can be illustrated where both conditions must be satisfied. In this case, a phenomenological approach that encompasses the overall process may be more useful than a mechanistic model because the mechanistic model may not accurately relate to mechanical property development. To achieve this overall goal the specific objectives of this experiment are:

1. To analytically model the cure of PMDI in a saturated steam environment,
2. Employ the use of \( \mu \)DEA in evaluating cure for model development,
3. Utilize an autocatalyzed model employing only one rate constant,
4. Compare single dynamic ramp and ASTM calorimetric methods of modeling, and

5. Relate the models to physical phenomenon.

**Methods and Materials**

Quaking aspen (*Populus tremuloides*) flakes were obtained and prepared to conduct μDEA (Harper 1998). A commercially available PMDI was applied at 3, 5, and 7 percent to the aspen strands with an atomized spraying technique on an oven dry mass basis. μDEA was performed to obtain a degree of cure and rate of cure for flake pairs pressed in an enclosed steam-producing press. Isotherms were performed at 110°, 120°, 130°, and 140°C in a saturated steam environment.

A series of dynamic DSC ramps were performed. 7% PMDI was applied to aspen strands (Harper 1998). The flake pairs were placed together, and 20mg was removed with a small hole punch and placed in hermetically sealed, stainless steel DSC pan. 2μl of distilled water was added to provide enough moisture to create a saturated steam environment. The DSC pan incorporated an o-ring to seal in all volatile gasses. Dynamic ramps were then performed from 30° to 200°C for heating rates of 1°, 5°, 10°, 15°, and 20°C/min. Degree of cure was calculated as:

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

Equation 16

Where, \(\alpha\) is the degree of cure, \(Q(t)\) is the residual heat at time, \(t\), and \(Q_0\) is the total heat of reaction. \(Q_0\) was calculated by numerically integrating the power with respect to time by the trapezoidal method. To obtain the rate of cure:
\[ \frac{d\alpha}{dt} = P(t) \frac{Q_o}{Q} \]  \hspace{1cm} \text{Equation 17}

Where, \( P(t) \) is the power at any time. An autocatalyzed model (\textit{Equation 15}) was applied to both isothermal and dynamic studies. The model was derived to find kinetic parameters that follow the Arrhenius relationship. By integrating \textit{Equation 11} comparisons were made between parameters and results previously obtained for PMDI cure (Harper 1998).

\textbf{Results and Discussion}

\( \mu \text{DEA} \)

An autocatalyzed kinetic model can be derived to determine kinetic parameters. Where \( \alpha \) is the degree of cure and \( m \) and \( n \) are reaction orders whose sum is the overall order of the reaction. The rate constant, \( k \), follows the Arrhenius relation. Starting with the autocatalyzed kinetic model,

\[ \frac{d\alpha}{dt} = k\alpha^m(1-\alpha)^n \]  \hspace{1cm} \text{Equation 18}

Where \( m + n = 1 \) for the assumption of first order kinetics.

\[ \frac{d\alpha}{dt} = k\alpha^{1-n}(1-\alpha)^n \]  \hspace{1cm} \text{Equation 19}

Rearrange to obtain a linear equation,

\[ \ln \left( \frac{d\alpha}{dt} \right) = \frac{1}{\alpha} \ln k + n \ln \left( \frac{1-\alpha}{\alpha} \right) \]  \hspace{1cm} \text{Equation 20}

A linear regression can be fit to this equation to determine \( k \) and \( n \). Thus, \( \ln k \) vs. \( 1/T \) can be plotted to find Arrhenius parameters. As an alternative to this method, a substitution
for \( \ln k \) in Equation 20 can yield Equation 21 that can be fit to a multiple linear regression.

\[
\ln \left( \frac{d\alpha}{dt} \right) = \ln A - \frac{E}{RT} + n \ln \left( \frac{1 - \alpha}{\alpha} \right)
\]

An alternative method for determining reaction orders is by finding the maximum rate of cure.

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

Equation 22

Take the derivative of Equation 22 at \( \alpha = \alpha_{\text{max}} \) where \( \alpha_{\text{max}} \) is the degree of cure at the maximum rate of cure.

\[
\alpha_{\text{max}} = m
\]

Equation 23

Comparisons to second order kinetics can be made by substituting \( m + n = 2 \). Such a comparison is used to validate the use of first order kinetics over higher orders. Thus Equation 20 will be changed to,

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

Equation 24

This will also influence the reaction order where,

\[
a_{\text{max}} = \frac{m}{2}
\]

Equation 25

This result for second order kinetics was achieved by Lam, 1987.
Figure 10: First order kinetic plot for 120°C platens and 5% PMDI with linear regression.

Figure 11: Second order kinetic plot for 120°C platens and 5% PMDI with linear regression.

Linear regressions were performed to compare first and second order kinetics (Figure 10 and Figure 11). A higher coefficient of determination ($R^2$) was achieved for the first order model than second order. Only the linear portion of the data was fit to a linear regression to determine rate constants and reaction orders. Towards the end of cure, the
reaction becomes diffusion controlled, which is not accurately represented in this model. Temperature dependence was observed in the reaction order (Figure 12). The temperature dependence of n could effect dynamic modeling studies where the reaction order is assumed to be independent, such as ASTM E698.

**Figure 12:** Temperature dependence of the n reaction order.

**Figure 13:** Determination of Arrhenius parameters for 5 percent PMDI by µDEA isotherms.
### Table 2: Arrhenius parameters obtained by the μDEA isotherms.

<table>
<thead>
<tr>
<th>% PMDI</th>
<th>E (kJ/mol)</th>
<th>$A \times 10^5$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>75.1</td>
<td>1500</td>
</tr>
<tr>
<td>5</td>
<td>65.5</td>
<td>73</td>
</tr>
<tr>
<td>7</td>
<td>82.6</td>
<td>3550</td>
</tr>
</tbody>
</table>

A linear regression was then performed to calculate the Arrhenius parameters (Figure 13 and Table 2). The differences between resin loads becomes more pronounced at the higher temperatures. A comparison between the predicted and experimental results for cure can be facilitated by integrating Equation 11 (Figure 14, Figure 15, Figure 16, and Figure 17). Although the model results are close to what is experimentally observed, an earlier completion of cure is generally predicted. Little difference is observed between the 3 and 7 percent PMDI models.

**Figure 14:** Comparison of data and model generated from kinetic parameters calculated by μDEA for 110°C.
**Figure 15:** Comparison of data and model generated from kinetic parameters calculated by μDEA for 120°C.

**Figure 16:** Comparison of data and model generated from kinetic parameters calculated by μDEA for 130°C.
Figure 17: Comparison of data and model generated from kinetic parameters calculated by $\mu$DEA for 140°C.

DSC

The ASTM E698-79 method is a very accurate and effective method for evaluating the kinetics of thermally unstable systems (Prime 1981). Kinetic parameters can be estimated from multiple dynamic ramps with different heating rates. For ASTM E698-79, a first order kinetic model is fit to the peak exotherm temperature ($T_p$), in DSC data. The basis for this model is that the peak occurs at a constant cure, $\alpha_{\text{max}}$, and that an nth order reaction is followed (Lam 1987). Both assumptions are often violated when evaluating autocatalyzed reactions. A slight temperature dependence of $\alpha_{\text{max}}$ was observed for the dynamic ramps (Table 3). The ASTM method was modified to fit autocatalized kinetics. Starting with first order kinetics and Equation 19,
\[
 f(\alpha) = \int \frac{d\alpha}{\alpha^{1-n}(1-\alpha)^n} = \int k dt = \int A e^{-\frac{E}{RT}} dt
\]

Equation 26

For \(\alpha_{\text{max}}\) and \(t_{\text{max}}\),

\[
 f(\alpha_{\text{max}}) = \int_{0}^{\alpha_{\text{max}}} \frac{d\alpha}{\alpha^{1-n}(1-\alpha)^n} = \int_{0}^{t_{\text{max}}} e^{-\frac{E}{RT}} dt
\]

Equation 27

For a constant heating rate, \(\beta\), where

\[
 \beta \cdot dt = dT
\]

Equation 28

\[
 f(\alpha_{\text{max}}) = \int_{0}^{\alpha_{\text{max}}} \frac{d\alpha}{\alpha^{1-n}(1-\alpha)^n} \approx \int_{0}^{T_{p}} e^{-\beta \frac{E}{RT}} dT
\]

Equation 29

The right hand integral can be solved using Doyle’s approximation (Doyle 1965, Prime 1981, Lam 1987)

\[
 f(\alpha_{\text{max}}) \approx \frac{AE}{R\beta} e^{-5.33 \cdot \frac{1.05E}{RT_{p}}}
\]

Equation 30

To obtain a linear form

\[
 \ln \beta + f(\alpha_{\text{max}}) \approx \ln \left( \frac{AE}{R} \right) - 5.33 - \frac{1.05E}{RT_{p}}
\]

Equation 31

The Arrhenius parameters can be solved by plotting \(\ln \beta + \ln f(\alpha_{\text{max}})\) vs. \(1/T_{p}\). By following the ASTM method for predicting activation energies, similar results to the modified method can be obtained. This method neglects the slight dependence of \(\alpha_{\text{max}}\) on temperature. \(A\) has been modified to fit autocatalyzed kinetics (Prime 1981),
where B is a stoichiometric ratio of reactants. B = 1 is assumed when the quantities of reactants are mixed. Results from the modified ASTM and modified A methods are E = 62.1 kJ/mol and A = 4.28 * 10^6 and E = 60.1 kJ/mol and A = 1.927*10^6 s^{-1} respectively. These results produce similar results for predicting cure (Figure 19, Figure 20, Figure 21, and Figure 22). The multiple dynamic ramps compare favorably with results previously obtained for completion of cure (Table 5) (Harper 1998).

<table>
<thead>
<tr>
<th>β (°C/min)</th>
<th>T (°C)</th>
<th>α_{max}</th>
<th>f(α_{max})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>79.6</td>
<td>71.8</td>
<td>1.99</td>
</tr>
<tr>
<td>5</td>
<td>105.4</td>
<td>68.9</td>
<td>1.93</td>
</tr>
<tr>
<td>10</td>
<td>118.8</td>
<td>68.3</td>
<td>1.91</td>
</tr>
<tr>
<td>15</td>
<td>126.3</td>
<td>67.1</td>
<td>1.89</td>
</tr>
<tr>
<td>20</td>
<td>134.0</td>
<td>67.3</td>
<td>1.89</td>
</tr>
</tbody>
</table>

**Table 3:** DSC dynamic ramps results reveal a slight temperature dependence of α_{max}.

**Single Dynamic Temperature Ramp**

Starting with Equation 19 and the Arrhenius equation, kinetic parameters can be estimated from a single dynamic temperature ramp.

\[
A \equiv \frac{E}{RT_p} \exp \left( \frac{E}{RT} \right)
\]

\[
\alpha_{max} = 2B \alpha_{max} + 2(\alpha_{max})^2 - 3(\alpha_{max})^2 - B
\]

Equation 32

The parameters can then be calculated by multiple linear or a nonlinear regression where \( m + n = 1 \) (Equation 34). Parameters calculated from a nonlinear regression showed
similar results for each dynamic ramp (Table 4). The nonlinear regressions were performed for up to 80 percent of cure. These parameters can then be used to predict cure for isothermal temperatures as previously discussed (Figure 18). The parameters obtained from the individual ramps produce similar results for all temperatures.

<table>
<thead>
<tr>
<th>Method/β (°C/min)</th>
<th>E (kJ/mol)</th>
<th>A × 10^5 (s⁻¹)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified ASTM</td>
<td>62.1</td>
<td>42.8</td>
<td>-</td>
</tr>
<tr>
<td>Modified A</td>
<td>60.1</td>
<td>60.1</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>61.3</td>
<td>24.2</td>
<td>0.52</td>
</tr>
<tr>
<td>5</td>
<td>55.3</td>
<td>4.00</td>
<td>0.51</td>
</tr>
<tr>
<td>10</td>
<td>55.5</td>
<td>3.88</td>
<td>0.50</td>
</tr>
<tr>
<td>15</td>
<td>55.5</td>
<td>3.96</td>
<td>0.49</td>
</tr>
<tr>
<td>20</td>
<td>55.5</td>
<td>4.08</td>
<td>0.51</td>
</tr>
</tbody>
</table>

**Table 4:** Kinetic parameters from single dynamic DSC ramps and the modified ASTM methods.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Partial Cure DSC (s +/- 15s)</th>
<th>Modified ASTM model (s)</th>
<th>Modified A (s)</th>
<th>10°C/min Single Dynamic Ramp (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>591</td>
<td>216</td>
<td>256</td>
<td>332</td>
</tr>
<tr>
<td>120</td>
<td>135</td>
<td>131</td>
<td>159</td>
<td>210</td>
</tr>
<tr>
<td>130</td>
<td>71</td>
<td>82</td>
<td>100</td>
<td>140</td>
</tr>
<tr>
<td>140</td>
<td>57</td>
<td>52</td>
<td>65</td>
<td>102</td>
</tr>
</tbody>
</table>

**Table 5:** Comparison of DSC results and models for the determination of the end of PMDI cure.
**Figure 18:** Cure estimated by DSC single dynamic ramps models at 120°C

**Comparison of Kinetic Models**

μDEA has been found to be more sensitive to the late stages and less sensitive to early stages of cure than DSC (Harper 1998). μDEA does indeed seem to be more sensitive late in cure at 110°C (**Figure 19**). However, at higher temperatures the chemical and physical cure appears to occur simultaneously for single dynamic temperature ramps and μDEA (**Figure 20, Figure 21, and Figure 22**). The multiple dynamic methods follow results previously obtained for DSC partial cure experiments (**Table 4**) (Harper 1998). The single dynamic ramp method, though consistent, overestimates cure as verified by the partial cure experiments.
Figure 19: Comparison of kinetic model results for all DSC and μDEA methods at 110°C

Figure 20: Comparison of kinetic model results for all DSC and μDEA methods at 120°C
**Figure 21:** Comparison of kinetic model results for all DSC and μDEA methods at 130°C

**Figure 22:** Comparison of kinetic model results for all DSC and μDEA methods at 140°C
Although similar results for degree of cure were obtained by the μDEA and single dynamic ramp models, A and E are still different. The high E for μDEA would suggest that more energy is needed for network formation than reactions that generate the majority of the heat. The two phenomena occur simultaneously late in cure as indicated by the single dynamic ramps. The modified ASTM methods indicate that chemical cure and vitrification is occurring simultaneously, but chemical cure is complete well in advance of dielectric cure.

**Conclusions**

μDEA analysis has been related to physical and mechanical properties of thermoset adhesives (Day et. al 1990, Harper 1998). Degree of cures and rates of cure calculated from μDEA data fit a first order autocatalyzed kinetic model. The end of cure calculated by the μDEA models was earlier than that of the data. This difference maybe associated with the reaction being diffusion controlled and that the adhesive crystallizes late in cure. Activation energy and frequency factors for PMDI in a saturated steam environment were higher for μDEA than those calculated by dynamic calorimetric techniques. The higher activation energy could be associated with the formation of long polymer chains and crosslinked networks. Kinetics from a single DSC dynamic temperature ramp consistently produced models that are similar to μDEA at high temperatures. Modified ASTM methods produce slightly higher activation energies, but the end of cure is predicted to be earlier. The end of cure for the modified ASTM methods corresponds closely to that observed earlier in partial cure study. All DSC
methods produced activation energies lower than that of \( \mu \text{DEA} \). This difference may indicate a higher sensitivity towards the onset of cure where amine, urea, and urethane reactions could be taking place before network formation. However, at higher temperatures both reaction schemes could be occurring simultaneously.
Literature Cited


CHAPTER 4
CONCLUSIONS

μDEA effectively monitored PMDI cure in a saturated steam environment. Peak and minimum values of dielectric conductivity relating to the cure of PMDI were clearly distinguishable from the signal of a coated aspen strand. Differences in morphology of the curing resin resulted from differences in cure rate and produced the observed changes in conductivity. A large drop in conductivity, slow reaction rate, and a shoulder in the rate plots may support the hypothesis of crystal formation. The diffusion rate and conductivity is lower for more closely packed crystalline structures than for a crosslinked amorphous polymer.

The interpretation of the observed kinetics suggests that the PMDI reaction is diffusion controlled for high degrees of conversion at low temperatures. Reduced lap-shear values at low temperatures may result from a reduction in crosslink density caused by increased crystallinity. The utilization of X-ray diffraction is recommended to validate the presence of crystal structures in the adhesive network.

A large reduction in isocyanate is observed early in the cure process, leading to no gain in physical or mechanical properties. The multiple ramp DSC kinetic models validated the large consumption of isocyanate well in advance of dielectric cure. Combined kinetic models derived from μDEA and DSC can be utilized to predict the consumption of isocyanate and mechanical strength development. In addition, models can be extended to wood-composite manufacture to evaluate the progression of chemical and physical interpretations of cure for the purpose of a) ensuring the reduction of free
isocyanate for safe storage and handling and b) preventing panel delamination. Rates of reaction and rate constants, which are controlled by processing parameters, can then be related back to mechanical testing.
APPENDIX A

FLAKE IMAGES
**Flake Images**

Flake images were obtained to check resin distribution. A solution of 0.01 percent toluidine blue O stain to water was prepared. Aspen strands were submerged in the solution and placed under a vacuum for 15 minutes (Kamke et. al 1996). The flakes were then rinsed in ethyl alcohol and dried flat in a 103°C oven. PMDI at levels of 3, 5, and 7 percent was applied to 88.9 x 25.4mm flakes at two flakes per resin level. Flakes were then cured at 130°C in the steam producing press for 10 minutes. Five images were taken for each flake at 6x magnification with illumination from a mercury lamp. Flake images show good resin distribution (**Figure 23, Figure 24, and Figure 25**). A large difference in the amount of resin covering the surface area for each level was also observed. Resin also was observed to wet very well along the grain of the wood.
Figure 23: Five images each for 3 percent PMDI coated flakes A and B.
Figure 24: Five images each for 5 percent PMDI coated flakes A and B.
Figure 25: Five images each for 7 percent PMDI coated flakes A and B.

**Literature Cited**

APPENDIX B

LAP-SHEAR ANALYSIS
**Lap-shear**

A finite element analysis was performed on a lap-shear setup to obtain the optimum geometry of the specimen. The specimen size was limited by the geometry of the press that has a diameter of 127mm. Therefore, a model was developed assuming a perfect bond between strands. Mechanical properties for aspen used in the analysis were obtained from Bodig and Goodman 1973. The load was applied in tension by holding one end fixed and displacing the opposite end 2.54 mm. A comparison of normal stress (perpendicular to the flake face) in the bond line was then made between lap-length (length of the bondline) of 6.35, 12.7, and 19.05mm. This comparison was made under the assumption that the idealized condition would be pure shear in the bondline (i.e. no normal stress). The results indicate that there are large stresses developing in the case of the 6.35mm sample, but the other two cases are comparable with the longer lap-length having the lowest stress (**Figure 26**). However, to reduce the overall length of the sample and leave more of the sample to be placed in the grips, a lap-length of 12.7mm was chosen. The final geometry of each flake was 63.5mm x 12.7mm x 0.6mm. With a gauge-length of 25.4mm and lap-length of 12.7mm the remainder of length was used to adhere wood tabs with a hot-melt adhesive that were placed in the grip. The tabs were adhered prior to resin application.
**Figure 26**: Normal stress in the bondline for varying lap-lengths as determined by finite element analysis.

**Ansys 3.2 Input File**

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/filnam, lap
/title, Wood lap shear specimen
/prep7

c*** Define specimen geometry (inches)
ft=0.01626
gl=1.50
ll=.5

c*** Define key points
k,1, 0, 2*ft
k,2,gl, 2*ft
k,3, 0, ft
k,4,gl, ft
k,5,gl+ll, 2*ft
k,6,gl+ll, ft
k,7,gl, 0
k,8,gl+ll, 0
k,9,2*gl+ll, ft
```
k, 10, 2*gl+11, 0

*** Define lines
mg=25   *Number of elements along gage
ml=15   *Number of elements along lap
mt=5    *Number of elements through thickness
1,1,2,mg  
1,3,4,mg  
1,6,9,mg  
1,8,10,mg 
1,2,5,ml  
1,4,6,ml  
1,7,8,ml  

*** 4 node plane strain element
et, 1, 42, 2

*** Define material properties
el=1e6
ex, 1, el*1.23     *el (quaking aspen in psi)
ey, 1, el*0.0452   *et
ez, 1, el*.1065    *er
prxy, 1, 0.50      *nlt
pryz, 1, 0.33      *ntr
prxz, 1, 0.37      *nlt
gyz, 1, el*0.01861 *gtr
gxy, 1, el*0.0833  *gtr
gxy, 1, el*0.0592  *glt

*** Create areas
mat, 1
elsize,, mt
a, 1, 2, 4, 3  
a, 2, 5, 6, 4  
a, 4, 6, 8, 7  
a, 6, 9, 10, 8  
amesh, all

*** Constrain nodes at x=0
nsel, s, loc, x, 0, 0
d, all, all, 0
nsel, all

*** Apply load at x=2*gl+11
nsel, s, loc, x, 2*gl+11, 2*gl+11, 0
c*** sf, all, pres, -10e3
d, all, uy, 0
d, all, ux, 0.01
nsel, all

wsort

finish

/solu
solve
Literature Cited