CHEMICAL AND PHYSICAL INTERPRETATION OF MDI CURE IN SATURATED STEAM ENVIRONMENTS

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SUMMARY

The cure of polymeric 4-4' diphenyhnethane diisocyanate, PMDI, in wood composite manufacturing has been the subject 'of much research. The exact contribution of polyurethane, polyurea, and polyurete formation to PMDI/wood bonding is still debated. This study foregoes the mechanism controversy and studies the cure from a panel consolidation process. Micro-dielectric analysis, μDEA, was utilized to monitor the cure of PMDI in a controlled environment of heat, steam, and pressure simulating those encountered during wood composite manufacturing. A small steam-generating chamber was mounted to a universal testing machine that produced saturated steam environments between 110° and 140°C. The degree of conversion calculated from μDEA provided a basis for further spectroscopic, calorimetric, and lap-shear analysis. Differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR) revealed a large consumption of isocyanate early in cure. However, lap-shear analysis showed that mechanical strength did not develop until late in cure. Low ultimate lap-shear strengths and a plateau in conversion rates were detected for bondlines cured at 110" and 120°C. These characteristics may indicate a transition to diffusion-controlled reaction resulting from a vitrification effect such as crystallization. A phenomenological approach to composite cure kinetics was applied to model isothermal μDEA and dynamic DSC data. Models successfully predicted cure that followed analytical results. Higher activation energies were obtained for μDEA than were generated from DSC methods. The observed differences in activation energy are interpreted in terms of differing mechanisms in the progression of chemical and physical cure.

INTRODUCTION

Wood composites are typically bonded with thermosetting adhesives. In the interior of a hot-pressed panel, these polymeric resins are subject to a constantly changing cure environment that is partially composed of water vapor. If the wood moisture content is relatively high or a steam-injection process is used, the pressurized internal panel environment often consists of saturated steam (Kamke and Casey 1988, Johnson *et* al 1993). A high moisture environment during pressing has many benefits to composite properties; however, the water vapor content influences the adhesive cure (Wang *et al* 1994). Polymeric 4-4' diphenylmethane diisocyanate (PMDI) has proven to be an effective wood binder when pressed at elevated moisture contents (Chelak and Newman 1991, Hawke *et al* 1993). This success results largely because PMDI reacts with water leading to the formation of polyurea, a major gap-filling component in the PMDI/wood bond (Wendler and Frazier 1996b, Rosthauser *et* al 1997).

Because the complex nature of wood composite manufacturing complicates the study of adhesive cure, much controversy exists over the different reactions leading to the PMDI adhesive bond. The possible bonding mechanisms of PMDI have been extensively discussed and investigated (Weaver and Owen 1992, Galbraith and Newman 1992, Wendler *et al* 1996a and b, Rosthauser *et* al 1997). Regardless what mechanism of bonding actually dominates, a need exists to understand the rate at which PMDI is converted into a network polymer. An effective description of cure must consider 1) the point at which the bond strength can resist delamination, and 2) reduction of free isocyanate levels for safe product storage and optimal resin use. Therefore, accurate analysis of cure and its relation to mechanical properties would lead to process models that optimize press-time and resin usage.

Evaluating Cure

Methods exist for evaluating the progression of cure 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 needed for pressing wood composites. Micro-dielectric analysis (μDEA) measures cure *in-situ* and have been shown to be compatible with curing PMDI (Wolcott and Rials 1995b). μDEA measures changes in conductivity of adhesives during cure, which relates directly to viscosity and therefore morphology (Day 1988). Bond strength development cannot be directly evaluated from μDEA.

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.

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), can measure the structure and quantities of reactants and products present. 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 (Rosthauser *et al* 1997).

OBJECTIVES

The overall goal of this research is to characterize the cure of the PMDI/wood bond from both a physical and chemical perspective. While providing data for kinetic analysis and interpretation of cure mechanisms, the three specific objectives of this research are:

1. Monitor PMDI cure in a saturated steam environment using μDEA;
2. Relate the progression of cure as interpreted by μDEA to conventional calorimetric, mechanical, and spectroscopic techniques.
3. Analytically model the progression of PMDI cure.

METHODS

Strand Preparation

Aspen (*Populus tremuloides)* strands (0.6-mm thick) were sectioned from the radial face of blocks using a microtome. The strands were dried between plate glass in a 103°C oven, sorted for defects, and allowed to equilibrate at room temperature for a minimum of two days before testing.

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

Steam Pressing

The coated strands were cured using a sealed 127-mm diameter press attached to a screw driven, universal testing machine. The press configuration included an internal water reservoir, two heated aluminium platens, and a corrugated polyurethane sleeve (Figure 1). Upon heating, liquid water was evaporated in the 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.

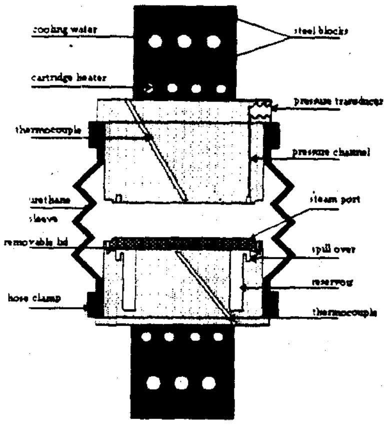

Figure 1: Environmental chamber mounted to a universal-testing machine. An integrated reservoir supplies steam to maintain a saturated steam environment.

Dielectic Analysis

Isothermal dielectric scans were performed at 110°, 120°, 130°, and 140°C inside the steam-press. A Micromet Eumetric System III dielectric analyzer equipped with a mid-conductivity signal conditioner and inter-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 a single side of 88.9 x 25.4-mm aspen strands. An IDEX sensor and thermocouple were placed between two sprayed strands, and the entire strand/sensor assembly was loosely secured at the ends with masking tape.

For resin-coated specimens, the maximum conductivity was taken as the onset of cure. Day *et al* (1990a) has shown this conductivity maximum to correspond with a minimum in viscosity and the beginning of network formation for epoxy resins. 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). Equation 1 defines a criterion for completion of cure.

$$\frac{d \log a(t)}{dt} = 0.01 \log(siemen) s^{-1} \qquad \text{Equation 1}$$

The degree of cure (a) is calculated by:

$$\alpha = \frac{\log \sigma_{max} - \log \sigma(t)}{\log \Delta\sigma} \qquad \text{Equation 2}$$

Where o(t) is the conductivity at any time, σ_{max} is the maximum conductivity, and $\Delta\sigma$ is the difference between the maximum and the minimum conductivity.

The degree of cure (Equation 2) determined from the μDEA experiments were 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. 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 exceed 30 seconds; however, this process did create an inherent time difference between μDEA and partial cure tests.

DSC

Seven percent PMDI was applied to the strands on a single side. The 7 percent resin load was used to obtain a sufficient heat of reaction for accurate measurement. A 25-mg sample was removed from the partially cured strands and placed in a large volume, 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 performed with a 1°, 5°, 10°, 15°, and 20°C/minute heating rate from 30” to 200°C, using a Perkin-Elmer Model DSC-7 instrument.

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:

$$\alpha = \frac{Q(t)}{Q_0} \qquad \text{Equation 3}$$

Where, *a* is the degree of cure, Q(t) is the residual heat at time, t, and Q_o 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 of the strands. Silicon-coated wood strands were placed in the un-bonded gauge lengths to ensure even pressing of the specimens. Tabs were adhered to the specimen ends with a hot melt adhesive prior to pressing.

Mechanical evaluation was performed using a screw-driven universal testing machine equipped with urethane coated mechanical grips. Specimens were tested at 1.27 mm/min to ultimate strength. Either wood or adhesive failures were noted by visually inspecting the failure surfaces.

FTIR

FTIR was performed on a Nicolet Model DXB-20 spectrophotometer for partially cured aspen strand pairs coated with 7 percent PMDI. Teflon@ cloth was placed between the strand pairs to prevent bonding. A 7 percent PMDI load was used to increase the isocyanate signal over 3 or 5 percent levels. Attenuated total reflectance spectroscopy (ATR) was performed by placing a strand on either side of the KRS-5 crystal in contact with the PMDI coated face. The isocyanate peak at 2275-2263cm^{-1} was pronounced despite the interference in other regions of the spectrum.

RESULTS AND DISCUSSION

Dielectric Cure

Moisture changes in the composite during composite manufacture have proven problematic for *in-situ* dielectric monitoring (Wolcott and Rials 1995a). However, using an 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 2). 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.

Influence of Resin Level

The influence of resin levels on conversion is shown in Figure 3. Higher levels of conversion are reached in less time for a 3 percent resin level when compared to the 5 and 7 percent loads. Late in the cycle, the 3 and 5 percent resin levels displayed faster cure rates than the 7 percent level. This decreased cure rate for 7 percent resin levels suggests that the cured resin may act as a barrier to slow the diffusion of water to the MDI molecules, thereby decreasing the reactant concentration and rate. Increased cure times at higher resin levels may also indicate a more diffusion-controlled reaction at higher resin levels.

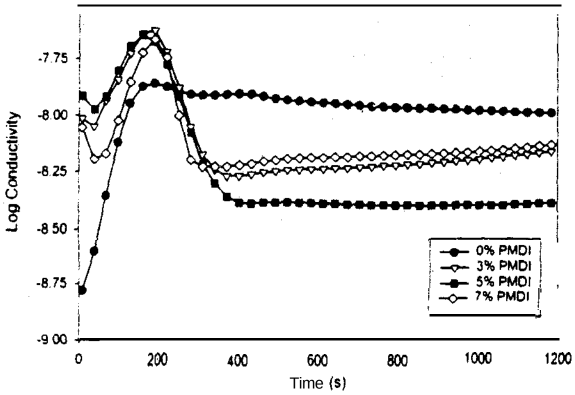

Figure 2: μDEA conductive response for wood and wood/PMDI at a 120 °C platen temperature for resin levels of 0, 3, 5, and 7 percent.

Strands coated with 5 and 7 percent resin levels displayed a larger change in conductivity ($\Delta\sigma$) than the 3 percent level (Table 1). The increased $\Delta\sigma$ indicates a difference in the polymer morphology of the cured adhesive layer. For resin levels with large $\Delta\sigma$, the resulting morphology impedes the ion flow to a greater extent than does the adhesive bond produced with the 3% resin level. Possible sources for morphological differences include crosslink density, crystallinity, or both. In PEEK. systems, morphology has a strong influence on moisture diffusion, thereby regulating reaction rate (Day *et al* 1990b).

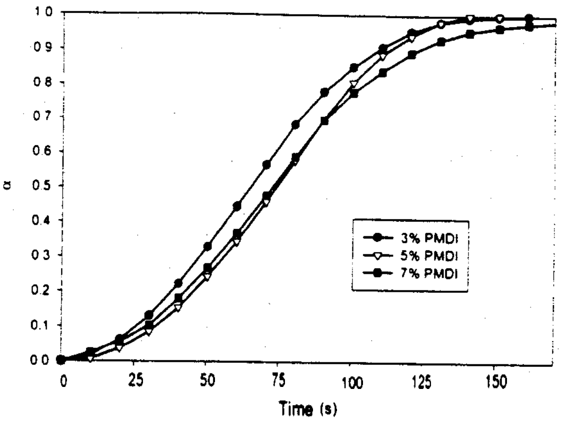

Figure 3: Degree of cure for a 130 °C platen temperature for varying resin levels. Degree of cure was calculated by a ratio of the change of conductivity at a given time to the total change in conductivity from the onset to cessation of cure.

Influence of Cure Temperature

The dielectric interpretation of cure rate ($d\alpha/dt$) is highly dependent on temperature. The maximum rate is found approximately midway through the cure cycle and increases with the isothermal cure temperature (Figure 4). Late in cure, a shoulder in the reaction rate occurs for the isothermal cure temperatures of 110° and 120°C. Although the shoulder occurs above 80 percent of cure, it contributes significantly to the total cure time required at low ‘temperatures (Figure 4). The presence of this shoulder in the dielectric signal indicates that an aberrant change in dielectric behaviour of the curing adhesive bond when approaching high degrees of cure. Ostensibly, this behaviour results from a change in the polymer morphology, reaction mechanism, or interaction between the two.

The long chain, linear structure and polar groups of polyureas favor the development of highly crystalline structures. Differences in conductivity can be observed between PMDI cured at low and high temperatures. A large drop in conductivity at 110°C of 0.96-1.30-log(siemen) indicates a difference in morphology between the low and high temperature cured adhesive bonds. The differences in conductivity become less apparent for cure temperatures above 120°C until a drop of only 0.41-0.65-log(siemen) at 140°C was observed. This drop in conductivity for low cure temperatures can be attributed to the crystallization of polyureas contributing to vitrification and impeding ion flow. Yadev *et al* (1996) found that slow cure rates in polyureas favored high degrees of crystallinity by supplying the time necessary for molecular alignment. Therefore, the reaction rate may overcome any negative effect of low temperature to favour high degrees of crystallinity at cure temperatures of 120°C and below.

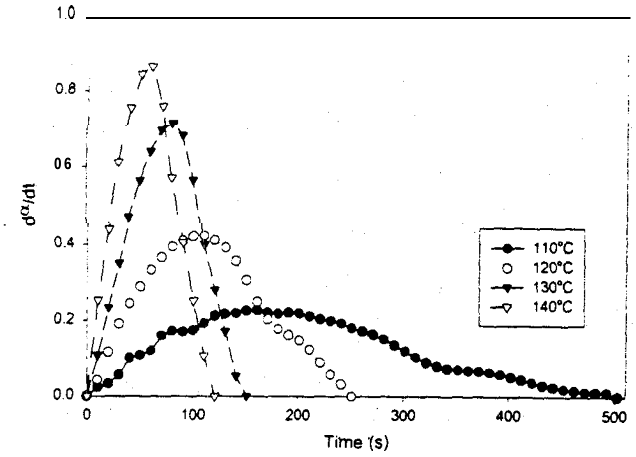

Figure 4: Rates of cure for vary platen temperatures at 5 percent PMDI. A shoulder in the cure rate exists at 350 seconds for 110 °C platen and 175 seconds for 120 °C.

The combined interpretation of these cure mechanisms suggests that the observed shoulders may be related to changes in crystallinity of the polyurea component. The crystalline structure itself may lower conductivity in the final drop of the shoulder. In addition, amorphous regions in polyureas increase diffusion rates over highly crystalline regions. Therefore, the formation of polyurea crystals may be decreasing the diffusion coefficient and limiting the reaction rate.

Differential Scanning Calorimetry

The interpretation of cure by DSC agreed well with that using μDEA for the isothermal cure temperature of 110°C. However, the agreement decreased with increasing temperatures. In fact, samples pressed at 130” and 140°C for only 25 percent of total cure as interpreted by μDEA, displayed virtually no residual heat of reaction. This latter observation is consistent with other research on network polymers (Day 1988). In these systems, much of the total heat of reaction is produced while increasing molecular weight of the oligomers. However, physical properties (e.g. viscosity) are most influenced by the increase in crosslink density, which occurs late in the cure cycle and typically produces little energy. The agreement of the DSC and μDEA data at low cure temperatures may suggest that crosslinking does not contribute strongly to the development of physical properties in these cases. This observation is consistent with the hypothesis that highly crystalline polyurea is primarily formed at low cure temperatures and high moisture environments.

Infra-Red Analysis (FTIR)

Using FTIR, a large drop in the isocyanate peak was observed for all isothermal cure temperatures during the time required to reach the onset of dielectric cure (Figure 5). This large decrease in isocyanate was consistent with the high degree of initial cure as measured by DSC for 130° and 140°C samples (Figure 6). However, the calorimetric interpretation of cure at low temperatures did not agree with the FTIR. The partial heat of reaction measured at the onset of dielectric cure were 98 and 47 percent of the total heat of reaction for samples cured at 110 and 120°C, respectively.

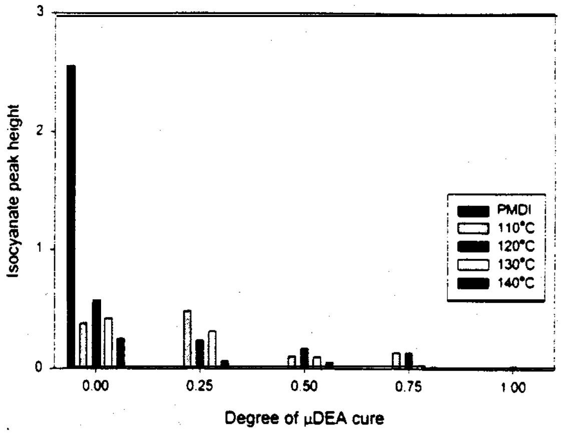

Figure 5: FTIR results for the reduction in the isocyanate peak. µDEA used as the basis for FTIR analysis with the exception of an uncured PMDI coated strand reported at 0 dielectric conversion.

Morphological differences could explain the observed discrepancy in FTIR and DSC cure interpretation for the low temperature samples. Considering the possible crystallization of polyureas, both the reaction of PMDI and the formation of crystalline regions are exothermic processes. If the curing mechanism of wood-PMDI below 120°C is dominated by the formation of polyurea as Wendler and Frazier (1996a) found, samples partially cured at these temperatures should display additional heat flow from the crystallization process.

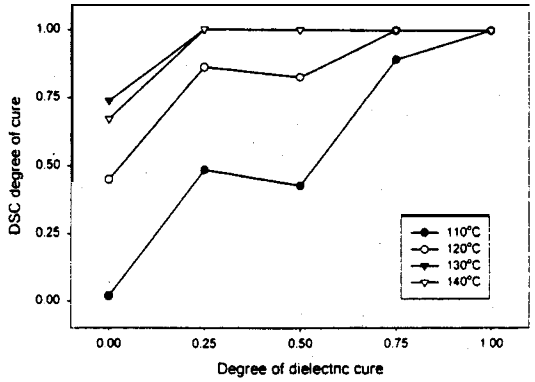

Figure 6: Comparison of DSC and µDEA results for PMDI cure. µDEA was used as a basis for partial DSC cure experiments at different platen temperatures.

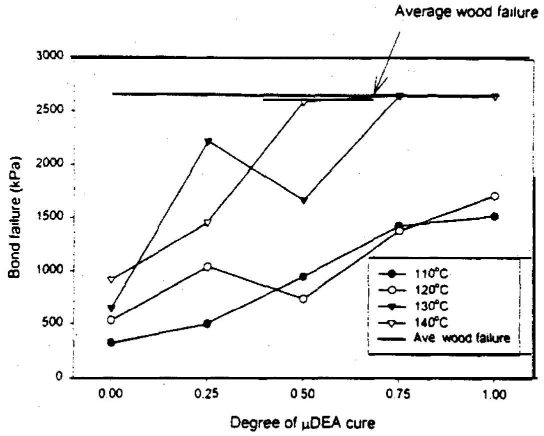

Figure 7: Average lap-shear results using µDEA cure as a basis at different platen temperatures. The average wood failures are presented as an upper limit to the test.

Bond Strength

A consistent increase of lap-shear strength with degree of dielectric cure was observed for all isothermal cure temperatures. This agreement is not surprising because the development of viscosity and bond strength reflect molecular weight build-up and network development, as well as changes in morphological characteristics. However, the actual mechanical strength of the bond cannot be directly related to µDEA observations. Whereas the lap-shear strength was higher for adhesive bonds cured at high temperatures, samples cured at 110°C displayed the largest drop in conductivity (Figure 7). If the polymer morphology of the bondline is different at high and low temperature, then relative changes in the dielectric signal will be the only relevant predictor for cure

Kinetic Modeling

Isothermal µDEA and dynamic DSC data were used to determine cure kinetics. A first order autocatalyzed kinetic model was employed (Equation 4). Procedures were followed to modify ASTM E698-79 test standard for the determination of kinetic parameters for multiple dynamic ramps (Prime 1981, Lam 1987). Also, kinetics was determined for single dynamic temperature scans (Provder *et al* 1983).

$$\frac{da}{dt} = k\alpha^{m}(1-\alpha)^{n} \qquad \textit{Equation 4}$$

Where k is the Arrhenius rate constant, and m and n are reaction orders.

µDEA has been found to be more sensitive to the late stages and less sensitive to early stages of cure than DSC. µDEA does indeed seem to be more sensitive late in cure at 110°C (Figure 8). However, at higher temperatures the chemical and physical cure appears to occur simultaneously for single dynamic temperature ramps and µDEA. The multiple dynamic methods follow results previously obtained for DSC partial cure experiments. The single dynamic ramp method, though consistent, overestimates cure as verified by the partial cure experiments.

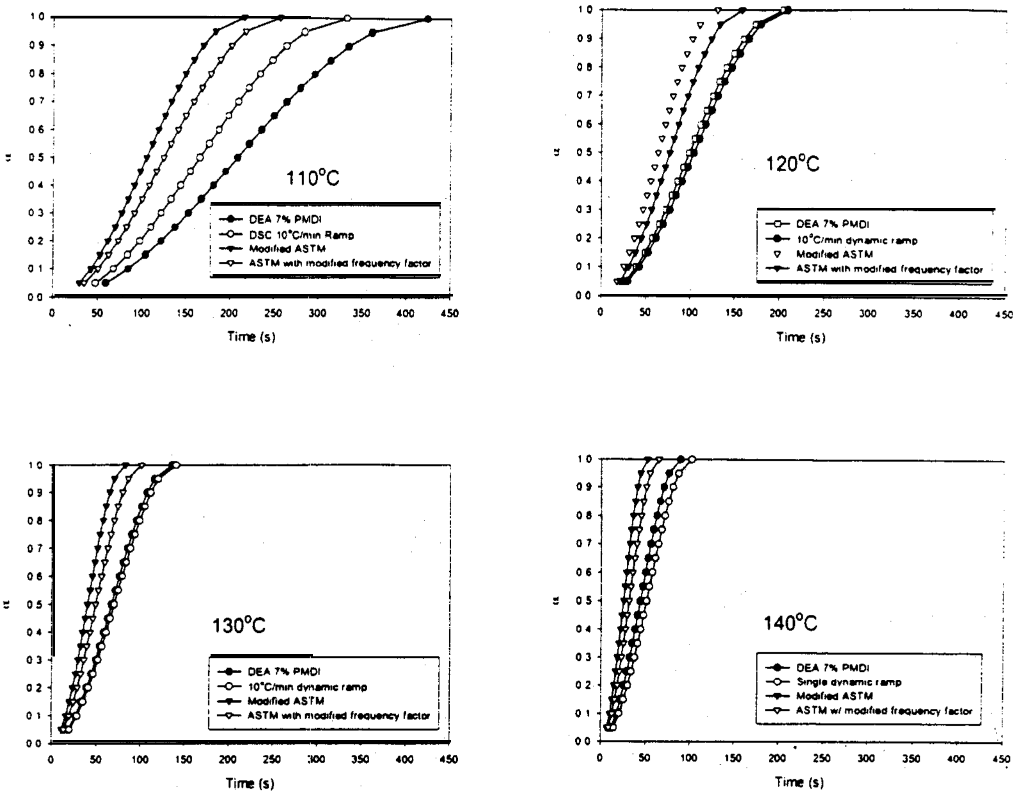

Figure 8: Comparison of kinetic results for DSC and μDEA methods.

CONCLUSIONS

μDEA has proven to be an effective tool in monitoring relative changes in the PMDI/wood bondline. These relative changes relate to differences in morphology during the progression of cure and were clearly discernible from changes due to moisture movement. A large drop in conductivity, slow reaction rate, and a shoulder in the cure-rate support the hypothesis of polyurea crystal growth at low temperatures. However, 130” and 140” C temperatures promote the formation of amorphous regions. The amorphous region is possibly the formation of a crosslinked network promoting, the rapid rise in bond-strength at higher temperatures as revealed by lap-shear analysis. Crystal structures appear to be detrimental to the development of bond-strength.

The large consumption of isocyanate early in cure leads to very little strength development and dielectric cure at low temperatures. This result indicates that most of the isocyanate is not being consumed early by chain building reactions, a view that is consistent with condensation polymerizations. The residual heat and dielectric cure result from the formation of polyurea and crystal structures. However, DSC analysis is not as sensitive to crosslinks late in cure as μDEA accounting for differences in observed cure at the higher temperatures. In addition, only small differences exist between isocyanate consumption for higher and lower temperatures at any stage of dielectric cure as compared to the initial availability. The kinetics of the curing system governs the distribution of the reaction products, which in turn governs bond strength development.

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