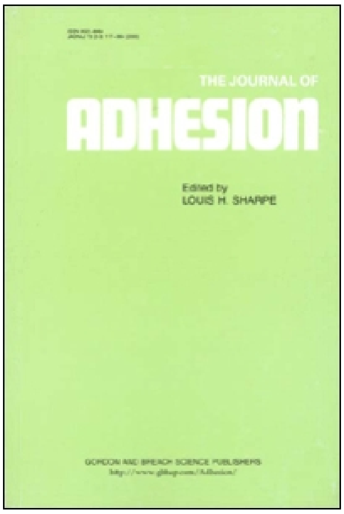

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Harper, David P. , Wolcott, Michael P. and Rials, Timothy G.(2001) 'Evaluating Cure of a pMDI-wood Bondline Using Spectroscopic, Calorimetric and Mechanical Methods', The Journal of Adhesion, 76: 1, 55 — 74
To link to this Article: DOI: 10.1080/00218460108029617
URL: http://dx.doi.org/10.1080/00218460108029617

J. Adhesion, 2001, Vol. 76, pp. 55-74
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Evaluating Cure of a pMDI-wood Bondline Using Spectroscopic, Calorimetric and Mechanical Methods

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(Received 16 July 1999; In final form 17 November 2000)

The cure of polymeric diphenylmethane diisocyanate (pMDI)/wood bondline in a controlled saturated steam environment was monitored using micro-dielectric analysis (μDEA). Saturated steam environments were produced between 110° and 140°C. The degree of cure calculated from μDEA was a basis for further spectroscopic, calorimetric, and mechanical evaluation. Interpretation of calorimetric and spectroscopic analysis revealed large consumption of isocyanate early in cure. However, mechanical strength, as revealed by lap-shear tests, did not develop until late in cure. Low lap-shear strengths and a plateau in conversion rates were detected for samples pressed at 110° and 120°C. Several components of the analysis suggest that low temperature cure may result in crystal formation, leading to diffusion controlled cure.

Keywords: Polymeric diphenylmethane diisocyanate; Dielectric analysis; Differential scanning calorimetry; Shear strength; Wood flakes; Saturated steam

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

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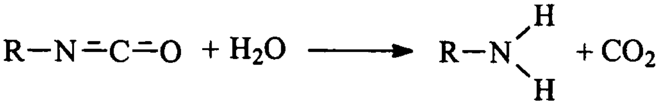
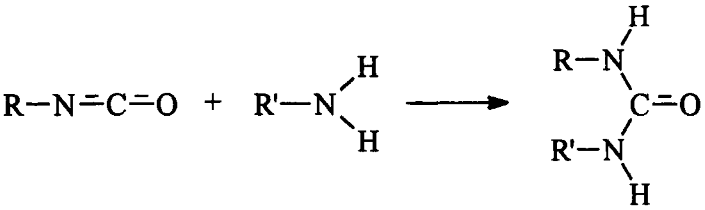
*Corresponding author. Tel.: 509-335-6392, Fax: 509-335-5077, e-mail: wolcott@wsu.edu composed of water vapor. If the wood moisture content is relatively high or if a steam-injection process is used, the pressurized internal panel environment often consists of saturated steam [1,2]. A high-moisture environment during pressing has many benefits to wood composite properties; however, the water vapor content influences the adhesive cure [3]. Polymeric diphenylmethane diisocyanate (pMDI) has proven to be an effective wood binder when pressed at elevated moisture contents [4–7]. 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 [8,9]. Microscopic investigations have shown the ability of pMDI to penetrate the cell walls and to fill cracks present in the wood [10].

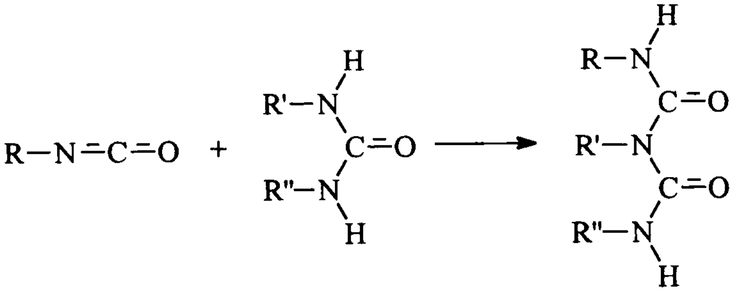
Much controversy exists over the different reactions leading to the pMDI adhesive bond because the nature of wood composite manufacturing complicates the study of adhesive cure. The possible bonding mechanisms of pMDI have been extensively discussed and investigated [8, 11–14]. Isocyanate reacts readily with water to form an amine (Scheme 1). The amine is highly reactive and quickly combines with pMDI to form ureas (Scheme 2). The difunctional ureas are known to form long chain polymers that can crystallize [15]. These polyureas may react with the remaining pMDI to form a biuret (Scheme 3), or polyuret. The trifunctional or higher molecules form crosslinked networks that are thermally reversible at temperatures as low as 106°C, but generally occur between 120° and 150°C [16].



SCHEME 1 Isocyanate reaction with water to form an amine.

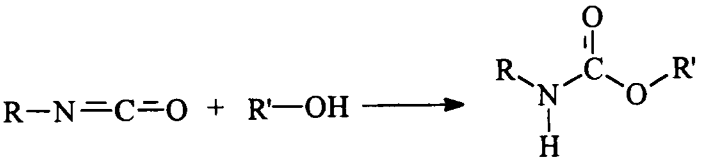


SCHEME 2 Amine and isocyanate reaction to form polyureas.

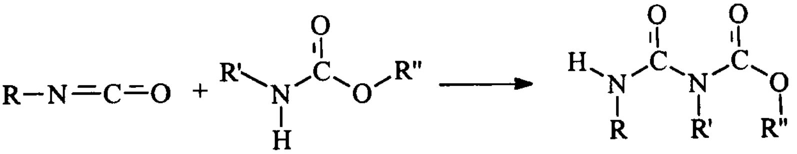


SCHEME 3 Polyureas react with isocyanate to provide crosslinking sites in the form of a biuret.

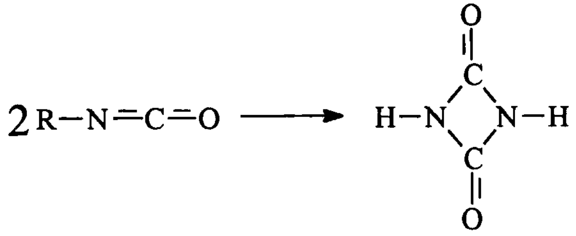
A potential for chemically bonding wood exists by the reaction of isocyanate and wood hydroxyl groups to form a urethane bond (Scheme 4). The urethane can further react with isocyanate to form an allophanate (Scheme 5), which provides sites for crosslinking. Like the biuret and polyuret, allophanate linkages are thermally reversible. There has been little solid evidence that the urethane reaction occurs in substantial quantities within realistic pressing conditions and with high molecular weight isocyanates [9, 11, 14]. Finally, isocyanate can react with itself to form difunctional uretdiones (Scheme 6) or isocyanurates (Scheme 7) for another possible crosslinking mechanism [16].



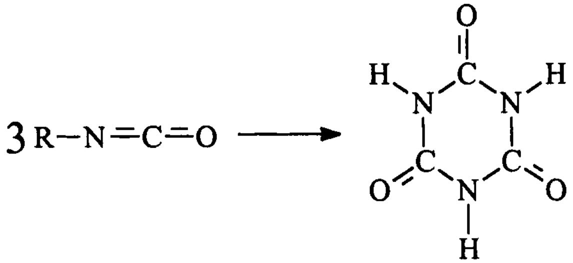
SCHEME 4 Isocyanate reacts with hydroxyls to form a urethane.



SCHEME 5 Crosslink sites can be formed with the reaction of isocyanate with urethane to form an allophanate.



SCHEME 6 Isocyanate reacts with itself to form a uretdione.



SCHEME 7 A cyclic structure can be formed in isocyanate reactions with itself in the form of isocyanurates.

Regardless of 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 the following: (1) the point at which the bond strength can resist delamination and (2) the reduction of free isocyanate levels for safe product storage and optimal resin use. Therefore, accurate analysis of cure and its relationship to mechanical properties would lead to process models, which optimize press times and resin usage.

Numerous 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.

Secondary methods of evaluating physical changes resulting from cure can be correlated to bond strength between adherents. Lap-shear tests succeed in characterizing cure of thermoset adhesives with wood substrates [17, 18]. 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 for thermoset cure analysis by *in situ* monitoring of 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 prior to vitrification [19]. In addition, the conductivity of a curing thermoset is affected by the morphology. The effects of diffusion, crystallinity and crosslink density have been detected by μDEA [20, 21]. μDEA is susceptible to moisture movement inside a panel encountered during manufacturing [22]. The cure of pMDI, however, dominates the dielectric response during the pressing of a particleboard [23].

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 for phenolic resins [18]. Spectroscopic techniques, including Fourier Transform Infrared (FTIR) spectroscopy 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, biuret and polyurea formation, but the amount of isocyanate still present can be reliably detected [9, 24].

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 μ-DEA;
(2) Evaluate the progression of cure as interpreted by μDEA using calorimetric, mechanical and spectroscopic techniques.
(3) Identify the mechanisms governing cure by observed relationships between the progression of physical and chemical cure.

METHODS AND MATERIALS

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 (Bayer Mondur 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 sealed 127-mm diameter press attached to a screw-driven, universal testing machine. The press was composed of an internal water reservoir, two heated aluminum platens, and a corrugated neoprene sleeve (Fig. 1). The sleeve fit over the platen and was clamped to form a seal. 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. Adhesion samples were assembled from two overlapping strands and 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 temperature oscillations at the set point, two heating rates were utilized, 6.5°C/min for 110°C, and 16°C/min

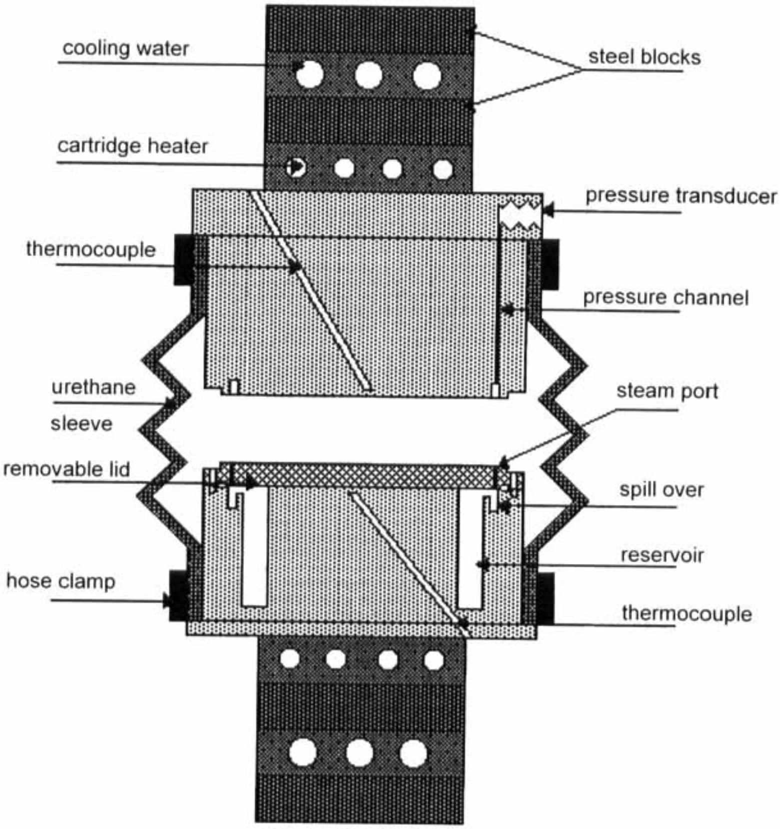


FIGURE 1 Environmental chamber mounted to a universal-testing machine. An integrated reservoir supplies steam to maintain a saturated steam environment.

for 120°, 130° and 140°C. Temperature and gas pressures were continuously monitored.

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, equipped with a mid-conductivity signal conditioner and integrated digitated electrode (IDEX) sensor was used for μDEA. Using a personal computer, data were acquired at 10-second intervals over four dielectric frequencies (1, 10, 100 and 1000 Hz), for

20 minutes. Resin levels of zero, three, five and seven percent were applied to 88.9 by 25.4-mm aspen strands using an airbrush. An IDEX sensor and thermocouple were placed between two sprayed strands. The entire strand/sensor assembly was loosely secured at the ends with pressure sensitive tape.

For resin-coated specimens, the maximum conductivity was taken as the onset of cure. Day *et al.* [21] has shown that this conductivity maximum corresponds 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 [21]. Equation (1) defines a criterion for completion of cure.

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

The degree of cure (α) is calculated by:

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

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

The degree of cure (Eq. (2)) determined from the μDEA experiment was used as a baseline for the subsequent differential scanning calorimeter (DSC), lap-shear, and FTIR experiments. The cure process was evaluated at zero (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. This process created an inherent time difference between μDEA and partial cure tests.

Calorimetric

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 stainless steel DSC pan sealed with a rubber O-ring. To maintain a saturated steam environment within the DSC pan, 2 µl of distilled water was added. Dynamic temperature scans were performed with a 20°C/minute heating rate from 30° to 200°C.

To determine the degree of 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:

$$\alpha = \frac{Q(t)}{Q_0} \tag{3}$$

where α is the degree of cure, Q(t) is the residual heat at time, t and Q_0 is the total heat as determined from an unpressed sample.

Mechanical

A pMDI dosage consistent with a three-percent resin level was applied to the bonded tip area of the strands. Silicone-coated wood strands were placed in the unbonded gauge lengths to ensure even pressing of the specimens. Tabs were adhered to the specimen ends prior to pressing with a hot melt adhesive.

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

Spectroscopic

FTIR was performed on partially-cured aspen strand pairs coated with seven percent pMDI. Teflon® cloth was placed between the strand pairs to prevent bonding. A seven-percent pMDI load was used to increase the isocyanate signal over three or five percent levels. The flake pairs were then pressed to achieve 0 to 100 percent of dielectric cure for 110° to 140°C in a saturated steam environment. Attenuated total reflectance spectroscopy (ATR) was performed on a Nicolet FTIR by placing a strand on both sides of the ATR crystal in contact with the pMDI-coated face. The isocyanate peak at 2275–2263 cm^{-1} was quite pronounced despite the noise in other regions of the spectrum.

RESULTS AND DISCUSSION

Dielectric Cure

Moisture changes in the composite during manufacture have proven problematic for *in situ* dielectric monitoring [22]. 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 (Fig. 2). This result is consistent with those achieved by Wolcott and Rials [20] where the dielectric response of the wood/water component is discussed in greater detail.

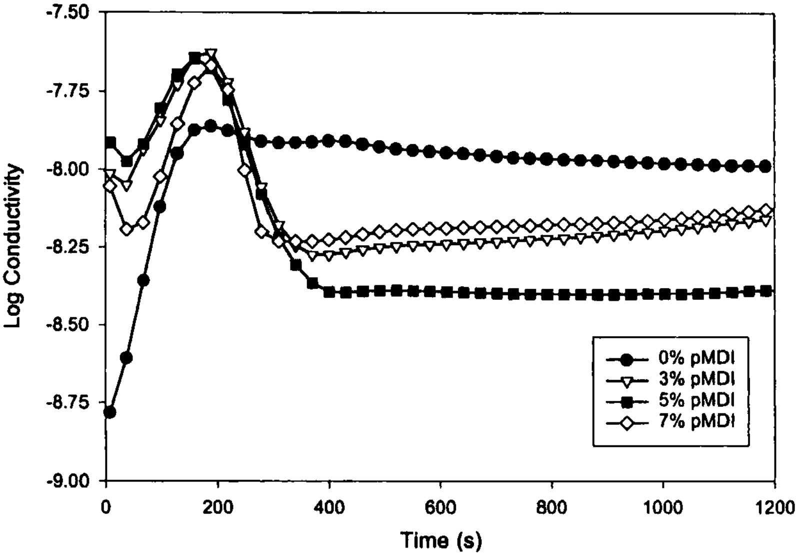


FIGURE 2 μDEA conductive response for wood and wood/pMDI at a 120°C platen temperature for resin levels of 0, 3, 5, and 7 percent.

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 three percent resin level when compared with the five and seven percent loads. Late in the cycle, the three and five percent resin levels displayed faster cure rates than the seven-percent level. This decreased cure rate for seven-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. For overall cure times, the coefficient of variation was estimated to be 8 percent by a series of five repetitions each over all resin levels. The variance suggests that cure times are different between the 3 and 7 percent resin loads. Increased resin levels and longer cure times may indicate a more diffusion-controlled reaction at higher resin levels.

Strands coated with five and seven percent resin levels displayed a larger change in conductivity ($\Delta\sigma$) than the three percent level with the exception of 120°C (Tab. I). The increased $\Delta\sigma$ indicates a difference in

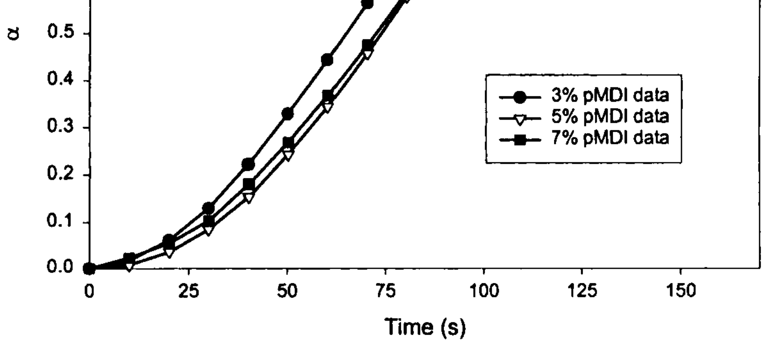


FIGURE 3 Degree of cure for a 130°C platen temperature for varying resin levels. Degree of cure was calculated by a ratio of the change of conductivity at a given time to the total change in conductivity from the onset to cessation of cure.

TABLE I 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

Temperature (°*C*)	*Resin* (%)	*Peak conductivity* (*log ohm*$^{-1}$)	*Minimum conductivity* (*log ohm*$^{-1}$)	*Difference* (*log ohms*$^{-1}$)
	3	−8.24	−9.20	0.96
110	5	−7.64	−8.73	1.09
	7	−7.61	−8.91	1.3
	3	−7.62	−8.28	0.66
120	5	−7.65	−8.39	0.74
	7	−7.54	−8.12	0.58
	3	−7.94	−8.61	0.67
130	5	−7.55	−8.35	0.80
	7	−7.62	−8.50	0.88
	3	−7.85	−8.26	0.41
140	5	−7.94	−8.59	0.65
	7	−7.67	−8.23	0.56

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 percent 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 [21].

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 (Figs. 4 and 5). Late in the 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 (Fig. 5). The presence of this shoulder in the dielectric signal indicates that an aberrant change in dielectric behavior of the curing adhesive bond occurs when approaching high degrees of cure. Ostensibly, this behavior results from a change in the polymer morphology, reaction mechanism, or both.

It is well known that several different polymer structures can form in a wood-MDI adhesive bond. Wendler and Frazier [8, 14] found that

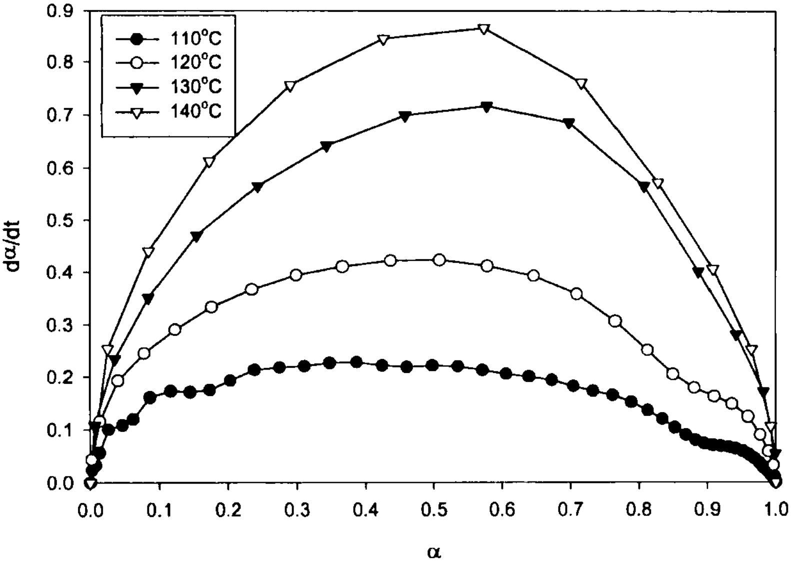


FIGURE 4 Cure rate for degree of cure at 5 percent pMDI. A shoulder exists in the cure rate at 0.85 cure for 110° and 120°C.

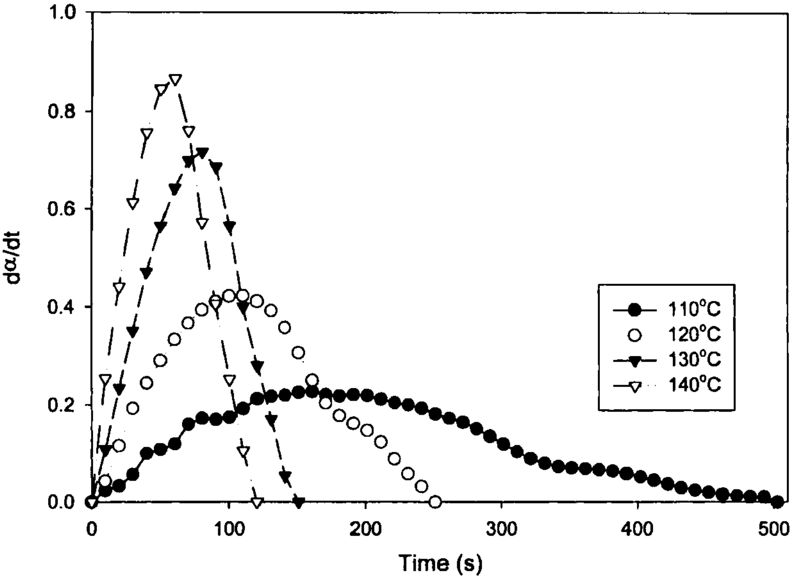


FIGURE 5 Rates of cure for various platen temperatures at 5 percent pMDI. A shoulder in the cure rate exists at 350 seconds for 110°C platen and 175 seconds for 120°C.

both wood moisture content and cure temperature resulted in different amounts of the various moieties. In this research, urea formation was dominant at temperatures of 120°C, below for 4.5 percent wood moisture, and above with biuret linkages present. However, at elevated temperatures, biuret formation was predominant. Evidence of polyurethane formation was found for 185°C temperatures and press times over four minutes only. Given that the shoulder in the dielectric cure rate was only evident at temperatures less than 130°C, any disturbance is likely to involve the polyureas.

Both biuret and allophanate structures are known to be thermally unstable. Saunders and Frisch [16] reported that allophanate and biuret dissociation occurs from 120 to 150°C. However, in studying MDI-bonded wood, Wendler and Frazier [14] noted biuret dissociation only at temperatures of 185°C or above. Although long times were required to complete cure of an MDI-wood bond at 120°C, the resulting polyurea network appeared to be thermally stable. The high temperatures required for disassociation mechanisms are likely to rule out this mechanism as a causal factor for the observed shoulder in the dielectric cure rate.

The long-chain 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 (Tab. I). 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 for cure temperatures above 120°C. This drop in conductivity for low cure temperatures can possibly be attributed to the crystallization of polyureas impeding ion flow. Yadev *et al.* [15] 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 favor high degrees of crystallinity at cure temperatures of 120°C and below.

Finally, diffusion controlled reactions occur when a reactant is limited and not held in close proximity to other reactants during cure. Polymer morphology has a strong influence on diffusion. Amorphous regions in polyureas increase diffusion rates over highly-crystalline regions [15]. In addition, the increased crosslink density afforded by biuret formation provides spatial separation and reduces intermolecular forces among the polymer chains. The spatial separation gives rise to the higher diffusion rates in amorphous polymers [16]. 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, 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 [19]. In these systems, much of the total heat of reaction is produced while the molecular weight of the oligomers is increasing. However, physical properties (*e.g.*, conductivity) 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 polyurea is primarily formed at low cure temperatures.

Infra-red Analysis

Using FTIR, large relative drops in the isocyanate peak were observed for 130° and 140°C cure temperatures prior to the onset of dielectric cure (Fig. 6). The FTIR data were normalized to the observed drops in absorbance as a function of μDEA cure and temperature relative to that observed at the onset of μDEA for 110°C. This large decrease in isocyanate was consistent with the high degree of initial cure as measured by DSC for 130° and 140°C samples (Fig. 7). The partial heats of reaction measured at the onset of dielectric cure were 98 and

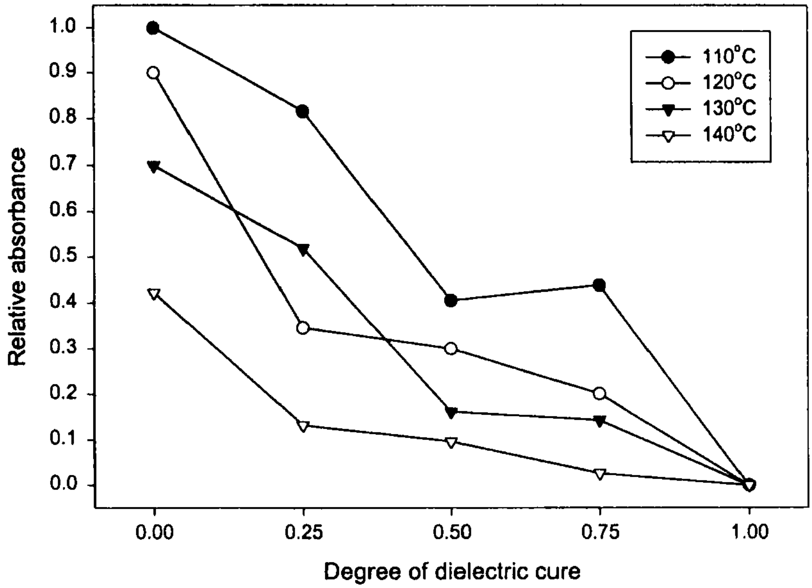


FIGURE 6 FTIR results for the reduction in the isocyanate peak. The results are normalized to the absorbance of the 110°C at 0 percent μDEA cure specimen for relative absorbance.

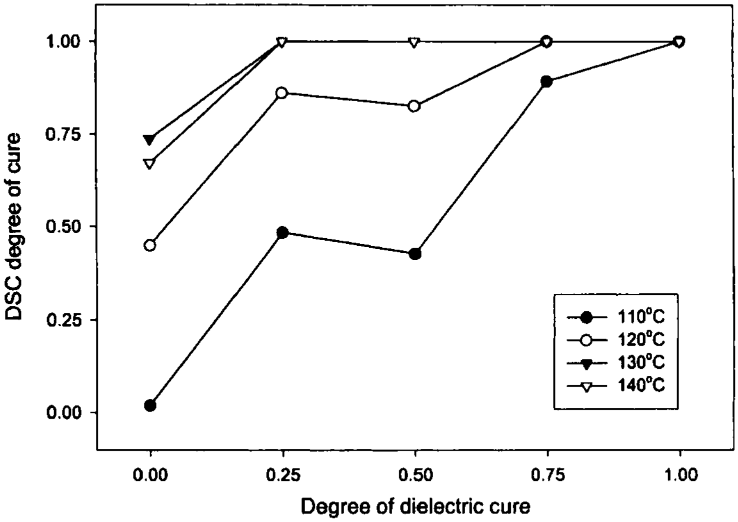


FIGURE 7 Comparison of DSC and μDEA results for pMDI cure. μDEA was used as a basis for partial DSC cure experiments at different platen temperatures.

47 percent of the total heat of reaction for samples cured at 110 and 120°C, respectively. The observed difference in isocyanate levels at the conductive peak illustrates the competitive response between reaction hardening and temperature softening during cure.

There are three explanations for the observed FTIR and DSC cure results for the low temperature samples. First, considering the possible crystallization of polyureas, both the reaction of pMDI and the formation of crystalline regions can generate the observed heat. If the curing mechanism of wood-pMDI below 120°C is dominated by the formation of polyurea [14] as found, samples partially cured at these temperatures should display additional heat flow from the formation of crystalline regions. Second, ATR is a near-surface technique and the penetration depth is not known for this system. It is impossible to investigate the increased concentrations for the reaction products because they are masked by the strong wood signal in that region of the ATR spectrum. Third, the majority of the isocyanate consumption occurs prior to the onset of μIDEA cure. A comparison could not be made with the initial amount of pMDI for the ATR method because of the differences in surface contact between the uncured and partially-cured samples. Partially-cured samples were prepared by pressing within a 1 percent tolerance for pMDI application between specimens. In contrast, the uncured samples were analyzed in a virgin, unpressed condition.

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 bond strength and changes in conductivity both depend on molecular weight increases and changes in morphological characteristics. However, the actual mechanical strength of the bond cannot be directly evaluated by μDEA. Bond strength began to exceed the strength of the wood for all tested specimens at 75 percent of dielectric cure for 130° and 140°C (Fig. 8). Further, tensile failures of the wood were observed at 25 and 50 percent of dielectric cure at the two highest temperatures: at 75 and 100 percent for 120°C, and 100 percent for 110°C. The inclusion of wood failures led to an increase in error for a sample set. Wood

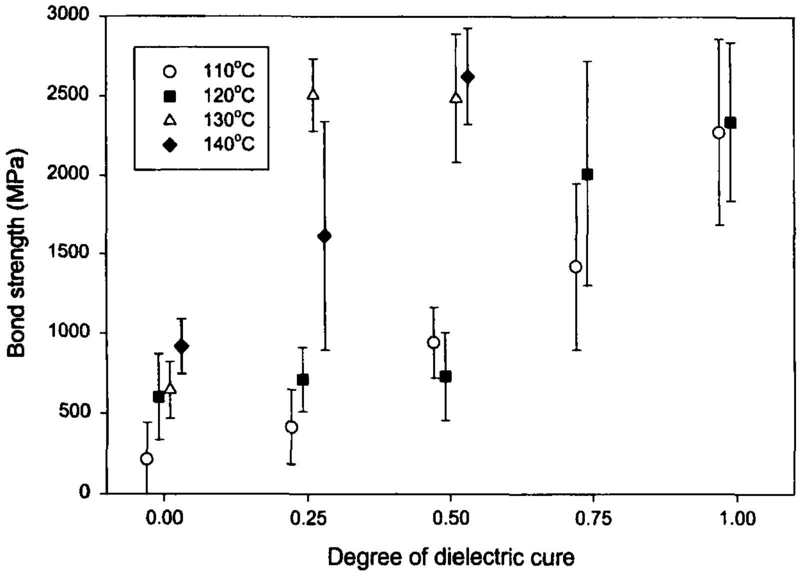


FIGURE 8 Comparison of lap-shear results at different platen temperatures normalized with respect to dielectric cure. All lap-shear specimens tested at 130° and 140°C for 75 and 100 percent of dielectric cure resulted in wood failure. The mean wood strength was 2651 MPa. The error bars represent a standard deviation.

failures were included as the lower limit of the possible bond strength for the specimen tested. The lap-shear strength was higher for adhesive bonds cured at high temperatures. Samples cured at 110°C displayed the largest drop in conductivity (Fig. 8, Tab. I). 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.

CONCLUSIONS

μDEA has proven to be an effective tool in monitoring relative changes in the pMDI/wood bondline. These relative changes relate to network structure development and differences in morphology during the progression of cure, and were clearly discernable from changes due to moisture movement. A large drop in conductivity, and a shoulder in the cure-rate, support the hypothesis of polyurea crystal growth at low temperatures. However, no shoulder was found at 130° and 140°C temperatures where biuret linkages preferentially form [14]. The formation of a crosslinked network promotes the rapid rise in bond-strength at higher temperatures as revealed by lap-shear analysis. Evidence of crystal structures may have been found and appear to be detrimental to the development of bond strength.

The consumption of isocyanate early in cure leads to very little strength development and increased changes in conductivity at low temperatures. This result indicates that most of the isocyanate is being consumed early by chain building reactions. The residual heat and dielectric cure may result from the formation of polyurea and crystal structures at low temperatures. DSC analysis is not as sensitive to crosslinking late in cure as μDEA, accounting for differences in observed cure at the higher temperatures. In addition, a large amount of iscocyanate is consumed prior to the development of bond strength or dielectric cure. Therefore, the majority of molecular weight development does not significantly influence the development of bond strength. The kinetics of the curing system appears to govern the distribution of the reaction products, which, in turn, governs bond strength development.

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