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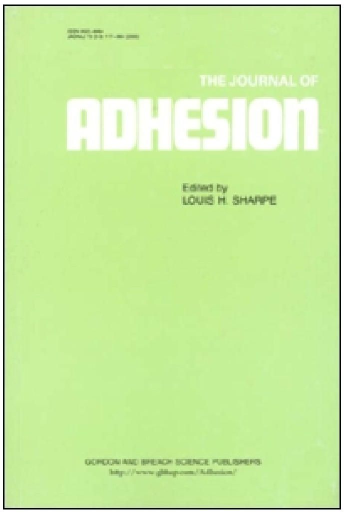

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Moisture-Curing Kinetics of Isocyanate Prepolymer Adhesives

Benjamin S. Lepene[a]; Timothy E. Long[a]; Andrew Meyer[b]; David E. Kranbuehl[b]
[a] Department of Chemistry, Center for Adhesive and Sealant Science, Virginia Polytechnic Institute and State University, Blacksburg, VA, USA [b] Department of Chemistry, College of William and Mary, Williamsburg, VA, USA

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MOISTURE-CURING KINETICS OF ISOCYANATE PREPOLYMER ADHESIVES

Benjamin S. Lepene and Timothy E. Long
Department of Chemistry, Center for Adhesive and Sealant Science,
Virginia Polytechnic Institute and State University,
Blacksburg, VA, USA

Andrew Meyer and David E. Kranbuehl
Department of Chemistry, College of William and Mary,
Williamsburg, VA, USA

The reaction between isocyanate-terminated prepolymers and atmospheric moisture produces urea linkages and results in a hydrogen-bonded network of linear high molecular weight polymers with adhesive properties. This study describes the synthesis of isocyanate-terminated prepolymers and investigates the use of in situ infrared spectroscopy as a technique for monitoring the chemistry of the polymerization reaction kinetics. In situ FTIR was successfully used as a means to monitor the residual isocyanate levels and the extent of the polymerization reaction. Frequency dependent dielectric sensing (FDEMS) using a thin, planar sensor has been used to monitor the reaction kinetics by monitoring changes in the mobility of ions in the reacting medium. A direct correlation of the extent of prepolymer cure was found using the normalized FTIR isocyanate absorbance spectrum and FDEMS imaginary permittivity at 500 Hz for the duration of the cure cycle. The results of this investigation demonstrate that FDEMS is an effective online method to monitor the extent of moisture cure in the bulk as well as in a coating or adhesive bondline.

Keywords: Moisture cure adhesives; Isocyanate; Cure monitoring; Frequency dependent dielectric sensing (FDEMS)

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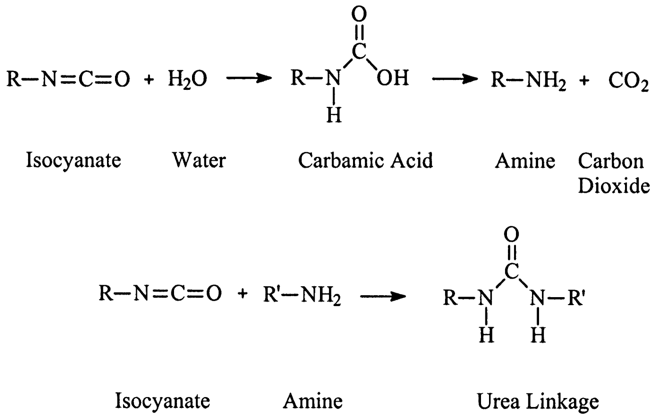
Address correspondence to Timothy E. Long, Department of Chemistry, 3107 Hahn Hall, Virginia Tech, Blacksburg, VA 24061-0212. E-mail: telong@vt.edu

INTRODUCTION

Isocyanate-terminated prepolymers react with atmospheric moisture to form hydrogen bond cross-linked polymeric adhesives [1–3]. The resulting adhesives are generally used to form moisture-, heat-, and solvent-resistant bonds with porous materials that contain inherent moisture. This study involves the preliminary investigation of moisture-curing isocyanate prepolymers and the cure kinetics associated with these adhesives. Previous FTIR spectroscopy cure studies have focused on the consumption of isocyanate near the prepolymer and air interface during covalent cross-linking reactions [4–6]. The emphasis of this paper is concerned with the formation of the hydrogen-bonded network within the bulk due to urea linkage formation. FTIR and dielectric measurements have been used in concert to monitor polymer growth during the moisture curing process [7–9].

The cure of urethane prepolymers results from the reaction between isocyanate end groups and hydroxyl-containing molecules, such as water, to form urea linkages. The reaction proceeds through a carbamic acid intermediate which dissociates to form carbon dioxide and an amine, as shown in Scheme 1 [1, 2]. The objective of this study is to determine an effective test method that can be used to monitor cure kinetics for the prepolymer and the formation of urea linkages during the polyurethane cure. Another objective is to determine whether moisture diffusion is the rate-determining step during the cure process and what chemical and environmental factors influence the relative moisture uptake and corresponding reaction rates.



SCHEME 1 Prepolymer chemistry.

The dielectric impedance of a material can be measured in order to monitor changes at the molecular level, which correlate with changes in macroscopic mechanical properties [10–14]. In dielectric measurements the two-parameter complex permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, is calculated from frequency-dependent measurements of the capacitance, C, and the conductance, G, according to the following equations:

$$\varepsilon'(\omega) = [C(\omega)\ \text{material}/Co]$$

and

$$\varepsilon''(\omega) = [G(\omega)\ \text{material}/\omega Co],$$

where $\omega = 2\pi f$, f is the measurement frequency, and Co is the air replacement capacitance of the embedded microsensor.

The earliest work using dielectrics to monitor the cure of a prepolymer measured the change in capacitance, C, and/or conductance, G, at one or only a few frequencies. Therefore, an understanding and isolation of the molecular origin of the resulting changes in the impedance, which is due to both changes in the translational mobility of ions and the rotational mobility of dipoles, was not available. In fact, the changes in capacitance and conductance with time varied with the frequency which, and which frequency signal to use and how to apply it to monitor cure was uncertain. The past decade has clearly shown that only through the measurement of C and G over many decades in frequency, thereby separately isolating and monitoring the change in the ionic mobility and/or the dipolar mobility, can cure be effectively monitored [7–14]. That is, it is the ionic mobility and/or the dipolar mobility that can be effectively used to monitor reaction advancement, viscosity, Tg increase, etc., as discussed in detail previously [10, 15–18].

The earliest work also suffered from the fact that it is very difficult to monitor the absolute values of a resin as it cures as a thin adhesive layer. This is because if measurements are made between two plates, the thickness is changing, and it is difficult, and usually impossible, to measure the thickness continuously during cure. This problem has been addressed by the use of interdigitated planar sensors [19]. They have a fixed geometry and are ideal for monitoring thin adhesive coatings.

The changes in the mobility of the ions is the focus of this article's use of planar interdigitated dielectric sensing to monitor a thin coating of adhesive during cure. The ionic mobility is identified from the frequency dependence of the impedance over a 6-decade, Hz to MHz range in frequency. The increase in Tg can also be observed from the changing position of the dipolar rotational peaks at high frequencies of the complex impedance plots versus time, but it will not be used here as only a few high-frequency peaks are readily identified for this adhesive system. Rather, the FDEMS dielectric signal is dominated by ionic mobility in these systems.

The conductivity, σ, of ions in the curing system is a function of the number of particles, Ni, times the particle ionic mobility in the medium, μi, or $\sigma = \sum Ni\mu$. It is calculated from FDEMS measurements when the product of $\omega\varepsilon''(\omega)$ is constant, using the relation

$$\sigma = \varepsilon o \ \omega\varepsilon''(\omega),$$

where εo is the permittivity of free space, 8.85 pF/m. The product of measurement frequency (ω) multiplied by the imaginary component of the dielectric permittivity ($\varepsilon''(\omega)$) can thus visually and quantitatively be used to monitor changes in ionic mobility when ε'' is dominated by the mobility of ions as verified by overlapping values of $\omega\varepsilon''(\omega)$.

EXPERIMENTAL

Materials

Dow Chemical Company generously supplied 4-,4′-methylenebisphenyl isocyanate (MDI) and poly(propylene glycol) having a hydroxyl number of 56.4 and an average functionality of 1.8. The polyol was dried at 120°C in the reaction flask under vacuum and constant agitation for 1 h prior to synthesis. The MDI was melted at 50°C prior to addition to the reaction flask. The catalyst, dibutyltin dilaurate (Dabco T-12) was supplied by Air Products and was used as received.

Prepolymer Synthesis

Four prepolymers were synthesized for this study. Samples with 4 and 10 wt% residual isocyanate level without catalyst and samples of both 4 and 10 wt% residual isocyanate level containing 0.004 wt % catalyst were synthesized. For example, a 2.2 isocyanate-to-hydroxyl molar ratio was utilized to prepare a 4 wt% isocyanate level. A three-necked, 500 mL flask was used for synthesizing the urethane prepolymers. A glass mechanical stirring rod was placed in the center port and a vacuum line was placed in the second port. A thermocouple and a nitrogen line were both sealed in the third neck within a septum. The temperature of the reaction was controlled using a heating mantle. Prior to the addition of the polyol to the reaction flask, all of the glassware was dried in a vacuum oven at 120°C. The polyol (117.51 g, 0.1181 mol) was charged to the reaction vessel and was dried in the reaction flask at 120°C under vacuum for 1 h. The reaction flask containing the dried polyol was cooled to 75°C under constant agitation and a nitrogen purge. The melted MDI (32.49 g, 0.2599 mol) was then charged into the reaction flask using a syringe. The temperature in the reaction vessel increased to 85°C during the first few minutes, but was maintained at 80°C for the remaining duration of the 2-h reaction period. After reaching 85°C, 0.004 wt% dibutyltin dilaurate catalyst (5.8 mL) was added to samples prepared with catalyst. At the completion of the reaction, the prepolymer was then titrated to ensure that the correct isocyanate level was achieved and stored in a dessicator inside a container that was purged with argon.

Characterization

An ASTM D 2572-91 titration procedure for urethane prepolymers was used in conjunction with in situ mid-infrared spectroscopy to monitor the residual isocyanate functionality levels accurately throughout the polymerization. Mid-infrared spectra were recorded at a rate of 2 scans/min during the prepolymer polymerization until the reaction endpoint had been reached. The infrared spectra were collected using an ASI ReactIR 1000 in situ Fourier Transform infrared spectrometer equipped with ASI data acquisition software. The reaction flask setup used for the IR data collection remained the same except for the addition of a fourth neck, which was used as the IR probe port.

Specimens for FDEMS cure studies were prepared as 0.025 mm films of prepolymer on a DekDyne interdigitated planar sensor with dimensions of $1\frac{1}{2}$ inches (3.8 cm) and 5 mm thick in an argon-purged atmosphere bag using a BYK-Gardner film casting knife blade. The FDEMS measurements were collected using a Hewlett Packard impedance bridge controlled with data collecting software. Measurements of capacitance, conductance, and temperature were taken at 10 frequencies from 5 Hz to 5×10^5 Hz, starting with 1 measurement taken prior to coating the sensors with the prepolymers and followed by continuous measurements throughout the entire cure process. The real and imaginary components of the complex permittivity were then calculated and recorded for each frequency. Five samples were prepared using prepolymers with 4 and 10 wt% residual isocyanate levels as well as a methanol-deactivated sample at ambient temperature and 40% relative humidity. The environmental conditions for each sensor are reported in Table 1. Desiccators containing saturated aqueous solutions of K_2SO_4 served as 40% relative humidity chambers.

TABLE 1 Isocyanate Prepolymers for FDEMS Measurements

Sample #	% Residual NCO	Catalyst
1	4.0	None
2	4.0	Dabco T-12
3	10.0	None
4	10.0	Dabco T-12
5	4.0 MeOH Deact.	None

An FTIR study of the curing 4% NCO prepolymer without catalyst was conducted using a MIDAC M-series FTIR to record spectra at selected time intervals during cure. Prepolymer was applied to NaCl plates using a BYK-Gardner film casting knife blade to produce a 0.025 mm thick film. The coated salt plate was then placed in a 40% relative humidity chamber until a spectrum was collected. For each FTIR scan, the plate was placed on a fixture in a vertical position within the instrument's nitrogen-purged atmosphere. The sample was placed back into the humidity chamber following the scan until the next measurement was collected. The coated plate remained in the vertical position within the instrument for approximately 60 s for each recorded spectrum.

RESULTS AND DISCUSSION

Figure 1 shows a three-dimensional waterfall plot of the urethane carbonyl absorbance (1724 cm^{-1}) versus time during the urethane prepolymer polymerization without catalyst. The growth in the absorbance as a function of time can be used to monitor the conversion of isocyanate functional groups to urethane groups during the reaction. The plot shows that the bulk of the carbonyl absorbance growth was finished after the normal 2-h reaction period, but further carbonyl formation was evident over longer times. This is presumably due to urea-forming side reactions resulting from the reaction of residual isocyanate groups and any moisture that may have diffused into the reaction flask around the IR probe joint. It is also useful to monitor the simultaneous decrease in the isocyanate absorbance peak at 2272 cm^{-1} and the increase in amide II absorbance at 1525 cm^{-1}.

Figure 2 shows the waterfall plot of the isocyanate consumption absorbance at 2272 cm^{-1}. This plot shows that the isocyanate levels continue to decrease well after the normal reaction time. Profiles of the isocyanate and urethane carbonyl peaks in Figure 3 show that

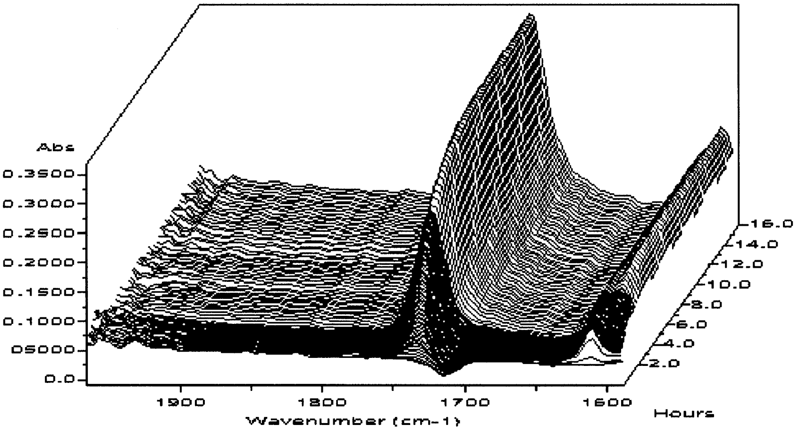


FIGURE 1 In situ IR plot showing the increase in the urethane carbonyl peak at 1724 cm^{-1} as the polymerization proceeds with time (80°C nitrogen atmosphere, no catalyst, 4% isocyanate).

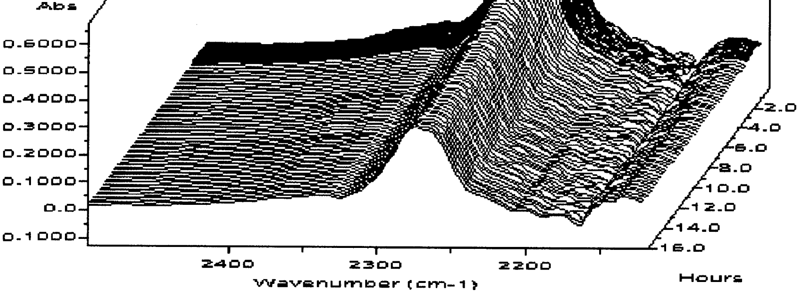


FIGURE 2 In situ IR plot showing the decrease in the NCO peak at 2272 cm^{-1} as the polymerization proceeds with time (80°C nitrogen atmosphere, no catalyst, 4% isocyanate).

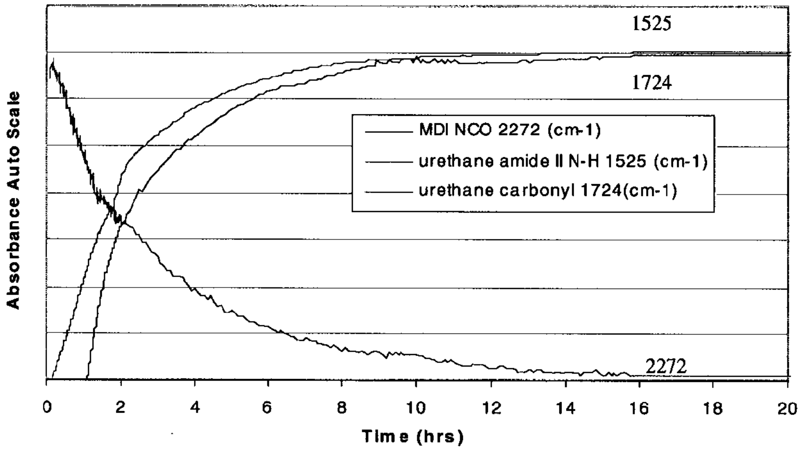


FIGURE 3 IR absorbance peak profile showing relative growth rates for the N-H (1525 cm^{-1}) and carbonyl (1724 cm^{-1}) peaks and simultaneous consumption of isocyanate at 2272 cm^{-1}. After the initial 2.5 h reaction, further growth and consumption resulted from urea formation due to controlled moisture ingress into the reaction flask (see Color Plate 1).

a urea-forming side reaction was taking place during the data collection due to water ingress. This was attributed to the reaction flask that was used in order to allow the IR probe to be placed into the flask during polymerization.

Titration measurements recorded during and immediately preceding the polymerization reaction verified the formation of urea and the steady consumption of isocyanate end groups. Although our primary goal was to produce urethane prepolymers without the presence of urea linkages, it was found that the in situ FTIR provided a valuable method for identifying isocyanate side reactions early during prepolymer polymerization. However, prepolymers for the cure study were prepared using the standard reaction flask setup, which did not include the addition of the IR probe as a source for moisture ingress. Titration of the prepolymers following the reaction was done to ensure that the reaction was complete and that urea linkages had not formed.

The FDEMS studies of the isocyanate prepolymers were significantly easier to conduct than the FTIR experiments, and thus a series of environments were examined. Figures 4a–d show the results of FDEMS in situ sensor measurements of the change in log $\varepsilon''(\omega)$ for 4 reacting systems at ambient temperature and 40% humidity: 4% NCO with and without catalyst and 10% NCO with and without catalyst. All

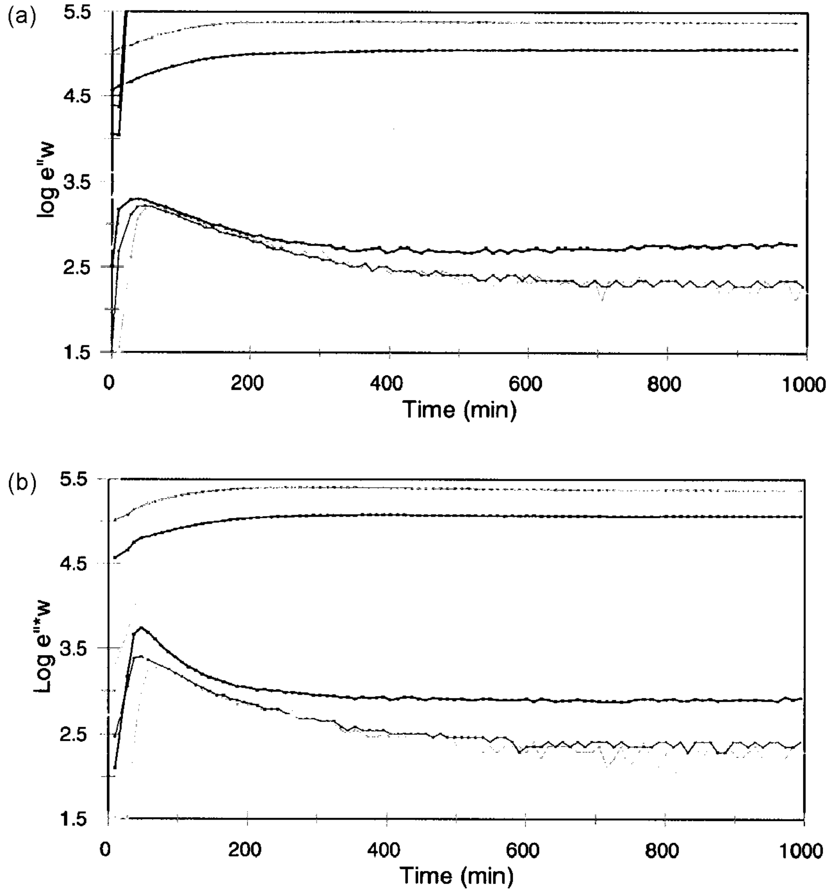


FIGURE 4 (a) FDEMS of a 4% residual isocyanate prepolymer without catalyst over a range of frequencies (50, 25, 5, 0.5, 0.25, 0.125, 0.050 kHz; frequencies plotted highest to lowest, top to bottom) during cure. (b) FDEMS of a 4% residual isocyanate prepolymer with catalyst over a range of frequencies (50, 25, 5, 0.5, 0.25, 0.125, 0.050 kHz; frequencies plotted highest to lowest, top to bottom) during cure. (c) FDEMS of a 10% residual isocyanate prepolymer without catalyst over a range of frequencies (50, 25, 5, 0.5, 0.25, 0.125, 0.050 kHz; frequencies plotted highest to lowest, top to bottom) during cure. (d) FDEMS of a 10% residual isocyanate prepolymer with catalyst over a range of frequencies (50, 25, 5, 0.5, 0.25, 0.125, 0.050 kHz; frequencies plotted highest to lowest, top to bottom) during cure (see Color Plate 2).

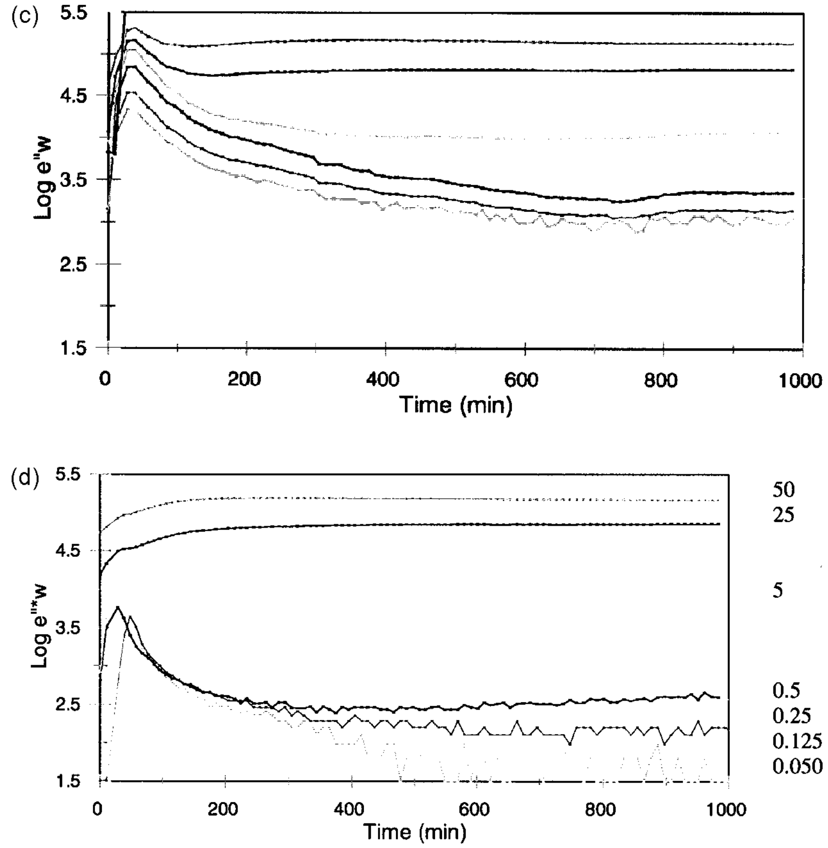


FIGURE 4 (*Continued*; see Color Plate 2).

of the systems show a relatively low conductivity as observed by the small overall values for log [$\omega\varepsilon''(\omega)$].

A related FDEMS study of pure isocyanate prepolymer with a similar value of log [$\omega\varepsilon''(\omega)$] has demonstrated that the mobility of residual ions is being monitored in the dielectric measurement and that the number of these residual ions is constant over cure. The cure chemistry of the isocyanate prepolymer adhesive suggests neither the creation nor consumption of ions (Scheme 1). Furthermore, the relatively low level of $\omega\varepsilon''(\omega)$ compared with epoxy and polyamide systems of higher viscosity and its comparable value with the isocyanate cure suggests that proton transfer is not a major mechanism for conduction. Conductivity is a function of the number of ions and their mobility, $\sigma = \sum Ni\mu i$. When the number of ions, Ni, can be assumed to be constant, then, as in this case, changes in conductivity are dominated by the changes of the ionic mobility during cure of the isocyanate system. These changes in conductivity are monitoring the decrease in mobility of the curing system and the corresponding increase in viscosity with the buildup of the urea network.

The FDEMS measurements of $\varepsilon''(\omega)$ are used to monitor the curing process. As one example, FDEMS plots of $\log \omega\varepsilon''(\omega)$ for the 4% NCO catalyzed and uncatalyzed systems show a time for completion of cure of about 600 min because, at this point, $\delta\varepsilon''(\omega)/\delta t$ reaches 0. Cure completion, represented by $\delta\varepsilon''(\omega)/\delta t = 0$, is the point where no further changes in ionic mobility can be detected. In general, this molecular measurement is more accurate than traditional macroscopic heat flow (DSC) or rheology measurements because impedance measurements are sensitive to changes of parts per 10^4 regardless of magnitude. No change in the conductivity with time suggests that the mobility of the ions in the system is constant and a full cure state for this temperature has been achieved. In these studies, the apparent increase in mobility in the bulk at $t = 0$ is due to initial measurements of $\varepsilon''(\omega)$ before the prepolymer was applied to the bare sensor.

A postcure study at 120°C showed little or no change in $\omega\varepsilon''$ after the system reached postcure temperature, verifying that the system had indeed reached high curing levels. Furthermore, the initial slope of $\delta\omega\varepsilon''(\omega)/\delta t$ for the catalyzed system is higher than that of the uncatalyzed system. This rate of change in $\omega\varepsilon''$ is monitoring the faster initial reaction rate for the catalyzed system.

The 10% NCO catalyzed and uncatalyzed systems show a greater difference in the time for reaction completion. The catalyzed system reaches $\delta\varepsilon''(\omega)/\delta t = 0$ at 500 min, while $\delta\varepsilon''(\omega)/\delta t$ approaches 0 for the uncatalyzed system at about 800 min. As in the 4% NCO study, the initial rate of cure is higher for the catalyzed system as monitored by $\delta\varepsilon''(\omega)/\delta t$ during the initial minutes.

Thus, this study qualitatively shows that the uncatalyzed prepolymer systems containing 4% residual isocyanate levels reach full cure at a greater rate than the systems containing 10% residual isocyanate levels, and the initial cure rates for both systems are increased with the addition of dibutyltin dilaurate catalyst. The data suggest that the addition of dibutyltin dilaurate catalyst either increased the water uptake rate or the coupling reaction rate during the initial 40% relative humidity exposure. Also, the decreased cure rate of the uncatalyzed prepolymer containing 10% residual isocyanate most likely can be attributed to a decreased reaction rate due to the absence of catalyst. However, the decreased cure rate of the bulk could also be due to an increased reaction rate on the surface of the prepolymer, which further decreases the diffusion rate of moisture into the prepolymer.

An additional dielectric study was conducted on a methanol-deactivated prepolymer. At the conclusion of the prepolymer polymerization, an excess of methanol was stirred into the prepolymer in order to react with the moisture-reactive isocyanate end groups. An FDEMS experiment was run with this deactivated sample, and plots of the real and imaginary components of permittivity as a function of time are shown in Figures 5a and b. A change in ionic mobility is observed over time for the deactivated system. The net decrease in both the permittivity and the imaginary component's conductivity (σ) reflects a

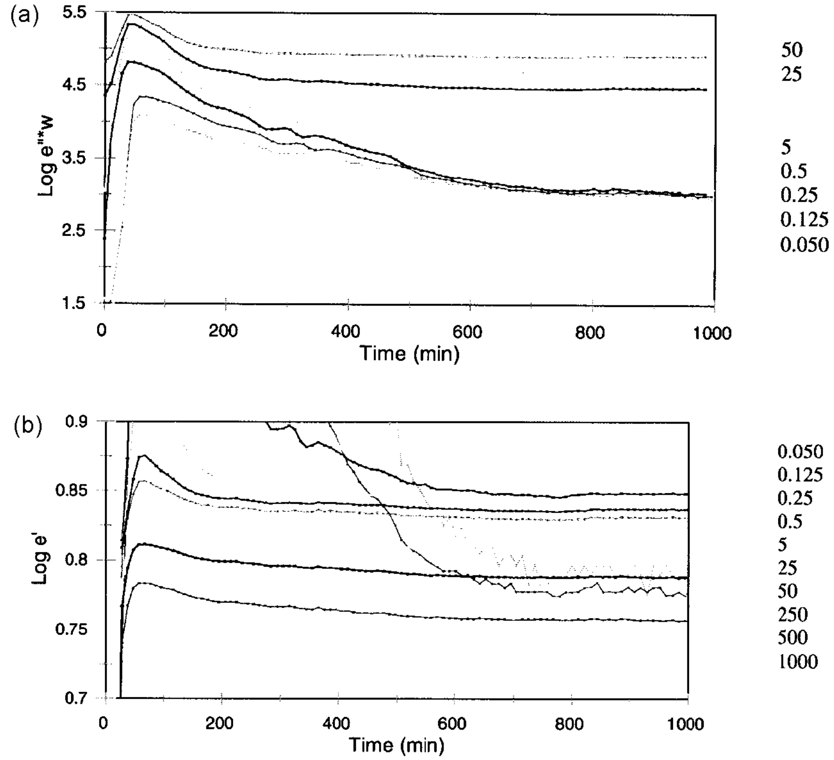


FIGURE 5 (a) FDEMS spectrum of a methanol-deactivated isocyanate prepolymer exposed to 40% RH (frequencies are 50, 25, 5, 0.5, 0.25, 0.125, 0.050 kHz; plotted highest to lowest, top to bottom). (b) FDEMS spectrum of a methanol-deactivated isocyanate prepolymer exposed to 40% RH (frequencies are 0.050, 0.125, 0.25, 0.5, 5, 25, 50, 250, 500, 1000 kHz; plotted lowest to highest, top to bottom) (see Color Plate 3).

decrease in ionic mobility as the system equilibrates with the 40% humidity environment. If significant amounts of proton conduction were present, an initial increase in $\omega\varepsilon''(\omega)$ and ε' would occur. This was not observed. The diffusion equilibrium process results in a decrease in ε' and $\omega\varepsilon''(\omega)$. The time for this process to reach completion is approximately 500 min. This time is close to the cure time and suggests that the diffusion of water vapor in the prepolymer is a rate-controlling step affecting adhesive cure, the buildup in viscosity, adhesive strength, and the corresponding decrease in ionic mobility. Thus, using FDEMS measurements of deactivated systems may lead to the determination of initial moisture diffusion rates in moisture-curing prepolymer systems.

FTIR was used as an additional method to monitor the urea-forming reaction by measuring the decrease in the isocyanate absorbance peak at 2272 cm^{-1} as a function of time. Many attempts were made to devise a method to use FTIR spectroscopy accurately for following the cure reaction in the bulk. However, the collected data were influenced by viscous flow on the surface of the NaCl FTIR plate because the plate was placed vertically in the instrument for data collection. ATR-FTIR is a potential method to monitor the reaction at the surface of the prepolymer, but we were more interested in a comparison of bulk properties with the FDEMS data. Figure 6 shows the spectrum from the noncatalyzed 4% residual isocyanate prepolymer cure as a function of time in a 40% relative humidity chamber. The plot reveals that the isocyanate absorption decreased at a decreasing rate throughout

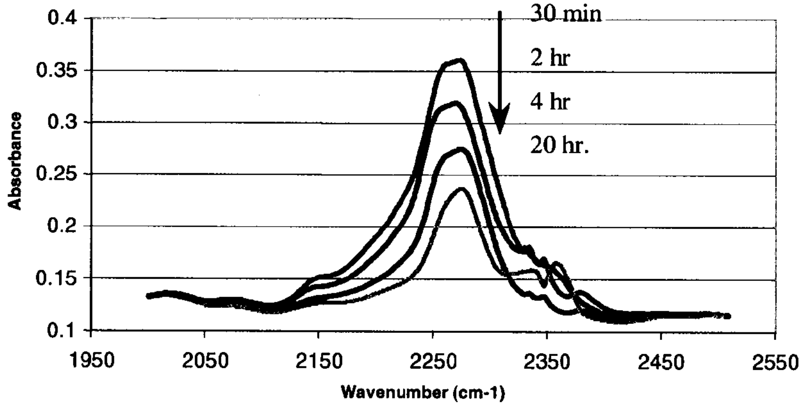


FIGURE 6 FTIR spectra showing the consumption of the isocyanate peak during cure at 2272 cm^{-1} (40% RH, 25°C, 4% isocyanate in the absence of catalyst) (see Color Plate 4).

the cure period as a result of urea formation and the developing hydrogen bond adhesive network. These data, coupled with the FDEMS data on the deactivated polymer, qualitatively support the concept that during prepolymer cure both the mobility of diffusing moisture in the prepolymer and the cure rate decrease. Finally, the direct correlation between the imaginary component of permittivity computed at 500 Hz and the disappearance of the isocyanate using FTIR was examined. Figure 7 depicts this correlation. Overall, the correlation between the change in isocyanate absorption, concentration, and the normalized change in molecular mobility of the ions as monitored by ε″ is very good. The extent of cure was calculated with the FTIR data by dividing the difference in the NCO absorbance and a constant baseline absorbance at a given time by the difference in the NCO absorbance and the constant baseline absorbance point prior to the moisture cure reaction. The FDEMS extent of cure ratio was calculated using the following equation to normalize the data:

$$R = \frac{\varepsilon''_t(\omega) - \varepsilon''_o(\omega)}{\varepsilon''_f(\omega) - \varepsilon''_o(\omega)},$$

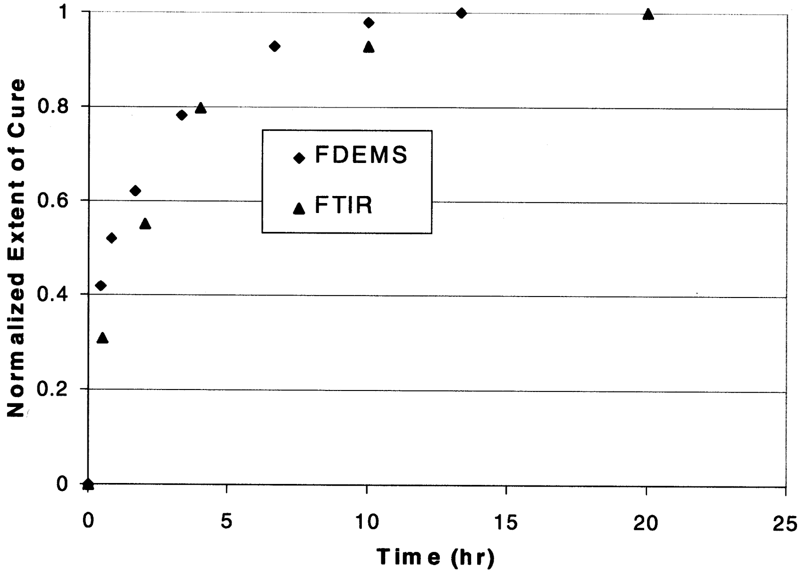


FIGURE 7 Direct comparison between the rates of urethane prepolymer cure monitored using FTIR and FDEMS at 500 Hz under similar environmental conditions (40% RH, 25°C, 4% isocyanate in the absence of catalyst) (see Color Plate 5).

where R is the extent of cure ratio and $\varepsilon''(\omega)$ are the imaginary permittivities at the given times.

The FTIR and FDEMS data collected from the cure of the uncatalyzed 4% residual isocyanate prepolymer were both recorded under the same environmental condition; however, the FDEMS technique has the advantage of online in situ monitoring throughout the curing process. FDEMS is suitable for laboratory experiments for coatings and adhesive bond lines [12–14] in any environment. Future investigations will involve studies to gain a more complete understanding of the role of $\varepsilon''(\omega)$ versus kinetic rate for moisture curing urethane prepolymers.

CONCLUSIONS

Urethane prepolymer reactions can be successfully monitored using in situ FTIR and titration during the synthesis of prepolymers with various residual isocyanate levels. Titration data confirmed that the absorbance peaks from the formation of the urethane carbonyl and the consumption of isocyanate can be used for determination of residual isocyanate levels. FDEMS data collected showed that the addition of dibutyltin dilaurate catalyst in the 10% NCO system during polymerization at 40% relative humidity increased the initial cure reaction rate, and the time required for complete cure was reduced by nearly 240 min by the addition of the catalyst. Furthermore, FDEMS data suggest that increased residual isocyanate levels decrease cure rate within the bulk of uncatalyzed systems. The FDEMS and the FTIR cure data both suggest that the urea linkage hydrogen bonding was formed as a result of the water vapor diffusion process. The FDEMS method for monitoring the moisture-curing reaction proved to be much more convenient and thereby more successful than FTIR because it allowed the capability of following the reaction with the sample on a horizontal plane as well as continuously and in situ in the environment of a coating [12, 13] or in an adhesive bondline [14]. A good correlation exists between the FDEMS changes in ionic mobility and the FTIR monitoring of the isocyanate during bulk curing of the 4% NCO system. Future integration of both test methods will lead to more quantitative results, additional studies on the reaction rates, and an understanding of adhesive properties as a function of the moisture diffusivity in the curing prepolymer. In addition, FDEMS measurements of systems deactivated by means such as alcohol addition at the reaction endpoint may lead to the determination of initial moisture diffusion rates in moisture-curing prepolymer systems.

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