

Evaluation of the Cure Kinetics of Isocyanate Reactive Hot-Melt Adhesives with Differential Scanning Calorimetry

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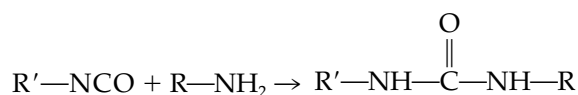
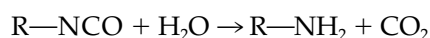
ABSTRACT: The matrix polymer of reactive hot-melt adhesive (RHMA) is an isocyanate-terminated urethane prepolymer based on oligoester or oligoether diols and diisocyanates. In this study, we explored wet cure kinetics with both isothermal and nonisothermal differential scanning calorimetry methods. Second-order autocatalytic models were successfully used to evaluate the cure process of both oligoester- and oligoether-based RHMAs. The autocatalyzation effect did not depend on the structure of diols but on the

reaction nature of the end isocyanates. The apparent energy of the overall cure reaction was 86.54 and 84.46 kJ/mol, respectively, which was based on nonisothermal DSC results. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2708–2713, 2003

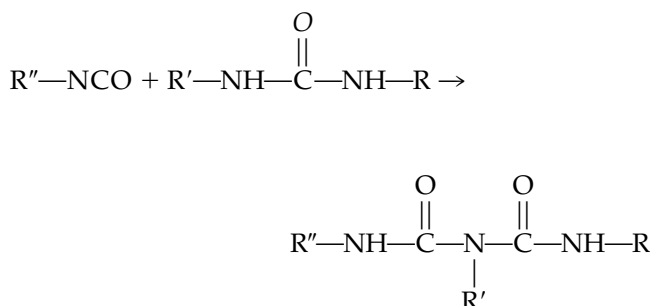
Key words: curing of polymers; kinetics (polym.); activation energy

INTRODUCTION

Reactive hot-melt adhesives (RHMAs) are drawing more and more attention from both theoretical and applied research fields because of their outstanding features, such as a high initial adhesion strength, excellent adhesion to a multitude of substrates, good resistance to heat, chemicals, and aging, and easy processing.^{1–3} The matrix resins of RHMAs are isocyanate-terminated urethane prepolymers based on oligoester and or oligoether diols and diisocyanates. After application, RHMAs exhibit green strength as a result of crystallization of the urethane prepolymer. Water absorption from the atmosphere results in a subsequent cure reaction as follows, which increases molecular weight:



A possible further reaction between urea, urethane, and a residual isocyanate group promotes the crosslinking of adhesive bulk.

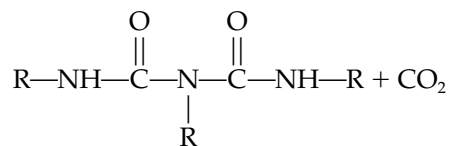


Thus, a consequence of the cure reaction is that the urethane prepolymer, which is first linear, now becomes crosslinked.³ As a result, the adhesion strength is greatly enhanced.

Understanding the curing process of thermosetting materials is of particular importance in the production of structural composites, coatings, adhesives, and so on. Kinetic modeling can be used to achieve a better understanding of the curing procedure. In the case of urethane chemistry, the cure reaction always involves the consumption of isocyanate groups. By monitoring the content of isocyanate groups, researchers can gain a quantitative insight into the cure kinetics of urethane resins. Fourier transform infrared spectroscopy (FTIR) is a powerful tool for conducting *in situ* monitoring of a certain group. With the FTIR technique, many researchers have investigated the cure behavior of urethane system.^{4–6} Sun and Sung characterized a model 4,4'-diphenylmethane diisocyanate (MDI)-based urethane reaction by means of the ultraviolet and fluorescence behaviors of MDI as the intrinsic sensor.⁷ MDI exhibits red spectral

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shifts and obvious fluorescence intensity enhancement as it reacts with alcohol to form urethane. These spectral changes were correlated to the extent of the reaction of MDI. Differential scanning calorimetry (DSC) is another important means of exploring the cure kinetics of thermosetting resins by the record of the heat flow traces caused by the cure reaction. Temperature-programmed DSC was used by Michael et al. to evaluate the cure kinetics of polymeric diphenylmethane diisocyanate resin.⁸ No research has elaborated on the curing behavior of urethane RHMA to the best of our knowledge. The primary challenge of studying the cure behavior of RHMA is that this adhesive cures in the solid state, which makes *in situ* FTIR or other spectroscopic methods invalid for monitoring the cure process. The curing reaction involves a series of polyaddition reactions, depending on the curing condition. Consequently, isolation and interpretation of individual reactions are difficult both to achieve and to quantify. However, a constant relative humidity should be created to ensure the wet cure kinetics of RHMA. The complex nature of the curing process makes a mechanical approach to modeling extremely difficult; the process favors phenomenological methods. DSC is a candidate because a saturated environment can be created inside a DSC pan during the cure evaluation. Standardized methods based on multiple-ramp calorimetric methods have been recommended to evaluate the cure kinetics of thermosetting resins.⁹ However, these methods should be modified to conform to this complex cure situation. When the saturated steam in the DSC pan is considered, the moisture could readily penetrate into the sample and result in subsequent crosslinking reactions. So it's reasonable to study the cure process as an overall reaction as follows:



The kinetic modeling is simplified in such a way. Flynn and Galwey and Brown reviewed many studies to summarize the kinetics research of heterogeneous, condensed-phase systems by thermal analysis.^{10,11} A basic rate equation relates the rate of cure to a function of cure by $k(T)$:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where α is the degree of cure and $k(T)$ is the temperature-dependent rate constant. The rate constant follows the Arrhenius equation

$$k(T) = A \exp(-E/RT) \quad (2)$$

where E is the activation energy, A is the frequency factor, R is the ideal gas constant, and T is the temperature in degrees Kelvin. The Arrhenius equation is indeed quite successful in describing the temperature dependence of the reaction rate.¹⁰ Two types of phenomenological kinetic models are related to the rate equation by $f(\alpha)$. In the case of an n th-order reaction, $f(\alpha)$ is described by $f(\alpha) = (1 - \alpha)^n$, where n is the overall reaction order. In contrast, autocatalyzed reactions take the following form: $f(\alpha) = \alpha^m(1 - \alpha)^n$, where m and n sum to equal the overall reaction order. Two general rules for the kinetic analysis of thermal data are to fit data from isothermal experiments to determine the parameters for $f(\alpha)$ and to fit the data from nonisothermal experiments to determine the parameters for $k(T)$.¹⁰⁻¹⁵ This research employed a method based on isothermal DSC and temperature-programmed DSC to evaluate the cure kinetic parameters of two kinds of isocyanate RHMA. The availability of these evaluations is also discussed.

EXPERIMENTAL

Preparation of RHMA

Urethane prepolymers were prepared for DSC in our lab. MDI (99% *para, para'* isomer) was a commercially available product from Aldrich (St. Louis, MO). MDI was used as received without further purification. Oligodiols were supplied by Dow Chemical Co. (Shanghai, China). One was a crystalline oligoester [number-average molecular weight (M_n) 3300], and the other was an amorphous oligoether with the same M_n . To avoid side reactions, oligodiols were dehydrated in an absolute dry flask at 120°C and 100 Pa for 1 h before the addition of MDI. Stoichiometric melt MDI, with an NCO/OH molar ratio of 2.05, was poured, and this addition reaction was carried out at 95°C for 1.5 h with a protection of an N_2 atmosphere. The prepolymers were degassed at 100°C and 100 Pa for 1 h. The two series prepared were oligoester-based urethane prepolymer (series A) and oligoether-based urethane prepolymer (series B).

DSC Analysis

A PE DSC-7 differential scanning calorimeter (PerkinElmer Scientific Instruments, CT) was used for the kinetics study. For isothermal DSC analysis, about 4–5 mg of the sample was hermetically sealed in a stainless steel DSC pan with 2 μ l of distilled water. Water was enclosed to provide enough vapors to ensure the development of the subsequent moisture cure of the RHMA sample. The sealed sample was heated

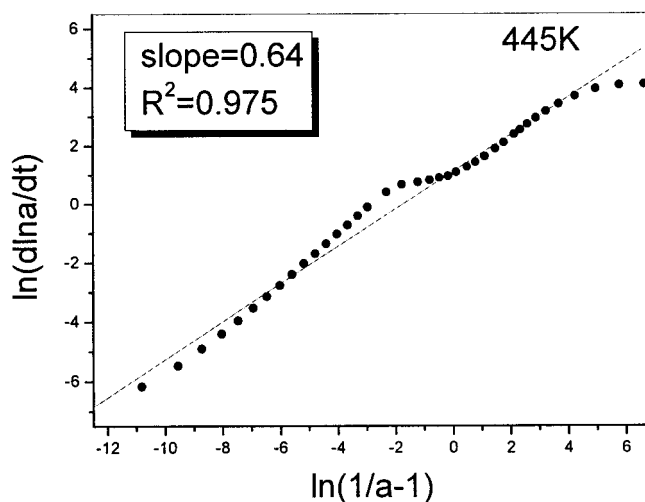


Figure 1 First-order kinetic plot of series A with linear regression for data obtained by an isothermal run at 445 K.

to 445 K as quickly as possible. With an ensuing isothermal run at 445 K, we monitored and recorded the heat generation of the whole cure duration. The degree of cure was calculated from the exothermal run as $\alpha = Q_t/Q_o$, where Q_t is the residual heat at time t and Q_o is the total heat of the cure reaction. The beginning of the cure reaction was appointed to the time corresponding to onset temperature of the exothermic peak. Q_o was calculated by the numerical integration of the power spectra with respect to time.

Nonisothermal DSC scanning were run from 300 to 480 K at 2, 5, 7.5, 10, 15, and 20 K/min (γ), respectively. A fresh sample was used for each DSC run. The peak temperature (T_p) for each heating rate was recorded. Each of the T_p values was refined through heating rate correction and thermal lag correction before it was used for plotting.

For both isothermal and nonisothermal tests, an important assumption for the application of DSC is that the measured heat flow, dH/dt , is proportional to the reaction rate, $d\alpha/dt$. The minor difference in the heat capacity (C_v) between the uncured and cured samples was neglected to simplify the modeling.

RESULTS AND DISCUSSION

Isothermal DSC

Two types of phenomenological kinetic models available for modeling thermosetting adhesives are n th-order and autocatalyzed models. Without knowledge of the exact mechanism of the cure reaction, both models can be summarized as a uniform equation as follows:

$$\frac{d\alpha}{dt} = k\alpha^{n-m}(1-\alpha)^m \quad (3)$$

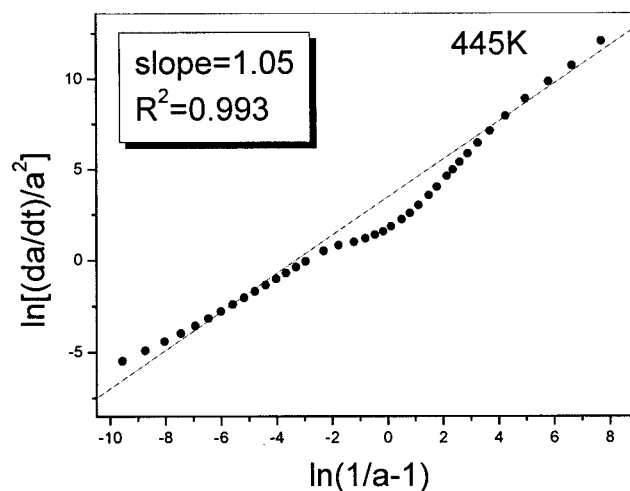


Figure 2 Second-order kinetic plot of series B with linear regression for data obtained by an isothermal run at 445 K.

where α is the degree of cure, k is the rate constant, n is the overall reaction order, and m is a parameter introduced to estimate the autocatalyzation effect during the cure process. In the case of nonautocatalyzed reactions, the parameter m is equal to zero.

When a first-order reaction where $n = 1$, eq. (3) can be rearranged as

$$\ln\left(\frac{d \ln \alpha}{dt}\right) = \ln k + m \ln\left(\frac{1-\alpha}{\alpha}\right) \quad (4)$$

For an isothermal cure process, k is a constant that depends on the reaction properties. Because an isothermal DSC run was available to correlate the degree of cure to reaction time, eq. (4) could be fitted to determine the value of m by plotting $\ln(d \ln \alpha/dt)$

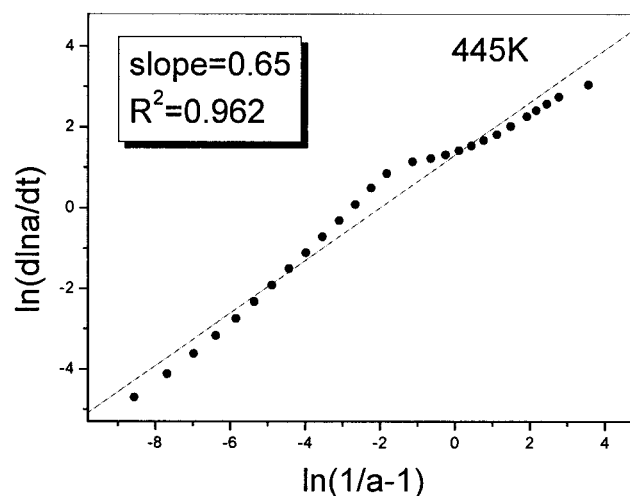


Figure 3 First-order kinetic plot of series A with linear regression for data obtained by an isothermal run at 445 K.

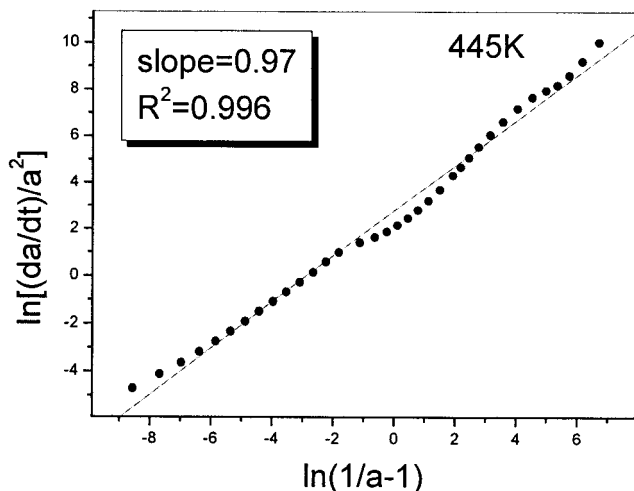


Figure 4 Second-order kinetic plot of series B with linear regression for data obtained by an isothermal run at 445 K.

versus $\ln(1 - \alpha/\alpha)$. If the overall reaction order was 2, eq. (3) was rearranged and expressed as

$$\ln\left(\frac{d\alpha/dt}{\alpha^2}\right) = \ln k + m \ln\left(\frac{1 - \alpha}{\alpha}\right) \quad (5)$$

The corresponding m could be obtained following a similar calculation. The coefficients of determination (R^2 values) of both linear regression results were used to evaluate the validity of the kinetic modeling.

Figure 1 plots $\ln(d \ln \alpha/dt)$ versus $\ln(1 - \alpha/\alpha)$, and Figure 2 plots $\ln[(d\alpha/dt)/\alpha^2]$ versus $\ln(1 - \alpha/\alpha)$ on the basis of the isothermal DSC results of series A. Figures 3 and 4 show two modelings of series B. To compare the validity of first-order and second-order models, linear regression treatments were performed to the two systems. Only the data of the linear part were fit to linear regression. The reaction became diffusion

controlled near the end of cure, and it was not accurately represented in this model.

For both series, higher R^2 values were obtained for the second-order modeling than for the first-order modeling. This demonstrates that the overall reaction favored a second-order reaction. Furthermore, the value of m , which describes the autocatalyzation effect of the cure reaction, was close to 1 for both series. It could be inferred that the extent that autocatalyzation affected the cure development did not depend on the structure of diols used but on the reaction nature of the end isocyanates. With regard to a second-order reaction, the cure rate could be expressed as

$$\frac{d\alpha}{dt} = k\alpha^{2-m}(1 - \alpha)^m \quad (6)$$

When the cure rate reaches a maximum, the first derivative of the right hand side of the equation with respect to t should be equal to zero. There exists a relation $\alpha_{max} = 1 - m/2$ between m and α_{max} , where α_{max} is the degree of cure at the maximum rate of cure. In the case of the RHMA system, the cure rate reached a maximum at about 40–50% cure, independent of diol structure.

Dynamic DSC

Temperature-programmed DSC was used to explore the detailed information of the cure reaction. It was extremely comprehensive for evaluating any individual reaction because of the complications in this reaction. Therefore, this research focused on studying the apparent activation energy (E) and apparent frequency index (A) of the overall reaction expressed previously. Kinetic parameters were determined and were then refined following the method suggested in

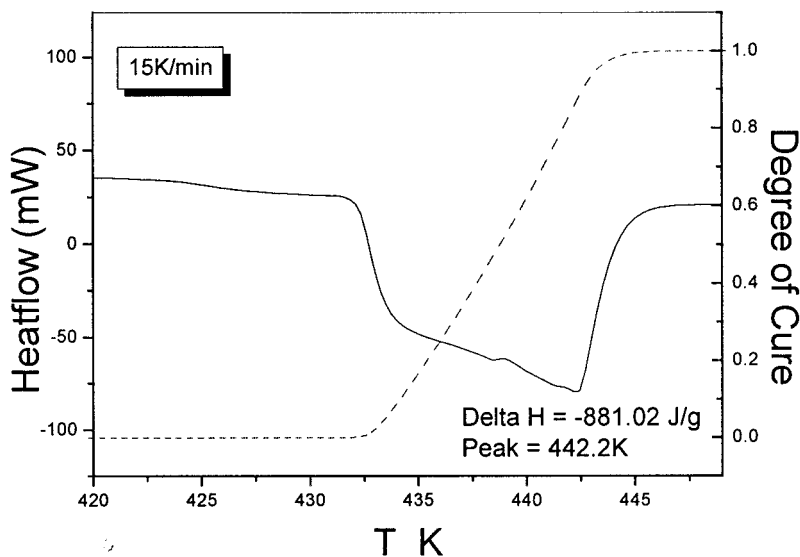


Figure 5 Typical cure trace and degree of cure of series A at a heating rate of 15 K/min.

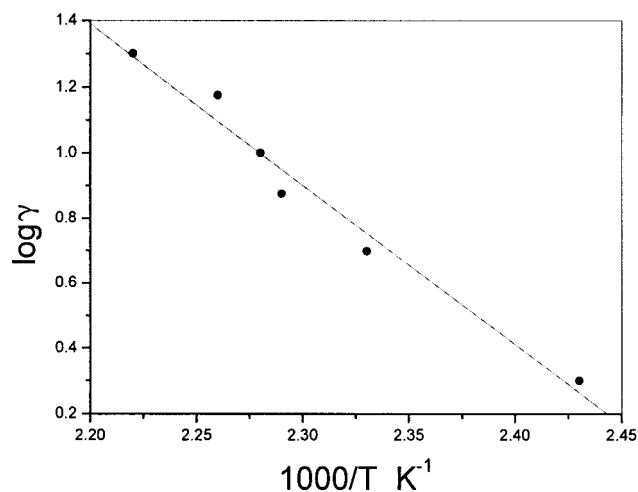


Figure 6 Determination of the Arrhenius parameters of series A from the plot of $\log \gamma$ versus $1000/T_p$.

ASTM E 698-79. From the dynamic DSC results, the plot of $\log \gamma$ versus $1/T_p$ would produce a curve from which E and A could be determined by the following equations:

$$E = -2.19R \left(\frac{d \log \gamma}{d(1/T_p)} \right) \quad (7)$$

$$A = \gamma E \frac{e^{E/RT}}{RT^2} \quad (8)$$

The value of E was refined after the standard method. Data of the heating rate of 10 K/min were used to calculate the value of A .

Figure 5 plots a typical nonisothermal DSC trace of series A with a heating rate of 15 K/min. The degree of cure, determined by $\alpha = Q_t/Q_o$ and obtained from

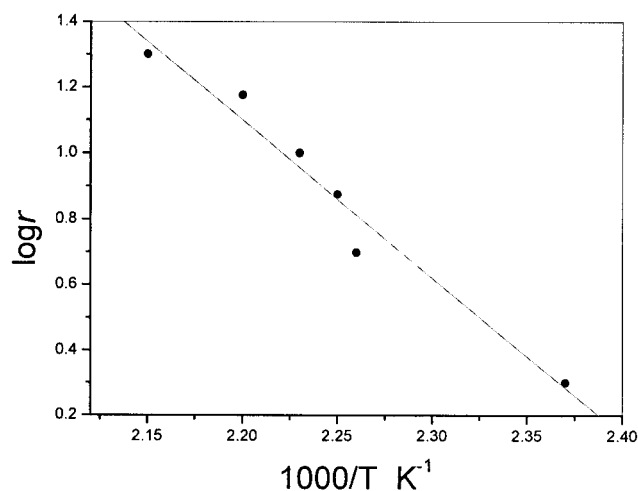


Figure 7 Determination of the Arrhenius parameters of series B from the plot of $\log \gamma$ versus $1000/T_p$.

TABLE I
Arrhenius Parameters of the Modeling
from Nonisothermal DSC

Series	$\frac{d(\log \gamma)}{d(1/T_p)}$	Approximate E_a (kJ mol ⁻¹)	Refined E_a (kJ mol ⁻¹)	A (min ⁻¹)
A	-4896	89.14	86.54	9.9e9
B	-4795	87.37	84.46	3.6e9

an integrated function in the DSC program, is also presented as dashed lines. The exothermal peak exhibited as a wide shoulder shape, which further confirmed the complexity of this cure reaction. It was difficult to evaluate the autocatalyzation effect of the reaction by analysis of the shape of the exothermal peak only, which was well used in other cure systems.¹⁶ However, the cure reaction included at least two steps during the cure development.

Figure 6 plots $\log \gamma$ versus $1000/T_p$ based on the temperature-programmed DSC scanning of series A, and Figure 7 shows the plot of series B. Linear fit results of both series are shown in Table I. E and A were also determined by eqs. (7) and (8), respectively. The activation energy (E_a) values of both series were very close, whereas series B showed a lower A than series A. The insignificant difference of E between these two systems demonstrated that the value of the energy barrier to carry out the cure reaction depended on the nature of the overall cure reaction. However, the results could be attributed to ready pervasion of vapor into RHMA bulk under these test conditions. The E_a obtained by this kinetic modeling was only an E , which expresses an energy barrier to the overall cure reaction. E does not surely equal a summation of the E_a of all of the individual reactions.

CONCLUSIONS

Isothermal and nonisothermal DSCs were used to explore the cure kinetics of RHMA. An autocatalyzed model was used to fit the cure reaction. Higher R^2 values were obtained for the second-order modeling than for the first-order modeling, independent on the structure of the urethane prepolymer. For the autocatalyzation effect, the cure rate was expected to be at a maximum at 40–50% cure. With the complexity of the cure reaction, this study was devoted to the evaluation of E of the overall reaction rather than that of individual reactions. The shape of the nonisothermal DSC trace revealed the complexity of the cure reaction. Further results showed an almost negligible difference in E for both series. They demonstrated that the energy barrier to carry out this cure process was in the reactions of isocyanates.

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