# Curing Kinetics of Polyurethane Reactions

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## Synopsis

The curing reactions of polyurethane resins are accelerated by electron donors (e.g., hydroxyl group) and electron accepting materials (e.g., carboxyl group and dibutyltin dilaurate). As the critical extent of reaction is reached, a three-dimensional cross-linked network is formed. Afterwards, most of the reactive functional groups are attached to the cross-linked network. The mobilities of these reactive functional groups are seriously restricted and the curing reactions become diffusion controlled. This could lead to incomplete extent of reaction. Based on elementary reaction mechanisms a kinetic model is developed. The concept of diffusion-limited reactions is used to describe the phenomenon of limiting extent of reaction. Changes in free volume are related to changes in the rate constants with extent of reaction. When the model is applied to experimental data available in the literature, agreement between the model predictions and experimental data is reasonably good.

## INTRODUCTION

A quantitative understanding of the curing kinetics is essential to assess the feasibility and design of commercial polyurethane processes. Properly formulated polyurethane coatings display fast drying time, excellent application properties, high gloss, and good chemical and solvent resistance. The reaction injection molding (RIM) process involves metering and mixing of reactants, mold filling, and fastcuring in the mold cavity. This study aims at developing a mechanistic model to describe the reaction dynamics of cross-linked polyurethane systems. The concept of free volume theory is used to deal with diffusion controlled reactions. This kinetic model may potentially improve the fundamental understanding of commercial polyurethane applications.

Macosko et al., modeled the curing kinetics of catalyzed polyurethane reaction using an $n$th order rate expression.[1,2] Such an empirical approach allows mathematical modeling but cannot differentiate between formulations with different ratios of reactants or different levels of catalysts.

Second-order reaction kinetics between isocyanate (NCO) and hydroxyl (OH) groups has been suggested by many research groups.[3-6] Squiller and Rosthauser investigated the reaction of catalyzed aliphatic isocyanate with excess alcohol which showed pseudo first-order kinetics.[7] Borkent and Van Aartsen studied the catalyzed polyurethane reaction in DMF solution.[8] The formulations with excess OH also followed pseudo first-order kinetics. Richter and Macosko studied the reaction kinetics of polyurethane catalyzed by dibutyltin dilaurate (DBTDL) and proposed four limiting cases.[9]

Bauer et al., studied the reaction of aliphatic isocyanate with acrylic resin systems and claimed that the reaction is not diffusion controlled even at a high extent of reaction.[5] Yang and Lee showed limiting conversion data (incomplete
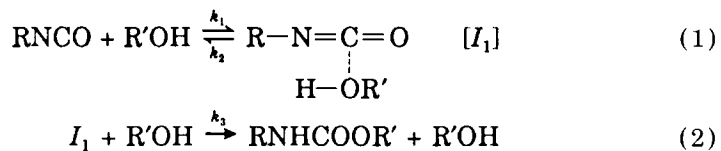
extent of reaction) for both bulk and solution polyurethane reaction during the later stage of cure.[10]

In step polymerization the original monomer or oligomer disappears very early in the reaction. After the formation of a three-dimensional cross-linked network, most of the reactive functional groups are attached to the network and their mobilities are very limited. This could result in a decrease in the reaction rate.

Recently, Chern and Poehlein developed a kinetic model for the curing reactions of epoxides with amines.[11] They treated diffusion controlled reactions with the concept of free volume theory. The reaction rate constants decrease exponentially with increasing extent of reaction after the formation of an infinite cross-linked network. This approach can be extended to polyurethane reactions to describe the phenomenon of limiting conversion.

## REACTION MECHANISMS

Baker et al., proposed a base catalyzed polyurethane reaction.[12-14] Without external catalyst the OH group (an electron donor) acts as a basic catalyst and interacts with an NCO group to form a complex. This complex then reacts with a second OH to produce a urethane unit and a free OH. This is termed the autocatalysis mechanism shown below.

$$RNCO + R'OH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \begin{array}{c} R-N=C=O \\ | \\ H-OR' \end{array} \quad [I_1] \qquad (1)$$

$$I_1 + R'OH \overset{k_3}{\rightarrow} RNHCOOR' + R'OH \qquad (2)$$

Please note that eq. (1) is not in equilibrium in Baker's treatment. Applying the assumption of pseudo steady state to intermediates $I_1$, the authors derived an equation for the reaction rate.

$$\frac{d[NCO]}{dt} = -\frac{k_1 k_3}{k_2 + k_3[OH]} [NCO][OH]^2$$

$$= -K_{OH}[NCO][OH]^2 \qquad (3)$$

where $K_{OH}$ is a lumped reaction rate constant and [NCO] and [OH] represent the concentration of NCO and OH groups, respectively. The rate constant $K_{OH}$ in eq. (3) is dependent on the curing temperature, [OH], and extent of reaction. Chang and Chen proposed an ion-pair mechanism for the formation of urethane and derived a similar rate expression.[15]

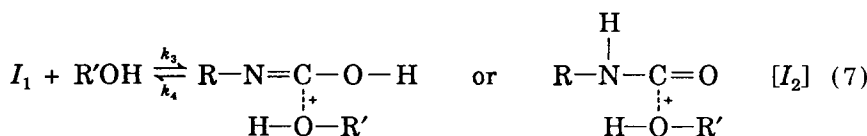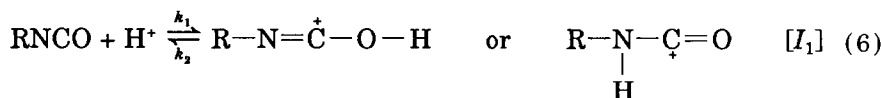If eq. (1) is in equilibrium and eq. (2) is the rate controlling step, then

$$[I_1] = k_1/k_2[NCO][OH] \qquad (4)$$

and

$$d[NCO]/dt = -k_3[I_1][OH]$$

$$= -k_1k_3/k_2[NCO][OH]^2$$

$$= -K_{OH}[NCO][OH]^2 \qquad (5)$$

In this case, $K_{OH}$ is not a function of $[OH]$.

Nakamichi and Ishidoya cured two-component acrylic urethane coatings and reported the catalytic effect of carboxyl group attached to the acrylic resins.[6] They postulated the following reaction mechanism to explain this effect.

$$RNCO + H^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R-N=\overset{+}{C}-O-H \quad \text{or} \quad R-\underset{\underset{H}{|}}{N}-\underset{+}{C}=O \quad [I_1] \quad (6)$$

$$I_1 + R'OH \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \underset{\underset{H-O-R'}{|+}}{R-N=C}-O-H \quad \text{or} \quad \underset{\underset{H-O-R'}{|+}}{\overset{\overset{H}{|}}{R-N}-C}=O \quad [I_2] \quad (7)$$

$$I_2 \overset{k_5}{\rightarrow} RNHCOOR' + H^+ \qquad (8)$$

A proton first attacks the oxygen or nitrogen of an NCO group, then the oxygen of an OH group attacks the carbon of the NCO. Following the same derivation procedure for the autocatalysis mechanism described above, the rate expression for the carboxyl group catalyzed polyurethane reaction can be written as
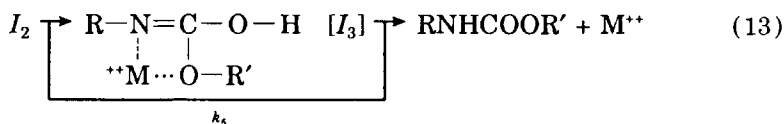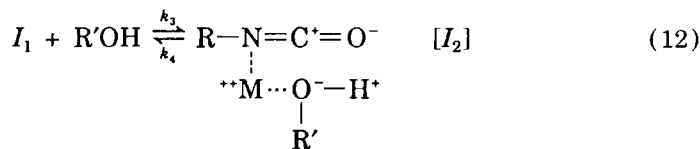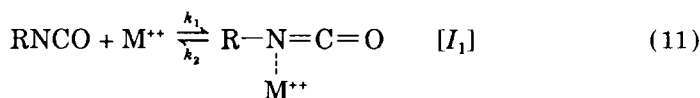
$$\frac{d[NCO]}{dt} = -\frac{k_1k_3k_5}{k_2(k_4 + k_5) + k_3k_5[OH]}[NCO][OH][COOH] \qquad (9)$$

$$= -k_1k_3k_5/k_2k_4[NCO][OH][COOH] \qquad (10)$$

$$= -K_{COOH}[NCO][OH][COOH]$$

where $K_{COOH}$ is the lumped rate constant and $[COOH]$ is the concentration of carboxyl group. In deriving eq. (9) the assumption of pseudo steady state is used for both $I_1$ and $I_2$. To derive eq. (10) it is assumed that eqs. (6) and (7) are in equilibrium and that eq. (8) is the rate determining step. Again, using the equilibrium-bottleneck approach, $K_{COOH}$ in eq. (10) is not dependent on $[OH]$.

Britain and Gemeinhardt proposed a reaction mechanism for urethane reactions catalyzed by metal compounds (such as DBTDL, an electron accepting reagent).[16] This scheme involves the formation of a ternary complex. Smith pointed out that this mechanism requires the attack of one electron deficient center on the other.[17] He suggested an alternate scheme in which the OH group and metal ion form a complex at a different site. Robins indicated that metal catalysts can increase the electrophilicity of NCO by coordinating either at the oxygen or nitrogen and can bring NCO and OH into closer proximity.[18] The proposed reaction mechanism is shown below.

$$\text{RNCO} + \text{M}^{+} \overset{k_1}{\underset{k_2}{\rightleftharpoons}} \underset{\underset{\text{M}^{+}}{|}}{\text{R}-\text{N}}=\text{C}=\text{O} \qquad [I_1] \qquad (11)$$

$$I_1 + \text{R}'\text{OH} \overset{k_3}{\underset{k_4}{\rightleftharpoons}} \underset{\underset{\underset{\text{R}'}{|}}{{}^+\text{M}\cdots\text{O}^--\text{H}^+}}{\text{R}-\text{N}}=\text{C}^+=\text{O}^- \qquad [I_2] \qquad (12)$$

$$I_2 \overset{}{\longrightarrow} \underset{{}^+\text{M}\cdots\text{O}-\text{R}'}{\text{R}-\text{N}=\text{C}-\text{O}-\text{H}} \quad [I_3] \overset{}{\longrightarrow} \text{RNHCOOR}' + \text{M}^{+} \qquad (13)$$

$$k_5$$

Equations (11) and (12) are in equilibrium, and the rate controlling step eq. (13) includes two steps: (i) $I_2$ is slowly converted into $I_3$ and (ii) the urethane and metal catalyst in $I_3$ are separated from each other. The rate constant for eq. (13) is $k_5$. The rate expression can be written as

$$d[\text{NCO}]/dt = -k_1 k_3 k_5 / k_2 k_4 [\text{NCO}][\text{OH}][\text{C}]$$

$$= -K_C[\text{NCO}][\text{OH}][\text{C}] \qquad (14)$$

where $K_C$ is the lumped rate constant and [C] is the concentration of metal catalyst.

Richter and Macosko proposed a Michaelis Menten type kinetics for DBTDL catalyzed polyurethane reaction.[9] The reaction rate is first order with respect to [NCO], [OH], and [C], respectively when cured at practical temperatures and catalyst levels (case 3). They also showed that the consumption rate of NCO by autocatalysis mechanism (eq. (3)) is not negligible compared to that by DBTDL catalysis (eq. (14)).

## MODEL DEVELOPMENT

### Kinetic Rate Expressions

The following assumptions regarding the reaction mechanisms are employed to simplify the kinetic model:

(a) Urethane reactions catalyzed by hydroxyl, carboxyl, and metal compounds are the only reactions taking place in the system. Other reactions catalyzed by the urethane group, allophanate formation reactions, and reactions between reactants and impurities are assumed insignificant.

(b) The carboxyl and metal compound catalysts are not consumed or generated during curing reaction.

(c) $K_{OH}$, $K_{COOH}$, and $K_C$ are only dependent on the curing temperature and extent of reaction (equilibrium-bottleneck approach).

(d) The curing reaction is isothermal.

(e) Nakamichi and Ishidoya observed interactions between COOH groups and DBTDL.[6] This jeopardizes the effectiveness of DBTDL as a catalyst. The

cause of this phenomenon is not known. To take into account this effect, a catalyst efficiency factor ($e$) is introduced ($0 \leq e \leq 1$).

Based on the above assumptions, the rate expression can be written as follows:

$$d[NCO]/dt = d[OH]/dt = -K_{OH}[NCO][OH]^2$$
$$- eK_{COOH}[COOH][NCO][OH] - eK_C[C][NCO][OH] \quad (15)$$

Equation (15) describes the curing dynamics and is subject to the following initial conditions:

at $\quad t = 0$

$$[NCO] = [NCO]_0, \quad [OH] = [OH]_0, \quad [COOH] = [COOH]_0, \quad [C] = [C]_0$$

where the subscript 0 represents the initial concentrations. The extent of reaction for NCO ($X_{NCO}$) and OH ($X_{OH}$) can be calculated by the following equations:

$$X_{NCO} = 1 - [NCO]/[NCO]_0 \quad (16)$$

$$X_{OH} = 1 - [OH]/[OH]_0 \quad (17)$$

## Diffusion-controlled Reactions

If the polyurethane curing reactions behave ideally during cure, all of the rate constants should remain constant over the entire extent of reaction range and complete conversion should be observed. In fact, this is not the case because in condensation polymerization the original monomer or oligomer disappears very early in the reaction. After the gel point, most of the reactive functional groups are attached to the three-dimensional cross-linked network and their mobilities are very limited. This could result in a decrease in the reaction rate even when there may be a significant level of NCO and OH groups available for curing reaction. Thus, the curing reaction will not be complete.

During the curing reaction, the critical extent of reaction for the onset of diffusion-controlled reactions is taken as the point at which a three-dimensional crosslinked network is formed. At the gel point the polymer molecular weight increases to infinity and, consequently, the viscosity of the reacting system increases dramatically. The gel point can be measured directly by a viscometry technique.[19] Carothers derived the following equations to correlate the extent of reaction at the gel point ($X_c$) with the average functionality ($f_a$) of the polymerization system in which the two reactive functional groups (e.g., NCO and OH) are at equal stoichiometry.[20]

$$f_a = \sum N_i f_i / \sum N_i \quad (18)$$

$$X_c = 2/f_a \quad (19)$$

where $N_i$ is the number of molecules of monomer $i$ with functionality $f_i$. The summations cover all the monomers present in the system.

As suggested by Chern and Poehlein, in step polymerization, changes in free volume are related to changes in the rate constants with extent of reaction.[11]

$$K_i/K_{i0} = \exp[-V^*(1/V_f - 1/V_{fc})] \tag{20}$$

where $K_i$ is the rate constant at a given extent of reaction, $K_{i0}$ is the chemical reaction controlled rate constant, $V_f$ is the fractional free volume of the curing system at a given extent of reaction, $V_{fc}$ is the critical fractional free volume at the gel point, and $V^*$ is an adjustable parameter. $V^*$ is a measure of the degree of diffusion control of the reacting system.

$V_f$ is a linear function of the temperature difference $T - T_g$. $T$ is the reaction temperature and $T_g$ is the glass transition temperature of the reacting system at a given $X$. In free radical polymerization, a propagating center adds many monomer units in a chain reaction and grows very rapidly to a large size. Thus, high molecular weight polymer is formed immediately. The polymer molecular weight is relatively constant during the reaction, except in the high conversion region associated with the gel effect. At any instant monomer, polymer, and propagating chains exist in the reacting system. Assuming additivity of the fractional free volumes of polymer ($V_{fp}$) and monomer ($V_{fm}$), $V_f$ can be calculated by the following equation:[21]
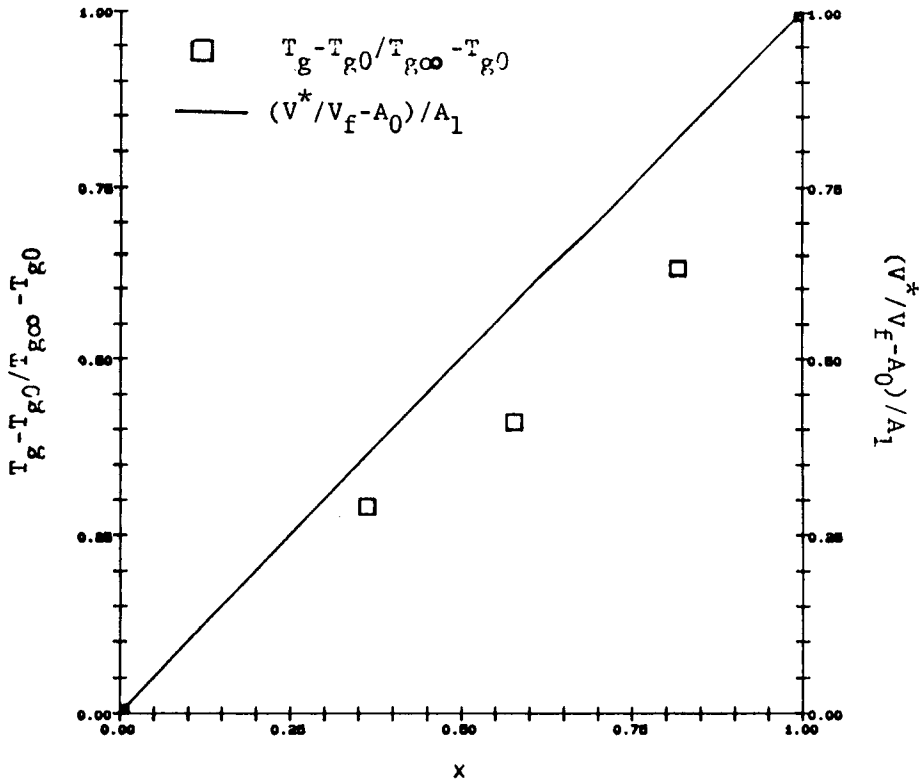


Fig. 1. Dimensionless Parameters of Glass Transition Temperature and Free Volume vs. Extent of Reaction.

| Parameter | Value | Units |
|-----------|-------|-------|
| $MW$ | | |
| NCO | 300 | g/mole |
| OH | 900 | g/mole |
| DBTDL | 632 | g/mole |
| $d$ | | |
| NCO | 1.21 | g/ml |
| OH | 1.07 | g/ml |
| DBTDL | 1.07 | g/ml |
| $f$ | | |
| NCO | 2.1 | |
| OH | 3.0 | |
| [NCO] | 2.51 | mole/l |
| [OH] | 2.51 | mole/l |
| [C] | $9.08 \times 10^{-6}$ | mole/l |
| $X_c$ | 0.69* | |
| | 0.81** | |
| $T$ | 60 | °C |

$MW$: molecular weight, $d$: density.
$T$: curing temperature.
*: viscometry (used in modeling).
**: Carothers eq.

$$V_f = V_{fm}\phi_m + V_{fp}(1 - \phi_m)$$

$$= [0.025 + \alpha_m(T - T_{gm})]\phi_m + [0.025 + \alpha_p(T - T_{gp})](1 - \phi_m) \quad (21)$$

where $\phi_m$ is the volume fraction of monomer in the reacting system. $T_{gm}$ and $T_{gp}$ are the glass transition temperatures of the monomer and polymer, respectively. $\alpha_m$ is the difference between the coefficients of volumetric expansion of monomer in the melt and glassy state, and $\alpha_p$ is the corresponding difference for the polymer. The value of 0.025 is the fractional free volume of pure polymer at its glass transition point.

Equation (21) is not applicable for the curing reaction of polyurethane. This is because in step polymerization the original monomer disappears early in the reaction. The polymer molecular weight, and consequently $T_g$, increases throughout the curing reaction.

Since the present model does not include a correlation between $V_f$ and $T - T_g$, the following approach is chosen to simulate the diffusion controlled reactions.[11] $V_f$ is closely related to the extent of reaction ($X$) and generally an empirical equation such as eq. (22) can be employed to describe the change of $V_f$ with $X$ during cure.

$$V^*/V_f = A_0 + A_1X + A_2X^2 + \ldots \quad (22)$$

where $A_0$, $A_1$, and $A_2$, etc., are constants that are dependent on the kind of reacting system and curing temperature. In this work, a linear relationship between $1/V_f$ and $X$ is used and eq. (20) can be written as

$$K_i/K_{i0} = \exp[-D(X - X_c)]$$                              (23)

## RESULTS AND DISCUSSION

Nakamichi and Ishidoya presented data on the change of $T_g$ with increasing $X$ for the polyurethane curing reaction.[6] Their experimental data are presented in a dimensionless form of $[(T_g - T_{g0})/(T_{g\infty} - T_{g0})]$-vs-$X$ in Figure 1 (squares). $T_{g0}$ and $T_{g\infty}$ are the glass transition temperature at $X = 0$ and $X = 1$, respectively. $T_{g\infty}$ and $T_{g0}$ are the extrapolated values. $T_g$ increases with increasing $X$. This leads to a decreased $V_f$. After $X_c$ is reached, the mobility of the reactive functional groups is seriously restricted and, consequently, the reaction becomes diffusion controlled. The calculated $[(V^*/V_f - A_0/A_1)]$-vs-$X$ curve is also shown in Fig. 1 (solid line). The deviation between the dimensionless $T_g$ data points and the dimensionless $V_f$ curve is not significant. This suggests that eq. (23) is a good approximation for the diffusion controlled reaction mechanism.

Yang and Lee cured poly(-caprolactonetriol) with 4,4'diphenylmethylene diisocyanate at 60°C using DBTDL as the catalyst.[10] The extent of reaction for NCO was followed using Fourier transform infrared spectroscopy. Their experimental data are used to assess the proposed kinetic model. The parameters necessary in the calculations are obtained from the literature or estimated from the curing conditions (Table I).

If NCO and OH are at equal stoichiometry, then $X_{NCO}$ equals $X_{OH}$. In this case, for concise nomenclature, $X_{NCO}$ is replaced by $X$. The extent of reaction data with and without DBTDL are shown as discrete points in Figure 2.

The second term in eq. (15) vanishes and the catalyst efficiency factor ($e$) equals unity because COOH is not present in the curing system. The only remaining parameters that need to be specified before computer modeling can be carried out are the rate constants ($K_{OH}$ and $K_C$) and empirical parameter $D$. The rate constants and $D$ are not totally decoupled; $K_{OH}$ and $K_C$ determine how fast the curing reactions react, and $D$ only has an effect after the three-dimensional network is formed after $X_c$. The computer modeling strategy is first to use $K_{OH}$ to best fit the $X$-vs-$t$ data without DBTDL in the chemical reaction controlled region and then to shape the curve with $D$ in the diffusion controlled region. With the knowledge of $K_{OH}$ and $D$ one can then best fit the DBTDL catalyzed $X$-vs-$t$ data by adjusting $K_C$.

The model predictions are presented as continuous curves in Fig. 2. The solid lines represent the calculated results with diffusion controlled reaction mechanism. Very good agreement between the predictions and experimental data is observed. For comparison, the dashed lines using constant $K_{OH}$ and $K_C$ throughout the curing reaction are also included. This model fails to predict the experimental data after $X_c$.

$K_{OH}$ and $K_C$ have best fit values of $1 \times 10^{-4}$ and $40 \ 1^2/\text{mole}^2 - \text{s}$ at 60°C, respectively. $D$ has a single best fit value of 10 for both catalyzed and uncatalyzed systems. This is probably due to the nature of the three-dimensional cross-linked network involved in such a thermosetting polymer system. A very small amount of DBTDL speeds up the curing reaction significantly, but it does not change the point at which the three-dimensional crosslinked network is formed
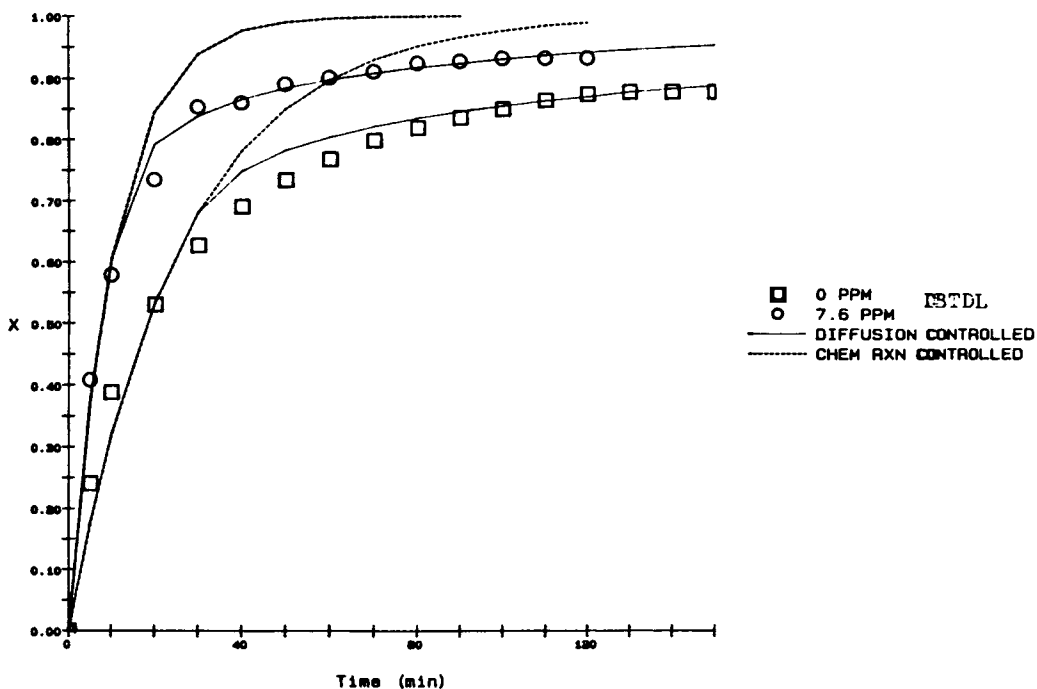
Fig. 2. Effect of DBTDL Level on Extent of Reaction.

($X_c = 0.67$ for both systems). After the gel point both systems experience the same degree of diffusion control of the reactions.

Figure 3 shows the change of $K_{OH}$ and $K_C$ with extent of reaction. In the chemical reaction controlled region (before 67% extent of reaction) $K_{OH}$ and $K_C$ remain constant. Thereafter, both rate constants decrease with increasing extent of reaction (decreasing free volume) in the diffusion controlled region.

Nakamichi and Ishidoya investigated the curing reaction between hydroxyl and/or carboxyl containing acrylic resins and a biuret of hexamethylene diisocyanate at different temperatures.[6] DBTDL was added as the external catalyst when required. The extent of reaction for NCO was measured by the thin film method of infrared spectroscopy. Most of the solvent in the thin film was assumed to evaporate prior to the curing reaction. Thus, the volume of the reacting system did not change significantly during the course of polymerization. Table II lists some physical parameters used in the computer simulations. Figure 4 shows the $X$-vs-$t$ profiles for resin $A$ cured at different temperatures. In this series of experiments COOH and $C$ are not involved in the curing reaction. Thus, the last two terms in eq. (15) disappear.

In Fig. 4 the discrete points are the experimental data, and the continuous curves represent the model predictions. The model predicts the experimental data very well. As expected, the curing rate increases with increasing temperature. The dotted line using constant $K_{OH}$ at 120°C is included. This model overpredicts the reaction rate after the gel point. The best fit values of $K_{OH}$ at different temperatures can be found in Table III. $D$ has a single best fit value
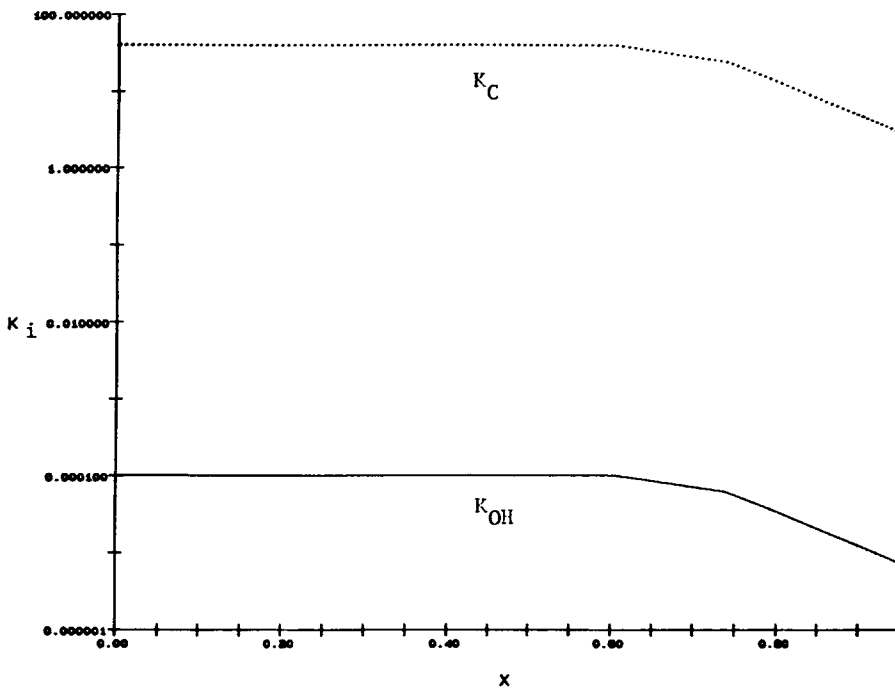
Fig. 3. Reaction Rate Constant vs. Extent of Reaction Profiles.

of 5 for this particular curing system. $K_{OH}$ and $D$ will be kept constant in the remaining computer modeling work.

The $X$-vs-$t$ profiles of the DBTDL catalyzed polyurethane reaction for resin A at 80°C are presented in Figure 5. The level of DBTDL ranges from 0 to 0.025 wt % based on total solids content. The experimental data are shown as discrete points. The continuous curves represent the model predictions. Agreement between the predictions and experimental data is reasonably good. The rate of polymerization increases with increasing catalyst concentration. The dotted line represents the simulation result with constant $K_{OH}$ and $K_C$ at 0.025 % DBTDL. Again, this model overpredicts the $X$-vs-$t$ data in the diffusion controlled region. The best fit value of $K_C$ is listed in Table III. This $K_C$ value will also remain unchanged in the computer simulations of other experiments with added DBTDL.

Figure 6 shows the $X$-vs-$t$ profiles for carboxyl containing resin B cured at various temperatures. The discrete points are the experimental data and the continuous curves are the model predictions. The model predictions agree reasonably well with the experimental data. The best fit values of $K_{COOH}$ are shown in Table III and these values will not be adjusted later.

The $X$-vs-$t$ profiles of the DBTDL catalyzed polyurethane reaction for resin B are illustrated in Figure 7. The discrete points represent the experimental results, and the continuous curves are the computer simulations. The catalyst efficiency factor ($e$) is taken as unity (i.e., no interaction between the carboxyl group and DBTDL). The model can predict the trend, but it does not fit the experimental data well, especially at high $X$. This indicates that, indeed, there

TABLE II
Parameters for Computer Modeling of Nakamichi's Data

| Parameter | Value | Units |
|---|---|---|
| $d$ | 1.1 | g/ml |
| $MW$ | | |
|    NCO | 478 | g/mole |
|    DBTDL | 632 | g/mole |
| Resin A | | |
|    $M_n$ | 8560 | g/mole |
|    $M_w$ | 21400 | g/mole |
|    [OH] | 1.1 | mole/l |
|    [COOH] | 0 | mole/l |
| Resin B | | |
|    $M_n$ | 8420 | g/mole |
|    $M_w$ | 20200 | g/mole |
|    [OH] | 1.1 | mole/l |
|    [COOH] | 0.128 | mole/l |
| Resin C | | |
|    $M_n$ | 8550 | g/mole |
|    $M_w$ | 20100 | g/mole |
|    [OH] | 1.1 | mole/l |
|    [COOH] | 0.327 | mole/l |
|    [NCO] | 1.1 | mole/l |
| $f$ NCO | 3 | |
| $f$ OH | 10.3* | |
| | 25.7** | |
| $X_c$ | 0.43* | |
| | 0.37** | |
| | 0.40*** | |

$M_n$: number average molecular weight, $M_w$: weight average molecular weight.
*: based on $M_n$, **: based on $M_w$.
***: used in modeling.

are some interactions between the carboxyl group and DBTDL. Varying the catalyst efficiency factor ($e$) does not improve the model predictions. The interaction mechanism is beyond the scope of this study.

Figure 8 shows the $X$-vs-$t$ profiles for resins $A$, $B$, and $C$ cured at 80°C. No external catalyst is used. The rate constants used in the calculations are listed in Table III. The experimental data are shown as discrete points and model simulations are represented as continuous curves. This series of experiments, again, demonstrates the predicting capability of the proposed kinetic model.

Figure 9 is the Arrhenius plot of the curing rate constants $K_{OH}$ and $K_{COOH}$. The activation energy ($E$) can be obtained from the slope. The calculated $E$ is 14.1 kcal/mole for $K_{OH}$ and 16.1 kcal/mole for $K_{COOH}$.

The extent of reaction for resin $A$ cured at 60°C is relatively low (12.4% at 120 min). Such a low curing level generally renders the coatings to be inferior in physical properties. The extent of reaction can be raised to a higher level by increasing the curing temperature. This process is simulated by keeping the curing temperature at 60°C from 0 to 200 min. Afterwards the temperature is brought up to 80°C rapidly. The system is further polymerized at this temperature until 400 min is reached as shown in Figure 10. The final extent of reaction
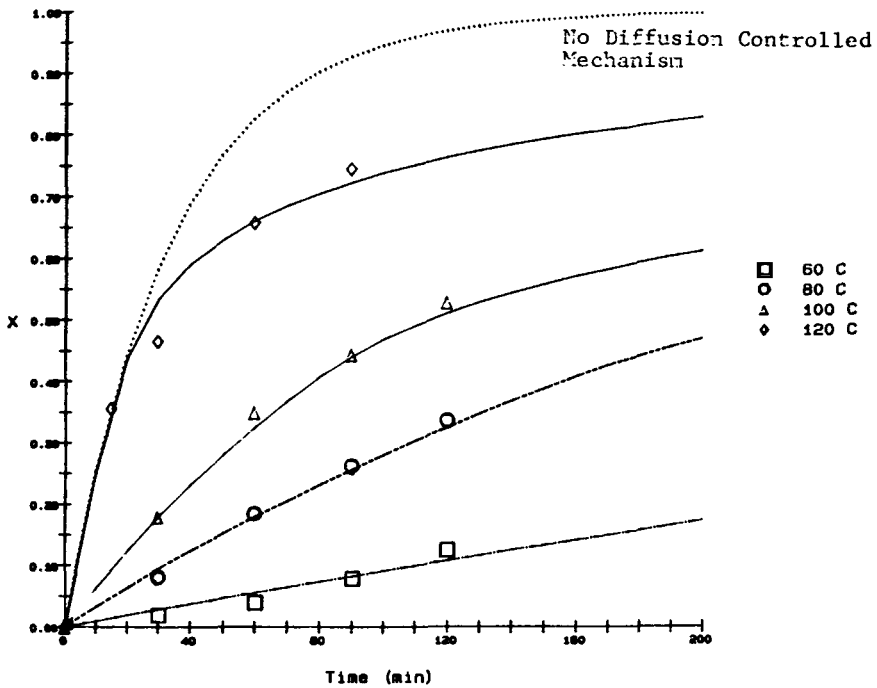
Fig. 4. Effect of Curing Temperature on Extent of Reaction Profiles for Resin A.

is about 50%, which is still short of completion due to the diffusion controlled reactions.

## CONCLUSIONS

The curing reactions of polyurethane resins can be accelerated by electron donors (e.g., hydroxyl group) and electron accepting materials (e.g., carboxyl group and DBTDL). The original monomer or oligomer disappears very early in the reaction. After the gel point most of the reactive functional groups are attached to the three-dimensional cross-linked network. When the mobilities of these reactive functional groups become seriously restricted, the curing re-

TABLE III
Best Fit Values of Rate Constants

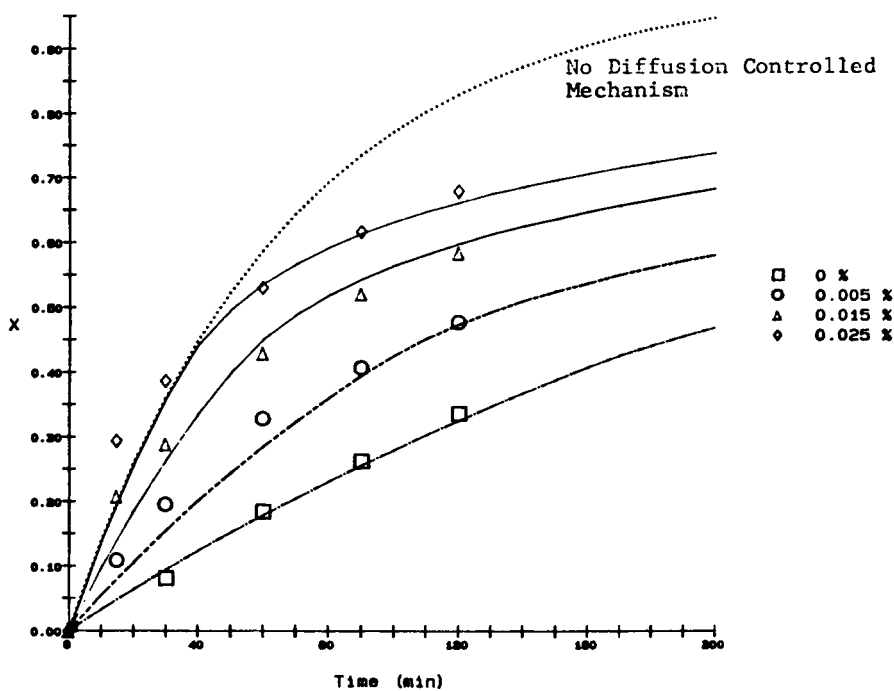|  | $T$ (°C) | | | |
| --- | --- | --- | --- | --- |
|  | 60 | 80 | 100 | 120 |
| $K_{OH} \times 10^5$ | 1.3 | 4.5 | 9.0 | 40.0 |
| $K_{COOH} \times 10^4$ | 4.5 | 15.0 | 50.0 | 200.0 |
| $K_C$ |  | 0.4 |  |  |

Units: $l^2/mole^2$ s.

Fig. 5. Effect of DBTDL Level on Extent of Reaction Profiles for Resin A Cured at 80 C.
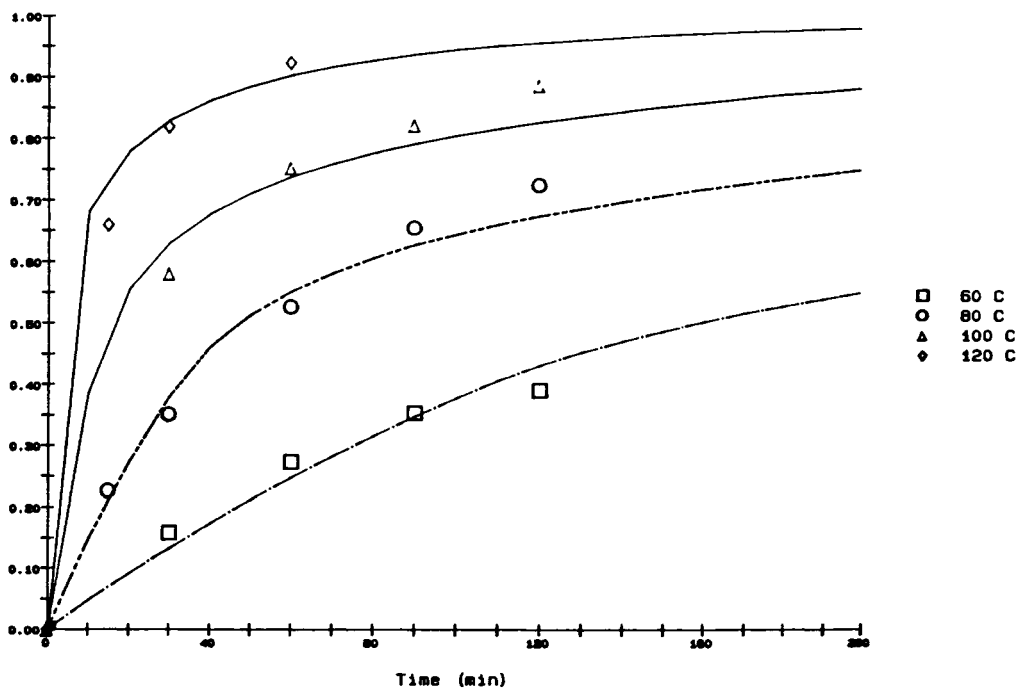


Fig. 6. Effect of Curing Temperature on Extent of Reaction Profiles for Resin B.
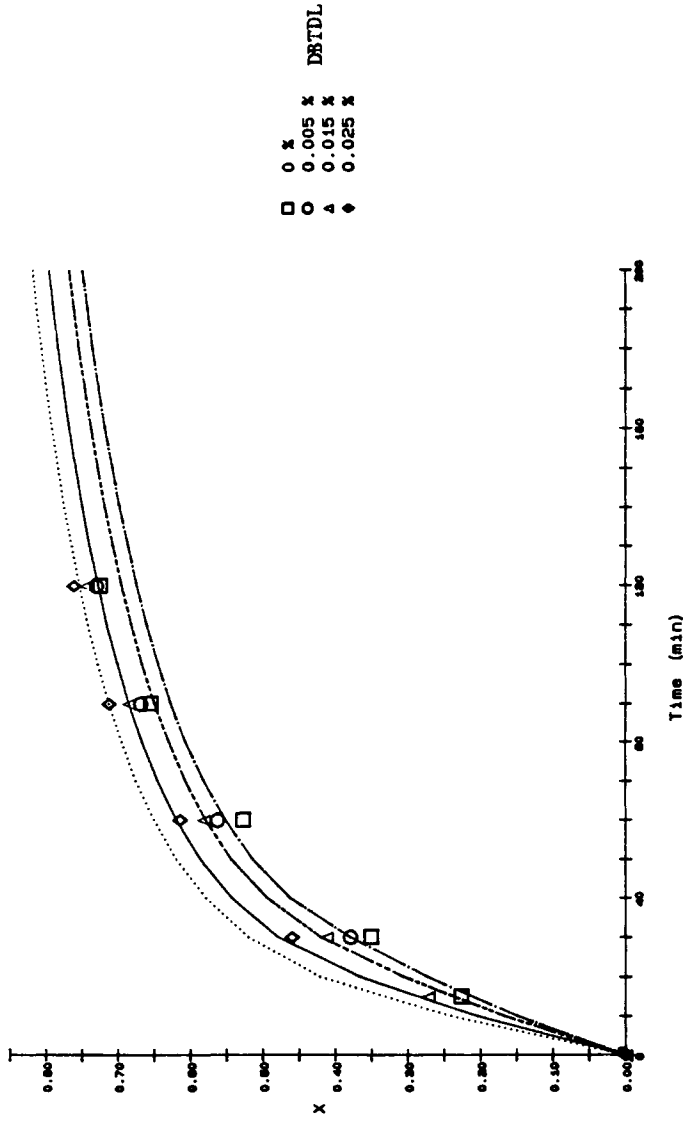
Fig. 7. Effect of DBTDL Level on Extent of Reaction Profiles for Resin B Cured at 80 C.
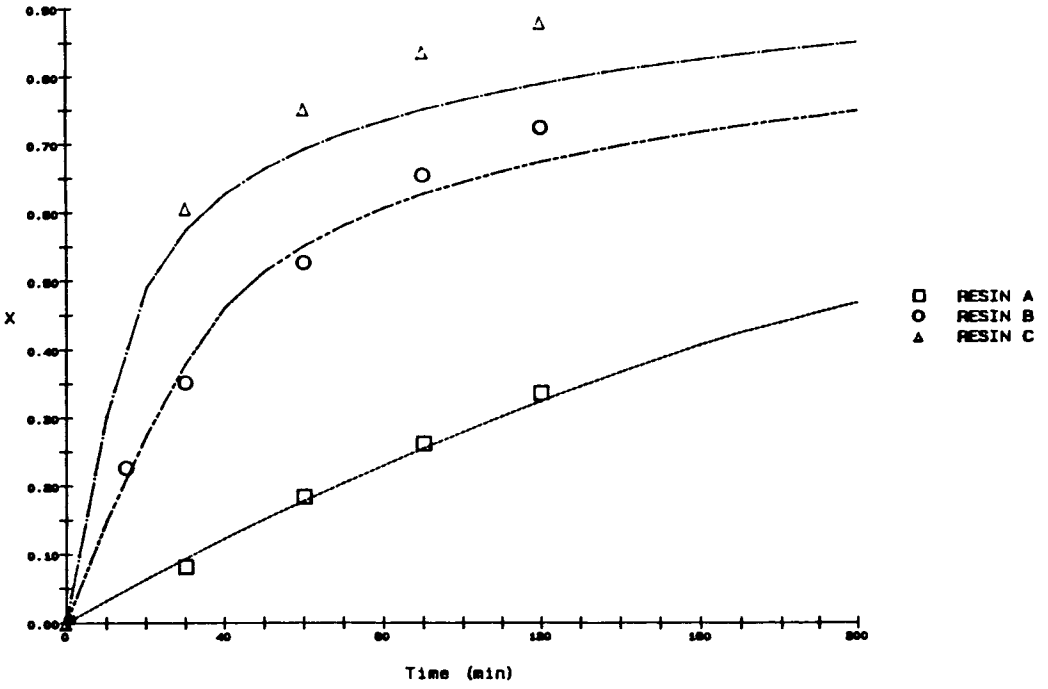
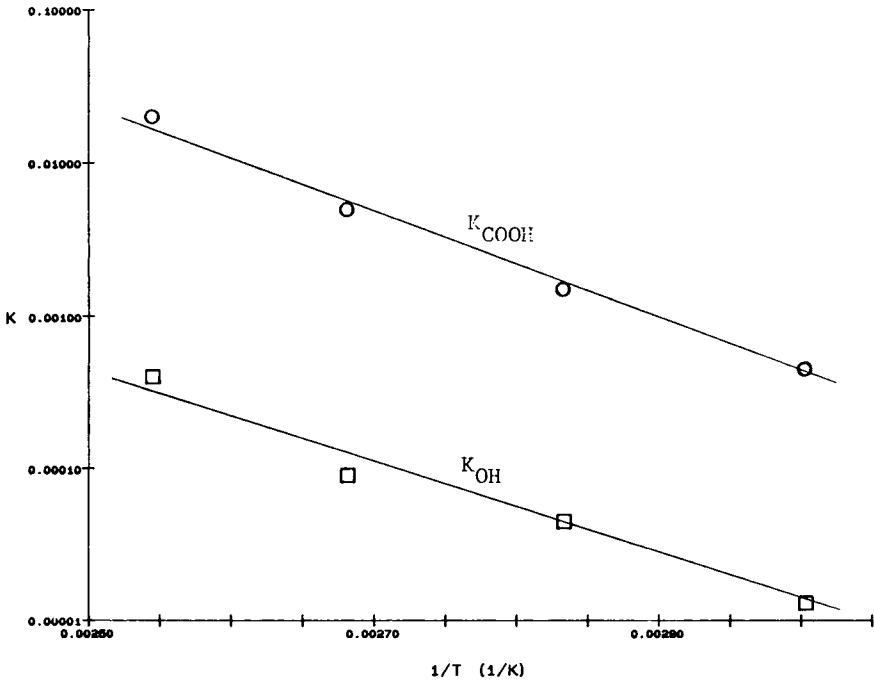Fig. 8. Extent of Reaction vs. Time Profiles for Resins A, B, and C Cured at 80 C.



Fig. 9. Arrhenius Plot of Curing Rate Constants $K_{COOH}$ and $K_{OH}$.
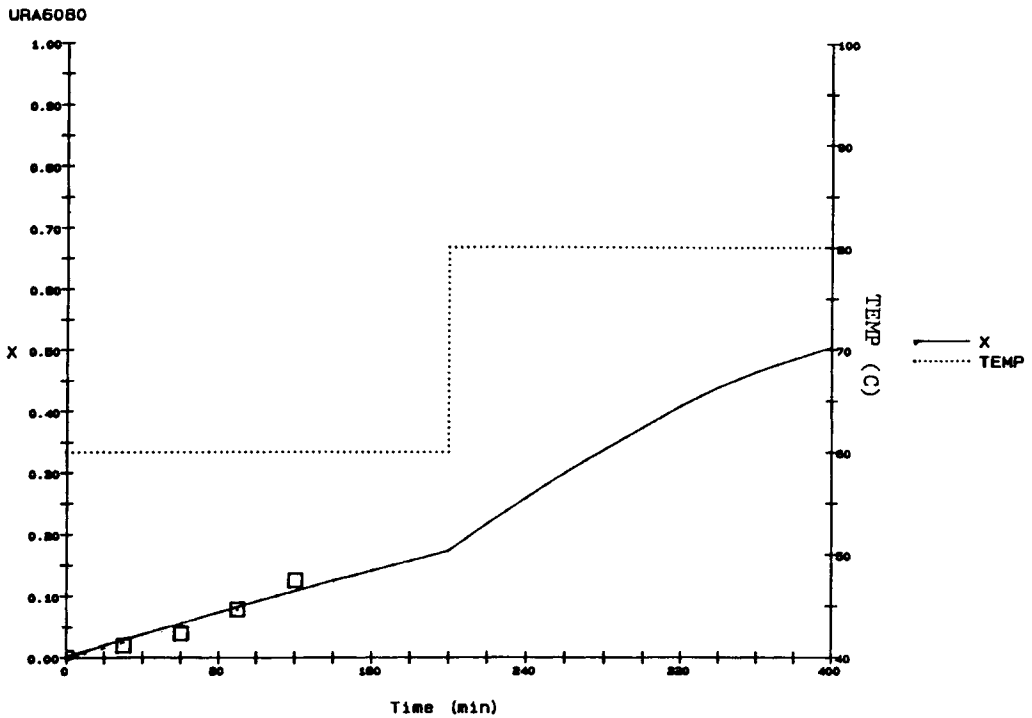
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Fig. 10. Effect of Curing Temperature on Extent of Reaction Profiles for Resin A.

actions become diffusion controlled. The curing rate decreases with increasing extent of reaction. This could lead to incomplete extent of reaction.

A kinetic model is developed based on elementary reaction mechanisms. The concept of diffusion controlled reactions is used to describe the phenomenon of limiting extent of reaction. Changes in free volume are related to changes in the rate constants with extent of reaction. The model is capable of predicting the curing dynamics of a polyurethane reaction. It can also differentiate between systems with different ratios of reactive functional groups or different levels of added catalysts. When experimental data available in the literature is used to test the proposed model, reasonable agreement between the model predictions and experimental data is observed.

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