

# Use of Isoconversional Methods to Analyze the Cure Kinetics of Isocyanate-Ended Quasi-Prepolymers with Water

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**ABSTRACT:** The curing of an isocyanate (NCO)-ended quasi-prepolymer by reaction with water in stoichiometric ratio was monitored by using differential scanning calorimetry both under isothermal and non-isothermal conditions. A quasi-prepolymer containing 16 wt % free NCO prepared by reacting trifunctional polypropylene glycol (PPG) with polymeric MDI was used in this study. The variation of the effective activation energy with the extent of the curing reaction was calculated by means of model-free differential and integral isoconversional methods. Both

isoconversional methods provided similar results showing that the activation energy depends on the extent of the reaction of the quasi-prepolymer with water. The dependence of the effective activation energy proved to be different under isothermal and non-isothermal curing conditions. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1049–1057, 2007

**Key words:** activation energy; differential scanning calorimetry (DSC); kinetics (polym); curing of polymers

## INTRODUCTION

Urethane prepolymers are isocyanate-ended macromolecular chains containing urethane groups in their backbone, and are usually obtained by reaction of a polyol with a molar excess of di- or polyisocyanate and typically contain free isocyanate (NCO) groups. Urethane prepolymers containing free NCO content of 15–30 wt % are called quasi-prepolymers because only part of the polyisocyanate monomer contributes to the formation of the backbone polymer.<sup>1</sup> Quasi-prepolymers are extensively used in the production of one-component polyurethane foams<sup>2</sup> in the building industry and in do-it-yourself adhesives.<sup>3</sup> When exposed to air moisture, the quasi-prepolymers cure as the reaction between the free isocyanate groups and the moisture from air and in the substrate occurs by formation of urea groups (Scheme 1). The release of carbon dioxide and its entrapment in the viscous quasi-prepolymer may lead to the formation of a cellular structure.

The curing process involves the transformation of a relatively low-molecular-weight liquid into a high-

molecular-weight poly(urethaneurea) solid that exhibit typical properties of thermosets.

Despite the industrial relevance of isocyanate-ended quasi-prepolymers, to our knowledge only a few studies have been devoted to the kinetics of the curing reaction of low free NCO content-ended prepolymers with water.<sup>4,5</sup>

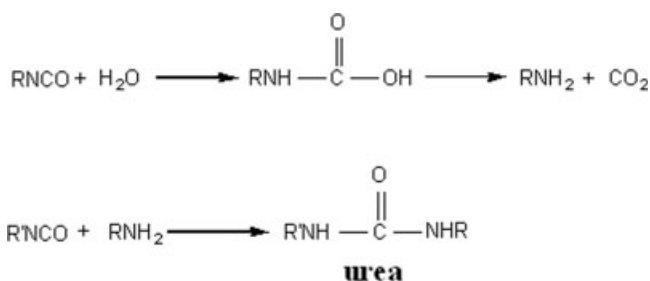
Differential scanning calorimetry (DSC) has been widely used for monitoring the curing process of thermosets. Several changes in the physical properties occur during the curing of a thermoset and they may affect the mechanism of the reaction. Usually, the reaction is kinetically controlled for lower conversion and becomes diffusion controlled at higher conversion. Because of the complexity of the curing process, an approach based on the fit of kinetic data to an assumed reaction model normally fails.

An alternative approach is the application of the model-free isoconversional methods. These methods allow for the evaluation of the activation energy as a function of the extent of the reaction, without assuming any kinetic model. Isoconversional methods reveal the variations in the reaction mechanism that are accompanied by changes in activation energy. These methods have been mostly used to analyze the curing of epoxy resin formulations but more recently their application to polyurethane systems have also been reported.<sup>6,7</sup>

In this study, the curing of a quasi-prepolymer with relatively high free NCO content by reaction with

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**Scheme 1** Formation of urea from the reaction between isocyanate groups and water molecules.

water was performed using isothermal and non-isothermal DSC experiments. Besides the traditional curve fitting approach, isoconversional methods were used to understand the complex curing process of urethane quasi-prepolymers.

### Mathematical aspects of isoconversional methods

The rate of a reaction ( $d\alpha/dt$ ) in condensed state is usually described as a result of two functions independent of each other: the  $k(T)$  function, which depends solely on the temperature  $T$  and follows the Arrhenius law, and the  $f(\alpha)$  function which depends on the conversion degree and is related to the mechanism of the reaction:

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \quad (1)$$

The main implication of eq. (1) is that the reaction rate at a constant conversion degree is only a function of the temperature, and this is the basic assumption of the so-called isoconversional methods. This assumption holds only for a single step reaction. For a multi-step kinetics the dependence of the activation energy ( $E_a$ ) with conversion ( $\alpha$ ) reflects the variation in relative contribution of single steps to the overall reaction rate.

The isoconversional methods are considered model-free because they provide the variation of the effective activation energy with the reaction progress, without assuming any kinetic model. Several isoconversional methods have been proposed in the literature. Starink<sup>8</sup> recently reviewed the accuracy of the different isoconversional methods, and differential and integral isoconversional methods may be defined.

### Isoconversional differential methods

Differential methods are frequently called Friedman methods due to the researcher who first derived this method.<sup>9</sup> The method derives from taking the logarithm of eq. (1):

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln[A_{\alpha}f(\alpha)] - \frac{E_{a\alpha}}{RT_i} \quad (2)$$

The activation energy ( $E_a$ ) is determined from the slope of the plot of  $\ln(d\alpha/dt)$  versus  $1/T$ , at a constant  $\alpha$  value. Subscript  $i$  is the ordinal number of an experiment performed under constant temperature (for isothermal conditions) or of an experiment performed at a given heating rate (for non-isothermal conditions). This method is rather accurate because it does not include any mathematical approximations. However, it is highly sensitive to the accurate determination of the baseline and calibration of the thermal analysis equipment and tends to be numerically unstable, especially when the rate is estimated by numerical differentiation of the experimental data.

### Isoconversional integral methods

Integral methods are used with the purpose of suppressing the high sensibility of the differential methods. They are called integral methods because they are based on the integral form  $g(\alpha)$ :

$$g(\alpha) \equiv \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = A \int_0^{t_{\alpha}} \exp\left(-\frac{E_a}{RT(t)}\right) dt = AJ[E_a, T(t_{\alpha})] \quad (3)$$

For isothermal conditions, the integration of eq. (3) leads to eq. (4):

$$\ln t_{\alpha,i} = \ln \left[ \frac{g(\alpha)}{A_{\alpha}} \right] + \frac{E_{a\alpha}}{RT_i} \quad (4)$$

and  $E_a$  can be determined from the slope of the plot of  $\ln(t)$  versus  $1/T$ , at constant  $\alpha$  value. For non-isothermal conditions, the integral of eq. (3) can be replaced by various useful approximations that may lead to simple linear equations for estimating the activation energy.<sup>8</sup> However, these assumptions introduce some systematic error in estimating  $E_a$  if it is a function of the extent of the reaction.

Vyazovkin<sup>10,11</sup> recently proposed an advanced integral method that allows for the calculation of the dependence of  $E_a$  with the extent of the reaction under non-isothermal conditions. According to this method,  $E_a$  is calculated as the minimum of the function  $\Phi[E_a(\alpha)]$ :

$$\Phi(E_a(\alpha)) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J[E_a, T_i(t_{\alpha})]}{J[E_a, T_j(t_{\alpha})]} \quad (5)$$

where subscripts  $i$  and  $j$  represent the ordinal number of two experiments performed under dif-

ferent heating rates. The integral  $J$  is calculated using eq. (6):

$$J[E_a, T_i(t_\alpha)] = \int_{t_\alpha - \Delta\alpha}^{t_\alpha} \exp\left[\frac{-E_a(\alpha)}{RT_i(t)}\right] dt \quad (6)$$

To avoid that each value of  $E_a$  becomes averaged over the entire conversion region (i.e., 0 to  $\alpha$ ), the integration is performed in a small segment  $[t_\alpha - \Delta\alpha, t_\alpha]$ . In eq. (6),  $\alpha$  varies from  $2\Delta\alpha$  to  $1 - \Delta\alpha$  with a step  $\Delta\alpha = (m + 1)^{-1}$ , where  $m$  is the number of the equidistant values of  $\alpha$  chosen for the analysis.

## EXPERIMENTAL

### Materials

The raw materials used to prepare the quasi-prepolymer were polymeric diphenylmethane diisocyanate (pMDI) and glycerine-propoxylated polyether triol (Voranol CP 1055). Both materials were supplied by Dow Chemical Company (Barcelona, Spain). The polymeric MDI used in this work has a free isocyanate content of 31.3 wt % and an average functionality of 2.7 and was used as-received. The polyol contains secondary hydroxyl terminal groups and has an average molecular weight of 1000 g/mol and an OH value of 156 mg KOH/g. The polyol was dried under reduced pressure ( $10^{-1}$  torr) at 60°C, for at least 3 h before use.

### Synthesis of the quasi-prepolymer

A quasi-prepolymer containing 16 wt % NCO was prepared by reacting 120 g dried polyol with 217 g pMDI in a three-necked 1000-mL glass flask, under dry nitrogen atmosphere. Inert atmosphere was used to avoid the reaction of isocyanate groups with moisture and the consequent formation of urea linkages. The system was kept at 70°C and mechanically stirred with a glass stirrer at 80 rpm for 3 h. The isocyanate content of the quasi-prepolymer was determined by titration of excess  $N,N'$ -dibutylamine with standard HCl.<sup>12</sup> After preparation, the quasi-prepolymer were stored under dry nitrogen in a glass container for further testing and characterization.

### Kinetic measurements

All calorimetric data reported in this work were obtained with a Q-100 differential scanning calorimeter (TA Instruments, New Castle, DE), calibrated with indium, using a continuous nitrogen flow of 50 mL/min.

The quasi-prepolymer was mixed with distilled water in a stoichiometric proportion and the mixture ( $\sim 50$  mg) was sealed in steel high volume DSC pan

with a capacity of 100  $\mu$ L. During the curing reaction, the samples expand due to the formation of carbon dioxide, and this was the reason to avoid the use of the standard aluminum hermetic pans because they were unable to retain the sample during the experiment, due to its expansion.

The calorimetric data of the quasi-prepolymer samples were measured using the following three different methods

1. *Postcuring dynamic DSC method:* The uncured samples were kept at 25°C for different curing times up to 7.5 h. The DSC experiment was then carried out by heating from  $-80$  to 200°C at the heating rate of 5°C/min to determine the residual enthalpy ( $\Delta H_r$ ). Because the reaction starts immediately after place in contact the water with the quasi-prepolymer and the DSC equipment needs some time to stabilize, the total heat of the reaction ( $\Delta H_{total}$ ) was calculated by extrapolation of the residual heat to  $t = 0$ . The molar conversion was calculated assuming that the heat involved during the curing reaction is proportional to the extent of the reaction. Additionally, the evolution of the glass transition temperature ( $T_g$ ) with the extent of the reaction was determined. The  $T_g$  of the fully cured system was obtained by temperature-modulated DSC (TMDSC). A stoichiometric mixture of quasi-prepolymer and water was kept at 25°C for 7 days, followed by heating at 80°C for 12 h. The foamed cured sample was compacted by pressing in a Muver hydraulic press (2 bar) for 2 h at ambient temperature, placed in a hermetic aluminum pan and then TMDSC experiments were carried out under nitrogen atmosphere. The amplitude and the period of the oscillation during TMDSC experiments were 1.2°C and 70 s, respectively. The dynamic scan was performed at 5°C/min and the  $T_g$  was determined from the reversible heat flow curve.
2. *Isothermal DSC method:* The extent of the reaction of the quasi-prepolymer with water at constant temperature was measured by DSC as a function of time. The measurements were performed for 6 h at 25°, 35°, and 50°C, followed by a dynamic DSC scan at 5°C/min to determine the residual enthalpy.
3. *Dynamic DSC method:* The uncured samples were heated from  $-80$  to 250°C at different heating rates (5, 8, 10 and 20°C/min).

The experimental results obtained by using the isothermal and the dynamic DSC methods were analyzed using two model-free isoconversional methods to obtain the dependence of the activation energy with the degree of conversion.

## RESULTS AND DISCUSSION

### Postcuring dynamic DSC method

Dynamic DSC heat flow curves obtained at 25°C at different curing times are given in Figure 1. As the reaction proceeds, the  $T_g$  increases and the residual enthalpy becomes lower. Furthermore, the endothermic peak centered at 0°C resultant from the water fusion decreases as a consequence on the reaction with the quasi-prepolymer. In some DSC curves, an endothermic peak at about -58°C can be identified, likely due to carbon dioxide formation during the curing reaction (depending on the pressure, carbon dioxide sublimates below -56.6°C<sup>13</sup>).

The extent of the reaction was obtained from eq. (7):

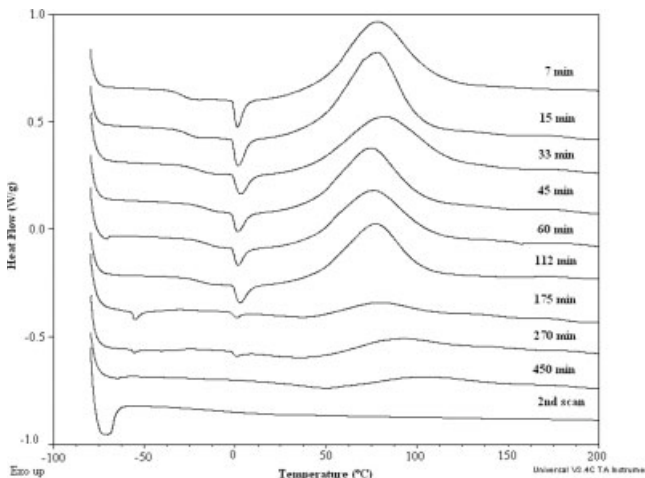
$$\alpha_t = 1 - \frac{\Delta H_r}{\Delta H_{\text{total}}} \quad (7)$$

where  $\Delta H_r$  is the residual enthalpy measured at a given curing time, and  $\Delta H_{\text{total}}$  is the total enthalpy.

Several studies on the correlation of the  $T_g$  data as a function of the conversion have been reported, although most of the data are for epoxy systems.<sup>14,15</sup> Numerous equations have been proposed to describe the  $T_g$  versus conversion data.<sup>16</sup> In some of these models, a statistical description of network buildup has to be available to calculate the concentration of junction points of different functionalities as a function of conversion. A different approach, based on the thermodynamic relationships has been proposed by Pascault and Williams:<sup>17</sup>

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda\alpha}{[1 - (1 - \lambda)\alpha]} \quad (8)$$

where  $T_{g0}$  and  $T_{g\infty}$  are the initial and at complete conversion  $T_g$ , respectively, and  $\lambda = \Delta cp_{\infty} / \Delta cp_0$  where



**Figure 1** DSC curves obtained at 25°C for the reaction of quasi-prepolymer and water. Postcured dynamic DSC method.

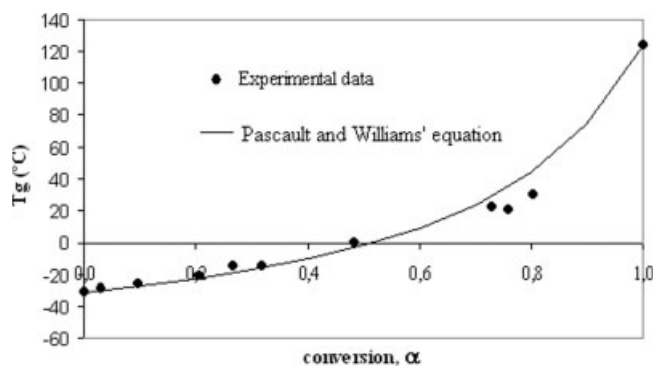
$\Delta cp_{\infty}$  and  $\Delta cp_0$  are the difference in the heat capacity before and after  $T_g$  for fully cured and uncured sample, respectively.  $T_{g0}$  and  $\Delta cp_0$  were determined by extrapolation of the  $T_g$  and  $\Delta cp$  values at  $\alpha = 0$ .  $T_{g\infty}$  and  $\Delta cp_{\infty}$  were determined by TMDSC, as described above.

$T_g$  was calculated as the temperature of the inflection point located at the  $T_g$  region in the DSC curves. For higher extent of cure, determination of the  $T_g$  was more difficult. At  $T_g$  values closer to the curing temperature, the system vitrifies and the reaction rate slows down, as the reaction becomes diffusion controlled. Owing to vitrification, a relaxation peak just near  $T_g$  inflexion was observed, which makes difficult the accurate determination of  $T_g$ . In these cases, to minimize the influence of the relaxation peak,  $T_g$  value was calculated as the fictive temperature of the transition by using the Universal DSC Analysis 2000 program from TA Instruments.<sup>15</sup> The fictive temperature ( $T_f$ ) is the temperature at which the structure is at equilibrium. At temperatures sufficiently far from the  $T_g$ , the system will remain in equilibrium at all curing times and  $T_f$  will be identical to the temperature of the system. However, during the  $T_g$  the system will not respond structurally to the changing temperature and  $T_f$  will differ from the temperature of the system.<sup>18</sup>

Equation (8) was derived on the basis of Couchman's analysis<sup>19</sup> for the compositional variation of the  $T_g$  of a solution, and assuming that a thermosetting polymer can be treated as a random mixture of a completely crosslinked network with the initial unreacted monomers. This equation has been applied with success to correlate experimental values of  $T_g$  versus conversion for many thermosetting polymers, using  $\lambda$  as an adjustable parameter.<sup>20-22</sup>

According to several investigators,<sup>15,16,22</sup> eq. (8) is mathematically equivalent to or based on DiBenedetto's equation.<sup>23</sup> DiBenedetto<sup>24</sup> has pointed out that the applicability of the principle he used to derive his equation is open to serious questions when applied to highly crosslinked systems, because of the great change in configurational entropy introduced by crosslinking. Consequently, the different forms of the DiBenedetto equation should only be appropriate to fit the  $T_g$  and conversion data of polymeric systems with relatively uncomplicated curing reactions. A report on the curing reaction of a modified bismaleimide resin system<sup>22</sup> has shown that eq. (8) is an inadequate model for high curing temperatures, when the crosslinking reactions responsible for three-dimensional network structures became dominant. Similar reports of  $T_g$  and conversion for polyurethane systems<sup>25</sup> are scarce and no analogous work was found for poly(urethaneurea) systems.

Figure 2 shows the dependence of the  $T_g$  as a function of the extent of the curing reaction of the



**Figure 2** Evolution of the glass transition temperature for the reaction of quasi-prepolymer and water as a function of the extent of reaction (25°C). Postcured dynamic DSC method.

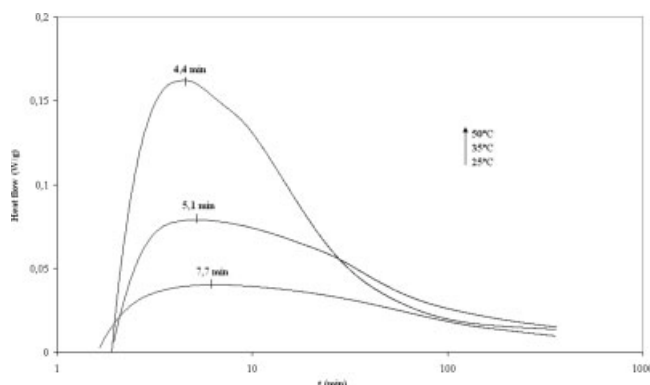
quasi-prepolymer and water. For lower conversion values this dependence is well described by eq. (8). Because the reaction was performed under isothermal conditions at relatively low temperature (25°C), we should expect that curing path consists on the chain extension as the result of urea linkage formation between prepolymer units, without relevant crosslinking reaction. With the progress of the chemical reaction, the difference between the transient  $T_g$  value and the cure temperature decrease. Molecular motion is significantly decreased together with the rate of reaction, vitrification occurs and consequently slows down the increase of the  $T_g$ . A previous study on isothermal cure of trifunctional polyurethane networks<sup>25</sup> attributes the decrease in the rate of the  $T_g$  increase in the later stage of the reaction to the formation of loops containing dangling ends during intramolecular reactions. This consumes free volume and does not restrict the movement of the chain as a crosslink would and therefore leads to a decrease in the rate of the  $T_g$  increase.

### Isothermal DSC method

DSC curves of the curing reaction of the quasi-prepolymer with water at different temperature are given in Figure 3. The area under the isothermal DSC curve at a given time  $t$  provides the heat of reaction,  $\Delta H_t$ . The extent of curing reaction  $\alpha_{ISO}$  at time  $t$  and temperature  $T$  was calculated from eq. (9):

$$\alpha_{ISO} = \frac{\Delta H_t}{\Delta H_{total}} \quad (9)$$

where  $\Delta H_{total}$  is the sum of the isothermal heat flow and the residual heat flow determined from the second DSC scan. The values of the ultimate extent of curing ( $\alpha_{T-ISO}$ ) were 0.84, 0.91, and 0.97 for 25°, 35°, and 50°C, respectively. As expected, the results obtained at 25°C are in agreement with those found



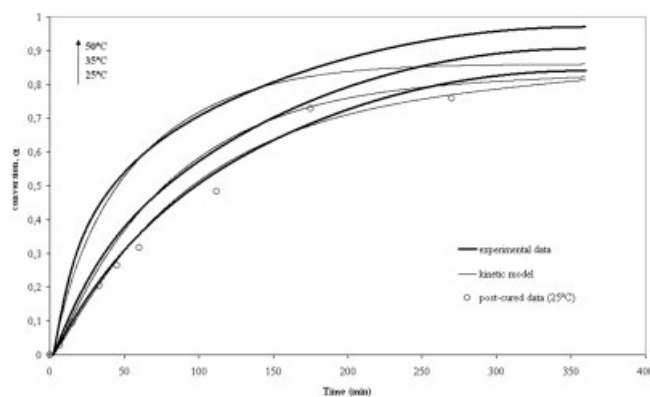
**Figure 3** DSC curves for the reaction of quasi-prepolymer and water, at 25°, 35°, and 50°C. Isothermal method.

by using the postcured dynamic DSC method (Fig. 4).

The curing process of thermosetting materials may be modeled using two types of kinetic models, the  $n$ th-order and the autocatalyzed models.<sup>26</sup> The reaction of the isocyanate groups with nucleophilic reactants can be catalyzed by both Lewis acids and bases.<sup>27</sup> Consequently, even in a catalyst-free system, the formation of urea groups during the curing process may be catalyzed by the existent urethane groups and the resulting urea. Without the knowledge of the exact mechanism of the cure reaction, both models can be summarized into one equation, i.e., eq. (10):

$$\frac{d\alpha}{dt} = k\alpha^m(1-\alpha)^n \quad (10)$$

where  $d\alpha/dt$  is the reaction rate,  $k$  is the rate constant and  $m+n$  is the global order of the reaction. Parameter  $m$  accounts for the autocatalytic effect during the reaction.



**Figure 4** Extent of the reaction of quasi-prepolymer and water as function of the curing time for different curing temperatures. Comparison with the kinetic model fit of eq. (10).



Considering that the reaction could be of first or second order, the kinetic parameters were calculated by fitting the experimental data to the logarithmic form of eq. (10), i.e., eq. (11):

$$\ln\left(\frac{d\alpha/dt}{\alpha^{m+n}}\right) = \ln k + n \ln\left(\frac{1-\alpha}{\alpha}\right) \quad (11)$$

The best correlation was obtained for the second-order reaction modeling. Figure 4 shows the fitted data and Table I includes the values of  $k$ ,  $m$ , and  $n$  as well as the activation energy.  $E_a$  was calculated assuming that the kinetic constant  $k$  follows the Arrhenius law, from the slope of the straight line of  $\ln(k)$  versus  $-1/T$  plot. According to Figure 4, only the initial part of the curing reaction follows the kinetic model described by eq. (10). For higher conversion values, this model fails.

The dependence of  $E_a$  on the extent of cure was calculated by using isoconversional methods. The application of the isoconversional methods for incomplete cures ( $\alpha_{T-ISO} < 1$ ) may introduce a systematic error in the determination of  $E_a$ , that can be eliminated by replacing the absolute extents of cure by the relative values  $\alpha'_{ISO}$ , i.e., eq. (12), which varies between 0 and 1.<sup>28</sup>

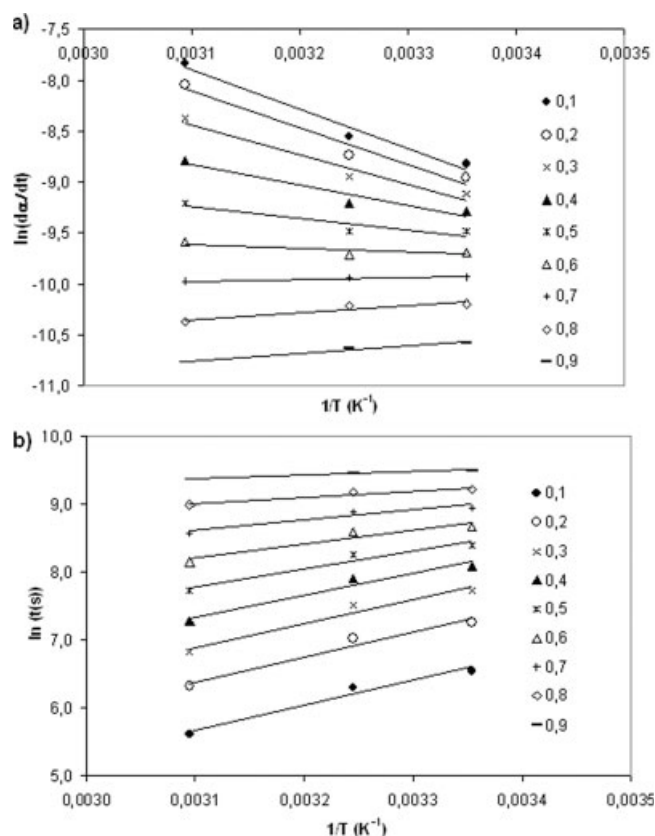
$$\alpha'_{ISO} = \frac{\alpha_{ISO}}{\alpha_{T-ISO}} \quad (12)$$

The dependence of  $E_a$  on  $\alpha'_{ISO}$  should then be reassigned to the absolute extents of cure ( $\alpha_{ISO}$ ), by multiplying  $\alpha'_{ISO}$  by  $\overline{\alpha_{T-ISO}}$  that is an averaged  $\alpha_{T-ISO}$  value for the series of isothermal experiments used to calculate  $E_a$ .

Figure 5 shows the determination of  $E_a$  for isothermal DSC cure by applying the Friedman and integral methods, corresponding to eqs. (2) and (4), respectively. The dependence of  $E_a$  with the extent of cure is shown in Figure 6. Both the Friedman and integral methods provide similar trends. The initial activation energy is  $\sim 30$  kJ/mol and decreases as the reaction progress. The activation energy calculated by applying the Arrhenius law is 24.7 kJ/mol (Table I). Because this value is calculated by assuming that  $E_a$  is constant during the curing process, a simple comparison with the results obtained with the isoconversional methods

**TABLE I**  
Kinetic Parameters of the Reaction of Quasi-Prepolymer with Water Determined from DSC Isothermal Experiments

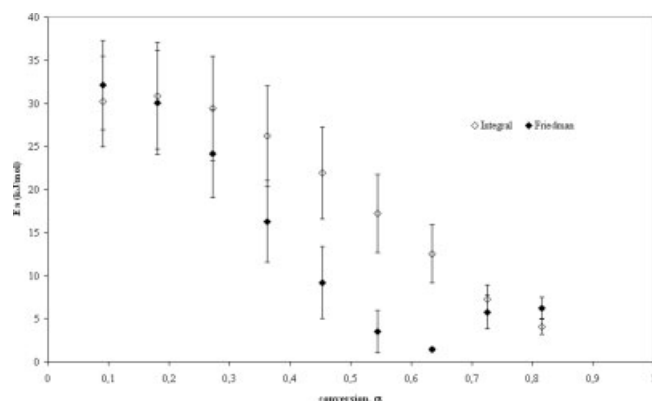
T (°C)	k (s <sup>-1</sup> )	m	n	E <sub>a</sub> (kJ/mol)
25	2.1 × 10 <sup>-4</sup>	0.17	1.83	24.7
35	2.7 × 10 <sup>-4</sup>	0.16	1.84	
50	4.5 × 10 <sup>-4</sup>	0.07	1.93	



**Figure 5** Determination of  $E_a$  for isothermal DSC cure of quasi-prepolymer and water, by applying the method of Friedman (a) and the integral method (b).

cannot be made. However, it seems that this value represents the average value of  $E_a$  in the range of conversion until 60° that is the range of conversion that supported the kinetic model.

The decrease of the activation energy can be ascribed to the increase in viscosity of the product as the degree of conversion increases. Similar behaviour was observed for isothermal curing of epoxy-amine<sup>29</sup>



**Figure 6** Dependence of  $E_a$  with the extent of isothermal DSC cure of quasi-prepolymer and water, obtained by the differential and the integral isoconversional methods.

and polyurethane systems.<sup>7</sup> As the reaction progresses, the molecular motion is restricted, the kinetics become diffusion controlled and the activation energy gradually decreases. The rate of conversion of the reactants into products becomes dependent on the chemical reaction rate as well as on the transport rate of the reactants and products in the reaction medium. The decrease in the effective activation energy ( $E_{ef}$ ) can be understood in terms of a kinetic model of a process encompassing both chemical and diffusion kinetics,<sup>30</sup> as expressed by eq. (13),

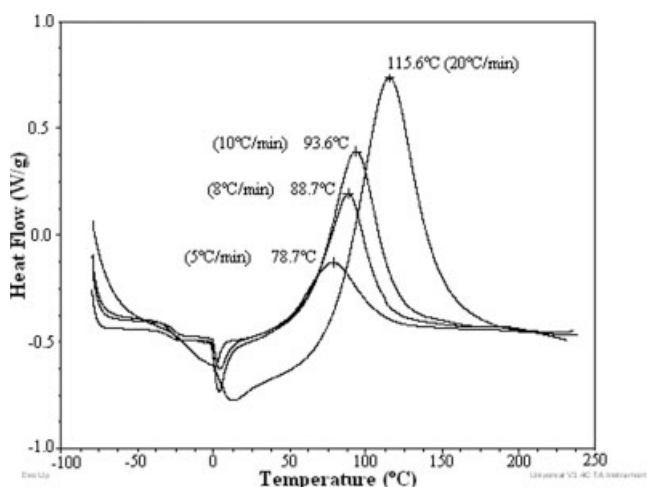
$$\frac{1}{k_{ef}} = \frac{1}{k_r} + \frac{1}{k_d}, \quad (13)$$

where  $k_{ef}$ ,  $k_r$ , and  $k_d$  are the effective, reaction, and diffusion rate constants respectively. If we accept the Arrhenius form for the temperature dependence of  $k_d$ , the effective activation energy will be a function of the activation energies of both chemical reaction ( $E_r$ ) and diffusion of reactants in the medium ( $E_d$ ):

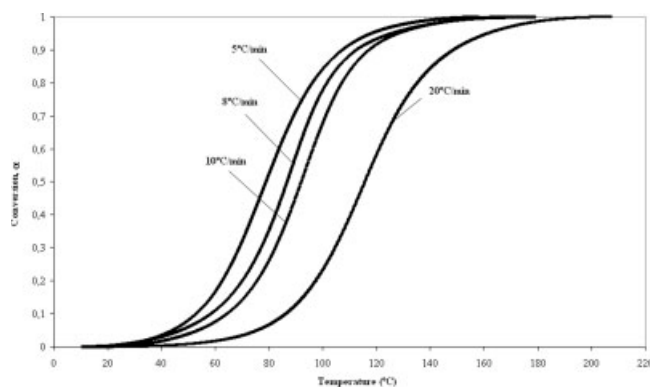
$$E_{ef} = -R \left( \frac{d \ln k_{ef}}{dT^{-1}} \right) = \frac{E_d k_r + E_r k_d}{k_r + k_d} \quad (14)$$

as described by Vyazovkin.<sup>31</sup> When one of the steps is much faster than another, the overall rate will be determined by the slowest step, and the experimental value of  $E_a$  will become the activation energy of this step. As the reaction progress,  $k_d$  begins to decrease, as a consequence of the restriction of the molecular motion, and the value of the effective activation energy decreases from  $E_r$  to  $E_d$ .

Based on eq. (14) and on the influence of the chemical reaction on the change in diffusivity, Vyazovkin<sup>32</sup> was able to describe the dependence of



**Figure 7** DSC curves for the reaction of quasi-prepolymer and water at different heating rate (5°, 8°, 10°, and 20°C/min). Dynamic DSC method.



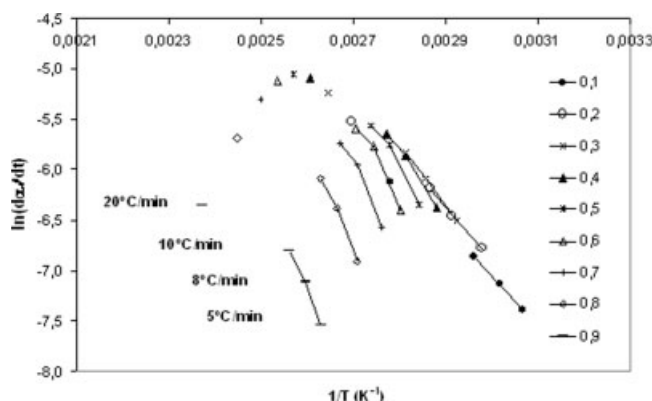
**Figure 8** Extent of the reaction of quasi-prepolymer and water as a function of the temperature at different heating rates. Dynamic DSC method.

the activation energy upon conversion during the curing of an epoxy-amine system.

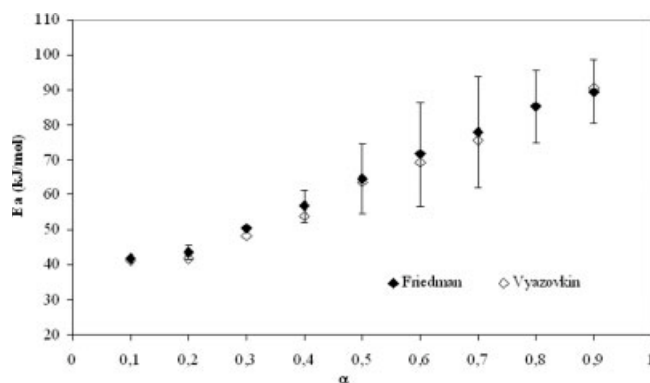
### Dynamic DSC method

The DSC curves for dynamic cure of quasi-prepolymer and water at different heating rates are shown in Figure 7, while Figure 8 gives the evolution of the extent of the reaction, calculated by using eq. (9), as a function of the temperature. Figure 9 shows the plots resultant of the application of the Friedman method to calculate  $E_a$  for a non-isothermal cure, i.e., eq. (2). For a heating rate of 20°C/min and high extent of cure, i.e. higher temperature, the system does not follow the linear relationship defined by eq. (2). This could be due to the thermal inertia of the high volume pans used in the DSC experiments. Then to obtain the variation of  $E_a$  as a function of  $\alpha$  the values obtained by using a heating rate of 20°C/min were not considered.

Figure 10 shows the variation of  $E_a$  with the extent of the reaction obtaining by applying the methods of



**Figure 9** Determination of  $E_a$  of the reaction of quasi-prepolymer and water, by using the isoconversional method of Friedman. Dynamic DSC method.



**Figure 10** Dependence of  $E_a$  on the extent of the reaction of quasi-prepolymer and water, by using different isoconversional methods. Dynamic DSC method.

Friedman and Vyazovkin. Both methods provide similar results. Activation energy varies between 40 and 90 kJ/mol and tends to increase with the extent of the reaction, showing that the curing is a complex process. The obtained results can be correlated with the earlier report by Cui et al.,<sup>4</sup> who have studied the kinetics of the reaction of reactive urethane prepolymers with steam. The overall activation energy for the dynamic cure of ether urethane prepolymers was 85 kJ/mol and the shape of the DSC trace revealed the complexity of the curing reaction.

The dependence of  $E_a$  on the degree of conversion under non-isothermal conditions suggests that parallel reactions take place simultaneously. In fact, it has been established<sup>33</sup> that isocyanate groups can participate in different secondary reactions, in such a way that urethane and urea groups can further react with isocyanate to form allophanate and biuret linkages. In addition, carbodiimides can be produced by heating isocyanate at elevated temperature. The observed trend was probably the result of the reaction of urethane and urea to form allophanate and biuret, and the decomposition of allophanate and biuret to urethane and urea at higher temperatures. Dissociation of allophanate and biuret into their precursors generally takes place at  $> 110^\circ\text{C}$ .<sup>34</sup> A similar trend was observed in the non-isothermal curing process of polymeric MDI with wood.<sup>35</sup>

## CONCLUSIONS

Isothermal and non-isothermal DSC experiments were used to study the cure kinetics of an isocyanate-ended quasi-prepolymer with water in stoichiometric proportions. It was found that the equation proposed by Pascault and Williams<sup>17</sup> might be used to correlate the  $T_g$  of the partially cured system with the extent of cure when the reaction is performed under isothermal conditions at  $25^\circ\text{C}$ .

A second-order kinetic model containing an autocatalytic contribution was successfully used to evaluate the cure process performed under isothermal conditions, at lower conversion values. For a higher degree of conversion the model fails probably because the reaction becomes diffusion controlled.

Differential and integral isoconversional methods provided similar results. However, the dependence of the effective activation energy with the extent of cure was different under isothermal and non-isothermal curing conditions. The increase in  $E_a$  as the reaction proceeds under non-isothermal conditions might be a consequence of the contribution of secondary reactions that may occur at higher temperatures, while the decrease in  $E_a$  with conversion when the reaction is performed under isothermal conditions suggests that after a certain conversion value the reaction becomes diffusion controlled.

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