

# Moisture Curing Kinetics of Isocyanate Ended Urethane Quasi-Prepolymers Monitored by IR Spectroscopy and DSC

Ana Luísa Daniel-da-Silva,<sup>1</sup> João Carlos Moura Bordado,<sup>2</sup> José Miguel Martín-Martínez<sup>1</sup>

<sup>1</sup>Adhesion and Adhesives Laboratory, University of Alicante, 03080 Alicante, Spain

<sup>2</sup>Department of Chemical Engineering, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisbon, Portugal

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**ABSTRACT:** The study of the kinetics of the curing of isocyanate quasi-prepolymers with water was performed by infrared spectroscopy and differential scanning calorimetry. The influence of the free isocyanate content, polyol functionality, and of the addition of an amine catalyst (2,2'-dimorpho-lynediethylether) in the reaction kinetics and morphology of the final poly(urethane urea) was analyzed. A second-order autocatalyzed model was successfully applied to reproduce the curing process under isothermal curing conditions, until gelation occurred. A kinetic model-free approach was used

to find the dependence of the effective activation energy ( $E_a$ ) with the extent of cure, when the reaction was performed under nonisothermal conditions. The dependence of  $E_a$  with the reaction progress was different depending on the initial composition of the quasi-prepolymer, which reveals the complexity of the curing process. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 700–709, 2008

**Key words:** urethane prepolymers; DSC; FTIR; kinetics; moisture curing

## INTRODUCTION

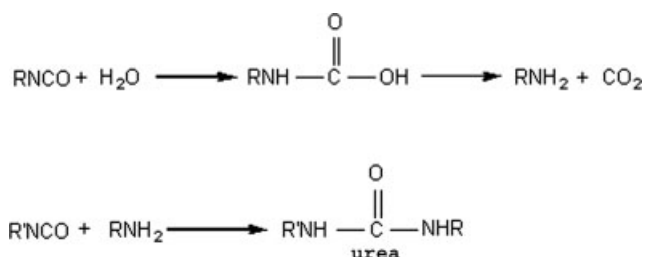
Isocyanate (NCO) terminated urethane quasi-prepolymers are used in the production of one-component polyurethane (PU) foams for building industry and do-it-yourself adhesives.<sup>1,2</sup> Their versatility arises from the possibility of producing tailored PU and poly(urethane urea) (PUU) materials through the addition of different chain extenders or by varying the quasi-prepolymer composition (polyol structure and functionality, amount of free NCO groups). In a previous study,<sup>3</sup> we have shown that the unreacted NCO content in the urethane quasi-prepolymer (usually between 15 and 30 wt %) was a critical factor governing not only the initial adhesion but also the adhesion of the moisture-cured urethane quasi-prepolymers.

When exposed to air, the free NCO groups in the quasi-prepolymer react with moisture from air and from the substrate, leading to the formation of urea groups. The reaction involves the formation of a carbamic acid intermediate that rapidly dissociates to yield carbon dioxide and an amine which further react with additional NCO groups to form urea linkage (Scheme 1).

By using nonlinear reactants, during the moisture curing process, the transformation of a relatively low molecular weight liquid into a high molecular weight PUU solid that exhibit typical properties of a thermoset is produced. In general, PUUs showed a two-phase morphology that results from the partial mutual insolubility of soft and hard domains. The soft domains derived from the polyol (soft segments, SS) and imparted softness and extensibility to the PUU, while the hard domains derived from the reaction of the NCO and the chain extender (water in this study) (hard segments, HS), and provided the cohesive strength to the PUU matrix. The hard domains act as physical crosslinks within the SS matrix.<sup>4</sup> Because of thermodynamic incompatibility between these two domains, microphase separation between hard and SS occurs and results a phase-separated morphology composed by SS rich matrix with HS rich hard domains. The performance of PUU is strongly dependent on the balance between microphase separation and microphase mixing.<sup>5</sup> Physical-chemical process that takes place during the curing reaction of a nonlinear quasi-prepolymer includes the chemical crosslinking reaction, the reaction-induced microphase separation, the hydrogen bonding formation and the vitrification. The extent of each of these processes will determine the polymer morphology, which is a key factor in determining the properties of the cured PUU thermoset, namely mechanical, thermal, and adhesion properties. Consequently, the understanding of the mechanism and kinetics of the

Correspondence to: A. L. Daniel-da-Silva (ana.silva@dq.ua.pt).

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

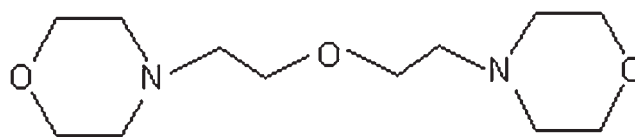
moisture curing of urethane quasi-prepolymers is very important in the understanding of structure-morphology-property relationship. Despite the industrial relevance of NCO ended urethane quasi-prepolymers, to our knowledge only a few studies have been devoted to the kinetics of the curing reaction of low free NCO content ended prepolymers with water.<sup>6,7</sup> More recently, we have shown the potential of using a model-free kinetic approach to better understand the complex curing process of NCO quasi-prepolymers.<sup>8</sup>

In this work we have focused our attention in the effect of the urethane quasi-prepolymer composition on the kinetics of the curing reaction with water. The influence of the unreacted NCO content, polyol functionality, and the addition of a morpholine-based catalyst were studied by monitoring the NCO consumption by Fourier Transform Infrared (FTIR) spectroscopy and by following the evolution of thermal properties by differential scanning calorimetry (DSC). Moreover, as the curing reaction proceeds, the interaction between the polyether soft segment and the formed urea HS will certainly change, and it should depend on the quasi-prepolymer composition. Since hydrogen bonding formation can provide information concerning the morphological structure of PUUs,<sup>9-11</sup> FTIR spectroscopy was also employed in this study to investigate the development of the PUU structure and changes in morphology during curing process.

## EXPERIMENTAL

### Materials

The raw materials used to manufacture the NCO urethane quasi-prepolymers were polymeric diphenylmethane diisocyanate (pMDI, Dow Chemical, Barcelona, Spain) and difunctional or trifunctional polypropyleneglycol (Voranol P1010 and Voranol CP 1055, respectively, Dow Chemical). The pMDI consists in a mixture of reactive monomers and oligomers of MDI<sup>3</sup> and the polyether polyols are mainly composed by secondary hydroxyl terminal groups. The tertiary amine 2,2'-dimorpholinediethylether (DMDEE, Struktol, Hamburg, Germany) (Scheme 2) was used as catalyst in one of the formulations. The DMDEE is a com-



**Scheme 2** Molecular structure of the catalyst 2,2'-dimorpholinediethylether (DMDEE).

monly used blowing catalyst that facilitates urea formation preferentially to urethane formation, and is frequently used in quasi-prepolymer-based systems as it confers excellent storage stability to urethane systems containing unreacted NCO groups.<sup>12</sup>

Table I shows some characteristic properties of the pMDI and the polyols used in this study. The polyols were dried under reduced pressure for at least 3 h at 60°C prior using, while the pMDI and the catalyst DMDEE were used as received.

### Synthesis of the NCO ended urethane quasi-prepolymers

The NCO ended urethane quasi-prepolymers were prepared by reacting the dried polyol with pMDI in a three-necked 1000 mL glass flask, under dry nitrogen atmosphere. Inert atmosphere was used to avoid the ingress of moisture and the consequent formation of urea linkages during synthesis. In absence of catalyst, the system was kept at 70°C and mechanically stirred with a glass stirrer at 80 rpm for 3 h. In the synthesis of the quasi-prepolymer containing DMDEE catalyst, the reaction was performed at ambient temperature and mechanically stirred with a glass stirrer at 80 rpm for 1 h. The NCO content in the urethane quasi-prepolymer was determined by back titration of excess *N,N*-dibutylamine with standard HCl.<sup>13</sup>

About 300 g each of four quasi-prepolymers differing in free NCO content, polyol functionality and catalyst content were synthesized. The DMDEE catalyst concentration used (5.4 g/eq polyol) is the typical for the manufacturing of one-component PU foams. The

**TABLE I**  
Some Characteristic Properties of the pMDI and the Polyols

Property	pMDI	Diol	Triol
Average functionality <sup>a</sup>	2.7	2	3
OH Content (mg KOH/g) <sup>a</sup>	–	110	156
NCO content (wt %) <sup>b</sup>	31.3	–	–
Molecular weight (g/mol) <sup>a</sup>	–	1000	1000
Viscosity 25°C (mPa s) <sup>c</sup>	50	145	250
Max. K + Na content (ppm) <sup>a</sup>	–	5.0	10.0

<sup>a</sup> Information provided by the supplier.

<sup>b</sup> Obtained by back titration of excess *N,N*-dibutylamine with standard HCl.

<sup>c</sup> Brookfield viscosity (10 rpm, spindle no. 1).

TABLE II  
Composition of the Urethane Quasi-Prepolymers

Prepolymer	NCO (wt %)	Polyol functionality	DMDEE (g/eq polyol)	pMDI mol (eq)	Polyol mol (eq)
N14D	14	2	0	0.46 (1.25)	0.13 (0.26)
N14T	14	3	0	0.54 (1.45)	0.13 (0.39)
N16T	16	3	0	0.60 (1.62)	0.12 (0.36)
N16T5,4	16	3	5.4	0.60 (1.62)	0.12 (0.36)

composition of the four quasi-prepolymers is given in Table II.

### Kinetic measurements

#### FTIR spectroscopy

FTIR spectroscopy was employed to monitor the reaction of the urethane quasi-prepolymers with moisture. Around 0.4 mg of each quasi-prepolymer was spread on a KBr pellet and then placed into the FTIR spectrometer chamber where the moisture curing was carried out at  $28 \pm 2^\circ\text{C}$  and 55 wt % relative humidity. FTIR spectra were recorded in a Bruker Tensor 27 spectrometer collecting 100 scans at a resolution of  $4\text{ cm}^{-1}$ . The NCO-water reaction was monitored by measuring the variation in absorbance decay of the free NCO stretching band at  $2270\text{ cm}^{-1}$ . To compensate the changes in thickness of the different samples, the C-H stretching band at  $2946\text{ cm}^{-1}$  was chosen as an internal standard to normalize the IR spectra.<sup>14</sup> The conversion of the NCO group  $\alpha_{\text{IR}}$  was calculated from eq. (1),

$$\alpha_{\text{IR}} = 1 - \frac{I_t}{I_0} \quad (1)$$

where  $I_0$  and  $I_t$  are the normalized peak heights of the NCO absorption bands at the beginning of the reaction and at time  $t$ , respectively.

#### DSC

DSC was used to study the kinetics of the curing reaction of the urethane quasi-prepolymers with water by direct addition of water to the quasi-prepolymer in stoichiometric proportions. Data reported in this study were obtained with a Q-100 differential scanning calorimeter (TA Instruments), calibrated with indium, using a continuous nitrogen flow of 50 mL/min. Urethane quasi-prepolymers were mixed with distilled water in a stoichiometric proportion and the mixtures ( $\sim 50\text{ mg}$ ) were sealed in steel high volume DSC pans with a capacity of 100  $\mu\text{L}$ . The calorimetric data of the sealed samples were collected performing the reaction under isothermal and nonisothermal conditions. In the isothermal conditions, the uncured samples were maintained at  $25^\circ\text{C}$  for different curing

times, and then, the samples were heated from  $-80$  to  $200^\circ\text{C}$  at a heating rate of  $5^\circ\text{C}/\text{min}$  to determine the residual heat ( $\Delta H_r$ ). The molar conversion at a certain time  $t$  ( $\alpha_t$ ) was calculated assuming that the heat involved during the curing reaction was proportional to the extent of the reaction, by using eq. (2). Because the reaction starts immediately and the DSC equipment takes some time to stabilize, the total heat of the reaction ( $\Delta H_{\text{total}}$ ) was calculated by extrapolation of the residual heat to  $t = 0$ .

$$\alpha_t = 1 - \frac{\Delta H_r}{\Delta H_{\text{total}}} \quad (2)$$

In the nonisothermal conditions, the uncured samples were heated from  $80$  to  $250^\circ\text{C}$  at different heating rates (5, 8, and  $10^\circ\text{C}/\text{min}$ ). The extent of the reaction was calculated by using eq. (3)

$$\alpha_T = \frac{\Delta H_T}{\Delta H_{\text{total}}} \quad (3)$$

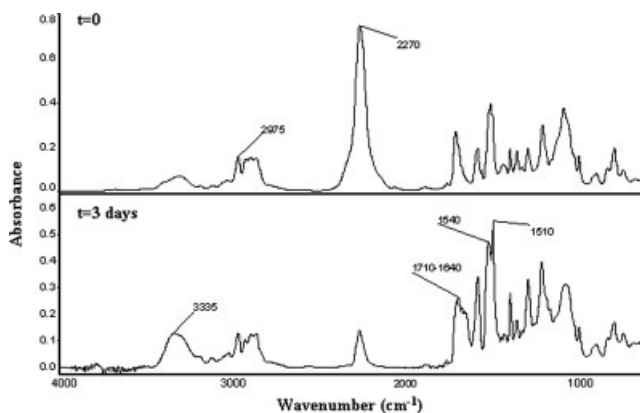
where  $\Delta H_T$  is the heat released up to a temperature  $T$ . The calorimetric data collected performing the reaction under nonisothermal conditions were analyzed using a model-free isoconversional method (Friedman method) to obtain the dependence of the effective activation energy with the degree of conversion.<sup>8</sup>

## RESULTS AND DISCUSSION

### FTIR spectroscopy

During the curing reaction of the urethane quasi-prepolymer, the free NCO groups react with water to form urea. Figure 1 shows as a typical example, the transmission IR spectra of the uncured and 3 days cured quasi-prepolymer N16T5,4. The intensity of the stretching band of the unreacted NCO groups ( $2270\text{ cm}^{-1}$ ) decreases as the reaction progress and new bands due to the formation of urea groups appear at  $3335\text{ cm}^{-1}$  (hydrogen bonded N-H stretching),  $1710$ – $1640\text{ cm}^{-1}$  (C=O stretching in urea),  $1510\text{ cm}^{-1}$  (N-H bending in urea), and  $1530\text{ cm}^{-1}$  (C-N stretching and N-H bending).<sup>15</sup>

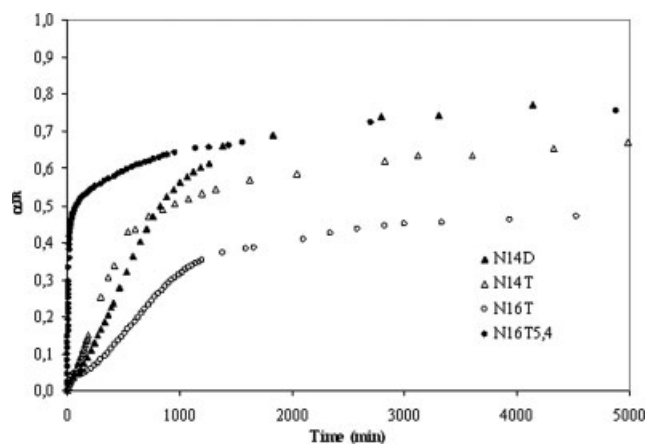
The extent of the moisture cure reaction of the quasi-prepolymers was calculated as the NCO con-



**Figure 1** FTIR transmission spectra for the quasi-prepolymer N16T5,4 (uncured and after curing for 3 days).

version [eq. (1)] and the results obtained are shown in Figure 2. Under the selected curing conditions, none of the quasi-prepolymers achieved complete conversion, even when the DMDEE catalyst is included in the formulation. The increase in the functionality of the polyol does not have a significant effect on the reaction rate in the initial stage of the cure reaction but the system becomes diffusion controlled at lower degree of conversion and the final conversion degree is also lower. The reaction rate decreases as the unreacted NCO groups content of the quasi-prepolymers increases and the final degree of conversion is also lower.

The curing of urethane thermosets starts by formation and linear growth of a chain and in the later stage involves the formation of a three-dimensional network through reactions among polyfunctional groups. In our study, because the reaction was performed under isothermal conditions at relatively low temperature (28°C), we should expect that curing path consists on the chain extension as the result of urea linkage formation between quasi-prepolymer units, without relevant crosslinking contribution from secondary reactions such as allophanate or biuret formation. The formation of biuret is much faster than that of allophanate and for temperatures below 60°C, formation of biuret and allophanate is very slow.<sup>16</sup> In the first stage of a typical curing reaction of a thermoset, the reaction is chemically controlled but after the gel point is reached the mobility of the reactive groups is restricted and the curing is controlled by diffusion rather than by chemical factors.<sup>17</sup> The gel point corresponds to the incipient formation of a three-dimensional network with an infinite weight-average molecular weight and depends of the stoichiometric, functionality, and reactivity of reactants and temperature. The gelation phenomenon is irreversible and the material becomes insoluble and acquires elastic properties not present in the pregel state.<sup>18</sup> A critical conversion value ( $\alpha_c$ ) for the onset of the diffusion controlled reactions, close to the gel point, can be



**Figure 2** Extent of cure versus curing time of urethane quasi-prepolymers determined with FTIR spectroscopy.

defined by fitting the first and the second part of the conversion curve,<sup>19</sup> the first part representing the chemically controlled reaction and the second part the diffusion controlled reaction. Also, the theoretical crosslink density ( $\nu$ ) of the PUU obtained from the completely moisture-cured urethane quasi-prepolymer was calculated by using the method developed by Miller and Macosko.<sup>20</sup> This method involves determining the probability that a given branch leads to a finite chain and is described elsewhere.<sup>21</sup>

The values obtained by applying the Miller and Macosko model are given in Table III, together with the critical conversion values for the onset of the diffusion controlled reaction ( $\alpha_c$ ) calculated from IR spectra. The  $\alpha_c$  value decreases and the theoretical crosslink density increases, with increasing the polyol functionality and the free NCO content of the urethane quasi-prepolymer. Both the increase of the polyol functionality and of the free NCO content (achieved by increasing the pMDI/polyol ratio) lead to an increment of the average reactants functionality. Polymeric MDI used in this study consists of a mixture of reactive monomers and oligomers of MDI with an average functionality of 2.7 and therefore, by increasing the excess of pMDI the introduction of chemical crosslinks into the system is favored. As expected, the theoretical crosslink density increases,

**TABLE III**  
Critical Conversion Degree Value ( $\alpha_c$ ) for the Onset of the Diffusion Controlled Reaction and Theoretical Crosslink Density ( $\nu$ ) of Moisture Cured Urethane Quasi-Prepolymers Estimated by Using the Model of Miller and Macosko

Prepolymer	$\alpha_c$	$\nu$ (mol m <sup>-3</sup> )
N14D	0.67	2972
N14T	0.44	3838
N16T	0.32	4056
N16T5,4	0.34	4056

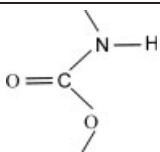
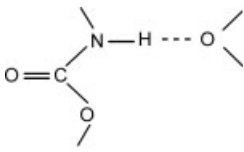
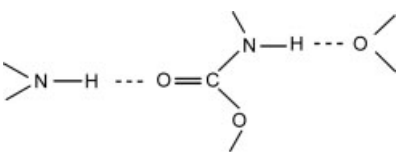
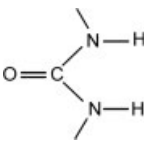
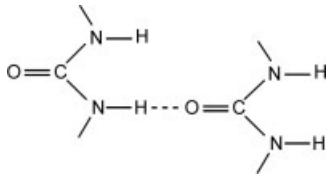
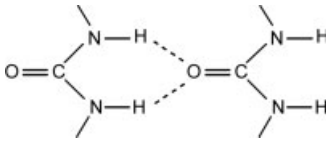


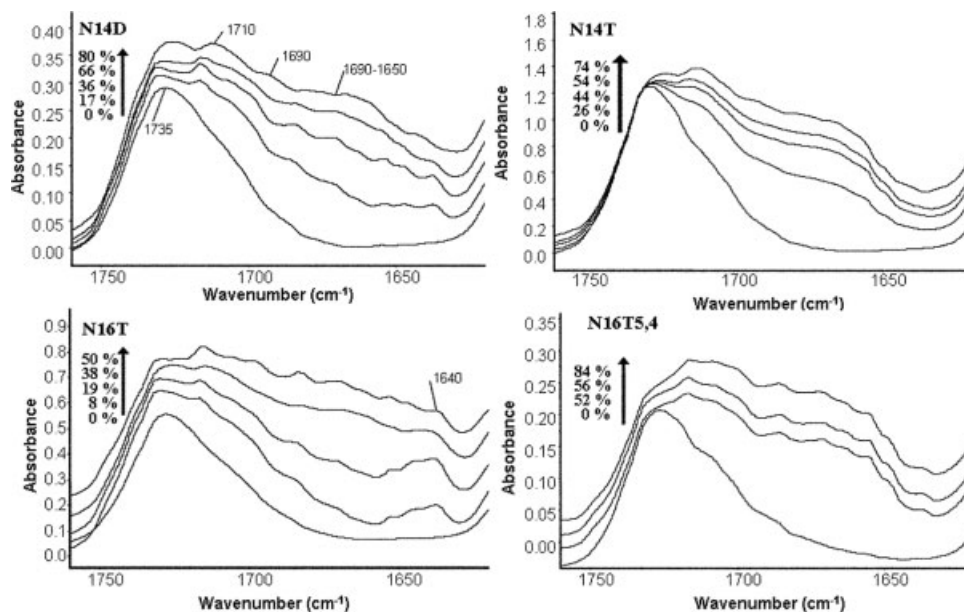
the reaction becomes diffusion controlled at low conversion values because of lack of mobility and the final conversion degree achieved under these experimental conditions is also low. The results are in agreement with a previous study<sup>22</sup> that indicates that the final degree of conversion achieved in the isothermal cure of thermoset materials decreases with increasing crosslink density.

By incorporating the catalyst DMDEE in the urethane quasi-prepolymer formulation, the reaction progresses more quickly. The addition of the catalyst does not affect significantly the gelation point neither the theoretical crosslink density. The amine DMDEE is one of the catalysts most widely used in moisture-cured quasi-prepolymers with application in the production of one-component PU foams and in reactive hot melt adhe-

sives, between other systems.<sup>23,24</sup> Despite the industrial importance of the DMDEE, to our knowledge very few studies regarding the catalytic activity of this compound have been performed.<sup>19,25</sup> The usual description of DMDEE is as a blowing catalyst that provides excellent shelf stability in systems containing free NCO groups, avoiding side reactions involving this group that could lead to the premature polymerization of the prepolymer. This is probably due to the steric hindrance of nitrogen atoms, exerted by the presence of morpholino groups. Also, it shows a tendency to catalyze the urea formation preferentially instead urethane formation that arises from its capacity to form chelates with water molecules. In a second step, the complex formed between water and the catalyst will attack the NCO, following the path presented in Scheme 1.

TABLE IV  
Infrared Stretching Band Assignments of the Carbonyl Group in Polyurethane Urea Systems<sup>5,9-11,27</sup>

Functional group	Wavenumber (cm <sup>-1</sup> )		Band assignment
ν(C=O) urethane	1740–1730		Free urethane
	1730–1725		H-bonded urethane HS/SS interaction
	1715–1700		H-bonded urethane HS/HS interaction
ν(C=O) urea	1700–1690		Free urea
	1690–1650		Monodentate urea (less ordered H-bonded urea)
	1650–1640		Bidentate urea (ordered H-bonded urea)



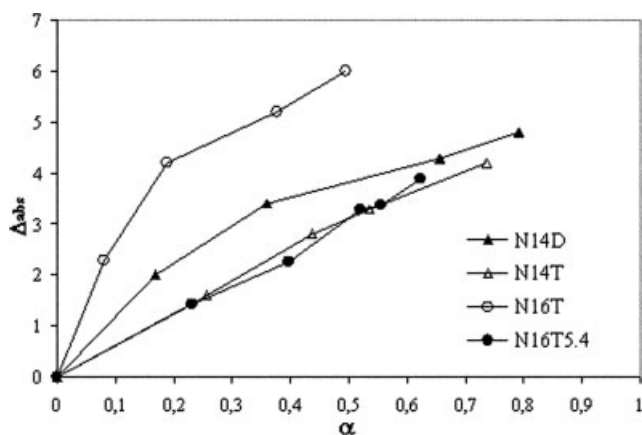
**Figure 3** Evolution of the carbonyl stretching IR spectral zone ( $1620\text{--}1760\text{ cm}^{-1}$ ) with moisture curing time for 0, 5, 10, and 23 h, and 8 days. Values of the extent of cure reaction are given for each IR spectrum.

To better understand the reaction chemistry and subsequent structural changes, the evolution of the IR spectral region of the carbonyl group during the moisture cure reaction of the urethane quasi-prepolymers was analyzed in more detail. Because of the formation of hydrogen bonds, the absorption band due to C=O stretching shifts to lower frequencies. The position of each band depends on the strength of the hydrogen bonds, which depends on the local geometry and the distance between the groups. An accurate assignment of each interaction may sometimes be difficult, because of some band overlapping or even because of inconsistent information in the literature. Besides, the analysis of hydrogen bonding in PUU is very complex because multiple hydrogen bonds may be formed between two kinds of proton donors, urethane N-H and urea N-H groups, and three kinds of proton acceptors, urethane C=O, urea C=O, and C-O-C groups. A summary of the frequency assignments to the specific functional groups, interactions, and types of hydrogen bonding in the carbonyl stretching zone found in the literature is summarized in Table IV.

Figure 3 shows the evolution of the absorbance in the carbonyl region in the IR spectra during moisture curing of the urethane quasi-prepolymers. Both free urethane ( $\sim 1730\text{--}1740\text{ cm}^{-1}$ ) and ether polyol hydrogen bonded urethane ( $\sim 1725\text{--}1730\text{ cm}^{-1}$ ) are present at the beginning of the reaction. As the curing reaction progresses free urea ( $\sim 1690\text{--}1700\text{ cm}^{-1}$ ) and disorder hydrogen bonded urea ( $\sim 1650\text{--}1690\text{ cm}^{-1}$ ) are formed to a considerable degree and an IR band centered at  $\sim 1710\text{ cm}^{-1}$  appears as consequence of the formation of hydrogen bonds between carbonyl ure-

thane and urea groups. These results suggest that interaction between HS takes place upon network growths. IR spectra show low development of bidentate urea that appears as a shoulder of the broad band of the disordered urea. Bidentate urea corresponds to the bifurcated hydrogen bonded urea groups as the oxygen in the carbonyl group is bonded to two hydrogen atoms of the same urea group. Its appearing indicates the organization of urea groups in more ordered domains ("hard" domains) and it has been identified in PUU systems presenting phase separation.<sup>11,27</sup> The low development of bidentate suggests that the PUUs prepared in this study present low amount of phase separation when compared with the degree of phase mixing. A similar morphology was observed in previous studies dealing with moisture-cured PU urea prepared with toluene diisocyanate and isophorone diisocyanate.<sup>26,28</sup> Nevertheless, the development of bidentate urea is more marked in N16T and the addition of the DMDEE catalyst inhibits its formation.

Figure 4 plots the increase in the intensity of the C=O stretching band ( $\Delta_{\text{abs}}$ ) of bidentate urea at  $1640\text{ cm}^{-1}$  as a function of the degree of conversion for the urethane quasi-prepolymers. The C—H stretching band at  $2946\text{ cm}^{-1}$  was chosen as an internal standard to normalize the spectra.  $\Delta_{\text{abs}}$  was calculated using the expression  $(I_t - I_{t0})/I_{t0}$ , where  $I_t$  and  $I_{t0}$  are the normalized peak absorbance at time  $t$  and at the beginning of the reaction, respectively. The tendency to form bidentate urea increases with increasing the free NCO content in the quasi-prepolymer. Therefore, the increase in the urea group content resulting from the higher unreacted NCO content in the quasi-prepoly-



**Figure 4** Variation of the normalized intensity of the C=O stretching IR band of bidentate urea ( $1640\text{ cm}^{-1}$ ) versus conversion degree.

mer will drive phase separation of the urea HS and their subsequent association via intermolecular hydrogen bonds to form HS domains. A higher degree of phase separation as a consequence of an increase in urea content was also proposed in a previous work<sup>5</sup> to explain the enhancement of the mechanical properties of elastomeric PUU with the increase in water content available during cure.

The ordered urea hydrogen bonding is disrupted by the introduction of triol or by the addition of the DMDEE catalyst to the quasi-prepolymer. While the effect of the triol may be explained by the introduction of chemical crosslinks that promote phase mixing and disrupt urea organization, the inhibitory effect of the DMDEE catalyst in the bidentate urea formation was unexpected. A previous study involving the blowing catalyst 2,2'-oxybis-(*N,N*-dimethylethylamine) suggested that the improvement of the mechanical properties of the elastomeric PU by increasing the catalyst content was due to a higher degree of microphase separation as a result of an extent of the bifurcated urea formation.<sup>5</sup> As the urea groups associate with each other, they form multifunctional physical network nodes responsible for the increase in the elastic moduli of the phase-segregated microstructure. Nevertheless the authors of reference<sup>5</sup> did not corroborate this hypothesis by adequate techniques such as FTIR spectroscopy. The effect of the addition of DMDEE catalyst observed in this study could be explained on the basis of the faster formation of the network that makes urea organization more difficult.

### Isothermal cure kinetics

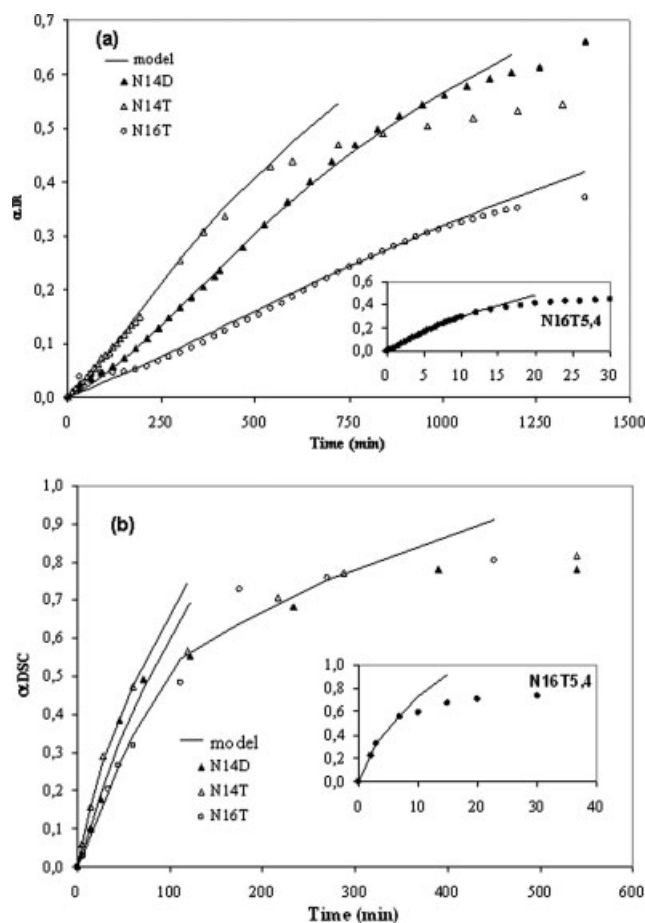
Water/diisocyanate reaction is a well-known second-order reaction.<sup>29</sup> Since the reaction of NCO groups with nucleophilic reactants can be catalyzed by both Lewis acids and bases, even in a catalyst-free system,

the formation of urea groups during the curing reaction of the quasi-prepolymers may be catalyzed by the existent urethane groups or even by the resulting urea.<sup>30</sup> Both *n*th order and autocatalyzed kinetic models can be summarized into one equation [eq. (4)]

$$\frac{d\alpha}{dt} = k\alpha^m(1 - \alpha)^n \quad (4)$$

where  $d\alpha/dt$  is the reaction rate,  $k$  is the rate constant,  $m + n$  is the global order of the reaction, and the parameter  $m$  accounts for the autocatalytic effect during reaction. Equation (4) has been successfully used in previous studies<sup>6,31</sup> for modeling the curing reaction of several systems containing unreacted NCO groups.

The experimental data obtained from the isothermal curing experiments of urethane quasi-prepolymers using FTIR spectroscopy and DSC were fitted to the logarithmic form of the kinetic model of the eq. (4), considering that the reaction was of first or second order. In both cases the best correlation was obtained for the second-order modeling. Figure 5



**Figure 5** Comparison between the experimental degree of conversion determined by FTIR spectroscopy (a) and DSC (b), and fitted results to a second-order autocatalyzed kinetic model.

**TABLE V**  
Kinetic Parameters of the Curing Reaction Performed Under Isothermal Conditions, Assuming a Second-Order Autocatalyzed Model, Determined by FTIR Spectroscopy and DSC (Values in Italics)

Prepolymer	$k$ (s <sup>-1</sup> )	$m$	$n$	$R^2$
N14D	$3.3 \times 10^{-5}$	0.43	1.57	0.985
	$3.5 \times 10^{-4}$	0.36	1.64	0.987
N14T	$3.7 \times 10^{-5}$	0.31	1.69	0.988
	$3.8 \times 10^{-4}$	0.24	1.76	0.999
N16T	$1.3 \times 10^{-5}$	0.27	1.73	0.933
	$2.5 \times 10^{-4}$	0.30	1.70	0.987
N16T5,4	$8.5 \times 10^{-4}$	0.10	1.90	0.994
	$4.8 \times 10^{-3}$	0.34	1.66	0.998

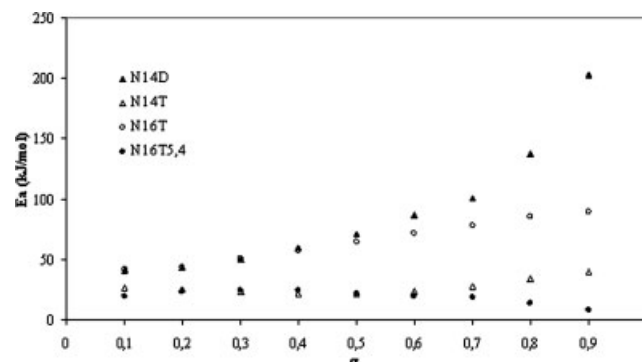
shows fitted data and Table V gives the values of the kinetic parameters  $k$ ,  $m$ ,  $n$ , and  $R^2$  (correlation coefficient of the fit) for the urethane quasi-prepolymers without catalyst. Figure 5 show that only the initial part of the curing reaction data supports the kinetic model of eq. (4). For higher extent of cure the reaction becomes diffusion controlled and the experimental degree of conversion is lower than the values calculated using the kinetic model. The kinetic constant values show the same dependence with the prepolymer composition, for both FTIR spectroscopy and DSC results. However, the  $k$  values determined by DSC are approximately one magnitude order higher than those obtained using FTIR spectroscopy. In fact, DSC and FTIR spectroscopy were used to monitor the curing reaction of quasi-prepolymers under different conditions, the former by adding the stoichiometric water amount to the system and the later by exposing the quasi-prepolymer to atmospheric air moisture. After placing the prepolymer on KBr pellet and exposure to the air, a skin of cured PUU could be quickly formed. This skin that becomes thicker as the reaction progress, likely acts as a barrier for permeation of moisture into the remaining uncured material. Because the urea formation occurs much faster than the rate of water vapor diffusion within the prepolymer, the overall reaction rate is limited by this parameter. The diffusion constraint may be surpassed through the addition of water to the system.

Table V shows that the kinetic constant values decrease with increasing the free NCO content of the quasi-prepolymer and that the effect of the functionality of the polyol in the kinetic constant is meaningless. These results are in agreement with the analysis of conversion degree curves obtained by FTIR spectroscopy (Fig. 2). Chattopadhyay et al.<sup>26</sup> have reported a similar effect of the NCO content in the moisture cure of toluene diisocyanate prepolymers. The value of  $m$ , which describes the autocatalysis during the cure reaction, decreases when the polyol functionality is higher and seems to be independent of the unreacted NCO content. Because of their nucleophi-

licity, urea groups or even intermediary amine compounds formed during NCO-water reaction are able to associate to water molecules. NCO groups will react preferentially with these activated complexes.<sup>30</sup> The formation of these associates certainly becomes more difficult as the functionality of the polyol increases, because of steric hindrance of nitrogen atom or to lower mobility of the polymeric chains, and consequently the autocatalytic effect should be less effective. The effect of the addition of the catalyst on the value of the parameter  $m$  depends on the experimental conditions used to perform the reaction. The reaction is less autocatalyzed in presence of DMDEE catalyst when exposed the quasi-prepolymer to air moisture, while no influence has been observed when water is directly added to the quasi-prepolymer. Therefore, the diffusion rate of water molecules may represent, in certain conditions, a limiting factor to the formation of the activated complexes in the autocatalysed path of the NCO-water reaction.

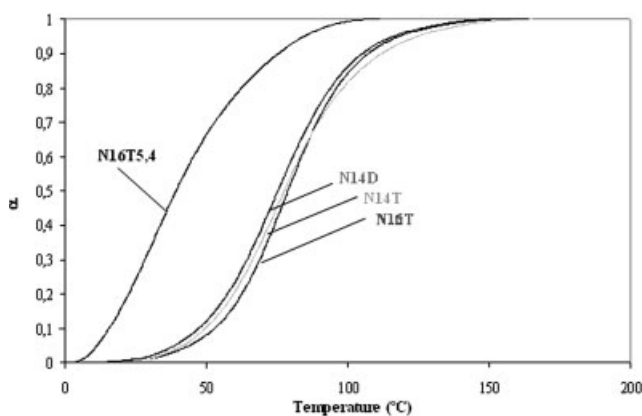
#### Nonisothermal DSC cure kinetics. Activation energy

The complexity of a reaction involving multiple steps can be detected by a variable value of  $E_a$  (effective activation energy). The effective activation energy is an empirical parameter accounting for the rates of several simultaneously occurring single steps of a reaction, each of which having its own energy barrier. Therefore, the effective activation energy will vary with the temperature and/or reaction progress.  $E_a$  values were calculated for the curing reaction performed under nonisothermal conditions, by applying the Friedman method,<sup>8</sup> a model-free kinetic approach. Actually, because of the complexity of the curing process, an approach based on the fit of kinetic data to an assumed kinetic model normally fails, as we reported above, and the use of model-free methods may be an alternative and advantageous approach. According to the Friedman method,  $E_a$  is calculated from the slope



**Figure 6** Dependence of the effective activation energy ( $E_a$ ) with the extent of the reaction for nonisothermal DSC cure (Friedman method).





**Figure 7** Variation of the extent of cure with temperature for nonisothermal DSC curing (heating rate = 5°C/min).

of the plot of  $\ln(dx/dt)$  versus  $1/T$ , at a constant  $\alpha$  value. The extent of the reaction was calculated using the eq. (3). Detailed mathematical aspects of the Friedman method are given elsewhere.<sup>8</sup>

Figure 6 shows the variation of the effective activation energy ( $E_a$ ) with the extent of the reaction, when the curing reaction of the urethane quasi-prepolymers is performed under nonisothermal conditions. In absence of catalyst, the initial value of the effective activation energy is  $\sim 25$ – $40$  kJ/mol and tends to increase with the extent of the reaction until  $40$ – $200$  kJ/mol, depending on the composition of the quasi-prepolymer. The activation energy increased slightly as the reaction proceed but increased more quickly at the higher degrees of conversion. A similar trend was reported earlier<sup>6,32</sup> for the nonisothermal cure of ether urethane prepolymers with steam and in the curing process of pMDI with wood. This behavior reveals the complexity of the curing reaction that probably is due to the contribution of secondary reactions such as the formation of allophanate and biuret and their decomposition into their precursors that takes place at relatively high temperatures. In absence of DMDEE catalyst, the nonisothermal curing reaction of the quasi-prepolymers is completed at  $\sim 150^\circ\text{C}$  (Fig. 7). Urea and urethane groups can further react with NCO to form allophanate and biuret linkages that are thermally decomposed at around  $110^\circ\text{C}$ .<sup>33</sup> Furthermore, carbodiimides can be produced by heating NCO at elevated temperature. Therefore, the effective activation energy calculated for the curing reaction performed under nonisothermal conditions should account not only for the NCO-water reaction but also for the contribution of several secondary reactions that take place in that temperature range. The increase of the effective activation energy as the reaction progresses is more pronounced for high free NCO content and for low polyol functionality quasi-prepolymers. The contribution of secondary reactions involving NCO groups should be more relevant as

the concentration of the NCO groups in the prepolymer increases. On the other hand, for high polyol functionality, the restriction of the molecular motion as the reaction progresses should be more marked and after a given moment the kinetics becomes diffusion controlled which contributes for a reduction of the value of the effective activation energy. This reduction is masked by the contribution of the secondary reactions to the effective activation energy and explains the less pronounced increase of the activation energy observed for the prepolymer prepared with high polyol functionality.

These trends can be better understood if a kinetic model of a process encompassing both chemical and diffusion kinetics is considered. The reciprocal of the overall constant rate ( $k$ ) is the result of the sum of the reciprocal values of the reaction ( $k_r$ ) and diffusion ( $k_d$ ) constant rates.<sup>34</sup> If the Arrhenius variation for the temperature dependence of  $k_d$  the effective activation energy is assumed, the effective activation energy will be a function of the effective activation energies of both chemical ( $E_r$ ) and diffusion of reactants in the medium ( $E_d$ ) reactions, as expressed by eq. (5).<sup>35</sup>

$$E = \frac{E_d \cdot k_r + E_r \cdot k_d}{k_r + k_d} \quad (5)$$

The activation energy of the chemical reaction ( $E_r$ ) includes the contribution of the NCO-water reaction together with the contribution of the secondary reactions. The later should become more important at higher temperatures which also correspond to higher degree of conversion values. Nevertheless, at high conversion degree the reaction becomes diffusion controlled and  $k_d$  begins to decrease as a consequence of the lack of molecular mobility. It is expected that this decrease will be more pronounced as the cross-link density of the polymer increases and therefore this would explain the differences observed in the variation of the effective activation energy of curing reaction of the prepolymers N14T and N14D.

When the DMDEE catalyst is added in the urethane quasi-prepolymer formulation, the initial value of  $E_a$  is lower ( $20$  kJ/mol) and decreases as the curing reaction progresses. In fact, in presence of DMDEE, the curing reaction is completed at temperatures below  $100^\circ\text{C}$  (Fig. 7) and therefore the contribution of secondary reactions that usually take place at high temperatures should be meaningless.

## CONCLUSIONS

FTIR spectroscopy and DSC experiments were used to study the cure kinetics of NCO ended urethane quasi-prepolymers with air moisture and with water added in stoichiometric proportion, respectively, under isothermal and nonisothermal conditions.

Under isothermal-curing conditions, the reaction rate increased for low free NCO content and through the addition of the DMDEE catalyst. The effect of the polyol functionality on the reaction rate was irrelevant although it affected the final degree of conversion. A second-order autocatalyzed model was successfully used, although it failed for high degree of conversion, probably because the reaction became diffusion controlled. The isothermal moisture-cured PUU showed loosely ordered HS domains but urea organization was induced for higher free NCO content and low polyol functionality and was suppressed by adding the catalyst DMDEE.

A kinetic model-free approach was used to find the dependence of the effective activation energy with the extent of cure, when the reaction was performed under nonisothermal conditions.  $E_a$  showed a variable value with reaction progressing which revealed the complexity of the curing process. Additionally, the addition of the catalysts DMDEE proved to invert the dependence of  $E_a$  with the extent of cure. The increase of  $E_a$  as the reaction progresses in absence of catalyst may result from the contribution of secondary reactions, while the decrease in  $E_a$  when DMDEE is added proves that the contribution of these reactions is less important when the curing reaction is completed at lower temperatures.

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