Revista Mexicana de Ingeniería Química

Vol. 12, No. 1 (2013) 155-163

A SIMPLE PROPOSAL FOR MODELING ISOTHERMAL CURE KINETICS

UNA PROPUESTA SIMPLE PARA MODELAR CINÉTICAS DE CURADO ISOTÉRMICAS

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Received 7 of June 2012; Accepted 15 of January 2013

Abstract

A simple model for cure kinetics, based on the Churchill-Usagi correlation, is presented here. This proposal, intended for engineering purposes, is capable of reducing computational time to facilitate, even with analytic solutions, the kinetics description, especially when more complex systems are being studied. In spite of the model's simplicity, fundamental kinetic parameters, including the reaction order and the rate constant, (composed of the Arrhenius constant and the activation energy) can be determined in the diffusion free zone. A four-parameter model accurately described the previously reported conversion evolution of a cyanate ester resin, from 140 to 190 ºC, presented as a case example. For the limit conversion and the Churchill-Usagi exponent, a linear dependence with reaction temperature was obtained.

Keywords: cure kinetics, cyanate ester resin, industrial applications, modeling and simulation.

Resumen

Se presenta un enfoque sencillo, basado en la correlación de Churchill-Usagi, para describir cinéticas de curado. Esta propuesta, destinada a aplicaciones industriales es capaz de reducir el tiempo de cálculo para facilitar, aún con soluciones analíticas, la descripción de la cinética de curado de resinas, especialmente cuando se estudian sistemas complejos. A pesar de la simplicidad del modelo, los parámetros cinéticos fundamentales, incluyendo el orden y la constante de reacción (compuesta por el pre-factor de Arrhenius y la energía de activación) se pueden determinar en la zona libre de problemas difusivos. Un modelo de cuatro parámetros describe con exactitud la evolución de la conversión de una resina de éster de dicianato (reportada previamente) de 140 a 190 ºC la cual se muestra para ejemplificar la propuesta. Tanto para la conversión límite como para el exponente Churchill-Usagi, se obtuvo una dependencia lineal con la temperatura de reacción.

Palabras clave: cinética de curado, resina de éster dicianato, aplicaciones industriales, modelado y simulación.

1 Introduction

The transformation of a low molecular weight liquid monomer(s) to a crosslinked polymer network is performed through the so-called curing reaction. At the beginning, the reaction kinetics is chemically controlled, but later, there is a decrease in the reacting species' mobility and curing becomes diffusion-controlled, because of an increase in the molecular mass and the crosslinking of the polymer molecules' entanglements. In addition, a free volume reduction occurs during the curing process that yields an increase in the glass transition temperature (T_g).

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Thermosetting resins play an important role in industry due to their dimensional stability and because they are stronger and support higher temperatures than thermoplastics. The most common molding processes for thermosetting resins include transfer molding, injection molding, compression molding, liquid injection molding, encapsulation, reaction injection molding, potting and impregnation (Halley and Mackay, 1996). Examples of thermosetting resins are: epoxy resins (Naffakh *et al*., 2006), rubbers (Arrillaga *et al*., 2007), phenol formaldehyde (Lei *et al*., 2006), polyurethanes (Kim and Macosko, 2000), silicones (Comyn *et al*., 1998), polyesters (Vilas *et al*., 2001), among others. Recently, a fluoromethylene cyanate ester $NCOCH_2(CF_2)_6CH_2OCN$ (DFCy) has been developed with the drawback of a low T_g (ca. 92 °C). Nevertheless, it has very low dielectric constant (2.3-2.6), refractive index (1.382-1.447) and optical loss, these characteristics make it interesting for optic-electrical applications (Zhao and Hu, 2007).

The polymer chains of the thermosetting resins are crosslinked (cured) by temperature, irradiation or chemical reaction. In industrial applications, a wide range of additives (e.g., catalysts, pigments, formulation agents, lubricants, fillers, UV protectors, etc.) are part of the curing system, which results in complex curing kinetics (Lei *et al*., 2006; Shojaei and Abbasi, 2006; Harsch *et al*., 2007). Therefore, a good description of the curing reactions is an important prerequisite for process simulation and optimization of composites properties.

According to Galwey (2004), there are two types of kinetic models: one which is phenomenological (or empirical) and other that is mechanistic. Both have advantages and disadvantages. The phenomenological approach assumes that an overall reaction and the kinetic data are fitted by regression with a simple model depicting the experimental data. In industry this is the preferred method due to its simplicity and computational time saving. In general, phenomenological models are not recommended for predictions outside the experimental data range. The mechanistic approach takes into account the reactions occurring during curing, and requires measurements of concentration of reactants, intermediate species and products. The mechanistic models are more complex than the phenomenological ones, but their advantage is that, in principle, they are not restricted to the original reaction conditions and have an extended prediction capability. Both phenomenological and mechanistic models can be built from data generated from isothermal and dynamic experiments. The isothermal mode has been criticized (Galeway, 2004), but it is the most reported in the literature. So far, the model used more often is the one reported by Kamal (1974), which has two reaction constants and two reaction order exponents. Another is that proposed by Chen and Macosko (1996), which attacks the problem in two parts: one kinetic equation before the diffusion effects appear (up to an onset conversion), containing one reaction constant and one reaction order exponent, and another kinetic scheme for the diffusion regime bearing another reaction constant, another reaction order exponent, and a parameter related to the maximum conversion of the system. It is worth mentioning that all the reaction rate constants have Arrhenius behavior. Other authors have included a reaction-order dependence on conversion to model cure kinetics (Zhao and Hu, 2007).

Other kinetic schemes have been reported in the literature (Halley and Mackay, 1996; Yousefy *et al*., 1997; Achilias, 2007). Usually, these models are not capable of describing the kinetics and diffusion effects, but they introduce the Rabinowitch (1937) expression, in which the inverse of the overall kinetic rate constant is equal to the sum of the inverse of the diffusion free kinetic constant and the diffusion limited inverse. Then the diffusion rate constant is represented by a Williams-Landel-Ferry equation related to the system's T_g, and of course, other parameters appear. Moreover, the forms of the diffusion-limited reaction constant can be found elsewhere (Halley and Mackay, 1996; Yousefy *et al*., 1997; Achilias, 2007).

Sometime ago, Churchill and Usagi (1972) proposed an empirical function that can be expressed as the m^{th} root of the sum of two asymptotes, related to two distinctive regimes of a given process, each one raised to a common power m. Even though this approach has been extensively applied in transport phenomena (Bahrami *et al*., 2006; Corcione, 2005; Sanitjai and Goldstein, 2004; Mitrovic *et al*., 2004; Petre *et al*., 2003; Fourie and Plessis, 2002; Romeo *et al*., 2002), only a few reports have been found in the literature concerning kinetics, such as microbial and enzymatic studies (Membre *et al*., 1997; Loo *et al*., 1978; Payne *et al*., 2007) and enzymatic reactions (Ho, 1991; Kazakov *et al*., 1994; Hayes *et al*., 2007).

Although several models can be used to fit curing kinetics, they usually require a large number of parameters, even in phenomenological approaches, which make computations slower and more complicated. From an industrial standpoint for process modeling and optimization, a simpler kinetic model is usually preferred (González-Romero, 1989;

Kim and Macosko, 2000; Abbassi and Shahnazari, 2004; Naffakh *et al*., 2006; Arrillaga *et al*., 2007; Kim and Macosko, 2000; González-Romero and Casillas, 1989; Abbassi and Shahnazari, 2004).

Here, we propose the application of the Chruchill-Usagi correlation to model cure kinetics with a simple algebraic equation, with few parameters, that can be applied in more complex modeling. To illustrate our approach, data of 2,2,3,3,4,4,5,5,6,6,7,7-dodeca fluoro octanediol dicyanate ester, (DFCy) reported recently, are used as a case example. The conversion evolution, materials and experimental procedure are reported elsewhere (Zhao and Hu, 2007).

2 Proposed methodology

The following proposal presents a simple model attempting to contain the least number of parameters to describe the isothermal curing of a cyanate ester resin (Zhao and Hu, 2007), applying the Churchill-Usagi correlation. The obtained kinetics function is intended for engineering purposes. However, as presented in this work, fundamental kinetic parameters can be also determined.

As was mentioned in the introduction, cure kinetics presents chemically controlled and diffusion-controlled rate stages. The Churchill-Usagi approach proposes the approximate overall behavior of a variable x as a function of the initial (x_0) and limit solution (x_∞) in a weighted-exponential sum, as follows:

$$x = (x_0^m + x_\infty^m)^{1/m} \tag{1}$$

To obtain these two solutions and the exponential weight parameter (m), we proceed as follows:

1. Interpolate the kinetic conversion data (x) during the chemically controlled regime (i.e., where no diffusion effects appear), at the different experimental temperatures, with a kinetic rate function given by:

$$x_0' = k(1-x)^n; \quad x_0 = 0 \tag{2}$$

where x_0' is the estimated conversion's derivative with respect to time t(s), to determine the kinetic rate constant k(s^{-1}) and the reaction order n (−). Then, the pre-exponential factor A (s^{-1}) and the activation energy E_a (kJ mol^{-1}), of the rate constant, can be determined from the typical Arrhenius' plot. The analytic solution of Eq. (2) (for $n \neq 1$) is:

$$x_0 = 1 - [(n-1)kt + 1]^{1/(1-n)} \tag{3}$$

Thus, the function x_0 can be determined from Eq. (3).

2. Obtain the limiting conversion (extent of curing) behavior from the conversion (x_∞) against time data; that is, the maximum conversion at each temperature, now x_∞, required in Eq. (1), can be determined.

3. With the two previous steps, find the exponent in Eq. (1) for each experiment, as follows:

$$x = \{([1-((n-1)kt+1)]^{1/(1-n)})^m + x_\infty^m\}^{1/m} \tag{4}$$

4. Next, determine the dependency of x_∞ and m on reaction temperature (T); that is:

$$x_\infty = x_\infty(T) \tag{5}$$

$$m = m(T) \tag{6}$$

5. Finally, perform an overall regression with Eqs. (5) and (6) along with:

$$x = \{([1-((n-1)kt+1)]^{1/(1-n)})^{m(T)} + x_\infty(T)^{m(T)}\}^{1/m(T)} \tag{7}$$

to obtain a general expression with the whole parameter set [contained in $x_\infty(T)$ and $m(T)$] for all the experimental runs.

3 Results

The above mentioned methodology was applied to a recently reported experimental data set for the curing of DFCy (Zhao and Hu, 2007). In step 1, the data fitting was reduced to conversions up to 60%, as explained in the *Discussion* section. Fig. 1 shows that there is a good agreement between the fitting curves Eq. 3 and the experimental data, up to 60% conversion for all temperatures. The obtained parameters are presented in the first two columns of Table 1. A plot of ln k versus $1/T$ follows a straight line (Fig. 2), from which the Arrhenius pre-exponential factor and the activation energy were obtained and their values are presented in Table 2. However, the reaction order did not show a temperature dependence as can be seen in Fig. 3. Here, it appears that for the first data points a decrease in reaction order seems to be apparent, however the data point at the highest temperature breaks this tendency. Nevertheless, if an average is taken (Fig 3. dashed line) it seems that this value represents well all the data points with a deviation of

Table 1. Fitted parameters. The reaction constant (k) and the reaction order (n) obtained in the chemically controlled regime (Eq. 3) considering experimental data up to 60 % conversion. The limiting conversions (x_∞) were taken to be the last experimental points (Fig. 4) and the Churchill-Usagi parameter (m) is obtained fitting Eq. 4 for each data set (Fig. 5).

Temp (°C)	$k \times 10^4$	n	x_∞	m
140	2.3864	2.378	0.7010	-18.256
150	3.7217	2.376	0.7364	-14.737
160	5.5661	2.318	0.7718	-12.857
170	7.8236	2.196	0.8027	-11.081
180	11.4022	2.161	0.8292	-10.621
190	17.9289	2.321	0.8616	-9.732

Table 2. Kinetic and Arrhenius parameters obtained for conversions up to 60%.

Kinetic parameters	Values
A (s^{-1})	55,574.00
E_a (kJ/mol)	66.477
n (−) average	2.29 ± 0.1

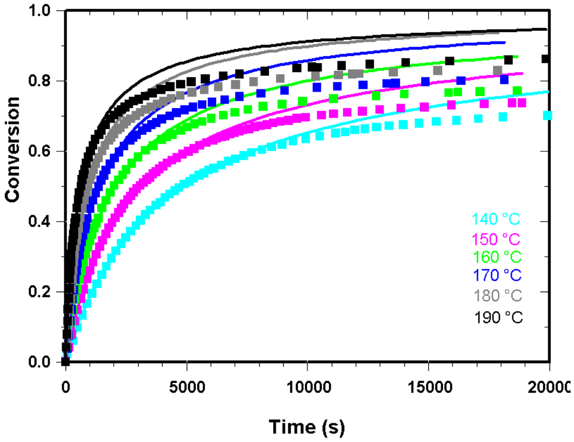

Fig. 1. Experimental data fitting (Eq. 3) conversion is taken into account up to 60% (below the diffusion effects). The continuous lines represent the model (Eq. 3) and the symbols represent the experimental data (Zhao and Hu, 2007).

less than 5%; therefore, an average (arithmetic) value was calculated (n = 2.29 ± 0.10) and the individual values are shown in Table 1.

Table 3. Parameters obtained from the overall fitting of the linear functionalities obtained for $x_\infty (= a_\infty + b_\infty T)$ and $m (= a_m + b_m T)$ with Eqs. (5-7).

Parameters	Overall
a_∞	15.152×10^{-2}
b_∞	4.451×10^{-3}
a_m	-16.179
b_m	5.848×10^{-2}

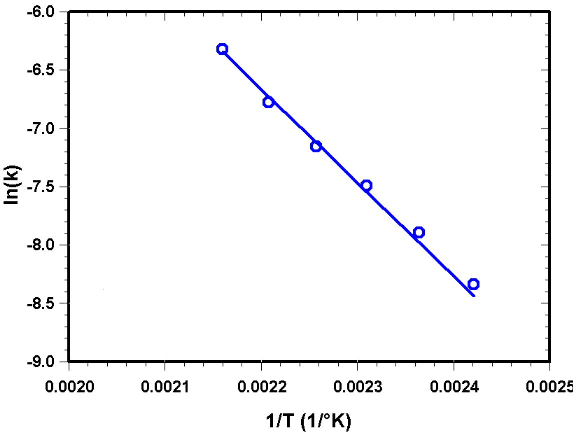

Fig. 2. Arrhenius plot of the rate constant, using experimental data up to 60% conversion. The continuous line is the best fit, and the symbols correspond to the individual experimental data at each temperature.

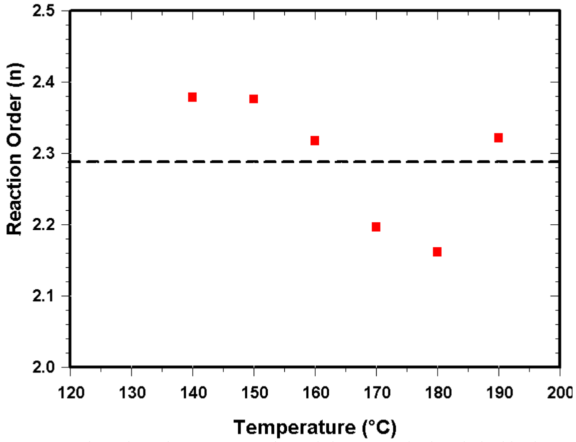

Fig. 3. Reaction order against temperature, the symbols represent the data obtained by the data fitting. The dashed line represents the arithmetic average of all the values.

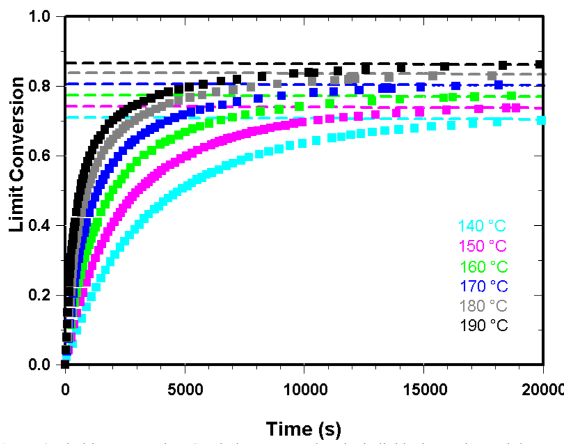

Fig. 4. Limiting conversion. Symbols correspond to the individual experimental data (Zhao and Hu, 2007) at each temperature. The horizontal (dashed) lines represent the limiting conversion, taken as the last conversion data points for each run.

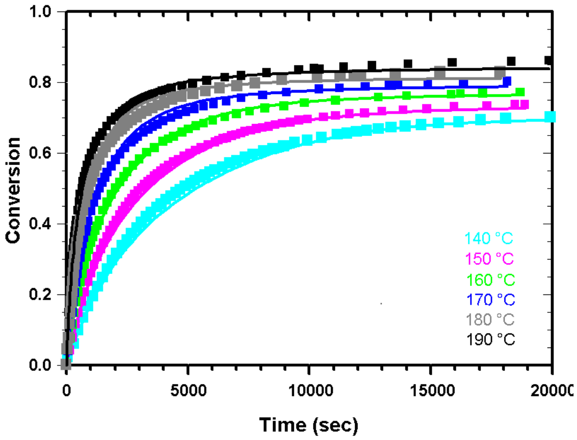

Fig. 5. Fitting m for each individual run (Eq. 4). Symbols correspond to the experimental trend (Zhao and Hu, 2007).

The limiting conversion was determined from the last experimental points, where the curve is asymptotic to the *time*-axis (indicated by the dashed lines in Fig. 4). The values for the maximum conversion (x_∞) are listed in the last column of Table 1. Once the limit behaviors have been determined, a regression is carried out with Eq. 4 to obtain (step 3) the weighted exponential (m). The results are shown in Table 1 and in Fig. 5; the limiting conversion and the Churchill-Usagi exponent plots against temperature are linear as presented in (the lower part of) Figs. 6 and 7, respectively.

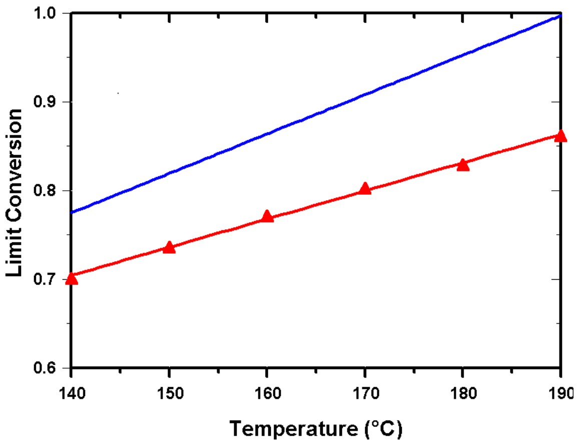

Fig. 6. Limit conversion against reaction temperature. The red line represents a linear fit from individual regressions. Symbols correspond to the experimental trend at each temperature, data taken from Fig. 3. The blue (upper) line corresponds to an overall regression performed fitting $x_\infty(T)$ and $m(T)$ (Eqs. 5-7).

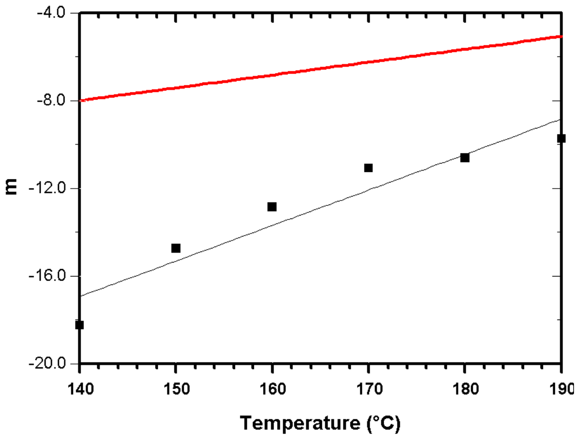

Fig. 7. Churchill-Usagi exponent (m) against temperature. The black (thin) line represents a linear fit from an individual regression performed over the experimental points (symbols) corresponding to individual fits. The red (thick) line corresponds to an overall regression performed, fitting linear fits on $x_\infty(T)$ and $m(T)$ (Eqs. 5-7).

When the basic parameters (A, E_a, n) in the kinetically controlled regime (Table 2) have been found, and both the limit conversion (Fig. 6) and the Churchill-Usagi exponent (Fig. 7) functional dependencies (found to be linear with reaction temperature in our case) have been determined, an overall fit is performed (step 5), leaving only four parameters free, two

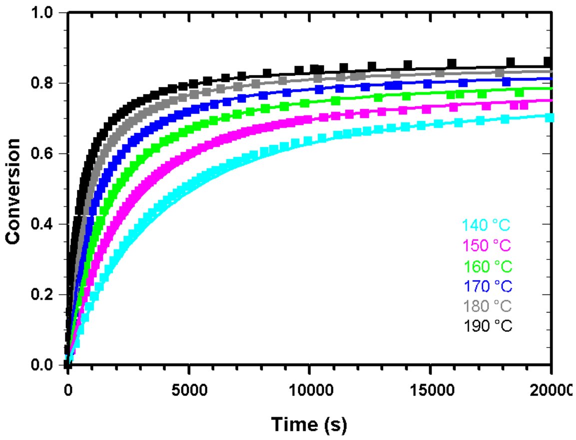

Fig. 8. Overall fit (Eqs. 5-7) (continuous lines) using the parameters shown in Tables 2 and 3. The experimental data (symbols) depicts the different temperature runs (Zhao and Hu, 2007).

(a_∞, b_∞) for $x_\infty(T)$ and two (a_m, b_m) for $m(T)$. The experimental and calculated conversions, as a function of time, are compared in Fig. 8, and the new overall parameters for $x_\infty(T)$ and $m(T)$ are shown in Figs. 6 and 7, respectively, in the upper part of the graphs. The obtained values for the overall fit are presented in Table 3.

4 Discussion

The criteria to select a conversion of 60% for the kinetically controlled rate stage was adopted because the trazine cycle that is formed can be considered as a tri-functional monomer (Chen and Macosko, 1996). Moreover, Carothers (1936) developed a relationship for the degree of polymerization (X_n), depending on the gel point conversion (x_g) and the monomer functionality (f) as follows: $X_n = 2/(2 - f x_g)$, and then, when the degree of polymerization becomes infinite, the gel conversion is 2/3 for a tri-functional monomer. As seen in Fig. 1, even though the fit was performed considering conversion data up to about 60%, the simplest model is capable of depicting conversions above 60%. Notice that the predicted conversion is larger as the reaction temperature becomes higher, probably because the molecules' segments have greater mobility as temperature augments. Therefore, a kinetic regime can be established in this case, performing the above criteria in a simple fashion. Regarding the occurrence of the diffusion effects, our results contradict those of Zhao and Hu (2007) because they observed these effects at conversions ca. 35%.

Once the simplest reaction scheme Eq. 3 had been fitted, the reaction constant was obtained, as presented in Fig. 2, where the traditional Arrhenius behavior is obtained, plotting ln (k) against the inverse of temperature (see Table 1). The reaction order does not show a clear trend with temperature (see Fig. 3), and individual values are reported in Table 1. Therefore, an (arithmetic) average value of 2.29 ± 0.1 was chosen to be representative for all experimental runs, having a small deviation of ca. 5%. This consideration simplifies the final calculation because an additional functionality for the reaction order is avoided. Zhao and Hu (2007) obtained a conversion-dependent reaction order [$n = 1.5 - \ln(1 - x)$]. Therefore, their reaction order varies from n = 1.5 (x = 0) to 2.1 (x = 0.6).

The Arrhenius parameters obtained here (Table 2) agree with the ones reported by Zhao and Hu (2007) (A = 63,704 s^{-1}; E_a = 67,240 J mol^{-1}). Up to this point, the description of the kinetically controlled stage has been described accurately, as shown in Figs. 1 and 2, and in Tables 1 and 2.

The limiting diffusion controlled conversion (x_∞) is shown in Fig. 4 and in Table 1. The comparison shown in Figs. 1 and 4 allows setting the beginning of this regime (named onset conversion in other works), but in our case, this is not required. One can observe in Fig. 4 and Table 1, that the limiting diffusion controlled conversion becomes larger as the reaction temperature is increased. This effect is also due to lesser diffusion limitations as the temperature is raised because diffusion is temperature dependent. This effect was also seen when analyzing the diffusion controlled regime in Fig. 1. The limiting conversion dependence with reaction temperature is linear, as shown in Fig. 6 (lower line), and this dependence can be used in an overall regression. Several functions have been documented to relate the diffusion limiting conversion with temperature. For instance, a linear dependence has been reported (Dusy *et al.*, 1987; Keny, 1994), a two-parameter negative dependence with curing temperature (diBenedetto, 1987; González-Romero and Casillas, 1989; Batch and Macosko, 1992), as well as a one-parameter exponential dependence (Hene *et al.*, 2004) have also been proposed. It is worth mentioning that in this work for simplicity a linear function was adopted, although Hene *et al.* (2004) criticized this dependence. However, the proposal of González-Romero and Casillas can also be fitted as well to the limiting diffusion conversion against temperature, obtaining two glass transition temperatures that can be related to the reacted ($T_{g\infty}$) and non-reacted material (T_{g0}).

Regarding the Churchill-Usagi exponent, in the literature (Crooke *et al*., 1981), attempts have been made to assign a physical meaning to this parameter. Usually, the two solutions are equated at the intersection point and conclusions are drawn from this treatment. The physical explanation of this parameter is beyond the purpose of this work, but with the analysis done so far, it can easily be seen that it does depend on the glass transition temperature of the reacted ($T_{g\infty}$) and un-reacted monomer (T_{g0}) (diBenedetto, 1987; González-Romero and Casillas, 1989). Readers who are further interested in this topic are directed to original reference (Crooke *et al*., 1981).

The Churchill-Usagi proposal Eq. (4) with the initial and final conversion behaviors, gave an excellent fit to each experimental run (shown in Fig. 5); however, the individual exponents in each run are slightly different (Table 1). On the other hand, Figs. 6 and 7 reveal that as a first approximation, the limit conversion and the Churchill-Usagi exponent against reaction temperature can be represented by a linear trend as a first approximation (lines over the symbols in these figures).

Once the obtained parameters were set (A, E_a, n, $x_\infty = a_\infty + b_\infty T$, and $m = a_m + b_m T$), an overall prediction for the six-run experimental set was performed, obtaining poor results. Usually the Churchill-Usagi procedure is applied to one set of parameters, and in our case this is a new application. Therefore, the parameters for the diffusion free regime (A, E_a, n) cannot be altered, but the constants contained in the linear behavior for x_∞ (a_∞ and b_∞) and m (a_m and b_m) were left free and an overall regression was then performed. The final values of these parameters are presented in Table 3. The overall fitting for x_∞, m and the overall conversion ($4x$) with these parameters are depicted graphically in Figs. 6-8, respectively. Figs. 6 and 7 (upper lines) show that the overall increasing trend with temperature is conserved, with small changes in the slope, but both dependencies are displaced upwards. Figure 8 indicates, however, that the overall prediction of the whole conversion follows the experimental data faithfully, which demonstrates the excellent description capability. It must be pointed out that once the diffusion free kinetic parameters are set, with a procedure already known in chemical kinetics, with only four additional parameters, (two for x_∞ and two for m), a complete description of the overall kinetic scheme from 140 to 190°C can be obtained. This approach, hence, is simpler and yields excellent results compared with others, including empirical approaches that use many more parameters. This simpler proposal can be very useful in chemical engineering applications where a more complex behavior is being modeled for example, in reaction injection molding or even cure behavior in an already molded part, where the temperature profiles are to be studied to obtain contained stresses at different conversions and, therefore, distinct mechanical properties. The proposed approach can reduce the computational time, especially because this kinetics problem and many others have an analytic solution.

Conclusions

A simple approach to model cure kinetics with a simple algebraic equation, based on the Churchil-Usagi approximation, has been presented. Four free parameters were capable of depicting accurately the cure kinetics of a cyanate ester resin from 140 to 190 °C. During the kinetically-controlled regime, the kinetic parameters (A, E_a, n) were determined in the traditional fashion. The overall conversion time-evolution predictions were performed, setting the parameters obtained in the diffusion-free zone and the two parameters that describe the limit conversion [$x_\infty = x_\infty(T)$], temperature dependence, and the two parameters depicting the Churchill-Usagi exponent temperature relationship $m = m(T)$. A much more convenient scheme than all phenomenological models containing more parameters, presented before, was therefore obtained. This methodology can be useful for engineering purposes in which computational time should be reduced. Nonetheless, the methodology is not limited to curing reactions and it can be applied to other polymerization systems that present diffusion limitations. In principle, the limit conversion and the Churchill-Usagi exponent might be assigned physical meaning.

Acknowledgments

The funds provided for this work, by UNAM (PAPIIT IN114212) and the exchange program between U de G and UNAM, are gratefully acknowledged.

Nomenclature

A	Arrhenius pre-exponential parameter [s^{-1}]
a_m	parameter used in the Churchill-Usagi exponent temperature dependence
a_∞	fitting parameter for the limit conversion temperature dependence
b_m	parameter used in the Churchill-Usagi exponent temperature dependence
b_∞	fitting parameter for the limit conversion temperature dependence
E_a	activation energy [kJ/mol]
k	kinetic constant [s^{-1}]
m	exponent in Churchill-Usagi correlation
n	reaction order [-]
T	temperature [°C]
x	monomer conversion
x'	monomer conversion time derivate
x_0	conversion versus time in the chemical regime
x_∞	asymptotic conversion in the diffusive regime

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