SIMULTANEOUS ESTIMATION OF KINETIC PARAMETERS USING GENETIC ALGORITHMS

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ABSTRACT

A procedure based on Genetic Algorithms (GAs) is applied to simultaneously estimate the six kinetic parameters associated with the model from Kamal and Sourour using dynamic differential scanning calorimetry data. Two estimation strategies are investigated and compared for the kinetic characterization of the curing of an epoxy resin. Despite strong correlations among all parameters, the results show the GA method is an effective tool in the simultaneous estimation of correlated parameters.

INTRODUCTION

In the development of composite fabrication processes, the ability to predict and monitor the curing process of the matrix material is a crucial issue. Such control requires the knowledge of the parameters of the kinetic model governing the degree of cure during material processing. Several kinetic models are available which provide relationships between reaction rate ($v=d\alpha/dt$), degree of reaction (α) and temperature (T). They are often referred to as describing autocatalyzed reaction rate mechanisms as the material contain substances that accelerate the reaction. The well known model from Kamal and Sourour (1) contains two rate constants K_1 and K_2 that depend on absolute temperature from the Arrhenius law and two exponents m and n to describe the order of the curing mechanism as shown in the Eq. below.

$$\frac{d\alpha}{dt} = \left(K_1 + K_2 \times \alpha^m\right)\left(1-\alpha\right)^n, \quad K_i = A_i \exp\left[-\frac{E_i}{RT}\right], \quad i = 1,2. \tag{1}$$

The parameters K_1 and K_2 represent the catalytic and the autocatalytic nature of the reaction, respectively. Using this model, one typically assumes known a combined order mechanism, which is generally a second order (2), and therefore the parameters to estimate are the rate constants K_1 and K_2. The most commonly used method of determining them involves the use of linear regression and isothermal Differential Scanning Calorimetry (DSC) data. The rate constants are identified at different temperatures from which the Arrhenius constants can be deduced. One of the disadvantages with this approach is that the Arrhenius constants cannot be estimated directly. An alternate approach involves the use of a minimization technique that can be used for nonlinear models, such as the Box-Kanemasu method. Assuming the exponents m and n to be known, this method has shown its effectiveness in the simultaneous estimation of the four Arrhenius constants associated with the curing of an amine epoxy system (2). However, due to correlations among the parameters when using dynamic DSC data, in order to be reliable, the estimation procedure was restricted to the use of isothermal DSC data. This limitation prevents the investigation of materials that react very fast and for which dynamic data can be obtained only. The need for an approach that do not require to set the exponents *m* and *n* to assumed values and to restrict the reaction analysis to isothermal runs has provided the motivation for this study.

The work summarized in this paper is part of an overall research effort to develop a robust estimation methodology based on Genetic Algorithms (GAs). Developed by Holland, these algorithms rely on genetic and selection mechanisms of nature and therefore, they do not require gradient information (3). Such information is known to be ill-defined when correlations are present among the parameters to estimate, limiting thus the application of gradient-based methods. In the present paper, the objective was to apply the proposed estimation methodology based on GAs to the kinetic characterization of the curing process of an epoxy resin using dynamic DSC data. The model from Kamal and Sourour (K&S) was selected because of the challenge associated with the simultaneous estimation of its six parameters and its popularity in the composite industrial world.

GENETIC ALGORITHMS

Genetic Algorithms belong to the field of Evolutionary Algorithms whose main idea is to simulate mechanisms derived from biology with an aim to modeling Evolution. Differing from conventional deterministic search techniques, these algorithms operate on populations of individuals and not on a unique one. Each individual represents a potential solution in the parametric search space. The initial population is randomly chosen in this space. The individuals/solutions are evaluated and ranked using a fitness function which can also be the optimization criterion. Then, the population progressively moves towards fitter regions of the search space by means of biological operators. The basic operators of a simple GA consist of selection, crossover and mutation. Following the Darwinian theory, an elitism operator is usually found in more elaborated GAs. These operators have all several variants which can be applied in a randomly and/or probabilistic –sometimes deterministic for some algorithms-process. Variants currently employed in the GA used at ISITEM follow the approach advised by Davis (4) which is to taylor the algorithm at hand. These variants are described in (5). A generation is accomplished when the sequence defined by the application of all operators to the individual *Parents* is completed, as illustrated in Fig. 1. The GA performs as many generations as necessary until the convergence criterion defined by the user is reached. The criterion used in our GA is satisfied when the best solution does not change -or roughly-during a fixed number of generations, this latter being limited by CPU time constraints. Note that if convergence is not reached, the run stops when the maximum allowable number of generations has been completed.

The functioning attributes of GAs allow them not to require gradient information of the measured variable with respect to the parameters to determine. Consequently, these algorithms are not limited by strong correlations among the parameters as traditional gradient-based methods are. The use of GAs in this study finds therefore all its rationale. Note that in the field of thermophysical property estimation, the GA technique has recently been shown to provide robust searches in spaces that include correlations among the parameters (5).

ESTIMATION PROBLEM FORMULATION

The estimation methodology used is based on Ordinary Least Squares (OLS). The objective function is the sum of squares function simply defined by the error between experimental and calculated data. The true parameter vector $\underline{\beta}$ sought to be estimated involves the six parameters (A_1, E_1, A_2, E_2, m and n) inherent to the K&S model whose mathematical form can be generalized into $v = F(T, \alpha, \underline{\beta})$. Dynamic Differential Scanning Calorimetry data are to be used in the kinetic analysis. Because the rate of heat generation is measured directly in DSC experiments, one logically thinks of using cure rate information in the estimation procedure. This latter is calculated from two steps assuming time and temperature to be known as shown in the scheme Fig. 2: first, the cure degree is determined from a Runge-Kunta analysis of order two to solve the first order differential equation; then, its value is used in Eq. 1 to find the reaction rate. However, the work form Scott and Saad (2) indicates that the degree of cure provides more information than the reaction rate and should be treated as the dependent variable. Therefore, a second estimation strategy was analyzed (schematic provided in Fig. 3), assuming that the measured quantity is the degree of cure α. The mathematical expressions for the two objective functions, S_v and S_α are for N_i measurements and N_j experiments:

$$S_v\left(\underline{\beta}\right)=\sum_{i=1}^{N_i}\sum_{j=1}^{N_j}\left[v_{ij}\left(\underline{\beta},\tilde{t}_{ij},\tilde{T}_{ij}\right)-\tilde{v}_{ij}\right]^2 \tag{2}$$

and $$S_\alpha\left(\underline{\beta}\right)=\sum_{i=1}^{N_i}\sum_{j=1}^{N_j}\left[\alpha_{ij}\left(\underline{\beta},\tilde{t}_{ij},\tilde{T}_{ij}\right)-\tilde{\alpha}_{ij}\right]^2 \tag{3}$$

To perform these estimation strategies, one therefore needs the set of experimental data $\left\{\tilde{t}_{ij},\tilde{\alpha}_{ij},\tilde{v}_{ij},\tilde{T}_{ij}\right\}$, where t is time, and $i = 1,\ldots,N_i$ measurements and $j = 1,\ldots,N_j$ experiments.

For both strategies, sensitivity coefficients were evaluated numerically using the simple but adequate finite differences. Recall that the estimation methodology based on GAs does not use sensitivity information. Nevertheless, it is meaningful to analyze dimensionless coefficients to obtain some insight in the estimation procedure. A dimensionless coefficient represents the product of the coefficient by its parameter value and scaled with respect to the measured variable by dividing by the maximum increase in the variable (Δv_{max} or $\Delta\alpha_{max}$).

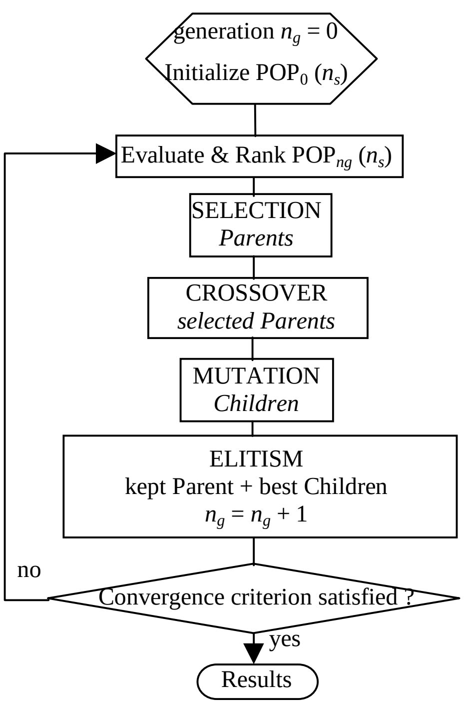

Figure 1: Flowchart for a typical Genetic Algorithm.

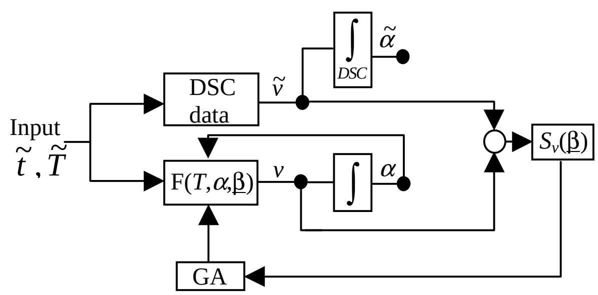

Figure 2: Schematic of estimation strategy S_v.

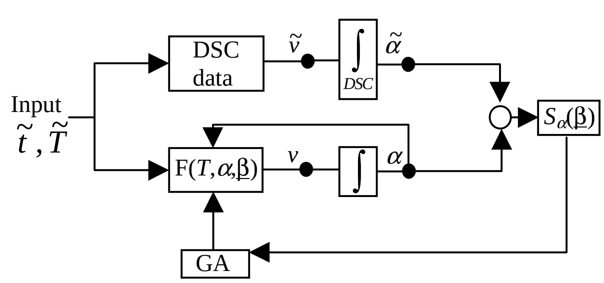

Figure 3: Schematic of estimation strategy S_α.

ANALYSIS OF THE CURING OF AN EPOXY RESIN

DSC Experimental Data

Experiments were performed using a Perkin Elmer DSC-7 apparatus, which operates using the power compensation mode. To generate dynamic data, six cycles were realized for which the temperature increased linearly with time and at different rates, V_T. The upper temperature value was chosen to ensure that the curing process was complete but still staying below a temperature level which could cause material degradation. Table 1 summarizes the number (N_j) and conditions of experiments for each resin. The maximum increase in cure rate for each cycle is given by Δv_{max} (min^{-1}). and $[\Delta v_{max}]_{av}$ designates the average maximum increase.

Table 1: Conditions of experiments performed using DSC.

Epoxy N_j **=6,** $T \in$ **[40-220 °C]**		
V_T **(°C/min)**	N_i	Δv_{max} **(min^{-1})**
2.5	447	0.1248
5	270	0.2325
7.5	186	0.3278
10	140	0.4165
12.5	118	0.4962
15	93	0.5692
	N_{tot} **= 1254**	$[\Delta v_{max}]_{av}$ **= 0.3612**

Treatment of the experimental heat fluxes recorded by DSC allowed to obtain the set $\left\{\tilde{t}_{ij}, \tilde{\alpha}_{ij}, \tilde{v}_{ij}, \tilde{T}_{ij}\right\}$ required in the estimation strategies as indicated previously. Note that data obtained by DSC before the cure started were used in the characterization of the inhibition time model which is not shown here. The rest of the data were used in the two estimation strategies S_v and S_α.

Estimation Procedure

For both strategies, the estimation of the kinetic parameters was proceeded as described in the following. Using large ranges for the kinetic parameters, two estimation were run for the three procedures, considering six and four parameters (without K_1), successively. The second run thus corresponded to the study of the simplified K&S model, which has a similar form to the equation suggested by Piloyan et al. (6). In these conditions, the numerical computation of the degree of cure required the initial value be set to a very small number. The objective functions obtained for these two initial runs were compared and the setting which provided the smallest sum of squares error was retained for subsequent trials. Note that even though the improvement of studying the complete K&S model over the simplified model was small, the simultaneous estimation of the six parameters was further investigated. This was in agreement with the motivation behind this work, which was the analysis of the complete K&S model. Following the choice between the complete and simplified model, four additional trials were conducted with the GA method, decreasing each time the parameter ranges used to generate the initial population. This ensured convergence towards the global minimum of the objective functions associated with the three estimation strategies. Eventually, the last run was considered to provide estimates, or a combination of estimates, that give a model close to the optimal one which can be reached with the K&S form.

Results and Discussion

Table 2 shows the detailed results obtained using the two estimation strategies S_v and S_α. For both strategies, the presence of the rate constant K_1 enables to better minimize the objective function, but slightly only. A look at the dimensionless sensitivity coefficients

Table 2: Detailed estimation results.

	Run	1	2	3	4	5	6
Strategy S_v	A_1 (min^{-1})	3.20×10^{14}	N/A	9.57×10^{6}	1.35×10^{20}	7.84×10^{10}	1.37×10^{15}
	E_1 (kJ/mol)	148.29		84.74	192.35	111.20	144.03
	$A_2 \times 10^{-9}$ (min^{-1})	8.08	11.63	7.69	5.14	6.28	5.89
	E_2 (kJ/mol)	78.61	80.00	78.35	76.94	78.12	77.40
	m	0.673	0.647	0.686	0.689	0.694	0.694
	n	1.774	1.771	1.790	1.787	1.786	1.786
	S_v (min^{-1})²	0.0734	0.0825	0.0730	0.0717	0.0708	0.0707
	$ITERG_f$	500	261	500	500	500	500
Strategy S_α	A_1 (min^{-1})	4.71×10^{45}	N/A	1.00×10^{40}	0.92×10^{37}	1.00×10^{37}	1.05×10^{37}
	E_1 (kJ/mol)	406.31		358.6	350.00	334.47	338.24
	$A_2 \times 10^{-10}$ (min^{-1})	1.37	1.49	1.36	1.35	1.35	1.35
	E_2 (kJ/mol)	80.68	80.95	80.66	80.64	80.66	80.66
	m	0.651	0.659	0.652	0.652	0.651	0.651
	n	1.586	1.594	1.586	1.586	1.584	1.584
	S_α	0.0954	0.0984	0.0953	0.0953	0.0952	0.0952
	$ITERG_f$	500	446	500	500	500	500

illustrated Fig. 4 and 5 for the curing at 15°C/min, indicates that both estimation procedures are much more sensible to the constant K_2 than to K_1, and more particularly, the sensitivity to the parameter A_1 is negligible. Furthermore, all coefficients are strongly linearly dependent as pointed out in Table 3 and Fig. 6. These ill defined estimation conditions make the GA method unable to converge before 500 generations which is the maximum number of generations allowed. This results in different combinations of the parameters that minimize as well the sum of squares error. Nevertheless, convergence towards solutions close to the global minimum is believed to be achieved. One can notice that the sensitivity coefficients from strategy S_v (Fig. 4) exactly represent the derivatives of those from strategy S_α (Fig. 5) in analogy with the fact that the cure rate is the derivative of the degree of cure. An interesting consequent feature is the magnification of all coefficients using strategy S_v.

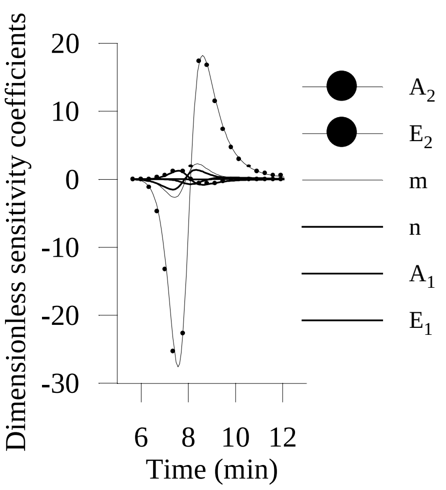

Figure 4: Dimensionless sensitivity coefficients with respect to the cure rate using estimates obtained with strategy S_v.

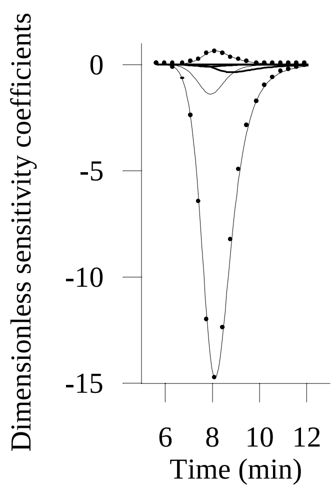

Figure 5: Dimensionless sensitivity coefficients with respect to the degree of cure using estimates obtained with strategy S_α.

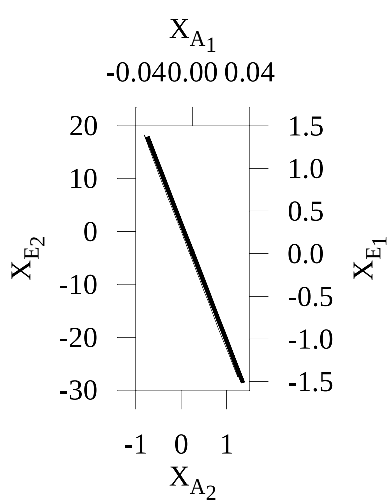

Figure 6: Linear dependence between dimensionless sensitivity coefficients represented in Fig. 4.

Table 3: Correlation matrices for the experiment at 15°C/min using the estimates obtained with both estimation strategies.

	Correlation Matrices					
Strategy S_v	1					
	0.99999889	1				
	-0.99292060	-0.99295367	1			
	0.98725702	0.98722365	-0.96308618	1		
	-0.97647893	-0.97636123	0.99062039	-0.93522729	1	
	-0.97662716	-0.97650803	0.99059672	-0.93553850	0.99999848	1
Strategy S_α	1					
	0.99999985	1				
	-0.99956251	-0.99957820	1			
	0.99975756	0.99974559	-0.99872098	1		
	0.98760610	0.98767961	-0.99155235	0.98468336	1	
	0.98754912	0.98762392	-0.99155332	0.98456435	0.99997955	1

With an aim to determining which estimation strategy should be used, Table 4 provides the values of the sum of squares errors S_v and S_α with their associated Root Mean Squares errors ($RMS = \sqrt{S / N_{tot}}$, $N_{tot} = \sum_{j=1}^{6} N_j$ given in Table 1) computed using both sets of final estimates (run number six). In addition, a third sum of squares error based on the cure rate as the measured quantity but computed using the experimental degree of cure data was calculated and is denoted by (S_v'). Note that the RMSs are also given as a percent of the maximum increase in the measured variable. The results show that the use of the kinetic parameter values estimated applying strategy S_v globally allows for the best minimization of the three objective functions. Indeed, on one hand, this set of estimates enables to generate cure rate data from both reconstructed (calculated using the Runge Kutta method) and experimental degree of cure data with a better fit than when using estimates obtained applying strategy S_α. On the other hand, it induces an RMS error associated with the degree of cure as the measured quantity below 2%. Figures 7 and 8 illustrate the reaction rate and degree of cure simulated using the K&S estimates obtained applying strategy S_v. As one can see, the K&S model is an appropriate choice for the kinetic characterization of the epoxy resin.

In order to appreciate the relative importance of the rate constant K_1, simulated isothermal cure rate data are plotted in Fig. 9 as a function of degree of cure. As one can see, no deviation in the cure rate initial values is encountered as temperature increases indicating thus a negligible effect of the constant K_1. This behavior is in good agreement with the information provided by the sensitivity coefficients.

Table 4: Summary and comparison of results using estimates obtained with both strategies.

	S_v (min^{-1})^2	**RMS_v (min^{-1})**	**RMS_v (% [Δv_{max}]$_{av}$)**	**(S_v)' (min^{-1})^2**	**RMS_v' (min^{-1})**	**RMS_v' (% [Δv_{max}]$_{av}$)**	**S_α**	**RMS_α**	**RMS_α (% $\Delta\alpha_{max}$=1)**
S_v	**0.07**	**0.0075**	**2.07**	0.19	0.0123	3.41	0.35	0.0167	1.67
S_α	0.147	0.0108	3.00	0.24	0.0138	3.81	**0.10**	**0.0087**	**0.87**

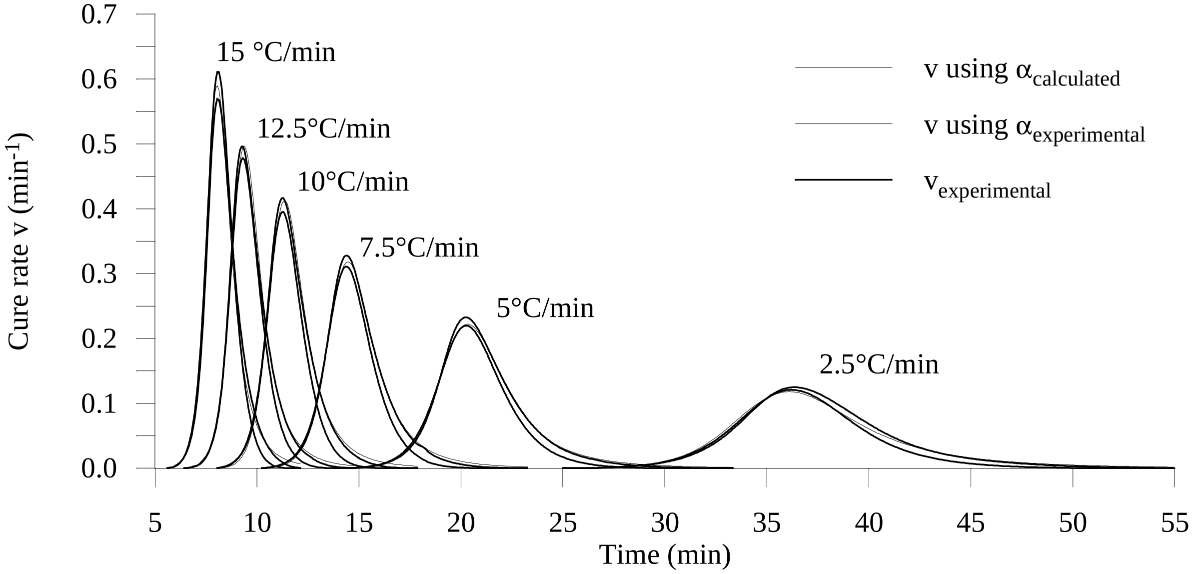

Figure 7: Simulation of the cure rate using estimates obtained with strategy S_v.

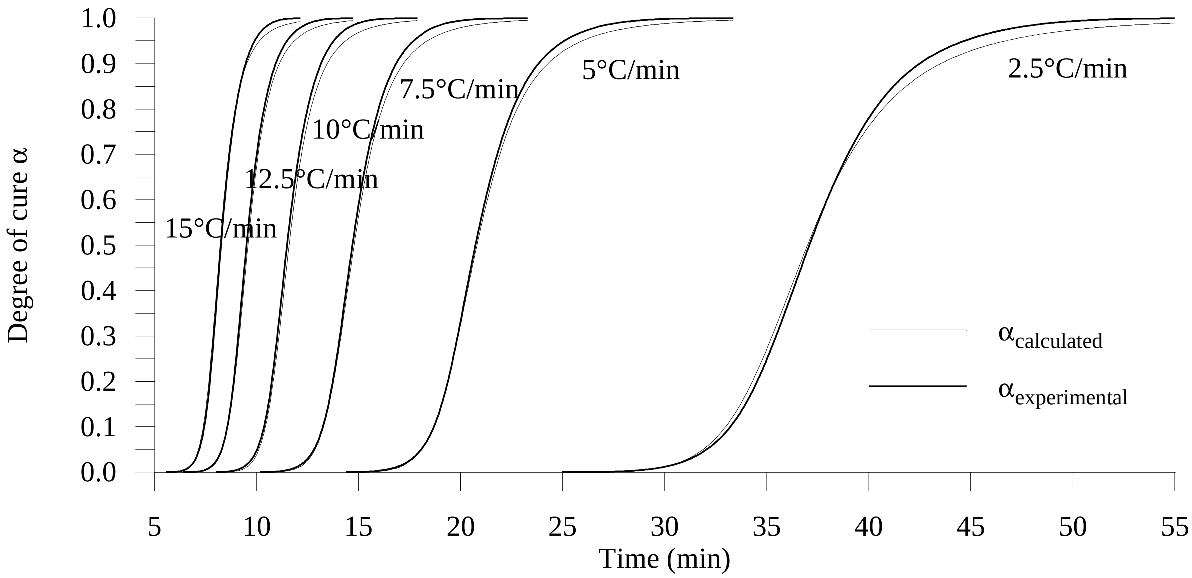

Figure 8: Simulation of the degree of cure using estimates obtained with strategy S_v.

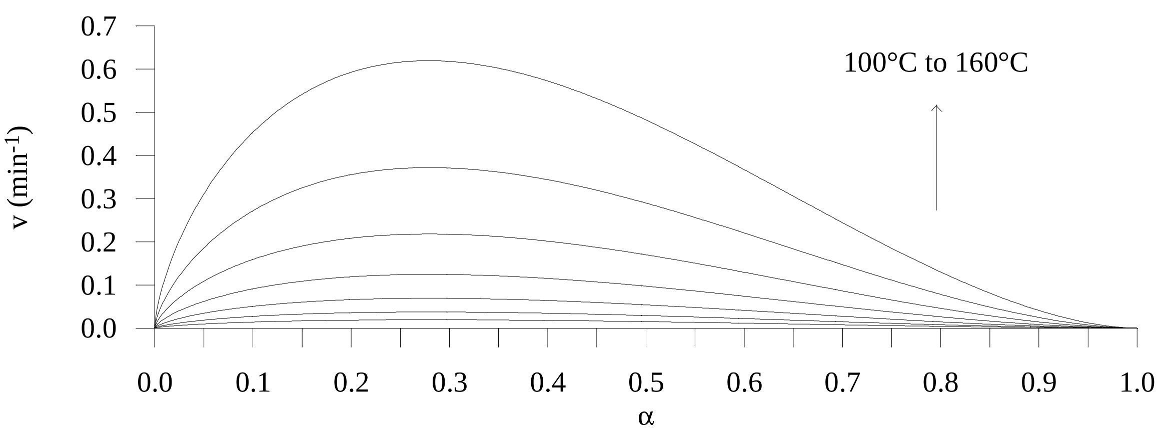

Figure 9: Simulation of isothermal cure rates using estimates obtained with strategy S_v.

SUMMARY AND CONCLUSION

This works presents the kinetic characterization of an epoxy resin using the Kamal and Sourour (K&S) model. The estimation procedure based on Genetic Algorithms allowed for the simultaneous estimation of the six parameters inherent to the K&S model, and this despite the strong ill-defined identification conditions. These latter included both a nearly negligible sensitivity to the rate constant K_1 representing the catalytic nature of the curing and strong linear dependences among all sensitivity coefficients. The results support that the proposed GA procedure is an effective tool in the simultaneous estimation of correlated parameters.

Two estimation strategies were investigated. The strategy based on the cure rate as the measured quantity provided globally better results than the one based on the degree of cure.

The K&S model seemed adequate for the epoxy compound. However, regarding the significance of using the complete K&S model, this study reveals that the rate constant K_1 could have been neglected. This implies that a model based on the separation of the dependent variables T and α could have been used. In this case, the model from Jarny et al. (7) in the form $F(T)\times G(\alpha)$ is thought to be a potential alternative to the K&S model.

NOTATION

$A_{1,2}$,	Arrhenius contants (min^{-1})
$E_{1,2}$	Arrhenius contants (kJ/mol)
F	Kinetic function
$K_{1,2}$	Rate constants (min^{-1})
m, n	Kinetic exponents
n_g	Generation number (Fig. 1)
n_s	Population size (Fig. 1)
N_I	Observation number
N_j	Experiment number
R	Gas constant
RMS	Root Mean Squares error (unit of corresponding S)
S	Least Squares error
t	Time (min)
T	Temperature (K)
v	Cure rate, $d\alpha/dt$, (min^{-1})
X	Dimensionless sensitivity coefficients
α	Degree of cure
$\underline{\beta}$	True parameter vector
Δv_{max}	Maximum increase in cure rate (min^{-1})

Subscript

I	Observation
j	Experiment
v	Considering cure rate as the variable
α	Considering degree of cure as the variable

Superscript

$\tilde{}$	Experimental data

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KEY WORDS

Kamal and Sourour kinetic model
Degree of cure
Cure rate
Thermosetting material
Differential Scanning Calorimetry
Dynamic data
Least Squares error
Simultaneous estimation
Correlation
Sensitivity
Genetic algorithm