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A new mathematical approach for determining kinetic parameters of curing process

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Abstract: We proposed a new algorithm (GMN) for determining pre-exponential and activation energy of curing process. This method is based on the combination of tanh fitting for the measured conversion values via least squares minimization technique and linear fitting for the kinetic parameters. Experimentally determined differential scanning calorimetry (DSC) data sets for an epoxy resin functionalized by single wall carbon nanotubes are used for the verification of the proposed method. The results obtained from the proposed algorithm are also compared with the methods reported in the literature.

Keywords: Computational material science, Numeical methods, Numerical simulation.

1 Introduction

Epoxy resins are extensively used in industry due to their good bonding adhesion to a variety of surfaces and a high chemical and thermal resistance [1],[2]. Since these materials can protect metals against corrosion, they have been employed for coating of internal and external surfaces of pipes [3]. Epoxy resin is mixed with its curing agent and curing process takes place in proper conditions to achieve the desired properties. Knowing the curing kinetics of epoxy can improve and enhance coating quality. There are different techniques to study the curing kinetic of thermosetting resins. Differential scanning calorimetry (DSC) is one of the most common and most accurate methods [4,6] in studying such processes. In the kinetic analysis of a chemical reaction such as resin curing, a mathematical equation between the conversion, conversion rate, and temperature is established [7]. Most of studies employ the model-fitting methods at nonisothermal conditions [8,9]. Although the model-fitting procedure is almost reliable for practical purposes, it does not provide a deep understanding of the detailed reaction mechanism [2]. Although, the most complex kinetics models cannot cover all the complexities of the reactions, to enhance the accuracy, the isoconversional method is recommended for analysis of reaction kinetics [7,10]. Isoconversional methods explain the kinetics of the curing process using several single-stage equations. Each of these equations is related to a specific range of conversion [7] and only one of them will determine the overall kinetics in each region [11]. In isoconversional methods, without considering any specific form of the reaction model, activation energy at a given extent of the conversion can be achieved. By obtaining the dependence of activation energy, kinetics analysis can be performed and a reliable prediction of the kinetics parameters could be provided [12]. Although, for analysis of dynamic data, model-free method is recommended [7], model-fitting method in complex models such as Kamal which can be used for practical applications is reliable as well. To our knowledge, there is no kinetics analysis on a specific epoxy based resin used for pipe lining. Therefore in this study, initially, an advanced model-free method was used. Then, Kamal model was applied to the dynamic data and its parameters were obtained by performing a simple fitting using genetic algorithm. At the end, the ability of both methods to predict the curing behavior of this epoxy resin was investigated.

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2 Kinetic Model

Curing reaction of an epoxy resin is an exothermic reaction. In the DSC measurements, the degree of cure α ranges from 0 (completely uncured) to 1 (fully cured) and is defined as follows:

$$\alpha = \frac{\Delta H_t}{\Delta H_R} \tag{1}$$

$$\frac{d\alpha}{dt} = \frac{(dH/dt)_t}{\Delta H_R} \tag{2}$$

where H_t is the amount of heat released in time t. $(dH/dt)_t$ is the rate of the heat generation and ΔH_R is the total heat of reaction.

It is commonly accepted in the kinetic analysis of chemical reactions by thermal analysis that any chemical process of reaction will obey a rate law of the form

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{3}$$

where $\frac{d\alpha}{dt}$ is the rate of reaction, $k(T)$ is the temperature dependent rate constant, and $f(\alpha)$ corresponds to the reaction model [15]. The temperature dependence of the reaction rate is generally defined through an Arrhenius expression [14]:

$$k(T) = A\exp(-\frac{E}{RT}) \tag{4}$$

where A is the pre-exponential factor, E is the activation energy, R refers to the universal gas constant and T corresponds to the absolute temperature. When the process is isothermal, the temperature is constant, but in the nonisothermal process the temperature usually increases according to a constant heating rate

$$\beta = \frac{dT}{dt} \tag{5}$$

where β is the heating rate. Combining the Eq. (3), (4) and (5) yields a resulting equation for non-isothermal conditions:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp(-\frac{E}{RT})f(\alpha) \tag{6}$$

Therefore, if the reaction model which describes the data is known, the conversion obtained at a given temperature or heating rate can be predicted using the above equations.

3 Experimental

In this study, single-wall carbon nanotubes (SWCNTs) were supplied from Pinhas Inc., Turkey. SWCNTs were manufactured by TUBALL^{TM}, Luxembourg. The outer mean diameter of SWCNTs is below 2 nm, and their length is higher than $1\mu n$. It contains high quality of SWCNT (G/D ratio $>$ 90) with an iron content of less than 15%. The resin system used consisted of solvent-type epoxy F- RES21. The viscosity of the resin is 400-650 mPa.s at 25 $^\circ C$. 800 tex carbon fiber (A-49 filaments) were provided from DowAksa Inc., Turkey, and used as reinforcing constituent.

Temperature variations during curing determine the degree of cure of the prepreg system. The degree of curing is highly dependent on the heat of reaction. The results of the DSC experiments are heat flux curves with respect to time and temperature. Samples consisting of $3-6$ mg mixtures were placed in aluminum pans. and 50mL/min of N2 purge in DSC 50. Dynamic scans for each sample were performed at different heating rates $2.5, 5, 10$ and 20 $^\circ C$/min) from room temperature up to 250 $^{\circ}C$ in a N2 atmosphere. The upward peaks formed in the DSC thermograms show that the reaction is exothermic.

4 A new numerical approach: Nonlinear fitting

Suppose that the experimental data $T = [a_1, a_2 \dots, a_n]$ and $\alpha = [b_1, b_2, \dots, b_n]$ temperature and conversion are given. Consider the activation function as follows:

$$\alpha(T) = A(\tanh(B(T_n - C) - 3) + 1) \tag{7}$$

where A, B and C are unknowns. We want to fit a function which has a form in Eq.(7). For this purpose, the nonlinear least square method is used.

4.1 Nonlinear least-squares data fitting

In this section we will explain nonlinear least square briefly. Error between the experimental result and and activation function is defined by the following function

$$E(A,B,C) = \sum_{n=1}^{N} (y_n - A(\tanh(B(T_n - C) - 3) + 1))^2 \tag{8}$$

Requirement of the nonlinear least square procedure is to find a minimum of error function. To find minimum, we set

$$\frac{\partial E}{\partial A} = 0, \qquad \frac{\partial E}{\partial B} = 0, \qquad \frac{\partial E}{\partial C} = 0. \tag{9}$$

Partial derivative of $E(A,B,C)$ with respect to A, B and C are

$$\begin{aligned}
\frac{\partial E}{\partial A} &= \sum_{n=1}^{N} 2(-\tanh(B(T_n - C) - 3)(y_n - A(\tanh(B(T_n - C) - 3) + 1)),\\
\frac{\partial E}{\partial B} &= \sum_{n=1}^{N} 2AB(\operatorname{sech}(B(T_n - C) - 3)^2)(y_n - A(\tanh(c_1(T_n - c_2) - 3) + 1)),\\
\frac{\partial E}{\partial C} &= \sum_{n=1}^{N} -2AB(\operatorname{sech}(B(T_n - C) - 3)^2)(y_n - A(\tanh(B(T_n - C) - 3) + 1)).
\end{aligned} \tag{10}$$

Combining (9) and (10), we obtain system of nonlinear equation as follows:

$$0 = \sum_{n=1}^{N} (-2\tanh(B(T_n - C) - 3)y_n + 2A\tanh(B(T_n - C) - 3) + 2A\tanh(B(T_n - C) - 3)^2), \tag{11}$$

$$0 = \sum_{n=1}^{N} (2AB(\operatorname{sech}(B(T_n - C) - 3)^2 y_n - 2AB\tanh(B(T_n - C) - 3)\operatorname{sech}(B(T_n - C) - 3)^2 - 2AB\operatorname{sech}(B(T_n - C) - 3)^2), \tag{12}$$

$$0 = \sum_{n=1}^{N} (-2AB\operatorname{sech}(B(T_n - C) - 3)^2 y_n + 2AB\operatorname{sech}(B(T_n - C) - 3)^2 \tanh(B(T_n - C) - 3) + 2AB\operatorname{sech}(B(T_n - C) - 3)^2). \tag{13}$$

When the partial derivative in Eq. (11), (12) and (13) are set equal to zero, the nonlinear system of equations are obtained. We use the Newton Method find the A, B and C. Iterative formula of Newton Method for nonlinear systems is given as follows:

$$z^{k+1} = z^k - J^{-1}(z^k)\begin{pmatrix} F(z^k) \\ G(z^k) \\ S(z^k) \end{pmatrix} \tag{14}$$

where $z^k = \begin{pmatrix} A^k \\ B^k \\ C^k \end{pmatrix}$ and J^{-1} is the inverse of the of the Jacobian matrix,

$$J(z) = \begin{pmatrix} \frac{\partial E}{\partial A} & \frac{\partial E}{\partial B} & \frac{\partial E}{\partial C} \\ \vdots & \ddots & \vdots \end{pmatrix}.$$

To start the Newton’s iterative method, an initial condition is needed. For convergent A, B, C values we choose appropriate initial condition, $z^0 = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$.

For calculations, Matlab solver is used. Finally we obtain the unknown as $A = 0.5$, $B = 0.0765$, $C = 358.3126$
Fig.1 shows the experimental conversion $\alpha(T)$ values and least square approximation of $\alpha(T)$ the activation function.

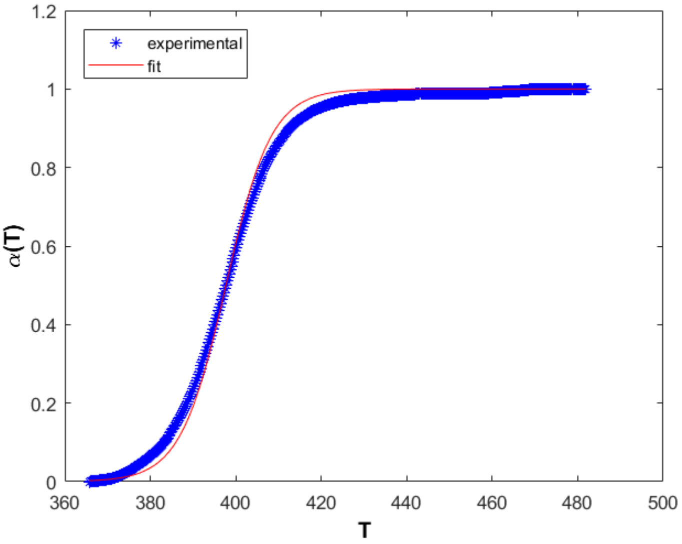

Fig. 1: Temperature and conversion (α) values are plotted from experimental data and activation function which is used fitting.

4.2 Data linearization technique

In this section, we will seek values of pre-experimental factor A and activation energy E which are given in Eq.(6). In Eq.(6), there is 4 unknows and they are A, E, α and $f(\alpha)$.

$\alpha(T)$ is obtained in previous section approximately. In the literature there are different choice of $f(\alpha)$. For the model most suitable choice is

$$f(\alpha) = \alpha^m(1-\alpha)^n$$

where m,n are pozitif real numbers. As a result, there are only two unknowns A and E in Eq.(6). To find these unknowns, data linearization technique is used.

The first step is to take the logarithm of both sides of the Eq.(6)

$$\ln\left(\frac{\beta}{f(\alpha)}\right)+\ln\left(\frac{d\alpha}{dT}\right)=\ln(A)-\frac{E}{RT}. \tag{15}$$

This results in a linear relation between the new values X and Y:

$$Y=\bar{A}+EX \tag{16}$$

where

$$\begin{aligned} Y&=\ln\left(\frac{\beta}{f(\alpha)}\right)+\ln\left(\frac{d\alpha}{dT}\right),\\ \bar{A}&=\ln(A),\\ X&=-\frac{1}{RT}. \end{aligned}$$

To calculate this unknowns, linear fitting method is used. In Table 2, E and $\bar{A}$ values are given for different samples.

Sample No	β	A	B	C	E	$\ln(A)$
1	2.5	0.5	0.0765	358.3126	89.8749	22.2212
1	5	0.5	0.0767	367.8309	85.5814	20.9993
1	10	0.5	0.0608	368.3936	73.3774	17.3604
1	20	0.5	0.0564	377.0870	70.3343	16.4869
2	2.5	0.5	0.0732	356.5693	82.7869	20.0338
2	5	0.5	0.0619	359.3702	71.0760	16.4988
2	10	0.5	0.0558	365.7544	66.7037	15.3149
2	20	0.5	0.0509	374.5726	69.8242	16.2947
3	2.5	0.5	0.0669	352.6327	73.1902	17.1211
3	5	0.5	0.0627	358.7051	68.1392	15.6939
3	10	0.5	0.0545	364.2501	63.2666	14.2895
3	20	0.5	0.0515	375.6366	64.49896	14.6932
4	2.5	0.5	0.0651	353.4174	73.7206	17.7973
4	5	0.5	0.0616	361.2695	76.1108	17.9529
4	10	0.5	0.0596	369.6381	73.5011	17.3437
4	20	0.5	0.0561	380.6521	73.1449	15.7400

Table 1: A, B, C obtain from nonlinear fitting and Data Linearization Technique provide getting E, $\ln(A)$ for different β.

Sample	Kissinger		KAS*		GMN	
No	E	$\ln(A)$	E	$\ln(A)$	E	$\ln(A)$
1	73.6	13.6	$75.5-61.5$	$15.2-10.38$	73.3774	17.3604
2	66.3	11.3	$69.0-54.3$	$13.3-8.2$	66.7037	15.3149
3	68.1	11.8	$61.1-51.6$	$10.6-7.8$	63.2666	14.2895
4	70.8	12.6	$64.9-68.6$	$11.6-10.6$	73.1449	15.7400

Table 2: Comparison of the optimum values of GMN method to with Kissinger and KAS* method.

Kissinger method gives average of activation energy for whole process containing all α values.

*The KAS method is an isoconversional method and changes depending on α. The range given in the table shows the values corresponding to the α value starting from 0.1 and reaching the value 0.9 with 0.05 increments.

5 Result and discussion

In this study, the non-isothermal curing behavior of an epoxy resin was studied by differential scanning calorimetry. Kinetic analysis was performed by a new mathematical approach based on the nonlinear least square fitting a tanh function and lumbarization method. This new algorithm is called as a GMN method. Experimentally determined differential scanning calorimetry (DSC) data sets for an epoxy resin functionalized by single wall carbon nanotubes are used for the verification of GMN method. The results obtained from the GMN algorithm are also compared with the methods reported in the literature. Finally, GMN algorithm was in good agreement with experimental data for calculation of the kinetic parameters.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

All authors have contributed to all parts of the article. All authors read and approved the final manuscript.

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