An Application of Non-Linear Regression Analysis for Predicting Cure Kinetic Model Parameters of Rubber Industry

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Abstract:

This paper presents a methodology to analyze a complex non-linear regression analysis for predicting the cure kinetic model parameters of rubber compounds. A potent approach is brought here to use the applicability of the 'SOLVER' function accessible in Microsoft (MS) Excel spreadsheet. In this present approach, a repetitive calculating process was proposed for minimizing the data error to achieve the optimal goodness of fit between experimental data and predicted data using an autocatalytic model. Curemeter is used to get a set of real data (torque- time) and is compared with the predicted data. The predictions of kinetic parameters using the model are close to experimental results. Therefore, the MS Excel Spreadsheet approach is an available tool for predicting cure kinetic model parameters.

Keywords: cure kinetics, Non-Linear Regression, rubber, and SOLVER.

1. Introduction

Rubber is a material, which exhibit properties of elasticity, viscosity to sustain deformation up to 1000 percent and quickly retracting to its original dimensions. The raw form of rubber is latex and harvested from the rubber tree by forming incisions on the bark; the collected fluid is milky in color, sticky and colloidal in nature. After refining process the raw form, is made suitable for commercial use. The vulcanized rubber [1] is the most commercially used form of rubber, which is brought to vulcanized form by the process called vulcanization. This process involves the formation of chemical and physical bonding between the macromolecules of rubber that results to vulcanizate mesh, and responsible for the properties of rubber [2]. Curing is a unique process and need to be determined to ensure the characteristics of the processed rubber; it is evaluated by a device called Curemeter gives a continuous cure curve and measures the development of torque with time at a predefined temperature [3].

The below **Figure 1** depicts the cure curve for sulfur vulcanization with three marked regions. The first region is induction period, second region is the curing reaction period and the third region is over curing period. Induction time provides a safe processing time; formation of cross- link network takes place in curing reaction period, which causes the stiffness of rubber; over curing region occurs as reversion, equilibrium, or marching cure behavior.

The Various methods are available to measure the cure kinetics of rubber [4] and among those the most preferred method is rheometer. The parameter such as k (T), m & n can be determined from the autocatalytic kinetic model.

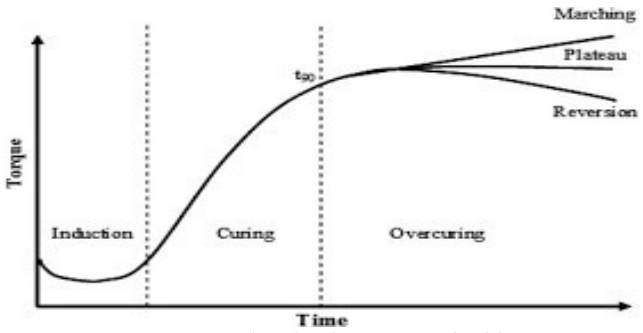


Figure.1. Vulcanization curve of rubber

The traditional method called least squares method used for calculating or predicting kinetics parameters of the most fitted models by converting the equation into a conventional linear form. The experimentally obtained data having the magnitude coefficients near to unity generally prefer these types of models in order to achieve goodness of fit [5].

A non-linear form of kinetic model is required to address the present context that can have an error analysis. Intervention of computer or artificial intelligence (AI) makes analysis of the data with great ease and fitting of data with simple functions such as a linear regression as compared to non-linear functions, which is more complicated. Another cost effective option is Microsoft Excel to fit non-linear functions as it is incorporated in the computer platform of Microsoft Office. It consists of an unique function called SOLVER, which ideally suits to fit the data with non-linear functions through an repetitive calculating process [6], which enables minimization of sum of the square differences among experimental data and predicted data. The purpose of this approach in the present study is to proposing and describing a approach of non-linear regression using the SOLVER function of Excel to predict the cure kinetic factors for the autocatalytic model.

2. Research Methodology

The followed methods which are described in this paper are: (i) prediction of the optimum values of cure kinetic parameters, (ii) finding out high fitness, and (iii) predicting the cure curve close-fitting with experimental values using Solver function. On this occasion, the formulated algorithm is carried out and the predicted curve is superimposed on the experimental data points. Degree of fit of predicted data is also calculated in order to measure the accuracy of fitting.

2.1 Model:

The isothermal cure kinetics for an autocatalytic reaction can be termed as below:

$$\mathbf{r} = \frac{\mathbf{d}\alpha}{\mathbf{dt}} = \mathbf{k(T)}\ \alpha^{\mathbf{N}}\ (\mathbf{1}-\alpha)^{\mathbf{n}} \qquad \mathbf{(1)}$$

Where ‘r’ is the rate of reaction; ‘k’ is the rate constant, N is the conversion (fractional), m and n are reaction orders of autocatalytic reaction, which is independent of temperature. The value of k(T), m and n was calculated using nonlinear regression fitting. The temperature dependency of the conversion rate is expected to lie in the constant (k) within the Arrhenius equation:

$$\mathbf{K} = \boldsymbol{Ae}^{-\frac{\boldsymbol{E}}{\boldsymbol{RT}}} \qquad \mathbf{(2)}$$

Where, A is pre-exponential factor, E_a is activation energy, R is the gas constant, and T is reaction temperature.

2.2 Goodness of fit:

Goodness of fit is a fundamental parameter that estimates how fit the curve (i.e. the predicted curve) set forth the data obtained by experiment. The traditional way is to change the non-linear data into a linear data which was then analyzed by

least square fit method. There are chances of errors arise due to inaccuracy in the measurements and predictions of the data. The data that cannot be described by a linear function are used with a protocol that makes the data suitable to fit into a form of non-linear function. The adaptable process for this protocol is known as iterative nonlinear least squares fitting. This adapted process will satisfy the desired goal which is used for linear regression, that is minimization of the value of difference between the sums of squared of experimental and the predicted data [11]. The initial parameters are assumed; based on best of the knowledge acquired by the set of experiments data and on a practical guess to fit the data. The following parameters are measured and arbitrated the goodness of fit: The concept of sum of square (SS) is the best fit of the given data is generated by taking the sum of squares and the least value can be obtained by the sum of squares is the best given data that fits in the identified model [12]. This is described by the function:

$$\mathbf{SS} = \sum_{\mathbf{i=1}}^{\mathbf{n}} [\propto_{\mathbf{Exp}} - \propto_{\mathbf{Model}}]^{\mathbf{2}} \qquad \mathbf{(3)}$$

Where, α_{exp} is obtained from the experimental data, α_{model} is the prediction from the model for curve at corresponding time t. In this model sum of square value is based on the guess (initial) parameters and second one is the variation in the values by minor changes in the quantity and which can be re-calculated by the sum of square concept. This process is repeatedly works on until a smallest possible value of SS is achieved. SOLVER is a reliable generalized reduced gradient (GRG) method and can be used as a simple iteration protocol. Its broad explanation about evolution and process is cited in the literature [8].

3. Results and Validation of Model

Cure meter works on the principle of applying cyclic strain to a test sample and measuring the respective force associated with it. The test process is a measure of an increase in the stiffness (modulus) of the test sample with respect to time. A typical data set collected from an experiment is given below in **Table-I.** Typical units used are: time (t) in minutes and torque(S) in dN-m. The degree of conversion (α) in curing reaction is defined as follows:

$$\propto = \frac{\mathbf{S_t - S_{Min}}}{\mathbf{S_{Max} - S_{Min}}} \qquad \mathbf{(4)}$$

Where, S_{min} reflects minimum torque value, S_t is the value of torque at given time of curing, and S_{max} is the maximum torque value.

Table-I: The experimental data over the time period

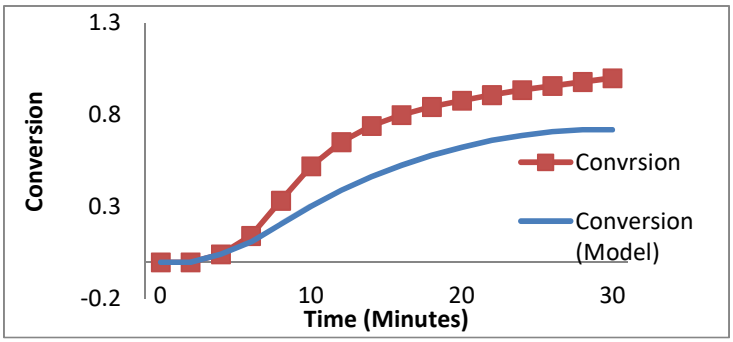
Time(Minutes)	Torque[dNm]	Conversion	Delta Conversion	Conversion (Model)	Delta Conversion (Model)	Error	Square of Error
0	0	0	0	0	0	0	0
2	3	0	0	0	0	0	0
4	3.36	0.0431138	0.0431138	0.0431138	0.03805671	0.00506	0.0000256
6	4.2	0.1437126	0.1005988	0.1097644	0.07170771	0.03395	0.001152
8	5.79	0.3341317	0.1904192	0.2070469	0.09728248	0.12708	0.016151
10	7.35	0.5209581	0.1868263	0.3046255	0.09757843	0.21633	0.0468
12	8.46	0.6538922	0.1329341	0.3908529	0.08622757	0.26304	0.06919
14	9.19	0.7412174	0.0874251	0.4645058	0.07365287	0.27681	0.076625
16	9.69	0.8011976	0.0598802	0.5270165	0.06251071	0.27418	0.075175
18	10.05	0.8443114	0.0431138	0.5800659	0.05304939	0.26425	0.069826
20	10.33	0.8778443	0.0335329	0.6247913	0.04472546	0.25305	0.064036
22	10.59	0.908982	0.0311377	0.6608831	0.03609177	0.2481	0.061553

24	10.82	0.9365269	0.0275449	0.6884227	0.02753956	0.2481	0.061556
26	11	0.9580838	0.0215569	0.7084545	0.02003183	0.24963	0.062315
28	11.18	0.9796407	0.0215569	0.7198471	0.01139261	0.25979	0.067493
30	11.35	1	0.0203593	0.7198471	0	0.28015	0.078486

The non-linear regression is the iterative procedure. In this process these needs to be initialize the initial value for each parameter. While choosing standard equation, program may provide the initial values automatically. The initial guess value of the kinetic parameters

K	0.13
M	0.6
N	0.8
S	0.7504

Data is plotted i.e. the values of t (x axis) vs. α (y-axis) obtain a graph, which provides the information about how degree of cure (conversion) changes with time at constant temperature.



Graph.1. Exponential graph of conversion and fitted model

The exponential **graph-1** of above model represents the conversion values at the initial parameters changes uniformly with respect to the time at constant temperature. From the graph it implies that traditional model of conversional values (∝) increases with respect to the time continuously over the period. It is proposed to use the following mathematical function (or model) for this purpose [9, 10]:

$$\mathbf{r = \frac{d\alpha}{dt} = k(T)\ \alpha^{N}\ (1-\alpha)^{n}} \qquad \mathbf{(5)}$$

where k, m and n are known as model parameters. There is not much difference, except the function is not a straight line rather a bowline, which is called as a "non-linear" function. If the value of k, m and n are known, we can "predict" the value of α for any given value of t. The guessed model parameters should be close to: **k = 0.13, m =0.6 and n = 0.8**. The mathematical model is used in Microsoft Excel for programming and predicting between guess values at fixed parameters and which is compared with against the experimental data is facilitated. The **Graph.1.** below represents the predictions appears to be in increasing trend, but the predictions does not fit the given data points well. It represents the bad fit to the given data points by calculating the absolute error between predictions and actual data. To minimize the error between both the data points the nonlinear regression model is the best fit in this approach point-by-point till end of the analysis.

Table-II: Non-linear regression and the built-in 'Solver' functions for executing the programmed algorithm.

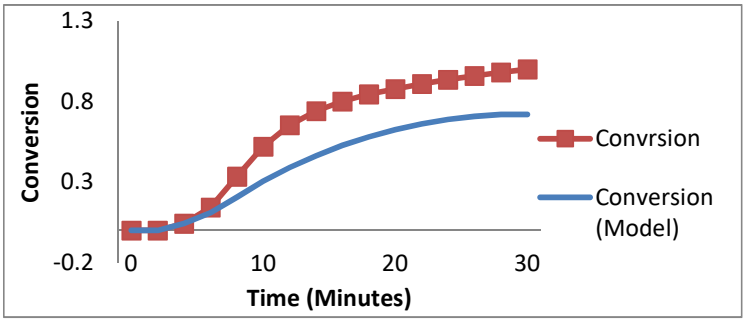
Time(Minutes)	Torque[dNm]	Conversion	Conversion (Model)
0	0	0	0
2	3	0	0
4	3.36	0.0431138	0.0431138

6	4.2	0.1437126	0.1097644
8	5.79	0.3341317	0.2070469
10	7.35	0.5209581	0.3046255
12	8.46	0.6538922	0.3908529
14	9.19	0.7412174	0.4645058
16	9.69	0.8011976	0.5270165
18	10.05	0.8443114	0.5800659
20	10.33	0.8778443	0.6247913
22	10.59	0.908982	0.6608831
24	10.82	0.9365269	0.6884227
26	11	0.9580838	0.7084545
28	11.18	0.9796407	0.7198471
30	11.35	1	0.7198471

The initial guess value of the kinetic parameters while using excel solver function

K	0.13
M	0.6
N	0.8
S	0.7504

From the above results of the **table I** and **II** exhibits the similar results from fitted model and using excel Solver function is identified. This reflects that for predicting rubber in a firm using non-linear regression Solver is the best approach for prediction and estimation of parameters, and which gives better results.



Graph.2. Exponential graph of conversion and fitted model

An easy approach to improve the fit is to play with the guess values. Following are the steps:

1) **To:** Selected Min button.

2) **Set objectives:** B24 set as a target. This simply implies your target is to minimize the value in cell B24.

3) **Changing of the variable cells:** You are asking the computer to vary these three parameters, in the cells B21, B22 and B23.

4) **Subject to constraints:** If need, implement the constraints on the values of model parameter.

5) Select GRG Non-linear, which is the default value

6) The click on solve.

SOLVER will automatically find the correct results and update the values of k, m & n (in cells B21, B22& B23) and

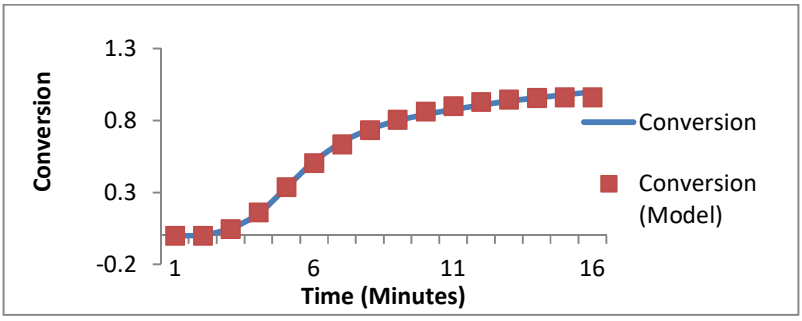
end result is a good-looking fit. It is seen that low total error in B24.The continuous dark line in **Graph.2.** demonstrates the best fit and it is found that it is an enhancement over the fit offered by the initial kinetic parameter values. It is found that the MS Excel SOLVER function - spreadsheet process achieved all the statistical measures to predict the real variance of probability of data obtained from the experiment.

Table-III: The sheet shows predicted parameters and fitted data curve along with experimental data curve

Time (Minutes)	Torque [dNm]	Conversion	Delta Conversion	Conversion (Model)	Delta Conversion (Model)	Error	Square of Error
0	0	0	0	0	0	0	0
2	3	0	0	0	0	0	0
4	3.36	0.0431138	0.0431138	0.0454727	0.04547269	-0.00236	0.00000556
6	4.2	0.1437126	0.1005988	0.1614764	0.11600373	-0.01776	0.000316
8	5.79	0.3341317	0.1904192	0.3374658	0.17598888	-0.00333	0.0000111
10	7.35	0.5209581	0.1868263	0.5045457	0.16705037	0.01644	0.00027
12	8.46	0.6538922	0.1329341	0.6355916	0.13107596	0.0183	0.000335
14	9.19	0.7413174	0.0874251	0.7338762	0.09828456	0.00744	0.0000554
16	9.69	0.8011976	0.0598802	0.8072159	0.07333972	-0.00602	0.0000362
18	10.02	0.8443114	0.0430038	0.8621123	0.05489636	-0.0178	0.000317
20	10.33	0.8778443	0.0335329	0.9028117	0.04069938	-0.02497	0.000623
22	10.59	0.908982	0.0311377	0.9308063	0.02799464	-0.02182	0.000476
24	10.82	0.9365269	0.0275449	0.9483027	0.01749369	-0.01178	0.000139
26	11	0.9580833	0.0215569	0.9583811	0.01007842	-0.0008	8.84E-08
28	11.18	0.9796407	0.0215569	0.9621801	0.00379898	0.01746	0.000305
30	11.35	1	0.0203593	0.9621801	0	0.03782	0.00143

Final guess value of curve kinetic parameters

K	0.4158
M	0.9051
N	1.379
5S	0.0045



Graph.3.Exponential graph of conversion and fitted model using SOLVER

From the above **Graph.3.** can conclude that the conversion values (∝) and solver model are coincident one to other. This represents the best fit to the model using Solver and mathematical model of nonlinear regression at kinetic approach. In addition to that the conversion values of the parameter (∝) is increases over the time with respect to constant temperature is observed.

4. Conclusions

The Autocatalytic model is an important cure kinetics model to predict the cure kinetic parameters. In this perspective, non-linear modelling is a potential technique for standardization of the experimental data. It is important that the data is fit in the model, for its analysis, and to arbitrate goodness of fit from computed estimate data. The MS Excel Solver function-spreadsheet technique shows robust results in terms of well-fitting of experimental data with a considerable high degree of fitness.

Acknowledgments

I would like to thank Prof. M. Krishna Reddy for his insightful comments and revisions that helped this article to be of higher calibre.

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