Interactive GUI Software for Natural Rubber Vulcanization Degree Numerical Prediction

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Abstract: A graphical user interface software called GURU suitable to fit rheometer curves in Natural Rubber (NR) sulphur vulcanization is proposed. Experimental data are loaded using Excel (experimental output comes from a moving die rheometer registration), normalized and fitted with a numerical model that follows the general scheme proposed by Han. Han's chemical model translates into mathematics by means of a first order ODE system, admitting a closed form solution for the crosslinking density. Three kinetic constants characterize the model and they must be found in such a way to minimize the absolute error between normalized experimental data and numerical predictions. GURU works to minimize the error by means of a trial and error procedure handled interactively by means of sliders, assigning a value for each kinetic constant and a visual comparison between numerical and experimental curves. An experimental case of technical relevance is shown as benchmark.

1 INTRODUCTION

The numerical study of Natural Rubber (NR) vulcanization with sulphur and accelerants is still a very challenging task. This is probably the reason why, despite the first utilization of vulcanized NR dates back to the second half of 19th century, the development of efficient numerical tools in standard curing conditions is still under study.

As well known in industrial practice, the most diffused laboratory device able to give operative information of the curing degree is the so called rheometer test. A rheometer is machine constituted by a chamber with either a fix and a moving part (MDR) or an oscillating disc inside (ODR), where a small rubber sample is cured at constant cure temperature and the torque applied to maintain a constant rotation of the moving part (moving die or oscillating disc) is measured.

Typically for NR vulcanized with sulphur torque generally slightly decreases during a so called "induction" period of time, followed by a significantly fast increase. Very frequently, in presence of sulphur, reversion is observed. Reversion is macroscopically a drop of the torque near the end of vulcanization. It occurs typically at high temperatures and it is commonly accepted to be a consequence of the degradation of polysulfidic (S-S or more) crosslinks (Milani and Milani, 2012; Tanaka, 1991; Coran, 1978).

In practice, it has been observed that the importance of the reversion depends strictly on curing temperature. Nevertheless, recent results, e.g. by (Leroy et al., 2013) and (Milani et al., 2011; 2013; 2014; 2015) tend to demonstrate that the ratio between thermally stable (short) and unstable (long) polysulfidic crosslinks is not significantly influenced by cure temperature.

Literature in the field of NR vulcanized with sulphur is certainly dated and superabundant, especially from an experimental point of view (Poh et al., 1996; 2001; 2002). Also, several kinetic models are at present available. Some of them are only phenomenological, essentially basing on experimental torque curve fitting (Kamal and Sorour, 1973; Milani and Milani, 2010; 2011). They are not considered here, because rubber producers need models with predictive capabilities at temperatures different from those considered in the rheometer chamber, to predict the behavior of rubber during curing of real items, without performing costly experimental campaigns. Some other models

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take into consideration the most important chemical reactions occurring during sulphur curing (Ding and Leonov, 1996; Ding et al., 1996), and are therefore more suited for the present application.

Unfortunately, all such models, either mechanistic (Coran, 1978; Ding and Leonov, 1996) or semi-mechanistic (Han et al., 1998) suffer from the important limitation of requiring the calibration of the kinetic constants by best fitting numerical procedures on the available experimental data. Here, the model firstly proposed by Han and co-workers (Han et al., 1998) is considered, because of its simplicity and diffusion in practice. It is an approach based on three reactions occurring in series and parallel (three kinetic constants should be therefore determined), has the advantage of providing a closed form expression for the crosslink density and may suitably reproduce reversion, usually encountered in sulphur vulcanization of NR. Induction is excluded from computations, because mostly related to viscous phenomena rather than formation/break of transversal sulphur bridges.

Recently (Leroy et al., 2013) derived a phenomenological model with the same formalism of (Han et al., 1998) and (Colin et al., 2007), which gives a continuous prediction of the induction/vulcanization/reversion sequence. Similar approaches following the same scheme may be also found in (Milani and Milani, 2011; 2014). Essentially, the phenomenological model proposed by (Leroy et al., 2013) assumes that the during the induction and vulcanization steps, the overall formation of sulphur crosslinks can be described by a classic (Kamal and Sourour, 1973) formulation, which supposes a catalytic and autocatalytic second order apparent reaction mechanism. The procedure has been recently refined by (Milani et al., 2013), where a complex kinetic scheme with seven constants is proposed, describing reversion by means of the distinct decomposition of single/double and multiple S-S bonds. Finally, the authors of this paper specialized Han's model in presence of two accelerators (Milani et al., 2015), whereas (Milani and Milani, 2015) have recently proposed an original approach to by-pass best fitting in Han's model, with a determination of the kinetic constants by means of a recursive approach.

However, in rubber farms, software users are usually unexperienced, not familiar with both best-fitting procedures and implementation of subroutines needing recursive computations.

Basing on some experimental results already utilized by the authors and here re-considered as benchmark, we present a GUI software (GURU) that runs under Matlab for experimental data fitting of rheometer curves in Natural Rubber (NR) vulcanized with sulphur. Experimental data are automatically loaded in GURU from an Excel spreadsheet coming from the output of the experimental machine (moving die rheometer).

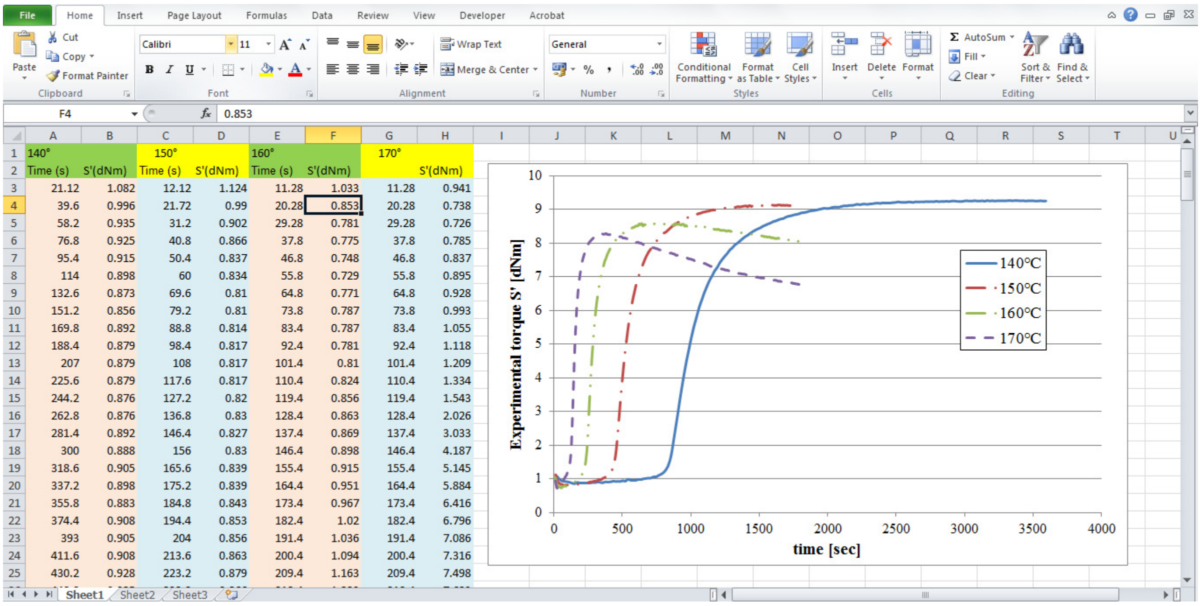
The numerical model essentially relies into a Graphical User Interface that can be managed even with unexperienced users and which allows an estimation of kinetic constants, to be used outside the range of concentrations inspected with predictive purposes, without the need of any particular optimization routine. The trend of variation of the kinetic constants is interactively checked in Arrhenius space providing useful hints on the effects induced by an increase in concentration of a particular ingredient.

To fit experimental data, the general reaction scheme proposed by Han and co-workers for NR vulcanized with sulphur is considered. As already pointed out, from the simplified kinetic scheme adopted, a closed form solution can be found for the crosslink density, and three kinetic constants must be determined in such a way to minimize the absolute error between normalized experimental data and numerical prediction. Usually, such a result is achieved by means of standard least-squares data fitting. On the contrary, GURU works interactively with the unexperienced user to minimize the error and, basing on GUI technology, allows the calibration of the kinetic constants by means of sliders, which allow the assignment of a value for each kinetic constant and a visual comparison between numerical and experimental curves. Unexperienced users will thus find optimal values of the constants by means of a classic trial and error strategy, also selecting the scorch point with a further slider.

A synoptically critical analysis of the numerical (kinetic constants) and experimental results obtained is reported in the paper for the benchmark considered, with a detailed comparison of the results obtained by (Leroy et al., 2013) and (Milani and Milani, 2015) with least-squares and iterative simplified solvers respectively.

2 INTERFACE WITH EXPERIMENTAL DATA

Experimental data loading occurs through the interactive window shown in Figure 1, where the user is asked to insert the name of the Excel file where



140°		150°		160°		170°	
Time (s)	S'(dNm)	Time (s)	S'(dNm)	Time (s)	S'(dNm)		S'(dNm)
21.12	1.082	12.12	1.124	11.28	1.033	11.28	0.941
39.6	0.996	21.72	0.99	20.28	0.853	20.28	0.738
58.2	0.935	31.2	0.902	29.28	0.781	29.28	0.726
76.8	0.925	40.8	0.866	37.8	0.775	37.8	0.785
95.4	0.915	50.4	0.837	46.8	0.748	46.8	0.837
114	0.898	60	0.834	55.8	0.729	55.8	0.895
132.6	0.873	69.6	0.81	64.8	0.771	64.8	0.928
151.2	0.856	79.2	0.81	73.8	0.787	73.8	0.993
169.8	0.892	88.8	0.814	83.4	0.787	83.4	1.055
188.4	0.879	98.4	0.817	92.4	0.781	92.4	1.118
207	0.879	108	0.817	101.4	0.81	101.4	1.209
225.6	0.879	117.6	0.817	110.4	0.824	110.4	1.334
244.2	0.876	127.2	0.82	119.4	0.856	119.4	1.543
262.8	0.876	136.8	0.83	128.4	0.863	128.4	2.026
281.4	0.892	146.4	0.827	137.4	0.869	137.4	3.033
300	0.888	156	0.83	146.4	0.898	146.4	4.187
318.6	0.905	165.6	0.839	155.4	0.915	155.4	5.145
337.2	0.898	175.2	0.839	164.4	0.951	164.4	5.884
355.8	0.883	184.8	0.843	173.4	0.967	173.4	6.416
374.4	0.908	194.4	0.853	182.4	1.02	182.4	6.796
393	0.905	204	0.856	191.4	1.036	191.4	7.086
411.6	0.908	213.6	0.863	200.4	1.094	200.4	7.316
430.2	0.928	223.2	0.879	209.4	1.163	209.4	7.498

Figure 1: Excel file used to load experimental rheometer curves (on the right the experimental curves obtained at four different temperatures).

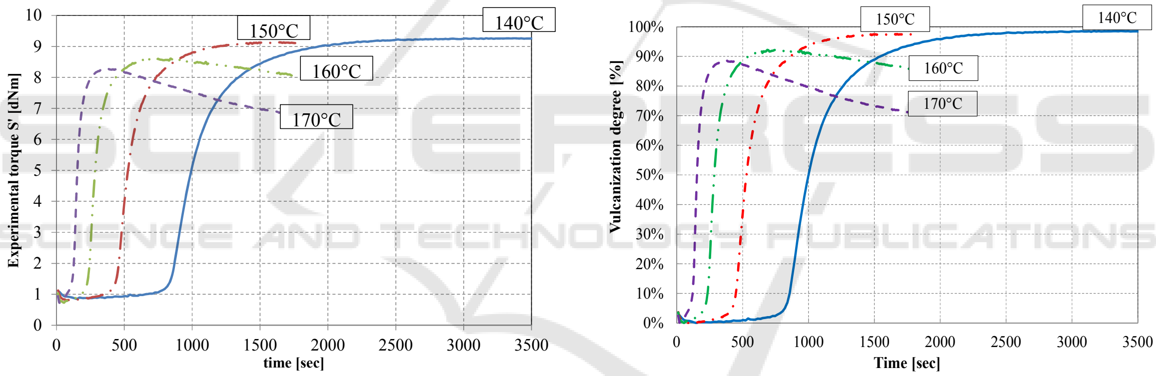
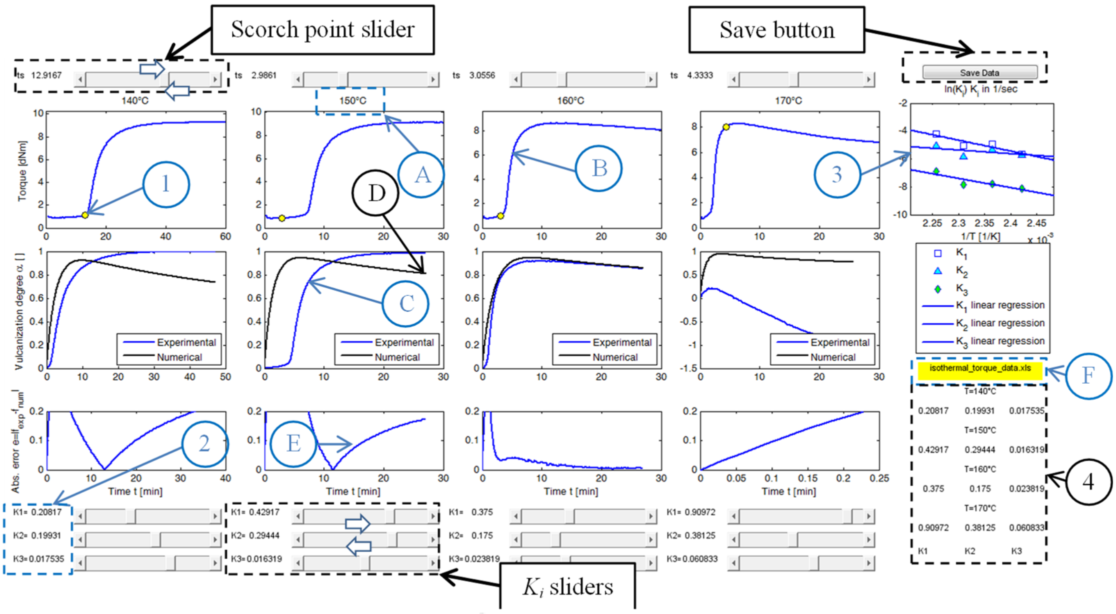


Figure 2: Experimental rheometer curves at temperatures from 130 to 170°C (left) and calculated vulcanization degree curves from Sun and Isayev (2009) relationship (note: induction, i.e. the curve before scorch point, is not excluded from computations).

experimental data are stored, with the range of variability to search the scorch point, at each curing temperatures. Times are typically expressed in minutes.

Experimental data are stored into a standard Excel file, which is classically constituted by two columns per experimented temperature, as illustrated in Figure 1, the first for the time and the second for the measured torque.

To test GURU, a benchmark of practical interest is considered relying into the isothermal curing of a natural rubber blend with properties reported in Table I. Data are at disposal from (Leroy et al., 2013) and (Milani et al.; 2013). The blend has been experimentally tested at five different temperatures, from 130 to 170°C, with a temperature step equal to 10°C. Curve at 130°C reported by (Leroy et al.; 2013) and (Milani et al.; 2013) is not loaded into GURU, because reversion is absent (as at 140°) and the behaviour is very similar to that found at 140°C. Optimization obtained in GURU at 130°C will be in any case shown at the end of the paper, in order to compare the kinetic constants so obtained with those predicted with alternative approaches. A Moving Die Rheometer MDR in dynamic mode (1 Hz) was used to collect the experimental curves.



ts 12.9167 · ts 2.9861 · ts 3.0556 · ts 4.3333

K1= 0.20817 · K2= 0.19931 · K3= 0.017535

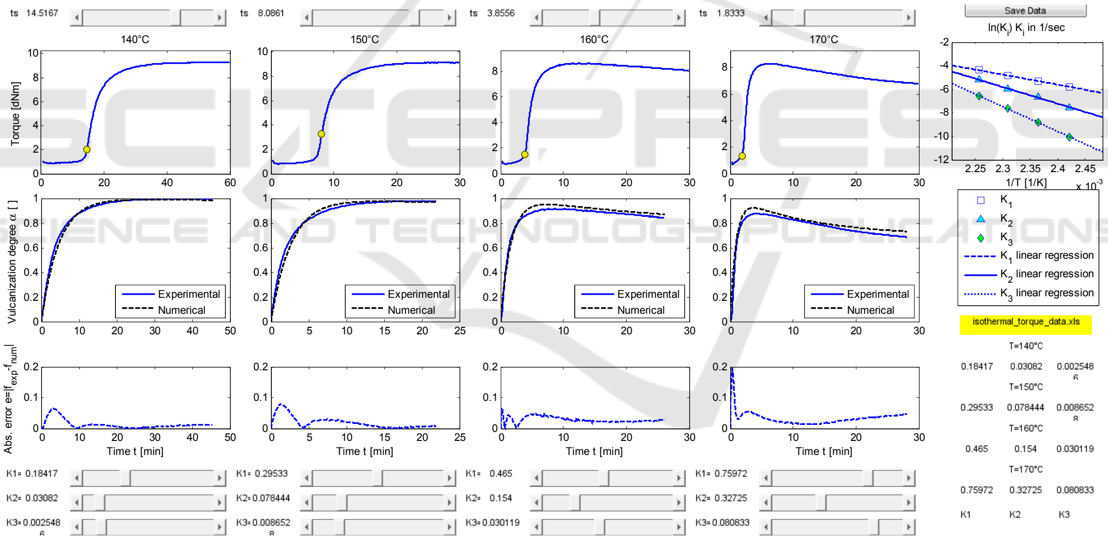
K1= 0.42917 · K2= 0.29444 · K3= 0.016319

K1= 0.375 · K2= 0.175 · K3= 0.023819

K1= 0.90972 · K2= 0.38125 · K3= 0.060833

K1	K2	K3
T=140°C		
0.20817	0.19931	0.017535
T=150°C		
0.42917	0.29444	0.016319
T=160°C		
0.375	0.175	0.023819
T=170°C		
0.90972	0.38125	0.060833

Figure 3: Explanation of the GUI software used to heuristically optimize the kinetic model on the available experimental data.



ts 14.5167 · ts 8.0861 · ts 3.8556 · ts 1.8333

K1= 0.18417 · K2= 0.03082 · K3= 0.0025486

K1= 0.29533 · K2= 0.078444 · K3= 0.0086528

K1= 0.465 · K2= 0.154 · K3= 0.030119

K1= 0.75972 · K2= 0.32725 · K3= 0.080833

K1	K2	K3
T=140°C		
0.18417	0.03082	0.0025486
T=150°C		
0.29533	0.078444	0.0086528
T=160°C		
0.465	0.154	0.030119
T=170°C		
0.75972	0.32725	0.080833

Figure 4: GUI after graphical optimization on experimental data.

The torque $S'(t)$ experimentally determined can be then used to estimate the vulcanization degree $\alpha_{\exp}(t)$, using the following relationship proposed by (Sun and Isayev; 2009):

$$\alpha_{\exp}(t)=\frac{S'(t)-S_{\min T}}{S_{\max T_0}-S_{\min T_0}} \qquad (1)$$

where $S_{\min T}$ is the S' minimum value at temperature T. Before reaching this minimum value, $\alpha_{\exp}(t)$ is considered equal to zero. $S_{\min T0}$ and $S_{\max T0}$ are the minimum and maximum torque values at a curing temperature equal to T0 low enough to allow neglecting reversion. In other words, the low temperature “reversion free” increase of mechanical properties during cure is taken as a reference, to estimate the influence of reversion at higher temperatures, which obviously results in a final degree of vulcanization lower than 100%. In our case the reversion free reference temperature is either 140 or 130°C, providing both temperatures very similar results.

Normalization Equation (1) is implemented into GURU and allows to pass from experimented torque to normalized torque, used to interactively fit numerical data.

Figure 2 shows the typical torque- curing time curves obtained experimentally at the different vulcanization temperatures. As can be noted, the reversion phenomenon, which can be clearly observed at 160 and 170°C, almost vanishes at 140°C, where the torque clearly reaches a horizontal plateau at the end of the experiments. A very similar rheometer curve is obtained at 130°C.

3 THE KINETIC MODEL BY HAN

The basic reaction schemes used in the software are classic, and basically refer to the so-called Han's model (Han et al., 1998).

As universally accepted, many reactions occur in series and parallel during NR cured with sulphur. After a viscous phase which characterizes the uncured rubber at high temperature and called "induction", the chain reactions are initiated by the formation of precursors, characterized by the kinetic constant K_1.

Table 1: Rubber blend composition tested in rheometer experimentation.

Component	**Parts** (by weight)
Rubber gum	100
Carbon black	25
Oil	5
(ZnO / Stearic acid)	6
Sulphur	3
amine antioxidant	2

Then, curing proceeds through two pathways, with the formation of stable and unstable unmatured cured rubber. The distinction between stable and unstable curing stands in the presence of single or multiple sulphur bonds respectively. Multiple S-S bonds are intuitively less stable, and the evolution to matured cross-linked rubber is again distinct between the single S link between chains and the multiple one, statistically much less stable and leading to break and backbiting with higher probability.

All the reactions considered occur with a kinetic velocity depending on the curing temperature, associated to each kinetic constant.

Let us assume that K_i is the i-th kinetic constant associated to one of the previously described phases, so that K_0 describes induction, K_1 and K_2 the formation of unmatured polymer, one stable and the other unstable, and K_3 describes reversion.

Within such assumptions, we adopt for NR the kinetic scheme constituted by the chemical reactions summarized in the following set of equations:

$$\begin{gathered}[A_c]+[S]\xrightarrow{k_0}[A_1^*]\\ [A_1^*]\xrightarrow{k_1}[R_1^*]\\ [A_1^*]\xrightarrow{k_2}[R_1]\\ [R_1]\xrightarrow{k_3}[R_1^D]\end{gathered} \tag{2}$$

In Equation (2), $[A_c]$ is a generic accelerator, $[S]$ is sulphur concentration, $[A_1^*]$ the sulphurating agent, $[R_1^*]$ the stable crosslinked chain (S-S single bonds), $[R_1]$ the unstable vulcanized polymer, $[R_1^D]$ the de-vulcanized polymer fraction (reversion). $K_{0,1,2,3}$ are kinetic reaction constants. Here it is worth emphasizing that $K_{0,1,2,3}$ are temperature dependent quantities, hence they rigorously should be indicated as $K_{0,1,2,3}(T)$, where T is the absolute temperature. In what follows, for the sake of simplicity, the temperature dependence will be left out.

The interaction between K_1 and K_2, from a chemical point of view, is associated with the formation of the activated complex and hence is linked to the activity and concentration of $[A_1^*]$. K_3 is reported by Han 0 to be responsible for reversion after the peak torque, as chemically confirmed by reactions in (2).

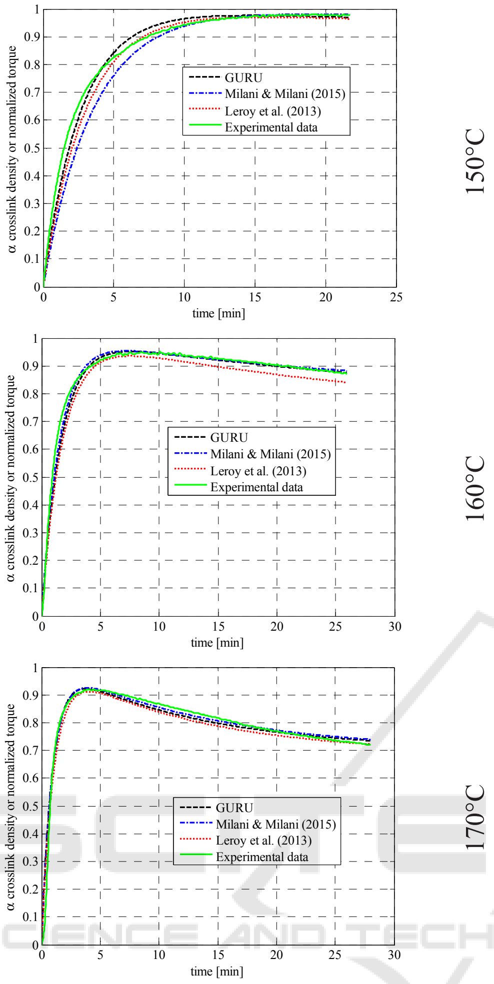


Figure 5: Numerical and experimental normalized rheometer curves. Comparison among GURU, Milani and Milani (2015) and Leroy et al. (2013) approaches.

K_0 is the kinetic constant representing the induction period, that can be excluded from the computations assuming that the induction is evaluated by means of a first order Arrhenius equation.

According to the reaction scheme (2), excluding induction, the following differential equations may be written:

$$\begin{aligned} \frac{d\left[A_1^*\right]}{dt} &= -\left(K_1+K_2\right)\left[A_1^*\right] \\ \frac{d\left[R_1^*\right]}{dt} &= K_1\left[A_1^*\right] \\ \frac{d\left[R_1\right]}{dt} &= K_2\left[A_1^*\right] - K_3\left[R_1\right] \end{aligned} \tag{3}$$

The first Equation (3) may be trivially solved by separation of variables, as follows:

$$\begin{aligned} \left[A_1^*\right] &= \left[A_1^*\right]_0 e^{-(K_1+K_2)(t-t_i)} \\ \frac{d\left[R_1^*\right]}{dt} &= K_1\left[A_1^*\right]_0 e^{-(K_1+K_2)(t-t_i)} \\ \frac{d\left[R_1\right]}{dt} &= k_2\left[A_1^*\right]_0 e^{-(K_1+K_2)(t-t_i)} - K_3\left[R_1\right] \end{aligned} \tag{4}$$

Once $\left[A_1^*\right]$ is a known analytical function, $\left[A_1^*\right]$ can be substituted into equations (b) and (c) in (4) to provide $\left[R_1^*\right]$ and $\left[R_1\right]$:

$$\begin{aligned} \left[R_1^*\right] &= \frac{K_1\left[A_1^*\right]_0}{K_1+K_2}\left[1-e^{-(K_1+K_2)(t-t_i)}\right] \\ \frac{d\left[R_1\right]}{dt} + K_3\left[R_1\right] &= K_2\left[A_1^*\right]_0 e^{-(K_1+K_2)(t-t_i)} \end{aligned} \tag{5}$$

The second Equation (5) is a non homogeneous first order linear differential equation, which admits the following solution constituted by a general and a particular root:

$$\begin{aligned} &\left[R_1\right] = \\ &= \frac{K_2}{K_1+K_2-K_3}\left[A_1^*\right]_0\left[e^{-K_3(t-t_i)} - e^{-(K_1+K_2)(t-t_i)}\right] \end{aligned} \tag{6}$$

The final concentration of vulcanized rubber is thus $\left[R_1^*\right]+\left[R_1\right]$:

$$\begin{aligned} \left[R_1\right]+\left[R_1^*\right] &= \frac{K_1\left[A_1^*\right]_0}{K_1+K_2}\left[1-e^{-(K_1+K_2)(t-t_i)}\right] + \\ &+ \frac{K_2}{K_1+K_2-K_3}\left[A_1^*\right]_0\left[e^{-K_3(t-t_i)} - e^{-(K_1+K_2)(t-t_i)}\right] \end{aligned} \tag{7}$$

(7) can be normalized with respect to $[S]_0$ as follows to provide the crosslinking density α :

$$\begin{aligned} \alpha = \frac{\left[R_1\right]+\left[R_1^*\right]}{[S]_0} &= \frac{K_1}{K_1+K_2}\left[1-e^{-(K_1+K_2)(t-t_i)}\right] + \\ &+ \frac{K_2}{K_1+K_2-K_3}\left[e^{-K_3(t-t_i)} - e^{-(K_1+K_2)(t-t_i)}\right] \end{aligned} \tag{8}$$

4 SOFTWARE ENGINE

GURU core appears to the user immediately after having stored the experimental Excel database, as in Figure 1.

With reference to Figure 3, where GURU interface is shown before any optimization, the software is roughly organized into five columns.

The first four columns from the left represent synoptically data at a given vulcanization temperature, starting for instance from 140°C with the column on the left and ending with 170° in the fourth column on the right (see detail A in Figure 3).

Each column represents on the top the crude experimental rheometer data (detail B), with an indication of the scorch time adopted (yellow dot moving on the curve after user's action 1 on the top slider in Figure 3), the performance of the numerical model (detail D) with respect to normalized experimental curve (detail C) in the central sub-figure and the absolute error of the numerical model when compared with normalized experimental curve (detail E).

Kinetic constants are dynamically modified by means of user's action on the sliders on the bottom (action 2). A user can dynamically move the slider by means of a trial and error procedure in order to graphically minimize the absolute difference between experimental and numerical curve. Scorch point can be adjusted as well. Typically, the optimization of the parameters takes few instants. The values of the kinetic constants are dynamically updated and registered in the table situated on the bottom left part of the screen (detail 4) and plotted in the Arrhenius space depicted on the top-left (detail 3). In the same sub-figure, the linear regression of each kinetic constant is also represented.

An indication of the stored Excel file name is also provided in a yellow box (detail F).

Finally, data obtained after proper trial and error interactive optimization can be saved by means of a standard "Save" button located on the top-right region of the interface. After having pressed the button, a standard saving interface appears. By default, it is possible to save data in a desired folder with any output name in ".dat" format, which is the standard binary format for Matlab. Files with extension ".dat" are immediately available at any time by any user, after proper reloading in a new Matlab session. By default GURU loads at the beginning a file called "output_data.dat". In this way, after a first optimization session, the user can modify in successive sessions the work previously saved and properly reloaded.

5 AN EXAMPLE OF TECHNICAL RELEVANCE

GURU reliability is tested on some existing experimental data from (Milani et al., 2013) and Leroy et al. (2013). Attention is focused exclusively on the fitting capabilities. GURU interface, after a quick trial and error optimization session is shown in Figure 4. As can be noted from the details of the fitting quality at each temperature and the estimated kinetic constants in the Arrhenius space, both good agreement with normalized experimental data and almost perfect linearity of the kinetic constants is experienced.

Since output data obtained may be saved in a proper database (file .dat into Matlab environment, with kinetic constant values directly at disposal in the command window for additional computations) with the dedicated "save" button on the top-right of GURU (see Figure 3), a more detailed insight into the fitting quality obtained with the graphical procedure can be also provided.

In particular, normalized rheometer curves obtained by means of GURU are depicted in Figure 5 and compared with normalized experimental data and numerical curves obtained in (Leroy et al., 2013) and (Milani and Milani, 2015) with a least square and interactive simplified semi-analytical approach, respectively.

GURU fits well experimental results, sometimes better than expensive least-squares approaches.

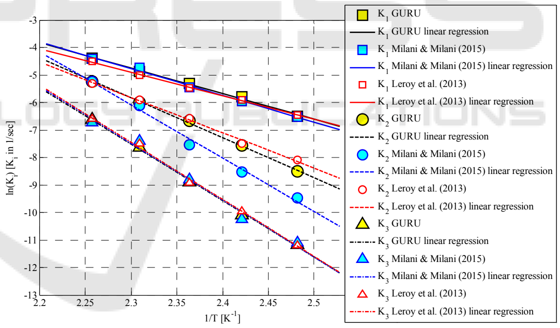


Figure 6: GURU performance in the Arrhenius space for the determination of Ki constants at different temperatures in the Arrhenius space. Comparison with other approaches presented in the technical literature.

The numerical rheometer curve is very near to the experimental one in absence of reversion, i.e. at low temperature (140°C), but appears extremely satisfactory even in presence of visible reversion (170°C). The absolute error appears constantly lower than 0.1 (i.e. with a relative error normalized on the unitary maximum torque equal to 10%) in case of both strong and zero reversion, a result which appears fully acceptable for practical purposes. From simulations results, it is interactively found that the kinetic constants follow reasonably well linearity in the Arrhenius space, see Figure 4 and a more detailed representation in Figure 6 also with data at 130°C. Ki numerical results found by (Leroy et al., 2013) and (Milani and Milani, 2015), with the corresponding linear regressions are also represented for comparison purposes. The agreement between GURU and (Leroy et al., 2013) is almost perfect, even with a more satisfactory linearity in GURU. When dealing with (Milani and Milani, 2015), the agreement is rather good for K_1 and K_3, but with visible deviation at lower temperatures (130°C and 140°C) for K_2, mainly related to an intrinsic limitation of the semi-analytical approach proposed in (Milani and Milani, 2015) (and hence independent from GURU software).

From simulations results, it is interactively found that the kinetic constants follow reasonably well linearity in the Arrhenius space, see Figure 4 and a more detailed representation in Figure 6 also with data at 130°C. Arrhenius law represents one of the most useful relationships in chemical kinetics, when an extrapolation of the behavior is needed outside the experimentally tested temperature range. In Figure 6, we represent also Ki numerical results found by (Leroy et al., 2013) and (Milani and Milani, 2015), with the corresponding linear regressions. Once again, we stress that (Leroy et al., 2013) use Han's model to fit experimental data and Ki are evaluated by standard least-squares. (Milani and Milani, 2015) again base on Han's kinetic scheme, but they propose, after few mathematical considerations on the closed-form solution found to estimate the crosslinking density, a semi-analytical approach to estimate Kis, thus circumventing the use of least-squares. As can be noted, the agreement between GURU and (Leroy et al., 2013) approach is almost perfect for all the kinetic constants, even with a more satisfactory linearity experienced for GURU. When dealing with (Milani and Milani, 2015) procedure, the agreement with GURU appears again rather good for K_1 and K_3 constants, but with visible deviation at lower temperatures (130°C and 140°C) for K_2. Such inaccuracy is not surprising, and mainly related to an intrinsic limitation of the semi-analytical approach proposed by (Milani and Milani, 2015) and hence independent from GURU software. As a matter of fact (Milani and Milani, 2015) closed form solution requires an evaluation of K_2 through the definition of the reversion percentage. When reversion is absent or very small, K_2 is clearly affected by high scatter. This also justifies the very good agreement at 170 and 160°C, where reversion is present.

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