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SoftwareX 5 (2016) 67–73
SoftwareX
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GURU v2.0: An interactive Graphical User interface to fit rheometer curves in Han's model for rubber vulcanization

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Received 26 February 2016; received in revised form 14 April 2016; accepted 20 April 2016

Abstract

A GUI software (GURU) for experimental data fitting of rheometer curves in Natural Rubber (NR) vulcanized with sulphur at different curing temperatures is presented. Experimental data are automatically loaded in GURU from an Excel spreadsheet coming from the output of the experimental machine (moving die rheometer). To fit the experimental data, the general reaction scheme proposed by Han and co-workers for NR vulcanized with sulphur is considered. From the simplified kinetic scheme adopted, a closed form solution can be found for the crosslink density, with the only limitation that the induction period is excluded from computations. Three kinetic constants must be determined in such a way to minimize the absolute error between normalized experimental data and numerical prediction. Usually, this result is achieved by means of standard least-squares data fitting. On the contrary, GURU works interactively by means of a Graphical User Interface (GUI) to minimize the error and allows an interactive calibration of the kinetic constants by means of sliders. A simple mouse click on the sliders allows the assignment of a value for each kinetic constant and a visual comparison between numerical and experimental curves. Users will thus find optimal values of the constants by means of a classic trial and error strategy. An experimental case of technical relevance is shown as benchmark.

Keywords: GUI optimization software; Natural rubber (NR) vulcanization; Kinetic numerical model; Experimental data fitting

Code metadata

Current code version	*V2.0*
Permanent link to code/repository used of this code version	https://github.com/ElsevierSoftwareX/SOFTX-D-16-00029
Legal Code License	*GNU*
Code versioning system used	*None*
Software code languages, tools, and services used	*Matlab/Scilab*
Compilation requirements, operating environments & dependencies	*Excel/OpenOffice/txt experimental data spreadsheet*
If available Link to developer documentation/manual	*Not available*
Support email for questions	Gabriele.milani@polimi.it

1. Introduction

The utilization of reliable kinetic software to predict the crosslinking degree after curing of Natural Rubber (NR) is still very low in industrial practice. The most diffused laboratory device able to give operative information of the curing degree is the rheometer. The rheometer is a machine constituted by a chamber with either a fixed and a moving part (MDR) or an oscillating disc inside (ODR). A small rubber sample is inserted into the chamber and cured at constant cure temperature. The torque applied to maintain a constant rotation of the moving part (moving die or oscillating disc) is measured.

For NR vulcanized with sulphur, torque generally slightly decreases during a so called "induction" period of time,

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http://dx.doi.org/10.1016/j.softx.2016.04.005

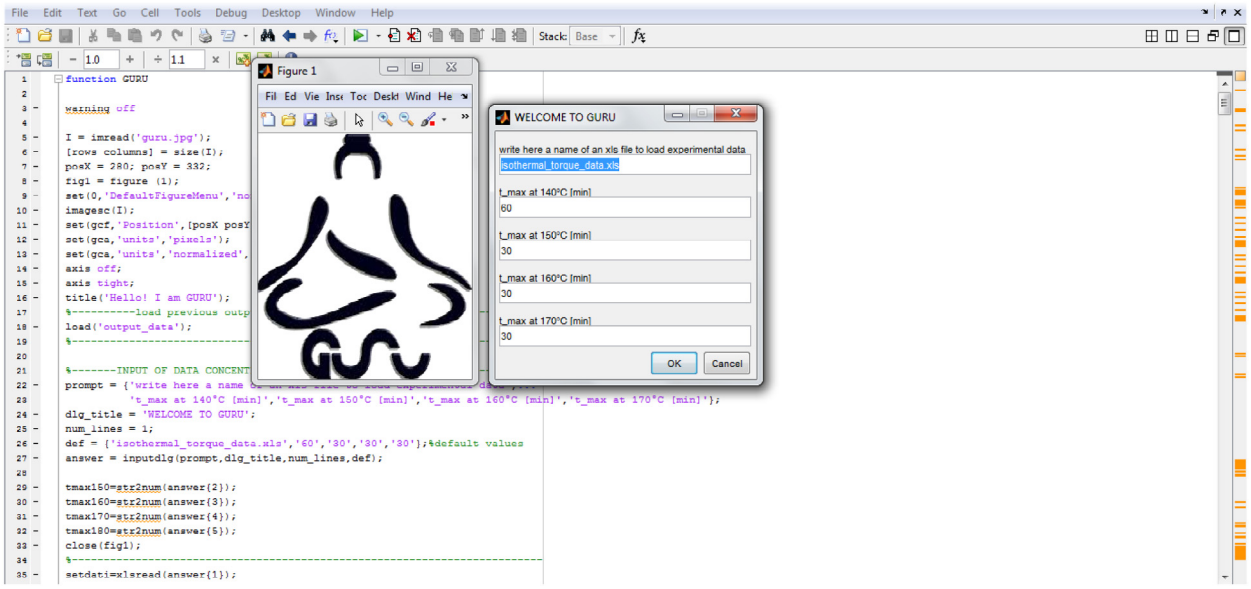

Fig. 1. Initial interface of the program and experimental data loading from Excel file.

followed by a significantly fast increase. Very frequently reversion (torque drop) is observed in the end. It occurs typically at high temperatures as a consequence of the degradation of polysulfidic (S–S or more) crosslinks [1–11].

Based on some experimental results already utilized by the authors in [12] and here re-considered as a benchmark, we present a Graphical User Interface (GUI) software called GURU that runs both under Matlab [13] or under the free software Scilab [14] 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 on a GUI 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 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 the experimental data, the numerical model proposed by Han and co-workers [15] for NR vulcanized with sulphur is utilized. A closed form solution can be found for the crosslink density. 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 allows the user to interactively minimize the error by means of GUI technology. In particular, the calibration of the kinetic constants is done by means of sliders, which allow the assignment of a value for each kinetic constant and a visual comparison between numerical and experimental curves. Users will thus find optimal values of the constants by means of a classic trial and error strategy. The position of the scorch point can be adjusted as well by 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 in [16] and [17] with least-squares and iterative simplified solvers respectively.

2. Experimental data loading

Experimental data loading occurs through the interactive window shown in Fig. 1, where the user is asked to insert the name of the Excel file where experimental data are stored, with the range of variability to search the scorch point, at each curing temperature. 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 Fig. 2, the first for the time and the second for the measured torque.

To test GURU, a benchmark of practical interest is considered relying on the isothermal curing of a standard natural rubber blend. Data are at disposal from both [12] and [16], but can come from any other experimental source.

In agreement with consolidated literature, GURU works on the experimental torque $S'(t)$ to estimate the vulcanization degree $\alpha_{\exp}(t)$, using the following relationship proposed by Sun and Isayev [18]:

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

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), $S_{\min T_0}$ and $S_{\max T_0}$ are the minimum and maximum torque values at a curing temperature equal to T_0. T_0 is a temperature low enough to allow neglecting reversion.

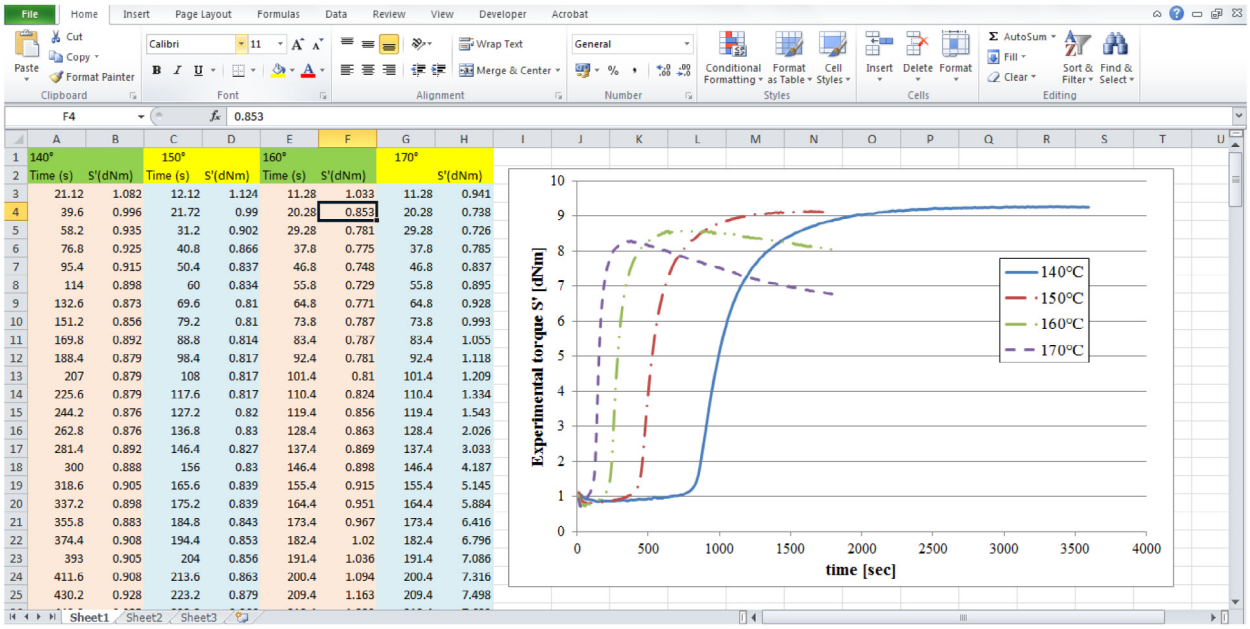

Fig. 2. Excel file used to load experimental rheometer curves (on the right the experimental curves obtained at four different temperatures).

3. Han's model and iterative evaluation of kinetic constants

The basic reaction schemes of the numerical model implemented in GURU are classic and refer to existing literature in the field [12,15,16,19–21].

We use the model given in [15]. After a viscous phase (induction) which characterizes the uncured rubber, the chain reactions are initiated by the formation of precursors. Then, curing proceeds through two pathways, with the formation of stable and unstable crosslinked unmatured rubber. Unstable rubber is more subjected to final reversion. All the reactions considered occur with a kinetic velocity depending on the curing temperature, associated to each kinetic constant.

If K_i is the ith kinetic constant associated to one of the previously described phases, then 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. To summarize, the reactions are the following:

$$\begin{aligned} &[A_c] + [S] \xrightarrow{K_0} \left[A_1^*\right] && \text{induction} \\ &\left[A_1^*\right] \xrightarrow{K_1} \left[R_1^*\right] && \text{Stable unmatured} \\ &\left[A_1^*\right] \xrightarrow{K_2} [R_1] && \text{Unstable unmatured} \\ &[R_1] \xrightarrow{K_3} \left[R_1^D\right] && \text{reversion.} \end{aligned} \tag{2}$$

In (2), $[A_c]$ is a generic accelerator, $[S]$ is sulphur concentration, $\left[A_1^*\right]$ the sulphurating agent, $\left[R_1^*\right]$ the stable crosslinked chain (S–S single bonds), $[R_1]$ the unstable vulcanized polymer, $\left[R_1^D\right]$ the de-vulcanized polymer fraction (reversion). K_i $(i = 0, 1, 2, 3)$ are kinetic reaction constants and K_0 is the kinetic constant representing the induction period, that is usually excluded from the computations. It is worth noting that in Eq. (2) square brackets indicate chemical concentrations.

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

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

After some mathematics, it has been demonstrated [15] that the crosslinking density α is:

$$\begin{aligned} \alpha = \frac{[R_1] + \left[R_1^*\right]}{[S]_0} &= \frac{K_1}{K_1 + K_2}\left[1 - e^{-(K_1+K_2)(t-t_i)}\right] \\ &+ \frac{K_2}{K_1 + K_2 - K_3}\left[e^{-K_3(t-t_i)} - e^{-(K_1+K_2)(t-t_i)}\right]. \end{aligned} \tag{4}$$

4. Core of GURU software

GURU interface is loaded automatically after the experimental Excel database, with the interface shown in Fig. 1 for the sake of clearness. GURU interface is shown in Fig. 3, before any optimization action by the user. As can be seen, GURU 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 Fig. 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 Fig. 3), the performance of the numerical model (detail D) with respect to normalized

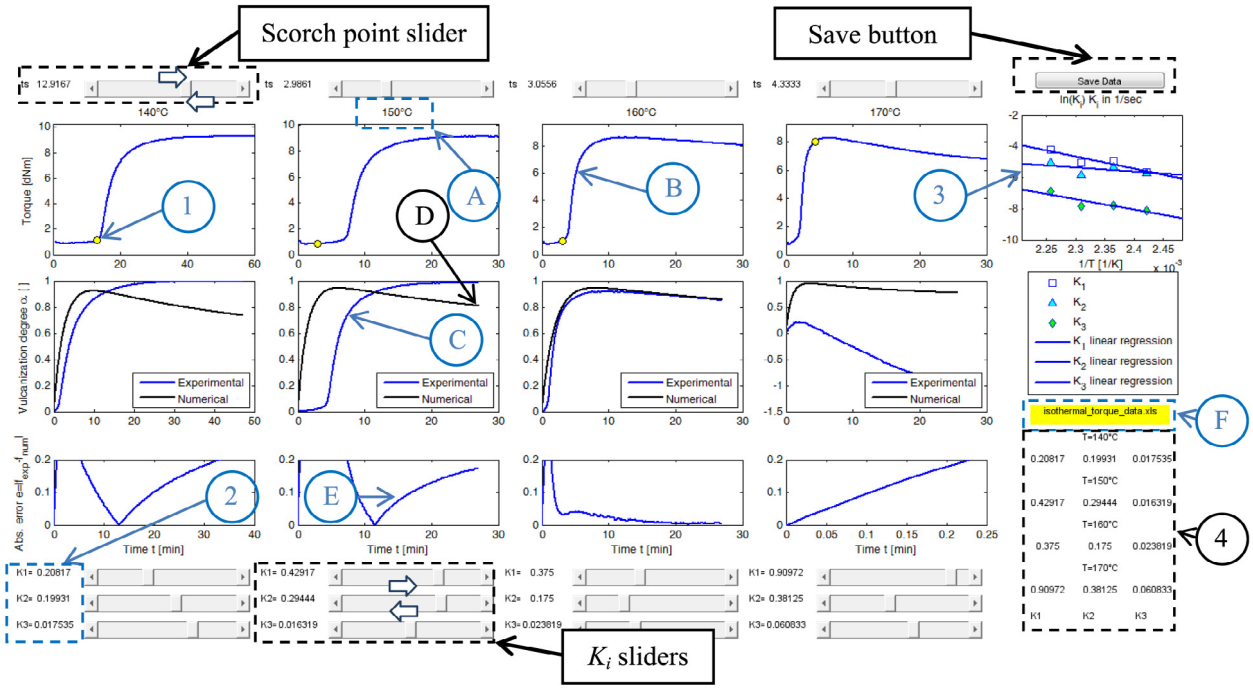

Fig. 3. Explanation of the GUI software used to heuristically optimize the kinetic model on the available experimental data. Detail 1: scorch point. Detail 2: values of the kinetic constants obtained moving the corresponding sliders. Detail 3: values of the kinetic constants in the Arrhenius space. Detail 4: final table of kinetic constants at different temperatures obtained moving the corresponding sliders. Detail A: vulcanization temperature considered. Detail B: experimental torque curve loaded from the Excel database. Detail C: normalized experimental torque curve. Detail D: numerical normalized curve obtained moving the corresponding sliders. Detail E: absolute error between normalized experimental and numerical curves. Detail F: Excel filename containing experimental data. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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 curves. 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 [13]. Files with extension ".dat" are immediately available at any time by any user, after proper reloading in a new Matlab/Scilab 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.

As it will be pointed out in the following section by means of a comprehensive comparison of all the numerical data produced, the experimental fitting is almost perfect in the majority of the cases. It is stressed that the determination of the kinetic constants of the rheometer curve investigated is almost immediate, because it occurs dynamically without needing any particular ability/mathematical knowledge by the user and without having at disposal non-linear programming routines.

5. Performance of the software for a benchmark of technical relevance

GURU reliability is tested on some existing experimental data from [12,16]. Attention is focused exclusively on the fitting capabilities. GURU interface, after a quick trial and error optimization session is shown in Fig. 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 are experienced.

Since output data obtained may be saved in a proper database (e.g. 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 Fig. 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 Fig. 5a and compared with

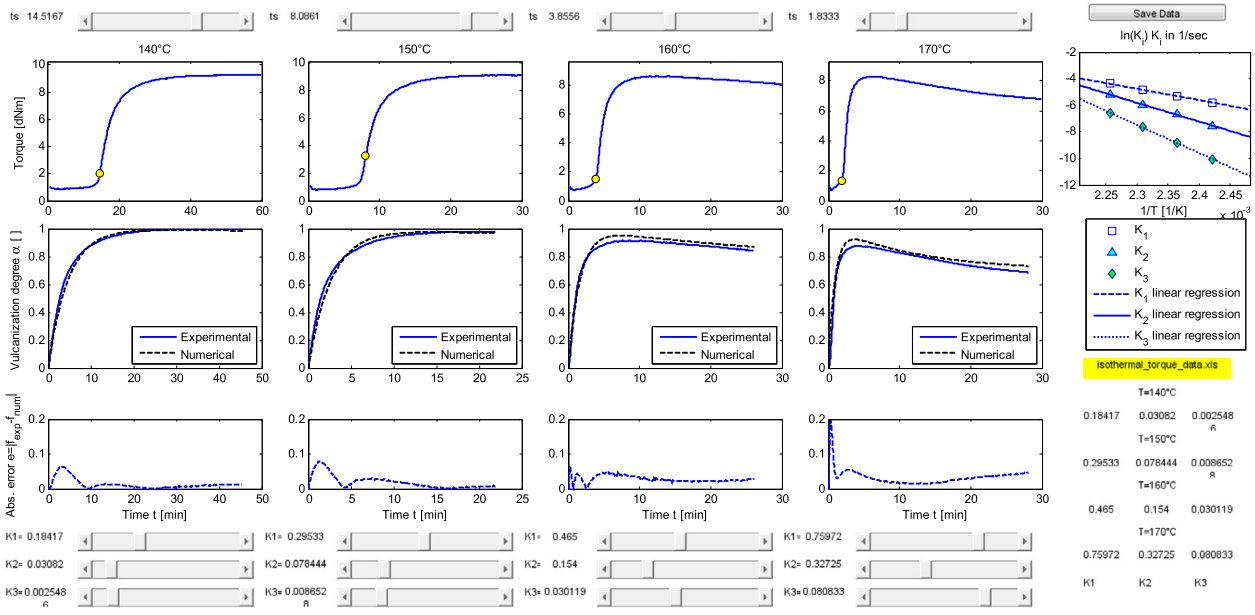

Fig. 4. GUI after graphical optimization on experimental data. First column from the left: temperature equal to 140 °C, experimental torque curve (top sub-figure), comparison between normalized and numerical torque curves (second sub-figure), absolute error estimation (third sub figure), kinetic constant values with corresponding sliders. Second, third and fourth columns: same data for temperatures equal to 150 °C, 160 °C, 170 °C respectively. First column from the right: kinetic constants in the Arrhenius space (top sub-figure) and table of the final kinetic constants at the different temperatures experimentally investigated.

normalized experimental data and numerical curves obtained in [16] and [17] with a least square and interactive simplified semi-analytical approach, respectively. Absolute errors against normalized experimental data are plotted in Fig. 5b in order to intuitively estimate a satisfactory agreement with experimental data and eventually estimate the local deviation.

As can be noted, GURU fits extremely well experimental results, sometimes better than expensive least-squares approaches, especially in the de-vulcanization range, when present. Small differences may be appreciated after a proper zoom of the curves at the very beginning or near the initiation of reversion in some few cases, however less evident than deviations of other models [17].

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 Fig. 4 and a more detailed representation in Fig. 6 also with data at 130 °C. K_i numerical results found by Leroy et al. in [16] and Milani & Milani in [17], with the corresponding linear regressions are also represented for comparison purposes. The agreement between GURU and [16] is almost perfect, even with a more satisfactory linearity in GURU. When dealing with [17], 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 [17] (and hence independent from GURU software).

6. Conclusions

We have presented a GUI software called GURU, which allows a fitting of experimental data with rheometer curves in Natural Rubber (NR) vulcanized with sulphur at different curing temperatures.

Experimental data are automatically loaded in GURU from an Excel (or OpenOffice or even a txt file) spreadsheet coming from the output of the experimental machine (moving die rheometer).

To fit experimental data, the general reaction scheme proposed by Han and co-workers for NR vulcanized with sulphur has been considered. Best fitting is achieved avoiding standard least-squares, working interactively by means of a GUI interface and calibrating kinetic constants by means of sliders, with a visual comparison between numerical and experimental curves.

An experimental case of technical relevance has been considered as benchmark. Rather close linearity has been found for all the kinetic constants so found in the Arrhenius space, with an impressive agreement with rigorous approaches.

The main achievement of the proposed software is that the user can estimate quickly and in a reliable manner optimal values of the constants by means of a trial and error strategy that does not require any knowledge about both optimization algorithms and chemistry of reaction. The results confirm the powerfulness of the interactive software proposed, which is put at disposal on Internet to all those practitioners interested, also in consideration of its adaptability in any experimental situation, with different concentrations and with any accelerator/loading agent [7,9,12].

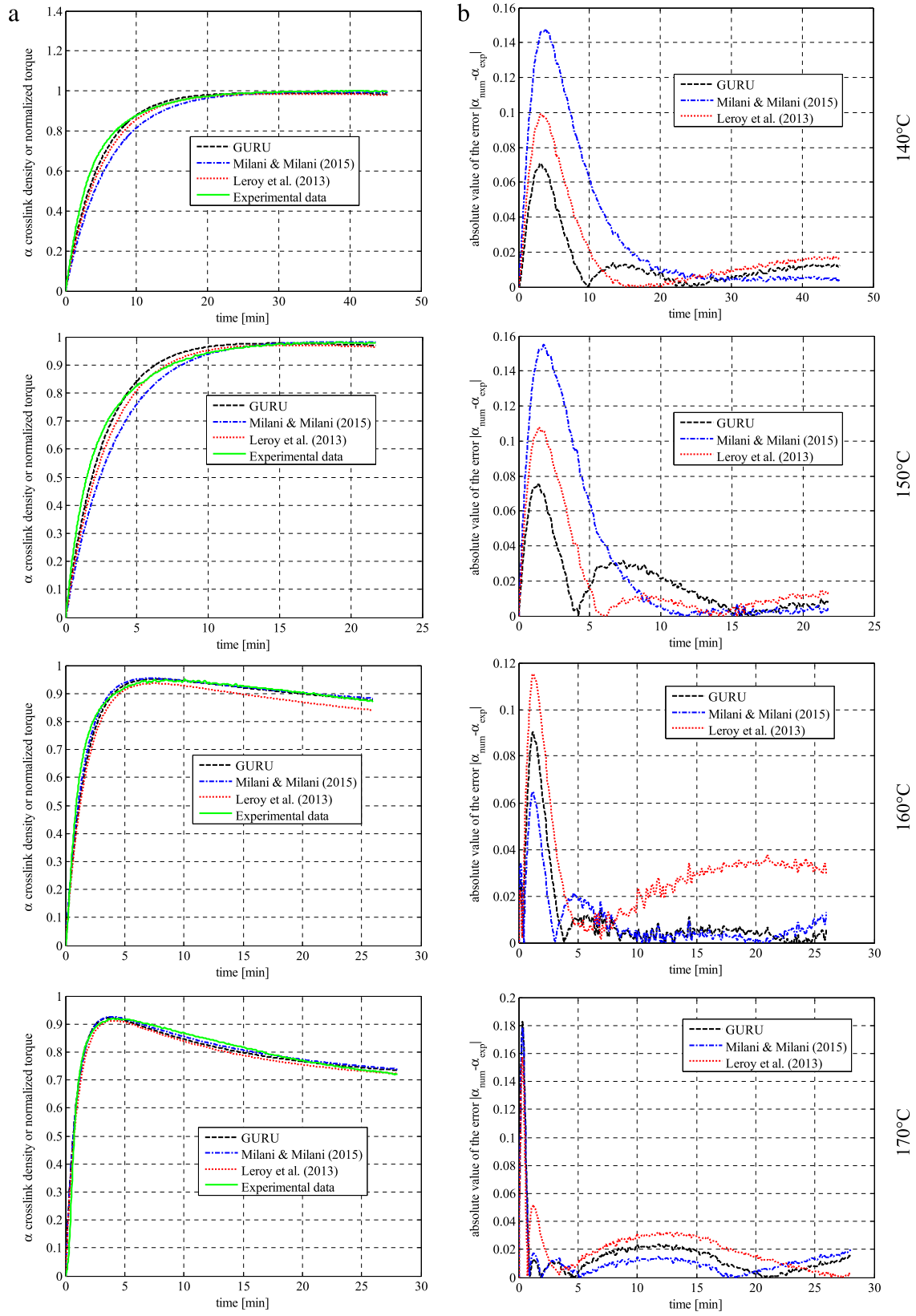

Fig. 5. (a) Numerical and experimental normalized rheometer curves and (b) absolute error estimation against normalized experimental data. Comparison among GURU, [16] and [17] approaches.

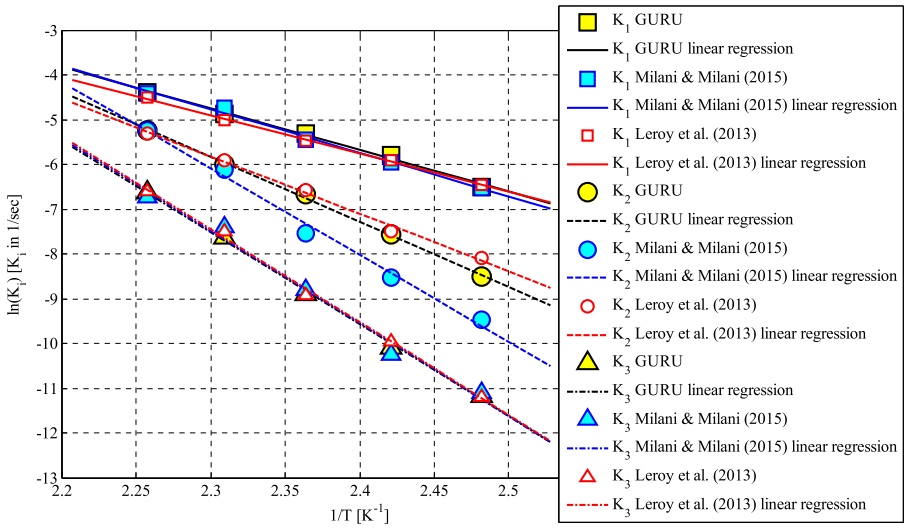

Fig. 6. GURU performance in the Arrhenius space for the determination of K_i constants at different temperatures in the Arrhenius space. Comparison with other approaches presented in the technical literature.

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