

# A closed form solution for the vulcanization prediction of NR cured with sulphur and different accelerators

G. Milani · T. Hanel · R. Donetti · F. Milani

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## 1 Introduction

The vulcanization with sulphur of natural rubber (NR) is particularly complex. This is the reason why, despite its first practical application dates back to the second half of nineteenth century, its chemical mechanisms are not still completely understood. Due to such theoretical lack, it remains difficult to develop efficient numerical tools to optimize the vulcanization process of items with big dimensions and to predict their final elasto-mechanical properties.

As well known, the crosslink density may be indirectly estimated by means of many macroscopic procedures, but the most diffused and simple one is the so-called rheome-ter test. A rheometer is a laboratory device where a small rubber sample is subjected to constant cure temperature and the torque applied to maintain a constant rotation of the moving part (e.g. oscillating disc, moving die, etc.) is measured. The torque generally starts to increase very slowly (or decreases) during an “induction” period of time, after which the main vulcanization reaction takes place with a significantly faster increase of the crosslink density and hence of the measured torque within the rheometer. Very frequently, for NR vulcanized with sulphur, it can occur that torque reaches a maximum and then starts to decrease, resulting in weaker mechanical properties of the vulcanizate for long curing times. This last phenomenon, called “reversion”, is well known for sulfur cured rubbers at high vulcanization temperatures (typically above 140 °C) and is attributed to the formation and subsequent degradation of polysulfidic (S–S or more) crosslinks [1–3]. Generally, in sulphur vulcanized rubber, it is commonly accepted that there are three types of polysulfidic structures namely C–S–C, C–S<sub>2</sub>–C and C–S<sub>x</sub>–C.

The primary reaction leading to polysulfidic structures involves the formation of reactive crosslinking precursors (which can contain between 2 and 8 S–S links) on a rubber chain by reaction with sulphurating agents. This precursor can then react either with another rubber chain, resulting in a crosslink, or with the same rubber chain, by a backbiting reaction resulting in a cyclic structure. In this latter case, the polysulfidic structure does not contribute to the increase of the crosslink density.

The evidence for these polysulfidic structures (both crosslinking and cyclic ones) is provided by an important physical chemistry literature, obtained by IR, UV, ESR and Raman characterizations [4,5] or with chemical methods [6], or by means of solid

G. Milani (✉)

Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milan, Italy  
e-mail: milani@stru.polimi.it; gabriele.milani@polimi.it

T. Hanel · R. Donetti

Pirelli Tyre, Via Alberto e Piero Pirelli 25, 20126 Milan, Italy

F. Milani

Chem.Co Consultant, Via J.F.Kennedy 2, 45030 Occhiobello, RO, Italy

state  $^{13}\text{C}$  nuclear magnetic resonance (NMR) studies [7], as done for instance in [8,9] for EPDM. In this latter case, the polysulfidic structures are consistent with predictions based on model compounds and the presence of three different allylic positions in the repeating unit of NR [7]. The percentages of each polysulfidic structure and the value of  $x$  depends on both rubber structure and reaction conditions, the most important being temperature and curing time [10]. It has been observed experimentally, that in the initial stage of the reaction, more crosslinking  $\text{C}-\text{S}_x-\text{C}$  ( $x = 4, 5$  or more) bonds are found. It is generally assumed that  $(\text{C}-\text{S}_x-\text{C})$  polysulfidic crosslinks can further react, leading either to shorter crosslinks  $(\text{C}-\text{S}-\text{C})$ , through a so called “maturation reaction”, or to cyclic polysulfidic structures by backbiting reactions. In such a case, the crosslink density decreases, and this chemically explains the macroscopically observed reversion.

In practice, it has been observed that the importance of the reversion depends strictly on curing temperature. Nevertheless, recent results by Leroy et al. [11] and Milani et al. [12, 13] tend to demonstrate that the ratio between thermally stable (short) and unstable (long) polysulfidic crosslinks is not significantly influenced by cure temperature.

The existing models that allow predicting such specific behavior regarding the kinetics of rubber vulcanization, by means of either a mechanistic (model of Coran [3], Ding and Leonov [14, 15]) or a semi-mechanistic (model of Han et al. [16]) base, suffer from important limitations, such as the need of evaluating kinetic constants by best fitting numerical procedures on the available experimental data and the generalist point of view, which does not take into account the actual accelerators present in the system.

Recently, Leroy et al. [11] derived a phenomenological model with the same formalism of Han et al. [16] and Colin et al. [17], which gives a continuous prediction of the induction/vulcanization/reversion sequence. Similar approaches following the same scheme may be also found in [12, 13]. Essentially, the phenomenological model proposed in [11] assumes that during the induction and vulcanization steps, the overall formation of sulphur crosslinks can be described by a classic Kamal and Sourour formulation [18], which supposes a catalytic and autocatalytic second order apparent reaction mechanism. Consequently, despite its practical interest for numerical simulations, such a phenomenological model remains not fully predictive, since it does not allow relating the global reaction kinetics to the current knowledge of the different individual reactions involved. The procedure has been recently refined by Milani et al. in [19], where a complex kinetic scheme with seven constants is proposed, describing reversion by means of the distinct decomposition of single/double and multiple  $\text{S}-\text{S}$  bonds. The limitation of [19] model remains however the need of solving numerically a differential equations system, evaluating the kinetic constants by means of a least squares procedure.

In the present paper, a novel and efficient closed form approach to determine the degree of vulcanization of NR cured with sulphur in presence of more than one accelerator is presented. The general reaction scheme proposed by Han and co-workers for vulcanized sulphur NR is assumed as the initial base to develop a suitably modified new model accounting for the single contributions of the different accelerators, focusing in particular on some experimental data [20], where a NR has been vulcanized at different temperatures (from 150 to 180 °C) and concentrations of sulphur, using

TBBS (*N* terbutyl, 2 benzothiazylsulphenamide) and DPG (*N,N* diphenyl guanidine) as co-agents at variable concentrations.

In the model, chain reactions initiated by the formation of macro-compounds responsible for the formation of the unmaturing crosslinked polymer are accounted for. It is assumed that such reactions depend on the reciprocal concentrations of all components and their chemical nature. In presence of two accelerators, reactions are assumed to proceed in parallel, making the assumption that there are no cross-reactions between the two accelerators. Despite there is experimental evidence of the existence of a process by which each accelerator affects the other, the reaction chemistry is still not well understood. For this reason, its real effect on vulcanization cannot be translated into any mathematical model. In any case, even disregarding such interaction, authors experienced a good numerical performance of the model on fitting experimental rheometer curves. From the kinetic scheme adopted, a closed form solution is found for the crosslink density, with the only limitation that the induction period is excluded from computations.

The main novelty of the model stands however in the closed form determination of the kinetic constants representing the rates of the single reactions in the kinetic scheme adopted. Such very straightforward procedure allows avoiding the utilization of numerically demanding least-squares best fitting routines on rheometer experimental data.

Two series of experiments available, relying into rheometer curves at different temperatures and different concentrations of sulphur and accelerators, are utilized to evaluate the fitting capabilities of the mathematical model. Very good agreement between numerical output and experimental data is experienced in all cases analyzed. The evaluation of kinetic constants at three vulcanization temperatures, after proper check of the linearity in the Arrhenius space, allows performing numerical simulations at curing temperatures outside the range experimentally inspected, making the model predictive in all those cases where a wide experimental campaign is not possible.

## 2 Experimental results

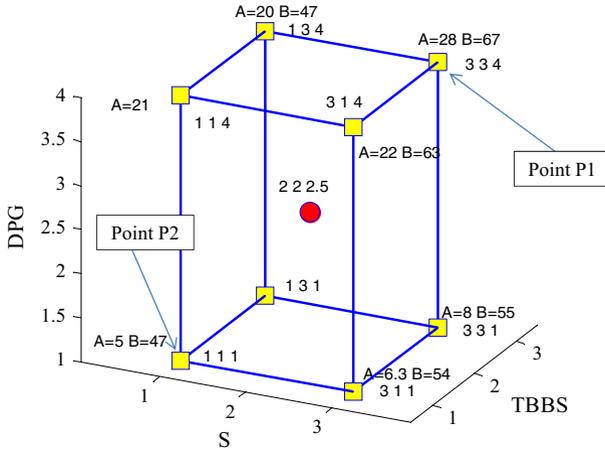
As base for the comprehensive validation of a newly conceived kinetic scheme ad-hoc developed by the authors, some experimental results [20] consisting of standard rheometer curves (MD rheometer tests) for NR vulcanized in various conditions have been considered.

The analyses focus on NR with different concentrations of S, TBBS and DPG at different temperatures. In particular, the same NR blend, with composition as in Table 1, was vulcanized with 9 different S–TBBS–DPG mutual concentrations, at four increasing curing temperatures equal to 150, 160, 170 and 180 °C. The final aim was to conduct a wide sensitivity analysis to have an experimental insight into the role played by the mutual concentration of the different accelerations on the (1) vulcanization level at the end of curing, (2) reaction velocity after scorch and (3) amount of reversion at different temperatures. The experimental campaign was designed in the S–TBBS–DPG space moving on the corners of the parallelepiped depicted in Fig. 1, with values of concentration (in phr) kept from previous experience of the authors in this field. A

**Table 1** NR blend composition (in phr) considered in the numerical simulations (zinc octoate at 3 phr was used in all cases)

Ingredients	(3,3,4) blend	(1,1,1) blend
NR	100	100
S	3	1
TBBS	3	1
DPG	4	1

NR Natural rubber SMR GP, S soluble sulphur, TBBS N terbutyl 2 benzothiazylsulphenamide, DPG N,N diphenyl guanidine



**Fig. 1** Sensitivity experimental analysis conducted on a same NR blend. Corners and centroid of the parallelepiped represent S–TBBS–DPG concentrations experimentally tested at four different temperatures. Letters A and B represent the experimental % reversion at 8 min at 150 and 180 °C, respectively

further set of rheometer curves at different temperatures was obtained considering the centroid of the parallelepiped, with the aim of evaluating the curing behaviour at an intermediate situation.

Since the discussion of the experimental results and the systematic application of the numerical model based on experimental data is the object of a parallel study [20], here the model is validated only on two corners of the parallelepiped for the sake of conciseness. In particular, points P1 and P2 in Fig. 1 are considered, corresponding to S–TBBS–DPG concentrations equal to 3-3-4 and 1-1-1, respectively. For the sake of clearness from here on, point P2 system will be named with NR+(S,TBBS,DPG)(1,1,1) and point P1 with NR+(S,TBBS,DPG)(3,3,4).

In Tables 2 and 3 a synopsis of the main properties exhibited by the rheometer curves is provided, as for instance time at which the maximum torque is reached, the value of the maximum torque, accelerators concentrations and curing temperature.

Crude experimental data obtained in the rheometer chamber are provided in Fig. 2 for (NR+(S,TBBS,DPG)(3,3,4) system and Fig. 3 for NR+(S,TBBS,DPG)(1,1,1).

**Table 2** Rheometer curves NR+(S,TBBS,DPG)(3,3,4) system

T curing	150	160	170	180
S phr	3	3	3	3
[S]	$9.40 \times 10^{-2}$	$9.40 \times 10^{-2}$	$9.40 \times 10^{-2}$	$9.40 \times 10^{-2}$
TBBS phr	3	3	3	3
[TBBS]	$1.02 \times 10^{-2}$	$1.02 \times 10^{-2}$	$1.02 \times 10^{-2}$	$1.02 \times 10^{-2}$
DPG phr	4	4	4	4
[DPG]	$1.89 \times 10^{-2}$	$1.89 \times 10^{-2}$	$1.89 \times 10^{-2}$	$1.89 \times 10^{-2}$
(TBBS+DPG)/S	2.33	2.33	2.33	2.33
([TBBS]+[DPG])/[S]	2.47	2.47	2.47	2.47
% reversion 8 min	20	40	56	67
t max [min]	3.2	2	1	0.8
Torque max	6.4	6.4	6.4	6.4

**Table 3** Rheometer curves NR+(S,TBBS,DPG)(1,1,1) system

T curing	150 °C	160 °C	170 °C	180 °C
S phr	1	1	1	1
[S]	$3.12 \times 10^{-2}$	$3.12 \times 10^{-2}$	$3.12 \times 10^{-2}$	$3.12 \times 10^{-2}$
TBBS phr	1	1	1	1
[TBBS]	$0.34 \times 10^{-2}$	$0.34 \times 10^{-2}$	$0.34 \times 10^{-2}$	$0.34 \times 10^{-2}$
DPG phr	1	1	1	1
[DPG]	$0.47 \times 10^{-2}$	$0.47 \times 10^{-2}$	$0.47 \times 10^{-2}$	$0.47 \times 10^{-2}$
(TBBS+DPG)/S	2	2	2	2
([TBBS]+[DPG])/[S]	2.1	2.1	2.1	2.1
% reversion 8 min	0	12	30	48
t max [min]	7.75	4.5	2.92	1.61
Torque max	4.2	4.1	3.9	3.77

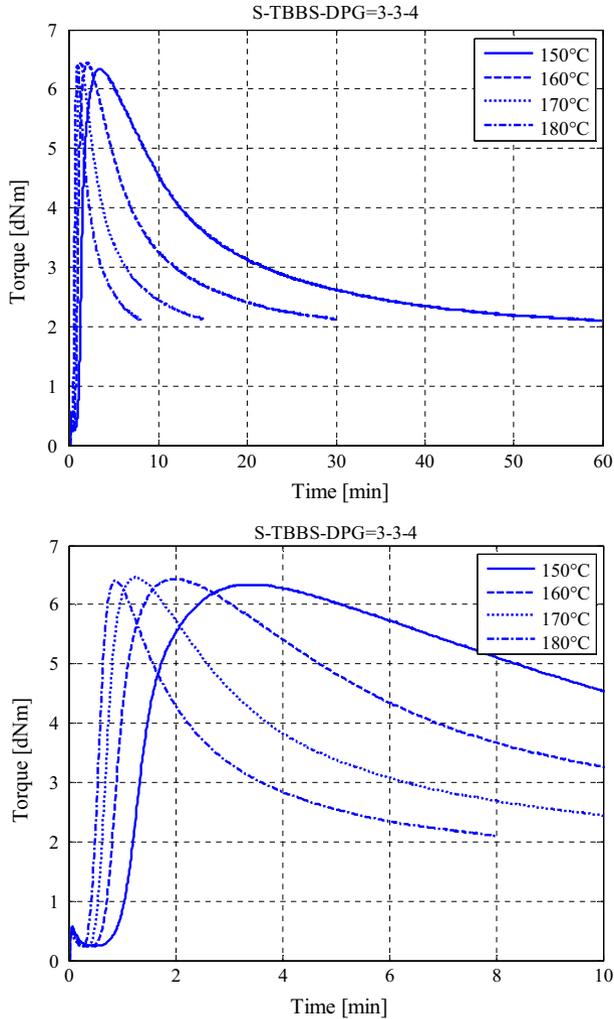
A normalization of crude experimental curves is necessary to apply the numerical model proposed hereafter, with the preliminary exclusion of the induction period.

One of the most diffused methods to heuristically link the vulcanization degree with experimental rheometer torque is the Sun and Isayev [21] procedure. In [21], the  $S'(t)$  torque is used as a measure to calculate the evolution of the vulcanization degree  $\alpha_{\text{exp}}(t)$  through the following formula:

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

where:

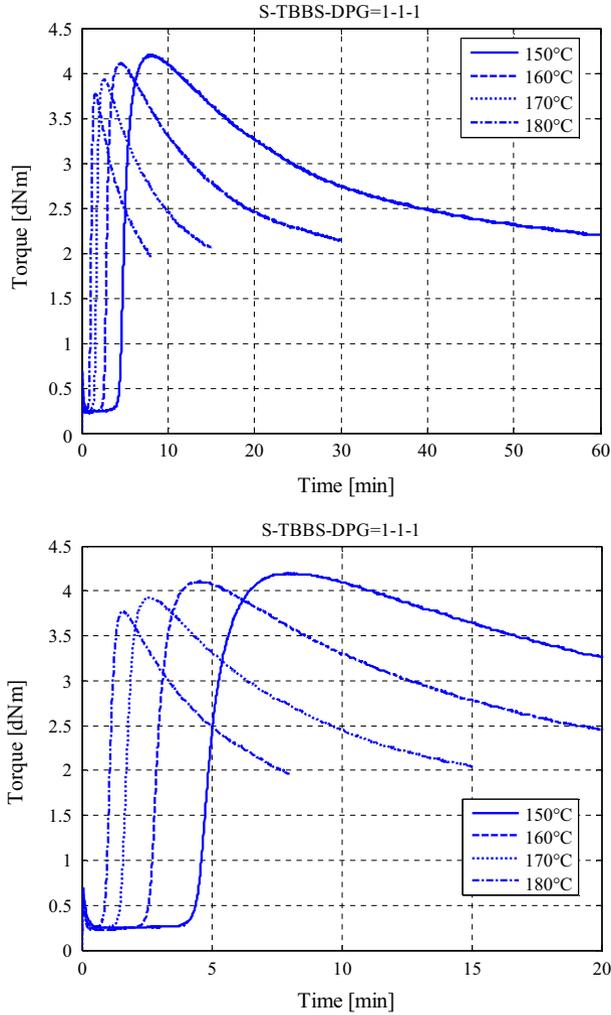
- $S_{\min T}$  is the minimum value of torque  $S'$  during a cure experiment at temperature  $T$ . Before reaching this minimum value,  $\alpha_{\text{exp}}$  is considered equal to zero.



**Fig. 2** Experimental rheometer curves, Table 2 dataset 1

- $S_{\min T_0}$  and  $S_{\max T_0}$  are the minimum and maximum torque values, obtained for a cure experiment at a temperature  $T_0$  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 results in a final degree of vulcanization lower than 100%.

In the present paper, a more straightforward but still effective normalization approach is adopted, relying into the exclusion from computations of rheometer data before scorch time and into the normalization of the torque values with the maximum



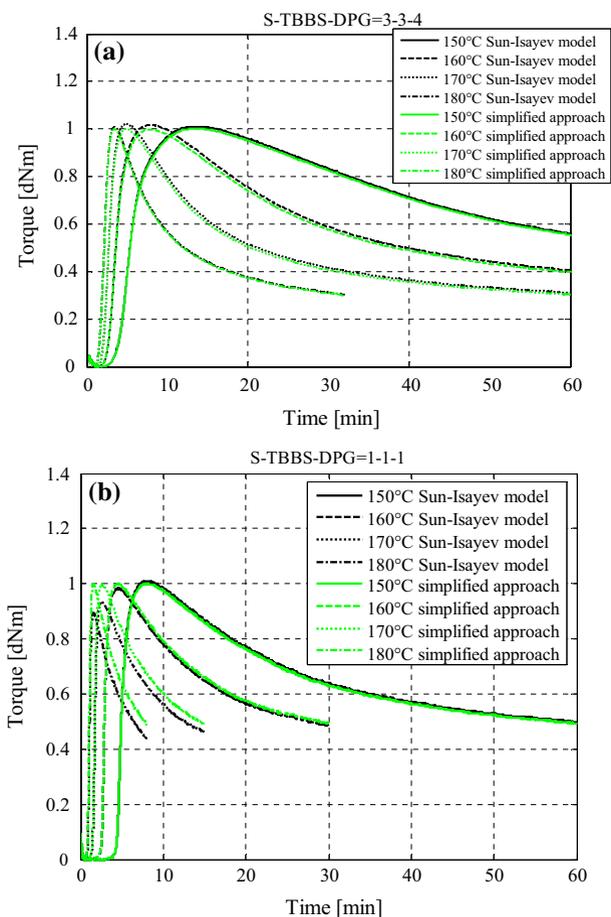
**Fig. 3** Experimental rheometer curves, Table 3 dataset 2

torque reached at that temperature. In other words, the following formula for  $\alpha_{\text{exp}}(t)$  is utilized:

$$\alpha_{\text{exp}}(t) = \frac{S'(t) - S_{\min T}}{S_{\max T} - S_{\min T}} \quad (2)$$

Note that using Eq. (2),  $\alpha_{\text{exp}}(t)$  is always between 0 and 1 at each temperature, whereas using Eq. (1) it may occur that the maximum value of  $\alpha_{\text{exp}}(t)$  is sensibly lower than 1, especially for high vulcanization temperatures.

A comparison of the two normalization procedures for the two cases analyzed in the paper is provided in Fig. 4. The induction period before the scorch time is still present, but no difference occurs if such data are deleted from the computations before



**Fig. 4** Comparison of experimental rheometer curves normalization by means of Eqs. (1) and (2). **a** NR+(S,TBBS,DPG)(3,3,4) system. **b** NR+(S,TBBS,DPG)(1,1,1) system

or after normalization. As can be noted, the difference is practically negligible (lower than 10% in the most unfavorable case, NR+(S,TBBS,DPG)(1,1,1) system at 150 °C) for all the curves considered. For this reason, the second normalization procedure is adopted for the sake of simplicity.

### 3 Revised kinetic scheme and mathematical closed form model

The basic reaction schemes assumed are classic and refer to existing literature in the field. Such schemes are known from the scientific literature, as mentioned above, see for instance [11, 14, 16, 19, 22].

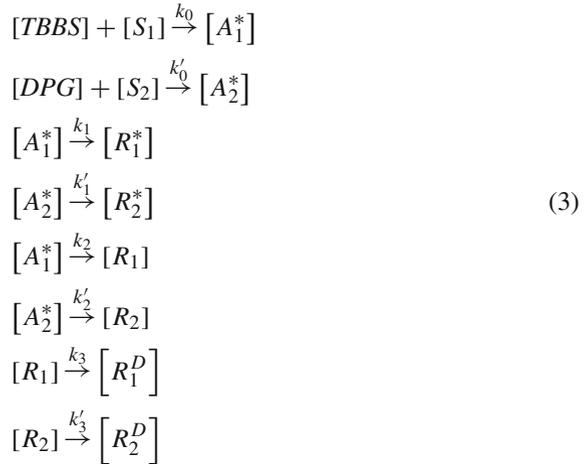
As universally accepted, many reactions occur in series and parallel during NR cured with sulphur. Typically, the chain reactions are initiated by the formation of

macro-radicals or macro-ions representing the intermediate cross-link precursor. Such reaction is associated to a velocity represented by the kinetic constant  $k_1$ .

The actual cross-linking proceeds through two pathways, which have been shown to be additive, namely the formation of the unmaturred crosslinked polymer and backbiting. In the first case, multiple S–S bonds on two contiguous polymer chains, whereas backbiting occurs when S–S bonds in the same back-bond chain. Since a multiple S–S bond is unstable, unmaturred crosslinked polymer evolves either to maturred crosslinked polymer exhibiting a single S or double bond between chains or leading to break of the bond and hence de-vulcanization, which occurs again with a backbiting of the bond in the same backbone chain. Potential interactions between DPG and TBBS can be hardly translated into mathematics and for this reason they are excluded from the model. All the reactions considered occur with a kinetic velocity depending on the temperature reaction, associated to each kinetic constant.

Let us assume that  $k_i$  and  $k'_i$  are the  $i$ -th kinetic constant associated to TBBS and DPG respectively and that index 1 (2) refers to concentrations of a chemical quantity reacting/formed with TBBS (DPG).

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



In Eq. (3),  $[S_1]$  and  $[S_2]$  are sulphur concentrations reacting with TBBS and DPG respectively,  $[A_1^*]$  and  $[A_2^*]$  the sulphurating agents,  $[R_1^*]$  and  $[R_2^*]$  the stable crosslinked chain (S–S single bonds),  $[R_1]$  and  $[R_2]$  the unstable vulcanized polymer,  $[R_1^D]$  and  $[R_2^D]$  the de-vulcanized polymer fraction (reversion).  $k_{0,1,2,3}$  and  $k'_{0,1,2,3}$  are kinetic reaction constants. Here it is worth emphasizing that  $k_{0,1,2,3}$  and  $k'_{0,1,2,3}$  are temperature dependent quantities, hence they rigorously should be indicated as  $k_{0,1,2,3}(T)$  and  $k'_{0,1,2,3}(T)$ , where  $T$  is the absolute temperature. In what follows, for the sake of simplicity, the temperature dependence will be left out.

Once established the stoichiometric ratio between sulphur reacting with TBBS and DPG respectively,  $[A_1^*]$  and  $[A_2^*]$  sulphurating agents follow two parallel and independent pathways.

$k_0$  and  $k'_0$  are kinetic constants 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 (3), the following differential equations may be written:

$$\begin{aligned}
 \text{(a)} \quad & \frac{d[A_1^*]}{dt} = -(k_1 + k_2) [A_1^*] \\
 \text{(b)} \quad & \frac{d[R_1^*]}{dt} = k_1 [A_1^*] \\
 \text{(c)} \quad & \frac{d[R_1]}{dt} = k_2 [A_1^*] - k_3 [R_1]
 \end{aligned} \tag{4}$$

Equation (4)(a) may be trivially solved by separation of variables, as follows [23]:

$$\begin{aligned}
 \text{(a)} \quad & [A_1^*] = [A_1^*]_0 e^{-(k_1+k_2)(t-t_i)} \\
 \text{(b)} \quad & \frac{d[R_1^*]}{dt} = k_1 [A_1^*]_0 e^{-(k_1+k_2)(t-t_i)} \\
 \text{(c)} \quad & \frac{d[R_1]}{dt} = k_2 [A_1^*]_0 e^{-(k_1+k_2)(t-t_i)} - k_3 [R_1]
 \end{aligned} \tag{5}$$

and, once known analytically  $[A_1^*]$  function, it can be substituted into equations (b) and (c) to provide  $[R_1^*]$  and  $[R_1]$ :

$$\begin{aligned}
 \text{(a)} \quad & [R_1^*] = \frac{k_1 [A_1^*]_0}{k_1 + k_2} \left[ 1 - e^{-(k_1+k_2)(t-t_i)} \right] \\
 \text{(b)} \quad & \frac{d[R_1]}{dt} + k_3 [R_1] = k_2 [A_1^*]_0 e^{-(k_1+k_2)(t-t_i)}
 \end{aligned} \tag{6}$$

(6)(b) is a non homogeneous first order linear differential equation, which admits the following solution composed by a general and a particular root:

$$[R_1] = \frac{k_2}{k_1 + k_2 - k_3} [A_1^*]_0 \left[ e^{-k_3(t-t_i)} - e^{-(k_1+k_2)(t-t_i)} \right] \tag{7}$$

The final concentration vulcanized polymer (related to TBBS) is thus  $[R_1^*] + [R_1]$ :

$$\begin{aligned}
 [R_1] + [R_1^*] &= \frac{k_1 [A_1^*]_0}{k_1 + k_2} \left[ 1 - e^{-(k_1+k_2)(t-t_i)} \right] \\
 &+ \frac{k_2}{k_1 + k_2 - k_3} [A_1^*]_0 \left[ e^{-k_3(t-t_i)} - e^{-(k_1+k_2)(t-t_i)} \right]
 \end{aligned} \tag{8}$$























assumption was derived in consideration of the quite similar molar ratio between the all activators and the sulphur.

Starting from previously presented models by the authors in this field, a detailed closed form approach with the straightforward analytical determination of kinetic constants of the model has been presented and discussed. The kinetic scheme is characterized by three main reactions per activator, occurring in series and parallel. The major improvement of the present approach when compared to existing literature is the derivation of a closed form expression for the crosslinking density and the determination of the kinetic constants without the need of utilizing least squares fitting routines. The model has been benchmarked on two series of experimental data at different concentrations of S, TBBS and DPG at four different temperatures. From simulations results, it was found that the kinetic constants follow reasonably well an Arrhenius law, which represents one of the most useful relationships in chemical kinetics, when an extrapolation of the behavior is needed outside the experimentally tested temperature range.

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