

Effective closed form starting point determination for kinetic model interpreting NR vulcanized with sulphur

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Abstract In this paper, a closed form analytical approach for a recently presented kinetic model proposed in Milani and Milani (Polym Test, 2013, under review) to interpret NR sulphur vulcanization in presence of either experimental or surrogate rheometer curves is proposed. The model has kinetic base and is aimed at predicting, by means of a very refined approach, the vulcanization degree of NR vulcanized with sulphur. It needs as input only rheometer curves to fit and provides as output kinetic constants of the single reactions occurring during the crosslink process. In Milani and Milani (Polym Test, 2013, under review) a cure chemical scheme constituted by five reactions occurring in series and parallel was adopted. The chemical scheme, translated mathematically into a differential equations system, was suitably re-arranged and a single analytical equation was derived, representing rubber crosslink degree evolution upon time. The main drawback of such procedure is that the five kinetic constants corresponding to each reaction were determined through a standard non-linear least squares procedure, trying to minimize the deviation of the analytical cure curve from experimental data. Such a limitation is here superseded and a major improvement is proposed utilizing (1) a closed form solution which does not require any optimization algorithm and (2) finding analytically a starting point for the unknown kinetic constants, very near to the actual solution and thus very convenient for a successive least squares minimization. In the model, it is shown how the analytical condition deduced from the scorch point (second derivative of the rheometer curve equal to zero) and two further conditions, e.g. the time at 90% of vulcanization and the reversion percentage, allow the simple direct evaluation of kinetic constants, providing a closed form ana-

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lytical formula to predict well the state of cure of the rubber under consideration. To assess the results obtained with the model proposed, several examples on two different NRs are discussed. The approach proved to be extremely robust and much faster when compared with the model proposed by Milani and Milani (Polym Test, 2013, under review).

Keywords Vulcanization · Natural rubber (NR) · Mathematical model · Closed form solution

1 Introduction

In its most general meaning, vulcanization may be defined as any treatment that decreases the flow of an elastomer, increases its tensile strength and modulus, but preserves its extensibility.

Methods for rubber curing have historically received considerable attention in manufacturing process, especially for rubber items with relatively large size, because in such cases, the different temperature profiles of the core and the skin occurring during vulcanization play a role into the resultant reticulation degree achieved at the end of the heating phase [2].

Among the others, vulcanization with sulphur is maybe the most popular technique for both natural rubber (NR) and its synthetic counterpart (IR), as well as for other synthetic rubbers such as polybutadiene (BR), styrene–butadiene rubber (SBR), nitrile rubber (NBR), butyl rubber (IIR), and ethylene–propylene–diene rubber (EPDM), only to indicate the most important in the market.

Sulphur is used in combination with one or more accelerators (e.g. delayed-action sulphenamides, thiazoles, thiuram sulphides, etc.) and an activator system, as for instance soluble zinc—which increases drastically the efficiency of crosslinking formation—and fatty acid. In this context, many reagents are nowadays at disposal associated with sulphur vulcanization of polydienes [3,4] allowing a drastic improvement of the basic cure capabilities obtainable with sulphur.

In general, it is commonly accepted that vulcanization with sulphur takes place roughly into three steps, namely induction, crosslinking and post-crosslinking.

The idea comes from the macroscopic interpretation of what happens to a sample during controlled temperature curing conditions in the rheometer chamber. The rheometer curve, which is simply the measure of the torque resistance of a sample subjected to fixed temperature cure at increasing time, typically exhibits an initial plateau with low and slightly decreasing torque, a rapid crosslinks formation with a significant torque increase and eventually a final degradation, i.e. a torque decrease, at sufficiently large vulcanization times, usually denoted with the term “reversion” [5–14]. Reversion is a key distinctive aspect of the vulcanization with sulphur and, from a macroscopic point of view, consists in a remarkable decrease or rubber vulcanized properties at the end of the curing process. It depends on a series of concurring factors, the most important being rubber type, its structure, % of double bonds [5], presence of additives, in particular the accelerators, and co-adjuvants, as well as vulcanization temperature.

Reversion is often associated with high-temperature curing. Loo [6] was probably the first to systematically demonstrate that, as the cure temperature rises, the crosslink density drops, thus increasing the degree of reversion. Chen et al. [7] shown that this phenomenon seems to appear when two reactions are competing during vulcanization, whereas Morrison and Porter [8] confirmed that the observed reduction in vulcanizate properties is caused by de-sulphuration and decomposition, which always proceed in parallel.

Chemical reactions associated with sulphur vulcanization are complex and involve only a few atoms in each polymer molecule; therefore, to propose a quantitative macroscopic model to predict vulcanization in terms of the physical properties of the rubber is, still now, a very challenging issue.

The so-called phenomenological approach was probably the first to be applied in practice and essentially relies into a mathematical scheme with constants obtained fitting experimental data, but without a clear kinetic interpretation connected to the reactions occurring during curing. Kamal and Sorour's [15] model, followed by many others in the recent and less recent past [16–18], belong to this category and essentially are conceived to mathematically fit the rubber behavior in a rheometer chamber by means of a macroscopic approach.

While such procedures are very effective in practice and are particularly suited for a direct implementation in common software for the curing industrial analysis of items with very complex geometries (as for instance tires) [2], their application is only possible after a costly experimental validation at different temperatures of the blend under study and does not provide any information on the actual chemical reactions occurring. They therefore fail to be predictive in different conditions than those tested experimentally.

With the increased understanding of the nature of the reaction, more attention has been paid to the so-called kinetic approach. Basically, the procedures belonging to this latter family rely into the determination of mathematical relations between degree of cure and time capable to fit experimental data, once that a chemical reaction scheme is hypothesized and translated into mathematical differential relations.

Ding and Leonov [9] and Ding et al. [10] were probably the first to propose a complex kinetic scheme for NR trying to interpret induction, crosslinking and devulcanization. The approach essentially relies into summing exponential laws, where crosslinking and devulcanization are ruled by two distinct kinetic constants, derived from the simplified kinetic scheme proposed by Coran [11].

Han et al. [19], recently, have provided a reasonable description of reversion, using a reduced number of kinetic parameters (with physical meaning), basing on the assumption that during vulcanization, after an induction period during which no crosslinking reaction takes place, both stable and unstable sulfur crosslinks can be formed by first order reactions, the latter being subject to subsequent degradation due to another first order reaction. The model was partially modified by Leroy et al. [20], and again by Milani et al. [21], where a quite complex but fully comprehensive mathematical model with 7 kinetic constants was proposed. The model has kinetic base and is aimed at predicting, by means of a very refined approach, the vulcanization degree of NR vulcanized with sulphur. It needs as input only rheometer curves to fit and provides as out-

put kinetic constants of the detailed single reactions occurring during the crosslinking process.

In order to supersede the major limitation of Milani et al. [21] approach, i.e. its complexity which does not allow dealing with closed form functions for the crosslinking degree, Milani and Milani [1] slightly simplified the kinetic scheme. Despite the introduction of such complexity downgrading, the model proved to fit reasonably well experimental data, at the same time allowing to rigorously deriving a closed form solution for the curing degree. The main limitation of this latter approach is that the determination of the unknown kinetic constant parameters passes through the utilization of non-linear least squares fitting where data to fit are rheometer curves. As well known, especially in presence of multivariable problems, the success of the least squares minimization is strictly connected to the starting point choice. In some cases, indeed, the algorithm may fail in finding the optimal solution or may require prohibitive computational times.

The aim of the present paper is to propose a rigorous strategy to determine analytically such starting point. In addition it is demonstrated how the function with kinetic constants derived analytically fits in the majority of the cases experimental data very well, meaning that the utilization of least squares may be by-passed. In the model, it is shown how the analytical condition deduced from the scorch point (second derivative of the rheometer curve equal to zero) and two further conditions, e.g. the time at 90 % of vulcanization and the reversion percentage, allow the simple direct evaluation of kinetic constants, providing a closed form analytical formula to predict well the state of cure of the rubber under consideration.

To assess the results obtained with the model proposed, two sets of experimental data available from [20] and [22] are considered.

The first set of data studied refers to a number of rheometer curves performed on the same NR blend in presence of different accelerators at variable concentrations, also in presence of moderate and strong reversion, whose a few specifics are available from the literature in [22]. To obtain full rheometer curves, the procedure proposed in [1] to obtain surrogate data from a few experimental information available, is applied and meta-data are treated as they were real experimental rheometer curves.

The second set of data is constituted by 5 rheometer curves obtained on the same blend in [20] at different temperatures, exhibiting strong reversion when the temperature is increased up to 170 °C.

In both cases, the procedure proved to be very fast and reliable and has the advantage of providing very accurate results even without the utilization of least-squares fitting.

The approach is general and can be used in presence of any rubber compound, provided that suitable but limited experimental data are at disposal to characterize crosslinking reactions at different temperatures.

2 The kinetic mathematical model revised

A mechanistic model, based on a simplified kinetic scheme, is here presented to numerically reproduced rheometer curves for NR vulcanized with sulphur. The uti-

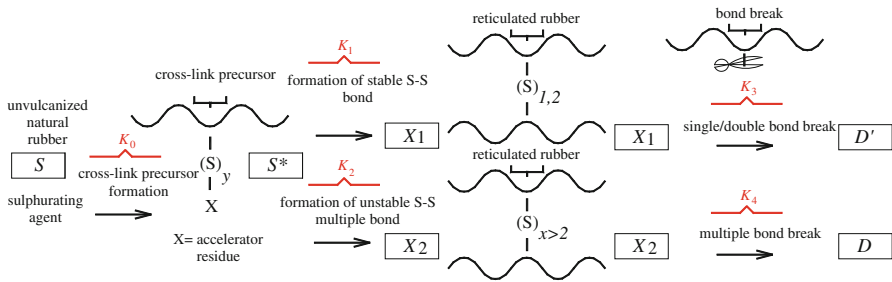


Fig. 1 Products and schematic reaction mechanisms of NR accelerated sulphur vulcanization

lization of a mechanistic model is particularly useful because it allows deducing kinetic constants at the base of the partial reactions characterizing final crosslinking of the blend, thus providing information on the behaviour of rubber under curing at different temperatures. The cure percentage obtained at the end of an industrial process may therefore be predicted without the need to perform extensive experimentation case by case [2].

A quite complex model for the vulcanization with sulphur of NR and requiring the iterated solution of an Ordinary Differential Equations System (ODES) has been recently proposed by the authors in [21]. Here, a new approach is proposed, which simplifies the mathematical formulation [21], but allowing to deduce a closed form equation for the degree of vulcanization as a function of time, with the possibility to suitably represent reversion when appropriate.

The basic reaction schemes assumed in the present paper are schematically represented in Fig. 1. Such scheme simplifies well established chemical interpretations available from the technical literature, see e.g. [9, 19, 20].

In particular, the scheme assumed may be regarded at the same time as a simplification of the procedure proposed in [21] and a modification with an increase of both the level of complexity and accuracy with respect to the well-known Han et al. [19] and Leroy et al. [20] model.

As can be seen, the main reactions that are considered relevant within the overall complexity of the vulcanization process are five, occurring in series and parallel.

The chain reaction is 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_0 .

The actual cross-linking proceeds through two pathways, which have been shown to be additive, namely the formation of more stable and unstable S–S bonds.

Since a multiple S–S bond is unstable, unmaturred crosslinked polymer evolves either to matured 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. All these reactions occur with a kinetic velocity depending on the temperature reaction, associated to four kinetic constants: K_1 , K_2 , K_3 and K_4 .

To summarize, adopting for NR the kinetic scheme constituted by the chemical reactions shown in Fig. 1, the following schematization holds:



In Eq. (1), S is the uncured polymer, S^* the unmaturred crosslinked polymer, which evolves into matured crosslinked polymer $X_1 + X_2$, with X_1 indicating the stable crosslinked part and with X_2 the unstable part. Part of both X_1 and X_2 may evolve into D and D' unvulcanized polymer due to multiple S–S chains breaks and consequent backbiting. $K_{0,\dots,4}$ are kinetic reaction constants. Here it is worth emphasizing that $K_{0,\dots,4}$ are temperature dependent quantities, hence they rigorously should be indicated as $K_{0,\dots,4}(T)$, where T is the absolute temperature. In what follows, for the sake of simplicity, the temperature dependence will be left out.

Differential equations associated to chemical reactions (1) are the following:

$$\begin{aligned}
 \text{(a)} \quad \frac{dS}{dt} &= -K_0 S \\
 \text{(b)} \quad \frac{dS^*}{dt} &= K_0 S - (K_1 + K_2) S^* \\
 \text{(c)} \quad \frac{dX_1}{dt} &= K_1 S^* - K_3 X_1 \\
 \text{(d)} \quad \frac{dX_2}{dt} &= K_2 S^* - K_4 X_2
 \end{aligned}
 \tag{2}$$

From Eq. (2)(a) we can derive directly the analytical function for S by separation of variables as:

$$\frac{dS}{S} = -K_0 dt \Rightarrow \ln \frac{S}{S_0} = -K_0 t \Rightarrow S(t) = S_0 e^{-K_0 t}
 \tag{3}$$

where S_0 is the initial concentration of $S(t)$, which is assumed unitary to fit normalized experimental data.

Substituting Eq. (3) into Eq. (2)(b), we obtain a first order non homogeneous linear differential equation (1ODE) as follows:

$$\frac{dS^*}{dt} + (K_1 + K_2) S^* - K_0 S_0 e^{-K_0 t} = 0
 \tag{4}$$

The solution of the characteristic polynomial for the homogeneous part of (4) is $\lambda = -(K_1 + K_2)$, whereas substituting the equation $S_p^* = K_0 S_0 / (K_1 + K_2 - K_0) e^{-K_0 t}$ into (4) we obtain an identity $0=0$, meaning that S_p^* is a particular solution for (4).

Therefore, the solution of the differential equation (4) turns out to be the following:

$$S^* = C_2 e^{-(K_1+K_2)t} + \frac{K_0 S_0}{K_1 + K_2 - K_0} e^{-K_0 t}
 \tag{5}$$

where C_2 is an integration constant. If we assume the reasonable initial condition $S^*(t) = 0$, then:

$$C_2 = -\frac{K_0 S_0}{K_1 + K_2 - K_0} \quad (6)$$

and:

$$S^* = \frac{K_0 S_0}{K_1 + K_2 - K_0} \left(e^{-K_0 t} - e^{-(K_1 + K_2)t} \right) \quad (7)$$

Substituting (7) into Eq. (2)(c) and (d) we obtain respectively:

$$\frac{dX_1}{dt} + K_3 X_1 = K_1 C_2 e^{-(K_1 + K_2)t} + \frac{K_1 K_0 S_0}{K_1 + K_2 - K_0} e^{-K_0 t} \quad (8)$$

and

$$\frac{dX_2}{dt} + K_4 X_2 = K_2 C_2 e^{-(K_1 + K_2)t} + \frac{K_2 K_0 S_0}{K_1 + K_2 - K_0} e^{-K_0 t} \quad (9)$$

Eqs. (8) and (9) admit the following similar closed form solutions:

$$\begin{aligned} X_2(t) &= C_4 e^{-K_4 t} - C_2 \frac{K_1}{K_1 + K_2 - K_4} e^{-(K_1 + K_2)t} \\ &\quad - \frac{K_1 K_0 S_0}{(K_0 - K_4)(K_1 + K_2 - K_0)} e^{-K_0 t} \\ X_1(t) &= C_6 e^{-K_3 t} - C_2 \frac{K_2}{K_1 + K_2 - K_3} e^{-(K_1 + K_2)t} \\ &\quad - \frac{K_2 K_0 S_0}{(K_0 - K_3)(K_1 + K_2 - K_0)} e^{-K_0 t} \end{aligned} \quad (10)$$

The role played by constants K_3 and K_4 in (10) is swapped: they represent reversion for X_1 and X_2 respectively. Assuming $X_1(0) = X_2(0) = 0$ it is possible to determine constants C_4 and C_6 as follows:

$$\begin{aligned} C_4 &= C_2 \frac{K_1}{K_1 + K_2 - K_4} + \frac{K_1 K_0 S_0}{(K_0 - K_4)(K_1 + K_2 - K_0)} \\ &= -\frac{K_0 K_1 S_0}{(K_1 + K_2 - K_0)(K_1 + K_2 - K_4)} + \frac{K_1 K_0 S_0}{(K_0 - K_4)(K_1 + K_2 - K_0)} \\ &= \frac{K_0 K_1 S_0 (K_1 + K_2 - K_4 - K_0 + K_4)}{(K_0 - K_4)(K_1 + K_2 - K_0)(K_1 + K_2 - K_4)} \end{aligned}$$

$$\begin{aligned}
 &= \frac{K_0 K_1 S_0}{(K_0 - K_4)(K_1 + K_2 - K_4)} \\
 C_6 &= \frac{K_0 K_2 S_0}{(K_0 - K_3)(K_1 + K_2 - K_3)} \quad (11)
 \end{aligned}$$

A closed form solution for the crosslink degree, intended as $\alpha = X_1 + X_2$, may therefore be deduced from relations (11), (10) and (6). In particular, the variation of the cure degree as a function of time t assumes the following form:

$$\begin{aligned}
 \alpha = X_1 + X_2 &= C_4 e^{-K_4 t} + C_6 e^{-K_3 t} - C_2 \frac{K_1}{K_1 + K_2 - K_4} e^{-(K_1 + K_2)t} \\
 &- C_2 \frac{K_2}{K_1 + K_2 - K_3} e^{-(K_1 + K_2)t} + \\
 &- \frac{K_0 K_1 S_0}{(K_1 + K_2 - K_0)(K_0 - K_4)} e^{-K_0 t} \\
 &- \frac{K_0 K_2 S_0}{(K_1 + K_2 - K_0)(K_0 - K_3)} e^{-K_0 t} \quad (12)
 \end{aligned}$$

Having indicated with C_2 , C_4 and C_6 the following integration constants:

$$\begin{aligned}
 C_2 &= -\frac{K_0 S_0}{K_1 - K_0 + K_2} \\
 C_4 &= \frac{K_0 K_1 S_0}{(K_0 - K_4)(K_1 + K_2 - K_4)} \\
 C_6 &= \frac{K_0 K_2 S_0}{(K_0 - K_3)(K_1 + K_2 - K_3)} \quad (13)
 \end{aligned}$$

And with S_0 the initial amount of unvulcanized polymer, which, as already mentioned, has to be put equal to 1 when the crosslink percentage α (ranging from 0 to 100 %) has to be determined.

3 Starting point determination

In order to evaluate kinetic constants of the model, a non-linear least squares routine—to fit with the mathematical model normalized rheometer curves—has to be used, see [23]. The utilization of non-linear optimization algorithms is not always effective, may fail in some cases in finding the minimum point or may require an excessive processing time. It is therefore interesting to analytically deduce a reasonable starting point for the algorithm, which furnishes predictions of the crosslinking degree via Eq. (12) near the experimental data.

A reasonable strategy to find such a starting point may be followed assuming no reversion, i.e. $K_3 = K_4 = 0$.

In this way, Eq. (12) simplifies as follows:

$$\alpha = X_1 + X_2 = S_0 - C_2 e^{-(K_1+K_2)t} - \frac{(K_1 + K_2)S_0}{(K_1 + K_2 - K_0)} e^{-K_0 t} \quad (14)$$

with:

$$\begin{aligned} C_2 &= -\frac{K_0 S_0}{K_1 - K_0 + K_2} \\ C_4 &= \frac{K_1 S_0}{K_1 + K_2} \\ C_6 &= \frac{K_2 S_0}{K_1 + K_2} \end{aligned} \quad (15)$$

It is worth noting that, as expected, in Eq. (14) $\alpha(0) = 0$ and $\lim_{t \rightarrow +\infty} \alpha(t) = S_0$.

In addition, it is interesting to underline that Eq. (14) is a function depending on the kinetic constants $K_1 + K_2 = K'$ and K_0 , i.e. it is possible to reduce kinetic constants from 3 (K_1 , K_2 and K_0) to 2 (K' and K_0).

Re-writing (14) and its first derivative in terms of K' and K_0 , we obtain:

$$\begin{cases} \frac{\alpha}{S_0} = 1 + \frac{K_0}{K' - K_0} e^{-K't} - \frac{K'}{K' - K_0} e^{-K_0 t} \\ \frac{1}{S_0} \frac{d\alpha}{dt} = -\frac{K' K_0}{K' - K_0} e^{-K't} + \frac{K' K_0}{K' - K_0} e^{-K_0 t} \end{cases} \quad (16)$$

The first derivative reported in Eq. (16) exhibits clearly a maximum point, which physically occurs in correspondence of the scorch point t_2 , being indeed t_2 defined as the time where there is a sign variation of the rheometer curve concavity (from concave to convex). t_2 time is hence evaluated equating to zero the second derivative of the crosslink function as follows:

$$\begin{aligned} \frac{1}{S_0} \frac{d^2\alpha}{dt^2} &= -\frac{K' K_0}{K' - K_0} \left(K' e^{-K't} - K_0 e^{-K_0 t} \right) = 0 \\ &\Rightarrow \left(K' e^{-K't_2} - K_0 e^{-K_0 t_2} \right) = 0 \\ &\Rightarrow \frac{K'}{K_0} = \frac{e^{-K_0 t_2}}{e^{-K't_2}} \Rightarrow \frac{K'}{K_0} = e^{-(K_0 - K')t_2} = e^{-K_1 \left(\frac{K_0}{K'} - 1 \right) t_2} \\ &\Rightarrow t_2 = \frac{\xi \ln \xi}{-K' (1 - \xi)} = \frac{\xi \ln \xi}{K' (\xi - 1)} \end{aligned} \quad (17)$$

where ξ indicates K'/K_0 ratio.

From (17), once time t_2 is known from experimental evidences, the kinetic constant K' may be estimated as a function of the ratio $\xi = K'/K_0$ as follows:

$$K' = \frac{\xi \ln \xi}{t_2 (\xi - 1)} \quad (18)$$

Imposing the passage of the function (14) through a point, say $(t_1 \alpha(t_1))$, we obtain the following non-linear equation which depends exclusively on the unknown ξ ratio:

$$\alpha(t_1) = 1 + \frac{1}{\xi - 1} e^{-\frac{\xi \ln \xi}{t_2(\xi - 1)} t_1} - \frac{\xi}{\xi - 1} e^{-\frac{\ln \xi}{t_2(\xi - 1)} t_1} \tag{19}$$

From Eq. (19) the following function $F(\xi)$ may be derived:

$$F(\xi) = -\alpha_1 + 1 + \frac{1}{\xi - 1} e^{-\frac{\xi \ln \xi}{t_2(\xi - 1)} t_1} - \frac{\xi}{\xi - 1} e^{-\frac{\ln \xi}{t_2(\xi - 1)} t_1} \tag{20}$$

According to authors' experience, $F(\xi)$ exhibits only one solution for ξ ranging within the expected interval, say from 1 to 3, which is the common variability range of the ratio between K' and K_0 . It is worth noting that it is expected that always $K' > K_0$.

The identification of the zero point for function $F(\xi)$ may be done graphically (plotting the absolute value of $F(\xi)$) or numerically and it allows to obtain an estimation for ξ to substitute into (18), and hence permits the evaluation of kinetic constants K' and K_0 by means of the following relations:

$$F(\xi) = -\alpha_1 + 1 + \frac{1}{\xi - 1} e^{-\frac{\xi \ln \xi}{t_2(\xi - 1)} t_1} - \frac{\xi}{\xi - 1} e^{-\frac{\ln \xi}{t_2(\xi - 1)} t_1} = 0$$

$$K' = \frac{\xi \ln \xi}{t_2(\xi - 1)} \tag{21}$$

Once K_0 and K' are known, reversion kinetic constants are evaluated on the original Eq. (12) with reversion, assuming at a first attempt $K_3 = 0$. Such hypothesis appears physically quite reasonable because K_3 is related to reversion of stable simple and double bonds. It is therefore expected that K_3 is much lower than K_4 .

Within such assumption, the equation expressing the crosslinking degree assumes the following form:

$$\alpha = X_1 + X_2 = C_4 e^{-K_4 t} + C_6 - C_2 \frac{\rho K'}{K' - K_4} e^{-K' t} - C_2 \frac{(1 - \rho) K'}{K'} e^{-K' t} +$$

$$- \frac{K_0 \rho K' S_0}{(K' - K_0)(K_0 - K_4)} e^{-K_0 t} - \frac{K_0 (1 - \rho) K' S_0}{(K' - K_0)(K_0)} e^{-K_0 t}$$

$$C_2 = - \frac{K_0 S_0}{K' - K_0}$$

$$C_4 = \frac{K_0 \rho K' S_0}{(K_0 - K_4)(K' - K_4)}$$

$$C_6 = \frac{K_0 (1 - \rho) K' S_0}{K_0 K'} \tag{22}$$

where the parameter ρ ranges from 0 to 1 and indicates the amount of K' due to K_1 , i.e. $K_1 = \rho K'$, and to K_2 , i.e. $K_2 = (1 - \rho) K'$. Such parameter should be a-posteriori determined by means of suitable experimentations identifying the percentage of single

and multiple bonds in the cross-linked rubber. In this paper, for the sake of simplicity $\rho = 0.5$ is assumed.

Imposing that Eq. (22) passes through point $P_3 = (t_3 \ \alpha_3)$ of the rheometer chart, where P_3 is placed in the reversion range far from the maximum of the rheometer curve, it is possible to estimate K_4 finding the zero of the following single variable function:

$$\begin{aligned}
 F_2 = & -\alpha_3 + \frac{K_0 \rho K' S_0}{(K_0 - K_4)(K' - K_4)} e^{-K_4 t_3} + \frac{K_0(1 - \rho) K' S_0}{K_0 K'} \\
 & + \frac{K_0 S_0}{K' - K_0} \frac{\rho K'}{K' - K_4} e^{-K' t_3} + \frac{K_0 S_0}{K' - K_0} \frac{(1 - \rho) K'}{K'} e^{-K' t_3} + \\
 & - \frac{K_0 \rho K' S_0}{(K' - K_0)(K_0 - K_4)} e^{-K_0 t_3} - \frac{K_0(1 - \rho) K' S_0}{(K' - K_0)(K_0)} e^{-K_0 t_3} \quad (23)
 \end{aligned}$$

4 Numerical applications

In this Section, a validation of the closed form approach proposed in the previous Section is performed considering two distinct sets of experimental data. The first is a NR blend vulcanized with sulphur in presence of different accelerators at the same curing temperature (144 °C). A few data of the rheometer curves are available in [22], representing the characteristic points of the cure curves. Due to the insufficient information available in [22], a meta-data approach, based on a numerical fitting of the experimental data available through a non-mechanistic model based on cubic splines has been used in [1], and surrogated rheometer curves so obtained will be used in this Section for the validation of the present model.

The second set of examples deals with a NR blend tested at five different temperatures in [20] and also in [21], where full rheometer curves are at disposal.

4.1 NR cured with different accelerators, meta data curves fitting

Experimental data utilized in the present sub-section for the validation of the mathematical model proposed may be found in [22], where the reader is referred for details.

In [22], only a few meaningful points representing the whole experimental cure curves are reported, as usually done in common practice to characterize cure properties of commercial blends. With the aim of deducing from such experimental available information, an estimation of the entire rheometer curves (not available), in [1] a procedure based on natural cubic splines has been proposed, which puts at disposal to users surrogate meta-data passing through the experimental points.

In this section, such meta-data will be considered as they were experimental cure curves to fit with the kinetic closed form approach proposed.

The composition of the blend considered within the present validation is provided in Table 1. Several accelerators are added to the same blend with the aim of testing their activity at a fixed curing temperature equal to 144 °C. Accelerators names, with their acronyms used, are summarized in Table 2, whereas in Table 3 a synopsis of the

Table 1 Composition of the 1st NR blend used for model validation

Component	phr
Natural rubber (SMR 5CV)	100
N330 carbon black	50
Naphthenic oil	5
Stearic acid	6
Sulphur	2
ZnO	5

Table 2 Typology of accelerators used experimentally to test the activity of different accelerators in NR vulcanization, 1st NR blend used for model validation

MBTS	benzothiazyl disulfide
MBS	<i>N</i> -oxydiethylen-2-benzothiazyl-sulfenamide
TBBS	<i>N</i> - <i>t</i> -butyl-2-benzothiazyl-sulfenamide
TSSR	2-ethylamino-4-diethylamino-6-heptyldithio-sym-triazine
PYSSPY	2,2'-dithiobispyridine- <i>N</i> -oxide
TSST	bis-(2-ethylamino-4-diethylamino-6-sym-triazinyl)disulfide
PSSR	beta-(di- <i>n</i> -butylphosphorodithioylthio)-propionic acid,methyl ester
TBBS	<i>N</i> - <i>t</i> -butyl-2-benzothiazyl-sulfenamide
ZDBDP	Zinc <i>O,O</i> -di- <i>n</i> -butylphosphorodithioate
CTP	<i>N</i> -(cyclohexylthio)phthalimide

experimented data-sets, the numerical simulations performed and the concentration and typology of accelerators used in the tests is reported.

As can be seen from Table 3, five different experimentation sets are considered for validation purposes. Some data are replicated, in particular 1-1, 2-1, 3-1 and 4-1 refer to the same accelerator TBBS with the same concentration (0.6 phr), 4-7 and 5-3 to PYSSPY and 4-5 and 5-2 to MBTS.

In Figs. 2, 3, 4, 5, 6 the performance of the closed form approach in fitting (surrogate) experimental cure curves is comparatively depicted.

Three numerical curves are compared with experimental data, namely (a) the closed form solution without reversion of Eq. (14), (b) the approach with reversion where kinetic constants are evaluated with the closed form procedure proposed in this paper, Eq. (22), and (c) the curve corresponding to the same Eq. (22) after least squares best fitting, with starting point corresponding to the collection of kinetic constants used to plot curve (b).

As it is possible to notice, for all cases analyzed, the correspondence with the curves to fit is almost always very promising. Obviously, the numerical curve without reversion, curve (a), fits well experimental data only before the range where reversion becomes relevant, i.e. at small curing times. The numerical performance of the second curve (with reversion), curve (b), is very satisfactory in almost all the cases analyzed,

Table 3 1st NR blend used for model validation. Synoptic chart of the data sets considered for the comparisons

Label	Data set #1			Data set # 2
	1-1	1-2	1-3	2-1
# numerical simulation	1	2	3	1
Accelerator concentration phr	TBBS 0.6	TBBS 0.2 ZDBDF 0.76	TBBS 0.2 ZDBDF 0.76 CTP 0.72	TBBS 0.6
Label	Data set # 2		Data set # 3	
	2-3	2-4	3-1	3-2
# numerical simulation	4	5	1	6
Accelerator concentration phr	TSST 0.7	TSSR 0.7	TBBS 0.6	TSSR 1.0
Label	Data set # 3		Data set # 4	
	3-4	3-6	4-1	4-4
# numerical simulation	7	8	1	9
Accelerator concentration phr	TSSR 0.5 PSSR 0.5	PSSR 1.0	TBBS 0.6	MBS 0.25 PYSSPY 1.0
Label	Data set # 4		Data set # 5	
	4-5	4-7	5-2	5-3
# numerical simulation	10	11	10	11
Accelerator concentration phr	MBTS 1.0	PYSSPY 1.0	MBTS 1.0	PYSSPY 1.0

also considering the fact that the utilization of non-linear least squares data fitting is not required.

Finally, curve (c) appears in the majority of the cases superimposable with the curves to fit, with a correct estimation of both initial curing rate and reversion percentage. In few cases, a small but still acceptable deviation in an initial range between numerical and meta-data is experienced, which appears more connected to the construction of the meta-data with a few experimental points instead of a lack of accuracy of the simplified mechanistic model of vulcanization proposed.

In addition, it is worth mentioning that the utilization of the kinetic constants used to plot curve (b) as starting point for curve (c) has the important advantage of both drastically increase the robustness of the non-linear algorithm and to reduce considerably the time needed to achieve convergence.

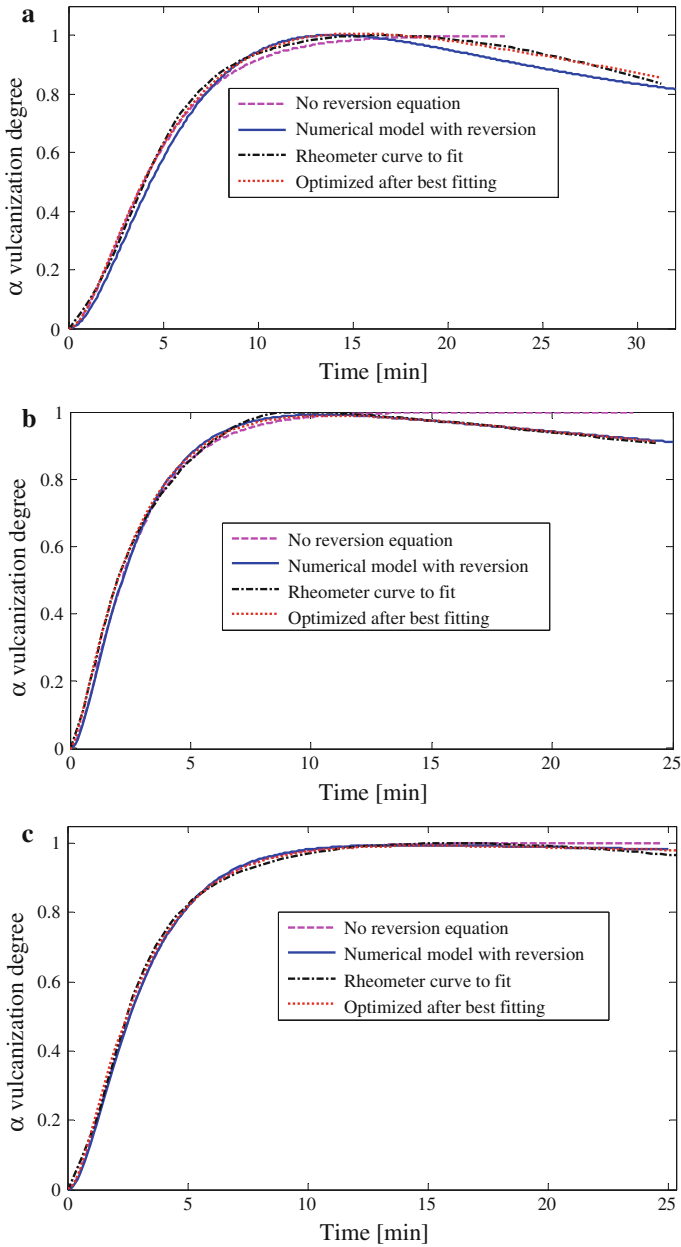


Fig. 2 1st NR blend, data set 1. **a** 1-1 data set, **b** 1-2 data set, **c** 1-3 data set

The convergence of the non-linear least squares routine is shown in Fig. 3 for the first data set. The convergence trend of the model applied to the other data sets is similar and is not reported here for the sake of conciseness. In Fig. 3, for each

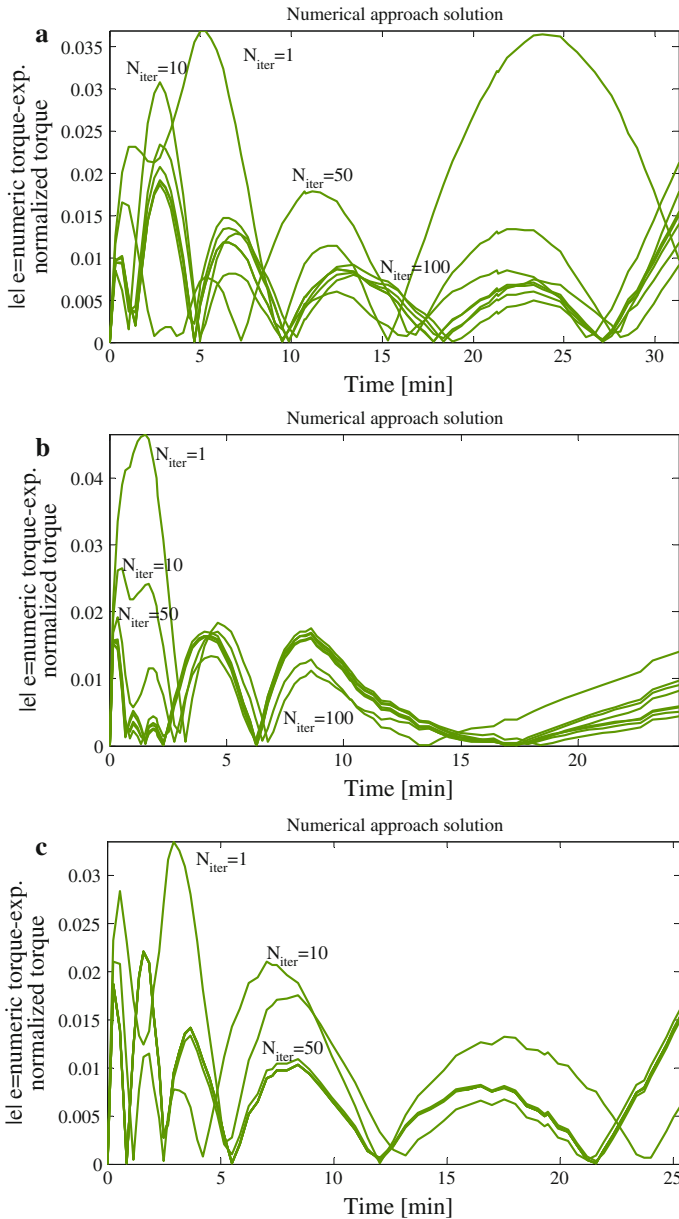


Fig. 3 1st NR blend, convergence performance during best fitting using the starting point proposed in the paper. **a** 1-1 data set, **b** 1-2 data set, **c** 1-3 data set

iteration, the absolute value of the difference between experimental normalized torque and numerical prediction is shown at increasing curing times. As can be noted, the deviation of the model from the target data is minimal and tends to quickly reduce after a few iterations. Typically, after 30–40 iterations, the algorithm may be considered near

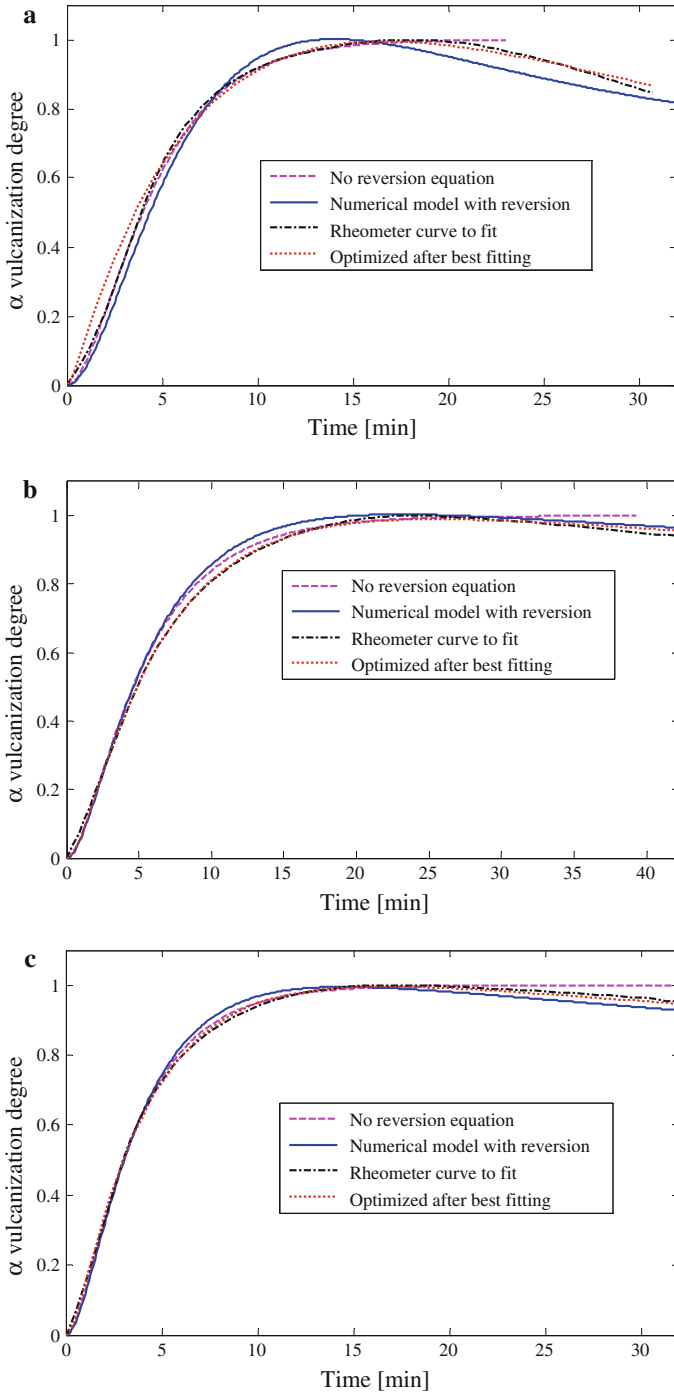


Fig. 4 1st NR blend, data set 2. **a** 2-1 data set, **b** 2-3 data set, **c** 2-4 data set

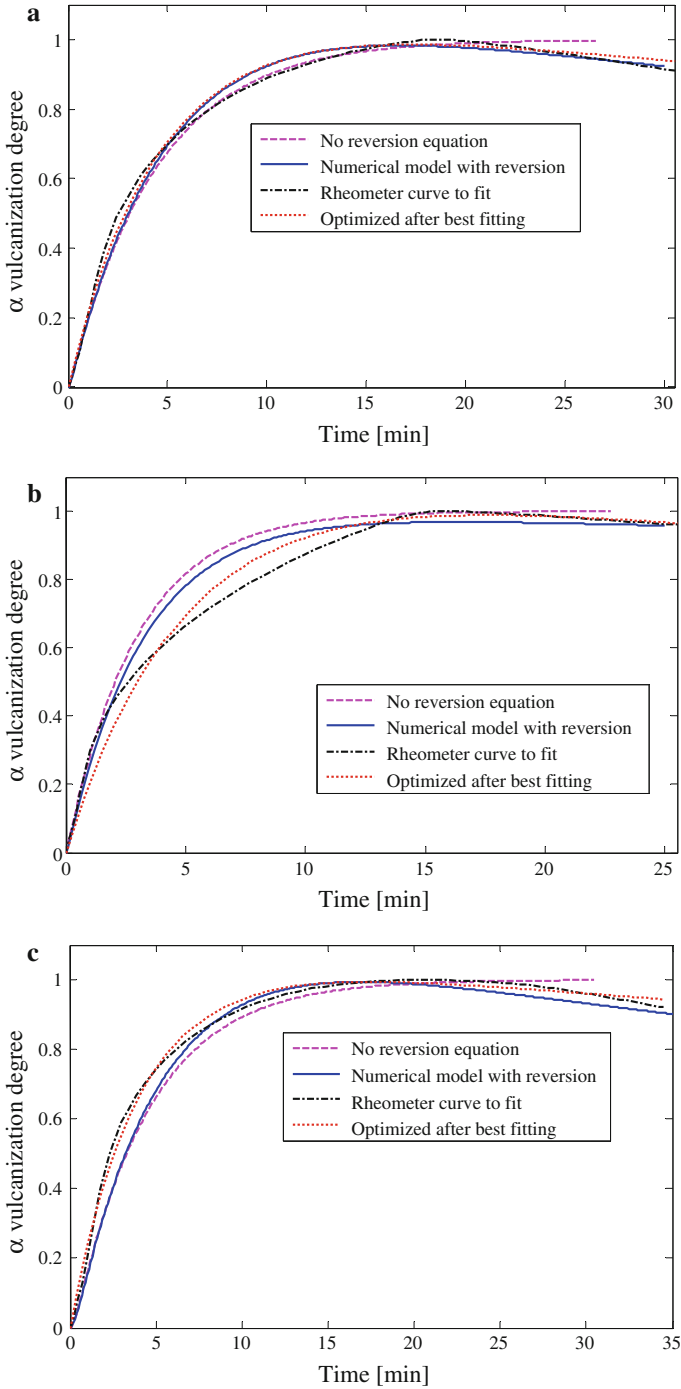


Fig. 5 1st NR blend, data set 3. **a** 3-2 data set, **b** 3-4 data set, **c** 3-6 data set

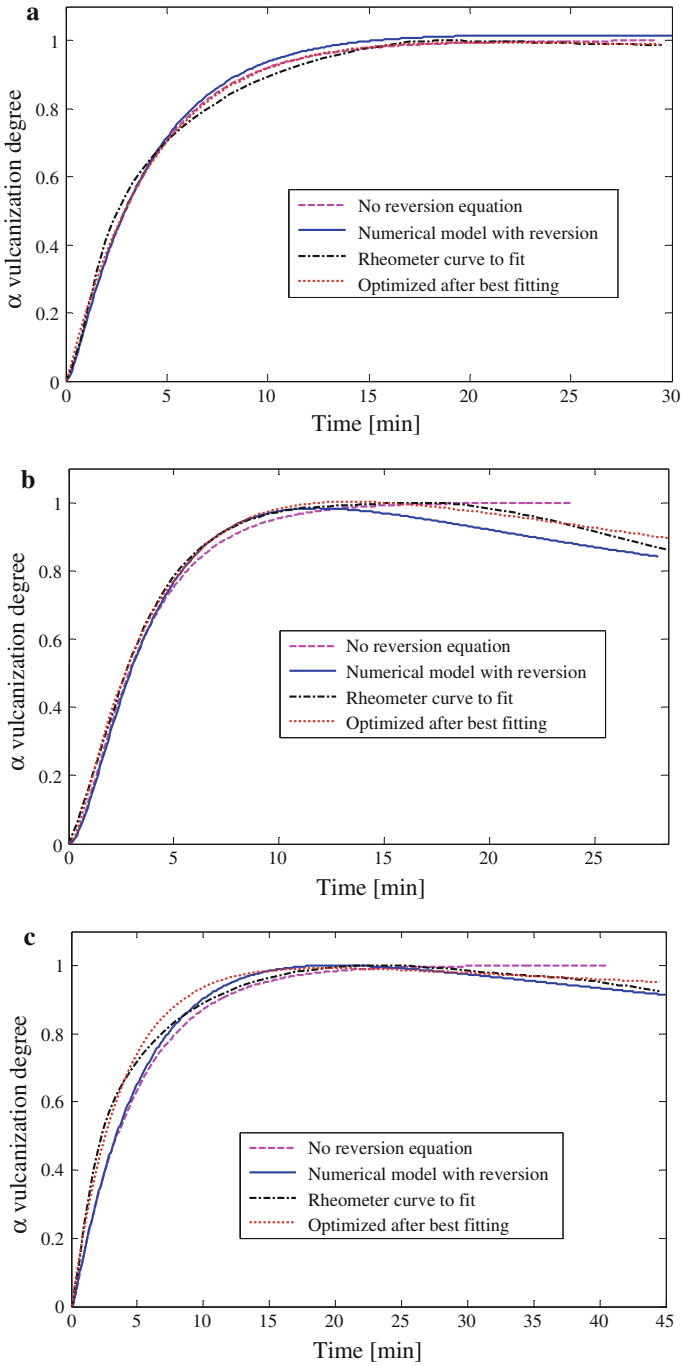


Fig. 6 1st NR blend, data set 4. **a** 4-4 data set, **b** 4-5 data set, **c** 4-7 data set

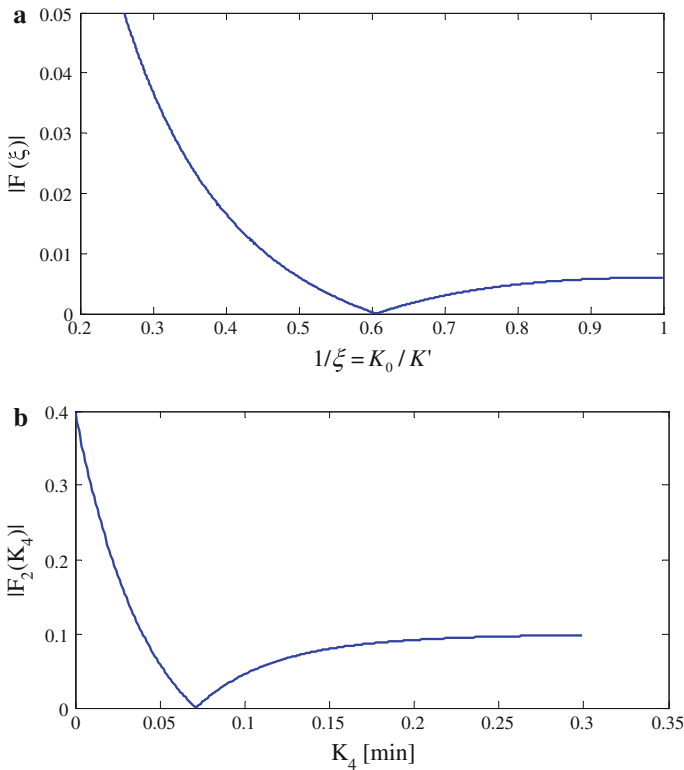


Fig. 7 Representation of functions $|F|$ and $|F_2|$ as a function of ξ and K_4 , data set 1-1

enough the optimal solution, meaning that the efficiency of the approach proposed is drastically improved assuming as starting point that analytically found with the procedure proposed.

In Fig. 7, for the sake of completeness, curves $|F|$ and $|F_2|$ where F and F_2 are represented in Eqs. (21) and (23) respectively, are plotted as a function of ξ and K_4 for one of the cases analyzed (data set 1-1). Figure 7 allows to graphically identify the points where $|F|$ and $|F_2|$ are equal to zero, which correspond to values of ξ and K_4 used to plot curve (b).

4.2 Experimentally tested NR blend at different curing temperatures

A NR blend experimentally tested in [20] at 5 different temperatures is here reconsidered to show the capabilities of the numerical-analytical approach proposed when data to fit are direct experimental instead of surrogate meta-data following a cubic spline low.

In [20], the isothermal cure of the NR compound with composition as in Table 4 was tested at 130, 140, 150, 160 and 170 °C respectively, using a Moving Die Rheometer MDR.

Table 4 Composition of 2nd NR blend used for model validation

Component	Parts (by weight)
Rubber gum	100
Carbon black	25
Oil	5
(ZnO / stearic acid) activator	6
Sulphur	3
Amine antioxidant	2

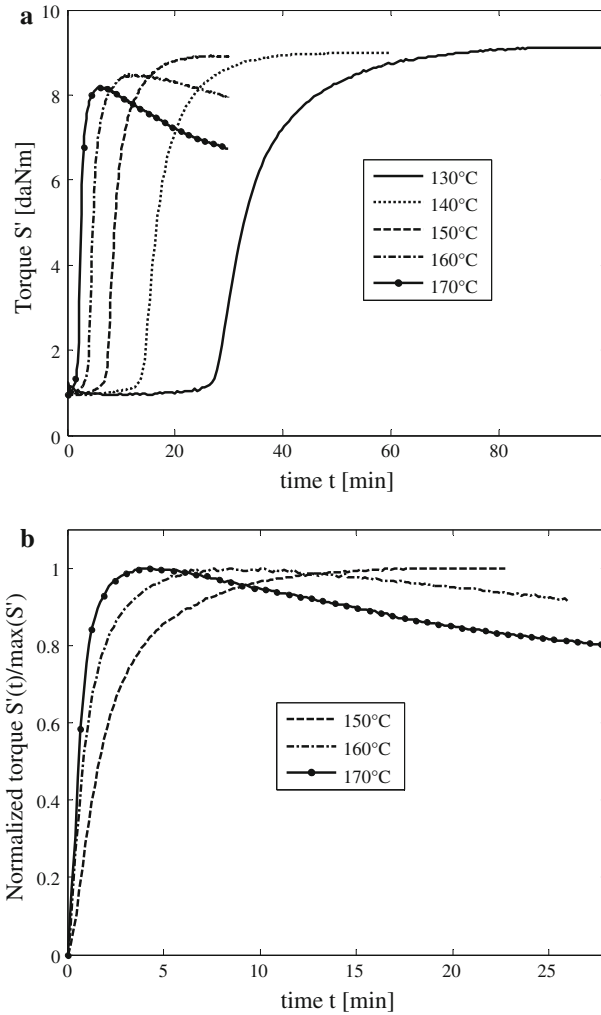


Fig. 8 Experimental torque curves (a) and normalized curves (b) used to validate the numerical/analytical model, 2nd NR blend

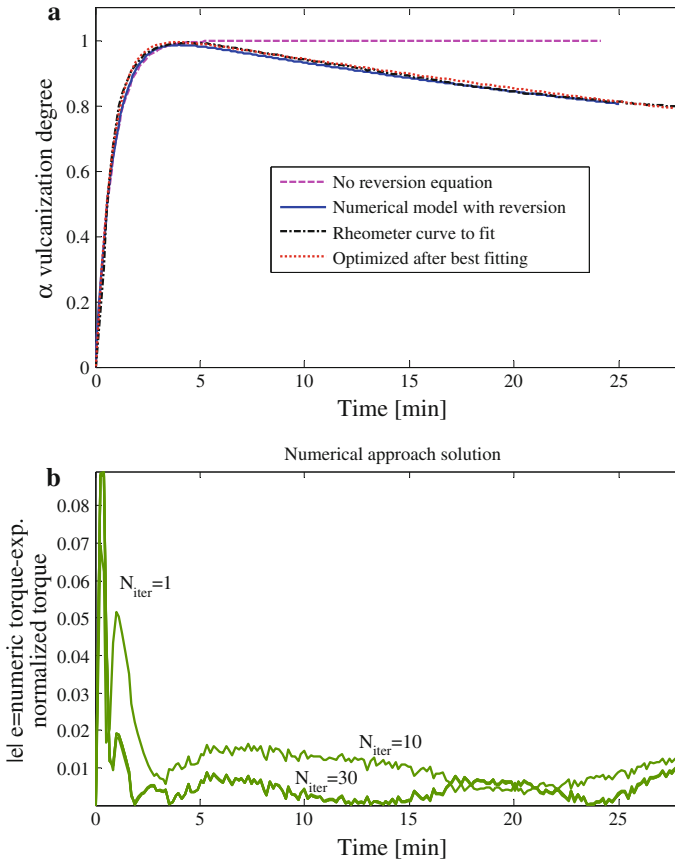


Fig. 9 2nd NR blend, cure temperature 170 °C. **a** Experimental versus numerical rheometer curves, **b** Convergence performance during best fitting using the starting point proposed in the paper

Since the aim of the present paper is to fit normalized experimental data, each torque curve is divided by the maximum torque at that temperature, provided that the induction phase is previously excluded from the analysis and curves are coherently translated into the origin. It is worth noting that such normalization does not take into account the experimentally observed decrease of the peak torque when the curing temperature is increased. In order to take into account such effect, the relation proposed by Sun and Isayev [24] to calculate the evolution of the vulcanisation degree $\alpha_{exp}(t)$ from rheometer $S'(t)$ curves should be used:

$$\alpha_{exp}(t) = \frac{S'(t) - S_{\min T}}{S_{\max T_0} - S_{\min T_0}} \quad (24)$$

where $S_{\min T}$ is the minimum value of torque S' during a cure experiment at temperature T , $S_{\min T_0}$ and $S_{\max T_0}$ are the minimum and maximum torque values at a temperature T_0 low enough to allow neglecting reversion.

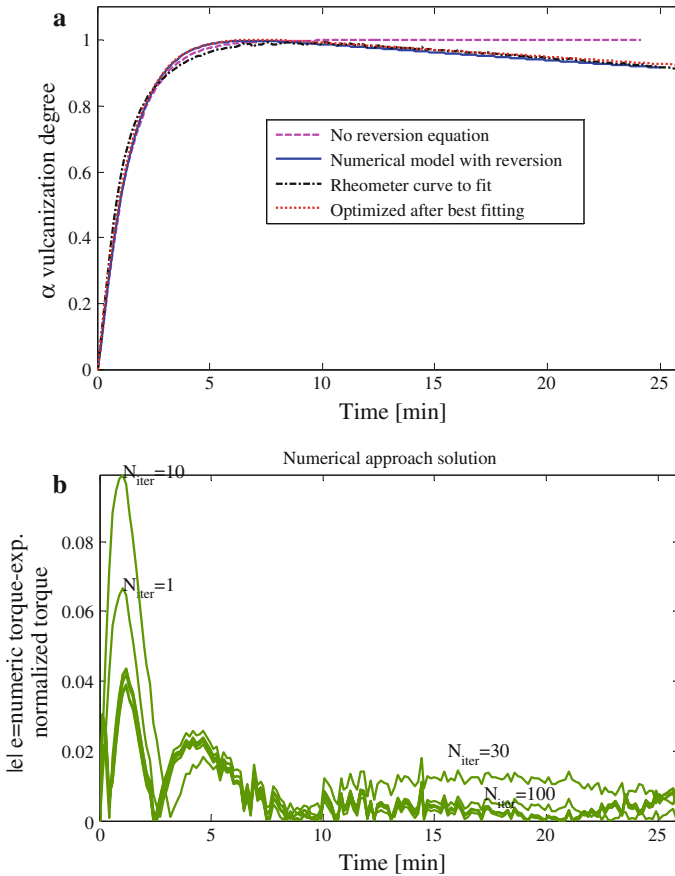


Fig. 10 2nd NR blend, cure temperature 160 °C. **a** Experimental versus numerical rheometer curves, **b** Convergence performance during best fitting using the starting point proposed in the paper

While the aim of the present comparison is only to fit experimental data, without making further considerations on the role played by high temperatures in reducing peak crosslinking degree, a normalization where the maximum normalized torque is always equal to a unitary value is adopted. The model is, however, capable of reproducing curves normalized by means of Eq. (24).

Figure 8a shows the typical torque vs. time curves obtained experimentally at the different cure temperatures. The reversion phenomenon, which can be clearly observed at 160 and 170 °C, becomes very weak at 150 and 140 °C, and at 130 °C is completely absent. Figure 8b shows normalized curves used for comparison purposes. For the sake of conciseness, only three temperatures are considered, namely 170, 160 and 150 °C. At 170 and 160 °C, indeed, a very marked reversion is obtained, whereas at 150 °C reversion is mitigated. Such three temperatures are therefore the most interesting and meaningful to fit numerically, because they allow to benchmark the model in presence of strong reversion and in absence of devulcanization. Lower temperatures correspond

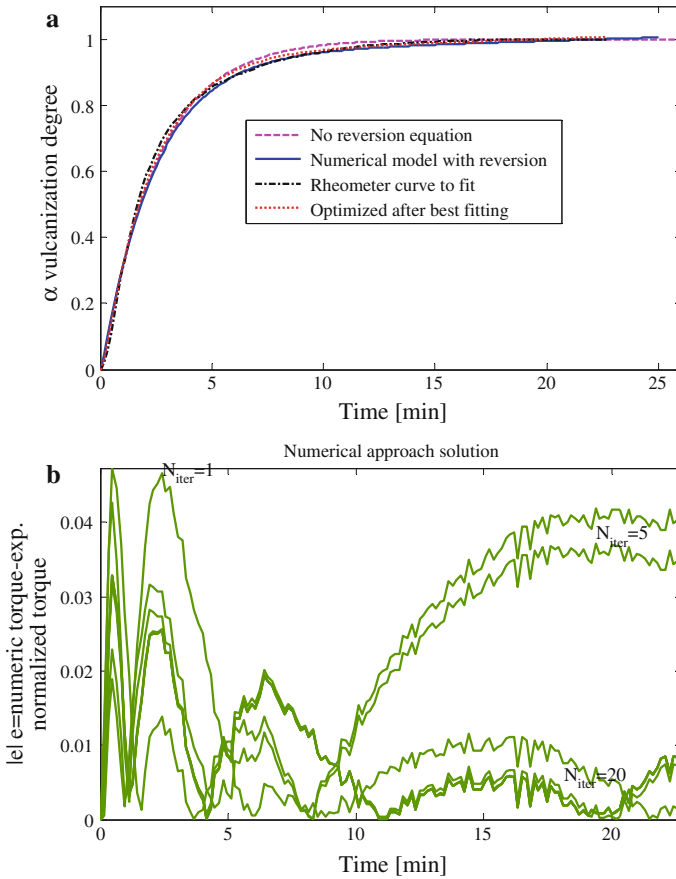


Fig. 11 2nd NR blend, cure temperature 150 °C. **a** Experimental versus numerical rheometer curves, **b** Convergence performance during best fitting using the starting point proposed in the paper

to curves exhibiting a stable unitary normalized torque under long time vulcanization and therefore, it is expected that the fitting quality of the model (even when dealing with the equation without reversion) is comparable to that observed at 150 °C, where reversion is very low.

Numerical cure curves are compared to normalized experimental evidences in Figs. 9a, 10a and 11a at 170, 160 and 150 °C respectively.

As it is possible to notice, the agreement with target data is almost perfect for all the three temperatures inspected, even near the end of the test (large curing times) in presence of strong reversion. In particular, even the curve obtained directly using kinetic constants analytically determined, seems to fit very well experimental data. Obviously, the same curve after best fitting through non-linear least squares and assuming as starting point the analytically determined one, improves further the accuracy of the approach, as it is shown by the convergence plot reported in Figs. 9b, 10b and 11b for temperatures equal to 170, 160 and 150 °C respectively.

Since the analytical model already provides very accurate predictions of the normalized torque, the improvement obtained through the application of the non-linear least squares is limited, but in any case allows a further reduction of the discrepancies between numerical predictions and experimental data.

5 Conclusions

Differently from a phenomenological approach, a kinetic numerical strategy allows to simulate the accelerated sulphur vulcanization of NR blends, providing quantitative information on the rate of reaction and crosslinking density, in all the vulcanization phases (induction, curing and reversion), thus indirectly allowing to control and to optimize the processing operation without the need of performing wide and costly experimental campaigns.

Depending on the level of complexity of the kinetic model proposed, more detailed or less precise information on the degree of curing, as well as on the single and multiple-bond percentage of resulting links may be retrieved. However, an increased complexity of the models results both into the impossibility to deal with closed-form predicting expressions for the cure percentage and in complex numerical best fits on experimental data available to estimate single kinetic constants representing the chemical scheme adopted.

In the present paper, a detailed closed form approach with direct analytical determination of kinetic constants has been presented. The kinetic scheme is characterized by five reactions occurring in series and parallel, and hence five kinetic constants, with the possibility to accurately reproduce the curing phase and, eventually, the presence of reversion, with a precise determination of the stable and unstable bonds and, separately, the amount of reversion due to the single/double and multiple bonds break.

The major improvement of the present approach when compared to existing literature, and in particular with reference to the closed form kinetic procedure presented in [1], is that (a) a closed form solution for the crosslinking density which does not require any optimization algorithm has been proposed and that (b) a starting point for the unknown kinetic constants, very near to the actual solution and thus very convenient for a successive least squares minimization, has been deduced.

It has been proved how the combination of three analytical conditions on the rheometer curves, namely position of the scorch point (second derivative of the rheometer curve equal to zero), determination of time corresponding to, e.g. 90% of cure and reversion percentage, allows a relatively simple direct evaluation of the kinetic constants characterizing the model. Such values, substituted into a closed form analytical formula representing the state of cure, permit a direct numerical estimation, in satisfactory agreement with experimental evidences, of the behavior of a given rubber compound during assigned vulcanization conditions, without the need to utilize optimization tools.

As well known, indeed, the non-linearity of the problem may result into convergence failure of non-linear optimization algorithms, especially if an unsuitable starting point is selected within the procedure.

In this context, it appears clear that the analytical knowledge of reasonable kinetic constants near to the optimized ones, eventually allows the successive utilization of non-linear least squares routines, increasing drastically their numerical convergence and reducing consistently the processing time needed to find the optimal solution.

To assess the results obtained with the model proposed, a wide and comprehensive validation of the procedure has been reported, studying in detail two different NR blends in presence of different accelerators and cure temperatures, exhibiting frequently marked reversion. The approach proved to be extremely robust, very reliable and much faster when compared with existing literature.

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