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Comprehensive Kinetic Numerical Model for NR and High-Cis Poly-Butadiene Rubber Blends

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A simple but robust kinetic mathematical model to predict the mechanical/thermal behaviour of NR and high-cis polybutadiene rubber blends is presented. The benchmark blend is a 70% NR with 30% high-cis polybutadiene blend vulcanized in presence of sulphur at 1 phr and single accelerants TBSS or DPG at concentrations equal to 1-0 and 0-1 respectively. Experimental rheometer curves are at disposal for both the NR-PB blend and single NR/PB rubbers at 170°C and 180°C. Rheometer curves at 150°C are utilized as reversion free references to normalize experimental data. The numerical model is based on a modification of Han's kinetic approach, where a linear interaction between NR and PB is accounted for. The determination of kinetic constants is possible by means of a constrained minimization approach that uses Sequential Quadratic Programming and fits through standard least-squares normalized rheometer curves. The procedure is benchmarked on 1-1-0 and 1-0-1 concentrations of S-TBBS-DPG at 170°C and 180°C. Quite good agreement is found against experimental data, with values of kinetic constants addressing a reduction of vulcanization rate with respect to pure NR and a beneficial reversion decrease due to PB contribution.

1. Introduction

The behavior of Natural Rubber NR and Poly-Butadiene PB blends under standard vulcanization with sulphur is at present scarcely investigated, both from an experimental and numerical point of view.

As commonly accepted, the standard laboratory methodology to provide a macroscopic estimate of the crosslinking degree is considered the rheometer test. A rheometer is a laboratory device 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. Consequently, any investigation regarding the crosslinking properties of a rubber blend passes throughout the determination of the kinetic behavior within the rheometer chamber.

The utilization of NR-PB blends is quite interesting for the rubber industry, because they are ordinarily used in tyre production. Pure NR cured with sulfur is characterized by small peak values of torque and generally a quite pronounced reversion at high vulcanization temperatures, which consists in a drop of the measured torque for relatively long curing times. The phenomenon is commonly thought to be a consequence of the degradation of polysulfide (S-S or more) crosslinks (Han et al. 1998, Schiraldi 2003, Milani and Milani 2014, Milani et al. 2016). On the contrary, PB exhibits much more stability as far as reversion is concerned, with much higher torque peak values. An advantage of NR is the quite fast vulcanization rate, which on the contrary is very slow for PB under the same vulcanization conditions and in presence of the same amount of accelerants, Milani and Milani (2017). In this context, the utilization of NR-PB blends has therefore the intuitive advantage to allow obtaining rubbers exhibiting higher torque than NR, a satisfactory vulcanization rate and reduced reversion. Another issue is represented by miscibility. Indeed, whilst many organic liquids at room temperature are fully or partially miscible, polymers, by virtue of the length of their molecular chains, are not easily miscible. Also in the case of NR and PB, we are in the case of partial miscibility, which strongly depends on molecular weight, molecular weight distribution and the solubility parameter. The present study is limited to 70%NR-30%PB blends in order to limit partial miscibility issues negligible.

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In particular, after a comprehensive experimental characterization of a 70%NR-30%PB blend under standard rheometer tests at 170 and 180°C, a robust kinetic mathematical model is proposed. Experimental data rely on a natural rubber and high cis-polybutadiene blend vulcanized in presence only of Sulphur (1 phr), Zinc octoate as co-adjuvant at constant 3 phr concentration and separately either the accelerator N-terbutyl, 2-benzothiazylsulfenamide TBBS (1 phr) or N,N-diphenylguanidine DPG (1 phr). Rheometer curves at 150°C are utilized as reversion free references to normalize experimental data. In the numerical model, we assume reasonably that the crosslinking reactions depend on the reciprocal concentrations of all the components and their chemical nature. In particular it is based on Han's kinetic approach for NR (Han et al. 1998, Milani and Milani 2014), a modification of Han's model proposed recently by the authors for PB (Milani and Milani 2017) and with a linear kinetic interaction model between NR and PB. No considerations are reported for possible aggregation reactions between NR and PB, as in Brener et al. (2009) or Dairabay et al. (2016). The determination of kinetic constants is possible by means of a constrained minimization approach that uses Sequential Quadratic Programming and fits through standard least-squares normalized rheometer curves. The procedure is benchmarked on experimental data available, finding quite good agreement, with resultant values of kinetic constants addressing a reduction of vulcanization rate with respect to pure NR, Milani and Milani (2014) and Milani et al. (2016), and a beneficial reversion decrease due to PB contribution.

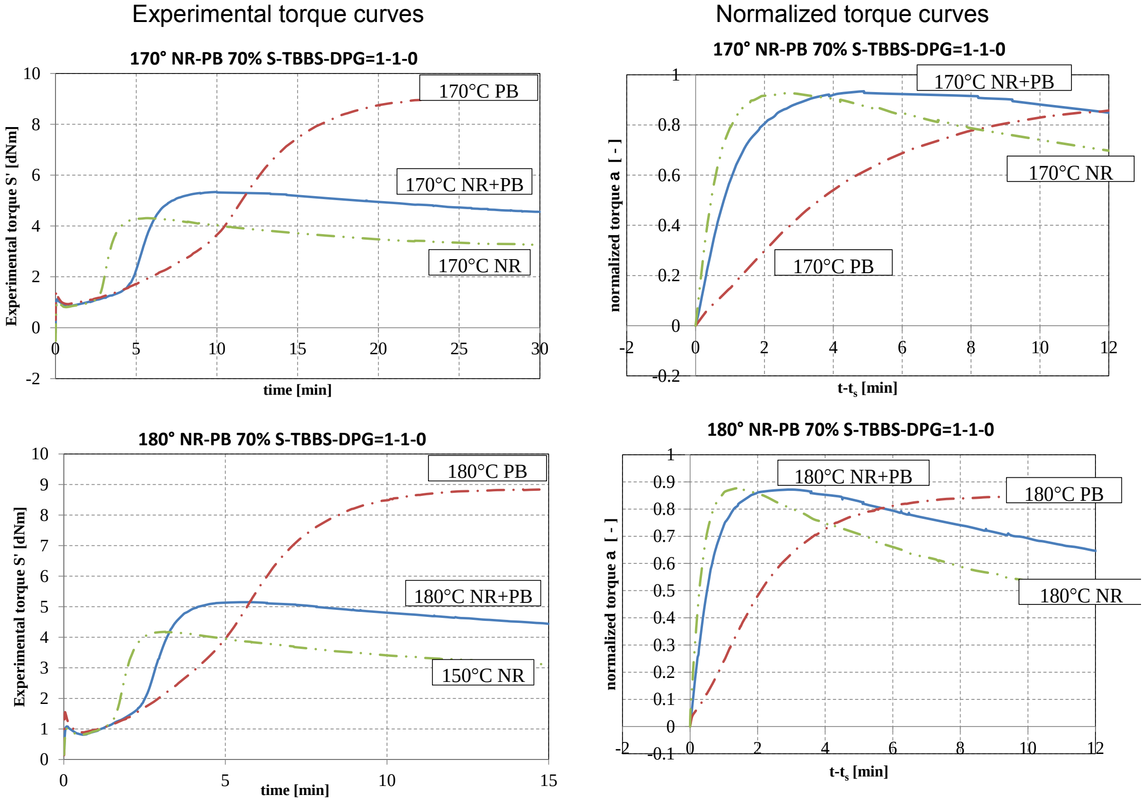

Figure 1: Experimental torque curves (left) and normalized curves (right) for natural rubber (NR), polybutadiene (PB) and 70% NR-30% PB blends at 170°C and 180°C Concentration of sulphur S and TBBS-DPG accelerants equal to 1-1-0.

2. Experimental

Natural Rubber used (SMR – 20) has the following molecular parameters: density = 0.917 g/cc, average molecular weight by number (Mn)=1.5x10^5 g/mol, Polydispersity = 4.5. PB used is a very high cis homo-polymer polybutadiene obtained with Ziegler-Natta catalysts, with a % of cis conformation more than 95. PB used has the following molecular parameters: average molecular weight by weight (Mw) = 6.5 x 10^5 g / mol, density = 0.91 g/cc, stereo-specificity cis conformation more than 95%. The accelerators used are the following: TBBS (N-t-butylbenzothiazole-sulfenamide) industrial name westco from Western Reserve Chemical, DPG (di phenyl guanidine) from Carlo Erba Reagents, sulphur in powder form Gasoilsulfur. Rubber blends were obtained using 70% NR and 30% PB. Rubbers were pre-blended and properly mixed homogenizing all ingredients. An internal mixer maintained at nearly 50°C, as recommended by ASTM D 3184-11, was used. Rubbers blends were conditioned at nearly 25°C for 24 h prior curing on a Monsanto oscillating Disc Rheometer fulfilling requirements by ASTM D 2084-81. Tests (rheometer curves) were carried out at four temperatures, namely 150, 160, 170 and 180°C. Here only comparisons at 170 and 180°C are discussed, because DPG has a melting temperature roughly equal to 150°C, too similar to 150 and 160°C to provide reliable numerical comparisons.

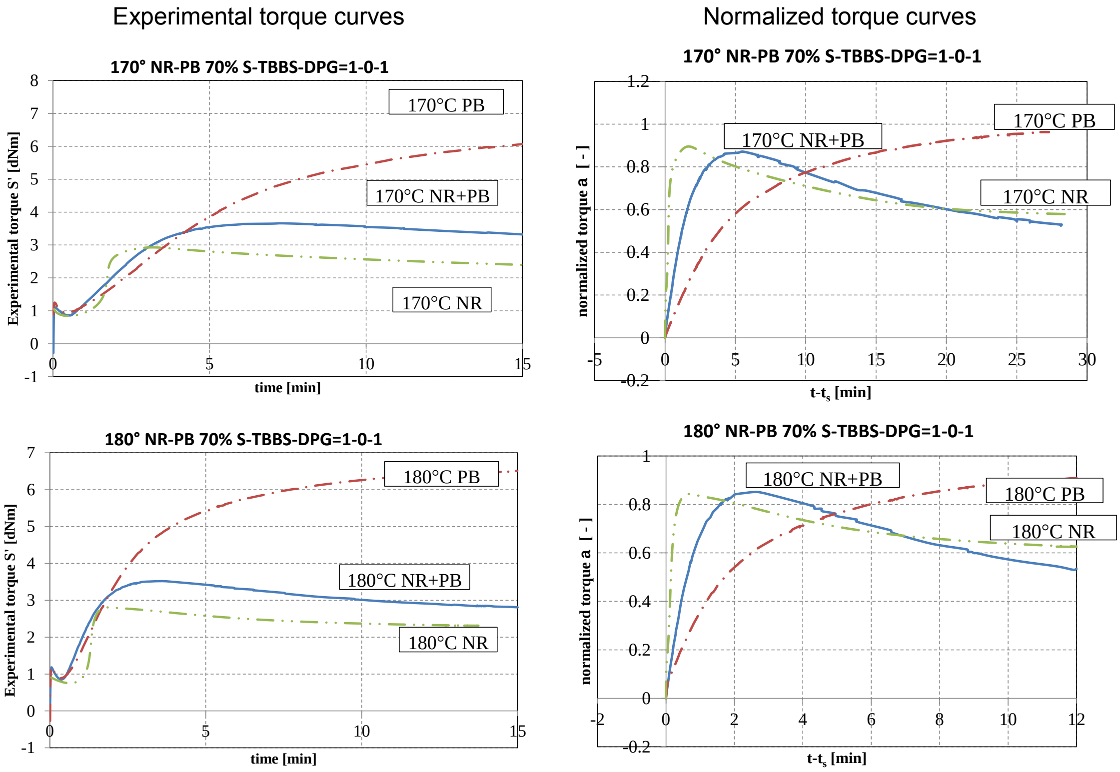

Figure 2: Experimental torque curves (left) and normalized curves (right) for natural rubber (NR), polybutadiene (PB) and 70% NR-30% PB blends at 170°C and 180°C Concentration of sulphur S and TBBS-DPG accelerants equal to 1-0-1.

The experimental campaign is conducted using two S-TBBS-DPG sulphur/accelerants concentrations, equal to 1-1-0 phr and 1-0-1 phr respectively, both at 70% NR and 30% PB concentrations.

Before any comparison with numerical data, rheometer curves should be normalized according to consolidated literature. In particular, experimental torque $S'(t)$ is traditionally adopted to estimate the experimental vulcanization degree $\alpha_{\exp}$, following the classic Sun and Isayev (2009) normalization law, that reads as follows:

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

Where S'_{minT} represents the minimum value of torque at temperature T. Before reaching this minimum value, $\alpha_{\exp}$ 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 low enough to allow neglecting reversion. Such temperature is chosen in this case equal to 150°C, even if for NR still there is reversion, because lower temperatures do not allow vulcanization of PB. 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 always lower than 1. Crude rheometer data for 1-1-0 and 1-0-1 formulations and corresponding normalized curves are depicted in Figure 1 and Figure 2 respectively. Only data at 170 and 180°C are reported for the sake of conciseness.

3. The numerical model

The basic reaction scheme assumed for NR is classic and in particular the model by Han et al. (1998), then optimized in the solution research by Milani and Milani (2014) and experimentally crosschecked in Milani et al. (2016), is adopted. Typically, after the initial induction viscous phase which characterizes the uncured rubber at high temperature, curing proceeds through two pathways, with the formation of stable and unstable un-matured cured rubber. The distinction between stable and unstable curing stand in the presence of single or multiple sulphur bonds respectively. Multiple bonds are subjected with higher probability to break and hence de-vulcanization (or reversion).

All the reactions considered occur with a kinetic velocity depending on the curing temperature, associated to each kinetic constant. Let us assume that K_1^{NR} is the kinetic constant associated to the formation of stable S-S bonds, K_2^{NR} to unstable multiple bonds and K_3^{NR} describes reversion.

Within such assumptions, the kinetic scheme adopted is constituted by the following reactions:

$$\left[(\rho-\xi)S_0\right] \xrightarrow{K_1^{NR}} \left[R_1^*\right] \qquad \left[(\rho-\xi)S_0\right] \xrightarrow{K_2^{NR}} \left[R_1\right] \qquad \left[R_1\right] \xrightarrow{K_3^{NR}} \left[R_1^D\right] \tag{2}$$

In Equation (2), $\left[(\rho-\xi)S_0\right]$ is the unvulcanized NR being ρ the NR fraction in the blend and ξ the part of NR that reacts with PB in a first order scheme as described in what follows, $[R_1^*]$ the stable crosslinked chain (S-S single bonds), $[R_1]$ the unstable vulcanized polymer, $[R_1^D]$ the de-vulcanized polymer fraction (reversion). $K_{1,2,3}^{NR}$ are kinetic reaction constants. K_3^{NR} is reported by Han to be responsible for reversion after the peak torque, as chemically confirmed by reactions in (2). According to the reaction scheme (2), it has been shown that the final concentration of vulcanized rubber is thus $[R_1^*]+[R_1]$:

$$\left[R_1\right]+\left[R_1^*\right]=\frac{K_1^{NR}\left[(\rho-\xi)S_0\right]}{K_1^{NR}+K_2^{NR}}\left[1-e^{-\left(K_1^{NR}+K_2^{NR}\right)(t-t_s)}\right]+\frac{K_2^{NR}\left[(\rho-\xi)S_0\right]}{K_1^{NR}+K_2^{NR}-K_3^{NR}}\left[e^{-K_3^{NR}(t-t_s)}-e^{-\left(K_1^{NR}+K_2^{NR}\right)(t-t_s)}\right] \tag{3}$$

Where t_s is the scorch time. Eq. (3) can be normalized with respect to $\left[S_0\right]$ as follows:

$$\alpha^{NR}=\frac{\left[R_1\right]+\left[R_1^*\right]}{\left[S\right]_0}=(\rho-\xi)\left\{\begin{array}{l}\dfrac{K_1^{NR}}{K_1^{NR}+K_2^{NR}}\left[1-e^{-\left(K_1^{NR}+K_2^{NR}\right)(t-t_s)}\right]+\\+\dfrac{K_2^{NR}}{K_1^{NR}+K_2^{NR}-K_3^{NR}}\left[e^{-K_3^{NR}(t-t_s)}-e^{-\left(K_1^{NR}+K_2^{NR}\right)(t-t_s)}\right]\end{array}\right\} \tag{4}$$

α^{NR} is commonly intended as a macroscopic estimation of the degree of vulcanization due to NR vulcanization. For PB, we assume a quite recent scheme proposed by the authors (Milani and Milani 2017), characterized by the following four reactions occurring in series and parallel:

$$\left[(1-\rho-\xi)S_0\right] \xrightarrow{K_1^{PB}} \left[R_2^*\right] \xrightarrow{K_4^{PB}} \left[R_2^{*D}\right] \qquad \left[(1-\rho-\xi)S_0\right] \xrightarrow{K_2^{PB}} \left[R_2\right] \xrightarrow{K_3^{PB}} \left[R_2^D\right] \tag{5}$$

In Equation (5), $\left[(1-\rho-\xi)S_0\right]$ is the uncured poly-butadiene reacting as PB, $[R_2^*]$ and $[R_2]$ represent crosslinked PB, with $[R_2^*]$ indicating the more stable crosslinked part and $[R_2]$ the less unstable part. Both of them may evolve into devulcanized polymers due to multiple S-S ($[R_2^D]$) or single/double ($[R_2^{*D}]$) chain breaks and consequent backbiting. $K_{1,\dots,4}^{PB}$ are kinetic reaction constants for PB. After standard algebra, Milani and Milani (2017) shown that a closed form solution for the vulcanization degree, intended as $\alpha^{PB}=\left(\left[R_2^*\right]+\left[R_2\right]\right)/\left[S_0\right]$, may be deduced as follows:

$$\begin{array}{l}\alpha^{PB}=(1-\rho-\xi)\left\{C_1e^{-K_4^{PB}(t-t_s)}+C_2e^{-K_3^{PB}(t-t_s)}-\left[C_1e^{-\left(K_1^{PB}+K_2^{PB}\right)(t-t_s)}+C_2e^{-\left(K_1^{PB}+K_2^{PB}\right)(t-t_s)}\right]\right\}\\ \text{with } C_1=\dfrac{K_1^{PB}}{K_1^{PB}+K_2^{PB}-K_4^{PB}} \text{ and } C_2=\dfrac{K_2^{PB}}{K_1^{PB}+K_2^{PB}-K_4^{PB}}\end{array} \tag{6}$$

NR and PB reacting together (ξ from NR and ξ from PB) are assumed to follow a Han kinetic scheme. Such portion of the model represents the linear interaction between NR and PB into NR-PB blends.

The reaction scheme is the following:

$$\left[2\xi S_0\right] \xrightarrow{K_1^{NR-PB}} \left[R_3^*\right] \qquad \left[2\xi S_0\right] \xrightarrow{K_2^{NR-PB}} \left[R_3\right] \qquad \left[R_3\right] \xrightarrow{K_3^{NR-PB}} \left[R_3^D\right] \tag{7}$$

In Equation (2), $\left[2\xi S_0\right]$ is the unvulcanized NR-PB part being ξ the NR/PB percentage that react together and vulcanize following a first order interaction scheme. According to Han's model, $[R_3^*]$ is the stable crosslinked chain (S-S single bonds), $[R_3]$ the unstable vulcanized rubber, and $[R_3^D]$ the de-vulcanized polymer fraction (reversion). $K_{1,2,3}^{NR\text{-}PB}$ are kinetic reaction constants of the interaction kinetic model. The amount of crosslinking derived from Eq. (7) is:

$$\alpha^{NR-PB} = \frac{[R_3]+[R_3^*]}{[S]_0} = 2\xi \left\{ \begin{array}{l} \dfrac{K_1^{NR-PB}}{K_1^{NR-PB}+K_2^{NR-PB}} \left[1-e^{-\left(K_1^{NR-PB}+K_2^{NR-PB}\right)(t-t_s)} \right] + \\ +\dfrac{K_2^{NR-PB}}{K_1^{NR-PB}+K_2^{NR-PB}-K_3^{NR-PB}} \left[e^{-K_3^{NR-PB}(t-t_s)} - e^{-\left(K_1^{NR-PB}+K_2^{NR-PB}\right)(t-t_s)} \right] \end{array} \right\} \quad (8)$$

The final vulcanization degree of the blend is:

$$\alpha = \alpha^{NR} + \alpha^{PB} + \alpha^{NR-PB} \quad (9)$$

The procedure followed to determine kinetic constants $K_{1,2,3}^{NR}$, $K_{1,\dots,4}^{PB}$, $K_{1,2,3}^{NR\text{-}PB}$ and variable ξ is a standard one, namely a least-squares type approach is utilized, within the following non-linear constrained minimization problem:

$$\begin{array}{l} \min\left(\alpha_{\exp}(t)-\alpha(t)\right)^2 \\ s.t. \left\{ \begin{array}{l} K_{1,2,3}^{NR} \geq 0 \quad K_{1,\dots,4}^{PB} \geq 0 \quad K_{1,2,3}^{NR-PB} \geq 0 \\ \qquad\qquad 0 \leq \xi \leq 1-\rho \end{array} \right. \end{array} \quad (10)$$

4. Numerical results and discussion

A proper numerical estimation of the kinetic constants according to Eq. (10) can be obtained by means of a robust medium-scale optimization code with engine constituted by a sequential quadratic programming SQP algorithm. The knowledge of the optimization variable at the converged solution allows estimating numerical crosslinking curves, to be compared with experimental normalized rheometer curves. Such comparisons are provided for S-TBBS-DPG concentrations equal to 1-1-0 and 1-0-1 respectively in Figure 3 and Figure 4. As can be noted, the agreement is almost perfect for all vulcanization times investigated. The good fitting is quantitatively shown also by the trend of the absolute error, reported in the bottom part of the figures within a green rectangle (the error is indeed in the majority of the cases negligible and much lower than 10%).

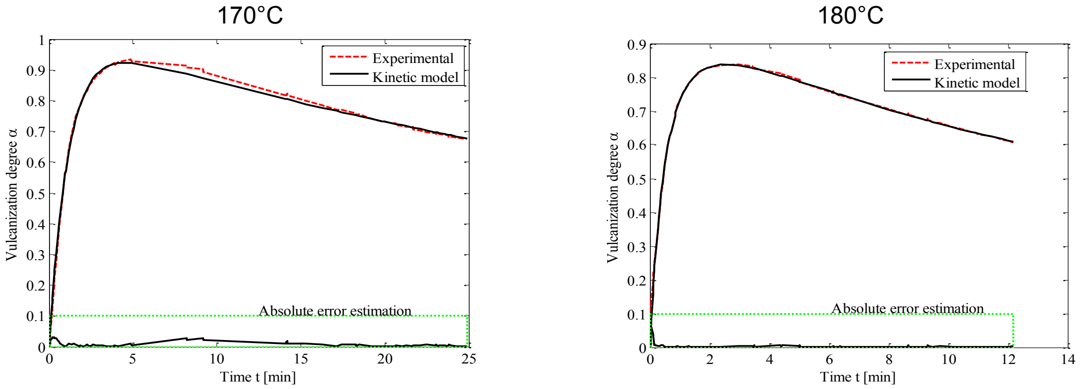

Figure 3: S-TBBS-DPG=1-1-0. Comparison between normalized experimental data and numerical results.

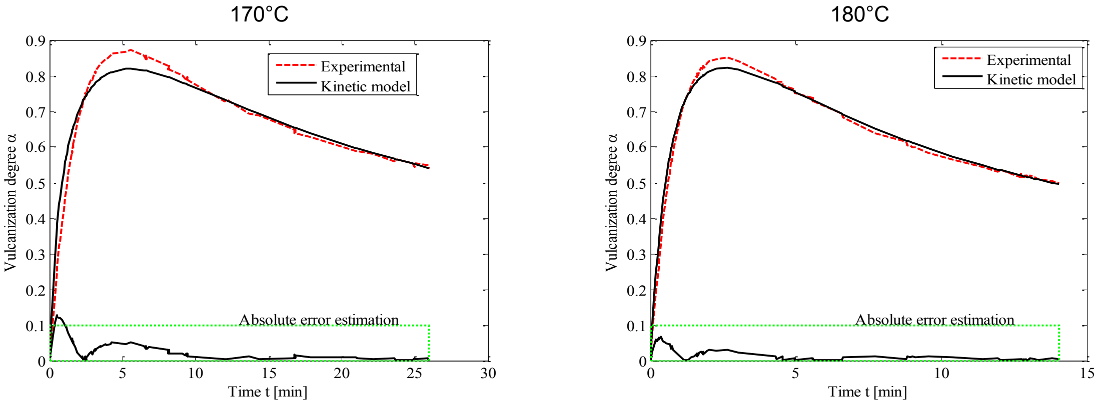

Figure 4: S-TBBS-DPG=1-1-0. Comparison between normalized experimental data and numerical results.

A comparison between kinetic constants estimated through optimization problem Eq. (10) and those previously evaluated for single NR and PB rubbers under the same vulcanization conditions and the same sulphur and accelerants concentrations is provided for both temperatures in Figure 5. On the horizontal axis kinetic constants for the NR-PB blends are reported, whereas on the vertical axis the same kinetic constants for NR and PB rubbers are depicted. Values of Kis for Eq. (8), i.e. NR-PB first order interaction scheme, are indicated on the horizontal axis, as well as the resultant ξ concentration found is usually very near to 0.3.

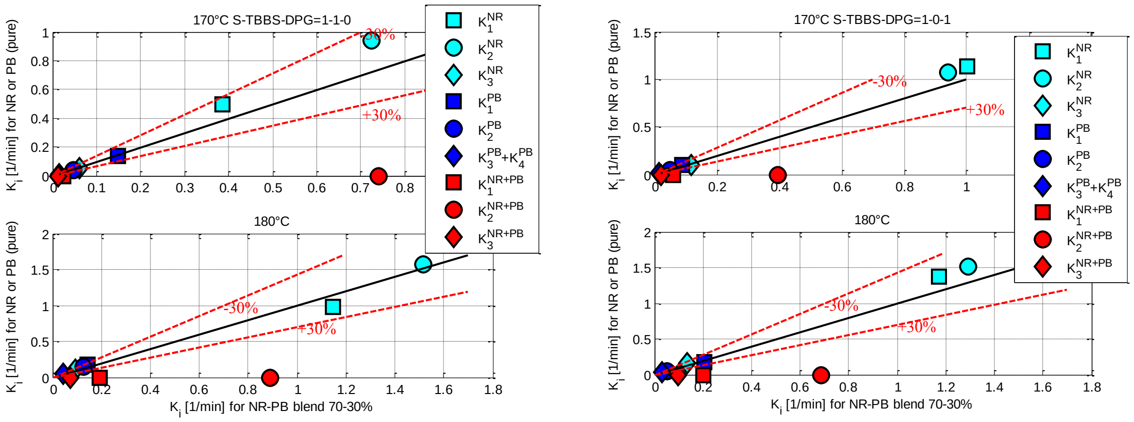

Figure 5: Comparison between Ki found for the NR-PB blend and Ki found for NR and PB pure.

5. Conclusions

A numerical model for the prediction of the kinetic behaviour of NR-PB has been proposed, which bases on a wide experimental campaign conducted by the authors and a kinetic scheme that combines linearly those of the constituent rubbers. Kinetic constants of the model are estimated through an optimization strategy that minimises the error against normalized experimental rheometer curves, Eq. (10). A comparison done between kinetic constant found for NR/PB blends and pure NR/PB rubbers shows that values found for kinetic constants $K_{1,2,3}^{NR}$ and $K_{1,\dots,4}^{PB}$ are very similar. Parameter ξ is usually very near to the upper bound, indicating that an amount of the total NR and almost the totality of PB vulcanize with a first order interaction, which follows a vulcanization rate driven by $K_{1,2,3}^{NR\text{-}PB}$. Values found for $K_{1,2}^{NR\text{-}PB}$ are lower than the corresponding ones for NR, and this justifies a lower crosslinking velocity exhibited by the NR-PB blend.

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