

Optimal Production of Tires Through an Integrated Experimental, Kinetic and Finite Element FE Modelling Approach

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An integrated three-step approach for the optimization of tires mechanical properties based on experimental characterization, kinetic steady-state model and Finite Element FE heat transmission modelling is presented. The first experimental characterization is needed to calibrate a kinetic numerical model (second step), directly nested in the last step into a FE software for the simulation of 3D heat transmission problems. The kinetic model is a phenomenological approach based on 3 kinetic constants, which allows predicting the initial curing rate, maximum crosslinking and reversion. Kinetic constants are deduced fitting normalized experimental rheometer curves. FE transient curing computations are carried out on a real car tire, discretizing the geometry through a refined mesh. All element of the tire (e.g. belts, carcass, core etc.) can be separately meshed, so the exact vulcanization process in different phases can be eventually accounted for.

1. Introduction

Blends of two or more rubbers are used to produce many items, in particular car tires, Milani & Milani (2018a & 2018b), because of the better mechanical properties obtained when compared with those of an elastomer alone (Arrillaga et al. 2007, Mansilla et al. 2015, Milani & Milani 2017).

The present paper discusses an integrated three-step numerical procedure for the optimization of tires final mechanical properties useful in industrial practice. The first step is the experimental characterization of the blend, the second step is a kinetic steady-state model which provides kinetic constants of the blend (according to Ding & Leonov 1996 approach) to implement in the last step into a FE code suitable to solve heat transmission problems in full 3D discretized models of complex geometries (such as tires). Knowing the temperature profile of each node of the mesh in step 3, from the kinetic model embedded into the FE code it is possible to estimate point by point the final degree of vulcanization of each node of the item and provide a reliable information on the local crosslinking density. The approach requires a rheometer characterization of the blend at 3 different temperatures and the calibration of a kinetic simple numerical model directly nested in a FE software. The kinetic model is a phenomenological approach based on 3 kinetic constants, which allows a reasonable prediction of the initial curing rate, maximum crosslinking conditions and reversion at high temperatures. For illustrative purposes, here the experimental characterization is carried out on two "idealized" blends constituted by Natural Rubber NR and High Cis Poly-Butadiene PB respectively at 70/30 and 50/50 concentrations, with sulfur at 1 phr and two accelerants, namely N-t-butylbenzothiazole-sulphenamide and Di-phenyl-guanidine (TBBS and DPG) at 1 and 3 phr, under standard steady-state vulcanization conditions from 150°C to 180°C. The utilization of NR-PB blends is quite interesting because they are common in tire production; NR is a good base, but also characterized by drawbacks as small peak torque and reversion at high temperatures. The phenomenon is due to degradation of poly-sulfidic (S-S or more) crosslinks, Han et al. (1998). On the other hand, whilst PB is much more stable with high peak torques, its vulcanization is slow and very difficult at 150°C, because near to its melting temperature. Blending NR with PB is a good compromise to obtain fairly good properties of the vulcanized product. Kinetic constants are here derived fitting normalized rheometer curves of the rubber through a semi-analytical approach, Milani et al. (2017). It is then possible to

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embed such kinetic model into a pre-existing FE code. The analytical solution of a realistic heat transmission problem is generally very difficult to find or even does not exist, and requires to tackle complex boundary value problems for partial differential equations. A FE formulation of the problem helps in estimating numerically such solution and results in a system of algebraic equations, because it approximates the unknown function over the domain subdividing a large system into smaller ones (2D and 3D finite elements), with the function inside the element a-priori known in its shape (shape function). The vulcanization of a real 3D item (e.g. a car tire) can be therefore simulated under transient curing conditions by means of a suitable refined discretization with 3D FEs. All elements of the tire (e.g. belts, carcass, core etc.) can be separately meshed with a full 3D approach, to reproduce the exact vulcanization process. The three-step procedure presented allows to find the best concentration ratio between rubbers, the optimal balance between strength and elastic characteristics, as well as the optimal time/temperature conditions to maximize average crosslinking density.

2. Experimental characterization (Step 1)

A standard NR with $M_n = 1.5 \times 10^5$ g/mol, and a very high cis homo-polymer polybutadiene with $M_w = 6.5 \times 10^5$ g/mol and a % of cis conformation more than 95% are used (M_n stands for the molecular weight by number and M_w for the molecular weight by weight). Accelerators used are TBBS (N-t-butylbenzothiazole-sulfenamide) and DPG (di phenyl guanidine). Blends are obtained with 50-50% and 70-30% NR-PB proportions. A Monsanto oscillating Disc Rheometer is used to produce rheometer curves at 150, 170 and 180°C. The following S-TBBS-DPG sulfur/accelerants concentrations are investigated: 1-1-0, 1-3-0, 1-0-1, 1-0-3 phr. Experimental rheometer curves are shown in Figure 1 for all the cases investigated. For the sake of comparison, rheometer curves for pure NR and PB are also depicted. Experimental values are represented with dots, whereas smooth colored curves are derived through a regularization technique with splines, fully described in Milani & Milani (2018b) where the reader is referred for further details, essential to apply the kinetic model discussed in the following Section. Figure 1-a depicts rheometer curves, whereas Figure 1-b shows time-vulcanization rate ($t-dM/dt$) relationships, evaluated from experimental values through finite differences and directly estimation of the first derivative of the spline approximation. Smooth vulcanization rate diagrams are again essential for the application of the kinetic model. Before any comparison with numerical data, experimental torque $M(t)$ is normalized (furnishing the experimental vulcanization degree α_{exp}) through Sun & Isayev (2009) method:

$$\alpha_{exp} = \frac{M - M_{minT}}{M_{maxT_0} - M_{minT_0}} \quad (1)$$

M_{minT} in Eq. (1) is the minimum value of torque at temperature T . Before reaching this minimum value, α_{exp} is considered equal to zero. M_{minT_0} and M_{maxT_0} are the minimum and maximum torque values at a curing temperature equal to T_0 low enough to allow neglecting reversion.

3. Kinetic numerical model in steady-state thermal conditions (Step 2)

The basic reaction scheme is classic for NR but can be adapted also in different situations, Milani & Milani (2018a & 2018b), as the present one, and is in particular due by Han et al. (1998). 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 stands in the presence of single or multiple sulfur bonds respectively. Multiple bonds are subjected with higher probability to break and hence they are responsible to macroscopic de-vulcanization (also known as reversion). The kinetic scheme adopted is therefore classically constituted by three reactions:



where $[P]$ is the unvulcanized rubber concentration, $[R_1^*]$ and $[R_2^*]$ the crosslinked rubber, one stable (K_1) and the other (K_2) subjected to reversion, and $[R_r^*]$ is the amount of rubber subjected to de-vulcanization.

Mathematically, the first two reactions occur in parallel, transforming unvulcanized rubber $[P]$ in crosslinked rubber $[R_1^*]$ and $[R_2^*]$. $[R_2^*]$, as already pointed out, is typically unstable, because of the presence of multiple S-S bonds between contiguous polymer chains, and it evolves –by means of a further reaction acting in series with the second one– into de-vulcanized rubber $[R_r^*]$.

Assuming the kinetic scheme of Eq. (2), after suitable mathematical passages not reported here for the sake of conciseness, it is possible to estimate in closed form the crosslinking density $\alpha = ([R_1^*] + [R_2^*]) / [P]$ as follows:

$$\alpha = K_1 / (K_1 + K_2) \left[1 - e^{-(K_1 + K_2)(t - t_s)} \right] + K_2 / (K_1 + K_2 - K_3) \left[e^{-K_3(t - t_s)} - e^{-(K_1 + K_2)(t - t_s)} \right] \quad (3)$$

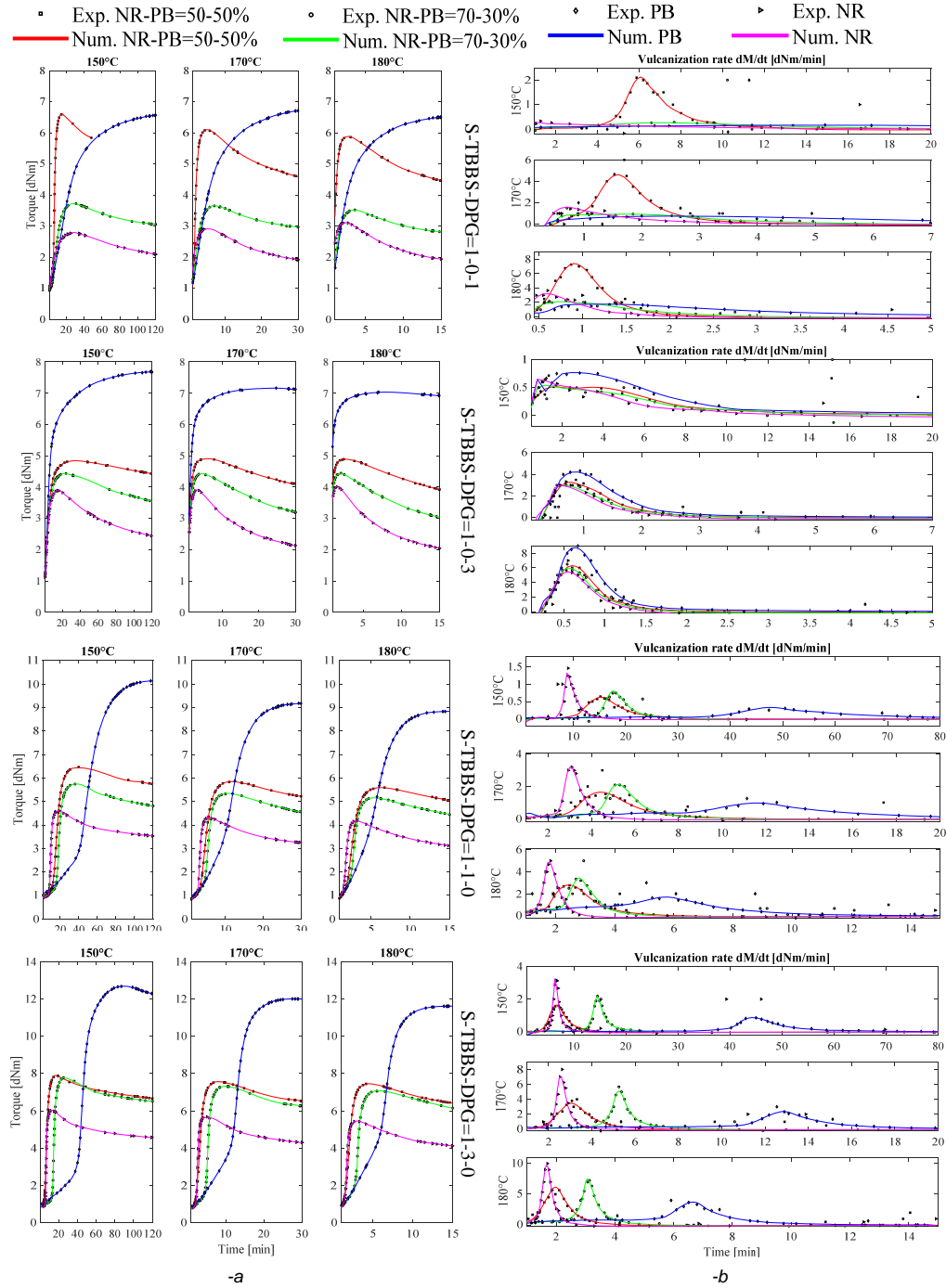


Figure 1: Spline fitting of rheometer curves after non-linear least squares optimization (-a) and comparison between numerical and experimental vulcanization rates (-b).

Han et al. (1998) suggest to evaluate kinetic constants by means of standard least-squares best fitting on experimental (or regularized) data, but Milani et al. (2015) have recently proposed a more efficient approach where kinetic constants are estimated in quasi-closed form.

This latter approach is adopted here and it consists in the following simple steps. In step 1, K_1 and K_2 constants are estimated knowing the crosslinking density at the end of the experimental test (α_R) and the vulcanization rate at scorch (α'_0), as $K_2 = \alpha'_0 (1 - \alpha_R)$ and $K_1 = \alpha'_0 \alpha_R$. Assuming the vulcanization degree α_P

known at a certain t_p , K_3 is estimated graphically in the second step as the intersection between the following curves:

$$y_1 = \frac{(\alpha_p - C_0)(C_3 - K_3)}{C_2} \quad y_2 = e^{-K_3(t_p - t_s)} - C_1 \quad C_0 = \frac{K_1 [1 - e^{-(K_1 + K_2)(t_p - t_s)}]}{K_1 + K_2} \quad C_1 = e^{-(K_1 + K_2)(t_p - t_s)} \quad C_2 = K_2 \quad C_3 = K_1 + K_2 \quad (4)$$

Where t_s is the time at scorch.

4. Industrial vulcanization or real items, FE heat transmission problem (Step 3)

The kinetic model proposed is semi-analytic, therefore its implementation into a Finite Element FE code for the thermal analysis of 3D items appear suitable and very straightforward. In the most general case of 3D items, temperature profiles for each point of the element are obtained solving numerically Fourier’s heat transmission law:

$$\rho_p c_p \frac{\partial T}{\partial t} - \lambda_p \Delta T - r_p \Delta H_r = 0 \quad (5)$$

where ρ_p , c_p and λ_p are rubber density, specific heat capacity and heat conductivity respectively, ΔH_r is rubber specific heat (enthalpy kJ/mol) of reaction (if any and if important for engineering applications), r_p is the rate of cross-linking (mol/m³sec); Δ is the Laplace operator.

Eq. (5) can be easily solved using a Finite Element FE discretization. In this case, FEs must be coupled with the kinetic model previously presented in order to predict point by point the final crosslinking density obtained. If for a node **P**, the temperature profile $T(\mathbf{P})=T(t)$ as a function of time is known from finite elements, then it is possible to show that deriving Eq. (3) the crosslinking rate at an instant t is the following:

$$\frac{d\alpha}{dt} = F_1 \left\{ 1 - e^{-[K_1(T) + K_2(T)]t} \right\} + F_2 e^{-[K_1(T) + K_2(T)]t} + F_3 \left\{ e^{-K_3(T)t} - e^{-[K_1(T) + K_2(T)]t} \right\} + \dots \quad (6)$$

$$\dots + \frac{K_2(T)}{K_1(T) + K_2(T) - K_3(T)} \left\{ F_4 e^{-K_3(T)t} + F_5 e^{-[K_1(T) + K_2(T)]t} \right\}$$

Functions F_1, \dots, F_5 are not reported here for the sake of conciseness and the interested reader is referred to Milani & Milani (2018b) for further details. Here it is worth noting only that functions F_i depend on the following parameters: dK_i/dt , K_i , dT/dt , T . It is interesting to point out that $K_i(T)$ is a function analytically defined by the well known Arrhenius relationship, i.e. $K_i(T) = \exp(\ln K_i^\infty - g'/T)$, where K_i^∞ is the i -th kinetic constant at an infinite temperature and g' is the absolute value of the slope of the Arrhenius law (linear) in the $\ln K_i - 1/T$ space. Temperature profile first derivative with respect to time t is again evaluated numerically by finite differences. All quantities appearing in Eq. (6) are therefore known either analytically or numerically: consequently, crosslinking rate during all the curing process is known for each node of the mesh. A final numerical integration allows to determine the crosslinking degree at each instant (including the final curing degree, which is the most important).

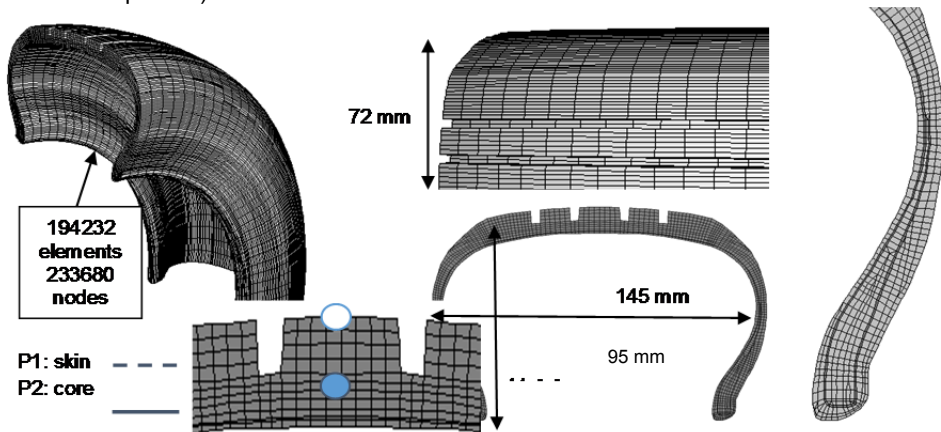


Figure 2: Common car tire analyzed numerically during vulcanization. Perspective view of ¼ of the tire (top-left), detail of the cross section with points on skin and core (bottom left), top view, transversal section and detail of the different parts of the tire (belts, core and carcass).

As practical example to analyze, a common car tire, whose transversal section, top view, perspective view and details in an already discretized version into FEs are depicted in Figure 2 is considered. The tire is a common 145/65 R15 type. The FE discretization is quite refined, being constituted by about 200000 3D elements.

Parameters used to define the heat transmission problem are provided in Milani & Milani (2018) and they are not repeated here for the sake of conciseness. Here it is only worth noting that data adopted in the simulations are in agreement with general literature indications. A vulcanization in axisymmetric chambers filled with nitrogen and then cooled at room temperature in air (this is possible opening the chambers) is assumed. Two different temperatures of vulcanization are considered, equal to 180°C and 170°C respectively, to simulate both a fast and a slightly slower realistic curing condition. The curing time is assumed equal to 25 minutes in both cases. The vulcanization rate and crosslinking degree are monitored everywhere in the mesh, but here attention is posed on a thick radial section, Figure 2, investigating curing on a point belonging to the skin (P1) and one in the core (P2). In Figure 3, the results obtained with the different blends and the different concentrations of accelerants are depicted. The first row shows the temperature profiles for P1 and P2 points obtained with the FE approach proposed. The other rows collect, for each S-TBBS-DPG concentration, the crosslinking degree evolution for P1 and P2 (blue curves, dashed for P1 and continuous for P2) and the vulcanization rates (red curves, dashed for P1 and continuous for P2). First and second columns refer to NR-PB at 50-50%, third and fourth columns to NR-PB at 70-30%. First and third columns depict results at a curing temperature equal to 170°C, second and fourth at 180°C. Results for S-TBBS-DPG equal to 1-1-0, 1-3-0, 1-0-1 and 1-0-3 are sketched respectively in diagrams belonging to rows 2, 3, 4 and 5 respectively. From an overall analysis of the results reported in Figure 3, the following considerations can be drawn: (1) As expected, in all cases the node on the skin exhibits a much faster heating with respect to the core node. At 180°C, this feature results into an almost immediate crosslinking (more than 80% in about 5 minutes for all the cases analyzed), but also the early activation of reversion, which induces de-vulcanization and does not allow rubber to exhibit good mechanical properties after the end of the curing process. The phenomenon is quantitative described by Figure 3, where a final crosslinking in some cases lower than 80% (e.g. for NR-PB=70-30%, S-TBBS-DPG=1-0-1) is found. The behavior of point P2 is obviously different: maximum crosslinking rate (usually around 30%/min) appears in the range 3-7 minutes (depending on the case considered). As a consequence, before 5 minutes, crosslinking is still insufficient (less than 20% in some cases, whereas at 5 minutes for P1 is maximum). (2) Results of Figure 3 show clearly that 25 minutes of curing at 180°C are not optimal and an over vulcanization is obtained in all the cases analyzed, with a final vulcanization degree that can be lower than 65% in few cases, as for NR-PB=70-30%, S-TBBS-DPG=1-0-3.

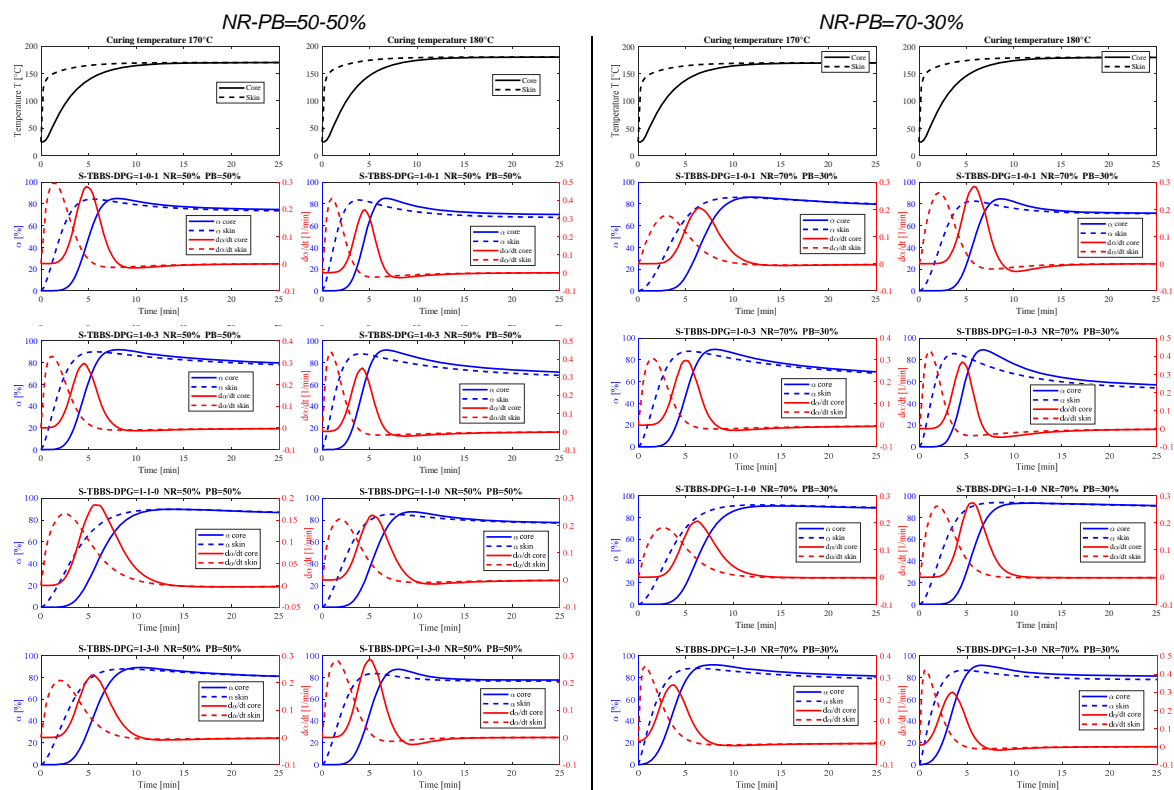


Figure 3: Vulcanization of a tire at 170°C and 180°C for 25 minutes. Analysis of the curing history of two points (P1-skin dashed curve, P2-core continuous curve) along tire thickness. Blue: vulcanization degree. Red curves to the vulcanization rate.

(3) When the vulcanization temperature is 170°C, the maximum crosslinking degree occurs in the majority of the cases between 5 and 10 minutes, for both the surface and the core of the item. Figure 3 clearly shows how an over-vulcanization is less critical than that at 180°C, and that a curing applied to 10-12 minutes is the condition assuring an average vulcanization that can reach 95%. (4) The effect of the accelerants in the vulcanization is evident, for instance DPG is always associated to over-curing and a rate of vulcanization very different passing from the skin to the core. When the skin starts to vulcanize, the core is still unreactive; conversely, when the core starts to vulcanize, the skin is in its reversion phase. On average, such effect is negative and reflects into poor final mechanical properties. Increasing DPG concentration at 3 phr is not beneficial; conversely, it results into an exacerbation of the drawbacks observed at 1 phr. (5) The blend NR-PB=70-30% seems to behave slightly better than that NR-PB=50-50%, exception made for S-TBBS-DPG=1-0-3, which in any case provides the worst results. The best results in terms of average crosslinking density are obtained for S-TBBS-DPG=1-1-0. When NR-PB=70-30% it is possible to obtain rather high curing degrees (very near to the optimized ones) both at 170°C and 180°C (more than 95%) with a vulcanization time of about 11-13 minutes. For NR-PB=50-50% the optimal temperature seems to be 170°C and the curing time must not exceed 12 minutes. An increase of TBBS concentration is not beneficial, because associated to more reversion.

5. Conclusions

The paper discussed a three-step numerical procedure which can be used in the production control of 3D rubber items to maximize the average crosslinking density and hence the final mechanical properties. The first step is the experimental characterization, the second a kinetic steady-state model which provides kinetic constants to implement in the last step into a FE code to solve heat transmission problems. The temperature profile knowledge of each node of the mesh in the last step allows to estimate locally the crosslinking degree, when a suitable kinetic model is hypothesized. The three-step procedure has been implemented in a commercial FE code by means of an Application Program Interface API function and tested on a real car tire geometry, changing the rubber blend used (a mixture of NR and PB) and concentrations of the accelerants adopted. In the specific case discussed, it has been found how a 50%-50% NR-PB blend with TBBS cured at 170°C is the most balanced providing good vulcanization of core and skin of the item.

References

- Arrillaga A., Zaldúa A.M., Atxurra R.M., Farid A.S., 2007, Techniques used for determining cure kinetics of rubber compounds, *European Polymer Journal*, 43, No. 11, 4783-4799.
- Ding R., Leonov A.I., 1996, A kinetic model for sulfur accelerated vulcanization of a natural rubber compound, *Journal of Applied Polymer Science*, 61, No. 3, 455-463.
- Han I.S., Chung C.B., Kang S.J., Kim S.J., Chung H.C., 1998, A kinetic model of reversion type cure for rubber compounds, *Polymer (Korea)*, 22, 223-230.
- Sun X., Isayev A.I., 2009, Cure kinetics study of unfilled and carbon black filled synthetic isoprene rubber, *Rubber Chem. Technol.*, 82, No. 2, 149-169.
- Mansilla M.A., Marzocca A.J., Macchi C., Somoza A., 1995, Influence of vulcanization temperature on the cure kinetics and on the microstructural properties in natural rubber/styrene-butadiene rubber blends prepared by solution mixing, *European Polymer Journal*, 69, 50-61.
- Milani G., Hanel T., Milani F., Donetti R., 2015, A closed form solution for the vulcanization prediction of NR cured with sulphur and different accelerators, *Journal of Mathematical Chemistry*, 53, No. 4, 975-997.
- Milani F., Milani G., 2017, Comprehensive kinetic numerical model for NR and high-cis poly-butadiene rubber blends, *Chemical Engineering Transactions*, 57, 1495-1500.
- Milani F., Milani G., 2018a, Rubber blends: kinetic numerical model by rheometer experimental characterization, *Journal of Mathematical Chemistry*, 56, 1520-1542.
- Milani G., Milani F., 2018b, Optimal vulcanization of tires: Experimentation on idealized NR-PB natural and poly-butadiene rubber blends, phenomenological smoothed numerical kinetic model and FE implementation, *Polymer Testing*, 72, 63-85.