Numerical Model for the Prediction of Final Mechanical Properties of EPDM Vulcanized with Peroxides
Part II Results

Gabriele Milani[1] and Federico Milani[2]

[1]*Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milan, Italy*
[2]*Chem.Co Consultant, Via J.F. Kennedy 2, 45030 Occhiobello (RO), Italy*

Keywords: Kinetic Numerical Model, EPDM Rubber, Peroxides, Comparison with Experimental Data.

Abstract: In the present Part II, the kinetic numerical model discussed in detail in Part I, is applied to the huge amount of experimental data collected by the authors. Rheometer curves are fitted numerically for three different curing temperatures, for all the curing agents investigated at a concentration equal to 150%, which have proved to be the most adequate to obtain optimal crosslinking of the EPDM under consideration. The comparisons with experimental data at three different temperatures allow estimating partial kinetic constants of the model as a function of the absolute temperature, with a direct comparison with simplified formulas provided by the peroxide producers. The application of the numerical kinetic model to a large variety of real scale examples allows a direct validation of the capabilities of the approach proposed, as well as an evaluation of the most suitable production parameters to use in practice (curing time and temperature, concentration and typology of the curing agents) in order to maximize rubber output mechanical properties and crosslink homogeneity, without the need to perform costly experimental campaign.

1 INTRODUCTION

To propose ad-hoc numerical models for the interpretation of vulcanization kinetics is paramount when producers are interested in a fast and less expensive (when compared with an experimental approach) evaluation of the most suitable production parameters to use in order to optimize rubber output mechanical properties, as for instance average tensile strength, elongation at break, tear resistance, etc., Hofmann (1989), Milani et al. (2013).

The procedure of optimization performed on production parameters includes –but it is not limited to- the evaluation of the curing temperature, typology and concentration of peroxide and exposition time to use to maximize an a-priori established characteristic of the vulcanized compound, Milani and Milani (Milani and Milani 2010), (Milani and Milani, 2012a), (Milani and Milani, 2013b).

Peroxides producers usually provide simplified kinetic mechanisms for their peroxides, which always follow a so called first order Arrhenius equation. By means of the knowledge of the so-called half-time life of the peroxide, it is possible to roughly identify a temperatures interval where the vulcanization has to be conducted. However, no information is provided on concentrations, which usually is fixed following well established rules of thumb and a change of few degrees in the curing temperature may result into a strong decrease of the final quality of the crosslinked items, especially for thick ones.

In addition, it can be affirmed that, while this simplified approach may be quite effective for a rough estimation of the most suitable peroxide to adopt within standard curing conditions, more sophisticated approaches are needed when mixtures of peroxides or extreme curing conditions are utilized.

Such conditions include drastic reduction of the curing time, always associated to high vulcanization temperatures and the uniform vulcanization of item with thickness varying from moderate to large.

For all the aforementioned cases, the adoption of simplified procedures progressives become no more effective and more quantitative approaches are required.

In this framework, it appears particularly interesting to utilize a comprehensive numerical

model, based on the actual partial reactions occurring during vulcanization. The kinetic model proposed in Part I, suitable to obtain a quantitative interpretation of the vulcanization process for EPDM rubber vulcanized with peroxides, is applied in the present paper to analyze the experimental results discussed in the companying paper. Rheometer curves obtained experimentally for the three curing agents considered are fitted numerically at three different curing temperatures, at a concentration equal to 150%, which have proved to be the most adequate to obtain optimal crosslinking of the EPDM under consideration. The comparisons with experimental data at different temperatures allow estimating partial kinetic constants of the model as a function of the absolute temperature, with a direct comparison with simplified formulas provided by the peroxide producers.

2 EXPERIMENTAL DATA NUMERICAL POST-PROCESSING

Normalized experimental rheometer curves are comparatively represented for the three different peroxides from Figure 1 to Figure 3. In particular, in Figure 1 results obtained using as curing agent M2 are depicted, in Figure 2 BC-FF data are represented, whereas in Figure 3 14S rheometer curves are summarized. Subfigures -a. –b and and –c refer to temperatures equal to 160°C, 180°C and 200°C respectively.

Normalization is conducted dividing each value of the torque by the maximum torque, Milani and Milani (Milani and Milani, 2011), (Milani and Milani, 2012b), (Milani and Milani, 2013a), which occurs at the end of the test, since no reversion is present for all the cases analyzed. The different curves represented refer to the different concentrations inspected in the experimental campaign, namely -50%, +/- 0%, +50%, +100%, +150%.

As it is possible to notice, there are small but perceivable differences among the normalized curves, meaning that curing agent concentration has some effects on the behavior of the compound during vulcanization. However, it is particularly evident that, increasing curing agent concentration, reticulation exhibits an asymptotic behavior, in all the cases analyzed. Indeed, rheometer curves corresponding to +100% and +150% are in practice superimposable, meaning that, beyond such

concentrations, the reticulation is fully independent from the curing agent concentration. Experimental evidences show that crosslinking optimality could be obtained with at least an amount of peroxide double with respect to the standard one (100% concentrations), implicitly stating that the standard +/- 0% peroxide concentrations provides suboptimal vulcanized items.
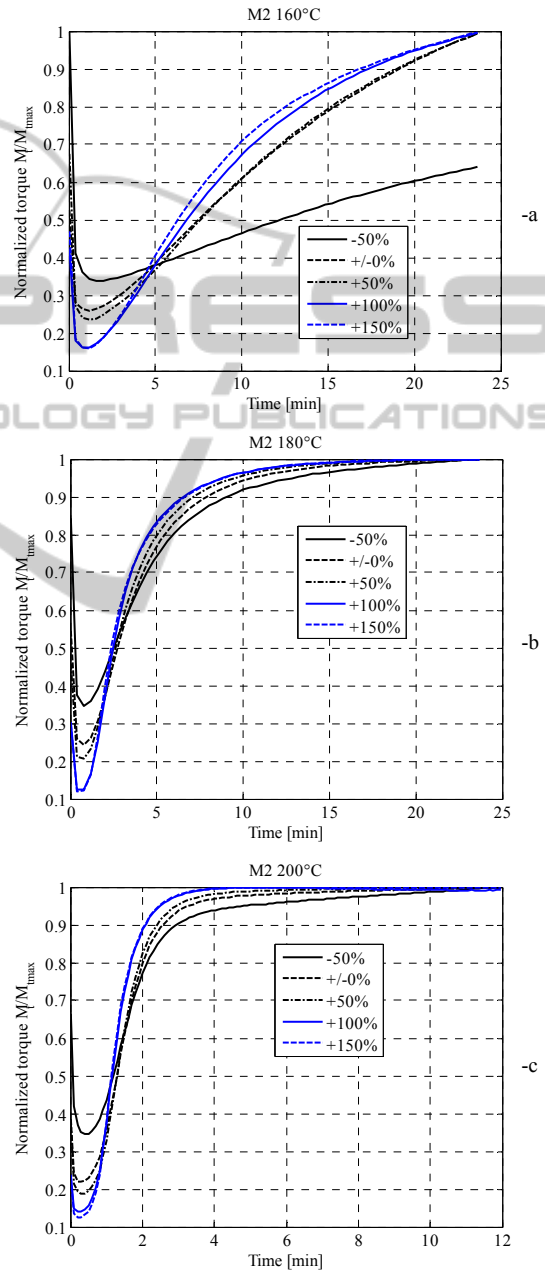

Figure 1: M2 peroxides mixture. Normalized experimental rheometer curves at different peroxide concentrations. –a: 160 °C. –b: 180 °C. –c: 200 °C.

On the other hand, it is worth noting that the numerical model proposed is independent from peroxide concentration. As a consequence, data to consider for the comparisons between numerical predictions and experimental results should be those provided with a 150% concentration of the peroxides.
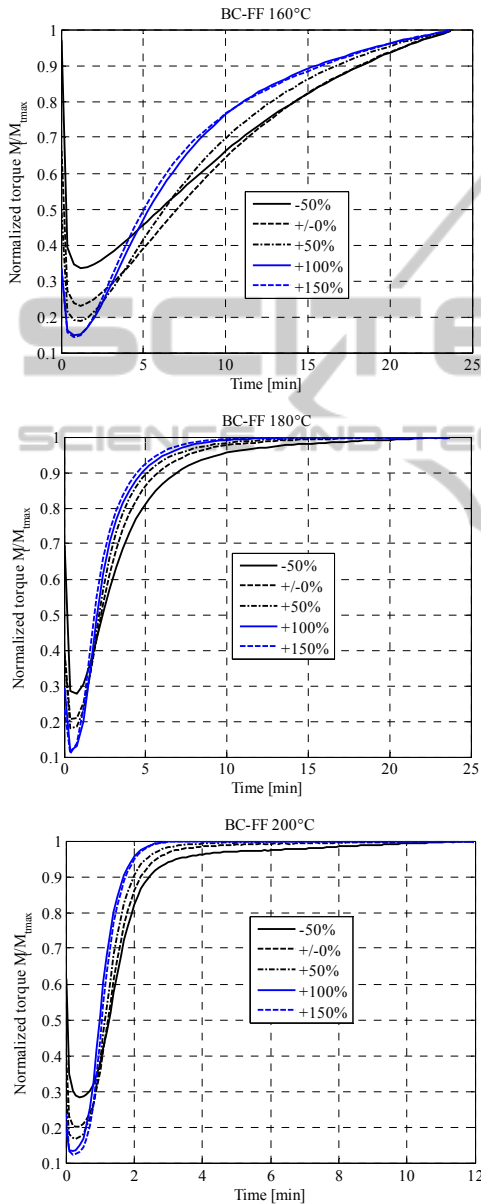

Figure 2: BC-FF peroxide. Normalized experimental rheometer curves at different peroxide concentrations. −a: 160 °C. −b: 180 °C. −c: 200 °C.
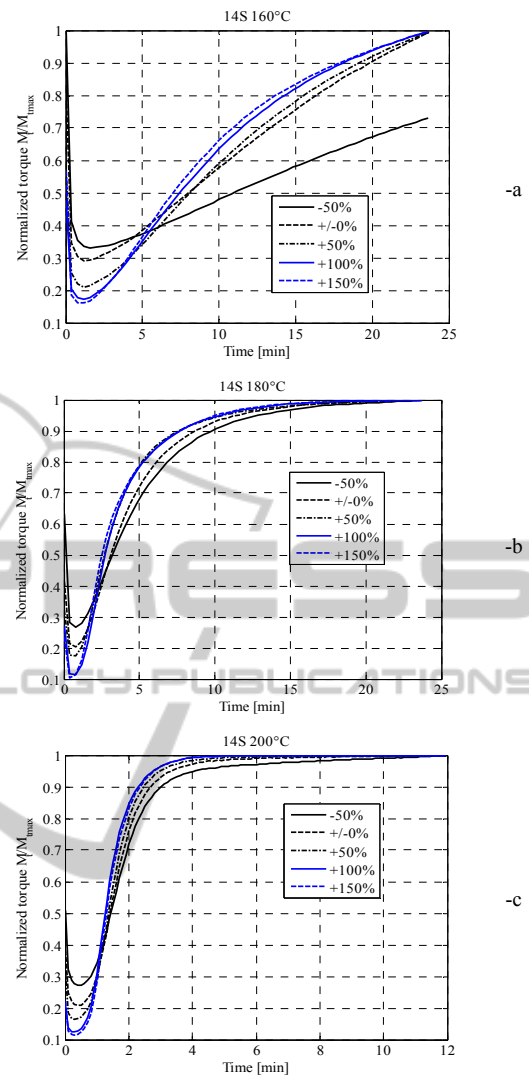

Figure 3: 14S peroxide. Normalized experimental rheometer curves at different peroxide concentrations. −a: 160 °C. −b: 180 °C. −c: 200 °C.
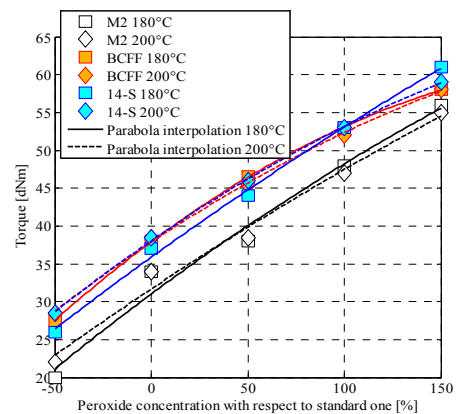

Figure 4: Peroxide concentration % versus torque. Experimental data (points) and parabolic numerical interpolation.
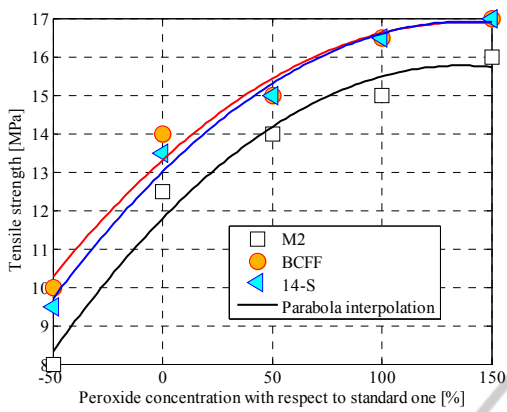
Figure 5: Peroxide concentration % versus tensile strength. Experimental data (points) and parabolic numerical interpolation.

To corroborate the idea that a greater concentration of peroxide with respect to the standard one results into an optimal crosslink of the EPDM under consideration, in figures from Figure 4 to Figure 6 a synopsis of the experimental results available is represented in graphical form. In particular, in Figure 4, peroxide concentration % versus torque is represented for all the curing agents and temperatures investigated. Experimental data are represented with points (squares and diamonds refer to 180°C and 200°C respectively, white, orange and cyan colors to M2, BC-FF) whereas continuous (180°C) and dashed lines (200°C) are parabolic numerical interpolations. In Figure 5, the same symbols are utilized to represent the relationship between peroxide concentration and tensile strength, whereas in Figure 6 tensile strength versus torque is represented. As it is possible to notice, especially from Figure 5 , it can be observed that tensile strength reaches an asymptotic value for 150% concentrations.
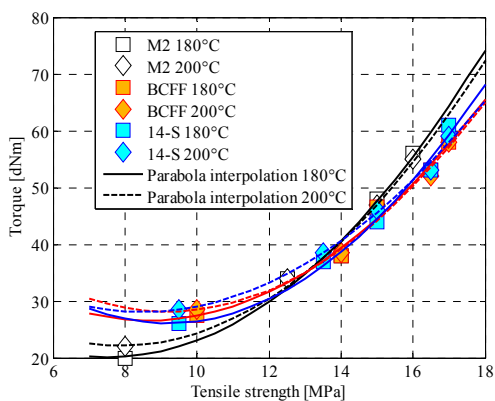

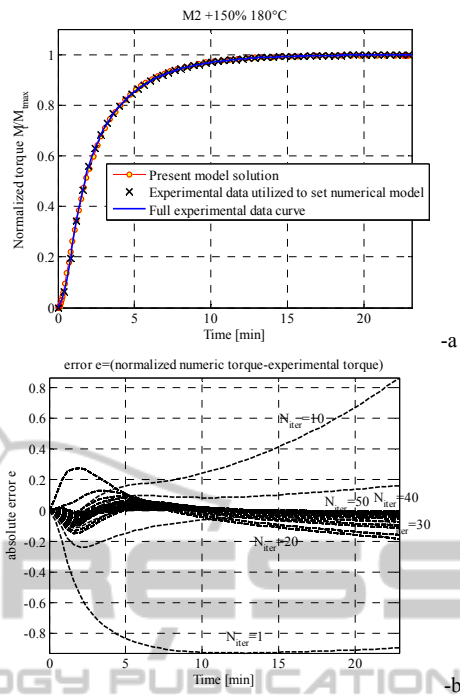Figure 6: Tensile strength versus torque. Experimental data (points) and parabolic numerical interpolation.

Figure 7: M2 curing agent, 180°C. Comparison between experimental data and numerical model. −a: full normalized curve. −b: difference between numerical model and experimental normalized torque at successive iterations.
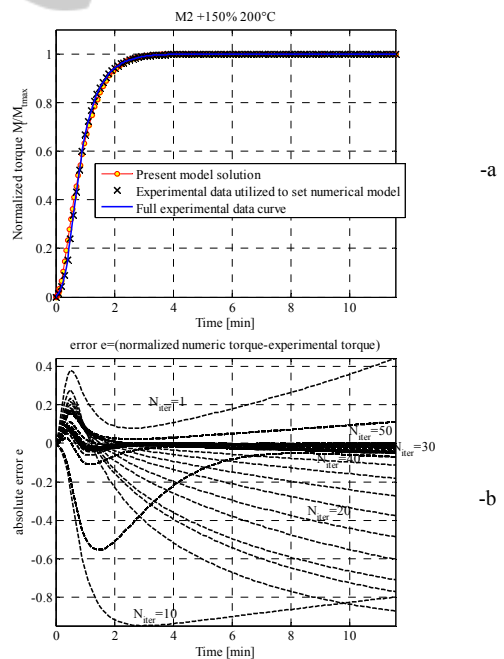

Figure 8: M2 curing agent, 200°C. Comparison between experimental data and numerical model. −a: full normalized curve. −b: difference between numerical model and experimental normalized torque at successive iterations.

To perform a numerical optimization of the kinetic model proposed, experimental cure values are normalized dividing each point of the curve by the maximum torque values, so that experimental data are always within the range 0-1.

A comparison between present numerical curves and experimental data is provided from Figure 7-a to Figure 12-a for EPDM vulcanized with M2, BC-FF and 14-S at 180°C and 200°C respectively. The resultant kinetic constants found numerically are summarized in Table 1.

Numerical curves are obtained using a non-linear least square procedure, for which the convergence performance is evaluated from Figure 7-b to Figure 12-b. In particular, in the figures, the absolute difference between normalized experimental torque and numerical predictions is represented, at successive iterations and at increasing instants between the initial and final time of experimentation. Obviously, as expected, passing from the initial iteration to the final, such difference decreases drastically, meaning that the least square routine is achieving convergence. As it is possible to notice, the gap between numerical models and experimental data tends to zero for almost the instants inspected, exception made for the initial simulation range, near scorch point.
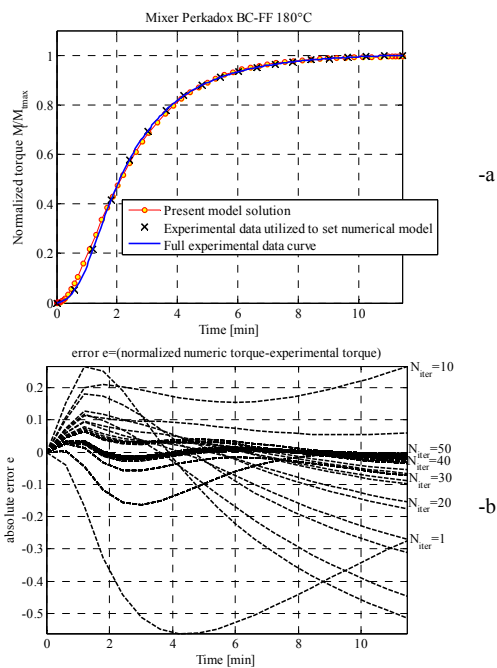

Figure 10: BC-FF, 200°C. Comparison between experimental data and numerical model. –a: full normalized curve. –b: difference between numerical model and experimental normalized torque.

Figure 9: BC-FF, 180°C. Comparison between experimental data and numerical model. –a: full normalized curve. –b: difference between numerical model and experimental normalized torque.
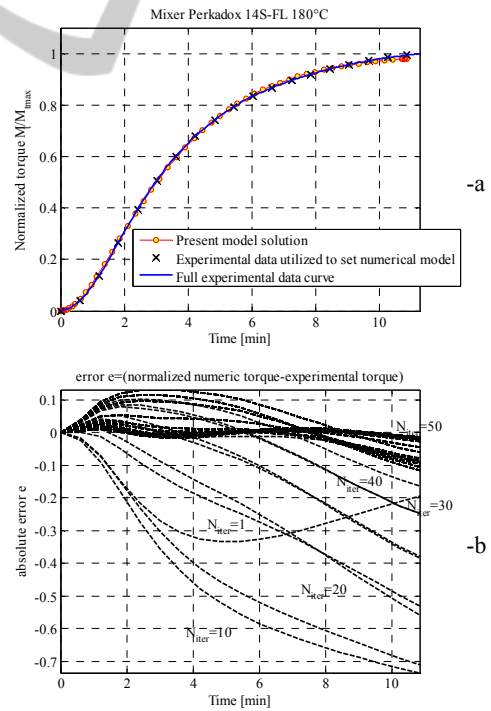
Figure 11: 14-S, 180°C. Comparison between experimental data and numerical model. –a: full normalized curve. –b: difference between numerical model and experimental normalized torque.
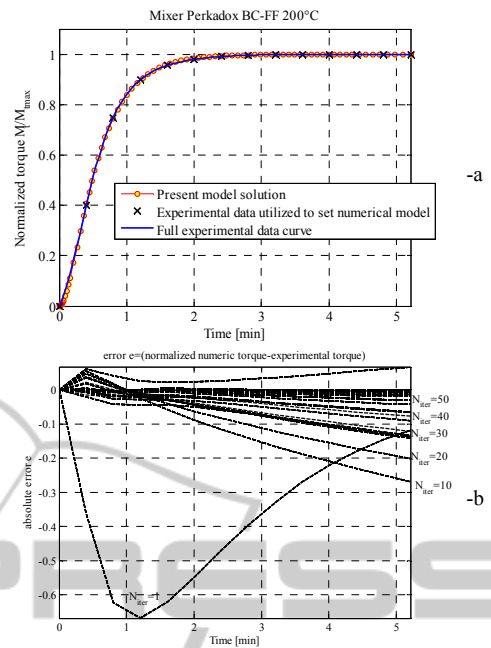
Table 1: numerical results obtained after least square optimization for kinetic constants K_i.

	Temp	K_1	K_2	K_3	K_4
	[°C]	1/min	1/min	1/min	1/min
M2	0.055	0.190	0.00	0.00	0.055
	0.327	0.513	0.00	1.28 e-4	0.327
	2.284	1.319	1.13 e-4	8.70 e-4	2.284
BC-FF	0.069	0.301	0.00	0.00	0.069
	0.491	0.602	0.0001	0.0002	0.491
	2.401	2.330	0.0002	0.0001	2.401
14-S	0.048	0.191	0.00	0.00	0.048
	0.312	0.473	0.00	0.00	0.312
	2.221	1.126	9.46 e-5	3.45 e-5	2.221

Figure 12: 14-S, 200°C. Comparison between experimental data and numerical model. –a: full normalized curve. –b: difference between numerical model and experimental normalized torque.
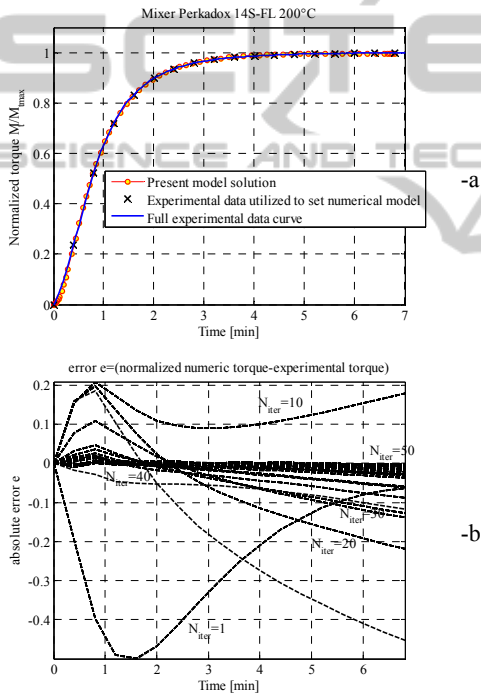
Here the experimental curve exhibits a sudden increase in the first derivate, meaning that the initiation of vulcanization is prone to occur. In any case, this stage is of little interest for the models proposed, which are designed for a reliable prediction of final reticulation level. In general, the agreement with experimental response seems rather promising, with an almost perfect superposition of the numerical curves with experimental data.

The convergence map of the least-square algorithm shows that after around 50 iterations the best fitting is always achieved, with errors in practice vanishing. The numerical values of the four kinetic constants defining completely the reaction kinetic are summarized for all peroxides investigated, in Table.
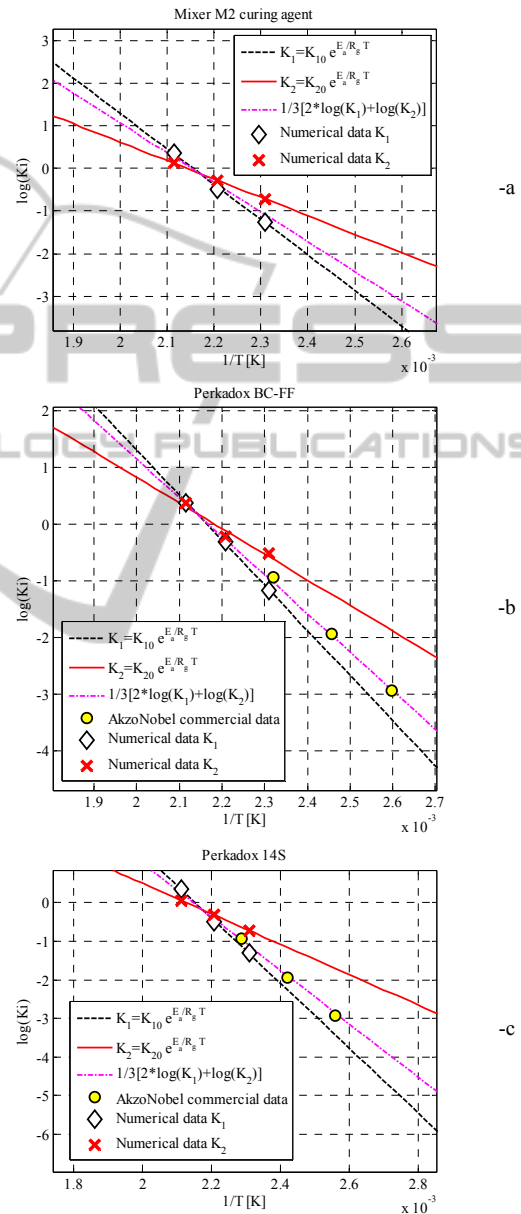

Figure 13: Linear regression interpolation of the kinetic constants K_1 and K_2 provided by the single differential equation model, the resultant linear regression obtained as $K_1 + K_2$ and comparison with commercial data provided by Akzo Nobel for the peroxide under consideration. –a: M2. –b: BC-FF. –c: 14-S.

Considering the numerical values obtained for the first two constants K_1 and K_2, reported in Table (the other constants are almost zero, indicating that no reversion is experienced) at two distinct temperatures, it appears interesting to plot the straight lines passing from such values in the Arrhenius plane. In such space, the horizontal axis is represented by the inverse of the absolute temperature, $1/T$, whereas the vertical axis is $\log(K_i)$, where K_i is the i-th kinetic constant. It is, indeed, commonly accepted that the variability of a single kinetic constant follows the so called Arrhenius law, which may be written as $K_i(T) = K_{i0}e^{\frac{E_{ai}}{R_g T}}$, where K_{i0} is the value of the i-th kinetic constant at an infinite temperature, E_{ai} is a constant typical of the reaction and R_g is the universal gas constant. In a $1/T$ - $\log(K_i)$ Cartesian plane, the Arrhenius law is thus represented by a straight line, intercepting vertical axis at $\log(K_{i0})$. Since experimental data are available at two distinct temperatures, and accepting that each single constant follows an Arrhenius law, it is possible to sketch $K_i(T)$ lines in the $1/T$ - $\log(K_i)$ plane, for both peroxides under consideration. Such representation is particularly useful from a practical point of view, because it allows a direct evaluation of the kinetic constants describing the velocity of the partial reactions at any vulcanization temperature. The straight lines numerically deduced are depicted inFigure 13. Subfigures refer to peroxides M2 (-a), BC-FF (-b) and 14-S (-c) respectively. Numerical data of Table 1, utilized to plot the straight lines, are also indicated for the sake of clearness. In order to evaluate if the numerical approach proposed is in agreement with simplified procedures commonly used in practice, it is also possible to compare numerical results with commercial data available for both peroxides under consideration. In particular, Akzo Nobel furnishes in tabular form values of the kinetic constants of both BC-FF and 14-S at three different temperatures, corresponding to a half-time life equal to 0.1, 1 and 10 hours respectively. It is implicitly assumed that the reaction describing peroxide decomposition is of first order and that the single kinetic constant associated to such a reaction follows and Arrhenius law. It is very straightforward the deduction of the numerical values of the constants at the three temperatures considered, from the experimental knowledge of the half time life

$t_{1/2}$, being simply $K_i \ln 2 = t_{1/2}$. No information is available for M2, which is indeed a mixture of peroxides.

Since in our numerical model, first and second reactions occur in series, and the first reaction produces $2R$ radicals, the comparison with the simplified practical approach above discussed, may be attempted considering the weighted average between constants K_1 and K_2, i.e. plotting the straight line 1/3*(2 $\log K_1$ + $\log K_2$), again deduced from present numerical results and represented with a dash-dot line in Figure 13-b and Figure13-c for Perkadox BC-FF and Perkadox 14S-FL respectively. In the same figures, data deduced from commercial catalogues provided by Akzo Nobel (2012) are represented with circles. As it is possible to notice, the agreement is almost perfect, meaning that the predictivity of the numerical procedure here presented is very promising.

3 CONCLUSIONS

In the present Part II, the numerical model proposed in Part I has been validated using the huge amount of experimental data obtained by the authors, in presence of three different curing agents with different concentrations at three increasing temperatures. The numerical model provides partial reactions kinetic constants, which are very useful in practice to determine the optimal industrial input parameters to use (as for instance vulcanization temperature and curing time) to obtain the maximum mechanical properties of the vulcanized items. A comparison with simplified approaches based on a single first order kinetic equation shows that very reasonable results are obtained and, at the same time, demonstrates that the model proposed supersedes the classic limitations of the simplistic procedures commonly used, especially in presence of reversion or when a mixture of peroxides is utilized. An interesting correlation between tensile strength and maximum torques has been also obtained.

The traditional methods used by producers to choose the most suitable production parameters, as for instance a-priori strategies (essentially based on the rheometer curves) or a-posteriori considerations (direct tensile tests on the vulcanized rubber) could be potentially avoided and superseded, after a careful calibration of the mathematical approach proposed, with an undoubted advantage in terms of

time and cost savings. The approach proposed, finally, may push the research forward when dealing with the preparation of new rubber compounds and vulcanization agents, once that a specific output parameter is considered as target to optimize at the end of the vulcanization process.

REFERENCES

AkzoNobel (2012). Brochure of organic peroxides, available at http://www.akzonobel.com/polymer/

Hofmann, W., 1989. Rubber Technology Handbook, *Hanser Publishers*, Munich.

Milani, G., Galanti, A., Cardelli, C., Milani, F., 2013. Peroxide cross-linking of EPDM for medium voltage cable applications: experimental insight. In: *Proc. 183rd Technical Meeting Akron*, Ohio Monday, April 22, 2013 - Wednesday, April 24, 2013

Milani, G., Milani, F., 2010. *Journal of Mathematical Chemistry* 47(1): 229-267.

Milani, G., Milani, F., 2011. *Journal of Mathematical Chemistry*, 48: 530–557.

Milani, G., Milani, F., 2012a. Computers & Chemical Engineering, 43: 173–190.

Milani, G., Milani, F., 2012b. *Journal of Applied Polymer Science*, 124(1): 311–324.

Milani, G., Milani, F., 2013a. Differential model accounting for reversion for EPDM vulcanized with peroxides. *Journal of Mathematical Chemisty, In press.*

Milani, G., Milani, F., 2013b. *Polymer Engineering and Science*, 53 (2): 353-369.