

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

Part I: Basis of the Numerical Model and Experimental Campaign

Gabriele Milani¹ and Federico Milani²

¹Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milan, Italy

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

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Abstract: In the paper, a simple but effective mathematical model having kinetic base, to predict the vulcanization degree of rubber vulcanized with peroxides, is presented. The approach takes contemporarily into consideration, albeit within a simplified scheme, the actual reactions occurring during peroxidic curing, namely initiation, H-abstraction, combination and addition, and supersedes the simplified approach used in practice, which assumes for peroxidic curing a single first order reaction. After a suitable re-arrangement of the first order system of differential equations obtained from the actual kinetic system adopted, a single second order non-linear differential equation is obtained and numerically solved by means of a Runge-Kutta approach. Kinetic parameters to set are evaluated by means of a standard least squares procedure where target data are represented by experimental values available, i.e. normalized rheometer curves. In order to assess numerical results, a wide experimental campaign is conducted, varying curing agents, vulcanization temperatures and concentration of the peroxides. Both rheometer curves to compare with those provided by the numerical model and stretch-strain curves of the vulcanized samples are obtained, to have a precise insight into the most suitable parameters to use during curing.

1 INTRODUCTION

The curing process of medium and high voltage electric cables with EPM/EPDM rubber having low molecular weight (Mooney viscosity ML), ethylene high content and low-medium amount of termonomer (generally 1,4-Hesadiene, ENB, DCPD and VNB) is made by peroxides.

In this paper, an industrial formulation with a terpolymer and VNB as third monomer (Vistalon, 1703) exhibiting a large molecular weights distribution, as shown in Figure 1, good processability suitable for the extrusion of medium-high voltage electric cables is considered. The peculiar characteristic of the industrial product analyzed is that unvulcanized rubber is produced in pellets, allowing absorption of the peroxide on the surface of each single element, satisfactory stocking stability and the possibility to vulcanize directly the compound by other factories.

On the base of such considerations and with the aim to determine the optimal reticulation conditions of real thick items, it appears therefore interesting to

propose a comprehensive numerical model based on the actual decomposition reactions occurring in reality, as close as possible to that observed experimentally, to predict with simple computer simulations the optimal curing time and temperature, Milani and Milani (2008, 2012a, 2013) and the most suitable peroxide to utilize in order to maximize the final crosslinking density of an item with given geometry, Milani and Milani (2010).

This work is part of a wider experimental/numerical program conducted by the authors on the same rubber recipe constituted by an EPDM elastomer, changing both peroxides used and controlled vulcanization temperature. In particular, test were conducted in a range temperature varying between 160 and 200°C, with a 20°C step, using different peroxides, changing their concentration and considering also a mixture of three of them. A huge amount of rheometric cure curves were obtained (one for each temperature, peroxide used and concentration) and quantitatively compared one each other, to have an insight into the most effective temperature and peroxide to use during such kind of

vulcanization, in terms of both vulcanization velocity and maximum torque reached.

In order to interpret theoretically experimental results obtained, a peroxide decomposition kinetic model is presented, considering the complex set of reactions that characterize peroxide crosslinking, namely homolytic cleavage of peroxide, hydrogen abstraction, polymer radicals formation, polymer radicals coupling, cross-link formation and polymer scission.

Starting from the above -most probable- kinetic scheme, a system of non-linear differential equations with few variables is obtained and solved numerically, after suitable variable substitutions, by means of a Runge-Kutta algorithm. Crosslinking density is thus evaluated numerically and compared to rheometer experimental curve, which may provide a reliable indication of the average cured rubber crosslinking, once suitably scaled to unitary values.

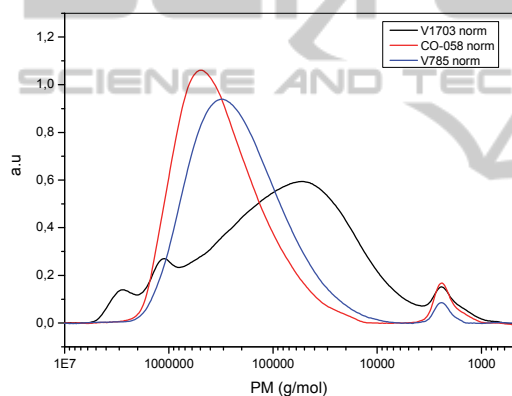


Figure 1: Molecular weight distribution of Vistalon 1703 compared with other two distributions of common industrial products.

By means of the numerical approach proposed, an estimation of the kinetic constants per single reaction, once known kinetic decomposition laws, may be evaluated and hence the activity of each peroxide may be estimated using a few experimental data at only two different temperatures.

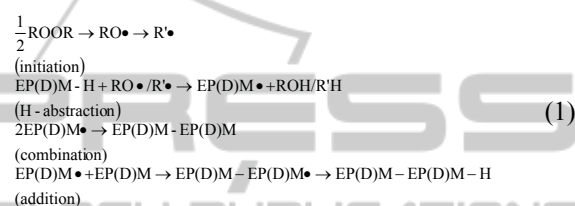
By means of the additional experimental and numerical evaluation of the stress-strain curves of the vulcanized samples, it is also possible to establish a correlation between tensile strength and maximum torque obtained with the rheometer test, again useful for an optimization of the production processes.

It has to be finally considered that, for thick items exceeding 5 mm, a numerical algorithm is already at disposal to determine the most suitable temperatures and exposition times to be used in the industrial production, in order to guarantee that the

core results not under-vulcanized and the skin not over-vulcanized.

2 RETICULATION KINETIC OF EPDM VULCANIZED WITH PEROXIDES

The basic chemistry in the generally accepted mechanism of peroxide cure of EPDM have been reviewed by van Duin and co-workers (Dees and van Duin, 2008); (van Duin, 2002), and may be summarized by means of the following partial reactions occurring in series and parallel:



The chain of free-radical reactions is initiated by thermal decomposition of the peroxide, yielding primary alkoxy (RO•) or secondary alkyl radicals (R•). Subsequent abstraction of H-atoms from the EPDM polymer results in the formation of EPDM macro-radicals (EPDM•). Calculations based on kinetic data for H-abstraction indicate that H-abstraction mainly occurs along the saturated EPM polymer backbone, Van Duin (2002), whereas several electron paramagnetic resonance (EPR) spectroscopy studies have shown the selective formation of allyl radicals derived from the diene monomer.

Considering the energy required for the abstraction of the H-atoms, see Figure 2, within the formation of the back-bone, the allyl radicals are more probable than the others, because of the lowest energy required by the abstraction of the H-atoms, Knox and Palmer (1961).

The actual cross-linking proceeds via two pathways, which have been shown to be additive. Two EPDM macro-radicals either combine or, alternatively, a macro-radical adds to an EPDM unsaturation. Visible spectroscopy has confirmed the conversion of the EPDM unsaturation upon peroxide cure, Dickland and van Duin (2002). It is noted that in practical EPDM/peroxide compounds usually co-agents, such as triallyl (iso)cyanurate, trimethylolpropane trimethacrylate or m-phenylenebis(maleimide), are included to increase the peroxide curing efficiency, Hofmann (1989), which obviously affects the mechanism of peroxide

cure.

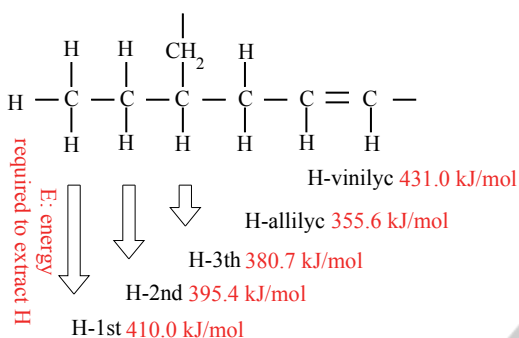


Figure 2: Energy required in order to extract hydrogen atom from the backbone of the macromolecules at 0 K. At 25°C add 1 Kcal.

In the paper, a simple but effective mathematical model having kinetic base, to predict the vulcanization degree of rubber vulcanized with peroxides is presented.

The approach takes contemporarily into consideration a large set of reactions occurring during peroxidic curing, i.e. initiation, H-abstraction, combination and addition, overcoming the simplified approach which assumes for peroxidic curing a single first order reaction. After a suitable re-arrangement of the first order system of differential equations obtained from the actual kinetic system adopted, a single second order non-linear differential equation is obtained and numerically solved by means of a Runge-Kutta approach. Kinetic parameters to set are evaluated by means of a standard least square procedure where target data are represented by experimental values available, i.e. normalized rheometer curves or percentage crosslink density experimentally evaluated by means of more sophisticated procedures.

Two cases of technical interest are critically discussed, the first relying into an EPDM crosslinked with di-cumyl peroxide, the second into a compound with high level of unsaturation exhibiting reversion at relatively high temperatures (175°C) near the end of the vulcanization process. A quite promising agreement is experienced, even in presence of reversion.

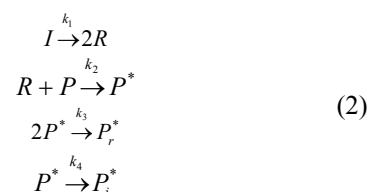
3 THE KINETIC MATHEMATICAL MODEL PROPOSED

The mechanism of EPM/EPDM peroxide curing and

the structures formed are still lacking, mainly due to the complexity of the system (large number of structures formed at low concentrations) combined with the relatively difficult in term of analytical accessibility to determine the cross-linked polymer networks.

The complex set of the reactions that characterize peroxide cross-linking involve homolytic cleavage of peroxide, oxy and alkyl radicals, hydrogen abstraction, radical coupling (cross-link formation), polymer scission and radical transfer. In the case of EPDM, the amount and type of the third-monomer, could be considered, but in first approximation it is not considered for the types of EPDM with lower concentrations of the third-monomer. Therefore, our cross-link scheme the different activity from alkyl and oxy radicals in the homolytic cleavage of peroxide and the secondary reactions as oxygenation and acid-catalyzed decomposition of peroxide. From these considerations, we have adopted for EPM/EPDM the kinetic scheme for the peroxide cross-link reactions summarized in Equation (1).

To circumvent limitations of such models in the application of EPDM rubber, the mechanisms at the base of vulcanization for such blend should be properly considered, Milani & Milani (2011, 2012b). In this framework, focusing exclusively on EPDM rubber, one possible polymerization scheme may be the following:



In Equation (2), I is the peroxide, R the primary alkoxy ($\text{RO}\bullet$) or secondary alkyl radicals ($\text{R}\bullet$), P the uncured polymer, P^* is the EPDM macro-radical, P_r^* and P_i^* the matured cross-linked polymers, and $K_{1,\dots,4}$ are kinetic reaction constants.. Here it is worth emphasizing that $K_{1,\dots,4}$ are temperature dependent quantities, hence they rigorously should be indicated as $K_{1,\dots,4}(T)$, where T is the absolute temperature. In what follows, for the sake of simplicity, the temperature dependence will be left out.

By means of the so called xyz method, independent variables may be established. From stoichiometry of the reaction, it can be argued that:

$$\begin{aligned}
 I &= I_0 - x \\
 R &= 2x - y \\
 P &= P_0 - y \\
 P^* &= y - 2z - q \\
 P_r^* &= z \\
 P_i^* &= q
 \end{aligned} \tag{3}$$

Obviously, from (3) it can be argued that independent variables are: $I(t)$, $R(t)$, $P_r^*(t)$, $P_i^*(t)$.
Indeed:

$$\begin{aligned}
 x &= I - I_0 \\
 y &= 2(I - I_0) - R \\
 P &= P_0 + R - 2(I - I_0) \\
 P^* &= 2(I - I_0) - R - 2P_r^* - P_i^* \\
 z &= P_r^* \\
 q &= P_i^*
 \end{aligned} \tag{4}$$

The aim is to provide an analytical expression for vulcanized rubber, i.e. concentration of P^* with respect to time.

From (2) and (3), the following set of differential equations is deduced:

$$\begin{aligned}
 \frac{dI}{dt} &= -K_1 I \\
 \frac{dR}{dt} &= 2K_1 I - K_2 R P \\
 \frac{dP}{dt} &= -K_2 R P \\
 \frac{dP^*}{dt} &= K_2 R P - K_3 (P^*)^2 - K_4 P^* \\
 \frac{dP_r^*}{dt} &= K_3 (P^*)^2 \\
 \frac{dP_i^*}{dt} &= K_4 P^*
 \end{aligned} \tag{5}$$

(a), (b) and (c) form a system of differential equations in three variables which may be solved as follows. (a) may be solved immediately by separation of variables:

$$I = I_0 e^{-K_1(t-t_0)} \tag{6}$$

(b)-(c) is:

$$\frac{dR}{dt} - \frac{dP}{dt} = 2K_1 I = 2K_1 I_0 e^{-K_1(t-t_0)} \tag{7}$$

Differentiation of (c) results into:

$$\frac{d^2 P}{dt^2} = -K_2 R \frac{dP}{dt} - K_2 P \frac{dR}{dt} \tag{8}$$

From (7), remembering from (5) that $R = -\frac{1}{K_2 P} \frac{dP}{dt}$

, the second order differential equation (8) may be re-written exclusively in terms of P as follows:

$$\begin{aligned}
 \frac{d^2 P}{dt^2} - \frac{1}{P} \left(\frac{dP}{dt} \right)^2 + K_2 P \frac{dP}{dt} + \\
 + 2K_1 K_2 I_0 P e^{-K_1(t-t_0)} = 0
 \end{aligned} \tag{9}$$

The non linear differential equation (9) may be solved numerically with a standard Runge-Kutta algorithm, Matlab (2011), to find concentration P(t). The knowledge of P(t) allows to determine R(t) and, from equation (5)(d), P^* :

$$\frac{dP^*}{dt} = K_2 R(t) P(t) - K_3 (P^*)^2 - K_4 P^* \tag{10}$$

Equation (10) is again solved using a Runge-Kutta numerical approach.

4 COMPARISON WITH EXPERIMENTAL DATA

A wide experimental campaign has been conducted by the authors in cooperation with Mixer Spa, Milani et al., (2013), on a same EPDM blend but varying a number of different parameters, as for instance curing agent, peroxide concentrations and vulcanization temperature.

Table 1: Experimental data set analyzed, EPDM composition in phr.

Polymer VISTALON 1703P Ethylene in wt. % 76.2 VNB - vinylnorbornene in wt. % 0.9 Mooney ML (1+4) 100°C 35.3 Manufacturer (Exxon)	54
Silane treated calcinated kaolin	30
Antioxidants	8
LDPE Riblene MR 10 MFI= 18.7 (ASTM D1238)	6
PE WAX	1
Peroxide	1

A huge amount of experimental data have been collected, including rheometer curves at different temperatures and stress strain curves of the vulcanized items.

The blend under consideration has the composition schematically reported in Table 1.

As it is possible to notice from the molecular

weight distribution of Vistalon 1703 reported in Figure 1, it is quite wider with respect to other common products available in the market stock.

The experimentation was conducted varying the following parameters:

- 1) Curing agent. Three different peroxides or a mixture of peroxides have been tested. The first, hereafter called M2 for the sake of clearness, is a mixture of three different peroxides utilized by the factory, AkzoNobel (2012), to industrially produce cured rubber. The three peroxides composing the mixture are the following: Trigonox T, Perkadox BC-FF and Perkadox 14S all in the same proportion. The sum of concentrations of the three peroxides used industrially are equal to around 1 phr and hereafter is labeled as +/- 0% concentration. The second and third peroxides investigated are commercial products provided by AkzoNobel, having commercial names as Perkadox BC-FF and Perkadox 14S-FL. They will be indicated in the following comparisons as BC-FF and 14S for the sake of conciseness. Perkadox BC-FF is dycumil peroxide whereas Perkadox 14S-FL is a di(tert-butylperoxyisopropyl) benzene. They exhibit a half time equal to 1 minute at 138°C and 146°C, respectively. The peroxides are therefore quite similar; nonetheless, some perceivable differences in the experimental rheometer curves of the EPDM under consideration were observed.
- 2) Concentration of the curing agent: five different concentrations for the different curing agents investigated were considered, hereafter labeled as -50%, +/- 0%, 50%, 100 % and 150% for the sake of clearness. Labels indicated the molar concentration of the curing agent with respect to the standard concentration (indicated as +/- 0%) utilized by Mixer within their production process.
- 3) Vulcanization temperature. Rheometer data were obtained in an oscillating disc curometer at three different temperatures, respectively equal to 160°C, 180°C and 200°C. A wider range of temperatures was experimentally investigated by the authors, namely from 120°C up to 220°C, but the activity of the curing agents resulted suboptimal out of the range 160°-200°C.

In figures from Figure 3 to Figure 7, detailed comparisons among the performances during vulcanization (rheometer curves) exhibited by the three different curing agents at different concentrations are shown. Such comparisons are

useful to have an insight into the most suited curing agent to be used at different temperatures. It is quite clear that the optimal behavior of all curing agents is obtained at 150% concentrations.

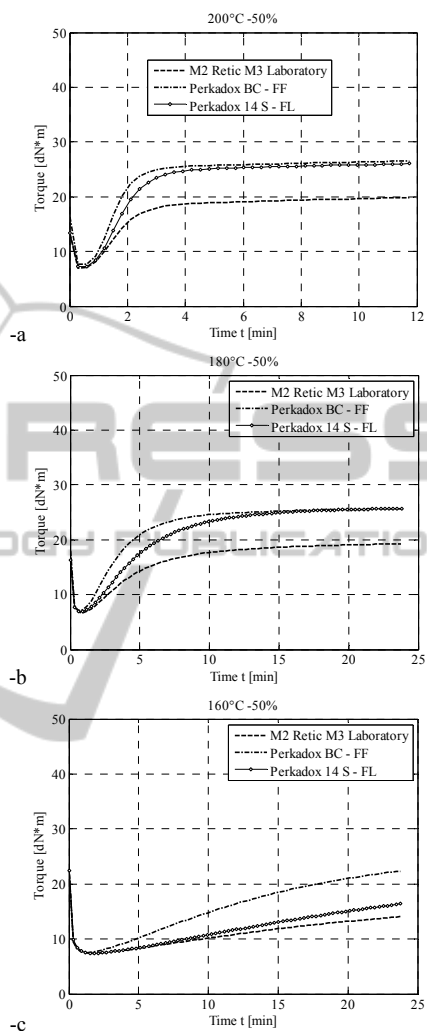


Figure 3: -50% Concentrations. Experimental rheometer curves at different peroxide concentrations. -a: 160 °C. - b: 180 °C. -c: 200 °C.

For such concentrations and for a curing temperature equal to 200°C, it can be observed that the maximum torque provided by all curing agents (M2, BC-FF and 14-S) is roughly the same (around 55 dNm, see Figure 7). Furthermore, the times needed to obtain 90% of the maximum torque (t_{90} values) seem very similar, meaning that also the kinetic constants at 200°C to be expected by the numerical model proposed should be very similar.

Two replicates for each vulcanization condition were considered within the experimental campaign, in order to reduce possible inaccuracies of the

experimentation. In this manner, a total amount of 90 different rheometer curves were experimentally determined.

Table 2: half-life temperatures of the peroxides analysed at 0.1, 1 and 10 hours.

Peroxide typology	$t_{1/2}$ in hours	0.1	1	10
TRIGONOX T		169	146	117
PERKADOX BC-FF		162	138	112
PERKADOX 14 S-FL		169	146	117

TRIGONOX T: ter-butylcumylperoxide
 PERKADOX BC-FF: dicumyl peroxide
 PERKADOX 14S-FF: di(tert-butylperoxyisopropyl) benzene
 Curing agent M2 is a mixture of BC-FF, 14S-FF and Trigonox T

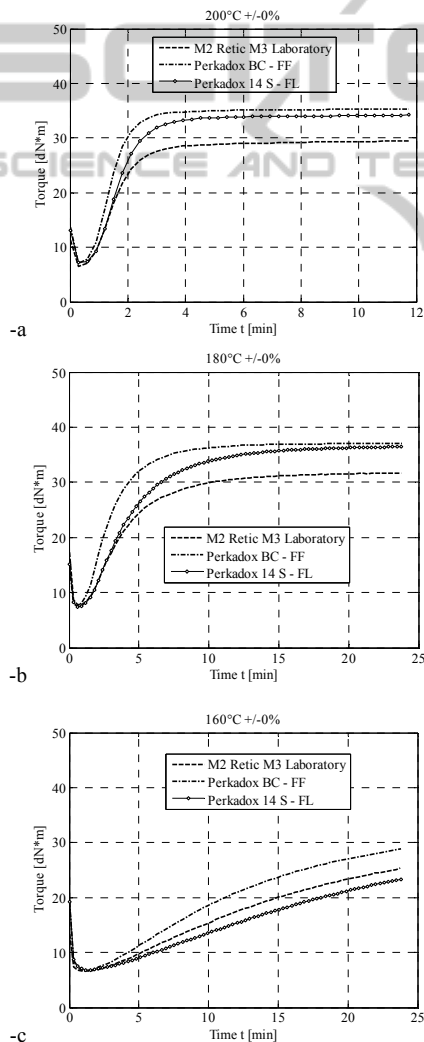


Figure 4: +/-0% Concentrations. Experimental rheometer curves at different peroxide concentrations. -a: 160 °C. -b: 180 °C. -c: 200 °C.

As expected, in all cases, experimental rheometer curves do not exhibit perceivable reversion, due to the low amount of unsaturations present in the EPDM utilized.

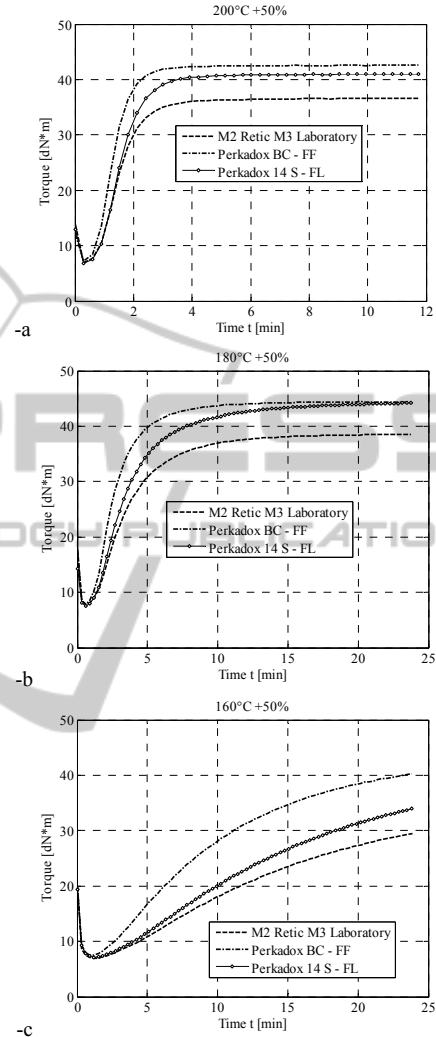


Figure 5: +50% Concentrations. Experimental rheometer curves at different peroxide concentrations. -a: 160 °C. -b: 180 °C. -c: 200 °C.

5 CONCLUSIONS

A combined numerical model and experimental campaign have been conducted with the aim of tuning and validating a complex numerical model with kinetic base, useful to predict the final crosslink density of rubber vulcanized with single peroxides or mixtures of peroxides. In the present Part I, the experimental results are presented and discussed. In addition, the theoretical base of the numerical model

is presented.

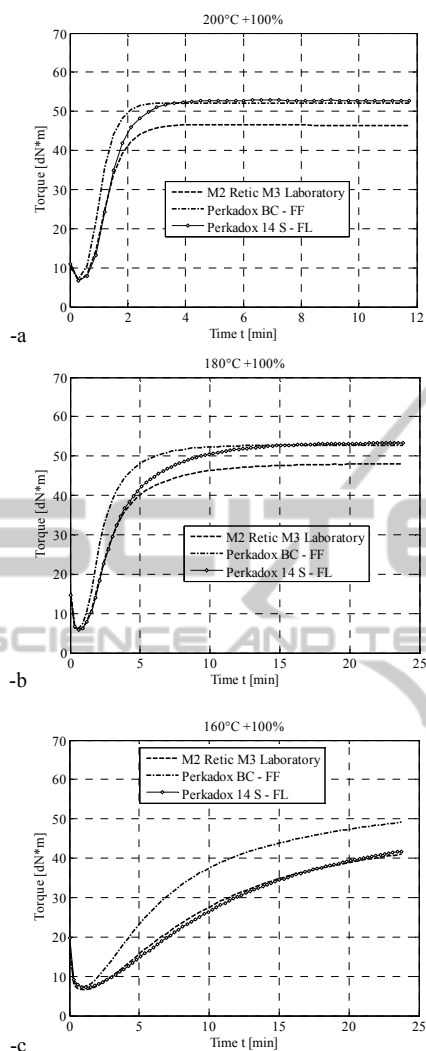


Figure 6: +100% Concentrations. Experimental rheometer curves at different peroxide concentrations. -a: 160 °C. -b: 180 °C. -c: 200 °C.

The experimental part is wide, since a number of different cases occurring in practice has been investigated in detail, varying curing agent typology, vulcanization temperatures and concentration of the peroxides. Both rheometer curves to compare with those provided by the numerical model and stretch-strain curves of the vulcanized samples have been collected, to have a precise insight into the most suitable parameters to use during curing.

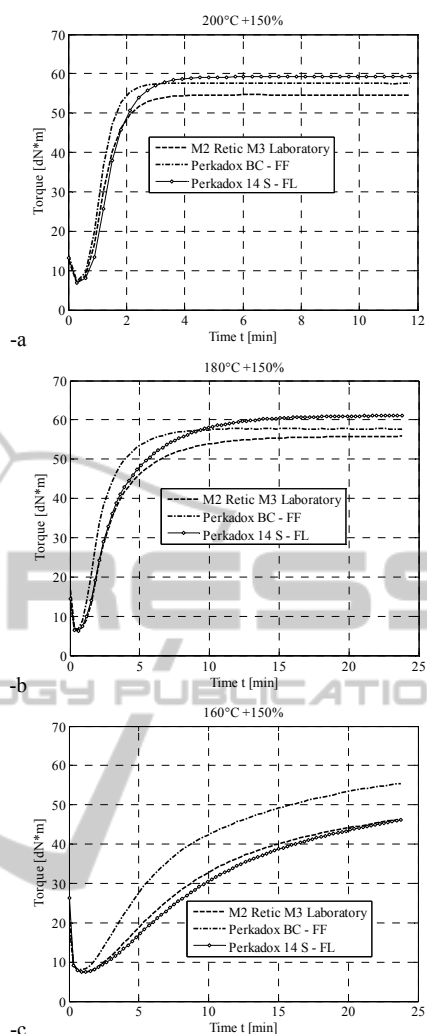


Figure 7: +150% Concentrations. Experimental rheometer curves at different peroxide concentrations. -a: 160 °C. -b: 180 °C. -c: 200 °C.

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