

Experimental/FEM Optimization of Medium Voltage Rubber Insulated Electric Cables Vulcanized with Steam Water

Differential Scanning Calorimetry (DSC) and Rheometer Experimental Results

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Abstract: The standard industrial process to produce medium voltage electric cables based on EPDM consists of crosslinking by peroxides with high temperature steam (pressurized water vapor). Suboptimal material crosslinking is usually due to a decrease of the temperature along the vulcanization pipe. Temperature variations are connected to variations in steam pressure into pipe system. In the present paper a combined numerical and experimental approach to optimize the production process of medium voltage rubber insulated electric cables vulcanized with steam water is presented. The numerical part, discussed in an accompanying paper, is based on the utilization of Finite Elements and an optimization Genetic Algorithm (GA) approach. Here, attention is focused on the experimental investigation. In particular, the final crosslinking degree is experimentally obtained by means of a DSC determination of non-decomposed peroxide from the external layer to the core of the cable insulation. The final task is to minimize the difference between numerically predicted and experimentally determined crosslinking degree using a steam temperature profile along the pipe to explain the variations. A preliminary evaluation of kinetic reaction constants of rubber cured with peroxides is here provided by means of a previously presented kinetic model.

1 INTRODUCTION

The continuous vulcanization process of cables has been developed more than fifty years ago. Nevertheless, the use of advanced mathematic studies to predict polymer compounds performance is not commonly applied, despite the fact it could play an important role in industrial technical development.

In the last few years, high voltage cables have been produced by using ethylene propylene co- and ter-polymers EPM/EPDM, Milani and Milani (2008), due to their good dielectric strength, aging resistance and partial discharges resistance. The capability to set up and to tune the plant conditions according to cable structure and compound properties plays a critical role in cable production and quality.

The industrial process of crosslinking, Roberts and Verne (1984), of power cables is usually obtained by means of horizontal (catenary continuous vulcanization CCV) systems, Figure 1.

In Figure 1 the CCV plant considered in the present paper is described.

Pressure, temperature and production speed should be kept under severe control in order to guarantee a designed crosslinking degree.

In order to prevent undesirable low level of crosslinking of the cable, authors conducted an experimental campaign crosslinking a medium voltage electric cable in four different conditions.

Preliminary rheometer characterizations at different temperatures and concentrations of the curing agents were performed to find out the most suitable crosslinking conditions. Several meters of cured samples were produced in order to measure the crosslinking degree. The level of crosslinking was evaluated through differential scanning calorimetry DSC, i.e. by the content of the unreacted peroxides, on five different radial positions of the cable, from the core to the external layer. Experimental results of DSC analysis are reported in the paper.

The determination of the unreacted quantity of

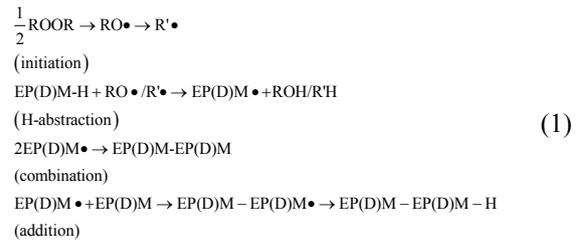
peroxide is not evaluable by the well-known relation between temperature and half time life of peroxide ($t_{1/2}$) because the curing agent used is a mixture of peroxides. To overtake this limitation, authors applied a recently proposed quite robust kinetic model based on multiple rheometer characterization, which has been integrated in the thermal analyses.

2 PEROXIDE CURING PROCESS, KINETIC MODEL FOR PEROXIDE MIXTURES

This section provides a numeric assessment of the results obtained experimentally and a brief description of the numeric model used to fit experimental data. The model is based on the kinetic of the reactions occurring in EPDM cured by peroxide through the following steps:

- Translation of chemical reactions into mathematical differential equations (set of first order ordinary differential equations, ODE system);
- Manipulation of the ODE system to reduce the problem to a single nonlinear ODE;
- Solving of the nonlinear equation through a standard numeric tool;
- Estimation of the kinetic constants entering into the model by means of standard least squares fitting of the experimental rheometer curves.

The basic chemistry of peroxide curing of EPDM has been reviewed by van Duin and co-workers (2002) and could be summarized by the following partial reactions that occur in series and parallel:



Where the exact meaning of the symbols can be found in e.g. Milani et al., 2014, where the reader is referred to.

In the numeric model we adopted the kinetic scheme for the peroxide crosslink reactions summarized previously because it reproduces the most important steps occurring during peroxide curing and it is simple to handle.

It can be proved that polymer concentration (P) vs time (t) can be estimated using xyz method after suitable mathematical manipulation:

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

Further details on equation derivation (2) could be found in Milani et al., (2014).

The nonlinear differential equation (2) may be solved numerically with a standard Runge-Kutta algorithm to find concentration P(t).

The knowledge of P(t) allows the determination of quantity R(t) and P^* (residual polymer after devulcanization):

$$\frac{dP^*}{dt} = K_2 R(t) P(t) - K_3 (P^*)^2 - K_4 P^* \tag{3}$$

Equation (3) is again solved using a Runge-Kutta numeric approach.

The combined application of equation (2) and (3) with least squares minimization allows to estimate the kinetic constants entering into reaction scheme.

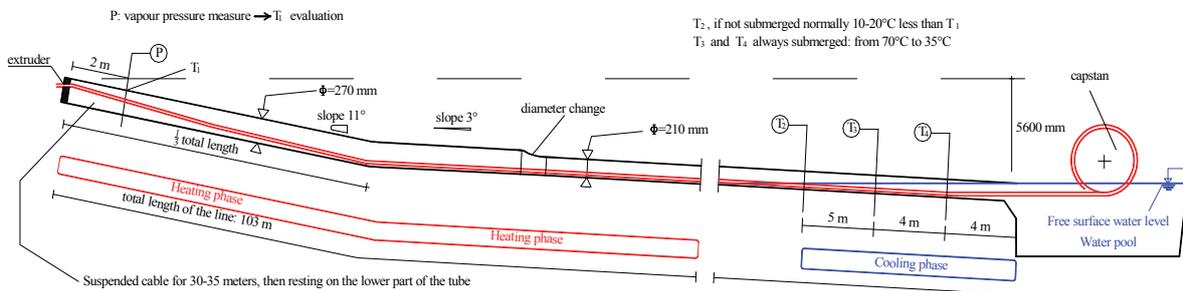


Figure 1: Real industrial production line considered.

3 DETERMINATION OF TEMPERATURE PROFILES IN THE VULCANIZATION TUBE

A short overview of the mathematical basis of the numeric approach employed for the determination of cable temperature profiles under curing is reported. The production line is supposed to be constituted by a vulcanization pipe (with water steam at high temperatures) followed by a water cooling phase (at lower temperature) as reported in Figure 1.

Steam temperature adopted by manufacturers usually depends on the peroxide employed for the EPDM crosslinking. Linear speed of the cable determines the exposition time at fixed pipe length. At fixed exposition time and temperature crosslinking degree of each layer can be numerically estimated applying standard heat transmission physical laws.

The analyses hereafter conducted refer to a real CV line. Its basic scheme is sketched in Figure 1. The head of the extruder is connected to the vulcanization pipe. After extrusion, the cable passes into a pipe containing water steam under pressure. Finally the tube is connected with a submerged equipment with cooling water. Linear speed of the cable is controlled by the capstan at the end on the line.

The CV pipe considered in this work is 103 meters long and exhibits an initial inclination of 11° for approximately one third of its length. After this zone, the pipe shows a slight residual slope of 3°. Diameter of the pipe is initially equal to 270 mm and reduced to 210 mm starting from one half of the length.

Two meters after the head of the extruder is located an analogic manometer used to measure the steam pressure acting during the vulcanization process. In the last 15 meters of the pipe, the cable is cooled by a water-pool at 35-40°C. Also the capstan is partially submerged. Considering as reference the free surface of the water in the pool the depth of the extruder head is equal to 5.6 meters. In the initial part the cable is suspended inside the pipe, but after 30-35 meters it rests on the lower part of the vulcanization device because of the combined action of gravity and slope change, posing also doubts on the effective symmetric crosslinking of the item under such physical conditions. Since the cable enters into the last portion of the line in correspondence of the lower part of the pipe, it immediately comes in contact with the cooling water-pool. Water level has therefore to be checked

with particular care in order not to vary significantly the length of heating zone.

Three thermometers are placed in the last 15 meters at a mutual distance of 5 meters and labeled in Figure 1 as T₂, T₃ and T₄ respectively. Theoretically, T₂ should measure the same temperature deduced from the pressure measure at the beginning of the line (i.e. T₁), but in practice this never occurs, because T₂ is usually 10-20 °C lower than T₁ near the surface of the water. This issue depends intrinsically on the design of the plant and partially on initial temperature imposed. In some cases, it occurs that T₂ section is submerged vanishing the temperature check at the end of the heating phase. No thermometer probes are installed in intermediate position from the beginning to the end of the heating phase. T₃ and T₄ thermometers have the role to monitor the temperature of the water-pool.

The experimental campaign has been conducted under the following four different crosslinking conditions:

- Test #1: temperature T₁=202°C, total curing time t_c=5.6 minutes;
- Test #2: temperature T₁=212°C, total curing time t_c=5.6 minutes;
- Test #3: temperature T₁=202°C, total curing time t_c=7.7 minutes;
- Test #4: temperature T₁=212°C, total curing time t_c=7.7 minutes.

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

Polymer VISTALON 1703P Ethylene in wt. % 76.2 VNB - vinylnorbornene in wt. % 0.9 Mooney ML (1 + 4) 100°C 35.3 Manufacturer (Exxon)	100
Silane treated calcinated kaolin	55.5
Antioxidants	14.8
LDPE Riblene MR 10 MFI= 18.7 (ASTM D1238)	11.1
PE WAX	1.8
Peroxide mixture M3	1.1

4 EXPERIMENTAL RHEOMETER CURVES AND KINETIC MODEL

The polymer used is a commercial EPDM, with properties furnished by the provider and summarized

in Table 1. The mixture (M3) of peroxides used as curing agent is a composition of three different peroxides: Trigonox T, Perkadox BC-FF and Perkadox 14S. For the composition and use of the mixture of peroxides M3 the reader is referred to Milani and co-workers (2014).

The amount of peroxide, referred to 100 grams of polymer, is variable. The chosen standard concentration, labeled as “+/-0%”, is equal to 5.037 millimoles per 100 g of polymer. It was considered as “reference” because this was the concentration used in the standard industrial production of the compound.

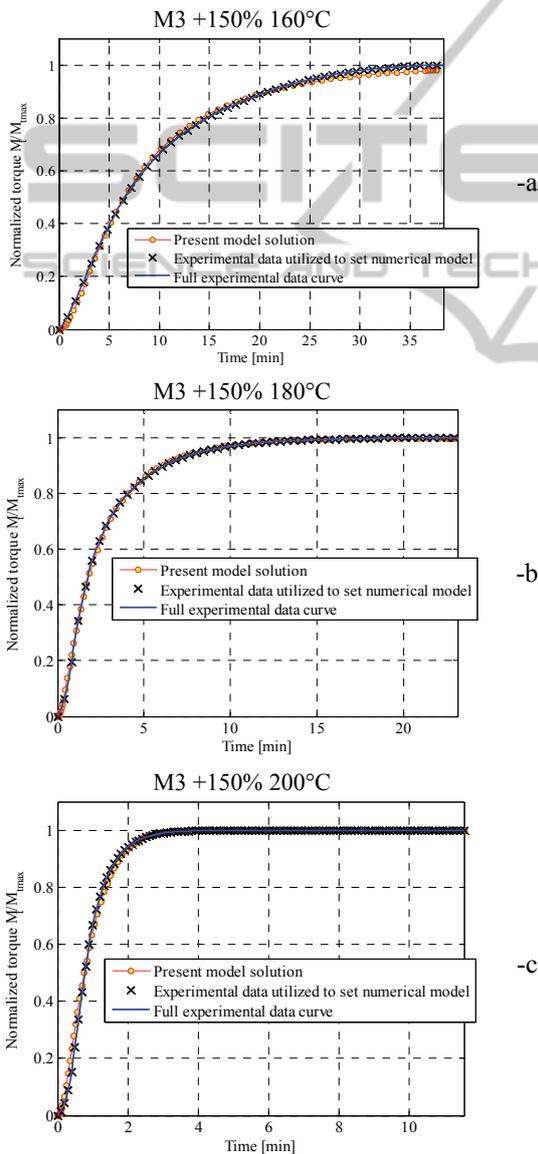


Figure 2: M3 curing agent. Comparison between normalized experimental rheometer curve and numeric model predictions. -a: 160°C. -b: 180°C. -c: 200°C.

Four additional concentrations were tested, called -50%, +50%, +100% and +150%. Labels indicate the molar concentration of the curing agent with respect to the standard concentration. For instance, a +50% concentration indicates that 1.5 moles with respect to the standard one were used. Three different vulcanization temperatures were inspected, typical for the curing of medium/high voltage electric cables, namely 160°C, 180°C and 200°C.

DSC analysis are used to quantify the unreacted crosslinking agents and Rheometer curves to obtain an indirect information on the state of cure or cure efficiency of the crosslinking agent, as extensively demonstrated by Sun and Isayev (2009).

The average $M(t)$ curves obtained may indeed be used to calculate the evolution of the crosslinking degree $\alpha_{exp}(t)$ using Sun and Isayev (2009) relation:

$$\alpha_{exp}(t) = \frac{M(t) - M_{minT}}{M_{maxT_0} - M_{minT_0}} \quad (4)$$

where:

- M_{minT} is the minimum value of torque S' during a cure experiment 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, obtained for a cure experiment at a temperature T_0 low enough to allow neglecting reversion. In this way, rheometer curves to fit always range between 0 and 1, with a maximum torque sensibly lower than 1 for high vulcanization temperatures.

Experimental results rely into a thermal characterization to determine the state of cure of each sample conducted by means of a standard ODR (oscillating disc rheometer), and mechanical characterizations, in particular tear and tensile strength tests.

5 THE NEW SIMPLIFIED MECHANISTIC MODEL PROPOSED

Experimental data exhibit a maximum torque close to 55 dNm that lowers at low concentrations (especially at -50%), whereas a concentration increase results in a beneficial effect.

The absence of reversion (decrease of torque after reaching the maximum) and the homogeneity

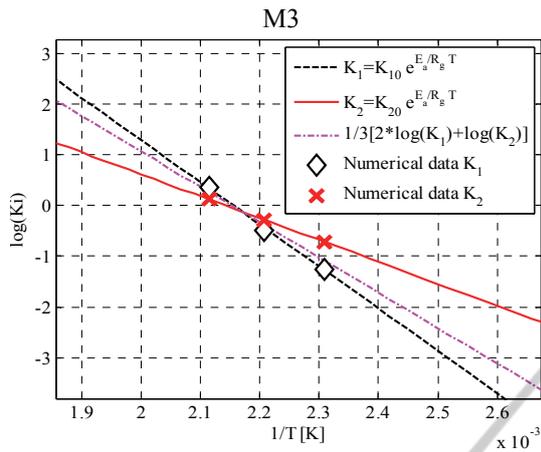


Figure 3: Linear regression interpolation of the kinetic constants K_1 and K_2 provided by the single differential equation model and the resultant linear regression obtained as weighted sum of K_1 and K_2

of minimum and maximum values of the torque at the three temperatures allow the normalization of the analysis simply dividing each value of the torque by the maximum torque, measure during the test. For the cases where reversion is present, the reader is referred to Milani (2013).

Experimental evidences show that maximum crosslinking density could be obtained with at double amount of peroxide in comparison to the standard one (+100% concentrations).

Kinetic constants of the mixture M3 are evaluated numerically with the kinetic model previously discussed. Numerically predicted rheometer curves resulting from the fitting process are depicted and compared with experimental ones in Figure 2 (-a: 160°C, -b: 180°C and -c: 200°C). The numeric fitting overlaps almost perfectly the experimental curves. Numeric curves were obtained using a nonlinear least square procedure. As extensively demonstrated in Milani and co-workers (2014), the fitting of experimental response is rather satisfactory by superposition of calculated curves with experimental data.

Considering the numeric values obtained for the two constants K_1 and K_2 at three distinct temperatures (the other constants are close to zero, indicating that no reversion is experienced), the lines passing from such values in the Arrhenius plane was plotted. In this 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. The calculated lines are plotted in Figure 3.

6 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The differential scanning calorimetry (DSC) has become the most used thermal analyzing technique. We have used this technique in order to quantify the vulcanization degree and hence the unreacted peroxide after the crosslinking process recovering samples across the sample section.

Five samples were cut at 1 mm of distance along the cross section (0.9 mm external surface, 1.8, 2.7, 3.6, 4.7 mm internal surface). The analyses were carried out on 10-15 mg samples in the temperature range from 0 to 230°C at the scanning rate of 20°C/min under inert atmosphere (N_2) in punched aluminum pans.

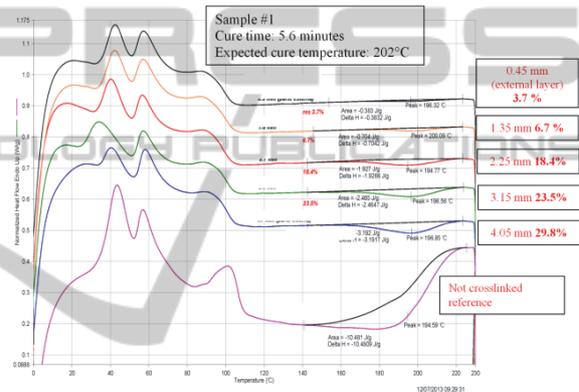


Figure 4: sample #1, DSCs on different positions from the external layer compared with DSC of the not crosslinked sample.

The residual unreacted peroxide has been calculated in order to evaluate the crosslinking degree according to the equation:

$$Res = \Delta H_r / \Delta H_0 \quad (5)$$

where ΔH_r is referred to the peroxide in the sample and ΔH_0 to the peroxide in the not crosslinked compound used as reference (100% of crosslinking residue).

In Figure 4 the results of the DSC performed for Sample #1 with the corresponding evaluation of the unreacted peroxide concentration are represented. In each figure six curves are reported. Five refer to the different positions across the cable section whereas the last one is the reference curve for the sample before crosslinking. The representation refers to the measured normalized heat flow plotted against temperature.

7 CONCLUSIONS

The experimental study on CV line crosslinked EPDM allows drawing the following considerations:

1. Optimization of final mechanical properties could be obtained with a detailed mechanical characterization at different concentrations of the curing agent;
2. A mixture of peroxides shows the interesting feature to reduce the gap between tensile and tear strength performances.

DSCs and classical rheometric curves are key tools to double check the unreacted peroxide concentration and the efficiency of the used curing agent. In an accompanying paper (Milani and Milani 2015) a comprehensive numerical investigation basing on the kinetic mathematical approach here presented and coupled with Finite Element computations will be presented and applied to the experimental case study here discussed, assuming in the numerical model a drop of the steam temperature along the length of the pipe to minimize the error between experimentally obtained data and numerically predicted output.

Residual values of peroxide are collected in Table 2 and Table 3, where the results of the DSC experimental campaign are synoptically represented.

Table 2: experimentally determined quantity of unreacted peroxide, test #2 and #4, temperature equal to 202°C.

Curing time	Distance from the surface				
	0.9 mm	1.8 mm	2.7 mm	3.6 mm	4.7 mm
5.6 min (#1)	3.7	6.7	18.4	23.5	29.8
7.0 min (#3)	0	0	0	2.1	3.7

Table 3: experimentally determined quantity of unreacted peroxide, test #2 and #4, temperature equal to 212°C.

Curing time	Distance from the surface				
	0.9 mm	1.8 mm	2.7 mm	3.6 mm	4.7 mm
5.6 min (#2)	0	0	0.9	3.6	11.4
7.7 min (#4)	0	0	0	0	0

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