MONITORING AND LIFETIME PREDICTION OF PVC CABLES: METHODOLOGY BY MULTISCALE AND MULTIDISCIPLINARY APPROACH

J. TIREAU*, R. MAURIN*, L. YUE*, G. MARQUE*, M. BEN HASSINE*, I. MKACHER*, F. DJOUANI[†], X. COLIN[†],

* EDF Lab les Renardières
Avenue des Renardières
77818 Moret-sur-Loing, France
e-mail: jonathan.tireau@edf.fr, web page: http://www.edf.fr

[†] Arts et Métiers ParisTech, PIMM
151 Boulevard de l'Hôpital
75013 Paris, France
e-mail : pimm-contact@ensam.eu, web page : http://pimm.paris.ensam.fr

Key words: Poly(vinyl chloride), Cables, Lifetime prediction, Monitoring, Multiscale, Plasticizers loss.

Abstract. Monitoring of the PVC cables as well as the prediction of their residual lifetime are important issues for the maintenance of the French nuclear power plants (NPPs). To date, the unanimously end of life criterion admitted for these cables is a 50% value of elongation at break and, to our knowledge, only destructive tests give access to this parameter. This study reports a relationship between elongation at break of the PVC and their plasticizer content. This correlation opens the door to a monitoring directly on site or by micro sampling since all classic laboratory techniques able to measure this content become ways to judge the condition of the PVC sheaths and insulators. In addition, this study demonstrates the feasibility of prediction of industrial PVC behavior changes. This model, adapted to the case of thin films, involved tools of chemical kinetics and the implementation of a constitutive model.

1   INTRODUCTION

In NPPs, electric cables represent about 1500 km per unit. To date, most of the French power plants currently in operation mainly have qualified electric cables on PVC. All these PVC cables are considered as "sensitive" because of their presence in large number in nuclear units and the high cost that the replacement would represent (cost including heavy maintenance and a long shutdown period).

In this context, EDF R&D manages research projects on PVC cables with the aim to improve the lifetime prediction accuracy of cables, to manage obsolescence and to develop non-

destructive exams to follow their aging on site.

To date, the end-life criterion unanimously adopted for cables is a mechanical one setting on a nominal value of the elongation at break (ε_r = 50%). To our mind, only tensile tests enable the measurement of the elongation at break of a material in a direct way. This technique has the double disadvantage of being destructive and to require sampling on nuclear material which is always a costly and heavy procedure. Thus, it is unbelievable to use this technique for monitoring PVC cables installed all over the French nuclear units.

Previous studies [1-2] conducted on PVC degradation give the demonstration that embrittlement of a plasticized PVC sheath is closely related to its loss of plasticizers. From this observation, EDF R&D decided:

- first, to simulate the physical loss of PVC plasticizers at different temperatures and determine the kinetics parameter of plasticizers evaporation;

- and then to access the elongation at break either by a simple multiscale relation between ε_r and plasticizer content or by the reproduction of the PVC tensile test curve using laws of behaviour.

2 MATERIAL AND AGEING CONDITIONS

2.1 Material and initial characterization

Pure PVC and phthalate plasticizers (DIOP, DEP, DINP, DIDP and DDP) were supplied by Sigma Aldrich. Pellets of industrial formulation were supplied by a cable producer. According to the information provided by this last supplier, this industrial PVC would be plasticized with phthalate. However, the exact formulation and initial plasticizer content were not communicated. Thus, the first stage of this work, carried out within the framework of Ines Mkacher's thesis [3], was to proceed to a shaping of the pellets and to an initial characterization of the industrial PVC films obtained.

The pellets were heat-pressed at 180 ° C for 30 seconds using a platen press. Thin films with a thickness of 130 ± 50 μm were formed. In the same way, thin model films of DIOP, DEP, DINP, DIDP and DDP plasticized PVC were pressed.

Characterization by infrared spectroscopy (IR), thermogravimetric analysis and gel permeation chromatography (GPC) highlight the presence, in the industrial PVC, of $CaCO_3$ fillers (35% by mass) and di-isodecyl phthalate phthalate plasticizers (DIDP, 27% by mass).

2.2 Ageing conditions and aged samples characterization

In order to simulate thermal aging of the PVC, the films were subjected to accelerated aging in a ventilated oven at different temperatures between 95°C and 160°C. Samples were regularly removed from the ovens to be analyzed by IR and tensile tests.

Mechanical characterizations, meaning stress and strain at break determination, were

performed on H2 shouldered test bars, at 23°C and 50% RH conditions, with a 100 N force cell and an elongation speed of 10 mm/min.

Residual content of plasticizers were determined by IR spectroscopy using the Beer Lambert law:

$$C = \frac{AO}{\varepsilon\,e}$$

C is the concentration of chemical species (here an ester of the different phthalates studied), AO is the absorbance also called operational amplitude, ε is the molar absorptivity and e the thickness of the sample crossed by the IR beam. The calibration lines were used to determine the molar absorptivity of the different phthalate. For example, the Figure 1 was used to determine the molar absorptivity of the DIDP plasticizers at 1723 cm^{-1} (ε_{DIDP} = 744 mol.l^{-1}.cm^{-1}). The DIDP having two groups of esters per molecule, the molar absorptivity of the ester function is ε_{ester} = 372 mol.l^{-1}.cm^{-1}. In the case of model films, infrared analyses were performed in transmission mode and so the e parameter corresponds to the thickness of the film. While in the case of industrial PVC films, the IR analysis were carried out in ATR mode due to the film opacity. The e parameter (e = 2.09 10^{-4} cm) was deduced from the ε_{DIDP} and the AO$_{ester}$ previously obtained on a PVC film with a well-known concentration of DIDP.

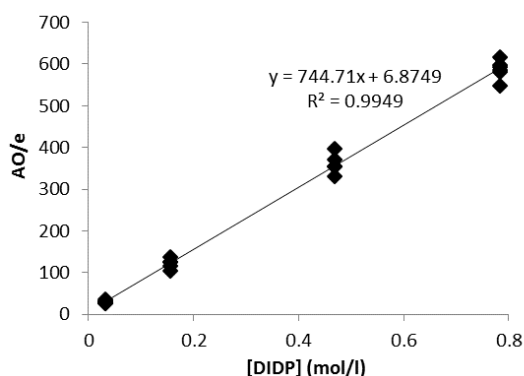y = 744.71x + 6.8749
R² = 0.9949

Figure 1: Calibration line obtained with data of ester functions absorbance of DIDP for PVC plasticized with content between 1% and 25% mass.

3   DETERMINATION OF EVAPORATION KINETICS OF PLASTICIZER

To illustrate the results obtained by IR on samples thermally aged, the example of PVC film plasticized with 30% mass of DIDP and exposed in ventilated oven for nearly 50 hours at 140°C can be used. Knowing the molar absorptivity of DIDP plasticizer, the Beer Lambert law enables to calculate the residual concentration of DIDP by simple measurement of absorbance at 1723 cm^{-1}. The concentrations obtained for each sample are summarized in Figure 2. Observations suggest a change occurring in two steps. A first phase, between 0 h and 25 h, during which the loss in plasticizers seems to be nearly linear with exposure time and, then, a second phase during which the losses appear to be zero due to a constant DIDP concentration. The literature showing no reactivity of esters of the DIDP during thermal ageing, observed losses can be correlated in totality to physical losses by evaporation.
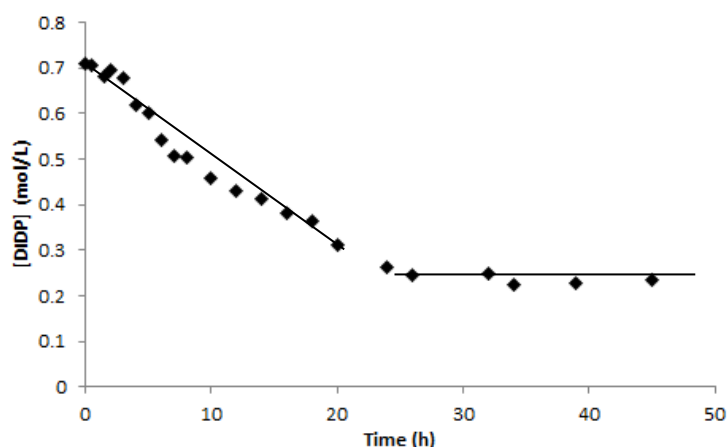
Figure 2: Evolution of DIDP concentration during exposure at 140 ° C of a thin film of a 30% mass plasticized PVC. Data obtained by IR measurements.

A description of the loss of plasticizers by evaporation was proposed by Audouin et al. [4] using the laws of heat transfer and Raoult equation. These authors assume the expression of evaporation rate to be as follow:

$$\frac{dC}{dt} = -\frac{r_{ev}C}{eC_s} = -\beta C \tag{1}$$

Where C is the concentration of adjuvant in the surface layer of the polymer, C_s the concentration at saturation of the adjuvant, e the thickness of the sample, r_{ev} the evaporation rate and β the evaporation kinetics coefficient.

The integration of equation 1 leads to the following relationship:

$$ln\frac{C}{C_0} = -\beta t \tag{2}$$

C_0 corresponds to the initial concentration of plasticizers.

With the aim to determine the kinetics of plasticizers evaporation, the infrared measurements were also performed on model PVC films exposed to different temperatures, such as 95°C, 105°C and 120°C. In the case of DIDP, the kinetics of evaporation obtained for each temperature is presented on the figure 3.
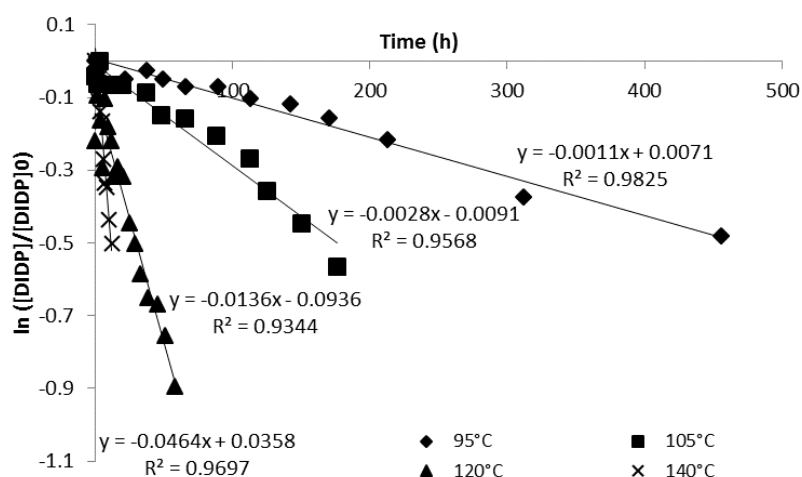
Figure 3: Logarithmic evolution of DIDP concentration in the case of thin film plasticized, initially with 30% mass of DIDP, versus exposure time for temperature between 95°C and 140°C. Data obtained by IR.

Figure 4 presents a logarithmic evolution of the evaporation coefficient (so the slope of the lines illustrated in figure 3) versus the inverse of the temperature. As evaporation is a phenomenon thermally activate, the evaporation coefficient can be expressed with the following equation:

$$\beta_{IR} = \beta_{IR0} exp(-\frac{Ea}{RT})$$ (3)

Where R is the perfect gas constant, so 8.314 J.mol^{-1}.K^{-1}
E$_a$ corresponds to an activation energy, here E$_a$ = 13.403 x R, so 111 kJ.mol^{-1}
And β_{IR0} corresponds to a pre-exponential factor equal to 1.88 10^9 s^{-1}
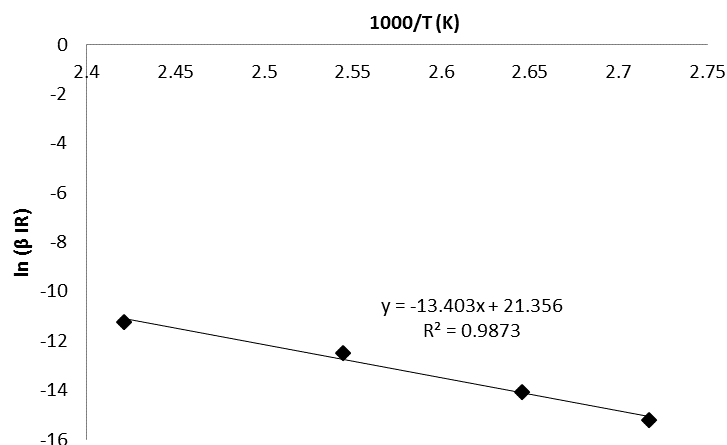

Figure 18: Logarithmic evolution of the DIDP evaporation coefficient versus the inverse of temperature in the case of thin PVC films, initially plasticized with 30% mass, for exposition under air at temperature between 95°C and 140°C. Data obtained by IR.

The same determination was used for DIOP, DEP, DINP and DDP. Table 1 summarizes all the kinetics parameters values obtained. A part of these data were previously published by

Djouani et al. [1].

Table 1: Kinetics parameters obtained for the evaporation of the five plasticizers studied

	DIOP	DEHP	DINP	DIDP	DDP
E_a (kJ.mol^{-1})	69	76	93	111	154
β_{IR0} (s^{-1})	8.61 10^5	3.65 10^5	1.28 10^7	1.88 10^9	1.11 10^{14}

3   MODELLING OF PLASTICIZER EVAPORATION

Virtual Polymer is a numerical tool internally developed by EDF which allows to simulate the aging of polymers using the resolution of differential equation (chemical kinetics) and transport (diffusion, evaporation ...).

The equations used for modeling the plasticizers evaporation are the equations 2 and 3:

$$C = C_0 \, exp(-\beta_{IR} t) \tag{2}$$

$$\beta_{IR} = \beta_{IR0} exp(-\frac{Ea}{RT}) \tag{3}$$

Figure 4 shows a comparison, in the case of industrial PVC films, of the evaporation results of plasticizers determined experimentally by IR spectroscopy and by modelling under Virtual Polymer.
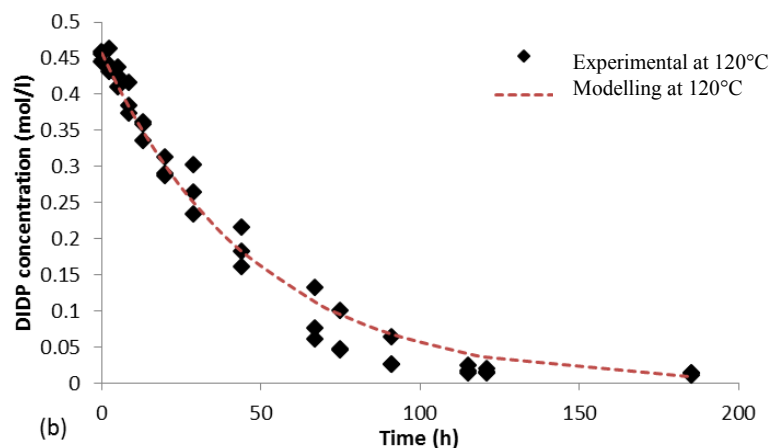

Figure 4: Evolution of the plasticizers concentration in a thin film of industrial PVC exposed to 120°C. Results obtained by modelling (Virtual Polymer) and IR analysis

4   MONITORING AND PREDICTION OF PVC EMBRITTLEMENT

4.1   Monitoring of PVC embrittlement

Linde and Gedde [5] showed, with experimental tests in the case of DIDP and DEHP plasticized PVC samples, that an increase of plasticizers concentration leads to an increase of the elongation at break of the material and to a reduction of its Young modulus. Since the current criterion of end of life of the nuclear cables is a 50% elongation at break value, our attention focus on the possible relation existing between plasticizers content and elongation at break of PVC.

As no relation was found in the literature, we decided to identify an experimental law from data obtained by IR spectroscopy and tensile tests on aged samples of industrial PVC. Figure 5 illustrates the found correlation and gives the empirical law determined.
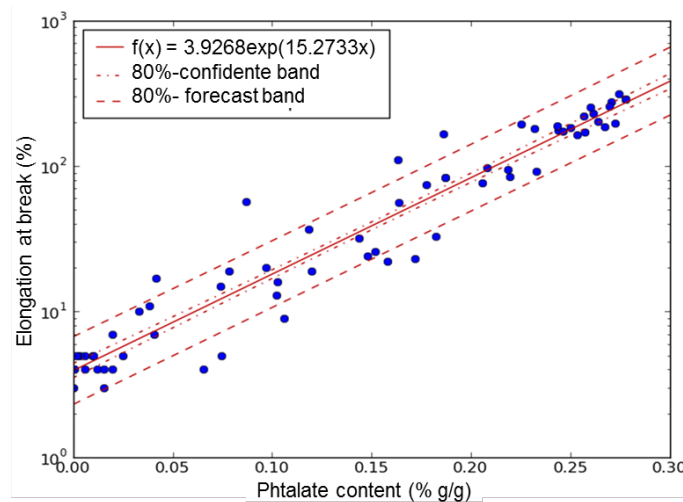

Figure 5: Evolution of the elongation at break (logarithmic scale) versus the concentration of DIDP plasticizers for industrial PVC thin films exposed to thermal ageing between 95°C and 160°C.

On the one hand, this relation opens the door to the estimation of the local mechanical properties of a PVC cable by non-destructive techniques (for example using portable infrared spectroscopy) or by a simple micro-sampling. With only 10 to 20 mg of material, it is possible to determine the plasticizers content (by classical IR spectroscopy, thermogravimetric analysis, gas chromatography, solvent extraction…) and finally to estimate elongation at break of the PVC without performing destructive tensile tests.

On the other hand, this relation indicates that $\varepsilon_r = 50\%$ is reached for a residual content of plasticizers of $17 \pm 3\%$.

4.2 Prediction of PVC embrittlement

Two approaches have been studied to simulate the evolution of mechanical properties of PVC films caused by plasticizers evaporation. One uses the empirical relation of section 3.1 and the other uses the reconstruction of a constitutive law using a phenomenological model

4.2.1 Empirical approach

This empirical relation, described in the §3.1, makes possible the transcription of the chemical data of plasticizers concentration in mechanics data of elongation at break. Thus, all the modelling of plasticizer evaporation can be used to model elongation at break changes. Figure 6 gives examples of comparison of elongation at break data obtained experimentally and by Virtual Polymer.
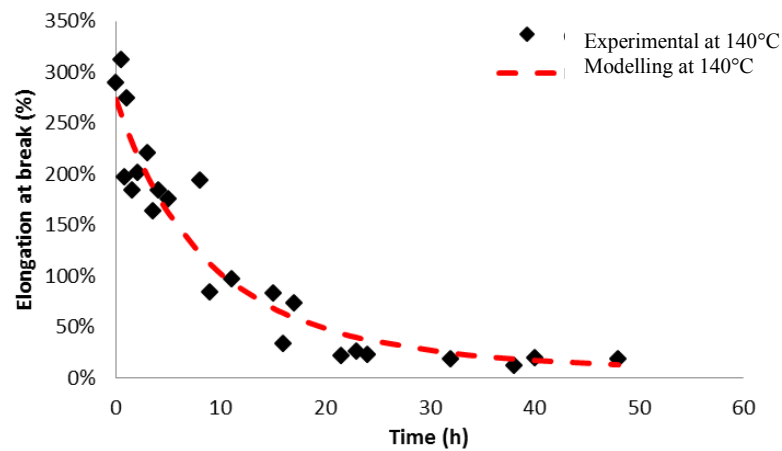

Figure 6: Evolution of the elongation at break of industrial PVC during the thermal ageing in air at 140 ° C. Comparison of numerical simulations to experimental data obtained by uniaxial traction.

The application of this elongation at break modelling at temperatures of 50°C and 70°C, temperatures which can punctually be meet on NPPs, offers the possibility to estimate, for thin film, evolution of the elongation at break in these conditions and to determine the time required to obtain a residual elongation of 50%. As shown in Figure 7, this time t_c is estimated after 3 and 40 years for thermal exposition at 70°C and 50°C respectively in the case of thin film of industrial.
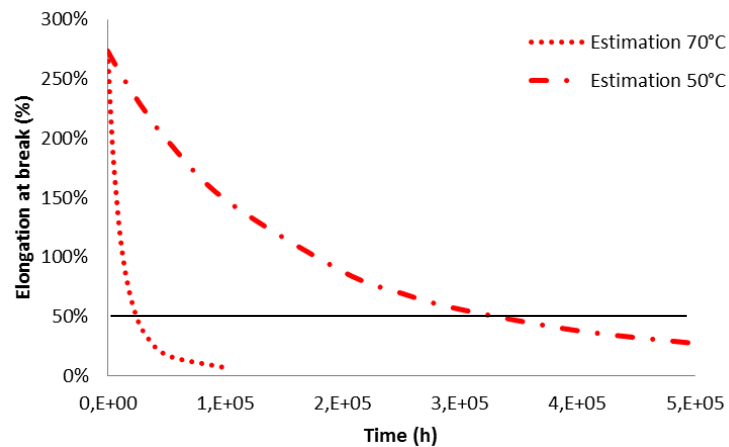
Figure 7: Estimation of the elongation at break of industrial PVC during thermal ageing under air at 50°C and 70 ° C. Data obtained by Virtual Polymer modelling.

4.2.2   Phenomenological approach

Mulliken [2] proposed a predictive model (Boyce-Mulliken model) of the stress-strain behavior of plasticized PVC. As illustrated in Figure 8, this model is composed of: (i) an elastic part (B) corresponding to the entropic hardening element and (ii) an elastic viscoplastic part (A) related to the rotation of macro segments of the main chains of polymer (α) and to the intermolecular resistance (β).
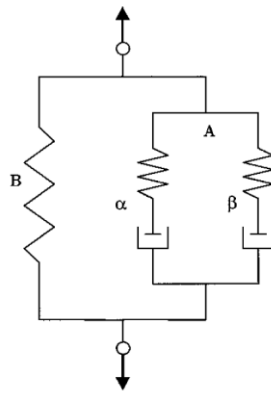

Figure 8: Proposed constitutive model for rate-dependent thermoplastic behaviour [2].

The implementation of the model of Boyce-Mulliken was done using the Mfront tool. Nine parameters of this law have already been identified by Mulliken [2] for DOP plasticized PVC. However, the formulation of our industrial PVC films and the tensile tests mode are different from that of the study of Mulliken [2], so a re-identification of some parameters was necessary.
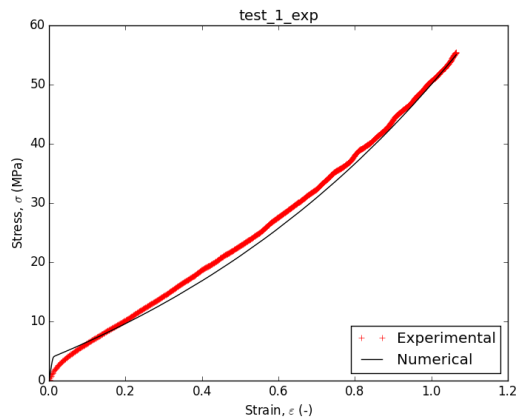
Figure 9: Result of the implementation of the Boyce-Mulliken model for an unaged film of industrial PVC.

As shown in Figure 9, the implementation of this model after re-identification of the parameters properly simulates the stress-strain curves of our industrial material in initial condition. However, for aged samples with a residual content of plasticizers below 17% mass, a discontinuity on one parameter appears. A parameter adjustment appears necessary to compensate this change in mechanical behavior. Figure 10 shows that the re-adjustment of parameter allows to frame all of the curves of traction obtained for the PVC containing 17% mass of plasticizers.
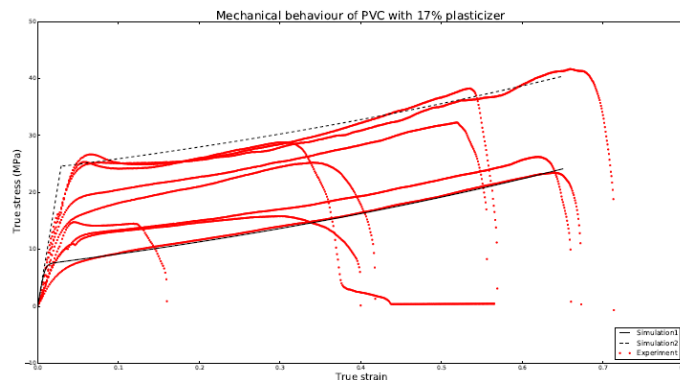

Figure 10: Comparison of the tensile curves obtained experimentally and using the model of Boyce-Mulliken in the case of industrial PVC film containing 17% mass of plasticizers.

The coupling of the kinetic model, used to calculate the plasticizers loss depending on time and temperature, and Boyce-Mulliken model, used to rebuild the tensile curve of a plasticized PVC, enables to simulate the evolution of the mechanical behavior of plasticized PVC films exposed to thermal aging. Figure 11 shows the result on our industrial PVC exposed to 70°C and gives the confirmation of an end of life criterion met after 3 years of exposure.
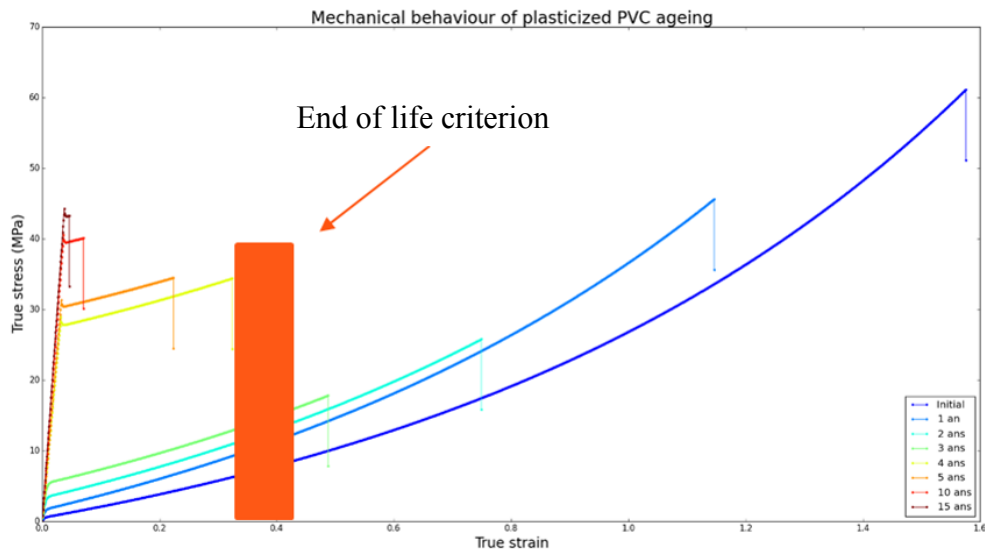
1168

Figure 11: Results of simulation obtained with the coupling of kinetics and Boyce-Mulliken models for industrial PVC films exposed to 70°C

5 CONCLUSIONS

This study reports a relationship between elongation at break of the PVC and their plasticizer content. This correlation opens the door to a monitoring directly on site or by micro sampling since all classic laboratory techniques able to measure this content become ways to judge the condition of the PVC sheaths and insulators. In addition, this study demonstrates the feasibility of prediction of industrial PVC behavior changes. This model, adapted to the case of thin films, involved tools of chemical kinetics and the implementation of a constitutive model.

The next part of this study will be to extend this model to the case of thick PVC in order to simulate the embrittlement of PVC sheaths (thickness of 3-4 mm). Chemical kinetics should take into account the phenomenon of diffusion of plasticizers in the thickness of the PVC sheaths and mechanical modelling should implement simulation in two dimensions.

REFERENCES

[1] Djouani, F. Mkacher, I. Colin, X. Brument Y. and Cristiano-Tassi A. Evaporation kinetics of DIDP plasticizer from PVC, *AIP Conference Proceeding*, (2014) 1599, 1:218-221.

[2] Mulliken, A. Soong, S. Boyce M. and Cohen, R. High-rate thermomechanical behaviour of poly (vinyl chloride) and plasticized poly (vinyl chloride), *J. Phys. IV Proceeding*, (2006) 134: 217-223.

[3] Mkacher, I. Vieillissement thermique des gaines PE et PVC de cables électriques. *Thesis of Arts et Métiers ParisTech* (2012).

[4] Audouin, L. Dalle, B. Metzger, G. Verdu, J. Thermal ageing of plasticized PVC. I. Weight loss kinetics in the PVC – didecylphtalate system. *Journal of Applied Polymer Science* (1992) 45(12):2091-2096.

[5] Linde, E. and Gedde, U.W. Plasticizer migration from PVC cable insulation – The challenge of extrapolation methods, *Polymer Degradation and Stability*, (2014) 101:24-31.