COMPARISON OF DIFFERENT METHODOLOGIES TO ASSESS THE LIFETIME OF CABLE

Jean-Christophe **GARD**, Karine **BIC**, Bernard **POISSON**, Silec Cable, (France)
jean-christophe.gard@sileccable.com, karine.bic@sileccable.com, bernard.poisson@sileccable.com

Francisco **ESPINOSA**, General Cable, (Spain), fjespinosa@generalcable.es

ABSTRACT

In the context of sustainable development, some customers require to provide the service lifetime of cables. The lifetime models specified in cable standards are very often based on an Arrhenius's diagram with failure criteria (elongation at break). Due to the extrapolation process in this method, the risk is in the error propagation which can lead to significant change in the final result. This article presents other kinetic models based on mechanical and chemical failure properties and show the influence of the sample shape on the prediction of the lifetime of a Low Smoke Zero Halogen sheath..

KEYWORDS

Ageing, Kinetic model, cable LSZH, lifetime

INTRODUCTION

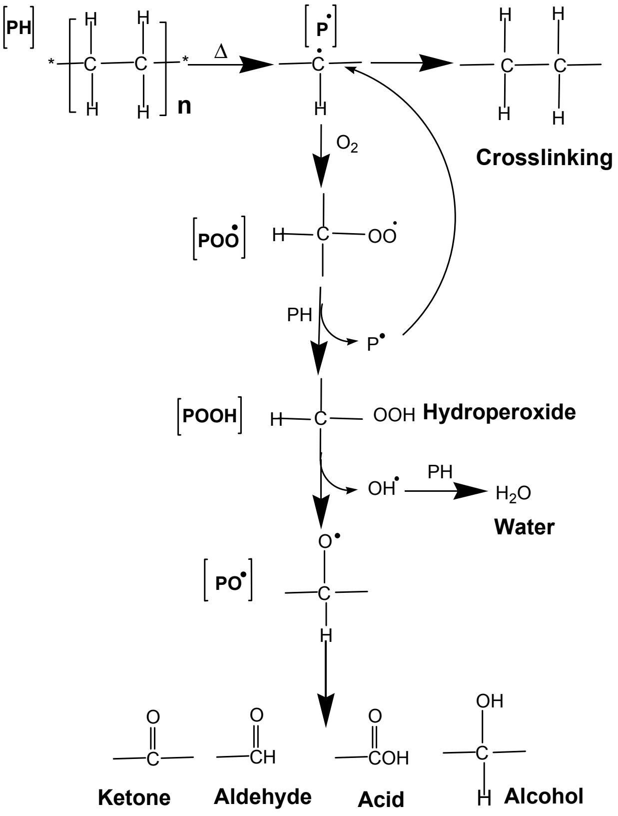
Sustainable development becomes a major issue for the cable manufacturer. In this framework, several customers such as railway rolling stock, nuclear or photovoltaic power plants require to provide the service life of cables.

The durability of polymeric materials is an important target for R&D teams who have to predict the lifetime of their products. The assessment of long-term behaviour is possible only from artificial accelerated ageing. The tests shall be representative of service life behaviour: chemical and mechanical evolutions must be of the same nature as those observed in reality.

MATERIAL AGEING

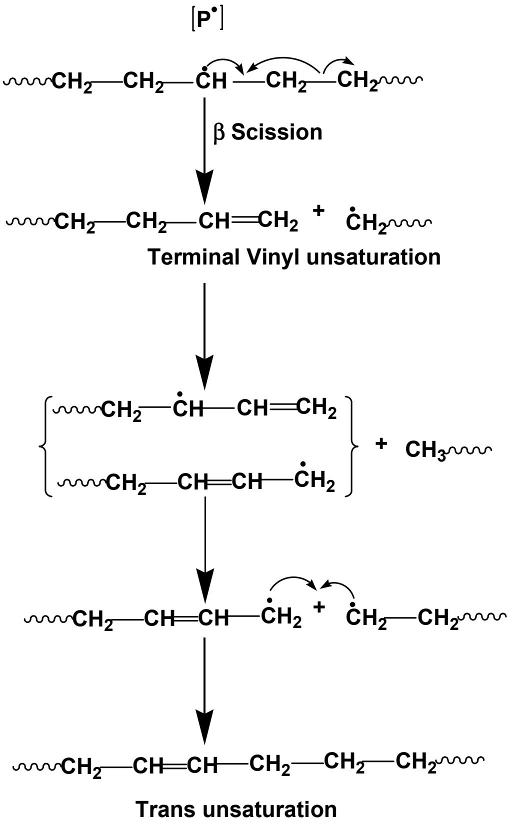
Degradation mechanisms that govern ageing of materials are well known [1-3] (Scheme 1)

The first stage of degradation of polyolefin (PH) is the formation of a macroradical ($P^\cdot$). The reaction with oxygen produces peroxy radical ($POO^\cdot$). This oxygen radical is transformed into hydroperoxide by abstraction of a hydrogen atom from the polymer. Hydroperoxides are very unstable and decompose to yield highly reactive free radical species ($PO^\cdot$) and ($OH^\cdot$). Further reactions lead by combination of two radicals ($PO^\cdot$) to peroxides (POOP), and by breaking chain to oxidized function such as ketone, aldehyde, acid, alcohol...:



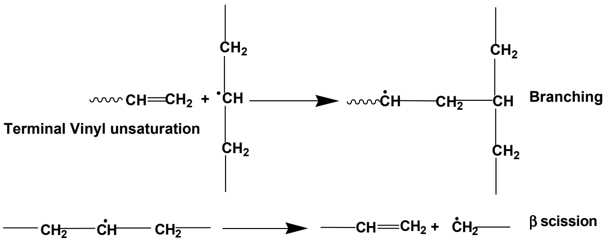
Scheme 1

The hydroxyl functions (water, alcohol, hydroperoxide ...) are observed by infrared spectroscopy around 3400 cm-1 while the carbonyl function appear around 1700 cm-1. During these various stages of degradation, the radical (P.) dimerises to form a macro polymer (crosslinking) and decomposes by intra and intermolecular reactions to generate Terminal Vinyl bonds (υ = 908 cm-1) and Trans Vinyl bonds (υ = 964 cm-1) [4-5] (scheme 2).



Scheme2

The macro radical polymer ($P^{\cdot}$) also reacts with Terminal Vinyls bonds to form branching and breaks by □ scission:



The competition between break and branching depends of many parameters (temperature, amount of unsaturation, stabilizer ....).

All of these reactions suggest that the main chemical entities generated during thermal oxidation of material are identified. The synergy between antioxidants and hydroperoxides decomposers in formulation shows a good knowledge of these secondary products.

However, the kinetic treatment of these mechanisms is still a difficult subject to master. Some models propose a purely mechanical approach (Arrhenius's plot, Dakin's law) or another model a physico-chemical approach.

We will compare these models on the determination of the lifetime of a LSZH sheath at 120° C.

EXPERIMENTAL PART

The thermal ageing is made without air ventilation ovens for at least 150 days at 3 temperatures 110°C, 135°C and 150°C according to IEC 60811-1-2. Several types of samples are tested:

a) Tapes of 1.8 mm thick and 40 mm wide taken on cable.
b) Samples of cables with a 2.2 mm thickness sheath.
c) Plaques of 200x200 mm 2 mm thick

RESULTS

The ageing is characterized by measuring the elongation at break on six H2 dumb bell. The result corresponds to the median of six values.

The lifetime is determined by a conventional criterion of end of life, it means an elongation at break of 50%.

Arrhenius model diagram

The mathematical model of Arrhenius is the most commonly used to study the thermal ageing [6]. This equation can be written as:

$$t = t_0 \exp\frac{Ea}{RT},$$

where t is the lifetime of the material, Ea the energy of thermal activation, R the gas constant, T the absolute temperature and t_0 a constant.

The principle is illustrated in Figures 1a-b where EB is the elongation at break of the material and EB_s is the criterion of end of life (50%)

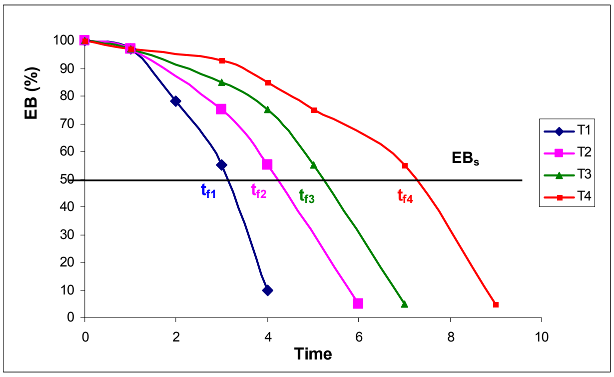


Figure 1a

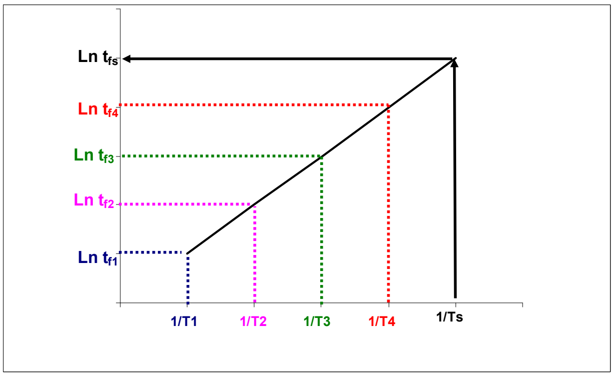


Figure 1b

The intercept represents the value of t_0 and the slope of the Arrhenius's plot allows to determine Ea. The lifetime of the material to service temperature (Ts) corresponds to the value Ln T_{fs}.

Ageing on tape

The curves representing the evolution of EB as a function of ageing time are shown in figure 2

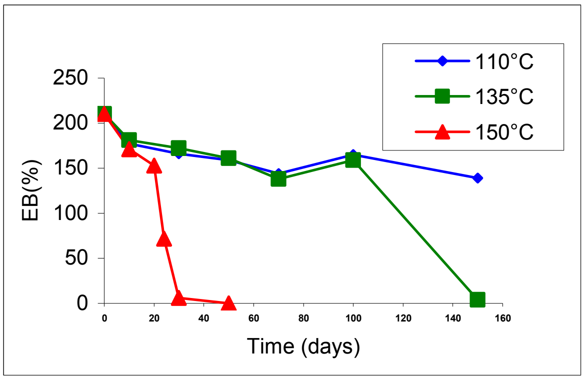


Figure 2

At 110°C, the elongation is moving very slowly. Only at temperatures of 135°C and 150°C, we can draw the plot (figure 3). The thermal activation energy is 159 KJ/mol.

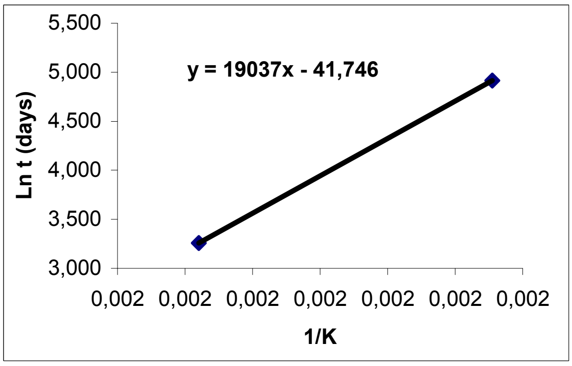


Figure 3

We calculated a lifetime of 808 days at 120°C (2.2 years).

Ageing on cable

The figure 4 shows the evolution of the elongation at break as a function of ageing time:

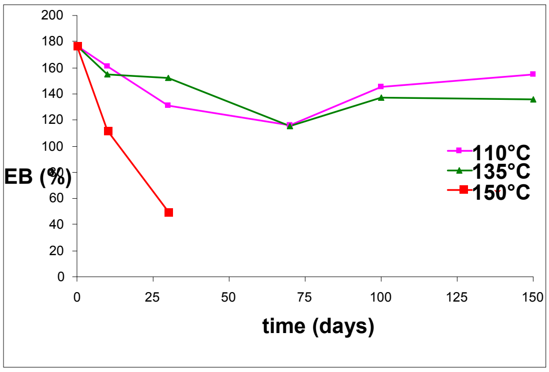


Figure 4

We can't draw the Arrhenius's plot because a significant change is observed only at 150°C. Increasing the ageing temperature is not possible because the degradation process will not be representative. The comparison of figures 2 and 4 indicates that ageing from tape is more severe than that on cable due to the exposure of the 2 sides of the sample to the external environment but cable is more representative of service condition.

Model from Dakin's law

Based on experimental results, EDF R&D has developed a kinetic model from the Dakin's law. This model has been the subject of 2 articles at conferences JICABLE 1995 [7] and JICABLE 2007 [8]. It describes the change in elongation at break with time and temperature as a "function of ageing." By extrapolation, it is possible to calculate the lifetime corresponding with an EB of 50% for a service temperature Ts.

The function of ageing is expressed as follows:

$$\frac{e}{e_0} = \left[1+(\beta-1)\cdot k'\cdot t\right]^{1/(1-\beta)} \quad \text{with } \beta\neq 1$$

$$\frac{e}{e_0} = \exp(-k't) \quad \text{with } \beta=1$$

With e = elongation at break measured at time t and temperature T

e_o = initial elongation at break

k '= rate constant for the reaction of degradation defined by the Arrhenius's law

k' = A exp (-Ea/RT)

β = constant characterizing the degradation reaction

The kinetic constants are calculated using the numerical computation software Scilab.

Ageing on tape

From the values of EB, we calculated the values of Ea, □ and K' at 135°C and 150°C.

T (°C)	k'(d^{-1})	β	Ea (KJ/mol)
135	7,11 E-3	1	170
150	4,07 E-2		

From these kinetic constants, we calculated at 120°C a lifetime of 1300 days (3.6 years).

Ageing on cable

From the set of curves obtained on samples aged over cable (figure 4), we determined the different constants of the ageing function:

T (°C)	K'(d^{-1})	β	Ea (KJ/mol)
110	2,78 E-2	17	22
135	3,67 E-2		
150	4,35 E-2		

A higher value of β for samples aged on cable than on tape confirms that the degradation of the material is less severe.

Close and Return

We calculated a lifetime was over 100 years at 120°C.

Physico-chemical approach [9]

For this study, we aged plaques (20 cm x 20 cm) with a thickness of 2 mm.

For mechanical properties, measurements are made from H2 dumb bell taken from plaques.

The curve of elongation at break at 135°C of test pieces aged on plaques is very close to the one obtained from test pieces on tape (figure 5).

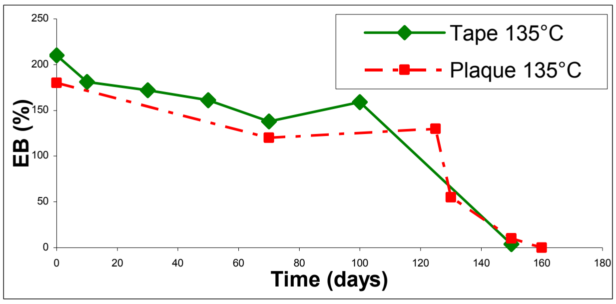


Figure 5

The long-term behavior of polymer can be evaluated on criteria such as the macroscopic elongation at break but also at the molecular scale that describes the chemical evolution of polymer backbone. The ageing of a polymer material involves the development of chemical entity (carbonyl products, hydroperoxides) responsible for the degradation of the physical properties. The characterization of the chemical evolution of a material in a process of thermal oxidation can be done by FTIR-ATR spectroscopy (analysis of the oxidized layer) and DSC-OIT (measuring the concentration of antioxidant). Figure 6 shows the FTIR spectra of the sheath after ageing at 150°C.

We observe an increase in the carbonyl peak at 1700 cm-1 characteristic of oxidation.

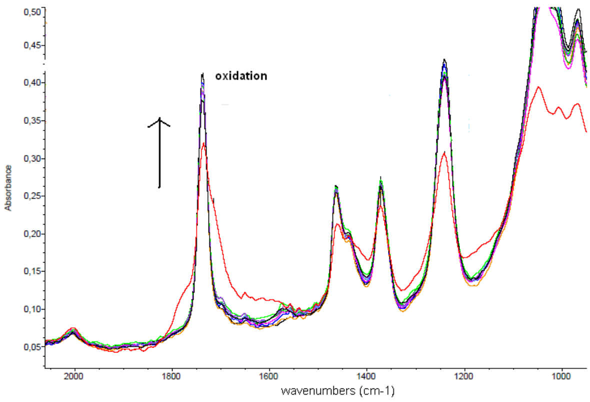


Figure 6

The DSC-OIT technique allows to determine the stabilization time of a material at 200°C under oxygen. This induction period is related to the concentration of antioxidant in the material. The graph (figure 7) shows a decreasing in the value of the OIT sheath after several hours ageing at 150°C. We observe a decrease from 300 minutes to less than 1 min after 700 hours. The FTIR analysis (figure 8) indicates that the surface oxidation of the polymer begins after the induction period of 700 h.

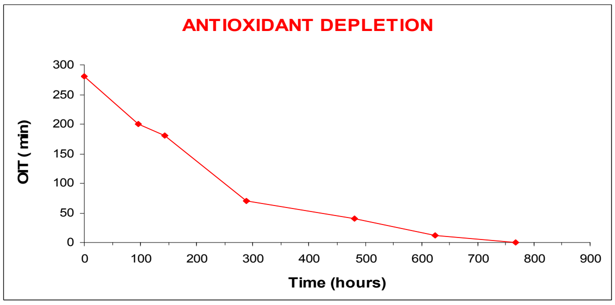


Figure 7

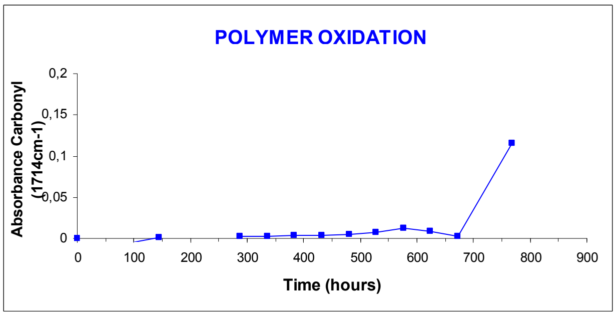


Figure 8

For different ageing temperatures 110°C, 135°C and 150°C, OIT values are measured as a function of exposure time (figure 9)

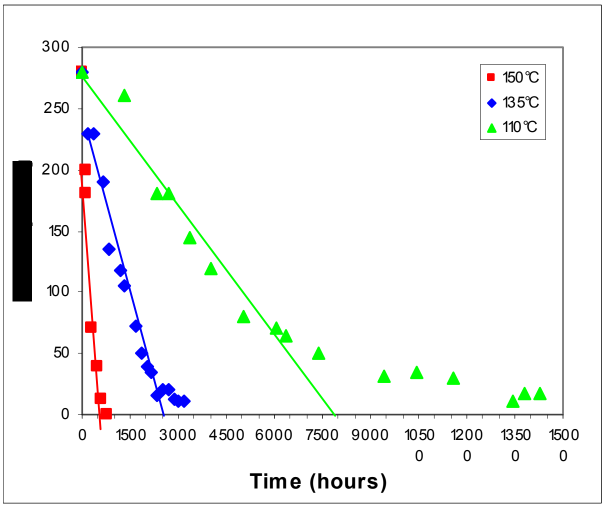


Figure 9

For the 3 temperatures, the slopes of the curves characterizing the rates of consumption of the antioxidant were determined.

T (°C)	T(K)	slope (S= min/h)	Ln S
110	383	0,0372	-3,29
135	408	0,124	-2,09
150	423	0,5	-0,69

The plot of the value Ln S versus 1/T (figure 10), whose slope is (-Ea/R), allows to calculate the thermal activation energy Ea of 87 kJ/mol and verify that ageing is linear between 150°C and 110°C.

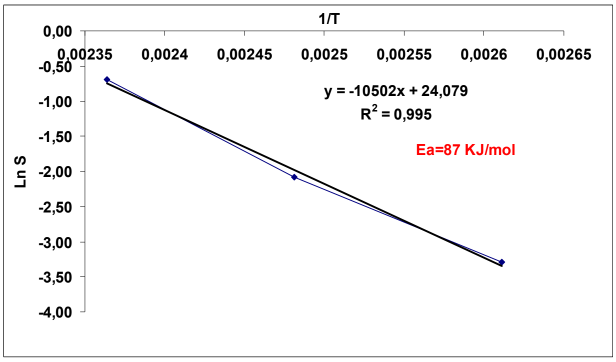


Figure 10

In order to correlate the chemical degradation and the effects on the mechanical properties, the measurement of elongation at break of 50% at 135°C (figure 5-plaques curve) is the basis to determine the kinetic constants at other temperatures (Table 1):

Temperatures test (°C)	T(K)	K_{130}/ K_t	Days
150	423	0,3	40
135	408	1,0	133
110	383	3,9	519

Table 1

To validate this model, we continued ageing the samples after 150 days at 110°C. Tests are in progress. We observe by DSC-OIT that the material contains no antioxidant after 541 days and therefore we should now begin to observe a drop of elongation at break which confirms our prediction of life of 519 days at 110°C. We calculated at 120°C a lifetime of 242 days.

CONCLUSION

The results of thermal accelerated ageing tests have established different predictions of lifetime at 120°C for a LSZH sheath according to the kinetic model chosen and the geometry of the samples.

Kinetic model	Geometry of sample	Lifetime at 120°C
Arrhenius's plot	Tapes	808 days
	Cable	undetermined
Dakin's law “ageing fonction”	Tapes	1300 days
	Cable	>100 years
Physico-chemical approach	Plaques	242 days

The results are very different depending on the model and also on the geometry of aged samples. The calculation of lifetime by the "Arrhenius's plot" approach is quick and easy, but this study shows that this methodology has some limitations because we can't calculate the durability of the sheath taken on cable.

The model suggested by EDF R&D based on the Dakin's law allows to determine a lifetime of material removed on tape and on cable, calculation which was not possible with Arrhenius's plot.

The physico-chemical approach is the one which allows to understand the relationship between chemical structures of materials-thermal behavior.

Whatever the model chosen, we observed that the oxidation kinetics depends strongly on the geometry of the sample (surface/volume ratio). For a better assessment of the quality of materials regarding to the thermal behavior, it is more appropriate to consider during accelerated ageing tests the representative geometry of the cable.

This study shows the difficulty in predicting lifetime at a service temperature of materials and the consequences to determine the strategies to stabilize the formulations.

REFERENCES

[1]: S.Goede, PhD 2006, Novel analytical approaches for studying degradation in polypropylene

[2] : G.Rames-Langlade, M.Milesi, 2005, Dégradations des thermoplastiques, Caoutchoucs et plastiques n°830

[3] : N.Khelidj, Thèse 2006, Vieillissement d'isolants de câbles en polyéthylène en ambiance nucléaire

[4] : T.Bremner, 1992, Effect of polyethylene molecular structure on peroxide crosslinking, Polymer Engineering and Science, vol 32, 939-942

[5] : P.Gijsman, 2008, Review on thermo-oxidative degradation of polymers during processing and in service, e-polymers, n°065, 1-34

[6] : E.Richaud, Thèse 2006, Durabilité des géotextiles en polypropylène

[7] : B.Pinel, F. Boutaud, Jicable 1995, A pratical model for the lifetime prediction of LOCA (EPDM-CSPE) and (PVC) cables in nuclear power stations

[8] : C.Monchy-Leroy, P.Therond, Jicable 2007, Nuclear cables and lifetime simulation

[9] : N.Siampiringue, 2011, Centre National d'Evaluation de Photoprotection