

## THE BEHAVIOR OF AN EVA COMPOUND UNDER THE SIMULTANEOUS ACTION OF HEAT AND OXYGEN PRESSURE

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*Abstract: This EVA compound, based on poly(ethylene-co-vinyl acetate) graft copolymer (79:21 parts by weight), antioxidants and fire proofing agents has been used as a jacket for I&C (instrumentation and control) cables for nuclear power stations. A synergetic degradation equation has been obtained for this material aged with heat and oxygen pressure using the laboratory techniques that RTL (radio-thermo-luminescence) for glass transition temperature, CL (chemiluminescence) for activation energy and TA (thermal analysis) to estimate the oxygen dependence factor. The relative elongation at break is a correlation parameter for synergetic degradation as well as other processes that develop during accelerated aging test.*

### INTRODUCTION

The accelerated aging of this EVA compound for cable jacket, under the simultaneous action of environmental conditions, creates many difficulties in the development of a unitary concept and an adequate mathematical formalism in order to obtain a synergetic model of degradation. In this paper we describe efforts to obtain a degradation equation for the relative elongation at break of the EVA cable jacket aged under simultaneous action of heat and oxygen pressure. During the accelerated aging, it is possible to observe whether crosslinking phenomena is accelerated or retarded in an EVA compound. These phenomena depend on chemical crosslinking agents, storage environment, storage period, or the generation of new crosslinking agents [1, 2]. In order to obtain all material coefficients for the degradation model from aging curves, it is necessary to obtain a number of experimental aging curves (isotherms and isobars). Using laboratory techniques such as radio-thermo-luminescence (RTL), chemiluminescence (CL), and thermal analysis (TA), useful results for estimating the coefficients for a degradation model [3] can be achieved.

### EXPERIMENTAL

The dumbbell samples have been prepared from EVA cable jackets. The samples were aged at 408K in an oven with forced air circulation and in a special installation at 408K and 400 kPa, 393K and 200kPa, 393 and 400kPa, 373K and 400 kPa, and the isotherm of 373K at 600kPa oxygen pressure. The tensile strength and elongation at break of the samples have been measured with a Monsanto T-10/E, equipped with pneumatic gripping. The tests were carried out on samples prepared by using a crosshead speed of 50 mm/min. The length of the test portion of the dumbbell was 20 mm, the width approximately 4 mm, and thickness 1 mm.

## RESULTS AND DISCUSSIONS

The initial average value of relative elongation at break is 224.2 %, and the corresponding average value of tensile strength is 14.73 MPa.

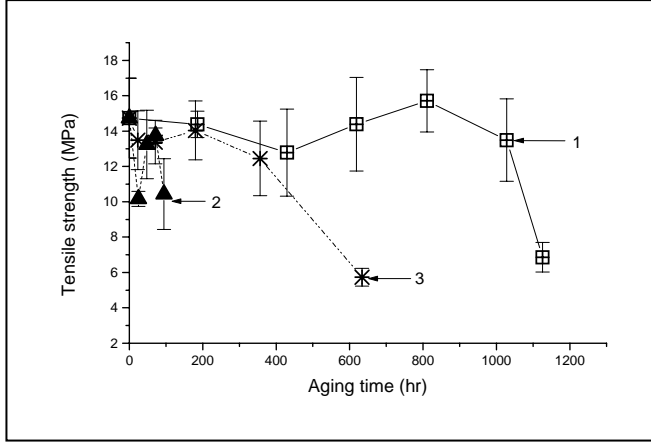


Figure 1 shows the dependence of tensile strength by time for three isotherms-isobars. In order to interpret the experimental data of this EVA jacket, a degradation model [3] has been elaborated, which is given by following equation:

**Fig. 1.** The tensile strength versus aging time for the following isotherms-isobars: 1- 408 K and 21 kPa O<sub>2</sub>; 2 - 408 K and 400 kPa O<sub>2</sub>; 3 – 393K and 200 kPa.

$$\pi(t) = \exp \left[ -Ap^{\omega} t^m e^{-\frac{E_A}{RT}} + Bt^n e^{-\frac{\delta}{T} - \beta \left( \frac{1}{T} - \frac{1}{T_g} \right)^2 - st} \right], \quad (1)$$

Where  $\pi(t) = \frac{E(t)}{E_0}$  is the ratio between relative elongation at break after aging time  $t$ ,  $E(t)$ , relative to the elongation at break of the non-aged material,  $E_0$ ,  $A$  is the preexponential factor,  $E_A$  is the thermooxidative degradation activation energy,  $R$  is the ideal gas constant,  $T$  is the thermodynamic temperature,  $p$  is the partial oxygen pressure of aging environment [4],  $\delta$ ,  $\beta$ ,  $\omega$ ,  $\gamma$ ,  $s$ ,  $B$  are material parameters,  $m$  and  $n$  are shape factors depending of aging temperature and glass transition temperature  $T_g$ .

We assume that the  $m$ ,  $n$ , and  $s$  parameters satisfy the following conditions:

$$\lim_{T \rightarrow T_g} m(T) = 0, \quad (2)$$

$$\lim_{T \rightarrow T_g} n(T, p) = 0, \quad (3)$$

$$\lim_{T \rightarrow 0} s(T, p) = 0., \quad (4)$$

In these conditions,  $m$ ,  $n$ , and  $s$  have following explicit expressions:

$$m(T) = b \left( \frac{1}{T} - \frac{1}{T_g} \right), \quad (5)$$

$$n(T, p) = c(p) \left( \frac{1}{T_g} - \frac{1}{T} \right), \quad (6)$$

$$s(T, p) = s_0(p)T, \quad (7)$$

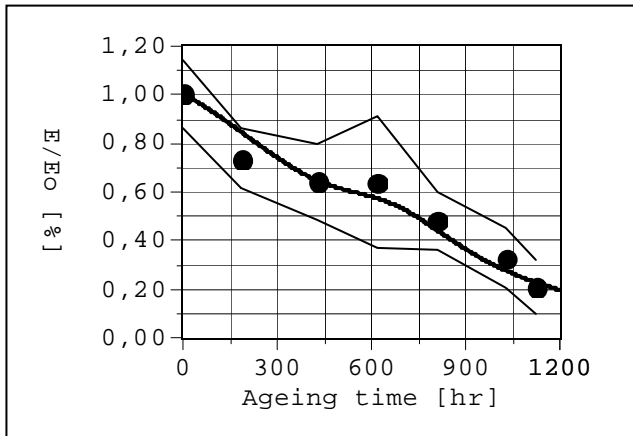
Where  $T_g$  is the glass transition temperature. Generally, the constant  $b$  will be determined from experimental data having to do with the calculated and measured glass transition temperature. For this synergetic experiment, the EVA glass temperature has been determined using a radio-thermo-luminescence technique. In addition, this compound type behaves in concordance with (1) for the case when  $\beta \rightarrow 0$ . The  $c$  and  $s_o$  material constants are:

$$c = \left[ \frac{b \left( \frac{1}{T_R} - \frac{1}{T_G} \right) \left( \frac{E_a}{R} - b \ln t_R \right)}{\left( 1 + A^{-1} p^{-\omega} t_R^{-m_R} e^{-\frac{E_a}{RT_R}} \ln \pi_m \right)} + b \left[ 1 - \left( \frac{1}{T_R} - \frac{1}{T_G} \right) \left( \frac{E_a}{R} - b \ln t_R - T_R \right) \right] \right] \times \left[ \left( \frac{T_R}{T_g} - 2 \right) \left( 1 + A^{-1} p^{-\omega} t_R^{-m_R} e^{-\frac{E_a}{RT_R}} \ln \pi_m \right) \right]^{-1} \quad (8)$$

Noted  $\varepsilon = E_A/R$  and with  $\pi_m = \max[\pi(t)]$ , below, equations will be simplified to writing.

$$s_0 = \left[ \frac{b - m_R (\varepsilon - b \ln t_R - T_R) + \Omega_R}{2(\varepsilon - b \ln t_R)} + n_R \right] (T_R t_R)^{-1} \quad (9)$$

$$\Omega_R = \left[ (b - m_R (\varepsilon - b \ln t_R - T_R))^2 + 4m_R (c + n_R T_R) (\varepsilon - b \ln t_R) \right]^{\frac{1}{2}} \quad (10)$$



The activation energy has been estimated using the chemiluminescence technique, resulting in an average value of  $E_A = 105,204$  kJ/mol, and confidence level is 99,54%. The oxygen dependence has been estimated using the value  $\omega=0.87$  with 95% confidence level.

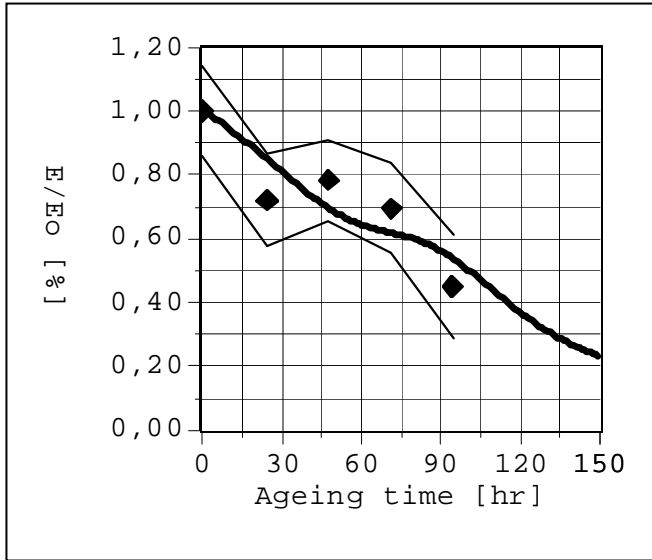
**Fig. 2.** Isotherm-isobar of 408 K in air (21 kPa O<sub>2</sub> partial pressure). The solid circles show experimental points, solid thick line is theoretical line conform to (1) for specific aging factors, and sleazy lines draw the line at the error envelope.

The material coefficients can be calculated with the following equations:

$$\delta = (b + c - s_0 T_R^2 t_R) (m_R - n_R + s_0 T_R t_R)^{-1} - \frac{b}{m_R} - c \ln t_R + s_0 T_R^2 t_R \quad (11)$$

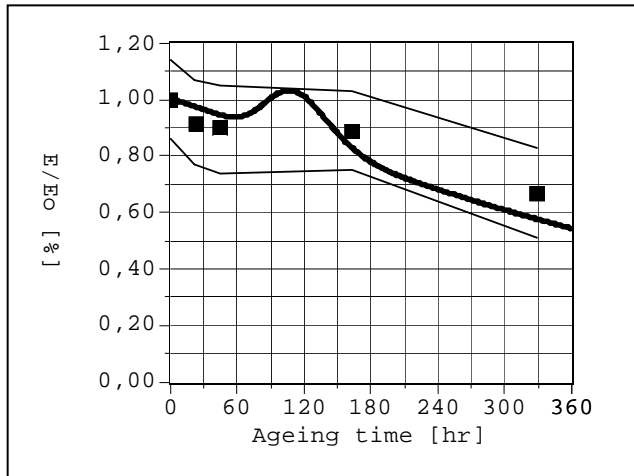
$$B = \left( \ln \pi_m + Ap^\omega t_R^m e^{-\frac{\varepsilon}{T_R}} \right) e^{\frac{\delta}{T_R} + s_0 T_R t_R - n_R \ln t_R} . \quad (12)$$

The pressure factor “ $\omega$ ” has been estimated using the integral volume of experimental data, but it may also be estimated with TA and DTA laboratory techniques [5,6].



Taking into account all experimental data and laboratory analysis, the following figures show experimental points and theoretical curves. This figure shows a good concordance between the experimental points and the theoretical curve, which has the parameters and coefficients, determined from these experimental points using statistical analysis.

**Fig. 3.** Isotherm-isobar of 408 K and 400 kPa O<sub>2</sub>. The solid diamonds show experimental points, solid thick line is theoretical line conforming to (1) for specific aging factors, and sleazy lines draw the line at the error envelope.

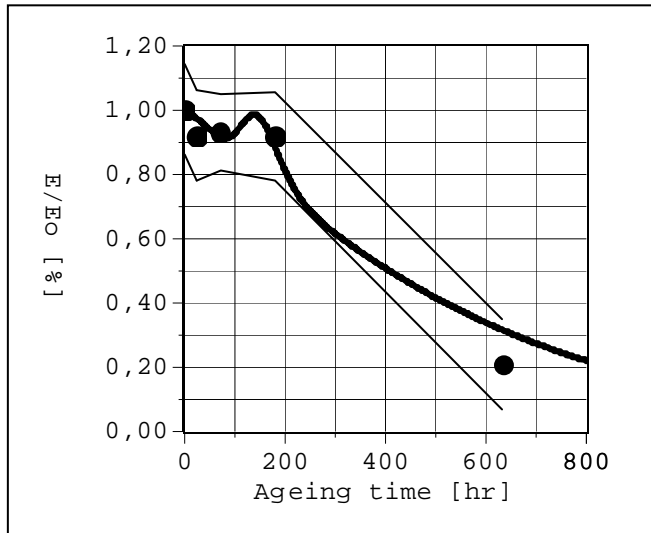


The error envelopes have been drawn taking into account the error interval for each experimental average value in order to calculate the error of the reported  $E/E_0$ . Generally, in zones where there is a peak of elongation at break, the experimental data dispersion would be increased.

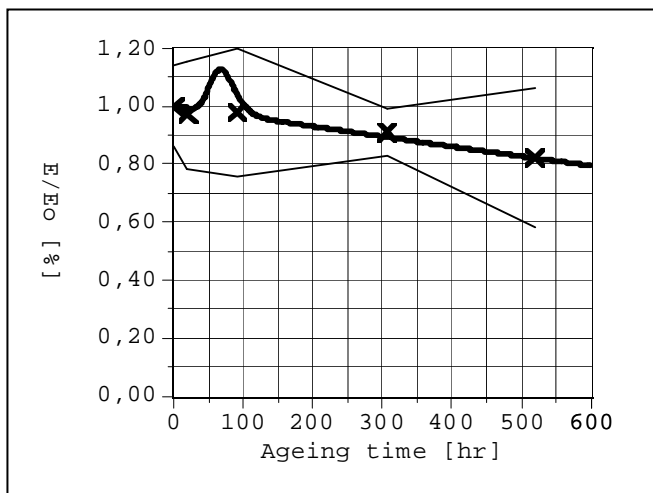
**Fig. 4.** Isotherm-isobar of 393 K and 400 kPa O<sub>2</sub>. The solid squares show experimental points, solid thick line is theoretical line conforming to (1) for specific aging factors, and sleazy lines draw the line at the error envelope.

The peaks are perhaps, generated by internal inhomogeneities that have an important dependence of aging temperature and a slow dependence on oxygen pressure (in practical mode it is not statistically detectable). The local peaks, from following figures, where the growth of elongation at break can be correlated with a corresponding growth of tensile strength, reflect a retarded crosslink. This crosslinking produces a growth of dispersion during

the aging process. Equation (7) and (9) define the capacity of copolymeric system that under certain circumstances produces a retarding crosslinkable process. Generally, the “ $e^{-st}$ ” term defines a probability of crosslinking after aging time  $t$ . All the same, it is difficult to correlate the “ $s$ ” factor value for a high molecular weight polymer as well as to make a connection with a configuration model. In the experimental errors limit “ $s_0$ ” coefficient has a dependence of partial oxygen pressure as shown in figure 7.

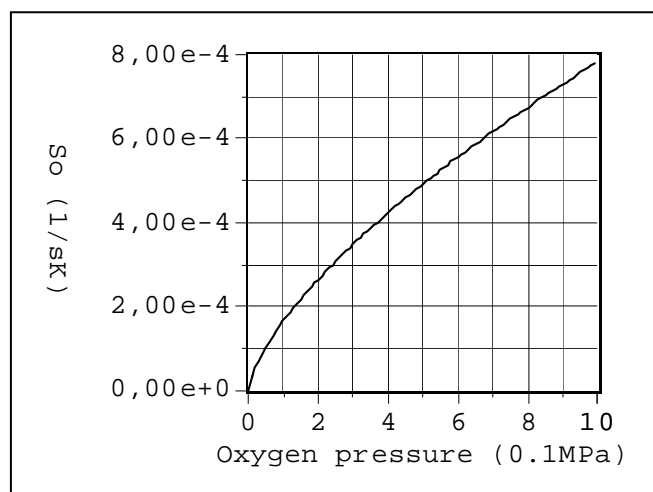


**Fig. 5.** Isotherm-isobar of 393 K and 200 kPa O<sub>2</sub>. The solid circles show experimental points, solid thick line is theoretical line conforming to (1) for specific aging factors, and sleazy lines draw the line at the error envelope.



**Fig. 6.** Isotherm-isobar of 373 K and 600 kPa O<sub>2</sub>. The bold X show experimental points, solid thick line is theoretical line conforming to (1) for specific aging factors, and sleazy lines draw the line at the error envelope.

The parameter “ $m$ ” is very important because it gives the trend of the isotherm degradation curve. It is specific for each polymer type (e.g. crosslinkable polyethylene) especially for mechanical properties [7]. The tendency for it to be zero near the glass transition temperature leads to an important property of this parameter, because it can be calculated from experimental data as well as measured using different techniques. It provides the possibility for verifying the calculations.



**Fig. 7.** The coefficient “ $s_o$ ” versus partial oxygen pressure.

## CONCLUSIONS

This thermo-oxidative degradation model may be developed for a number of polymer types (elastomers, polyolefins etc) especially for estimation of lifetimes [3]. It successfully assesses the evolution of a polymeric material subjected to the action of aging factors. It is a synergetic degradation model, which can be extended as well to the aging in radioactive environments [3]. In addition, it accommodates a number of parameters. It has been used to develop a number of degradation models of polymeric materials especially for insulation applications in nuclear power stations. The retarding crosslink process generates many difficulties for the prediction of lifetimes because the implicated aging factors will have different unknown magnitudes during the accelerated aging test. On the other hand, oxygen pressure is an important factor in reducing the accelerated aging period, not only for the EVA compound used as I&C cables jacket, but also for other polymer systems. It should be noted that there was a difference between the samples taken from aged I&C cable segments and dumbbells aged after removing from unaged cables.

## REFERENCES

1. Munteanu, D and Turcu, S. “Evaluation of kinetic parameters of the thermal decomposition of polyethylene-vinyl acetate graft copolymers”, J. Thermal Anal., Vol.20, pp. 281, 1981.
2. Marcilla, A. and Beltran, M., Kinetic study of thermal decomposition of polystyrene and EVA graft copolymer by thermogravimetric analysis, Polym. Deg. and Sab. 50(1995) pp. 117-124.
3. Mares, G. “Predictive Modelling”, Report on the IAEA Research Co-ordination Meeting, 4-8 October, Prague CR, pp.114-130, 1999.
4. Mares G., Budrugaec P., Chap. X, Elastomer Technology Handbook, CRC Press, Boca Raton, London, Tokyo, 1993.
5. Budrugaec P., Accelerated Thermal Aging of NBR and other Materials under Air or Oxygen Pressures, Die Angewandte Makromolekulare Chemie, 247 (1997) pp. 19-30 (4422).
6. Budrugaec P., The Effect of Oxygen Pressure on the Kinetics of Thermo-oxidative Degradation of Copolymer EVA and Nitrile-Butadiene Rubber, Journal of Applied Science, Vol. 75, pp. 1453-1457 (2000).
7. Mares G., Setnescu R., The Accelerated Ageing of a XLPE Cable Insulation under the Simultaneous Action of Heat and Stationary Electric Field, 2001 IEEE 7<sup>th</sup> International Conference on Solid Dielectrics, June 25-29, Publication 01CH3711, pp. 62-65.