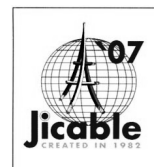




KINETIC MODELLING OF PHENOL STABILISER EFFICIENCY IN POLYETHYLENE SUBMITTED TO NUCLEAR ENVIRONMENTS



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ABSTRACT

This work is aimed to build a non-empirical kinetic model for the lifetime prediction of electrical cable insulators exposed at low dose rates at room temperature in air, in nuclear plants. Previous studies have been devoted to the first stage of our approach, i.e. establish a kinetic model efficient for neat PE matrices whatever temperature and dose rates. This work deals with the second stage of our approach. It consists in proving that this approach is possible for stabilized matrices, in introducing the stabilisation reactions into the model and showing the performances of a first very simple model.

KEYWORDS

Lifetime prediction, kinetic modelling, polyethylene, phenolic antioxidants.

INTRODUCTION

1 – Typical approach for lifetime prediction

It has often been proposed that lifetime (denoted t_F) for insulating cables could be predicted by laws such as:

Thermal ageing:
$$t_F = t_{F0} \cdot \exp\left(-\frac{E}{RT}\right) \quad [1]$$

Radiochemical ageing:
$$t_F = t_{F0} \cdot I^{1/2} \cdot \exp\left(-\frac{E}{RT}\right) \quad [2]$$

T being the absolute temperature (K), I the dose rate (Gy s^{-1}). Nevertheless, it can be recalled that in case of thermal ageing (at low dose rates), such laws could be not well adapted because mechanisms significantly change with temperature. For example, true lifetime curve against reciprocal temperature is “down bended” whereas law 1 predicts a linear variation (Fig 1a) [1].

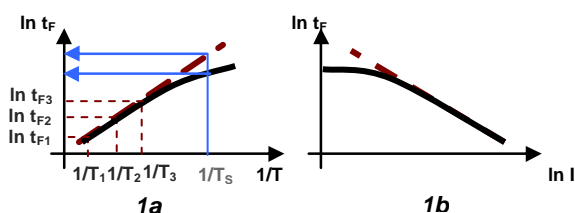
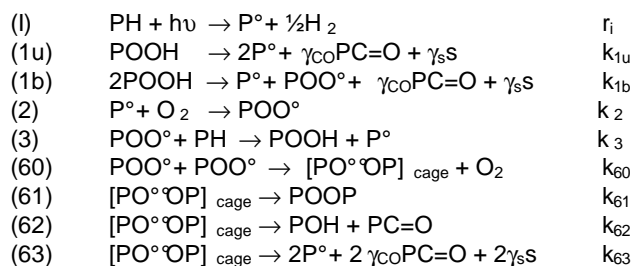


Figure 1: Methods for lifetime estimation from empirical laws (full lines) and shape of experimental lifetimes curves (dashed lines)

Law 2 is quite well adapted to accurately estimate lifetime at strong dose rates but at lower rates, it is now well established that lifetime is shortened by thermal oxidation processes (Fig 1b). Consequently, the aim of researches performed in our laboratory is to develop a non empirical tool for lifetime prediction being able to predict ageing kinetics whatever the mechanism (radio, thermal, or radio and thermal oxidation), this one being of course adapted to the material nature (chemical structure of polymer matrices and formulation).

2 – Lifetime prediction by kinetic modelling: case of pure PE radio-thermal oxidation

This approach is based on the mechanism of chemical (microscopic) structure changes:



In the classical frame of chemical kinetics, a system of differential equations is derived from this scheme:

$$\frac{d[\text{P}^\bullet]}{dt} = r_i + 2k_{1u}[\text{POOH}] + k_{1b}[\text{POOH}]^2 - k_2[\text{P}^\bullet][\text{O}_2] + k_3[\text{POO}^\bullet][\text{PH}] + 2k_{63}[\text{PO}^\bullet\text{OP}]_{\text{cage}} \quad [3]$$

$$\frac{d[\text{POO}^\bullet]}{dt} = k_{1b}[\text{POOH}]^2 + k_2[\text{P}^\bullet][\text{O}_2] - k_3[\text{POO}^\bullet][\text{PH}] - 2k_{60}[\text{POO}^\bullet]^2 \quad [4]$$

$$\frac{d[\text{POOH}]}{dt} = -k_{1u}[\text{POOH}] - 2k_{1b}[\text{POOH}]^2 + k_3[\text{POO}^\bullet][\text{PH}] \quad [5]$$

$$\frac{d[\text{PO}^\bullet\text{OP}]_{\text{cage}}}{dt} = k_{60}[\text{POO}^\bullet]^2 - (k_{61} + k_{62} + k_{63})[\text{PO}^\bullet\text{OP}]_{\text{cage}} \quad [6]$$

$$\frac{\partial[\text{O}_2]}{\partial t} = -k_2[\text{P}^\bullet][\text{O}_2] + k_{60}[\text{POO}^\bullet]^2 + D_{\text{O}_2} \cdot \frac{\partial^2[\text{O}_2]}{\partial x^2} \quad [7]$$

Where:

$$k_i = k_i(T)$$

$$r_i = \alpha I$$

$$[\text{O}_2] = s_{\text{O}_2} \times P_{\text{O}_2} \quad (s_{\text{O}_2} \text{ being the oxygen solubility in polymer})$$

In other words, instead of using environmental strains (T , I ,