Validation of a generic tool of kinetic simulation of cable ageing

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ABSTRACT
The aim of this work is to present a generic tool used to model kinetics ageing of polymers in order to predict their service life. The adopted approach consists to use an accelerated ageing procedure in view of establishing of a validated non-empirical kinetic model. In the present study, our interest is focused on the impact of thermal-oxidation on the chemical structure of Ethylene-propylene-diene monomer rubber (EPDM). Obtained results validate this new generic tool at the molecular scale and allow us to take with confidence the next step of our multi-physics and multi-scale approach for lifetime prediction, i.e. the prediction of macromolecular changes.

KEYWORDS
Polymer ageing, Thermal oxidation, molecular changes, kinetics modelling.

INTRODUCTION
Polymer materials are extensively used in electric power applications. In fact, due to their mechanical properties and excellent thermal stability, polymers are mainly used as sheaths of cables and insulators. In service, these materials are subjected aggressive environmental conditions such as high temperature by the Joule effect (heating due to electric current transit). In these ageing conditions, chemical degradation can take place and affect the mechanical integrity of rubber pieces, reducing their lifetime. Generally, FTIR spectroscopy is used to evaluate the chemical changes in certain functional groups of material due to thermal oxidation. The major products formed during the oxidation of polymers and, in particular EPDM, include carbon–carbon double bonds, carbonyl groups, and ester groups, were found to be generated by the thermal oxidation of EPDM [1-4]. Thermal ageing of rubbers consists in a several complex reactions, not fully elucidated, that proceed simultaneously and still the object of a vivid scientific debate [5-7]. Since the early 2000s, the EDF R&D team of polymers is interested in the study of the multi-scale analysis ageing of polymers (at the molecular, macromolecular and macroscopic levels) used in nuclear power plants, such as cables, pipes or paintings [8-11]. This understanding of the mechanisms of aging allows, among others, to develop a universal approach for life time prediction or monitoring the aging of these materials on-site. The establishment of structure/property relationships remains the major problematic in any non-empirical approach for lifetime prediction. Recently, Polymers team has developed a generic tool to model kinetics ageing of polymers.

In this study, our proposal is to present the first step of this approach which is the development of a generic tool used to model the thermal oxidation kinetics, at the molecular scale, of an EPDM rubber used in cables. The approach taken to establish the physical model validation of polymer ageing consists in first, the integration of a system of non-linear differential equations derived from an established mechanistic scheme for describing the polymer ageing process in the simulation code; then, the comparison of chemical experimental results [12] (obtained by FTIR spectrophotometry) and numerical resolution (obtained both with Matlab software and the new simulation tool named Virtual Polymer).

MATERIAL AND EXPERIMENTAL PROCEDURE

Material
The material investigated in this work is an EPDM rubber with a density of 0.86 and a Tg of -57±2°C. It contains: 66.1 mol.% ethylene, 33.1 mol.% propylene and 0.8 mol.% norbornene (ENB) (Fig.1).

![Fig.1. Chemical structure of EPDM based on ENB diene.](image)

Accelerated ageing procedure
Isothermal ageing experiments of purified EPDM films were performed between 70 and 170°C in air-ventilated ovens (regulated at ± 2°C) for several hundreds of hours.

Ageing analysis
EPDM films were regularly removed from ovens to be analyzed mainly using Fourier transform infrared (FTIR) spectroscopy in a transmission mode. This technique permits to examine changes in concentration of thermal degradation products. Analysis was conducted on the thermal aged samples of about 100 µm thick and using a Perkin-Elmer Instruments with 32 scans analysis and a resolution of 4 cm⁻¹. All the spectral calculations were performed using Spectrum software. The changes in the concentration of both chemical groups were determined using the classical Beer-Lambert’s law:

\[ A = \varepsilon c \]

Equation 1

Indeed, the Beer-Lambert’s law allows deducing, from absorbance signal, the changes in concentration of thermal degradation products.