

STUDY OF THE STABILIZATION OF POLYETHYLENE AND ETHYLENE-PROPYLENE COPOLYMERS BY A PHENOLIC ANTIOXIDANT

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ABSTRACT

The present article outlines a non-empirical kinetic model for the lifetime prediction of electric cable sheaths and insulators made of polyethylene or ethylene-propylene copolymer (with a fraction of ethylene units higher than 70 wt%) stabilized by a multifunctional phenol antioxidant. Examples of simulation showing the good predictive value of the model are reported. The model predicts satisfyingly the consumption and evaporation kinetics of phenol antioxidant, the oxidation kinetics of methylene groups, and then the polymer lifetime in a nuclear environment.

KEYWORDS

Polyethylene, Ethylene-propylene copolymer, Phenolic antioxidants, Thermo-oxidation, Radio-oxidation, Kinetic modeling, Lifetime prediction.

INTRODUCTION

The monitoring and evaluation of the durability of electric cables installed inside the nuclear power plants is one of the EDF's main concerns for many years. In a cable, the weak links are the polymer constituents, i.e. the outer sheath and the inner insulator. Both constituents are frequently made of polyethylene (PE) or ethylene-propylene copolymer (EPR). It is now well established that they can perish oxidation. Depending on dose rate and temperature, oxidation can be initiated by the polymer radiolysis, the thermal decomposition of hydroperoxides or by these two mechanisms together [1].

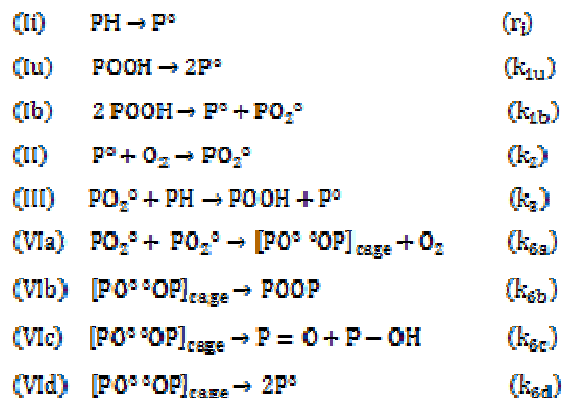
During the last decade, EDF has collaborated with ARTS ET METIERS ParisTech to develop a new methodology for lifetime prediction based on the kinetic analysis and modeling of the thermo-oxidation and radio-oxidation processes [2-3]. The main outcome was the proposal of a realistic mechanistic scheme for the complex thermo-radio-oxidation process, from which has been derived a non-empirical kinetic model using the common concepts of chemical kinetics. Then, the polymer lifetime has been predicted using a structural endlife criterion characterizing the ductile/brittle transition.

Such a non-empirical kinetic model has been established for pure PE, but can be generalized with confidence to pure EPR as the fraction of ethylene units is higher than typically 70 wt%. Now, the challenge is to extend gradually the model to complex industrial sheath and insulator formulations by taking into account all effects of adjuvants and fillers.

The present communication is devoted to the stabilizing effects of phenol antioxidants.

THEORY

The mechanistic scheme for the thermo-radio-oxidation of pure PE was established in previous studies [2-3]. In its simplest form (in oxygen excess), it can be written:



where I_i, I_u and I_b are initiations by polymer (PH) radiolysis and by unimolecular and bimolecular thermal decomposition of hydroperoxides (POOH) respectively.

II and III are propagations by oxygen (O₂) addition to alkyl radicals (P[•]) and hydrogen abstraction by peroxy radicals (PO₂[•]).

VIa is the formation of a complex composed of two alkoxy radicals (PO[•]) in a cage.

VIb, VIc and VI d are bimolecular terminations and non terminating processes of alkoxy radicals in a cage.

r_i (in mol.l⁻¹.s⁻¹) is the initiation rate due to polymer radiolysis. It is proportional to dose rate I (in Gy.s⁻¹):

$r_i \approx 10^{-7} \times G_i \times I$, G_i being the radical yield expressed in number of radicals P[•] per 100 eV absorbed.

k_{1u} , k_{1b} , k_2 , k_3 , k_{6a} , k_{6b} and k_{6c} (in l.mol⁻¹.s⁻¹ or s⁻¹) are rate constants.