



# Thermodynamic analysis of the degradation of polyethylene subjected to internal partial discharges

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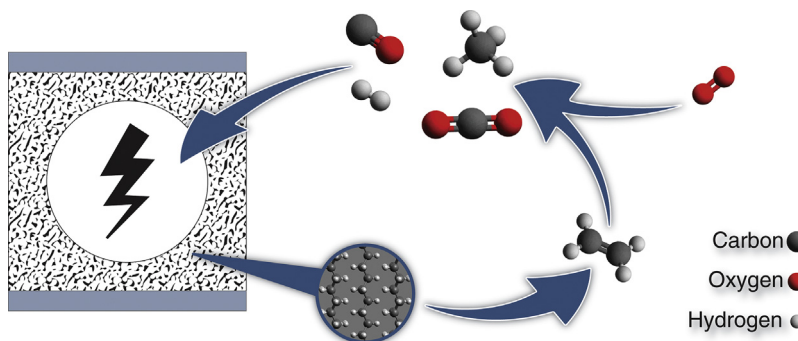
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## HIGHLIGHTS

- A thermodynamic model is employed to study the evolution of a partial discharge within a cavity.
- The computational predictions are in qualitative agreement with previous experimental results.
- The increase of the cavity volume can be related to the energy introduced by partial discharges.
- Two energetic regimes are possibly active in the degradation of PE by partial discharges.
- At low energy only gaseous species are produced; at high energy graphite is also formed.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The field of electrical insulation has improved considerably after the introduction of the first synthetic polymeric dielectrics. However, these materials are often considered the “weakest link” as they tend to degrade and eventually fail, thus compromising the reliability of devices and equipment. Such degradation is related to the occurrence of partial discharges (PDs), a phenomenon that is difficult to measure in actual applications.

In the present work, the chemical evolution of the gas phase composition and polyethylene degradation in a polyethylene microcavity subject to a PD were studied using a thermodynamic model. Thermodynamic parameters for the depolymerization of polyethylene into ethylene were obtained using density functional theory calculations. The system evolution is studied minimizing the Gibbs free energy subject to the constraints of energy conservation explicitly considering the polyethylene surface among the reacting species.

The model results can be interpreted in terms of the density of energy introduced by the partial discharge. At low discharge energy densities methane and carbon monoxide are the most abundant species produced by the discharge. As the energy density increases the model predicts that ethylene is formed in the gas phase because of the depolymerization of the polymer. At high energy densities carbon may be formed at the surface. In these conditions, the most abundant gas phase species predicted by the model are methane, carbon monoxide, hydrogen, water, and carbon dioxide. This is in good agreement with experimental observations reported in the polyethylene PD literature. In addition, the model is able to

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correlate the energy of the partial discharge to the increase of volume of the microcavity, thus providing a tool that may be used to predict polymer degradation due to PDs dissipated power.

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## 1. Introduction

Polymeric materials have been extensively employed in the electrical power industry as insulators due to their remarkable and wide-ranging properties. Particularly, in the last decades, great attention has been paid to the use of polyethylene (PE), especially in its cross-linked form (XLPE), to insulate high-voltage (HV) cables (Englund et al., 2009; Wutzet et al., 2015). However, under normal operation conditions, the polymer is subject to several concurrent stresses (e.g. mechanical, thermal, electrical, chemical, etc.) that lead to its degradation and, in some cases, to its definitive failure.

It is generally agreed that the main cause of degradation of the polymeric insulator is the occurrence of partial discharges (PDs) (Leon-Garzon et al., 2015). They take place due to the existence of microcavities in the matrix of the polymer and/or at the interface between the polymer and another material. These microcavities are formed during manufacture, handling or use of the dielectric and their density is around  $10^3 \text{ mm}^{-3}$ – $10^7 \text{ mm}^{-3}$ , while their size ranges from  $1 \text{ }\mu\text{m}$  to  $5 \text{ }\mu\text{m}$  (Mayoux et al., 2013). For this reason, some efforts have been devoted to the reduction of their size and density.

A partial discharge event takes place when the electric field within a microcavity exceeds the breakdown strength of the contained gas thus leading to the formation of an electron avalanche (Fig. 1) (Illias et al., 2011). Under certain conditions, an electron avalanche is able to trigger excitation and ionization processes of the gas producing further electrons, ions, free radicals and excited species. These species lead to deleterious chemical transformations in the polymer due to their prolonged bombardment over the surface (Novak and Bartnikas, 1995).

As a result, several structural and chemical transformations occur in the polymeric insulator. The main structural transformation consists in the formation of damage paths inside the dielectric. These paths can take different forms ranging from expanse structures that resemble the branches of a tree (Fig. 2a) to more dense structures that are similar to a bush (Fig. 2b). Due to its shape, such phenomenon is usually known as electrical treeing. The chemical nature of such formations has been analyzed by Vaughan et al. (2006), who identified the G and D Raman bands of a C–C  $sp^2$  bonded system that can be attributed to the formation of graphitic carbon.

According to Morshuis (2005), chemical transformations lead to the formation of several degradation products resulting from the sustained discharge within the polymeric dielectric (in this case

polyethylene and epoxy resin). Such products are present in gaseous, liquid or solid phase. Gaseous degradation products include carbon monoxide, carbon dioxide, methane and hydrogen.

Several approaches have been used to model the degradation of PE by partial discharges. Many are statistical models using adaptive parameters to fit experimental PD data, thus without any need of a physical insight into the phenomenon (Montanari, 2013). On the other hand, life models that included some physical description of the chemical reactivity of the polymer, triggered by the injection of energy due to the discharge, do not take into consideration the chemical evolution of the gas phase inside the cavity (Ding and Varlow, 2005; Dodd, 2003; Mazzanti et al., 2007).

In the present work, we propose a thermodynamic approach that is suitable to study the partial discharge within a microcavity that explicitly considers the decomposition of PE, the gas phase chemical evolution, and the formation of solid carbon as a co-product of PE decomposition. Though a partial discharge is essentially a non-equilibrium phenomenon, the modelling of various types of plasma discharges has been done employing a thermodynamic analysis in several cases, ranging from the monitoring and treatment of atmospheric contaminants, to the synthesis of thin films by chemical vapor deposition and to the conversion of hydrocarbon fuels. For instance, Sakano et al. (2001) employed a thermodynamic analysis to study the application of radiofrequency plasmas to the treatment of fly ash in atmospheric gases, while Masi et al. (1998) used a similar approach to study the Plasma Assisted Chemical Vapor Deposition of diamond like carbon. Vacher et al. (2001) interpreted atomic emission spectral lines of trace metals in  $\text{N}_2/\text{O}_2$  mixtures in inductively coupled plasma through thermodynamic computations. Cota-Sanchez et al. (2005) employed a thermodynamic analysis to study the effect of temperature and pressure on the synthesis of fullerenes by induction plasma. Always throughout thermodynamic calculations, Sassi et al. (2002) studied the competition between the formation of  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  in the deposition of thin dielectric films by electric-discharge-assisted chemical vapor deposition. Moreover, the primary assessment of the efficiency of partial oxidation reforming of hydrocarbons assisted by plasma discharges has been approached through a thermodynamic analysis by several authors (Lutz et al., 2004; Minutillo, 2005; Rollier et al., 2008; Rusu and Cormier, 2003). Finally, a thermodynamic analysis was done to study the ablation of vapors from polymeric materials by electric arcs in circuit breakers. A first analysis was done supposing decomposition only to gaseous components (André, 1996), whereas a second analysis was done to include the formation of condensed carbon in its graphitic form (André, 1997).

This paper is structured as follows: the partial discharge modelling strategies are described in Section 2, while the modelling results are presented and discussed in Section 3. Finally, in Section 4 we present the conclusions.

## 2. Theory

The model here proposed relies on the following simplified description of the chemical events initiated by the partial discharge. Initially, the PD leads to a release of a certain amount of energy in the gas phase of the microcavity, which is a complicated function of the shape and size of the microcavity as well as of the local electric field. Thus, it was decided to consider it as a param-

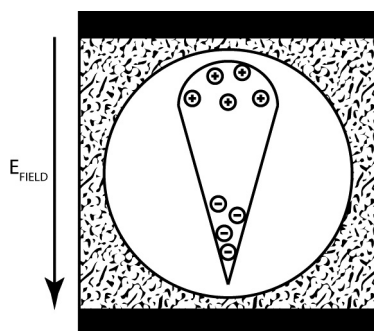


Fig. 1. Partial discharge in a microcavity.

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