

Lumped Mechanism for Polymeric Dielectric Degradation Under High Electrical Fields

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Since the introduction of the first synthetic polymeric dielectrics, several improvements have been introduced in the field of electrical insulation at the same pace that electrical apparatuses have evolved in complexity throughout time. The implementation of polyethylene as an electric insulator in the early 1960s marked an important breakthrough allowing to pass from low-voltage (a few kilovolts) to high-voltage applications (>15 kV) thanks to diverse contributions from engineers, physicist and chemists. Even though the significant improvements achieved in the field, the mechanism responsible for the degradation or aging of polymeric dielectrics is not completely clear as the material is under several types of stresses (e.g. electrical, chemical and mechanical). In the present study a possible mechanism for the degradation of polymeric dielectrics from a chemical perspective is introduced. It is supported on the hypothesis of the occurrence of ionic and excited species inside the microscopic voids present in the material which are caused by the high voltage field the dielectric is typically subject to. Then, we put into consideration the numerous effects of such ionic/excited species on the backbone chain of the polymeric dielectric, and in particular on polyethylene as it is one of the most employed dielectrics on electrical insulation and to its simple molecular structure. A model of the mechanism is subsequently introduced based on a streamer discharge with the inclusion of the surface boundary chemical phenomena.

1. Introduction

Thanks to their remarkable properties and their wide ranging characteristics, synthetic polymers are employed in a variety of fields and are the most important type of materials for the modern age. Particularly, in the electric power industry, polyethylene (PE) and cross-linked polyethylene (XLPE) are extensively used due to their low dielectric permittivity and loss factor; and their good mechanical, thermal and chemical stability (Sarathi et al., 2004). However, despite their proven advantages as insulators, these materials suffer from electrical degradation and their quality decline with time up to the point where the insulator fails (breaks down) causing economic losses and safety issues.

Several ageing models have been proposed in literature, most of them resorting to a kinetic approach using an Arrhenius model such as that proposed by Dakin (1948) or a thermodynamic approach employing an Eyring model such as that proposed by Crine (1990). However, they rely on experimental data fitting or accelerated life testing data and do not explain the underlying mechanism and are employed generally for health monitoring (Makdessi et al., 2013). Thus, understanding the phenomena from a microscopic level would permit to explain the elementary processes that lead to the macroscopic breakdown of the polymeric dielectric and, according to Teysseudre and Laurent (2013), is a current trend in modern insulating material research and the main core of the present work.

As a result, despite the wide literature on partial discharges available nowadays and the enormous advance in the field, the breakdown mechanism of polymeric dielectrics is still not completely elucidated and is still highly

debated among researchers so, paraphrasing Montanari (2013), it is crucial to understand the real phenomena occurring to the insulator and the causes for its accelerated aging and breakdown in order to focus on the important aspects of insulation design and performance. The paper is structured in this way: in section 2 the partial discharge phenomena is introduced while in section 3 and 4 we proposed a mechanism for the degradation of polyethylene together with a mathematical model to describe it.

2. Partial discharge principles

The degradation phenomena in polymeric dielectrics is related to the occurrence of partial discharges (PD), these can be corona, surface or internal discharges (Kao, 2004); however, great attention has been made to surface and internal partial discharges as these are the most common due to the presence of microcavities in the matrix of the polymer or in the interface between the polymer and another material; such microcavities are formed while manufacturing, handling or utilization of the dielectric and even though several efforts have been made to reduce their quantity and size, their density is still around 10^3mm^{-3} to 10^7mm^{-3} and their size range around $1 \mu\text{m}$ to $5 \mu\text{m}$ (Mayoux et al., 2013).

Under the right conditions the electric field within a microcavity can exceed the breakdown strength of the gas that fills it creating an electron avalanche (Figure 1) and resulting in an internal partial discharge (Illias et al., 2011). This discharge is characterized by the occurrence of excitation and ionization processes that produce electrons, ions, free radicals and excited species that would lead to deleterious chemical transformations due to their prolonged bombardment in the polymer surface (Novak and Bartnikas, 1995).

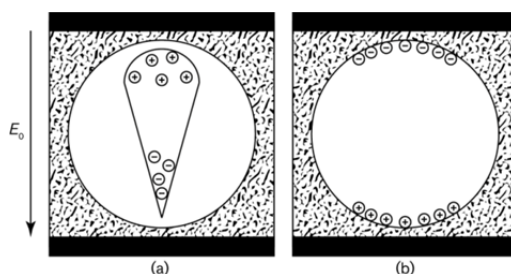


Figure 1: Partial discharge in a microcavity. In (a) streamer discharge and (b) species bombardment

Throughout the aging process structural and chemical transformation occur; structural transformation refer to 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 (Figure 2(a)) to dense structures that are similar to a bush (Figure 2(b)), as a result such phenomena is called treeing due to its particular shape.



Figure 2: Electrical tree structures in a XLPE cable insulator. In (a) a branch-like structure while in (b) a bush-like structure (Xiangrong et al., 2011)

On the other hand, according to Morshuis (2005) the chemical transformation refer to the formation of several degradation products resulting from the sustained discharge of polymeric dielectric (in this case polyethylene and epoxy resin). Such products are present in gaseous, liquid or solid phase; gaseous devolatilization products include carbon monoxide, carbon dioxide, methane and hydrogen; liquid decomposition products are present in the form of carboxylic acid droplets (e.g. formic and acetic acid); and the solid decomposition product is mainly in the form of hydrated oxalic acid crystals.

3. Polyethylene degradation mechanism

Polyethylene was chosen as the material of interest due to its widespread utilization as insulator in the power industry and specially in high voltage transmission cables. It is a saturated hydrocarbon composed of a long chain of an even number of carbon atoms attached each other by a covalent bond, each carbon atom is paired with two hydrogen atoms except for the chain extremities that are essentially methyl groups (see Figure 3).

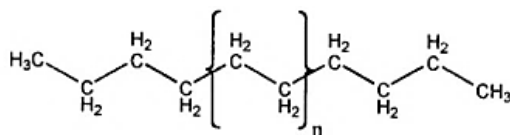


Figure 3: Structure of polyethylene (Peacock, 2000)

Internal partial discharges are considered to induce several chemical transformations to the polymer, however, they are usually modelled through a strictly physical approach without considering the chemical degradation of the material. This work is aimed at accounting for the presence of air within the microcavities, that subject to a partial discharge, will produce a weakly ionized plasma; the ionization and excitation of the main components of air (i.e. nitrogen, oxygen and water) will produce free electrons and several other subspecies (e.g. ions, radicals, etc.) able to attack the polymer structure and causing its degradation. Such process will involve three main steps: initiation, propagation and termination.

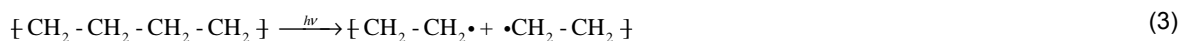
3.1 Initiation

According to Dissado and Fothergill (1992) the most crucial factor in the degradation of polymeric dielectrics is the presence of oxygen as dischargers in nitrogen are unable to initiate a chemical attack, this has also been verified experimentally by Sekii (2010). Therefore, the most active species will be molecular oxygen and its subspecies with a transient long enough to be able to reach the surface of the microcavity in order to interact with the material. Employing plasma simulations of atmospheric discharges Gordillo-Vázquez (2008) suggests that the species $O(^3P)$ (atomic oxygen), $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g^+)$ and OH exhibit long transients, of these, only $O(^3P)$ and OH (both of the radicals) are able to initiate an attack on the material through a reaction of hydrogen abstraction (Dorofeev, 2004):

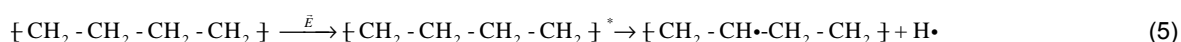


The probability of such attack is higher in the secondary hydrogen as the primary hydrogens in the chain extremities are less reactive and their number is greatly reduced in comparison with secondary hydrogens, thus, there is an equal probability of an attack occurring on any central secondary hydrogen to produce a macroradical able to propagate in other reactions.

According to Wheale et al. (1998), photodegradation could play an important role in the region nearest to the surface as such phenomena could produce the scission of C-C and C-H bonds:



On the other hand, employing molecular dynamics Bealing and Ramprasad (2013) suggest that the electric field could be able to cause an electronic excitation of the polyethylene resulting in a triplet state for which the cleavage of the C-H bond is thermodynamically favored:

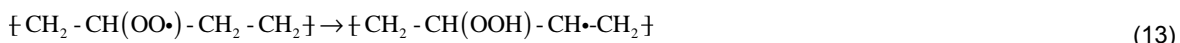
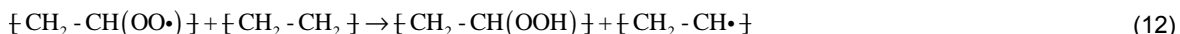
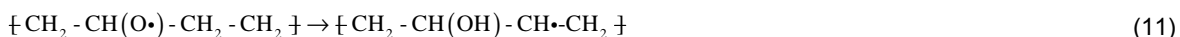
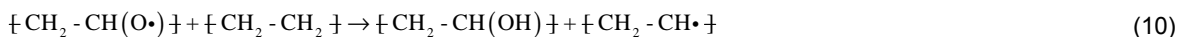


Therefore, the formation of molecular hydrogen could be explained either by process (4) and (5) by the abstraction of a second hydrogen atom in an adjacent chain or by the combination of free hydrogen radicals:

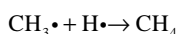


3.2 Propagation

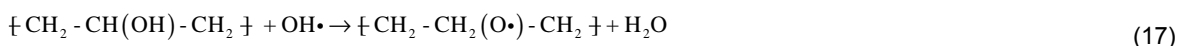
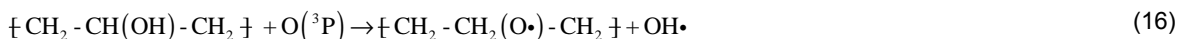
The macroradicals further react with atomic oxygen to form an alkoxy radical or with molecular oxygen to form a peroxy radical, these eventually form alcohols and a hydroperoxides by an intermolecular or intramolecular H-abstraction, the intramolecular attack is favoured by a ratio 1:5 (Dorofeev, 2004):



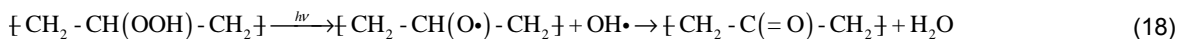
β -scission of end-chain methyl groups are responsible for the formation of methane (CH_4) while aldehydes are formed by the β -scission of alkoxy radicals (Wheale, Barker, and Badyal, 1998):



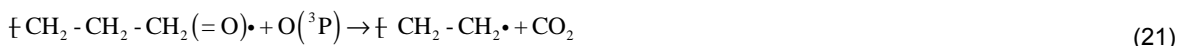
Alcohol groups are able to react with atomic oxygen and hydroxyl radicals to form once again a macroradical:



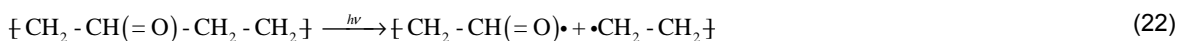
Ketones can be formed by the decomposition of hydroperoxide groups by a cage reaction (Gardette et al., 2013)



Acyl radicals are formed by the reaction of aldehyde groups with atomic oxygen and hydroxyl radicals, these are transformed into carbon dioxide (CO_2) by further reaction with atomic oxygen:



Acyl radicals are also form by the Norrish reaction type 1, while vinyl groups are formed in the type two mechanism :



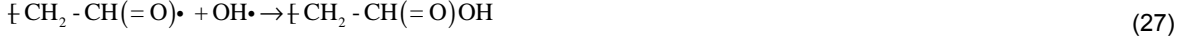
Decarbonylation of acyl radicals occurs by the participation of a photon, thus, explaining the formation of carbon monoxide (CO) :



3.3 Termination

Hydrogen atoms and hydroxyl radicals compete in the termination reactions to saturate alkyl macroradicals, alcohols and carboxylic acids (Dorai and Kushner, 2003):





Even though there are several other reactions that might participate in the degradation process these were not include mostly because the unavailability of proper mechanism and data and also to avoid increasing the complexity of the model.

4. Mechanism modelling

In order to simulate an internal partial discharge we must consider the transport and reaction of all the species that participate in the phenomena such as electrons, negative ions, positive ions and neutrals (i.e. radicals, ground species and excited species) along the three domains that compose the system, these are, the low-density media Ω^a (i.e. air), the high-density media Ω^s (i.e. the polymeric matrix) and the interface between them Γ (see Figure 4).

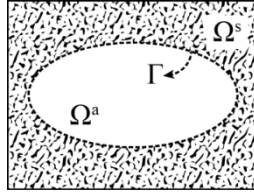


Figure 4: Gas-filled cavity inside a polymer matrix

As a result, the model is composed of the continuity equations of the species of interest together with an electrostatic equation (Poisson's equation) that takes into account of the modification of the electric field due to the electron avalanche inside the microcavity as seen in Table 1.

Table 1: Set of equations governing an internal partial discharge

	Air domain	Interface	Solid domain
Continuity equations	$\frac{\partial n_e^a}{\partial t} - \bar{\nabla} \cdot (n_e^a \mu_e^a \bar{E}) = R_e^a + Ph$	$\frac{\partial n_e^\Gamma}{\partial t} - \bar{\nabla} \cdot (n_e^\Gamma \bar{\mu}_e^\Gamma \bar{E}) = \frac{1}{e} (\bar{J}_n^a \cdot \bar{n}^a) + \frac{1}{e} (\bar{J}_n^s \cdot \bar{n}^s)$	$\frac{\partial n_e^s}{\partial t} - \bar{\nabla} \cdot (n_e^s \mu_e^s \bar{E}) = R_e^s$
	$\frac{\partial n_{n,i}^a}{\partial t} - \bar{\nabla} \cdot (n_{n,i}^a \mu_{n,i}^a \bar{E}) = R_{n,i}^a$	$\frac{\partial n_h^\Gamma}{\partial t} - \bar{\nabla} \cdot (n_h^\Gamma \mu_h^\Gamma \bar{E}) = \frac{1}{e} (\bar{J}_p^a \cdot \bar{n}^a) + \frac{1}{e} (\bar{J}_p^s \cdot \bar{n}^s)$	$\frac{\partial n_{h,i}^s}{\partial t} - \bar{\nabla} \cdot (n_{h,i}^s \mu_{h,i}^s \bar{E}) = R_{h,i}^s$
	$\frac{\partial n_{p,i}^a}{\partial t} - \bar{\nabla} \cdot (n_{p,i}^a \mu_{p,i}^a \bar{E}) = R_{p,i}^a + Ph$	$\frac{\partial n_{m,i}^\Gamma}{\partial t} = R_{m,i}^\Gamma$	$\frac{\partial n_{et}^s}{\partial t} = R_{et,i}^s$
	$\frac{\partial n_{m,i}^a}{\partial t} - \bar{\nabla} \cdot (D_{m,i} \bar{\nabla} n_{m,i}^a) = R_{m,i}^a$		$\frac{\partial n_{ht}^s}{\partial t} = R_{ht,i}^s$
Electrostatic equations	$\bar{\nabla} \cdot (\epsilon^a \bar{E}) = \frac{e}{\epsilon_0} (n_p^a - n_e^a - n_n^a)$	$\epsilon^a \bar{E}^a \cdot \bar{n}^a + \epsilon^s \bar{E}^s \cdot \bar{n}^s = e (n_h^\Gamma - n_e^\Gamma)$	$\bar{\nabla} \cdot (\epsilon^s \bar{E}) = \frac{e}{\epsilon_0} (n_h^s + n_{ht}^s - n_e^s - n_{et}^s)$

The subscripts e, n, p and m denotes respectively electrons, negative ions, positive ions and neutral species while et, h and ht denotes the trapped electron, holes (i.e. electron hole) and trapped electron holes in the solid phase. The source and loss term of species (i.e. chemical reactions) i is noted indicated as R_i and its density as n_i while the photoionization term is noted as Ph . The term μ_i and $\bar{\mu}_i$ denote the mobility and surface mobility of charged species while $D_{m,i}$ is the diffusion coefficient for neutral species. The flux of charged species migrating towards the surface and from the solid is noted as \bar{J}_i , the electric field is \bar{E} and ϵ^a, ϵ^s and ϵ_0 is the permittivity of air, solid and free space respectively. Therefore, the mechanism described in section 3 is contained in the reaction term $R_{m,i}^\Gamma$ and a comprehensive model of plasma chemical reactions is contained in R_i^a .

5. Conclusions

In the present work we developed a mechanism for the degradation of polymeric dielectrics (in particular polyethylene) under high electric fields. The model is based on an internal partial discharge as this phenomena is associated to the loss of performance of polymeric dielectrics. Such mechanism is able to explain the production of the different sub-products reported in literature and consist of a radical reaction scheme initiated by the impact of the different actives species produced in the ionization of the air contained in the microcavities. The mechanism resembles the modification of polymers treated by atmospheric plasmas, a process usually employed in industry to improve the surface characteristic of the material. Finally, a model for the simulation of an internal partial discharge has been developed and coupled with the mechanism resulting in a comprehensive chemical model of an internal partial discharge and the degradation of polymeric dielectrics.

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