Chapter 9

Models for Ageing of Electrical Insulation: Trends and Perspectives

9.1. Introduction

In the world of electrical engineering, device reliability is widely determined by the durability of the insulating materials' properties. Electrical equipment failure is often associated with the *dielectric breakdown* phenomena of the insulation. These phenomena can occur for electrical fields clearly weaker than the estimated breakdown field. This is widely due to the insulating materials' *electrical ageing*, a generic term which groups together all of the mechanisms by which the general characteristics of materials, and particularly their electrical properties, evolve over time under the action of working stresses.

Solid insulating materials have been introduced in a wide range of electrical equipment, from transport and distribution to the use of electrical energy. In particular, polymers are widely used for cables, capacitors, alternators, transformers and motors. We also find them in electronic devices, i.e. as coatings and in power components [LAU 99].

Although the main function of the polymer is to maintain electrical insulation, it also needs to have a good resistance to mechanical and thermal stresses. The understanding of ageing processes leading to either the loss, reversible or not, of functional properties, or to the dielectric breakdown of organic solid insulating

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materials must allow the behavior of this type of material to be predicted, according to the system's life (30 to 40 years, for example, for energy transport cables or alternators [LAU 99]). This behavior obviously defines the lifetime of systems in which these materials are integrated.

In this sense, the characterization of the physico-chemical properties of insulating materials and the understanding of complex relationships between their structure, whatever the scale (micro, nano, etc.), their properties and ageing, are key steps in the process of the development of new materials, allowing their improvement and the reliability of systems.

It is therefore fundamental to be able to develop a modeling approach leading to the prediction of materials' long term behavior, and to develop short classical laboratory tests, if possible.

This approach must take into account the fundamental recovering mechanisms typical of amorphous materials, elastic and plastic deformation, and the nonlinear character of these mechanisms when the conditions exceed a certain level, e.g. rate of rise, frequency, temperature. Charge transport phenomena, mechanical or electrical breakdown, bond energy ranges, the probable reversibility of breakdown and reactions also all need to be considered.

We now propose to briefly present existing models which could be good starting points for researchers interested in this area. Readers are obviously invited to refer to the bibliography for more detailed information.

Current trends and perspectives will be revealed by this analysis of the different ageing scenarios which have inspired the models.

9.2. Kinetic approach according to Zhurkov

9.2.1. *Presentation*

This model originated from experiments led by Zhurkov [ZHU 65], [ZHU 66], destined for measuring the breakdown time, under uniaxial mechanical stress on a series of different materials such as metals, crystals or polymers. This study is closely related to that of the application of a purely electrical stress, knowing that the electrical field could generate electromechanical stresses [DIS 97], [PAR 97], [BLA 95].

Taking polymers as an example, the experimental results led the author to write the following relationship:

$$\tau = \tau_0 \exp\left[\frac{U_0 - \gamma\sigma}{kT}\right]$$ [9.1]

with τ the lifetime, τ_0 a pre-exponential factor, k the Boltzmann constant, T the absolute temperature, σ the mechanical tensile stress, U_0 and γ being coefficients subsequently defined for the understanding of the physical sense of the experimentally established relationship [9.1].

The author could thus define, in the same experimental frame, the coefficient τ_0 whose value coincides with the value of the thermal oscillation period of atoms in a solid. τ_0 is of the order of 10^{-13} s independently of the structure and the chemical nature of the material. By writing equation [9.1] in the form:

$$kT\ln\left(\tau/\tau_0\right) = U_0 - \gamma\sigma$$ [9.2]

where the left part of this equation is identified with an energy U which represents the barrier to be crossed in order to initiate a breakdown. τ_0 being determined, we can draw the curves from previous results and $U(\sigma)$ shows a linear relation between the effective barrier U and the applied stress. The extrapolation for a null stress gives values of U_0 for materials placed under testing. The comparison of these values with those of interatomic bond dissociation energies deduced from the thermal destruction of polymers, has led Zhurkov to identify U_0 to an atomic bond energy.

The follow-up of the fracture kinetics of the polymer subjected to a mechanical stress has been made by electron spin resonance (ESR) experiments through which the authors have observed the rate of free radical formation increasing in an exponential manner as a function of the applied stress [ZHU 66]. Zhurkov thus estimated that the breakdown of polymers is essentially due to the breaking of covalent bonds [ZHU 65], [ZHU 66], [ZHU 83]. This mechanism is debatable.

In Figure 9.1, Zhurkov evoked the possibility of the creation of a cavity or a free space smaller than a micron, due to chemical bonds breaking which lead to free radicals. Indeed, Figure 9.1(a) illustrates the thermo-mechanical breaking of a covalent bond leading to the creation of two radicals. These two highly reactive radicals, in Figure 9.1(b), will then interact with the adjacent molecule and thus create two new radicals. A chain reaction is produced (see Figure 9.1(c)). The final result of this process is represented in Figure 9.1(d) by a submicronic cavity into which partial discharges may be initiated, after coalescence for example, under size

and gas pressure conditions (the Pashen Law), leading to the breakdown of the material.
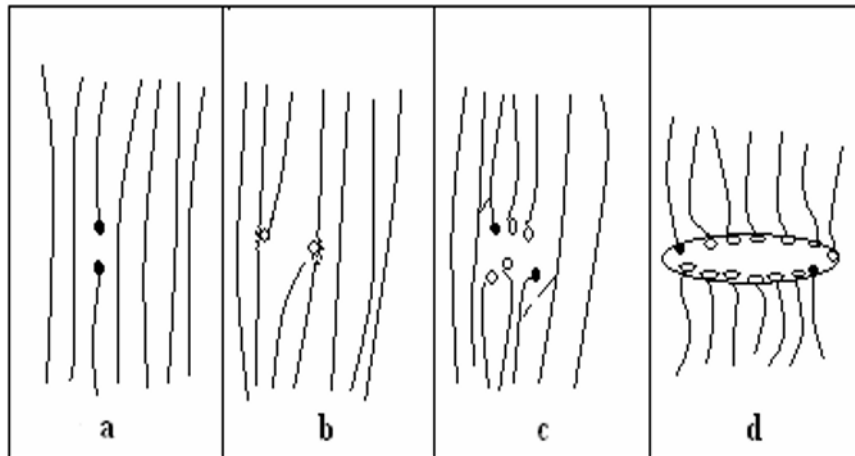

Figure 9.1. *Mechanism of a submicronic cavity generation, from [ZHU 72]*

The coefficient γ represents the volume which undergoes the stress, i.e. an activation volume. In a paper published in 1983, Zhurkov [ZHU 83] expressed the coefficient γ as a function of the parameters suited to the material structure, i.e. the calorific capacity, the linear thermal expansion coefficient, Young's macroscopic modulus and a surcharge coefficient. Unfortunately, the paper did not demonstrate the means by which this term can be expressed as a function of the different variables which are at the same time macroscopic and microscopic.

9.2.2. *Interpretation of the process and introduction to the notion of a dilaton*

The base of this kinetic theory of breakdown is the overloading of some chemical bonds with respect to the constrained polymer volume. The probability of their breakdown is quite high, in such a way that they become initiator sites for the insulating material breakdown [ZHU 69].

The vibration frequency of the molecules of a polymer depends on the amplitude of the strength applied, the atomic bond energy and the valence angles. The deformations of these bonds and angles modify the vibration frequency of the principal chain. From this, Zhurkov and his team [ZHU 69] determined the amplitude of real mechanical stresses acting on the polymer chains by following the vibration frequency changes, through infrared spectrophotometry.

The coefficient γ related to the structure allows, for a given strength and temperature, the activation volume as well as the emergency time of a submicronic breaking to be known. This coefficient is defined by the relationship:

$$\gamma = \frac{C.\chi}{\alpha.Y} \qquad\qquad [9.3]$$

where C is the specific heat, χ an overloading coefficient proportional to the mean free path of a phonon Λ, α the linear thermal dilation coefficient and Y the Young's macroscopic modulus.

The kinetic approach presented by Zhurkov makes the local breakdown appear like a thermal fluctuation process, which could bring into play the breaking or the rearrangement of atomic chains, or both simultaneously. The preexisting defects, or those created under stress because of thermal fluctuations, are localized in an element of the material volume. The notion of dilatons was thus introduced and has been tackled by different authors (see below).

9.2.2.1. *Definition according to Zhurkov (1983)*

Zhurkov refers to an ancient idea, that of Smoluchowski (1908), who was the first to define the concept of negative fluctuation of density [ZHU 83]. This phenomenon appears spontaneously in a solid as the consequence of a random atom displacement, or the superimposing of elastic waves describing network vibrations. The interatomic bonds are then stretched and weakened. The density of the region concerned decreases and this zone thus becomes a trapping site for phonons (these latter being defined as energy *quanta* of an elastic wave, their mean free path Λ representing the dimensions of the density fluctuation region, which is called a *dilaton*). The amplitude of Λ and that of the dilaton both depend on the structure of the existing defects, the impurities, etc.

9.2.2.2. *Definition according to Kusov (1979)*

Kusov uses the previous idea but excludes the necessity of the presence of a defect. The defects play the role of catalysers in the breakdown process, by favoring the conditions required for the outbreak of dilatons [KUS 79]. In return, he mentions the importance of anharmonicity in the process of thermal fluctuation formation. This anharmonicity allows trapped energy to favor the thermal dilation of the zone concerned. To better explain this process, Kusov considers a linear chain of carbon atoms, as represented in Figure 9.2 where AB is the fluctuation zone, r is the distance between two neighboring atoms which do not belong to the fluctuation zone, and r' is the distance between two neighboring atoms situated in the fluctuation zone. The chain is at temperature T, and the atoms can only make longitudinal vibrations.
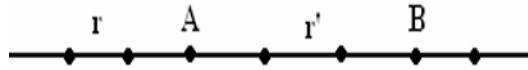
Figure 9.2. *Linear chain of carbon atoms*

AB is the zone where local fluctuations and density are negative. In other words, it is the zone where the atoms are more spread out from one another which we call the dilaton. d is the fluctuation dimension and $-\Delta_{loc}$ is the fluctuation intensity, such that:

$$\Delta_{loc} = (r - r')/r \qquad\qquad [9.4]$$

Kusov showed that a phonon exchange between the dilaton region and the rest of the chain causes an energy accumulation in the fluctuation region AB. Because of the relaxation phenomena, a competition appears between the increase and the decrease of the fluctuation intensity (Δ_{loc}). If the initial fluctuation density is sufficiently important, thermal expansion prevails ($\Delta_{loc} \geq \Delta_{critical}$) and wins over the relaxation. In the dilaton region, the energy accumulation can lead to the chain breaking.

9.2.2.3. *Definition according to Petrov (1983)*

Oscillations in a solid imply collision processes of phonons. The collisions could take place between phonons, defects or surfaces. Petrov therefore took into account the mean free path Λ of the phonon to define the spatial dimension of the fluctuation. An accumulation of phonons is similar to a local increase of thermal energy which leads to a deformation of the medium. This deformation has a limit when a stress is applied. Petrov views dilatons as sub-systems having spatial characteristics Λ, an interatomic distance a, and a volume $V = \Lambda.a^2$. The dilaton is an elastic deformation region which absorbs the phonons which traverse it [PET 83].

9.2.2.4. *Universal breakdown kinetics*

In conclusion, the approach of a breakdown mechanism of interatomic bonds developed by Zhurkov's team to establish universal breakdown kinetics on metals and polymers deserves attention. However the γ parameter which depends essentially on the structure of the material cannot be used to predict the breakdown time of the insulating material. Within this latter, a vacuole resulting from the submicronic cavities, is created and its insulating properties are damaged in an irreversible manner. It is important to point out in this model that the parameter γ

represents an activation volume; this volume is presented in the following model which relies on thermodynamic processes.

9.3. Thermodynamic approach according to Crine

The model proposed by Crine is founded on a simple thermodynamic concept, taking into account thermodynamic parameters such as intermolecular cohesion energy, the amorphous phase thickness of a material [CRI 90], breakdown theory related to the free volume proposed by Artbauer [ART 96], the concept of submicronic cavity initiation, and the fact that the first stage of electrical ageing is essentially a molecular process. This model, applicable to ageing under alternative stress, supposes that the deformation of macromolecular chains is a fatigue process accelerated by frequency. Of course, purely electronic concepts described by numerous models are brought into consideration during the final breakdown mechanism.

The fact that processes such as electrical conductivity, dielectrical or mechanical relaxation depend on temperature, implies that they are most often expressed by the Arrhenius relationship:

$$X = X_0 \exp\left(-E / KT\right) \qquad [9.5]$$

where X_0 is an empirical factor and E the apparent activation energy.

Crine presented a simple thermodynamic interpretation of the compensation law applicable to polymers. An equation is then proposed by Crine relating Gibbs' free energy of activation theory to the fundamental thermodynamic parameters [CRI 84].

From Eyring's theory, the reaction which allows the passing from an active state to an upper state follows the relationship:

$$K_f = (kT / h)\exp(-\Delta G^{\#} / kT) \qquad [9.6]$$

where $\Delta G^{\#}$ is the activation free energy. This free energy relates the activation enthalpy, the activation entropy and the temperature by the relationship:

$$\Delta G^{\#} = \Delta H^{\#} - T.\Delta S^{\#} \qquad [9.7]$$

We can then rewrite relationship [9.5] in the form:

$$X = X_0 \exp(\Delta S^{\#} / k)\exp(-\Delta H^{\#} / kT) \qquad [9.8]$$

A few years ago, a theoretical interpretation was proposed by Lawson [LAW 57] and Keyes [KEY 58] to demonstrate that, for a process having a weak activation volume $\Delta V^{\#}$, the following expression takes place:

$$\Delta H^{\#} = \Delta V^{\#} / K.\beta \qquad [9.9]$$

where β represents the isothermal compressibility coefficient and K a dimensionless constant. Subsequently, $\Delta S^{\#}$ can be expressed as:

$$\Delta S^{\#} = \Delta V^{\#}.(\alpha / \beta) \qquad [9.10]$$

where α represents the thermal dilation coefficient. We can then deduce the Gibbs free energy as a function of thermodynamic parameters (α and β), the activation free volume $\Delta V^{\#}$, the K parameter and the temperature, which gives:

$$\Delta G^{\#} = \left[(\alpha / \beta).\Delta V^{\#} \right].\left[(K.\alpha)^{-1} - T \right] \qquad [9.11]$$

In order to verify this equation, it is important to know the signification of the K parameter. From Keyes [KEY 58] and Barker [BAR 67], this latter can be better understood if associated to the Grüneisen constant (γ) of polymers. This constant measures the anharmonicity of intermolecular vibrations in solids and is related to thermal and mechanical properties by the relationship:

$$\gamma = \alpha.V / \beta.C_V \qquad [9.12]$$

where V is the molar volume and C_V, the molar calorific capacity at constant volume. Knowing K, $\Delta S^{\#}$ or $\Delta H^{\#}$, α and β, it is possible to evaluate the activation free volume $\Delta V^{\#}$ for a given process.

An important fact is to note here: the value of the activation volume $\Delta V^{\#}$ is close to the volume obtained by Zhurkov [ZHU 65], [ZHU 66], from the coefficient γ for purely mechanical tests. This reinforces the logic of the approach which was elaborated by using thermodynamic parameters and supposing that the first stage of ageing is a molecular fatigue process.

Parpal and Crine [PAR 97] proposed a model which takes into account a critical electrical field beyond which submicronic cavities can be created and then become the seat of discharges, leading to final polymer breakdown. The value of this field can be determined by knowing the cohesion energy of the polymer; this leads to a simple

lifetime relation, which only takes into account two physical parameters: ΔG_0 representing the activation energy of the process distorting the chains being considered, and λ_{max} representing the maximum size of submicronic cavities created.

The major characteristic of this model is the presentation of electrical ageing as a phenomenon which is not necessarily associated with an electron displacement under the action of an electrical field but, rather, with a fatigue phenomenon under an alternative field. The proposed ageing process happens in two very distinct steps:

– the first step is a purely molecular process. It consists of a rearrangement of the polymer's free volume, induced by an electromechanical deformation of macromolecular chains under the action of a field beyond a certain value;

– the second process is an electronic avalanche. When the microcavities are created, the charges injected and accelerated under the action of the electrical field acquire enough kinetic energy (from the electrical field) to break the bonds and consequently increase the size of the microcavities. Bigger cavities then become available, allowing the electrons to break the intramolecular bonds, leading to the final breakdown.

Above a certain critical energy, the weakest bonds (Van der Waals) can be broken under the effect of electromechanical deformations due to an applied alternative electrical field [PAR 97]. This hypothesis is reinforced by work done on cables extruded with PE where a cyclic deformation was observed during the application of the alternating field [DAV 94]. After the breaking of the bonds under consideration, the macromolecular chains can move and create a sort of rearrangement of the free volume.

The breakdown process is controlled by an energy barrier of a height equal to the activation energy $\Delta G^{\#}$. Parpal and Crine [PAR 97] established the fact that this energy barrier does not represent a simple trapping or detrapping phenomenon of entities, but rather the phenomenon of bond breaking. This implies that the displacement of carriers under a high field preferably appears in the void present in the submicronic cavities created, rather than in the hopping phenomenon from one electronic trap to another.

Following the analysis of over 200 publications, it appears that the inverse power law [$t = A.F^{-n}$] does not satisfy ageing data corresponding to long periods [DAN 96]. The results from experiments on LDPE, XLPE, and EPR follow an equation of the type:

$$t = (h / 2kT) \exp(\Delta G_0 / kT) \csc h(e\lambda F / kT) \tag{9.13}$$

where t is the time required to reach the state corresponding to broken bonds, or, in other words, the time required to get over the free energy barrier of height ΔG_0; h and k are, respectively, the Planck and Boltzmann constants, λ is the deformation distance of the molecular chains and e is the charge of the electron.

The interpretation of the phenomenon is as follows: when an electrical field F is applied, the macromolecular chains are distorted over a distance λ, and ΔG_0 is then reduced to a quantity equal to the deformation energy applied to the barrier, which is $W = e\lambda F$. We shall see later that, in order to correlate his model with a thermodynamic parameter of the polymer, i.e. its cohesion energy (E_{coh}), Crine calls on the energy brought into play during the application of an electromechanical stress σ on an activation volume ΔV. W can then be written in the form $W = \Delta V.\sigma$.

For fields $F > F_c$ (critical field), equation [9.13] is reduced to:

$$t = (h / 2kT) \exp[(\Delta G_0 - e\lambda F) / kT] \qquad [9.14]$$

which means that for high fields, there is a regime where t varies exponentially with F. Knowing ΔG and λ from the exponential regime, it is then possible to calculate t for weak fields ($F < F_C$), i.e. by using equation [9.14]. However the experimental results of Equation [9.14] indicate that λ is constant only in the exponential regime and it varies with F for weak fields. It is therefore fundamental to determine the value of this critical field F_C from experimental data, which are the thermodynamic parameters suitable for polymers.

For a large range of temperatures (from 77 K to fusion temperature), Crine *et al.* showed that the dielectric behavior of numerous polymers depends on the cohesion energy density of the polymer defined as the cohesion energy (E_{coh}) divided by the molar volume (V).

If the Van der Waals bond breaking is the first stage of the mechanical breakdown, it implies that the deformation energy W is greater than the cohesion energy E_{coh} of the polymer:

$$W \succ E_{coh} = \Delta H_{vaporization} - kT \qquad [9.15]$$

where ΔH is the vaporization heat of the polymer [CRI 97].

By hypothesis, W then corresponds to a strain exerted on the polymer, which is:

$$W = \Delta V * \sigma \qquad [9.16]$$

We easily deduce from equations [9.15] and [9.16] the critical stress σ_c, above which the submicronic cavities can be initiated:

$$\sigma_c = E_{coh} / \Delta V \tag{9.17}$$

The critical electrical field required to significantly distort the Van der Waals bonds is that which brings an energy (or effort) greater than the cohesion energy, so:

$$E_c = E_{coh} / e\lambda_{max} \tag{9.18}$$

The most interesting aspect of the Crine model is that it permits the parameter λ to be adapted to the morphology of the polymer. With a weak field, the value of λ deduced from equation [9.13] is weaker than that deduced from equation [9.14]. This allows us to say that λ varies with the field F until a maximum value λ_{max} for $F_c > 20$–40 kV/mm.

According to Crine, we can then:

− deduce the fundamental thermodynamic parameters. The value of the free volume $\Delta V^{\#}$ of an activated process can be calculated by using activation enthalpy and entropy and not the activation energy which is often difficult to identify;

− determine the required time for the breaking of intermolecular bonds from a critical field (F_c), i.e. the required time for the creation of submicronic cavities and therefore breakdown initiator sites. This threshold is also identifiable from thermodynamic parameters such as cohesion energy (E_{coh}) and parameters specific to the polymer;

− affirm that the first electrical ageing process of polymers is a fatigue phenomenon induced by the application of an alternative electrical field. This phenomenon is accelerated by frequency. It essentially constrains the Van der Waals type bonds, i.e. intermolecular bonds; hence, this is the principal difference between this model and that of Zhurkov, which does not show interest in electron displacement because covalent bonds are involved.

Amongst the parameters that the Crine model does not take into account, we particularly note the space charge (see Chapter 6), which other authors have been very interested in [DIS 95], [DIS 92], and the distribution of submicronic cavities, etc.

9.4. Microscopic approach according to Dissado–Mazzanti–Montanari

According to Dissado, Mazzanti and Montanari, any damage is associated with the presence of micro rather than macro defects. Microscopic or mesoscopic defects are associated with the presence of space charge regions. These latter are chiefly trapped at the extremities of cavities present in the insulating material or are localized at the level of inclusions and contaminant, whether conductors or not. They significantly modify the local field, increasing the ageing reaction rate and can introduce new degradation modes. Therefore, the distribution of these space charges in the material creates local fields. This is the basis for the development of the Dissado, Mazzanti and Montanari model (DMM) for ageing related to space charges [DIS 97].
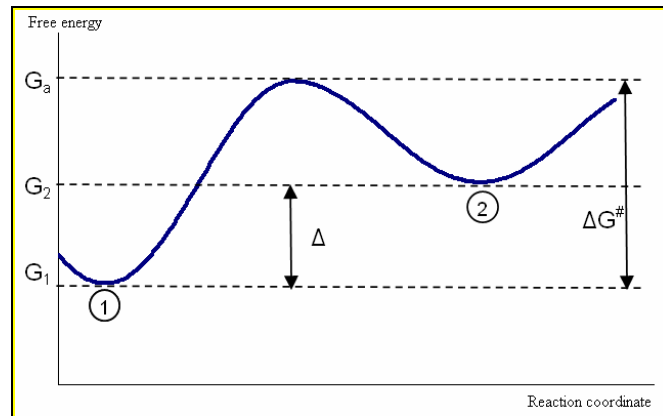

Figure 9.3. *Diagram of the free energy in the absence of electrical current [DIS 95]*

This model is therefore based on a thermodynamic approach describing the degradation rate of insulating materials submitted to thermal and electrical stresses. A polymer insulation is composed of a set of units each subjected to local reactions. The degradation of the material is the consequence of the net evolution of those local reactions which changes the morphology of the polymer in such a way to set off a rapid dielectric breakdown process. The ageing process is described according to a reaction which allows the polymer to pass from a initial non-aged state (state 1) to an aged final state (state 2), the passage from (1) to (2) possibly being reversible. To each of these two states is associated a free energy for each entity (Gibbs energy), G_1 and G_2 respectively (Figure 9.3). These two alternative states are connected by an energy barrier ΔG^* and the two reversible reactions take place with rates depending on species concentrations in both local states and the energy barrier height which links these two states [DIS 95].

9.4.1. *Thermal ageing*

Beyond a critical temperature which allows a thermal degradation phenomenon to be set off, the fraction of concentrations in a dielectric, defined by A = c_2 / (c_1+ c_2) (where c_1 and c_2 are the species concentrations present in states 1 and 2, respectively) undergoes a passage towards a value at the equilibrium A_{eq}. This value essentially depends on the absolute temperature T and the difference of the free energy for each entity between states 1 and 2:

$$A_{eq} = \frac{1}{1 + \exp(\Delta / kT)} \qquad [9.19]$$

with $\Delta = G_2\text{-}G_1$ and k the Boltzmann constant. In the absence of applied external stresses, the conversion to a new equilibrium value is supposed to be weak in insulating materials. The application of external stresses leads to a change in local energies, thus causing the reduction of Δ and favoring a conversion towards the equilibrium state.

The value of A at an ageing time t, $A(t)$ is given by the expression:

$$\ln\left[\frac{1 - A(t)/A_{eq}}{1 - A(0)/A_{eq}}\right] = -(K_1 + K_2)t \qquad [9.20]$$

With $A(0)$ the initial value of A which will subsequently be supposed to be zero, K_1 and K_2 are the rate constants of the degradation reversible reaction in both directions, for 1 and 2 respectively.

The breakdown takes place when a critical quantity of units passes from the initial to the final state. The fraction of concentrations then reaches a limit value A^*.

Thus equation [9.20] is written in the following way by replacing A by A^* and t by L (the lifetime of the insulating material):

$$L = (K_1 + K_2)^{-1} \ln\left[\frac{1}{1 - A^* / A_{eq}}\right] \qquad [9.21]$$

By introducing the expressions of K_1 and K_2 in equation [9.21], we get:

$$L(T) = \frac{h}{kT} \frac{\exp(\Delta_G / kT) \ln[A_{eq} /(A_{eq} - A^*)]}{\exp(-\Delta / 2kT) + \exp(\Delta / 2kT)} \qquad [9.22]$$

where h is the Planck constant, and $\mathit{\Delta G}$ is a parameter depending on the activation free energies of states 1 and 2, as follows [DIS 01]:

$$\Delta_G = G_a - \frac{G_1 + G_2}{2} \qquad\qquad [9.23]$$

The necessity to reach a critical value of conversion A^* justifies the existence of a threshold temperature for the damaging of insulating materials [DIS 95]:

$$[9.24]$$

$$T_{th} = \frac{\Delta}{kT \left[\ln \left(\frac{1 - A^*}{A^*} \right) \right]}$$

9.4.2. *Ageing under electrical field: space charges effect*

According to Dissado, Mazzanti and Montanari, when an electrical field is applied, space charges injected from electrodes, semi-conductors or discharge phenomena move towards sites where they can be trapped. In organic materials, the distribution of the charge trapping sites is not uniform within the material. This is the case for PE in which the sites are situated at the interface of the amorphous and crystalline zones. Consequently, local charge concentrations are formed. This local aspect takes place especially around morphological defects, inclusions and impurities. The shape, size and density of microcavities can vary significantly according to the materials and the insulating systems [DIS 95].

The Dissado, Mazzanti and Montanari (DMM) model describes the formation time of defects (microcavities, holes) in the insulating materials as a function of the electrical field and the applied thermal stresses. The model was initially developed in direct regime. The model parameters significantly change when dealing with data in an alternating current. Consequently, an addition, for an alternating regime, was then proposed.

In order to simplify the analytical approach for obtaining the model, the following hypotheses have been taken into account:

− charges accumulated at the charge centers are injected from electrodes such that the injection current is insufficient to generate a direct breakdown. The trapped charges get to equilibrium in a much shorter time than the insulation life;

− close to the charge centers, the external field (Laplacian) E is negligible with respect to the field created by the space charges;

− charge centers are spherical, of radius r_0, with a uniform charge density and all possess the same amount of charge q_c which depends on the applied field, $q_c = CE^b$;

− a number N_m of species or "moieties" is affected on average in each microcavity. These species reside within a thin shell of thickness λ at the cavity wall;

− the material is homogenous at the macroscopic scale [MAZ 05].

In the presence of an electrical field, the system reaches a global disequilibrium state and goes through modifications over time, in order to reach a new thermodynamic equilibrium.

The effect of trapped space charges is to increase the local electrical field which reaches its maximum value at the extremities of the space charge regions. Consequently, elementary electrostatic and electro-mechanical stresses and strains are created in these regions with a local storage of electrostatic and electro-mechanical energy. This effect concerns the species in their initial state whose free energy G_1 increases by a value ΔG_m (see Figure 9.4), according to the equation:

$$G_1(E) = G_1 + \Delta G_m \qquad [9.25]$$

with:

$$\Delta G_m = AW_{es} + BW_{em} \qquad [9.26]$$

where W_{es} and W_{em} are, respectively, the electrostatic and electro-mechanical energies, A and B are proportionality constants with A and B $\leq$ 1. The detailed expressions of the energy variation are explained in [DIS 95].

The energy barrier of the degradation reaction (direction 1) decreases (whilst that of the reaction in the opposite direction increases) proportionally to the stored electro-mechanical energy and so a net transfer to the reaction products (state 2) takes place. The breakdown is related to the fact that the fraction of the degraded species A exceeds, locally, a critical value A^* which corresponds to the creation of cavities sufficiently large to set off partial discharges, and consequently electrical arborescence phenomena.

Thus, the ageing process is essentially a sort of apparition of local progress, and rather than the time to break down, the DMM model determines the time required for the formation of voids in critical amount to trigger a breakdown.
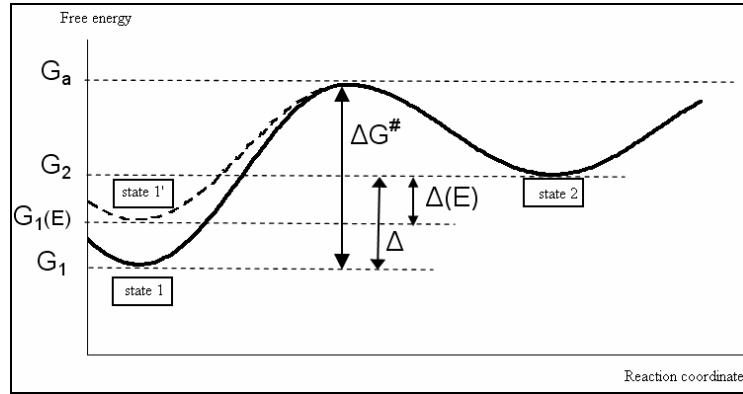
Figure 9.4. *Diagram of free energy in presence of electrical current [DIS 97]*

After the analytical development of these hypotheses, the final expression of the DMM model under a direct field is the following:

$$L(E,T) = \frac{h}{2kT} \exp\left[\frac{\frac{\Delta H}{k} - \frac{C'E^{2b}}{2}}{T} - \frac{\Delta S}{k}\right] \ln\left[\frac{A_{eq}(E)}{A_{eq}(E) - A^*}\right] \left[\cosh\left(\frac{\frac{\Delta}{k} - C'E^{2b}}{2T}\right)\right]^{-1} \quad [9.27]$$

$$\text{with: } A_{eq}(E) = \left[1 + \exp\left(\frac{\frac{\Delta}{k} - C'E^{2b}}{T}\right)\right]^{-1} \quad [9.28]$$

with $A_{eq}(E)$ being the value of A at equilibrium between both the reactions (in opposite directions), T is the absolute temperature, ΔH and ΔS are, respectively, the activation enthalpy and entropy for each species, and Δ is the free energy difference between the reactants and the products. C' is a constant which essentially depends on the properties of the materials:

$$C' = \frac{B\alpha_E \delta\lambda C^2}{16\pi\varepsilon^2 r_0^2 N_m k} \quad [9.29]$$

where B is a proportionality constant between the stored electro-mechanical energy and its contribution to the free energy barrier of the degradation reaction, δ is the elementary deformation and α_E is the electrostriction coefficient. C and B relate the previous expression to the relationship between the stored charges in the charge centers and the applied field [MAZ 05].

To conclude, the proposed thermo-electrical model essentially relies on the idea that, following the application of a thermo-electrical stress, the space charges trapped within an insulating polymer material contribute considerably to the ageing phenomenon of the material. The effect of the space charges is to create local fields concentrated around charge centers. This local aspect generates electro-mechanical stresses which modify the free energies associated with two states brought into play for the definition of the ageing reaction. Since the ageing reaction rate is led by these free energies, it will in turn be modified by them.

9.5. Conclusions and perspectives

All these approaches allow us to consider that the long-term breakdown of insulating materials is not, in general, a direct and simple consequence of the application of a voltage, but a much more complex process related to a synergy of environmental stresses, such as the accumulation of charges, a local temperature increase, direct or induced mechanical stresses, UV radiation, humidity rate, etc.

These many factors contribute to a deterioration of physical properties of the material and, consequently, to its reliability as an electrical insulation.

A high number of mechanisms are involved in the description of the ageing process of organic insulating materials. Two principal approaches have been tackled. First, the model presented by the Russian school, which could be considered as a macroscopic approach. This approach keeps a global description of the degradation process based on the study of solid insulating samples or on systems. Second, the Crine and Dissado, Mazzanti and Montanari models offer a more microscopic approach where, on the one hand, we place ourselves upstream from previous phenomena and, on the other hand, the behavior of the solid insulating material is taken into account at the molecular scale.

The first two theories which we have briefly analyzed have the mechanical behavior of the polymer in common, but with an essential difference concerning the nature of this behavior. The tensile stress studied by Zhurkov leads to the breaking of interatomic chemical bonds, and is revealed in particular by the formation of free radicals. Covalent bonds are then involved and the breakdown is irreversible. This theory does not tackle the study of displacement phenomenon within the material of entities such as electrons, space charges, etc. Tensile stress would cause, according to Crine, deformation and chain rupture in the free volume where the Van der Waals bonds are especially affected. In this case the damage remains reversible until a critical value of the deformation is reached. In both theories, breakdown leads to the initiation of submicronic cavities which could become the site of discharges.

In the theoretical approach tackled in the DMM model, the ageing phenomenon essentially takes place because of the formation of space charge centers during the application of a field. A threshold voltage is then defined as a value from which the local field created by the charge centers is sufficient to accelerate the ageing phenomenon and trigger a rapid breakdown within the material.

The theorical approaches of breakdown mechanisms of electrical insulating materials have, of course, the simple understanding of phenomena as a first objective, then their application to real systems for which security and lifetime problems are posed. The prediction of a long or short-term breakdown is difficult to make if we want to take into account all of the intervening parameters.

Thus, it can be seen that there are numerous attempts at ageing models, each with their own difficulties. A two-site model has been systematically proposed by different authors for the representation of the free energy variation between two states to define the ageing phenomenon. However, the energies in polymers are associated with distribution and relaxation functions. In this case, the two-site model is not representative in defining the nature of entity displacements within a polymer material.

Among the simplifications of the existing models, one consists of considering the structure of the organic material as homogenous. However, most industrial electrical organic insulating materials are semi-crystalline, i.e. constituted of an amorphous and a crystalline phase; hence, the necessity of introducing in these models the notions of anisotropy and heterogeneity. Further, several parameters which could have an influence on the ageing phenomenon are not considered in the already existing models. We could mention, for example, the role of the temperature to which the material is exposed with respect to the characteristic temperatures of that material, such as the glass transition temperature T_g, the melting temperature T_m and the crystallization temperature T_c.

Thus, the issues of ageing and the breakdown of solid organic insulating materials are, and will no doubt remain for many years to come, the subject of long investigations.

9.6. Bibliography

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