

A MOLECULAR APPROACH TO THE ELECTRICAL AGING OF XLPE CABLES



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ABSTRACT

The relation between electrical aging and breakdown of XLPE and its molecular characteristics is examined. We show that our new aging concept describes the electrical aging process of XLPE and, in fact applies to all polymers with free volume. The physical significance of the basic parameters (activation energy and volume) is discussed and it is shown that XLPE cable aging directly depends on the breaking of C-C bonds. The influence of samples size is briefly discussed as well as the influence of temperature cycles. Testing under high frequency might be reliably translated to power frequency condition with our model.

KEYWORDS

Electrical aging, testing, molecular properties, size effect.

INTRODUCTION

Electrical aging of polymer insulated cables is still poorly known and customarily accelerated aging results are plotted according to an inverse power law, such as $t = CF^{-n}$, where t is the time, F is the applied field, C and n are constants characteristic of the cable. We have shown in previous work (1,2) that life extrapolations made from such graphs are, at best, dubious since the linear relation between log field and log time does not hold for long aging times (1,2) and it is not always evident at short aging times. In fact, results fit much better a semi-log plot between F and $\log t$. We have proposed an aging model that describes very well actual accelerated aging data (1,2). There are few other models able to predict lifetime at the temperatures where most transmission cables operate (3-6). The Crine (1,2), Dissado and Montanari (3-4), and Lewis (5-6) models of aging predict the times to failure more accurately than the empirical inverse power law model that is currently used in cable design. Some of the models have constants that have to be determined experimentally, and it is likely that these constants will vary according to the extrusion conditions. The three models predict a threshold electrical stress, below which there is little or no electrical aging. Above the threshold stress, the times to failure decrease with increasing electrical stress. One major theoretical question often raised concerns the physico-chemical origin of the basic parameters (i.e. the activation energy and volume) in our model and their evolution with the aging conditions. One objective of this paper is to answer this question.

It should be made clear that these models do not entirely solve all the complexities involved in the electrical aging of

actual cables in service. One difference between accelerated aging in the laboratory and service is usually the size difference of the cable samples. It is well known, although poorly understood, that breakdown decreases with increasing insulation thickness and with the cable length (1,7,8). We present preliminary calculations attempting to correlate the sample size with the activation volume of the tested samples. Another problem is that some cables are successfully operated at ~ 15 kV/mm, and some have undergone prolonged aging tests at stresses greater than 20 kV/mm, which are well above the so-called threshold field, i.e. in a domain of accelerated aging. Although we do not have a complete answer to this apparent paradox, we nevertheless submit some ideas that might explain the significant difference between tests performed at constant temperature and aging in service under temperature cycles. The implication on the significance of accelerated aging tests on the prediction of cable life in service is also discussed. Finally, the accelerating influence of frequency on electrical aging is discussed and calculations are presented to show it is possible to significantly and reliably shorten the duration of aging tests by using high frequencies fields.

THE BASIC PARAMETERS IN OUR AGING MODEL

Our model based on the rate theory has been presented elsewhere and we will give here only the main equation. The time t needed to reach the final (aged) state is given by

$$t = (h/2fkT) \exp (\Delta G/kT) \operatorname{csch}(\frac{1}{2} \epsilon_0 \epsilon' \Delta V F^2/kT) \quad (1)$$

where f is the field frequency; the factor 2 comes from the fact that there 2 changes of polarity for each field cycle. Equation 1 predicts that at zero field, t will be equal to infinity since $\operatorname{csch}(0) = \infty$. Thus, there will be some sort of "tail" at low fields, where t will slowly tend toward ∞ . At high fields, Eq. 1 reduces to

$$t = (h/2fkT) \exp [(\Delta G - \frac{1}{2} \epsilon_0 \epsilon' \Delta V F^2)/kT] \quad (2)$$

which predicts a linear relation between F^2 and log time. In Refs. 1,2 we have shown that various dry aging results of XLPE cables are well described by the linear relation at high fields (Eq. 1) and the tail (Eq. 2) at low fields (see Fig. 1). From the slope and intercept of the high field regime in F^2 vs. $\log t$ plots, it is then possible to determine $\square V$ and $\square G$,

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respectively. It appears that at 22°C the activation energy value is in the $1.95\text{-}2.1 \times 10^{-19}$ J range. The activation volume varies more widely and seems sensitive to the sample volume (1,2) as shown later.

The threshold field is in the 9-12 kV/mm range for XLPE at 22°C; an equation giving its exact definition will be presented in a subsequent publication. Note that the value of this threshold field is the same whatever the theoretical model used. Note also that its value decreases with increasing temperature but little is known regarding the influence of temperature cycles.

The activation energy and the strength of C-C bonds

When Eq. 2 is applied to a wide variety of cable aging results, it appears that the activation energy ΔG is almost the same for all cables aged at 22°C in air, that is around 2.05×10^{-19} J (1.28 eV). Intuitively, one would expect that this energy should be related to the strength of the C-C bonds of the PE molecular chains. However, the dissociation energy D for C-C bonds is 5.6×10^{-19} J, that is more than 2 times larger than the average ΔG value. Another major difficulty is to explain the breaking of bonds, whose strength is 3.5 eV, by modest applied stresses, mostly below 0.2 eV. In order to resolve that problem, several earlier models explained mechanical failure by a chain slip process induced by the applied stress. Zhurkov and co-workers (9) have proposed long ago that mechanical breakdown was a kinetic bond scission process and in support of their affirmation they detected free radicals during the aging and breakdown processes. Assuming that strained bonds might relax during deformation, results in a C-C bonds strength value reduced to 30-40% of its original value (10).

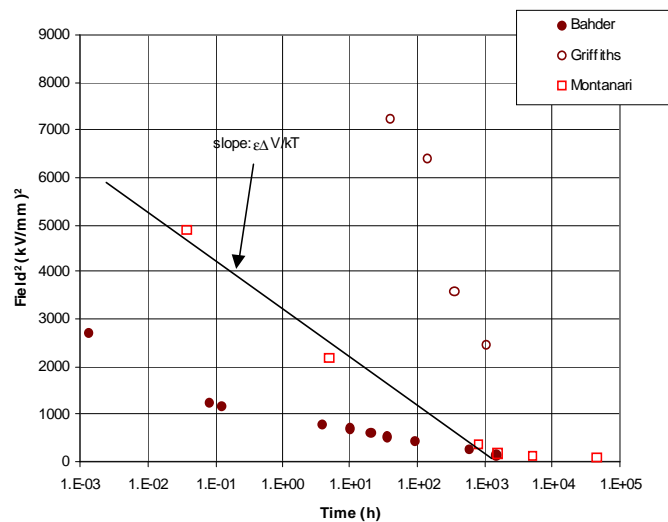


Fig. 1- Comparison between experiments (symbols) and calculations (lines) using Eq. 2. Results taken from Refs. 3, 6, 8.

If indeed the C-C bonds relax after the stress application, we may suppose that the dissociation energy D varies with stress and time according to

$$D_F = D \exp(-t/\tau) \quad (3)$$

where τ is the lifetime under stress given by Eq. 2. At breakdown, $t = \tau$ and therefore $D_b = 0.367 D = 2.06 \times 10^{-19}$ J. This value is in excellent agreement with the average value deduced from electrical aging of XLPE. It then seems reasonable to assume that the activation energy for electrical aging at room temperature is 2.06×10^{-19} J (1.287 eV). This means that the physical process at play during electrical aging is the breaking of C-C bonds and breakdown would occur when a given number of bonds have been broken. Note that the generation of free radicals under stress will enhance, and thus accelerate, the bonds breaking rate. Further detail will be given elsewhere.

The Activation Volume And Nanocavities

Polymers are all composed of molecular chains and nanocavities (the so-called free volume). These nanocavities have well known sizes and in LDPE/XLPE their average size is $1.8\text{-}2 \times 10^{-28}$ m³, that is a diameter (assuming spheres) of ~0.9 nm. At low and moderate stress, the nanocavities will be compressed by the compressive Maxwell stress induced by the field. Nanocavities are much easier to deform than the much more rigid molecular chains. Note that under moderate stresses, only some nanocavities will be deformed and those located near chain ends and in the amorphous phase are more likely to be the first to be deformed. When a given number of nanocavities have been entirely deformed, some bonds will be broken, free radicals will be induced and the aging process will considerably accelerate. This corresponds to the onset of the threshold field (more detail elsewhere). The activation volume is then the inverse of the concentration of completely deformed nanocavities. That concentration depends on the sample size, as empirically shown in Fig. 2. A more theoretical definition will be given in a subsequent publication. From a practical point of view, the results in Fig. 2 indicate that extrapolation from small laboratory samples to full size cables might be dangerous if the size effect is not taken into account. This definitely needs more work from a theoretical standpoint in order to give a reliable and comprehensive explanation to this very significant effect.

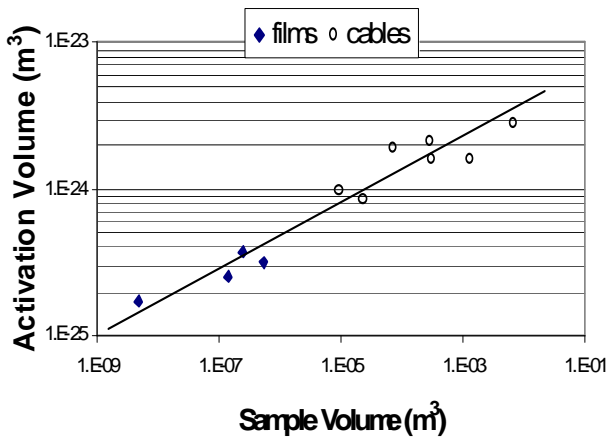


Fig. 2- Influence of sample size on the activation volume ΔV for cables and films aged at 22°C in air under ac fields (1,2).

Interestingly enough, the above given interpretation of the physical sense of ΔG and ΔV implies that both parameters are varying with time during the aging process. At short aging times, ΔG would be very large and ΔV very small, meaning very little aging, whatever the field. It also means that breakdown obtained under exactly the same field but after different times might not be the statistical fluctuation often assumed, but more likely a reflection of local disorders yielding different ΔV (i.e. deformed nanocavity concentration) values. We have shown in Fig. 3 typical results obtained by Yoda et al. (11) illustrating this possibility. Yoda et al. aged various similar cable samples under the same fields and obtained different breakdown times. We have calculated the corresponding ΔV values from Eq. 2 and plotted them as a function of time in Fig. 3. Quite obviously, the activation energy, that is the degree of local deformation, is varying exponentially with time. This means that trying to simulate the life of cable from an average value for ΔV might be misleading. The use of statistics is definitely recommended but the interpretation requires some care.

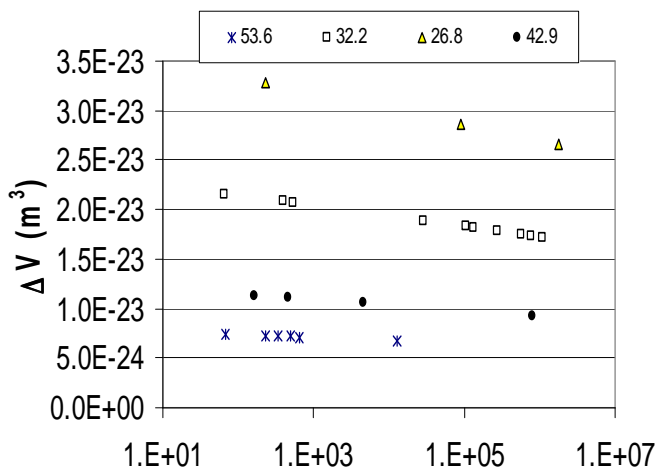
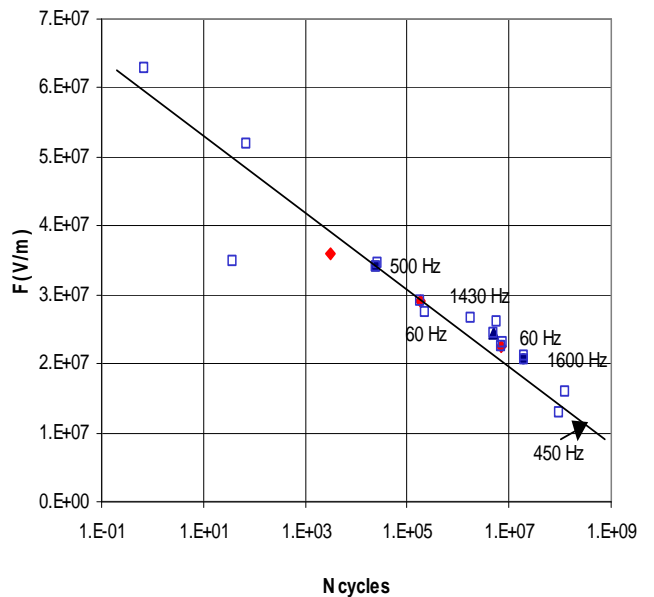


Fig. 3 – Activation volume deduced from the results of Yoda et al. (11) and Eq. 2 for four constant fields (in kV/mm). Note the exponential variation with breakdown time.

FREQUENCY, BREAKDOWN AND AGING

Equations 1 and 2 show the influence of frequency via the factor $2f$ (2 changes of polarity per cycle). Of course, aging under dc would be much longer, as indeed observed, since $2f$ is then equal to 1. What is particularly interesting in this approach is the fact that the duration of the aging tests might be considerably reduced by using higher frequencies. Results should be plotted not as function of time but as a function of the number of polarity changes. A good example is shown in Fig. 4 where results obtained under various frequencies by Bahder et al. (8) are plotted as a function of polarity changes. The expected straight line in F^2 vs. $\log t$ plots is indeed observed indicating that the same aging process was at play, whatever the frequency.

This also explains the different values of the breakdown fields obtained under various ac (or dc) ramps or under impulses. Assuming that electrical breakdown and aging are controlled by the same energy barrier, breakdown may be considered as a very short aging experiment. Thus, the time to breakdown will also depend on the number of broken bonds and under higher frequency, this concentration will be attained much more rapidly than under low frequency.



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Fig. 4- Variation of breakdown field in XLPE cables obtained under various frequencies (8) as a function of the number of field cycles (changes of polarity).

INFLUENCE OF TEMPERATURE CYCLES

Figure 5 is a good example of the positive influence of temperature cycles on XLPE cable life. Quite clearly, the cycles resulted in a longer life for the same fields or higher fields were needed to achieve breakdown in the same time than at room temperature. Several possibilities might explain this effect:

- heating and slowly cooling the polymer leads to some sort of annealing and therefore some previously deformed nanocavities might have recovered from their strained condition;
- the above suggested annealing is likely to give a more crystalline structure. Some limited experimental data indicates that indeed the insulation crystallinity has increased after several temperature cycles (1,13);
- during heating, there are more room between the molecular chains and therefore they may move more easily, allowing the recombination of some broken bonds. The influence of temperature (i.e. above 50°C) on radicals generation is unknown and it might play a very significant role on the insulation "regeneration" during the heat cycle.

The major problem is that there is almost no data on the influence of the heat cycles on the polymer morphology and to the best of our knowledge there is only one publication showing the evolution of some electrical properties of PE films submitted to a dc field (14). Therefore, there is a need for more work in this area if one wants to understand the influence of temperature cycles. If proven, it might be a simple way to improve XLPE cables life.

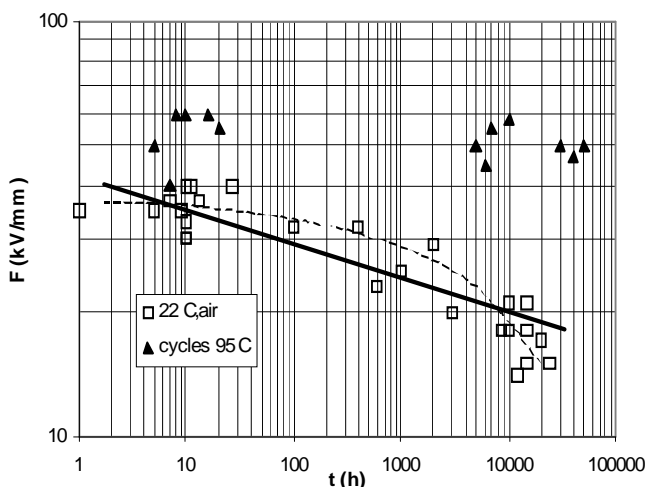


Fig. 5- Aging results obtained at 22°C and under temperature cycles (12) plotted on a log field vs. log time graph.

CONCLUSION

The proposed aging model describes very well experimental data on electrical aging and breakdown. Both processes appear to be controlled by the rate of c-c bonds breaking. However, it was stressed that translating laboratory results to actual full size cables is not a simple thing and several factors must be considered. The sample size is one major parameter and a formal equation relating ΔV and size has to be developed. Temperature cycles have a very positive influence on cable life but there is no theory to support it and we are limited to some unverified speculations due to the almost nonexistent information. Finally, time and frequency are also affecting the electrical aging of cables. Testing under high frequency might prove to be a cost efficient option. In summary, one may wonder if the present day way of testing and interpreting tests results is giving the expected reliable and useful information tests are supposed to give.

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