Multi-Sectioned Kinetics for the Degradation of Cable Insulation

Yuan-Shang Chang and Ali Mosleh

B. John Garrick Institute for the Risk Sciences, and Department of Materials Science & Engineering
University of California, Los Angeles (UCLA)
yensun@ucla.edu, mosleh@ucla.edu

INTRODUCTION

Cables are essential components in nuclear power plants, and they transmit power and communication signals. Cross-linked Polyethylene (XLPE or PEX) is a major material for cable insulation.[1] The insulation degrades due to thermal energy[2] and becomes brittle, which may render the exposure of the metallic core of a cable and cause short circuit, clearly a safety issue. Developing models to predict the degradation of the insulation, therefore, is an important topic for power plant safety, particularly in relation to plant life extension.

In field application, the degree of the brittleness of cable insulation has been defined by elongation at break (EAB).[3-6] The EAB of non-degraded insulation can range from 300% to 500% while the degraded one can be lower than 20%.[7] There are two well-known models addressing the change in the EAB in the literature: Time Temperature Superposition (TTS) and Dose to Equivalent Damage (DED) models.[8] Both models use a single value for the activation energy (ΔG) in the shift-factor equations to represent the EAB curves in different aging conditions. However, the concept of the shift factor in TTS and DED models can be replaced by a different modeling approach to improve the prediction.

This paper has applied the Dichotomy Model[9-11] to the insulation made from XLPE. One EAB curve is divided into multiple sections with different ΔG values. The physical significance of this multi-ΔG approach will be validated by the experimental data of XLPE insulation.

MODEL & VALIDATION

According to the Dichotomy Model, the degradation of the EAB can be modeled by the combination of equations (1) and (2).[9-11] V_d is degradation ratio with no unit. δ is normalized EAB. ν is drop-off rate whose unit is [1/time]. t is time. τ_0 is incubation time. $(t - \tau_0)$ must be equal to or larger than zero, which means the drop off of the EAB begins after the end of τ_0.

$$\delta = 1 - (V_d)^{(1/3)} \tag{1}$$

$$V_d = 1 - e^{-\nu(t-\tau_0)} \tag{2}$$

To validate these equations, we use the experimental data of the FR-XLPE cable insulation made by Company B under thermal degradation.[7] In Fig. 1, the discrete patterns are the experimental data[7] while the continuous lines are plotted by equation (1) and equation (2). The corresponding parameters are listed in Table 1. The two sections represented by the horizontal lines and the curves in Fig. 1 indicate different reaction kinetics in each isothermal condition.

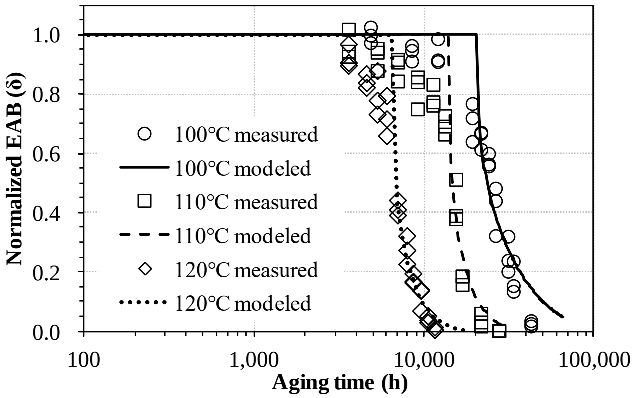

Fig. 1. Normalized EAB in thermal aging

Table 1. Values of the parameters in equation (2)

Aging Temperature (°C)	ν = [x10^{-5}/hour]	τ_0 = [hour]
100	4.4	20,500
110	19	14,000
120	40	6,500

DISCUSSION

The concept of drop-off rate (ν) is similar to that of degradation rate in chemical reactions. However, ν in this research is determined by the EAB rather than chemical reactions. To evaluate whether the values of ν determined by the Dichotomy Model are reasonable, the simplest way is to compare the fitting between the modeled lines and experimental data in Fig. 1. Besides, Arrhenius equation represented by equation (3) and its logarithmic form, equation (4), can be used to double-check the ν values. By plotting (1/T) on the x-axis and ln(ν) on the y-axis corresponding to Table 1, the linear fit as shown in Fig. 2 indicates that the values of ν are reasonable and of physical significance. The value of ΔG in equation (3) can be determined by the slope of the line. In this case, ΔG is 16.233×8.314 KJ/mol.

$$\nu = \nu_0 \times \exp\left(\frac{-\Delta G}{RT}\right) \tag{3}$$

$$\ln \nu = \frac{-\Delta G}{R} \times \frac{1}{T} + \ln \nu_0 \tag{4}$$

where ΔG is activation energy in [energy/mole]. ν_0 is a constant in [1/time]. R is ideal gas constant. T is absolute temperature.

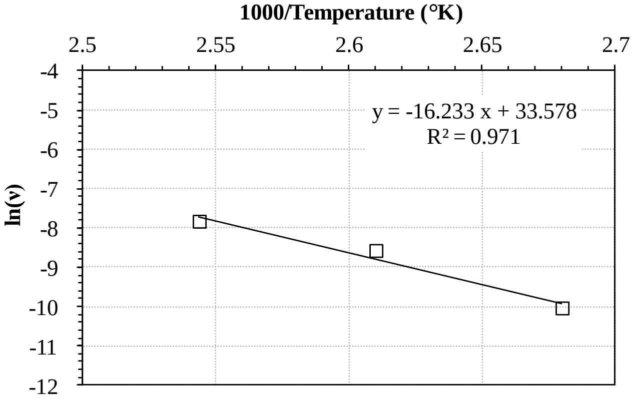

Fig. 2 Drop-off rate vs. aging temperature

According to equation (2), τ_0 determines the offset of the curved section in Fig. 1. Within τ_0, the drop off of the EAB is insignificant. This phenomenon has been measured in the previous study.[7, 8, 12] The end of τ_0 represents the start of the drop off of the EAB. The length of τ_0 regularly decreases as the aging temperature increases, as shown in Fig. 3. Although Fig. 3 shows a monotonically decreasing trend, its physics-based kinetics has not been developed in our study. Nevertheless, Fig. 3 can help us double-check if a determined τ_0 follows the trend corresponding to the aging temperature when Dichotomy Model is applied.

τ_0 may result from the high concentration of the antioxidant, and the transition from mechanical to chemical cross-links in the insulation. The antioxidant is typically added when the insulation is manufactured.[13] It can significantly slow down the oxidation which is one of the major chemical reactions causing the brittleness of cable insulation.[14] In the incipiency of the aging, the concentration of the antioxidant is sufficient, so the oxidation rate is too slow to be discernible.[14] Therefore, in this period of time (τ_0), the reduction of the EAB is negligible. On the other hand, when the insulation is made, in order to increase the entropy, the polymer chains spontaneously tangle with one another. The nodes between the chains are mechanical cross-links restricting the relative movement of the chains while the insulation is elongated. Exposure to heat or radiation can cause some of the mechanical cross-links to transform into chemical cross-links due to the formation of covalent bonds near the nodes. Meanwhile, the overall effect of the cross-links contributing the EAB has not been significantly changed. This is the second reason causing the time period (τ_0) with a negligible drop-off rate.

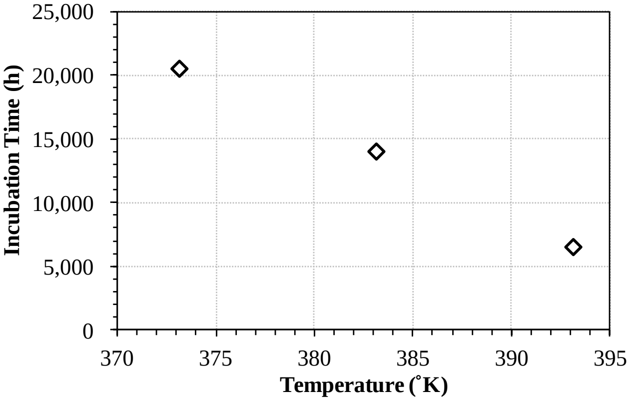

Fig. 3. Incubation time vs. aging temperature

V_d is the degradation ratio in the Dichotomy Model.[9-11] It is the integral of ν against time. V_d calculated by equation (2) and Table 1 is visualized in Fig. 4. Since V_d is modeled by the change of the EAB rather than the chemical reactions in the insulation, each line in Fig. 4 shows two sections: incubation section where the drop-off rate is negligible, and drop-off section where the curve is modeled by equation (2). This modeling approach can determine the values of the ΔG directly based on the Arrhenius equation represented by equation (3), which is different from the widely-used shift factor discussed in the literature.[8]

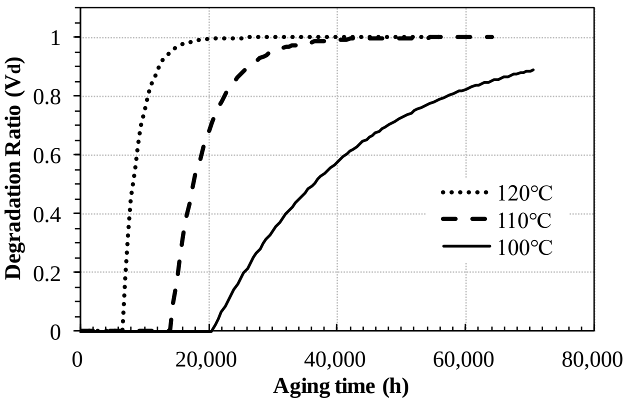

Fig. 4 Degradation ratio vs. aging time

The shift factor in TTS model cannot accommodate the shape change of the EAB curve versus time for different aging conditions.[15] DED model also uses shift factor to represent the offset along the dose-rate axis corresponding to different aging temperatures, and the ΔG of this shift factor is determined by trial and error.[8] Besides, DED model does not model the trend of the EAB along a time axis; only one EAB value is considered in one DED plot. Furthermore, when the targeted EAB value is changed, the ΔG determined by DED model changes as well.

The facts discussed above are caused by the shift factor which is the ratio of two Arrhenius equations respectively representing two aging conditions, and both Arrhenius equations have the same ΔG. However, even in one aging condition, it is obvious that ΔG is not constant since ΔG in the related research[7, 8] is determined by the EAB. The experimental data shows during the early stage of aging, the EAB does not drop significantly,[7] which means the ΔG of incubation section is much higher than that of drop-off section according to the trends of the EAB. Moreover, the loss of the antioxidant in aging can also decrease the value of ΔG. Figure 8 of the reference[14] shows the loss of the antioxidant in thermal aging. Figure 2 of the same reference[14] shows the drop-off rates of the EAB are different when the content of the antioxidant is varied although the aging temperature is fixed. Different drop-off rates indicate that the values of ΔG are not the same when the concentration of the antioxidant varies in the isothermal condition. Therefore, the degradation of the EAB may be modeled by disparate sections such as the horizontal section represented by τ_0 and the curved section plotted by equation (1) in Fig. 1. More sections can be added to Fig. 1 if the drop-off rate is further changed during aging.

CONCLUSION

The degradation of cable insulation is a topic of concern in nuclear power plant safety. The proposed Dichotomy Model predicts the decrease of the EAB due to aging. The experimental data of the XLPE samples have been used to validate the model.

There are two parameters in the model: drop-off rate and incubation time. Drop-off rate is similar to the degradation rate in a chemical reaction. It is measured by the EAB instead of chemical methods. The values of drop-off rate follow Arrhenius equation. As for incubation time, it may be caused by the high concentration of the antioxidant significantly slowing the degradation rate and by the transition from mechanical to chemical cross-links. The values of incubation time regularly decrease when aging temperature increases.

In our model, one EAB curve is modeled by an incubation section and a drop-off section having different ΔG, respectively. Unlike the shift factor in TTS and DED models represented by a single ΔG value, multiple ΔG values can not only accommodate the shape change of the EAB curve but also provide equations for the EAB curves as a function of time.

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NOMENCLATURE

XLPE = Cross-linked Polyethylene
EAB = Elongation at Break
TTS = Time Temperature Superposition
DED = Dose to Equivalent Damage
ΔG = activation energy
τ_0 = incubation time
ν = drop-off rate
δ = normalized elongation at break
V_d = degradation ratio
T = temperature
t = aging time

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