Changes on structural and electrical properties of retired cross-linked polyethylene (XLPE) cable insulation under electro-thermal aging test

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Abstract. In order to study the insulation performance of two retired high voltage cross-linked polyethylene (XLPE) cables with service years of 16 and 32 and evaluate the reliability of reusing these cables for actual operation, a 180-day electro-thermal aging test was exerted on a section of these two cables to inspect the changes on structural and electrical properties. Several diagnostic measurements including fourier infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and breakdown field strength were carried out on the untreated and treated samples. The measured results show that the crystalline structure of the 16 years cable has been improved after the accelerated aging test probably because of the reduction of the impurities and the annealing effect, which further improve the electrical property. Even though the molecular chains of the 32 years cable insulation has been damaged and a slight degradation happens on the crystalline structure under the intensive aging test condition, which is responsible for the decline in the electrical property, the cable still have the potential to resist the stresses properly under the actual operation condition for a long time from the perspective of the XLPE. Therefore, it can be expected that the rest of these two retired cables still have the ability to reuse in the long-term actual operation condition.

1. Introduction
Crosslinked polyethylene (XLPE) has been widely used as an insulating material for high-voltage cables because of its excellent electrical and thermal properties [1-3]. Under its working condition, the cables are subjected to the thermal, electrical, mechanical stresses and environment factors, which eventually leads to the aging phenomenon [4]. Research on the aging mechanism and evaluation on the status of the cable insulation are a highlight of the operation and maintenance power department. Currently, the assessment of the insulation properties of XLPE has been analysed from the perspective of the material ultimate endurance, which is quite different from the actual operation condition of the cables. This will lead to the design lifetime ranging of 30–40 years of the XLPE cables is not accurate and suitable. In recent years, an increasing number of high voltage cross-linked cables are decommissioned because of transmission line relocation or design service life limitation. In the face of the situation that lacks extensive experimental research on reusing retired cables for practical operation, they are dismissed to be a waste. In fact, a large quantity of experimental studies on retired
cables demonstrate that relevant parameters still comply with quality standards and still meet the requirements for continuous operation [5-7].

Cross-linked polyethylene (XLPE) is a high molecular polymer consisting of two mutually intermixed phases, the crystalline and amorphous phases and its microstructure plays a decisive role in its electrical properties. Actually, the influence of the thermal effect and electric effect on the polymers are a complicated process and the insulation properties can be improved in some certain situations [8,9]. In this paper, in order to investigate the deterioration of XLPE insulation of the retired cables under high strength conditions, a 180-day electro-thermal aging test is conducted on a section of two retired cables with different service years. This paper aims to explore the changes on structural and electrical properties of the retired cables and to evaluate the reliability of reusing the rest of those cables for practical operation.

2. Experimental

2.1. Preparation of XLPE samples

A section of two 110 kV high voltage cross-linked polyethylene cables with the service years of 16 and 32 were selected as the testing samples. Overheated operation was not reported for the two retired cables, which means that the temperature in the insulation layer remained below 90℃ during the cable operation. It can be seen that the cable sheath and the insulating layer were not damaged, and there was no water permeation before the electro-thermal aging test. The critical parameters of the cables are shown in table 1, where the terms of XLPE-16 and XLPE-32 are defined as the cables with the service years of 16 and 32 before the electro-thermal aging test, respectively.

| Sample     | Voltage Level (kV) | Conductor Area (mm²) | Conductor Diameter (mm) | Insulation Diameter (mm) | Manufacturer | Operation Period |
|------------|--------------------|----------------------|-------------------------|--------------------------|--------------|------------------|
| XLPE-16    | 110/63.5           | 630                  | 32                      | 68                       | Showa        | 1999-2015        |
| XLPE-32    | 110/63.5           | 700                  | 39                      | 77                       | Showa        | 1985-2017        |

2.2. Electro-thermal aging test

180-day electro-thermal aging test was adopted for a section of the two testing cables with the length of 15 m and the two cables were connected in series form. A high voltage of 1.7 U₀ (108 kV, U₀ = 63.5 kV) was applied to the circuit, and the current were applied to the cables metal conductor with high-current generation. The insulation of the cables was heated for at least 8 h to the preset temperature of 90 ~ 95℃ and kept for 2 h, then cooled to the room temperature at least for 16 h during the test. There was no insulation breakdown phenomenon during the electro-thermal aging test. Therefore, the untreated samples and accelerated aging samples were obtained for diagnostic measurements.

2.3. Diagnostic measurements

Fourier transform infrared spectroscop (FTIR), differential scanning calorimetry (DSC) measurement, and breakdown field strength measurement were adopted to analyse the changes on structural and electrical properties of each sample after accelerated aging test.

Micro-structure changes on each sample were performed by VERTEX 70 infrared spectrometer manufactured by German. Each sample was tested at 32 scans in the range of 600~3600 cm⁻¹ with a resolution of 4 cm⁻¹.

Aggregation structure changes on each sample were analysed by DSC NETZSCH-DSC 214 instrument manufactured by German. 5 mg samples were prepared for the test with the program of a heating phase of 30~140℃ and a cooling phase of 140~30℃ at a constant rate of 10℃/min under N2
atmosphere to avoid the oxidant process.

Electric properties changes of the samples were analysed by the ZJC-100 kV voltage breakdown tester manufactured by China. Each sample was cut into a square of 5×5 cm to test the valid breakdown field strength 5 times and obtain the average values.

3. Result and discussion

Samples were peeled radially from untreated and accelerating aged cables and the tape-like XLPE peels were obtained. Peels near the inner semi-conductive layer were taken as the test samples because these locations suffered the most serious electrical and thermal stresses. We define the untreated samples of the cables with different service years of 16 and 32 as 16-0 and 32-0, while samples of the 180-day accelerating aged cables with different service years of 16 and 32 as 16-180 and 32-180.

3.1. Result and discussion of FTIR spectroscopy measurement

Cross-linked polyethylene (XLPE) is a high molecular polymer whose methylene groups (-CH₂) is the most characteristic group of XLPE. This absorption peak appears at a wavelength of 720 cm⁻¹, and it is confirmed by the peaks that locate at 1471 cm⁻¹, 2856 cm⁻¹ and 2937 cm⁻¹ [9]. Dicumyl peroxide (DCP) is commonly used as cross-linking agent and its by-product mainly consists of acetophenone, cumyl alcohol and α-methylstyrene. The corresponding characteristic groups of these compounds are phenyl, carbonyl (=C=O) and hydroxyl (-OH), and the infrared absorption peaks appear at 1600 cm⁻¹, 1680 cm⁻¹ and 3371 cm⁻¹, respectively [10]. In addition, absorption peaks ranging from 1700 cm⁻¹ to 1800 cm⁻¹ can be considered as the thermo-oxidative products [3]. Among of them, carboxylic acid absorption appears at 1701 cm⁻¹, ketone absorption locates at 1718 cm⁻¹ and aldehyde absorption situates at 1741 cm⁻¹. The peak at 1635 cm⁻¹ is assigned to the unsaturated groups absorption, which can indicate the decomposition process. In order to judge the oxidation and decomposition situation of each samples under the different equivalent accelerated aging test condition, carbonyl index and double band index were chosen for research. The indexes are shown in table 2.

| Sample   | Carbonyl index (I₁741/1471) | Unsaturated band index (I₁605/1471) |
|----------|----------------------------|-----------------------------------|
| 16-0     | 0.035                      | 0.336                             |
| 16-180   | 0.020                      | 0.167                             |
| 32-0     | 0.059                      | 0.197                             |
| 32-180   | 0.044                      | 0.248                             |

From figure 1, we can find that distinct absorption peaks appear at 1600 cm⁻¹, 1680 cm⁻¹ and 3371 cm⁻¹ in 16-0. That means a certain number of cross-linking by-products still remain in the cable with service years of 16. After the electro-thermal aging test, a significant drop of these peaks in 16-180 indicates the decreasing of cross-linking by-products. This phenomenon is ascribed to the positive influence of thermal effect, which reduces the inside impurities by evaporation or migration. On the contrary, it can be observed that absorption intensity of these three peaks of 32-0 are relatively low comparing to 16-0, which infers that the cross-linking by-products have been reduced during its long-term operation. After the electro-thermal aging test, these three peaks become expanded because of decomposition in the macro-molecules.

In order to quantify the process of oxidation and decomposition under the thermal effects, carbonyl index and unsaturated band index are chosen for research. The two indexes are shown in table 2. Where carbonyl index is the relative intensities of the carbonyl band at 1741 cm⁻¹ (aldehyde absorption) to the methylene band at 1471 cm⁻¹, unsaturated band index is the relative intensities of the unsaturated group at 1635 cm⁻¹ to the methylene band at 1471 cm⁻¹ [11]. We can observe that the carbonyl index of 16-0 and 32-0 are both reduced after the electro-thermal aging test, which signifies the process of oxidation degradation does not happen basically during the accelerated aging test. On
the other hand, we can figure that the unsaturated band index decreases in 16-0 but increases in 32-0 after the electro-thermal aging test. With regard to the cable with service years of 16, this phenomenon can be deduced for the secondary reaction of cross-linking. As to the cable with service years of 32, it can be attributed to the damage of XLPE macro-molecules and formation of more polar groups and broken chains, leading to a certain decomposition process happened under the severe accelerated aging condition.

![FTIR spectrum](image)

**Figure 1.** FTIR spectrum of the samples before and after the electro-thermal aging test.

3.2. Result and discussion of DSC measurement

With the DSC measurement program running, two phases were analyzed, including the heating and cooling phase that can be analysed on the current crystalline structure and the ability to recrystallize of the samples. Figures 2(a) and 2(b) show the thermograms in the phases of heating and cooling of each sample. The critical parameters are listed in table 3, where $T_m$ is melting peak temperature, $\Delta H_f$ is enthalpy of fusion, $L$ is melting range, $T_c$ is the crystallizing peak temperature, $\Delta H_c$ is the enthalpy of crystallization and $\Delta T = T_m - T_c$ is degree of supercooling, which is proportional inversely to the crystallization rate.

![DSC thermogram](image)

**Figure 2.** DSC thermogram of the samples before and after the electro-thermal aging test. (a): heating phase, (b): cooling phase.
Table 3. Parameters obtained from DSC spectrum of each layer.

| Sample | $T_m$ (°C) | $\Delta H_f$ (J/g) | $L$ (°C) | $T_c$ (°C) | $\Delta H_c$ (J/g) | $\Delta T$ (°C) |
|--------|------------|-----------------|-------|---------|-----------------|-------------|
| 16-0   | 103.8      | 109.8           | 14.9  | 88.1    | -96.1           | 15.7        |
| 16-180 | 106.3      | 108.5           | 14.2  | 85.6    | -97.9           | 20.7        |
| 32-0   | 107.2      | 116.7           | 14.7  | 90.1    | -104.4          | 17.1        |
| 32-180 | 106.5      | 113.2           | 13.0  | 90.9    | -104.9          | 15.6        |

After the electro-thermal aging test, the changes of aggregation structure on 16-0 and 32-0 have changed inversely. As is shown in figure 2(a), a sharp endothermic peak which characterizes the melting process of crystalline structure, has emerged in all the samples [11]. The heat flow curve of 16-0 drifts slightly to higher temperature and the melting range of the main DSC peak becomes narrowed after the accelerated aging test. Therefore, it can be considered that the crystalline structure becomes uniform and solid because of the adequate chains mobility and impurities reduction. As to 32-0, we can see that the main melting peak moves towards lower temperature and the melting enthalpy is decreased accentuately after accelerated aging test, which indicated a certain degradation happens on the crystalline structure during the severe testing condition.

From figure 2(b), an exothermic peak which symbolizes the process of recrystal of the polymer, was observed in all the samples. We can observe that the heat flow curve of 16-0 shifts to higher temperature, exothermic peak area is enlarged and the lifting of supercooling degree $\Delta T$ after the electro-thermal aging test. That means the recrystalline structure becomes compact which is probably attributed to integrity and regularity of the XLPE macromolecules and decreasing of impurity molecules. As to 32-0, a slight displacement of the exothermic peak moves towards lower temperatures and the drop of supercooling degree $\Delta T$ indicate that certain damage in the XLPE macromolecules leading to drop of the ability to recrytallize and degradation on the re-crytal structure under the severe testing condition.

Further, the DSC Endotherms indicate a range of melting process that can be related to the crystallinity and lamellar thickness variations. The crystallinity and main lamellar thickness [7,11] can be calculated by formulas (1) and (2). The calculating formulas are as follows:

\[
\chi(\%) = \frac{\Delta H_f}{\Delta H_f^0} \times 100
\]

\[
T_m = T_{m0}(1 - \frac{2\sigma_e}{\Delta H_m L})
\]

Where $\chi$ (%) is crystallinity; $\Delta H_f^0$ is the enthalpy of fusion of an ideal polyethylene crystal per unit volume, which is 293 J/g; $T_m$ is the observed melting temperature (K) of lamellar of thickness L, $T_{m0}$ is the equilibrium melting temperature of an infinitely thick crystal, $\sigma_e$ is the surface-free energy per unit area of basal face, $\Delta H_m$ is the enthalpy of fusion of an ideal polyethylene crystal per unit volume, and L is the lamellar thickness. The used values for calculation were as follows: $T_{m0} = 414.6$ K, $\Delta H_m = 2.88 \times 10^8$ J/m$^3$ and $\sigma_e = 93 \times 10^{-3}$ J/m$^2$. The crystallinity and lamellar thickness are shown in table 4.

Table 4. Crystallinity and lamellar thickness at the main endothermic peak.

| Sample | $\chi$ (%) | $L$ ($\times 10^{-10}$) (m) |
|--------|------------|----------------------------|
| 16-0   | 37.5       | 71.1                       |
| 16-180 | 37.0       | 76.2                       |
| 32-0   | 39.8       | 78.2                       |
| 32-180 | 38.6       | 76.6                       |

It is hard to judge the status of crystalline structure just from the crystallinity. Therefore, the analysis should be combined with the change of lamellar of thickness obtained at the main
endothermic peak. After the electro-thermal aging test, we can see that crystallinity of 16-0 has decreased slightly, while the lamellar thickness at the main endothermic peak becomes thicker, which means the main crystalline structures are compact and the secondary crystals are inapparent. The possible reason can be ascribed to adequate movement of the molecular chains and the decreasing of the impurities that are prone to hinder the development of crystal. With regard to 32-0, we can notice that both the crystallinity and lamellar thickness at the main endothermic peak are declined, which indicates the crystalline structures have been broken slightly. This phenomenon is attributed to the generation of smaller chain segment, resulting from the broken of XLPE macromolecules under the severe testing condition.

3.3. Result and discussion of breakdown field strength measurement
In table 5, we present the changes of the valid average breakdown field strength according to the inverse relationship of average breakdown voltage and thickness. We can observe that average breakdown field strength has changed in different way for 16-0 and 32-0 after the electro-thermal aging test, which increases with 9.3% and decreases with 8.2%, respectively.

| Sample    | Thickness (mm) | Average breakdown voltage (kV) | Average breakdown field strength (kV/mm) |
|-----------|----------------|-------------------------------|----------------------------------------|
| 16-0      | 0.7            | 38.36                         | 54.81                                   |
| 16-180    | 0.7            | 41.94                         | 59.92                                   |
| 32-0      | 0.5            | 31.10                         | 62.20                                   |
| 32-180    | 0.5            | 28.54                         | 57.07                                   |

The significant lift in breakdown field strength in regard to the 16 years cable after aging is probably due to the improvement of the crystalline structures, which are partly antioxidant free, and the diminution of cross-linking by-products, which disrupt the crystalline order of the XLPE. On the other hand, a slight drop of the breakdown field strength on the 32 years cable after aging demonstrates the deterioration on the crystalline structures because of the scission on the molecular structure induced by the intensive aging test condition.

4. Conclusion
In this paper, a 180-day electro-thermal aging test was exerted on the retired high-voltage cross-linked cables with service years of 16 and 32 to evaluate the reliability of reusing these cables for actual operation. Relevant diagnostic measurements were adopted to analyse the changes on structural and electrical Properties.

The crystalline structure of the 16 years cable is improved after the accelerated aging test probably because of the reduction of the impurities and the annealing effect, which further improve the electrical property. On the contrary, even though the molecular chains of the 32 years cable insulation has been damaged and the crystalline structure has been slightly degraded under the intensive aging test condition, which is responsible for the decline in the electrical property, the cable still have the potential to resist the stresses properly under the actual operation condition for a long time from the perspective of the XLPE. Therefore, it can be expected that the rest of these two retired cables still have the ability to reuse in the long-term actual operation condition.

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