Thermal Annealing on the Thermal Performance of XLPE from Retired Cables

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Abstract. In the present paper, different annealing methods were performed on cross-linked polyethylene (XLPE) from three retired cables, the effects on thermal performance were discussed. The cables with length of 15 cm were prepared and the insulation layers were peeled, and the peels near the inner semi-conductive layer were used as the test samples. Isothermal treatment and heat recycling treatment were performed on the samples at temperatures of 85, 90, 95, and 100°C, and the temperature holding hour \( T_h \) in the heat recycling treatment were 8, 16, and 24 h. Each kind of heat treatment was repeated 20 times, and the duration of the isothermal treatment was the same as that for the heat recycling treatment with 24 h temperature holding hour. Then, differential scanning calorimetry (DSC) were performed. The results show that the melting point, crystallinity, lamellar thickness increase and melting range decreases as the annealing temperature increases; the optimal values appear as the samples were annealed at 95°C. With longer \( T_h \), the cables annealed at 95°C exhibit decreased melting range and increased crystallinity, melting point, lamellar thickness.

1. Introduction
Annealing, a widely adopted heat treatment method used in the research on crystalline polymer materials. Two different annealing methods, isothermal treatment and thermal cycling treatment have shown their superiority in improving the morphological structure of XLPE at a proper temperature [1]. With annealing occurring at a temperature above the glass transition temperature during cable operation, evolution of the crystal-amorphous structure in the insulation layer has been widely observed in retired cables [2]. The reason for the enhancement has been summarized as a “crystal second evolution process”, with molecular chains forming an orderly arrangement, imperfect crystals being converted to perfect ones, thin lamellae becoming thick lamellae, and new crystal formation accompanying the reduction of the amorphous region.

In this study, two different annealing methods are performed on three retired cables with 0, 15, and 30 years of service, considering the cable operation conditions. The effects of annealing on the morphology and electrical performance of the cables are compared, and the selection of a method for cable rejuvenation is discussed.

2. Experimental Details

2.1. Sample Preparation
Three 110 kV AC cables are used in the present study, some important specific parameters are listed in Table 1. Two of the cables are retired cables with the service year of 15 and 30, the last cable is a spare
cable. Overheated operation was not reported for the two retired cables, which means that the temperature in the insulation layer remained below 90°C during the cable operation. The cable insulation was peeled parallel to the conductor surface, and the peels near the inner semi-conductive layer were taken as the test samples.

2.2. Sample Treatment

The samples were divided into 4 groups and annealed by four different heat treatment methods. The first three are thermal recycling treatments, with temperature holding hour $T_h$ of 8, 16, 24 h. The last one is the isothermal treatment in which the temperature is increased to the preset temperature and maintained until the heat treatment is finished. A thermal recycle process including a heating, holding, and cooling phase, and the same cycle repeats 20 times. The samples annealed at same preset temperature with different $T_h$ of 8 h, 16 h, 24 h, and isothermal treatment are labeled as S-1, S-2, S-3, and S-4, and cables annealed by the same method are named according to their service year: XLPE-0, XLPE-15, and XLPE-30.

| Sample    | $M_i$ | $M_C$ | $d_{IS}$ | $d_I$ | $d_{OC}$ | $S_C$ | $O_P$ |
|-----------|-------|-------|----------|-------|----------|-------|-------|
| XLPE-0    | XLPE  | Cu    | 2        | 19.8  | 2        | 700   | -     |
| XLPE-15   | XLPE  | Cu    | 2        | 19.8  | 2        | 700   | 2000-2015 |
| XLPE-30   | XLPE  | Cu    | 2        | 19.8  | 2        | 700   | 1985-2015 |

$M_i$: insulation material, $M_C$: conductor material, $d_{IS}$: inner semiconductor thickness in mm, $d_I$: insulation thickness in mm, $d_{OC}$: outer semiconductor thickness in mm, $S_C$: conductor area in mm$^2$, $O_P$: operation period. Other parameters such as cross-linking method are unknown.

2.3. Parameter Measurement

Differential scanning calorimetry (DSC) was performed with a Q200 (TA Instruments, USA) instrument to measure the thermal properties of the samples. A sample with a weight of 5 mg was used in each measurement. The temperature was increased from 25 to 140°C at a rate of 10°C a/min and maintained at 140°C for 5 min, and then cooled to 25°C. This scanning was repeated twice per measurement, and 5 measurements were performed for each sample.

3. Results and Discussion

Due to the vast amount of data in the measured DSC spectra for all the samples, only the DSC spectra of XLPE-0 are adopted and shown in the following figures.
Figure 1. DSC spectra observed for XLPE-0 in the first heating spectra.

Figure 1 shows the DSC spectra of XLPE-0 measured in the first heating phase. In each graph, the melting point shifts to a higher temperature and the melting range narrows as the increases in annealing temperature. The highest melting point and the smallest melting range are observed when the samples were annealed at 95°C. When the samples were annealed at 100°C, the melting point shifts to a lower temperature and the melting range becomes larger when the cable is annealed. The change in the melting range, primarily concentrated below the melting point occurs because many thin lamellae convert into thicker lamellae, leading to a denser crystalline distribution. The melting point corresponding to the thickest lamellae shifts to a higher temperature also indicates that the thickest lamellae was further thickened. When the sample is annealed at a higher temperature of 100°C, the melting point decreases and the melting range broadens as a result of melting of the thicker lamellae and emergence of the thinner lamellae [3].

Generally, the DSC spectra in the second heating phase are also highly important. And the DSC spectra of XLPE-0 from the second heating phase are shown in Figure 2. In each graph, each curve shows similar heat flow at each temperature, and the same melting point. Slight difference is observed among the four graphs, indicating that similar crystal-amorphous structures form with all the crystals completely melted when the sample is heated to 140°C in the first heating phase and recrystallized in the first cooling phase. As the sample cools to 25°C at the same rate, a similar crystal-amorphous structure emerges that means no change in the molecular chain, indicating that the annealing process at these temperatures did not result in further damage to the molecular chain.

The highest melting point and smallest melting range in Figure 2 consistently show that the optimal values appear when the cable is annealed at 95°C regardless of the temperature holding hour. To clearly illustrate the differences observed for the sample annealed at 95°C with different $T_h$, Figure 3 shows the DSC spectra of XLPE-0 annealed at 95°C. The higher melting point and smaller melting range observed correspond to longer $T_h$, and the optimal values appear for the sample S-4.
Figure 2. DSC spectra observed for XLPE-0 in the second heating phase.

Figure 3. DSC spectra observed for XLPE-0 after annealed at 95 °C in the first heating phase.

Comparing Figures 1 and 2, the DSC spectra measured in the first heating phase provide more detailed information about the effect of annealing on the morphological change of XLPE. Based on the DSC spectra measured in the first heating phase for all the samples, the melting point was obtained directly, and the crystallinity $X$, lamellar thickness $L$ and melting range $T_{mr}$ were calculated using the following three equations [4-6],

$$X = \frac{\Delta H_m}{\Delta H_m^0} \times 100\%$$

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

and  

\[ T_{mr} = T_{me} - T_{ms} \]  

where \( \Delta H_o \) is the observed fusion enthalpy per unit volume and \( \Delta H_m \) is the value for an ideal polyethylene crystal, \( 2.88 \times 10^8 \) J·m\(^{-3} \). Furthermore, \( T_{m0} \) is the melting point of polyethylene for an infinitely thick crystal, 414.6 K. In addition, \( \sigma_e \) is the surface-free energy per unit area of the basal face, \( 9.3 \times 10^{-2} \) J·m\(^{-2} \), \( T_{ms} \) is the starting melting point, and \( T_{me} \) is the ending melting point.

Figure 4 shows the values of melting point, crystallinity, lamellar thickness, and melting range as a function of annealing temperature. From Figure 6(a) to (c), the changes in these three values exhibit the same trend: the values increase with increasing annealing temperature and the maxima appear at the annealing temperature of 95°C. The melting range shown in Figure 6(d) decreases with increasing annealing temperature, and the smallest value appears at the same temperature as the previous three values. For the sample annealed at 100°C, the formal three values decreased identically, and the melting range increased.

![Figure 4](image_url)

**Figure 4.** Melting point, crystallinity, lamellar thickness, and melting range as a function of annealing temperature. Solid symbols (■, ●, ▲) represent XLPE-0, XLPE-15, XLPE-30. Solid line (---): S-1, short dash line (---): S-2, short dot line (-----): S-3, short dash dot line (-------): S-4.

To compare the effectiveness of the different heat treatment methods on the morphological structure, Figure 5 shows the melting point, crystallinity, lamellar thickness, and melting range values
for the samples annealed at 95°C. The values in Figure 5(a) to (c) increase with increasing $T_h$, and the value in Figure 5(d) decreases with increasing $T_h$. If we ignore a slight exception, the optimum values are observed in S-4. It is well known that XLPE is an original symmetric molecular chain, polar groups and impurities emerge from degradation, and their movement impedes the crystal emergence. For the sample annealed at a temperature below the optimum point, a longer $T_h$ means more time for molecular chain movement over larger distances, gradually, thicker and uniform lamellae emerge.

4. Conclusions
When the annealing temperature was 85, 90, and 95°C, heat treatment led to a positive effect on the cables. The annealing temperature of 100°C led to a negative effect on the cables. The optimal values of the melting point, crystallinity, melting range, and lamellar thickness were observed when the cables were annealed at 95°C. For the three cables annealed at 95°C, longer temperature holding hour greatly enhanced the thermal properties and the isothermal treatment yielded the best results.

![Figure 5. The values of melting point, crystallinity, lamellar thickness, and melting range as a function of $T_h$ as the samples annealed at 95°C. Solid symbols (■, ●, ▲) represent XLPE-0, XLPE-15, XLPE-30. Iso is the abbreviation of isothermal treatment.](image)

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6. References
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