Research on Thermal Endurance Properties of XLPE Aged in Different Media

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Abstract. In this paper, XLPE samples were placed in air and silicone oil for thermal aging, respectively. Besides, the samples were tested by differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA). Then the thermal endurance properties of XLPE were also investigated. The results show that the variation of the thermal endurance properties of XLPE with aging time was highly related to the content of antioxidants in the samples. When the content of antioxidants was above the critical value, the melting temperature and initial decomposition temperature of XLPE just drop slightly and the variation of the melting temperature and initial decomposition temperature is irrelevant to the heating media. In contrast, when the content of antioxidants was below the critical value, the melting temperature and initial decomposition temperature of XLPE aged in air would drop sharply. In addition, when the samples are aged in silicone oil for a long but limited time, the variation of thermal endurance properties is close to the results of running cables.

1. Introduction

High-voltage XLPE cable has been widely used in the grid because of its excellent thermal endurance properties and electrical properties. However, XLPE will age with the increase of run time and it is not clear whether the decrease of thermal endurance properties will affect the safety of the cable operation or not in this process. Although many scholars have studied the thermal endurance properties of XLPE and got considerable research results, these research results mostly focus on the aging properties of XLPE in air [1, 2, 3]. However, aging in air is much different from the main insulation condition of high-voltage XLPE cable. As a result, these research results are difficult to evaluate the state of running cables. Therefore, researching the thermal endurance properties of XLPE in different media is significant to ensure the safety and reliability of the grid.

The physical and chemical properties of silicone oil are steady. The silicone oil does not swell with XLPE and can be used for a long time at a temperature below 200°C without obvious oxidation reaction [4]. In this paper, the samples were aged in air and silicone oil, respectively. The samples were placed in the silicone oil to simulate the low-oxygen environment of the main insulation during running, therefore the thermal endurance properties of XLPE aged in different media can be investigated.
2. Experimental Methods

2.1. Samples preparation and aging tests

110kV commercial XLPE cable without service was used. The main insulation of the cable was cut into a long strip with width of 100mm and thickness of 0.5mm by numerically controlled machine tool. In addition, the samples were processed into square of 100×100×0.5mm.

After preparation of the samples, the aging test in air was carried out in a single-chamber oven in accordance with the provisions of IEC60216-4-1:2006 [5]. And the aging test in silicone oil was realized by beaker and oven. The placement of the samples in beaker was shown in figure 1.

![Figure 1. The placement of the samples in beaker.](image)

The aging conditions were shown in table 1. In this paper, the unaged sample was named F0, the sample was named A1 aging in air for 6h, and the sample was named A2 aging in air for 12h, and so on. The sample was named B1 aging in silicone oil for 120h, the sample was named B2 aging in silicone oil for 240h, and so on.

| Heating Media | Aging Temperature (°C) | Aging Time (h) | Samples Number |
|---------------|-------------------------|----------------|----------------|
| Unaged        | -                       | 0              | F              |
| AIR           | 180                     | 6              | A1             |
|               |                         | 12             | A2             |
|               |                         | 18             | A3             |
|               |                         | 24             | A4             |
|               |                         | 30             | A5             |
|               |                         | 36             | A6             |
| OIL           | 180                     | 120            | B1             |
|               |                         | 240            | B2             |
|               |                         | 360            | B3             |
|               |                         | 480            | B4             |
|               |                         | 600            | B5             |
|               |                         | 720            | B6             |
|               |                         | 840            | B7             |
|               |                         | 960            | B8             |

2.2. OIT and DSC test

Both the oxidation induction period (OIT) and the DSC were tested by the Swiss MettlerDSC822e.
For OIT test, the mass of the samples was 6±2%mg, the test temperature was from 30°C to 200°C (In nitrogen, the flow rate of nitrogen was 60ml/min, heating rate was 10°C/min). Then the temperature was hold on 200°C, the nitrogen was switched to oxygen (flow rate of oxygen was 60ml/min) after 10 minutes. After that, the test was finished when an obvious endothermic peak appeared.

For DSC test, the test was in nitrogen with the flow rate of nitrogen at 60ml/min. The mass of the samples was 7±5% mg. The test temperature was from 30°C to 150°C, firstly. Then the temperature was from 150°C to 30°C. Finally, the temperature was from 30°C to 150°C again. Both heating and cooling rates were 10°C/min in this process.

2.3. TGA test
The samples were tested by MettlerTGA/SDTA851e. The test was in nitrogen with the flow rate of nitrogen at 60ml/min. The mass of the samples was 7±5%mg. The test temperature was from 50°C to 600°C with a heating rate of 20°C/min.

3.  Experimental Results and Discussion

3.1. The results and discussion of OIT

![Figure 2. OIT of the samples in air.](image1)

![Figure 3. OIT of the samples in silicone oil.](image2)

RH+O2→R·+OOH                   \( (1) \)

R·+O2→ROO·                  \( (2) \)

ROO·+RH→R·+ ROOH              \( (3) \)

2ROOH→RO·+ ROO·+H2O          \( (4) \)

Figure 2 and figure 3 show the relationship between OIT and aging time. It can be seen that the OIT of the samples in air and silicone oil decreases with increasing of aging time, this is because the samples will undergo the oxidation reaction shown from equation (1) to equation (3) during thermal aging. Under the influence of heat, the ROOH (hydrogen peroxide compound) will decompose to produce new ROO· (free radical) as shown in equation (4). Then the ROO· will react with XLPE to produce new R· (free radical) and ROOH [6]. The accumulation and decomposition of ROOH accelerates the reaction rate of oxidation reaction, which is considered as the main cause of automatic oxidation reaction [7]. However, antioxidants will capture the free radicals and form stable compounds to inhibit the automatic oxidation reaction in this process. The research results of Shimada A et al. [8] show that, the inhibitory effect of
antioxidants is almost not affected when the content of antioxidants in XLPE is above a certain critical value. However, the oxidation reaction rate would increase rapidly when the content of antioxidants is below this critical value.

From figure 2, it can be seen that the OIT of the samples decrease sharply from A5 (aging in air for 30h) to A6 (aging in air for 36h). Since the OIT of A5 is 483s, it can be judged that the critical value of the content of antioxidants in the samples is between 0 and 483s. In contrast, it can be seen that the content of antioxidants for B8 (aging in silicone oil for 960h) is still above the critical value from the figure 3. In addition, it also can be seen that the OIT of A6 is 0 which indicate that the time required for the samples to be oxidized is negligible when the content of antioxidants is below the critical value. Considering the quality error of the samples is no more than ±2%, the OIT can be used to represent the content of antioxidants in the samples.

3.2. The results and discussion of DSC

![Figure 4. DSC curves of the samples in air.](image)

![Figure 5. DSC curves of the samples in oil.](image)

Figure 4 and figure 5 are the DSC secondary melting curves of the samples. It can be seen that the DSC curves of aged samples shift to the left compared with the DSC curve of F0 (unaged sample), and the DSC curve of A6 is obviously distorted. Here, the parameter of the peak temperature is extracted in order to analyze the thermal aging endurance of the samples in detail. The variation of the peak temperature is shown in figure 6 and figure 7.

![Figure 6. Peak temperature of the samples in air.](image)

![Figure 7. Peak temperature of the samples in oil.](image)
Figure 6 and figure 7 show the relationship between peak temperature and aging time. When the content of antioxidants is above the critical value, it can be seen that the variation of the peak temperature of the samples in air and silicone oil is similar. Firstly, the peak temperature of A1 (aging in air for 6h) and B1 (aging in silicone oil for 120h) are all dropped to 104.4-105°C. This is because both samples come from the cable without service. Besides, the aging temperature of 180°C is enough to cause the decomposition of the residual DCP in the samples. Then the decomposition of the residual DCP triggers secondary cross-linking reaction. So the peak temperatures of A1 and B1 decrease because the increase of the degree of cross-linking is not conducive to crystal growth [9]. Secondly, the decrease of the peak temperature is no more than 1°C in air and 0.5°C in silicone oil, when the antioxidants are above the critical value. It means the samples do not occur intrinsic aging in this process. Therefore, it can be proved that the decrease of the peak temperatures is not caused by intrinsic aging for A1 and B1 from the side.

The results of the samples in air and silicone oil are also different in the test. According to the figure 6, the peak temperature of the samples decreases sharply from A5 to A6. It means oxidation reaction rate greatly increases in this process. The oxidation reaction leads to severe cracking of XLPE molecular, which causes the crystallization area of the samples to be destroyed, then the size of the crystal shrinks further, and the peak temperature decreased sharply.

3.3. The results and discussion of TGA

Figure 8 and figure 7 are the TGA curves of the samples. It can be seen that the thermal decomposition of XLPE is mainly divided into three stages. The first stage is about 50-300°C, which is mainly the volatilization of additives and their by-products. The second stage is about 300-520°C, where the samples lose weight significantly. The third stage is about 520-600°C, the mass of the samples tends to be stable again. In addition, it also can be seen that the residual rate is close to 0, which means that the thermal decomposition of XLPE is dominated by the formation of volatile small molecules. In order to analyze the thermal endurance properties of the samples in more detail, the initial decomposition temperature is extracted. Here, the temperature (at the intersection of the tangent line at the first stage and the tangent line of the maximum slope at the second stage) is chosen as the initial decomposition temperature of the samples.

Figure 10 and figure 11 show the relationship between initial decomposition temperature and aging time. From figure 10, it can be seen that the initial decomposition temperature of the samples in air decrease only slightly before A5 and the initial decomposition temperature of A5 is 461.6°C. However, the initial decomposition temperature of A6 drops sharply from 461.6°C to 436.52°C. This is because oxidation reaction leads to the relative molecular mass of A6 declines seriously. From figure 11, it can
be seen that the initial decomposition temperature of the samples in silicone oil decreases less than 0.5°C and the initial decomposition temperature is still 462.13°C when the sample is aged to 960h.

3.4. The results and discussion of other unaged samples
The table 2 shows the OIT, peak temperature and initial decomposition temperature of some unaged samples. The S1 comes from the cable which has running for 20 years, the S2 comes from the cable which has running for 20.58 years, and the S3 comes from the cable which has running for 23.42 years.

| Samples Number | Operating Time (Year) | OIT(s) | Peak Temp. (°C) | Initial Decomposition Temp. (°C) |
|----------------|-----------------------|--------|----------------|----------------------------------|
| S1             | 20.00                 | 852.6  | 106.80         | 460.18                           |
| S2             | 20.58                 | 734.4  | 106.94         | 457.02                           |
| S3             | 23.42                 | 701.4  | 106.27         | 460.87                           |

Although these cables were produced in different cable works and ran in different environments, the OIT of all samples is above the critical value. As a result, the peak temperature of these samples is no less than 106.27°C and the initial decomposition temperature is no less than 457.02°C. In addition, it can be inferred that when the samples are aged in the silicone oil for a long but limited time, the variation of thermal endurance properties is closer to the results of running cable. This is because the OIT of these samples is much larger than the critical value and these samples are all from the cables that have been ran for more than 20 years.

4. Conclusion
The following conclusions could be obtained from the results above:
1. The variation of the thermal endurance properties of XLPE with aging time is closely related to the content of antioxidants in the samples. When the content of antioxidants is above the critical value, the peak temperature of the samples aged in different media would be higher than 104°C and their initial decomposition temperature should be no less than 461°C. Meanwhile, the variation of the thermal endurance properties of XLPE aged in different media is similar. When the content of antioxidants is below the critical value, the thermal endurance properties of the aged XLPE would drop sharply in the air.
2. The OIT of cables running for more than 20 years is above the critical value, which indicates that when the samples aged in the silicone oil for a long but limited time, the variation of thermal endurance properties is close to the results of operating cable.

Acknowledgments
This study was performed as a part of a project No.GDKJXM20172792. The authors would like to thank the financial support of China Southern Power Grid.

References
[1] Xu J, Wang X D, et al. Effect of Thermal Aging on the Physicochemical Structure of XLPE Cable Insulation [J]. Insulating Materials, 2013, 46 (02): 33 - 37.
[2] Zhan W P, Chu X L, et al. Study on Aggregation Structure and Dielectric Strength of XLPE Cable Insulation in Accelerated Thermal-oxidative Aging [J]. Proceedings of the Chinese Society for Electrical Engineering, 2016, 36 (17): 4770 - 4778.
[3] Li H, Li J Y, et al. Degradation Trend of Thermal and Mechanical Properties of XLPE Cable Insulation Thermal Aging at Different Temperatures [J]. Insulating Materials, 2018, 51 (01): 57 - 63.
[4] Feng S Y, Zhang J, et al. Polymer of organic silicon and its application [M]. Beijing Jing: Chemical Industry Press, 2004.
[5] Information IEC60216-4-1: 2006, Electrical insulating Materials Thermal endurance properties, [S].
[6] Li J Y, Li H, Zhou F, et al. Copper-catalyzed oxidation caused by copper-rich impurities in cross-linked polyethylene cable insulation [J]. Journal of Materials Science-Materials in Electronics, 2016, 27 (1): 806 - 810.
[7] Wu S Z, Xie D R, et al. Electrical Insulation Materials Science and Engineering [M]. Xi’an: Xi’an Jiao Tong University Press, 2007.
[8] SHIMADA A, SUGIMOTO M, KUDOH H, et al. Degradation distribution in insulation materials of cables by accelerated thermal and radiation aging [J]. IEEE Transactions on Dielectrics and Electrical Insulation, 2013, 20 (6): 2017 - 2116.
[9] Guo H X, Wire and Cable Material [M], Bei Jing: China Machine Press, 2012.