Study on XLPE Temperature-Frequency Aging Based on Combined Analysis of Laser Induced Breakdown Spectroscopy and Gas Chromatography

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Abstract. The aging mechanism of polymer materials such as cross-linked polyethylene (XLPE) has been paid close attention. This paper built a temperature-frequency heat aging platform, which is compared with constant temperature heat aging. The acceleration efficiency of XLPE frequency change heat aging and constant temperature heat aging was compared by Fourier transform infrared spectroscopy. Combined with laser induced breakdown spectroscopy (LIBS) and gas chromatography, the dynamic characteristic of XLPE aging process was explored and the thermal aging mechanism of XLPE and other polymer materials was revealed. It found that the aging effect of frequency-induced heat aging on XLPE was more serious, and the artificial accelerated aging time can be shortened by this method. The content of C, H and O elements increased with the increase of aging time, showing three processes of gradual-increasing-smoothing, corresponding to the three aging stages of the material. The results of gas chromatography showed that XLPE mainly released isobutylene gas in the early stage of aging, and the content of oxygen-containing organic compounds released during the middle and late aging period increased and the isobutylene content decreased.

1. Introduction
In recent years, with the increasing demand for renewable energy and long-distance transmission, high-voltage DC cables have developed rapidly and Cross-linked polyethylene (XLPE) insulated DC cables have been widely used in power transmission systems. Thermal aging and electrical aging is a key factor that restricts the long-term safe and reliable operation of polymer cables. Among them, the heat aging process will not only affect the physical and chemical properties of XLPE cable insulation, but also affect its electrical properties, water branch characteristics, etc[1-6].

Since the middle of the 20th century, researchers at home and abroad have done large amounts of research on the aging mechanism, life model and state evaluation methods of XLPE cable insulation. Wang Xuedong and others from Xi’ an Jiao tong University found that the carbonyl index increased with the aging time during heat aging at different temperatures. The low temperature heat aging was
beneficial to the crystallization of XLPE, and the high temperature heat aging had a significant destructive effect on the crystal morphology of XLPE [7]. Wang Zhiling and others from Chongqing University used NMR to study the longitudinal relaxation time and molecular structure of XLPE after heat aging, and obtained more intuitive aging results [8]. Huang Xingyi and others of Shanghai Jiao tong University have found that thermal oxidation has the most serious impact on the production and growth of XLPE cable insulation surface water trees [9].

At present, a lot of research focuses on the analysis of physicochemical properties, electrical properties and mechanical properties of XLPE constantly heat aging. This paper built a temperature-frequency thermal aging platform (Fig.1.) and uses Fourier transform infrared spectroscopy to analyze the difference of the samples aged in the thermal aging platform and the incubator. The comparison of aging samples revealed the further acceleration of temperature-frequency thermal aging courses. At the same time, the combination of plasma spectroscopy and gas chromatography can further explain the thermal aging mechanism of XLPE and explore the aging characterization parameters, which is expected to reveal the aging reaction of XLPE materials and other polymer materials.

2. Experiment

2.1. Principle
With the XLPE undergoing an aging reaction in the presence of air, a peroxy group and other oxygen-containing groups are formed in the molecular chain. In the high temperature environment, a series of physical and chemical reactions occur in the XLPE. In this paper, the XLPE is undergoing thermo-oxidative aging at 473.5K. It has been found through experiments that the XLPE will change into soft and transparent form in the 473.5K incubator. A large number of literatures indicate that the XLPE has a melting temperature in the range of 378.5 to 388.5 Kelvin. In this paper, the temperature-frequency aging method is adopted to make the XLPE continuously change between the crystalline state and the molten state to achieve the effect of accelerating aging.

2.2. Equipment
The groups of the XLPE aged samples were analyzed by Thermo Nicodet 6700 infrared spectrometer. The change in elemental content of aged samples was analyzed by ChemReveal 3000 Series LIBS laser induced breakdown spectrometer. The composition and content of oxidative aging gas of XLPE were studied by Agilent 7010B gas chromatography-mass spectrometer.

2.3. Preparation of aged samples
The temperature-frequency variable device is used to carry out temperature-frequency aging and constant-thermal aging of the XLPE sample. In order to ensure that the sample is uniformly aging, a sample of 3 cm*1.5 cm*1mm size is taken for experiment. The rise and fall rate of sample temperature
is shown in Fig. 2, and the temperature varies from 293.5 to 473.5 Kelvin. The sample is heated and keep the temperature constant for 55 minutes, then it is lowered to room temperature in 5 minutes. While the normal heating aging sample is aged at a constant temperature of 473.5K in the incubator. The sampling interval of constant temperature aging and temperature-frequency aging experiment is 6 hours. In order to avoid the error caused by the temperature rise and fall time, the aging sample is prepared to ensure that the heating time does not exceed 5 minutes, and the cooling time does not exceed 3 minutes. According to the aging condition of the sample, 5 rounds of aged samples were taken for experimental analysis.

2.4. Preparation of aging gas
In this paper, gas chromatography-mass spectrometry was used to analyze the composition and content of gas produced by temperature-frequency aging of XLPE. The experiment used varying temperature heating aging on quantitative XLPE in an airtight device, and collected aging gas every 6 hours. In order to avoid the analysis error of the result caused by insufficient oxygen, the airtight device is evacuated after each gas collection.

3. Result and Discussion

3.1. Characterization of XLPE
Fig. 3 shows the results of FTIR for the edge and center of the 18h aged sample. It can be seen from the figure that compared with the center of the 18h aged sample, the edge portion of the aged 18h sample has obvious absorption peaks in the 1100-1250cm\(^{-1}\) band and the 1600-1750cm\(^{-1}\) band. The corresponding characteristic groups of these bands are C-O and C=O. It indicates that the thermal aging of XLPE is a process that occurs from the edge and gradually diffuses into the center. This is due to the higher temperature at the edge of the sample, which intensifies the thermal aging of the XLPE edge. And the following test results are all based on the center of sample.
Figure 3. The edge and center of heat 18h aging sample.

Fig. 4 shows the infrared spectrum of the constant temperature heat aging and temperature-frequency aging sample at the same aging time of 30 hours. The result shows that the characteristic absorption peaks of the temperature-frequency aging sample are higher than the constant temperature heat aging test in the 1100-1250 cm$^{-1}$ band (corresponding to the CO bond vibration) and the 1607-1550 cm$^{-1}$ band (corresponding to the C=O bond vibration). The two characteristic groups correspond to the fatty ethers, carboxylic acids, esters, aldehydes and ketones produced by the oxidation reaction of XLPE. It shows that the sample of temperature-frequency aging is more damaged than the sample of constant temperature heat aging. In the process of temperature-frequency aging, the repeated melting and crystallizing of XLPE deteriorates the crystallization zone to a certain extent, and the crystallization
zone changes to the amorphous zone, resulting in a decrease in the crosslinking degree of XLPE and chain relaxation. It increases the chance of Oxygen reaction.

![Infrared Spectrum of Aging Samples](image.png)

**Figure 5.** Different aging samples of temperature-frequency aging.

Compare the infrared spectrum of unaged samples with 6-30h temperature-frequency aging samples, it can be seen that with the aging promoted, the characteristic absorption peak area of 1100-1250cm\(^{-1}\) (corresponding to CO bond vibration) and 1600-1550cm\(^{-1}\) (corresponding to C=O key vibration) bands gradually increases. It indicates that with aging time increasing, the degree of aging of temperature-frequency aging samples is aggravated. In addition, the characteristic absorption peak areas of the 1350-1450cm\(^{-1}\) and 2750-3000cm\(^{-1}\) bands (the bending and vibration peaks corresponding to the methylene groups of the two bands respectively) increase at first and then decrease as the aging time increasing. And reached a maximum at aging 12h. This is because when the sample aging less than 12h, the XLPE just undergoes thermal cracking which will break the molecular chain, resulting in a slight increase in the C-H bond in the sample. After aging more than 12 hours, the XLPE reacts with the oxygen in the air to break C-H key in the molecular chain. It can be seen from the figure that after the sample is aged more than 12 hours, the C-O bond and the C=O bond vibration absorption peak appear, which confirms that the XLPE only undergoes thermal cracking of the molecular chain when aging less than 12 hours.

### 3.2. Emission Spectra of Different Samples

Figure 6 shows the elements spectral intensity distribution of new XLPE in two wavelength ranges, the peak at 388.1nm is relative to C-N spectral, and the spectral peaks at 656.4nm and 777.3nm are attributed to H and O elements, respectively. The LIBS test is performed in air atmosphere, so the detected plasma spectrum is affected by air. The C element in XLPE and the N element in the air form the CN bond, and a certain O element spectral peak will appears in the new material. Fig. 7, Fig. 8 and Fig. 9 are the curves of the C, H and O elements in the new XLPE with the number of laser pulses under the same energy, respectively. The results show that the spectral intensity of C-N fluctuates with the number of pulses, but the overall trend is stable, which is related to the spatial confinement effect of plasma. The spectral intensity of the H element and the O element also exhibits the above trend, so averaging the 23 laser pulse plasma spectra can result in a highly reliable elemental spectral.
Figure 6. The spectral intensity of new XLPE in two different wavelength ranges.

Figure 7. The spectral intensity of C-N in pure XLPE in different pulse number.

Figure 8. The spectral intensity of H in pure XLPE in different pulse number.
Figure 9. The spectral intensity of O in pure XLPE in different pulse number.

Figure 10 shows the variation of the C element spectrum of XLPE with aging time. Fig. 7 shows that the C element content changes slightly before 12h aging time. The spectral intensity of the C element increases sharply between 12h and 18h, indicating that the material begin to take some chemical reactions during this heat aging stage. After 18 hours of heat aging, the spectral intensity of C element tend to be gentle, indicating that the aging of XLPE material has entered the final aging stage. After 21h, there is a slight decrease of the C element spectrum, which may be due to the relaxation of the molecular chain structure in the aged sample and the volatilization of small molecular substances at high temperatures.

Figure 10. The spectral intensity of C-N of XLPE versus aging time.

The variation of the spectral intensity of H element with aging time is shown in Fig. 11. The results show that the spectral intensity of H element increases linearly with the aging time. It may be the damage of crystallization zone in XLPE due to the high temperature, resulting in the volume of the amorphous
region increased and the interaction force between the chains weakened. Thus the ablation volume is increased at the same pulse energy, resulting in the increase in the spectral intensity of the detected H element.

![Figure 11. The spectral intensity of H of XLPE versus aging time.](image)

Figure 11 shows the variation of the spectral intensity of O element with aging time. The result shows that oxygen does not react with XLPE between 0h to 12h aging time. The sharply increase of oxygen element between 12h and 18h indicates that oxygen begins to participate in the aging process of the material, indicating that the reactivity of the group on the molecular chain increases in this stage and the oxidation reaction with oxygen continues to form some groups such as the carbonyl group, et al. After 18h aging time, the spectral intensity of O element tends to be flat, showing that the material has been completely aged and the groups or molecular chains which are prone to react with oxygen have been completely oxidized. This change rule is highly similar to the change of spectral intensity of C element in Figure 10.

![Figure 12. The spectral intensity of O of XLPE versus aging time.](image)
According to the above curve, the heat aging stage of XLPE can be roughly divided into three aging stages. In the early stage of aging, the depolymerisation of the XLPE molecular chain and the destruction of the crystallization zone are dominant. At this stage, no oxygen is involved in the aging process. In the second stage, the oxygen starts to participate in the reaction, mainly manifested by oxidation of the group in XLPE and further fracture of the main chain. The end of aging stage is mainly manifested by the further oxidation of residual groups that are not involved in the oxidation reaction and the volatilization of some small molecular substances generated by thermal oxygen aging.

3.3. Analysis of XLPE Materials Based on Gas Chromatography

Figure 13 shows the data of gas chromatography detection.

The results of gas chromatography analysis show that the stable organic gas products in the temperature-frequency aging process are mainly isobutylene C4H8 (the first peak) and oxygenated organic matter (the second peak), and other organic substances are relatively more unstable and less. Therefore, for the XLPE aged gas, comparative analysis was carried out by the proportion of isobutylene and oxygenated organic matter and the total organic matter.

3.3.1. Analysis of content of the isobutylene gas. Figure 14 show the relationship between the volume of isobutylene produced by aging sample in every 6 hours and aging time. And Figure 15 show the relationship between the total volume of isobutylene and aging time. The specific calculation formula is as follows:

\[ \delta_i = \frac{\sum_{k=1}^{6} V_i}{N_i} (i = 1, 2, 3, 4, 5, 6) \]  \hspace{1cm} (1)

\[ \delta_k = \frac{\sum_{i=1}^{6} V_i}{\sum_{i=1}^{6} N_i} (k = 1, 2, 3, 4, 5, 6) \]  \hspace{1cm} (2)

\( \delta_i \) is the proportion of isobutylene in the organic gas, which is produced by the aging sample in 6 hours in round I, \( V_i \) is the volume of isobutylene in the organic gas, which is produced by the aging sample in round I, \( N_i \) is total volume of organic gas produced by the aging sample in round I, \( \delta_k \) is the proportion of total volume of isobutylene in the organic gas, which is produced by the aging sample in 6*k hours.
As shown in Fig. 14, the amount of isobutylene gas produced by the aged sample-XLPE every six hours presents a straight line, and the linear fit is used to obtain a fitting degree of 96 percents. The results show that with the aging time increases, the amount of isobutylene produced by the thermal aging of the crosslinked polyethylene decreases linearly. The visible light analysis of the experimental samples shows that the thermal oxygen aging of the cross-linked polyethylene will lead to yellowing of the sample, but the degree of color change of the sample is significantly slowed down to the end of aging. The sample is shown in Figure 16, which is consistent with the results of meteorological chromatographic analysis. At the same time, comparing with the results of laser induced breakdown spectroscopy (combustion mainly occurred before 12h), isobutylene gas is mainly the product of thermal cracking of crosslinked polyethylene, which indicates that the degree of thermal cracking gradually decreases with the increase of aging time.
3.3.2. Analysis of content of oxygenated organic matter (the second peak). Figure 17 shows the relationship between the volume of oxygenated organic matter produced by aging sample in every 6 hours and aging time. And Figure 18 shows the relationship between the total volume of oxygenated organic matter and aging time. The calculation formula is the same as the calculation formula of isobutene.

![Aging samples](image)

**Figure 16.** Aging samples.

![Graph](image)

**Figure 17.** The proportion of oxygenated organic matter produced in every 6 hours.

![Graph](image)

**Figure 18.** The proportion of oxygenated organic matter produced by aging sample.
It is shown in Fig. 17 that under different aging time periods, the amount of oxygen-containing organic matter continuously increases with the degree of aging in XLPE, but the growth rate decreases, which is opposite to the change trend of isobutylene. This is because the unaged XLPE does not contain oxygen. In the early stage of aging, it produces relatively less oxygen-containing organic matter. As the thermal oxygen aging progresses, a large amount of oxygen-containing groups are producing on the molecular chain. At this time, the oxygen-containing organic gas produced by the aging of the cross-linked polyethylene increases. By the end of aging, the oxygen in the cross-linked polyethylene has been fully saturated, so the rate of production of oxygen-containing organic matter gets lower. Comparing the results of laser induced breakdown spectroscopy, the change of oxygen content shows S-type growth, which also indicates that the thermal oxygen degradation of aging of XLPE is mainly concentrated in the middle of aging.

4. Conclusion

In this paper, XLPE thermal frequency accelerated aging and constant temperature accelerated aging were compared. Based on laser induced breakdown spectroscopy and gas chromatography, the XLPE material elements and aging gas were analyzed with the increase of aging time. The results show that the temperature frequency change causes more serious aging on the XLPE material than the constant temperature. This method can improve aging efficiency of the material. The change of the spectral intensity of the element can be expressed as the change of the element content. The results show that the content of C, H and O increases with the aging time, which prove the three aging stages of the material. Gas chromatography results show that XLPE releases isobutene gas in the early stage of aging, and the content of oxygen-containing organic compounds is increased and the isobutylene gas content is decreased during the middle and late aging period.

Acknowledgments

This work was financially supported by The National Engineering Laboratory Open Fund Project for Ultra High Voltage Engineering Technology (Kunming, Guangzhou, and NEL201710).

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