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Research on Thermal Aging Behavior and Thermal Decomposition of Insulating Material XLPE

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Abstract. In this paper, accelerated thermal aging experiment was used to simulate the thermal aging behavior of XLPE, and FT-IR, DSC, TG and other test techniques were used to characterize the materials with different aging periods. The results show that with the aging time, the oxygen-containing groups in XLPE increase, and the crosslinking degree of molecular chains decreases. At the same time, the melting peak of the endothermic peak of the material shifts and the endothermic enthalpy decreases. After aging, the high temperature resistance of XLPE decreases and decomposition occurs more easily. The thermal decomposition of XLPE before and after thermal aging was carried out at different temperatures, and the corresponding thermal decomposition gases were collected. According to GC-MS analysis, the thermal decomposition gas products were all small molecule unsaturated olefin, small molecule containing oxygen and long carbon chain containing oxygen, and the content changed significantly before and after aging.

Keywords: high voltage switchgear; Insulation materials; Thermal degradation characteristics; Thermodynamics; dynamics

1. Introduction

Cross-linked polyethylene (XLPE) is regarded as one of the most commonly used insulating materials for high-voltage switchgear due to its good heat resistance and excellent insulation properties [1,2]. During long-term operation, the internal XLPE material often ages due to electrical, thermal and other environmental stresses, resulting in a decrease in its insulation performance [3-5]. During the thermal aging process of XLPE, it will be accompanied by a certain degree of decomposition and chain scission, and the composition and content of the generated gas products are generally analyzed by techniques such as chromatography-mass spectrometry [6-8]. However, due to the long period of traditional aging experiments, it is difficult to collect the thermal decomposition gas of XLPE materials in real time, so there are few reports on the thermal decomposition characteristics and thermal decomposition gas of XLPE insulating materials [9].

Based on this, this paper selects the industrial-grade XLPE insulating material commonly used in high-voltage switchgear as the research object, and uses accelerated thermal aging experiments to simulate the thermal aging of XLPE insulating materials in actual operation. TG), differential scanning calorimetry (DSC) and other test techniques were used to characterize and analyze XLPE with different aging cycles, and to explore the structural changes, thermogravimetric laws and thermal decomposition characteristics of XLPE matrix under different aging cycles. The composition and relative content of thermal decomposition gas were analyzed by GC-MS, and the thermal decomposition law and the type of thermal decomposition gas were determined. This paper has a certain reference value for exploring the thermal aging behavior, condition monitoring and service life of industrial-grade XLPE in the actual use of high-voltage switchgear.

2. experiments

2.1 Thermal aging test

In the experiment, the industrial-grade 10 kV XLPE insulating sleeve material commonly used in high-voltage switchgear provided by Yueqing Saipu Electric Co., Ltd. was selected. After surface

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cleaning, a sample with a length × width of 4 cm × 2 cm and a thickness of 0.5 cm was prepared. The thermal aging experiment was carried out in the DHG-9030A air aging test box, the temperature was 120 °C, one cycle for 7 d, and four aging cycles were carried out. The sample number T0 before aging, with the increase of the aging cycle, the sample number is T1, T2, T3, T4 in sequence.

2.2 Thermal decomposition experiment

Thermal decomposition experiments were carried out on the samples before and after aging by using OTF-1200X tube furnace. The samples were washed with 95% absolute ethanol and deionized water in turn, and dried at 60 °C. Cut the sample into small pieces of 1 × 1 cm, take about 1.5 g of the sample, and put it into the porcelain boat. After installing the tube furnace, nitrogen was introduced to exhaust the residual air in the furnace tube, and the temperature was programmed at a heating rate of 10 °C/min. The temperature was kept at 120 °C, 200 °C, and 285 °C for 30 min respectively, and the gas collecting device was connected synchronously. Carry out gas collection. The specific parameter settings are shown in Figure 1.

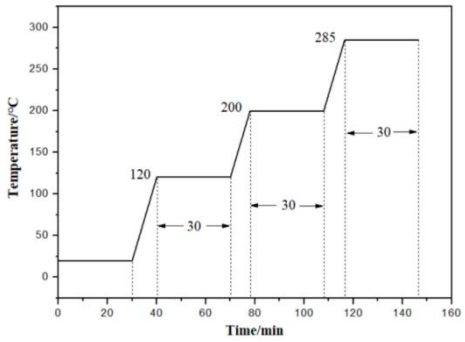

Figure 1. Thermal decomposition experiment parameter setting

2.3 Characterization method

FT-IR characterization: Using Nicolet Is50 Fourier transform infrared spectrometer, the scanning range is 4000~500 cm-1, 32 scans, and the spectral resolution is 4 cm-1.

DSC characterization: Mettler differential scanning calorimeter DSC 3 was used, indium was used for temperature calibration, the sample mass was 3-5 mg, nitrogen atmosphere, gas flow rate was 50 mL/min, heating rate was 10 °C/min, temperature range was 60 ~350°C.

TG characterization: STA-409PC/PG synchronous thermal analyzer was used, the sample mass was 2-4 mg, nitrogen atmosphere, gas flow rate 50 mL/min, heating rate 10 ℃/min, temperature range 30-800 ℃.

GC-MS characterization: QP2010 PLUS gas chromatography-mass spectrometer was used, the selected chromatographic column was SH-Rtx-Wax (30 m × 0.25 mm × 0.25 μm), and the temperature was increased at 10 °C/min to 250 °C and held for 10 min , carrier gas He, split ratio 30:1. The MS detector uses an EI ion source with an electron energy of 70 eV and a mass scan range of 29 to 450 (m/z) amu.

3. Results and Discussion

3.1 Analysis of FT-IR results

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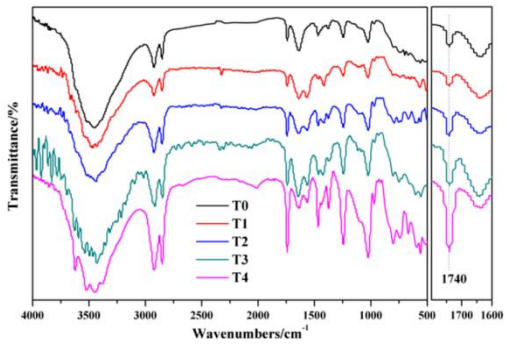

Figure 2. Infrared spectra of XLPE in different aging cycles

The infrared spectra of XLPE samples with different aging cycles are shown in Figure 2. It can be seen from Figure 2 that the absorption peaks in the 2750cm-1-3000 cm-1 band are attributed to the characteristic absorption peaks of saturated carbon-hydrogen bonds-CH, methylene-CH2, and methyl-CH3. The absorption peak around 1635 cm-1 corresponds to the C=C stretching vibration of olefins. The absorption peak near 1740 cm-1 corresponds to the stretching vibration of carbonyl C=O, and the absorption peak of carbonyl is usually used as a characteristic peak to characterize thermal-oxidative aging. In addition, the absorption peaks around 800 cm-1 usually correspond to unsaturated hydrocarbon functional groups [10]. With the extension of thermal aging period, the position and intensity of its main characteristic absorption peaks changed accordingly. In the early stage of aging, the structural change of the material is small, and the internal oxygen-containing groups are less, the possible reason is that the antioxidant added in XLPE inhibits the thermo-oxidative degradation process [5]. In the later stage of aging, the main chain is broken and the molecular chain is relaxed, the reaction between the molecular chain and oxygen is deepened, the oxygen-containing groups in the molecular chain are slowly increased, and the sample is gradually oxidized. The intensity of the carbonyl absorption peak in the later stage of aging increased significantly, and the unsaturated olefins gradually increased.

3.2 Analysis of DSC results

In order to simulate the actual situation of the high-voltage switchgear running at a lower temperature, the experiment mainly tested the DSC curve of XLPE at 60-350 ℃, and the results are shown in Figure 3. It can be seen from Figure 3 and Table 1 that the DSC curves of XLPE with different aging cycles have the same shape, and the position of the crystal melting peak has changed significantly. The melting peak peak 1 at low temperature shifts to high temperature with the prolonging of aging time, and the area of the endothermic peak gradually decreases, and the endothermic enthalpy decreases. It may be due to the destruction of the XLPE crystalline region due to thermal aging, the spherulite size of the material changes, and the crystallinity becomes smaller. As the aging time increases, the melting peak peak 2 at high temperature shifts to the low temperature direction, and the area of the endothermic peak gradually decreases, the endothermic enthalpy decreases, and the high temperature resistance of the material decreases .

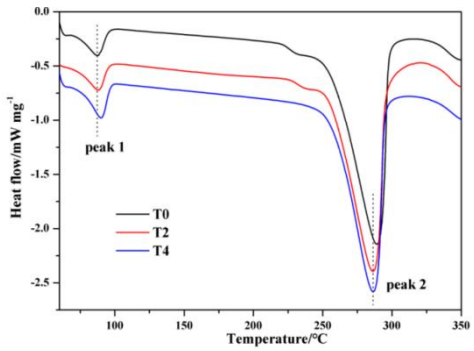

Figure 3. DSC spectra of XLPE with different aging cycles

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Table 1. Data of DSC endothermic peak of XLPE insulation materials with different aging cycles

different cycles	Peak 1		Peak 2	
	Peak temperature/℃	Endothermic enthalpy/mJ	Peak temperature/℃	Endothermic enthalpy/mJ
T0	87.07	-115.80	289.13	-1259.76
T2	88.28	-114.51	286.76	-1069.41
T4	90.15	-113.44	285.82	-891.88

3.3 Analysis of TG results

Figure 4 shows the TG spectrum of the XLPE material, and the thermogravimetric properties of the sample can be divided into three stages. Comparing the TG spectra of T0 before thermal aging of XLPE and T4 after four cycles of aging, it can be seen that the weight loss rate of T4 sample is slightly higher than that of unaged XLPE (T0), and the residual mass of the sample is lower. In the first stage of the TG spectrum, the temperature of the first weight loss platform of the two is similar. Compared with the curve T0, the weight loss is about 6.5%, and the weight loss of T4 is more, which is 7.1%; in the second stage, the XLPE material undergoes In the third stage, the curve T4 also showed more obvious weight loss, and the residual rate of the sample was lower, only 28.1%. The results of TG analysis show that thermal aging will destroy the molecular chain structure inside the XLPE material, causing irreversible defects or structural damage, which makes the material more prone to decomposition during the heating process.

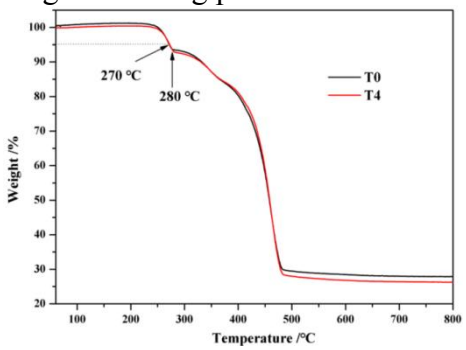

Figure 4. TG spectra of XLPE before and after thermal aging

Table 2. Analysis of thermal decomposition characteristics of XLPE insulation materials

weightlessness stage	temperature/℃	Weight loss analysis	Analysis of decomposition characteristics
The first stage	60-280	About 7% weight loss	Corresponding to the volatilization of water, small molecules, cross-linked by-products and other organic additives (such as DOP) in the sample
second stage	280-485	Rapid weight loss of the sample	In the early stage of decomposition, random decomposition mainly occurs, and the quality remains basically unchanged; in the later stage of decomposition, the decomposition products volatilize at high temperature, causing the quality of XLPE to drop rapidly.
The third stage	485-800	Quality tends to be stable	The residual rate remains basically unchanged, and the remaining parts are mainly carbonized products and inorganic fillers, etc.

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3.4 Analysis of GC-MS results

According to the test results of DSC and TG (Figure 5), combined with the actual situation of the high-voltage switchgear used at lower temperatures, the thermal decomposition temperature and holding time of the XLPE sample were determined. The results are shown in Figure 1.

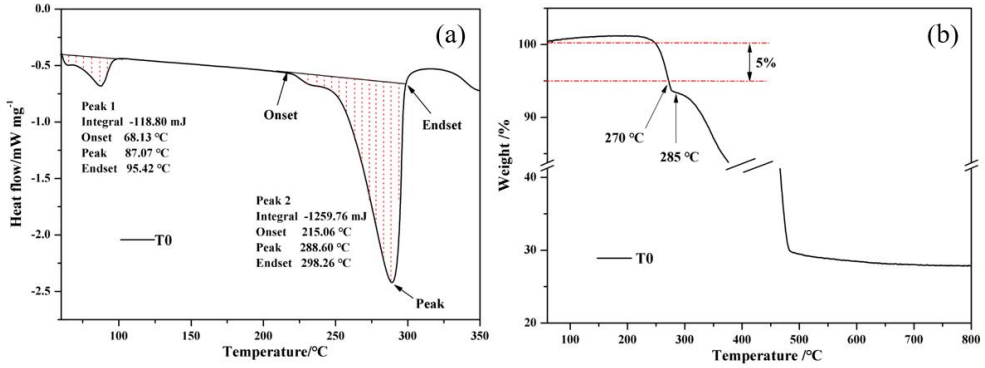

Figure 5. DSC spectra(a) and TG spectra(b) of unaged XLPE

The thermal decomposition gas of unaged XLPE was analyzed, and the results are shown in Figure 6. It can be seen from Figure 6 that at the selected thermal decomposition temperature (120 ℃, 200 ℃, 285 ℃), the types of gases decomposed by XLPE are basically the same, namely ethylene, succinic anhydride, formamide, vinyl formate, ethylene di acid and dioctyl phthalate. The gases corresponding to each peak in the gas total ion current spectrum of unaged XLPE at different thermal decomposition temperatures are shown in Table 3.

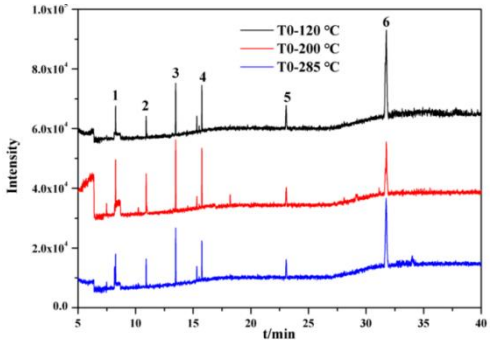

Figure 6. Gas total ion flow spectra of unaged XLPE at different thermal decomposition temperatures

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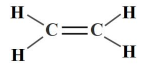
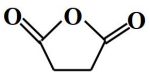
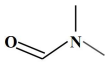
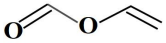
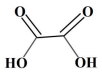
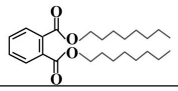
Table 3. Summary of thermal decomposition gases in XLPE non-aging T0 sample

serial number	keep time	molecular weight	molecular formula	Molecular Structure
1	8.265	28	C_2H_4	
2	10.920	100	$C_4H_4O_3$	
3	13.475	73	C_3H_7NO	
4	15.745	72	$C_3H_4O_2$	
5	23.080	90	$C_2H_2O_4$	
6	31.750	390	$C_{24}H_{38}O_4$	

In order to compare and analyze the thermal decomposition gas and decomposition law of XLPE samples before and after thermal aging (T0, T4), the components and relative contents of the collected gases were analyzed by GC-MS. Figure 7 shows the total ion chromatograms of thermally decomposed gas samples of XLPE (T0, T4) at different temperatures (200 °C, 285 °C).

The mass spectral characteristic ion peak area of each characteristic component in Figure 7 is normalized, and the relative content of the obtained gas is shown in Table 4. It can be seen that at the same thermal decomposition temperature, the gas content decomposed by the XLPE material before and after aging has changed significantly. The thermal decomposition gases before aging are mostly unsaturated hydrocarbons, and the content is higher than that of the samples after aging. Compared with the oxygen-containing small molecule gas products, it can be seen that the content of such gases is relatively higher under the condition of lower decomposition temperature (200 °C). After increasing the thermal decomposition temperature (285 °C), the oxygen-containing gas products appeared in the form of longer carbon chains. After four cycles of thermal aging, the oxygen content in the gas product increased significantly. Peak 6 corresponds to dioctyl phthalate (DOP), a common plasticizer. By comparative analysis of No. 6 peaks, it is found that the unaged samples have released such gases at a lower temperature (120 °C). After aging treatment, the decomposition phenomenon is more obvious. It may be that DOP continued to decompose during the aging process. After 4 cycles of aging, the content of DOP in the material decreased significantly, and the material performance deteriorated gradually.

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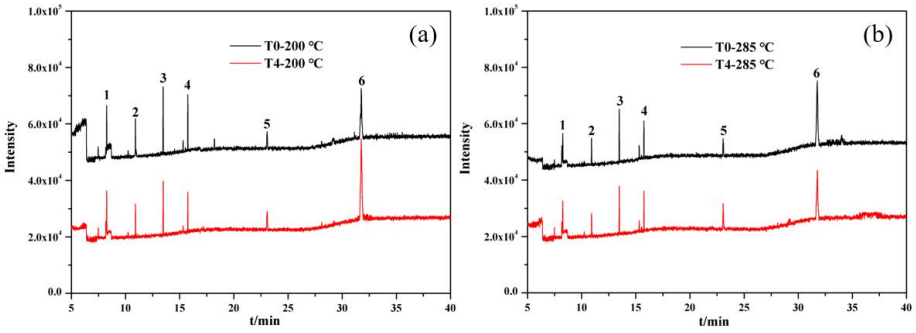
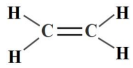
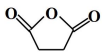
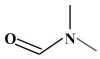
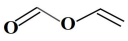
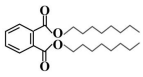


Figure 7. Comparison of total ion flow spectra of XLPE pyrolysis gas samples at different temperatures before and after thermal aging

Table 4. Summary of total ion flow spectra of XLPE gas samples before and after thermal aging

serial number	Molecular Structure	Normalized peak area (200 ℃)			Normalized peak area (285 ℃)		
		T0	T4	T0/T4	T0	T4	T0/T4
1		34636	29589	1.171	29611	27266	1.086
2		20958	17960	1.167	17420	12378	1.407
3		43022	31484	1.366	33725	28882	1.168
4		29301	17987	1.629	18095	17276	1.047
5		23391	29963	0.781	24236	31735	0.764
6		130989	236943	0.553	187595	129277	1.451

4. Conclusion

(1) With the prolongation of aging time, the oxygen-containing groups inside the XLPE material increase, the cross-linking degree of the molecular chain decreases, a large number of aging products are generated, and the unsaturated hydrocarbons gradually increase.

(2) With the prolongation of aging time, the endothermic melting peak of the sample shifted and the endothermic enthalpy decreased slightly, corresponding to a decrease in the high temperature resistance of XLPE after aging; the types of gases generated by thermal decomposition of the sample before and after aging Basically the same, the main gas types are small molecular unsaturated olefins, oxygen-containing small molecules and oxygen-containing long carbon chain gases, but their contents have changed significantly before and after aging.

(3) Both the aging period and the thermal decomposition temperature have a certain influence on the thermal decomposition characteristics and decomposed gas of the XLPE insulating material, and show a certain regularity.

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References

[1] [SHAN Weiwei, WANG Jian. Review on the combustion and thermal aging of insulation materials for electric wires and cables[J]. Plastics, 2020, 49(03): 151-155.

[2] [LIU Meibing, YANG Kaijun, TU Demin. Comparative analysis of performances in HV XLPE cable materials[J]. Electric Wire & Cable, 2014(2):21-25.

[3] ZHANG Jing, LUO Chuanxian, YANG Fengyuan, et al. Study on experimental characteristics of leakage current and partial discharge for DC XLPE cables[J]. High Voltage Apparatus, 2019, 55(02): 140-148.

[4] ZHAN Weipeng, CHU Xuelai, SHEN Zuojia, et al. Study on aggregation structure and dielectric strength of XLPE cable insulation in accelerated thermal-oxidative aging[J]. Proceedings of the CSEE, 2016, 36(17): 4770-4778.

[5] ZHANG Y, WU Z J, QIAN C, et al. Research on lifespan prediction of cross-linked polyethylene material for XLPE cables[J]. Applied Sciences, 2020, 10: 5381-5393.

[6] Tang Ming, Wei Lue, Gao Yuan, et al. Research and algorithm design of the gas detection system for volatile organic compounds of XLPE cables[J]. Electrical Measurement & Instrumentation, 2018, 55(23): 82-89.

[7] [ZHANG Zhenyu, JIN Tao, WANG Tianzheng, et al. Insulation defect recognition of air switchgear based on gas detection[J]. Engineering Journal of Wuhan University, 2021, 54(08): 761-768.

[8] ChenKe, YuanShuai, GongZhenfeng, et al. Ultra-High sensitive photoacoustic spectrometer for trace gas detection based on Fiber-Optic acoustic sensors[J]. Acta Optica Sinica, 2018, 38(03): 185-190.

[9] HE D, ZHANG T, MA M, et al. Research on mechanical, physicochemical and electrical properties of XLPE-Insulated cables under Electrical-Thermal aging[J]. Journal of Nanomaterials, 2020, 2020: 1-13.

[10] ZHANG Y, HOU Z, WU K, et al. Influence of oxygen diffusion on thermal ageing of cross-linked polyethylene cable insulation[J]. Materials (Basel), 2020, 13: 2056-2067.