Analysis of electrical tree ageing in silicone rubber by physicochemical approach

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Abstract. In this paper, the characteristics of electrical tree ageing in silicone rubber (SIR) under AC voltage were studied. The electrical tree initiation rate is 20% after the application of 6 kV AC voltage for 1000 hours. Samples are separated into three kinds according to processes of electrical tree formation: virgin samples without voltage application, non-treed samples without electrical tree formation after 1000 hours and treed samples with electrical tree formation after 1000 hours. Certain physicochemical diagnostic tests were carried out to understand the degradation of material, ascribed to long-time voltage application, using differential scanning calorimetry (DSC) and thermogravimetric–differential thermal analysis (TG–DTA). Physicochemical analyses, especially the DSC results, show that no additional phases are formed in the processes of electrical tree ageing in SIR. Reduction of the melting point and crystallinity of SIR is observed in the sequence of virgin samples, non-treed samples and treed samples. The activation energy values were calculated from the TG-DTA data. Compared to virgin samples, obvious reduction of activation energy value is observed in non-treed samples. Degradation in SIR has already occurred before electrical tree formation and charge injection and extraction by high field electrode under AC voltage is regarded as the reason.

1. Introduction
With the increase of voltage level, electrical tree ageing is found to be a formidable problem for power cable systems including cable and cable accessories, which are increasingly used in urban areas, hydropower station and pumped-storage power station [1, 2]. Silicone rubber (SIR), as an advanced internal insulating material, has been widely used in high voltage cable accessories due to its excellent insulation and mechanical performance. Although electrical tree phenomena have been found in SIR, enough attentions have not yet been paid. Studies on SIR were mainly concentrated in the external insulation characteristics like flashover characteristics, hydrophobic, weathering aging properties, and so on [3-9]. So it is necessary and urgent to study the electrical tree phenomena of SIR for the stable operation of electrical power system and the development of insulation materials. In this paper, the characteristics of electrical tree ageing in SIR under AC voltage were studied.

The process of electrical tree initiation in SIR is a highly complicated process. Under normal operating voltage, some defect site in SIR, such as gas cavities, conducting inclusions and intrusions, may lead to partial breakdown. Depending on the size and shape of the defect, the stress distribution in the insulation material is altered, causing joule heating/oxidation of the material and a reduction in
breakdown strength/local erosion forming prebreakdown channels. In one case, these channels, formed around the defect site in the dielectric structure, resemble branches of a tree and thus the term “electrical tree” is given to the deleterious process. In other cases, although the structure of insulating material around the defect site has already changed, but defect structures that resemble tree branches are not seen and thus the term “electrical tree ageing” should be given to this deterioration process. In this paper, physicochemical approaches are used to analyze the characteristics of electrical tree ageing in SIR to supply an available method to detect the invisible degradation processes in electrical tree ageing.

2. Experimental details
The classical needle-plane electrode was chosen to study the electrical tree ageing characteristics of SIR. The schematic structure and dimension of sample with needle and plane electrodes is shown in Figure 1. The high voltage electrode and ground electrode are all semi-conductive SIR electrode. A stainless steel needle electrode with diameter 250 µm, needle tip 30°, tip curvature radius 2 µm, was used to simulate the defect in SIR. The distance between the needle tip and plane electrode is 4±0.1 mm. The raw material used in this paper was two components liquid SIR. After two components of liquid SIR were mixed, needle electrode was put into the liquid unvulcanized rubber. Then the mixed rubber with needle electrode was put into the prefabricated mould and was heated to 100°C to vulcanize. The micrograph of sample with needle electrode is shown in Figure 2.

![Figure 1. Schematic structure and dimension of sample with needle and plan electrodes.](image1)

![Figure 2. Micrograph of sample with needle electrode.](image2)

According to the former studies [10], the mean value of tree initiation voltage at power frequency is 9.7 kV and the minimum value is 7.2 kV. Consequently, 6 kV AC voltage with frequency of 50 Hz was applied on 20 samples to study electrical tree ageing characteristics of SIR. Electrical tree processes were observed by a digital image processing set consisting of a microscope, a digital camera and a computer. In order to increase the efficiency of experiment, a digital micro-observing system for electrical tree experiments of multi samples, as shown in figure 3, were designed and the application number of Chinese patent is 200810238886.8.

The electrical tree initiation rate is 20% after the application of 6 kV AC voltage for 1000 hours. Samples were separated into three kinds according to processes of electrical tree formation: virgin samples without voltage application, non-treed samples without electrical tree formation after 1000 hours and treed samples with electrical tree formation after 1000 hours. Certain physicochemical diagnostic tests were carried out to understand the degradation of material, ascribed to long-time voltage application, using differential scanning calorimetry (DSC) and thermogravimetric–differential thermal analysis (TG–DTA).
3. Result and discussions

3.1. Differential scanning calorimetry (DSC)

This technique involves the measurement of energy necessary to establish a zero temperature difference between the specimen and a reference material when the two specimens are subjected to thermal degradation. The melting behaviour of the specimens was observed using a Perkin–Elmer model DSC-2C apparatus (Perkin Elmer Cetus Instruments, Norwalk, CT). The experiments were performed in a nitrogen atmosphere, at a heating rate of 10°C/min. Alumina was used as a standard.

DSC currents of different kinds of silicone rubber samples are shown in Figure 4 and the calculated melting point, caloric content and crystallinity of different kinds of silicone rubber samples are shown in table 1. The DSC results show that no additional phases are formed in the processes of electrical tree ageing in silicone rubber. Reduction of the melting point and crystallinity of silicone rubber is observed in the sequence of virgin samples, non-treed samples and treed samples.

Silicone rubber is a highly micro filled polymer system composed basically of polydimethylsiloxane (PDMS) polymer and ‘micro’ fumed silica filler. Silicone rubber is composed of the chain of –Si–O– and there are two symmetric methyl groups in the side chain of Si atom. Because of the good solid stereoregularity of the chain and the small steric hindrance of substituent, crystallization can occur in silicone rubber at low temperature. Meanwhile, the aggregation structure of silica and interactions of silica and PDMS has a great influence on the crystallization properties.

Because the silica and PDMS are connected by hydrogen bonding formed by the hydroxyl in the surface of silica and oxygen atom of PDMS, microcrystalline area is formed with silica as nucleation. The increased physical crosslinking points of the filling system reduce the dynamic mobility of molecular chain and the packing density of macromolecular, and then lead to the slowdown of crystallization. As shown in table 1, the melting point of SIR increases in the sequence of treed...
samples, non-treed samples and virgin samples. That means, as the extent electrical tree damage increases, the melting point moves to a higher temperature.

Charge injection and extraction is considered to be an intrinsic factor. When external electrical field was applied to the samples, the electrons in the bulk of SIR or injected from the needle electrode would be accelerated in negative half cycle, and be drawn back in the positive half cycle. If the electrons drift under the applied field and the excitation energy after accelerated is large enough, avalanches will occur, and, hydrogen bond of SIR molecular will be cut by collision with carrier, resulting in the decrease of physical crosslinking points. At the same filling quantity, the more combined PDMS the surface of silica adsorbed, the more orderly connections there are and then the higher the crystallinity of SIR is. Consequently, according to the analyses of DSC, it can be concluded that electrical tree ageing leads to the destruction of the chemical connection between silica and PDMS.

![Heat Flow vs Temperature Graph](image)

**Figure 4.** Differential scanning calorimetry currents of different kinds of silicone rubber samples.

**Table 1.** Melting point, caloric content and crystallinity of different kinds of silicone rubber samples

|                | Virgin samples | Non-treed samples | Treed samples |
|----------------|----------------|-------------------|--------------|
| melting point  | -44.6          | -44.8             | -47.1        |
| caloric content| 24.4           | 22.1              | 19.0         |
| Crystallinity  | 65%            | 59%               | 51%          |

3.2. *Thermogravimetric–differential thermal analysis (TG-DTA)*

The TG–DTA study was carried out with Netzsch STA 409C equipment. The experiments were performed in a nitrogen atmosphere, in the range 50°C to 900°C. Alumina was used as a standard catalyst. The TG and DTA methods are very effective techniques to study the chemical and physical phenomenon as a function of temperature. Figure 5 shows the thermogravimetric–differential thermal analysis currents of different kinds of silicone rubber samples at the heating rate of 10°C per minute.
In order to evaluate the thermal stability of degradation area in SIR further, degradation kinetics of virgin samples and non-treed samples were studied. Samples were heated from 50°C to 900°C in high purity nitrogen protection area with an increase rate of 5°C, 7°C, 10°C, 15°C, 20°C per minute, and their weight change curves were recorded. Because there is only one reaction in the protection of nitrogen, the thermal degradation processes can be described by Arrhenius equation. The rate of weight loss can be described by [11]:

\[
\frac{dc}{dt} = (1 - c)^n A \exp\left(\frac{-E}{RT}\right)
\]  (1)  

\(n\)–reaction order,  
\(A\)–factor,  
\(E\)–activation energy,  
\(R\)–gas constant,  
\(T\)–Kelvin temperature.

The heating rate is

\[ r = \frac{dT}{dt} \]  (2)

Consequently,

\[
\frac{dc}{dt} = r \frac{dc}{dT} = (1 - c)^n A \exp\left(\frac{-E}{RT}\right)
\]  (3)

**Figure 5.** Thermogravimetric–differential thermal analysis currents of different kinds of silicone rubber samples at the heating rate of 10°C per minute.
The boundary condition of equation 2 is:

\[(1 - c)_{t=0} = 1 \quad T_{t=0} = T_a\]  \hspace{1cm} (4)

\(T_a\) is the room temperature. According to the equation of Kissinger [11],

\[\frac{A}{r} = \frac{E}{R T_{\text{max}}^2} \exp\left(\frac{-E}{RT_{\text{max}}}\right)\]  \hspace{1cm} (5) \cite{11}

\(T_{\text{max}}\) is the temperature at which the weight loss rate is the largest. So,

\[\ln\left(\frac{R T_{\text{max}}^2}{r}\right) = -\frac{E}{R} \cdot \frac{1}{T_{\text{max}}} + \ln\frac{E}{A}\]  \hspace{1cm} (6)

Fitting currents of degradation kinetics of virgin samples and non-treed samples according to Arrhenius equation are shown in Figure 6. The activation energy values were calculated from the TG-DTA data, as shown in Figure 7. Compared to virgin samples, obvious reduction of activation energy value is observed in non-treed samples.

**Figure 6.** Fitting currents of degradation kinetics of virgin samples and non-treed samples according to Arrhenius equation.
4. Conclusion
Physicochemical analyses, especially the DSC results, show that no additional phases are formed in the processes of electrical tree ageing in SIR. Reduction of the melting point and crystallinity of SIR is observed in the sequence of virgin samples, non-treed samples and treed samples. The activation energy values were calculated from the TG-DTA data. Compared to virgin samples, obvious reduction of activation energy value is observed in non-treed samples. Degradation in SIR has already occurred before electrical tree formation and charge injection and extraction by high field electrode under AC voltage is regarded as the reason. Physicochemical approaches supply an available method to detect the invisible degradation processes in electrical tree ageing.

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