Electrical Tree Aging of Epoxy-Based Nanocomposites at Cryogenic Temperature

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Abstract. Electrical insulation at cryogenic temperatures is a key technology in the development of superconducting cables and superconducting current limiters. Due to their improved electrical, mechanical and thermal properties, the application of epoxy nanocomposites in high voltage power systems has shown a broad outlook. In this paper, tests were conducted to investigate the electrical tree aging phenomenon in epoxy resin/Al₂O₃ nanocomposites in liquid nitrogen under AC voltages. The test samples were prepared with six levels of nanofiller content: 0 wt %, 1 wt %, 2 wt %, 3 wt %, 4 wt %, and 5 wt % by weight ratio. Experimental results showed that nanofillers below 3% are easy to cause the electric field distortion at the needle tip, which reduces the tree inception voltage in the composite sample compared to that in the neat epoxy sample. At low temperature, the effect of electric field distortion on the tree inception voltage is significantly weakened and the tree growth rate decreases sharply with the increase of the content of the nano-filler.

1. Introduction
Due to its excellent insulation and mechanical properties, epoxy resin was widely used as an insulating and support material for cryogenic power equipment, especially for superconducting cables and superconducting current limiters [1-4]. However, in the process of production and installation, some small defects such as air gaps, micropores and impurities are inevitably introduced into the insulating materials, which may even cause cracking of the insulating material at cryogenic temperatures[5, 6]. These defects will cause ununiform electric field distribution and local stress concentration which lead to further PD and carbonized electrical tree channels in the insulating material [7, 8]. The appearance of carbonized channels means
the degradation of materials and the reduction of service life.

In order to solve this problem, epoxy nanocomposites (mainly inorganic nano-fillers) with superior mechanical strength and electrical insulation properties have attracted more and more attention as new insulating materials, which can improve insulation reliability and optimize the structural design of cryogenic power equipment. In earlier investigations, nanofillers uniformly dispersed in polymers have brought significant improvements in properties such as electrical strength, mechanical strength, and thermal conductivity. Epoxy nanocomposites can improve the resistance to PD and tree growth inside the matrix polymer. Stephanie Raetzke et al found that tree initiation V-t characteristics were improved obviously for the epoxy/nanoclay composite compared to the neat epoxy resin [9]. Ohta et al confirmed that the voltage lifetime of the epoxy resin with 30 phr of magnesium hydroxide was approximately 100 times longer than the neat epoxy resin [10]. Nanofiller can also effectively improve the thermal conductivity of epoxy resin insulation [11]. When the insulating material is in PD state at cryogenic environments, the nanofiller of high thermal conductivity can effectively conduct the heat generated by PD to the outside environments, thereby preventing further carbonization of the material. At the same time, higher thermal conductivity can better prevent the accumulation of space charge in the material.

The limited investigations of epoxy nanocomposites in the electrical insulation field at cryogenic temperatures make it difficult for superconducting power devices to determine better insulation materials and optimal insulation dimensions. In this work, we focused on PD and tree resistance of epoxy nanocomposites in liquid nitrogen. In order to verify the application possibilities of epoxy nanocomposites at cryogenic temperature, we performed electrical tree tests of epoxy/Al$_2$O$_3$ nanocomposites. In addition, COMSOL Multiphysics® software was used to simulate the electric field at needle tip in the neat epoxy resin and epoxy/Al$_2$O$_3$ nanocomposites.

2. Material prepared for the test

2.1. Nanoparticle modification

In this work, nano-Al$_2$O$_3$ was used as the filler, and the particle size was concentrated at around 100 nm. Since nano-Al$_2$O$_3$ and epoxy resin are difficult to be directly compatible, the inorganic nanoparticles were surface treated with silane coupling agent KH–560, which can change the physicochemical properties of their surface and improve their bonding with epoxy resin. The reaction during the silane coupling agent with the surface of nano-Al$_2$O$_3$ was shown in figure 1. The silane coupling agent is hydrolyzed to form active silanol and then the silanol forms a hydrogen bond at the surface of inorganic nano-particle. The FTIR spectra of the surface treated inorganic nanoparticles were shown in figure 2. It can be found that the C-H vibrational stretching peaks of -CH$_3$ and -CH$_2$ appear at 2927 cm$^{-1}$ and 2870 cm$^{-1}$, respectively, indicating that the coupling agent has been bonded to the surface of nano-Al$_2$O$_3$. 

Figure 1. The reaction during the silane coupling agent with the surface of nano-Al$_2$O$_3$.

Figure 2. FTIR spectra of (a) treated nano-Al$_2$O$_3$; (b) untreated nano-Al$_2$O$_3$.

2.2. Preparation of neat epoxy resin and epoxy composite materials

Two types of samples were prepared: (a) neat epoxy (without fillers), (b) epoxy composites (with spherical Al$_2$O$_3$ fillers). The scale of the filler was around 100 nm. The filler content was fixed at 1%, 2%, 3%, 4%, 5% (parts per hundred parts of resin by weight ratio, for example, 1% means 1 g of alumina filler was mixed to 100 g of epoxy resin). The epoxy resin employed for this work was commercially available high active and low viscous liquid bisphenol F (Araldite GY-285) and the hardener was commercially available low viscosity liquid aromatic amine (Aradur 5200). For all samples, the epoxy resin and hardener (100:24 by weight ratio) were mixed with the fillers at 70 °C for 30 min. The sample mixtures were degassed in a vacuum chamber at room temperature for 60 min and then poured them into a stainless steel mold with a pre-inserted needle electrode. The mixture was cured at 70 °C for 7h, followed by a further 5h at 130°C. As shown in figure 3, the size of the sample was 20 mm × 20 mm × 4 mm (length × height × width) and the needle electrode was 0.18 mm in diameter. The radius of curvature and the cone angle of the tip are 2 μm and 30°, respectively. The distance between the needle tip and the bottom of the test sample is 2 mm.
2.3. Experimental set-up

A 50 Hz AC voltage was applied to the samples at a continuously rising speed (1 kV/30s) to measure tree initiation voltage. An AC voltage test system (model BGCZX) with a capacity of 5 kVA was used as shown in figure 4(a). The test sample was held tightly between the high voltage electrode and the ground electrode by two non-conductive polytetrafluoroethylene (PTFE) screws, as shown in figure 4(b). The prepared epoxy samples were immersed in liquid nitrogen and insulating oil, respectively, to compare the electrical tree growth characteristics of the samples at different temperatures.

Figure 3. The test sample for treeing experiments.

Figure 4. AC test system and electrodes configuration. (a) 5 kVA AC test system, (b) sample jig for AC breakdown test.

3. Results and discussion

3.1. Effect of nano-filler on electrical tree inception voltage

The tree inception voltage was defined as the voltage at which the tree length observed by the CCD camera had exceeded 10 μm. Once a tree had been observed, the voltage is retained to keep the tree propagation. Figure 5 shows the tree inception voltage for epoxy and composite samples in liquid nitrogen and insulating oil. It can be found that when the filler content is less than 3%, the average tree inception voltage of the "without filler" samples is higher than that of the "with filler" samples. When the filler content is higher than 3%, the trend is the opposite, which is not completely consistent with previous investigations [12, 13]. It’s suggested that the difference in dielectric constant between the filler and the resin causes the distortion of the electric field at the needle tip, which makes the region at the needle tip a weak region that
prevents PD and reduces tree inception voltage.

**Figure 5.** The tree inception voltage for the neat epoxy resin and nanocomposites in liquid nitrogen and insulating oil.

COMSOL Multiphysics® software was used to simulate the electric field at needle tip in the neat epoxy resin and epoxy/Al₂O₃ nanocomposites. As shown in figure 6(a), the electric field at the needle tip in neat epoxy material is 53.9 kV/mm, while the electric field at the needle tip in the nanocomposite is as high as 991.8 kV/mm, which is about 18 times higher than that in neat epoxy material. It seems a perfect explanation for the reason why the filler reduces the tree inception voltage, but this model is not suitable when the filler is greater than 3%. In fact, there are so many possibilities for the distribution of nanofillers near the needle tip. The filler may just wrap the needle tip completely, or it may be partially wrapped, or even completely separated from the needle tip like figure 6(b). Different distributions will cause different degrees of distortion of the electric field near the tip. But one thing we can fully confirm is that the higher content of the filler means that the more particles are distributed inside the sample, the more likely it is to wrap the needle tip, resulting in an increase in tree inception voltage.

**Figure 6.** The electric field at needle tip in the neat epoxy resin and nanocomposites

From the figure 5, It can be found that the tree inception voltages of all samples in the liquid nitrogen is nearly double those in the insulating oil, and the electric field distortion caused by the filler is significantly weakened in the liquid nitrogen. The high thermal conductivity of the nano- Al₂O₃ may be responsible for this result. When the insulating material is in PD state
in the liquid nitrogen, the nanofiller with high thermal conductivity can effectively conduct the heat generated by PD to the outside, thereby increasing the tree inception voltage. Based on our previous work, the state of the oxygen inside the material is also one of the reasons for the increase of tree inception voltage[14].

3.2. Effect of nano-filler on electrical tree propagation

The changes in tree length over time in the samples in insulating oil are shown in figure 7. The tree length is defined as the distance between the needle tip and the tip of the furthest tree branch. It can be found that the introduction of nanofillers significantly inhibits the propagation of trees in the sample. An interesting phenomenon is that before 120 min, the tree propagation in the composite sample is always faster than that in the neat epoxy sample when the nano-filler content is less than 3%, which is related to the distortion of the electric field at the needle tip caused by the nano-fillers. After 120 min, the tree propagation in the neat epoxy sample is in the lead. When the nano-filler content is higher than 3%, the above phenomenon does not occur any more, which indicates that nano-fillers with high content can inhibit tree propagation more effectively.

![Graph](image)

**Figure 7.** The changes in tree length over time in the samples in insulating oil.

The changes in tree length over time in the samples in liquid nitrogen are shown in figure 8. It can be found that the tree length in the sample in liquid nitrogen is much shorter than that in the sample at room temperature, which means the tree propagation in the sample at low temperature is inhibited strongly. It is worth noting that when the nano-filler content is less than 3%, the effect of the electric field distortion caused by the nano-fillers on the tree propagation is obviously weakened at a low temperature. At low temperature, the tree growth rate decreases sharply with the increase of the content of the nano-filler. It can be predicted that nano-fillers with higher content will inhibit the tree growth in the material more strongly, but whether the changes in thermal and mechanical properties of materials caused by higher content can be better applied to the low-temperature environment is also worth considering in the future.
Figure 8. The changes in tree length over time in the samples in liquid nitrogen.

4. Conclusion
We focused on the electrical tree characteristics of the neat epoxy and composite sample in liquid nitrogen. Tree inception voltage and tree length measurements were carried out at different temperatures. The following conclusions can be drawn:

(1) Nano-fillers below 3% are easy to cause the electric field distortion at the needle tip, which reduces the tree inception voltage in the composite sample compared to that in the neat epoxy sample, while the nano-fillers above 3% will wrap the needle tip with great probability, causing the increase of tree inception voltage. The effect of this distortion on the tree inception voltage is significantly weakened at low temperature.

(2) The electric field distortion caused by the nano-fillers below 3% promotes the tree propagation in composite samples at room temperature before 120 min. After 120 min, the tree propagation in the neat epoxy sample is in the lead. At low temperature, the tree growth rate decreases sharply with the increase of the content of the nano-filler.

5. References
[1] Y. Yu, B.X. Du, J.X. Jin, T. Han, J.G. Su, Effect of Magnetic Field on Electrical Treeing Behavior of Silicone Rubber at Low Temperature, Ieee Transactions on Applied Superconductivity, 26 (2016).
[2] I. Sauers, D.R. James, A.R. Ellis, M.O. Pace, High voltage studies of dielectric materials for HTS power equipment, Ieee Transactions on Dielectrics and Electrical Insulation, 9 (2002) 922-931.
[3] D.J. Swaffield, P.L. Lewin, G. Chen, J.K. Sykulski, Cryogenic dielectrics and HTS power apparatus: Research at the University of Southampton, Ieee Electrical Insulation Magazine, 22 (2006) 29-37.
[4] J.Y. Koo, Y.J. Lee, W.J. Shin, Y.H. Kim, J.T. Kim, B.W. Lee, S.H. Lee, Insulation design of cryogenic bushing for superconducting electric power applications, Physica C, 484 (2013) 338-342.
[5] N. Shimizu, T. Nagata, K. Horii, K. Fukushima, M. Nagao, M. Kosaki, Thermal contraction and cracking of extruded polyethylene electrical insulation at cryogenic temperatures, Cryogenics, 26 (1986) 459-466.

[6] G. Bahder, M. Rabinowitz, M. Sosnowski, Bulk solid dielectric for cryogenic cables, Cryogenics, 23 (1983) 95-101.

[7] M.G. Danikas, G. Adamidis, Partial discharges in epoxy resin voids and the interpretational possibilities and limitations of Pedersen's model, Electrical Engineering, 80 (1997) 105-110.

[8] A. Mahajan, K.E. Seralathan, N. Gupta, Ieee, Modeling of Electrical Tree Propagation in the Presence of Voids in Epoxy Resin, Ieee, New York, 2007.

[9] S. Raetzke, Y. Ohki, T. Imai, T. Tanaka, J. Kindersberger, Tree Initiation Characteristics of Epoxy Resin and Epoxy/Clay Nanocomposite, Ieee Transactions on Dielectrics And Electrical Insulation, 16 (2009) 1473-1480.

[10] T. Ohta, K. Iida, Dehydration Reaction Effect of Metal Hydroxide on AC Voltage Lifetime of Epoxy Composites, Ieee Transactions on Dielectrics And Electrical Insulation, 23 (2016) 2294-2302.

[11] T. Tanaka, Dielectric nanocomposites with insulating properties, Ieee Transactions on Dielectrics And Electrical Insulation, 12 (2005) 914-928.

[12] L. Harvanek, J. Hornak, V. Mentlik, P. Trnka, T. Dzugan, Ieee, Influence of Nano and Microparticles on the Development of Electrical Trees, 2016.

[13] R. Kurnianto, Y. Murakami, M. Nagao, N. Hozumi, Investigation of filler effect on treeing phenomenon in epoxy resin under ac voltage, Ieee Transactions on Dielectrics And Electrical Insulation, 15 (2008) 1112-1119.

[14] Y. Wang, R. Huang, C. Li, C. Zhang, F. Shen, J. Li, H. Dong, H. Zhang, H. Zhang, L. Li, Electrical tree characteristics of epoxy resin under AC voltage at 77 K, Cryogenics, 99 (2019) 123-129.

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