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Analysis of DC insulation and properties of epoxy/ceramic composites with nano-sized ZnO/TiO_2 fillers

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A molded transformer is maintenance-free, which makes it unnecessary to replace the insulating material, like in an oil-filled transformer, because the epoxy, which is a molded insulating resin, does not suffer variations in its insulating performance for heat cycles over a long time, as compared to insulating oil. In spite of these advantages, a molded transformer may still be accessed by the user, which is not good in regards to reliability or noise compared to the oil transformers. In particular, a distrust exists regarding reliability due to the long-term insulating performance. These properties have been studied in regards to the improvement of epoxy composites and molded transformer insulation. There have nevertheless been insufficient investigations into the insulation properties of epoxy composites. In this study, it is a researching of the epoxy for insulating material. In order to prepare the specimens, a main resin, a hardener, an accelerator, and a nano/micro filler were used. Varying amounts of TiO2 and ZnO nano fillers were added to the epoxy mixture along with a fixed amount of micro silica. This paper presents the DC insulation breakdown test, thermal expansion coefficient, and thermal conductivity results for the manufactured specimens. From these results, it has been found that the insulating performance of nano/micro epoxy composites is improved as compared to plain molded transformer insulation, and that nano/micro epoxy composites contribute to the reliability and compactness of molded transformers.

Key words: DC Insulation, ZnO/TiO2, Epoxy composite, Epoxy resin, Thermal expansion coefficient.

Introduction

An epoxy resin is a resin that is thermally hardened by heat which has great chemical-resistance stability and superior electrical/mechanical characteristics. In addition, since it is very compatible and harmonious with various kinds of fillers, it is relatively easy to obtain various characteristics which cannot be obtained with epoxy resins alone, leading to a wide range of uses. Recently, epoxy has been widely used as a macro-molecular electric insulation material, ranging from a large rotary machine, molded transformers and other kinds of transformers, to bushings, insulators, and electric devices. The best ratio between micro and nanoparticles contents can be determined as indicated by a reduced space charge accumulation [1], considering the fact that ZnO is an important wide band-gap semiconducting material with potential for different applications [2] and Nano-TiO_2 fillers in the epoxy resin part enhance insulation breakdown. Consequently, TiO_2 fillers have superior insulation properties [3].

This work aims to study the effects of nanosize fillers breakdown behaviors of epoxy nanocomposites. The effects of the filler type on the epoxy nanocomposite insulating properties were investigated. The mixture of micro filler (SiO_2) and nano filler (ZnO, TiO_2) was used in this study. The experiment measured the glass transition temperature to determine the DC insulation breaking strength at temperatures above Tg and the thermal expansion coefficients were measured as well.

Experiment

The preparation process

The specimens used in the experiment consisted of resins (Bakelite EPR 845 by Hexion Co.), hardeners (Bakelite EPH 845 by Hexion Co.), accelerators (Bakelite EPC 845 Hexion Co.), along with a micro-filler and various quantities of nano-fillers. SiO_2 was used for the micro-filler; TiO_2 (nano-filler size 50 nm) and ZnO (nano-filler size 10 nm) were used for the nano-fillers. The compound rate is shown in Table 1. First, the resins and micro/nano-filler accelerators compounds were mixed with an agitator for 15 minutes at 60 °C Afterwards, with a hardener added, it was again mixed with an agitator for 15 minutes at 60 °C. Second, epoxy resin filled with micro/nano fillers was mixed by planetary centrifugal mixer with 1000 rpm for 10 minutes. Third, the compound epoxy composite was poured into a stainless steel mold painted with variants. A vacuum of 10^{-3} torr was applied for

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Table 1. The Epoxy Composite Specimen Component Ratios.

specimen \ contenta	Resin [phr]	Hard-ener [phr]	Accel-erator [phr]	Micro-SiO2 [phr]	Nano-ZnO [phr]	Nano-TiO2 [phr]
EMNZ3	100	82	1.5	335	3	-
EMNZ5	100	82	1.5	335	5	-
EMNZ7	100	82	1.5	335	7	-
EMNT3	100	82	1.5	335	-	3
EMNT5	100	82	1.5	335	-	5
EMNT7	100	82	1.5	335	-	7

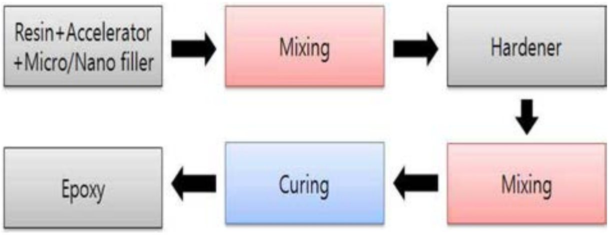

Fig. 1. The specimen manufacturing process.

10 minutes at 60 °C Finally, after locking the frame, the epoxy nano-composites were obtained by curing at 80 °C for 4 hours and 130 °C for 16 hours. Each test specimen's diameter was 100 mm and 1 mm thick. The process of making specimen is summarized in Fig. 1.

The thermal property experiments

The thermal expansion coefficient and glass transition temperature were measured using a TMA2904 and a DSC2910 (TA Instruments), respectively.

The difference between the thermal expansion coefficients of the metal and epoxy insulation material in a transformer that has been in operation over a long period of time causes the generation of voids at their interface. Therefore the insulating characteristics are eliminated when these differences are repeated [4]. Therefore, it is critical to match the thermal expansion coefficient of the insulation material with that of the metal. The thermal expansion coefficient was measured by increasing the temperature by 2 °C per second from 30 to 150 °C; the glass transition temperature was measured by changing the temperature at a rate of 10 °C per minute until it reached 200 °C.

DC the breakdown strength experiments

In order to measure the insulation breaking strength, a high-voltage transformer, a sphere-to-sphere electrode system, and an oil circulator were required. Fig. 2 shows the circuit schematic diagram used to measure the DC insulation breakdown strength. The direct current high-voltage generator can generate a total of 200 kV. When using the measurement electrode system, the gap may be smaller than the diameter of an electrode when measuring the voltage, but in reality, the diameter

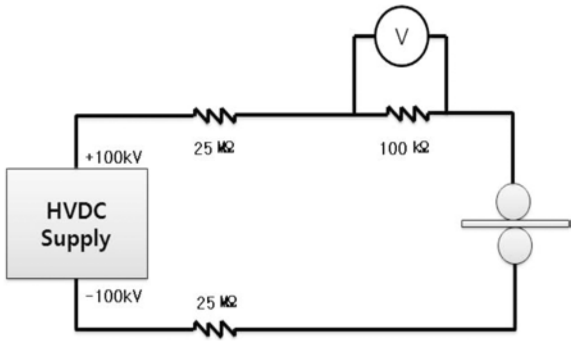

Fig. 2. The electrical circuit schematic diagram.

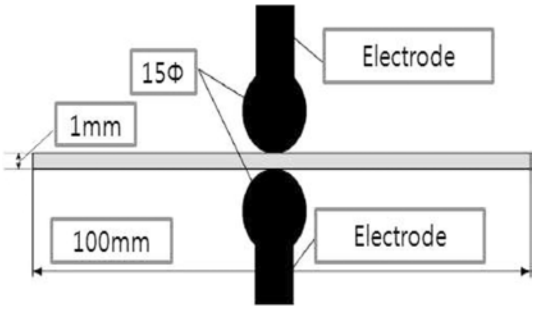

Fig. 3. The sphere-to-sphere electrode system.

of an electrode is recommended to be 10 times larger than the gap. Therefore, stainless steel 15 mm diameter sphere-to-sphere electrodes were used in their stead; the specimens and their electrodes were immersed in insulating oil to prevent surface flashovers. The insulation breaking strength was measured at room temperature (25 °C) and below and above the glass transition temperature. In order to sustain a regular temperature for the specimen during the experiment, an insulating oil bath with a heater and circulator were used.

Fig. 3 shows the sphere-to-sphere electrode system in detail. It was designed to be sufficient to supply protection from flashovers; the specimens were manufactured to have a sphere size over 10 times larger than the specimen thickness.

Results and Discussions

The thermal properties

In regards to the glass transition temperature measurement, the heat flow is largely divided into three sections. As shown in Fig. 3, sections are provided at some points where the heat flow decreases at a regular gradient according to the increase of the temperature after a rapid slop-decreased section. Out of them, the temperature in the middle between the starting point and the ending point is called the glass transition temperature, Tg. The epoxy resin properties undergo great changes at Tg. In Fig. 4, all of the specimens have a steep gradient from 75 °C to 85 °C. Therefore, the dielectric breakdown tests were done at 70 °C and 90 °C.

Table 2 shows the measured thermal expansion

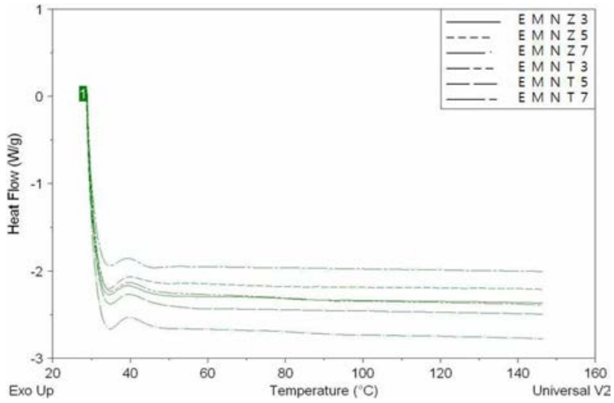

Fig. 4. The glass transition temperatures.

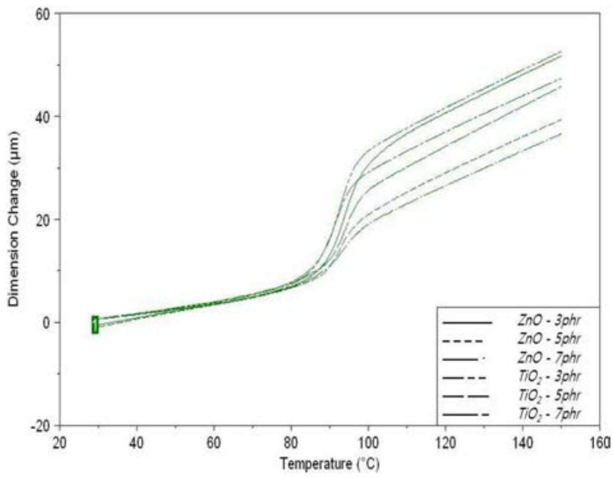

Fig. 5. The TMA analysis results.

coefficients. Below the glass transition temperature of the copper or aluminum used as a conductor, the thermal expansion coefficient is about 2 ~ 3 (17 and 23) ppm/K, whereas the thermal expansion coefficient of pure epoxy resin is 6 ~ 7 (60~70) ppm/K, most of the specimens showed a lower thermal expansion coefficient than that of the pure epoxy resin. Considering only the thermal expansion coefficients, it was found that the specimen combined with EMNZ7 had a thermal expansion coefficient most similar to that of metal. Therefore, it can be posited that the epoxy resin using the ZnO filler is good for aluminum devices.

The DC breakdown strength

Fig. 4 shows DC breakdown strength of insulation material according to different temperatures in contrast with the content. In the case of the ZnO mixture, the insulation breakdown strength was found be best using EMNZ5, and in the case of the TiO_2, EMNT3 was found to have the best insulation breakdown strength. Consequently, it was determined that as the content of nano-filler increases, the breakdown strength decreases. These results can be explained by Nordiem's rule:

$$\rho_l = CX(1-X) \qquad (1)$$

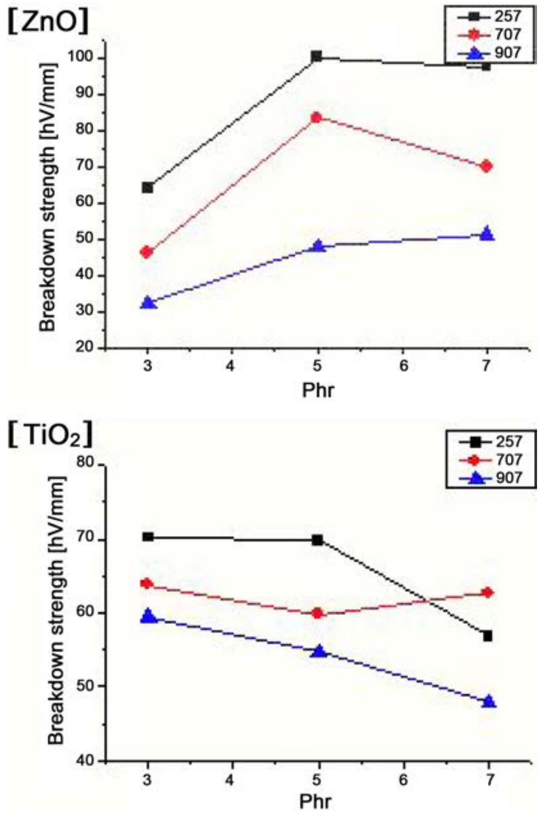

Fig. 6. The DC breakdown strength of the insulation material (ZnO/TiO2).

Table 2. The Thermal Expansion Coefficient.

Specimen	Thermal Expansion Coefficient [ppm/K]
EMNZ3	5.81
EMNZ5	5.37
EMNZ7	4.9
EMNT3	5.94
EMNT5	5.38
EMNT7	6.04

where C is the coeffcient and X is the ratio of the composites. When the amount of nano filler is small ($X \ll 1$), the resistivity is CX($\rho_l = CX$) because the nano filler act like an impurity in the composition. The mobility of the composite decreases due to the impurity, increasing the resistivity. After X is bigger than 1($X > 1$), the resistivity ρ_l decreases. It is thought that the nano-filler no longer acts as an impurity after X becomes bigger than 1.

In order to quantitatively compare the effects according to different temperatures, the insulation breakdown strength and temperature dependence coefficient are defined and compared using:

$$TDC = -\frac{1}{Eb(at\ 70°C)} \times \frac{\partial Eb}{\partial T} \times 100 \qquad (2)$$

Table 3. The Temperature Dependence Coefficient.

Specimen	TDC
EMNZ3	0.66
EMNZ5	0.46
EMNZ7	0.75
EMNT3	0.45
EMNT5	0.43
EMNT7	1.12

Table 3 shows the calculated temperature dependence coefficient. As a result of examining the temperature dependency alone, it was found that the EMNT3 epoxy had the least change according to temperature. The EMNT7 specimen, however, formed lower glass transition temperatures than the other specimens, indicating that there was an error taking place during the measuring process of the insulation breakdown strength for that specimen, or that as the content of nano-filler increased, the insulation breakdown strength decreased due to defects caused by a foreign substance.

Conclusions

This study investigated the DC insulation breakdown and measured the thermal expansion coefficient in order to determine the electrical and thermal characteristics of insulation resins used in molded transformers. As a result of measuring the epoxy thermal expansion coefficient, it was found that the EMNZ7 epoxy resin showed the least value at 4.9 ppm/K, Therefore, it is thought that the epoxy resin using the ZnO filler is good for aluminum devices. As a result of the DC insulation breakdown experiment, it was found that the EMNZ5 epoxy resin had the best performance. Nano ZnO epoxy composites have higher breakdown strength than that found for the TiO2 composites. It is thought that the nano-ZnO acts like an impurity compared to the nano-TiO2 in the composites; the mobility of composite is decreased by impurities and then resistivity. The results of the examination of which specimen had the smallest breakdown strength change according to temperature showed that the EMNT3 epoxy resin was the most appropriate.

We confirmed that there are effects from the nano filler that make the electrical properties good but the degree of this effect is unpredictable. The filler amount is not proportional or inversely proportional. There are optimal ratios between filler and resin. Therefore, a study regarding the optimal ratios between nano fillers and other materials and the theory of the phenomena need to be conducted. It is required to carry out further studies into how to decrease the thermal expansion coefficient by changing the kinds of nano-fillers and content.

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