PARTIAL DISCHARGE INCEPTION VOLTAGE OF TIO2 NANOCOMPOSITE AFTER APPLYING SEVERAL THERMAL SHOCKS

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Abstract: The particles smaller than 100 nm called nano particles. They are one of the important subjects of the current century technologies. This technology would be nowadays in different fields of industry, so that adding a small percentage of nano fillers to epoxy resins can influence their electrical, dielectric, mechanical and chemical features. To study the influence of thermal shock on the electrical and dielectric properties of nanocomposite, an indoor epoxy resin system based on bisphenol-A was used. TiO_2 was selected at different percentages by weight as nano filler. Nano fillers were mixed with the resin carefully using ultrasound device and high speed mixer at the same time. By means of transmission electron microscopy, the homogeneous distribution of the fillers was proved. The measurements were done under inhomogeneous (rod-plane) electrical field. The influences of the amount of the nano fillers up to 10% by weight on the partial discharge inception voltage of the specimens during totally four thermal shock cycles from -25 till 130°C at room temperature and 90°C, 150°C and 180°C were investigated.

1 INTRODUCTION

Nanotechnology deals with characteristics of particles in nanometer size and/or microscopic regions on materials and functional devices [1]. More than half century has passed since a famous physicist Richard P. Feynman (1959) predicted its possibility by his talk on " There is Plenty of Room at the Bottom" on December 29th 1959 at the annual meeting of the American Physical Society at the California Institute of Technology.
Mesoscopic substances between bulks and molecules or atoms can be considered to represent nanomaterials. They tend to manifest unique surface properties in addition to bulk performances due to the limited number of constituent atoms and molecules, and enable to exhibit even quantum effects in their mesoscopic regions.
Nanocomposits are composed of host and guest materials in general. They should be fabricated so that they may be endowed with super performances of the guest materials, while keeping original performances of the host materials. In general, inorganic materials are excellent in optical, electrical, mechanical and thermal properties, while organic materials are known with light weight, flexibility, and processability [2].
In this research epoxy resin based on bisphenol-A and related micro filler are the same for all produced specimens and TiO_2 was considered as nano filler to see if the nano fillers can improve the partial discharge behaviour of the insulation material after several thermal shock cycles. This improvement is important because epoxy resin and conductor have different expansion coefficients, what can make problem for the insulation material during time. This problem for example happens, when a dry type transformer becomes warm and cool under different loading conditions or different atmospheric temperatures. As the expansion coefficient of epoxy resin is about four times greater than the thermal expansion of copper, it can cause crack and also space between conductor and insulation material and consequently an increase of partial discharge. Using nano filler in insulation material can put the material in better condition physically, so that keeping the mechanical and electrical resistivity in a proper situation, it causes the cracks not to happen or not to grow during different loading process of the dry type transformer easily.
Al_2O_3, TiO_2, ZnO nano fillers are the most famous nono fillers which would be used for researches [3]. To evaluate the influence of nano fillers on the electrical and dielectric properties of bisphenol-A epoxy resin, TiO_2 at different concentrations including 0%, 1%, 3%, 5% and 10% by weight in combination with the conventional micro fillers was used. Using electron microscope observation, it was shown that the area surrounded by dispersed micro-scale silica fillers was also filled with the nano-scale fillers. Nano fillers can fill the spaces between micro fillers and as a result can improve partial discharge (PD) characteristics. Furthermore, the estimate of spacing between the fillers and the filler/epoxy resin interface area shows a more densely packed structure of the filler mixture composite than the conventional filled epoxy resin. The epoxy resin is usually filled with a large amount of micro-scale fillers, for example Quartzmehl, Wollastonit, Silica or Alumina. Using Silica or Alumina results the same low thermal expansion as aluminum or copper conductors. The conventional filled epoxy with low thermal expansion avoids exfoliating between the epoxy casting part and the conductor caused by heat-cycle. So, it is noticeable that adding a very low volume of nano fillers to

epoxy resin results a better dielectric performance [4].
The key parameter of the partial discharge inception voltage was evaluated under inhomogeneous electrical field after several temperature cycles.
As mixing nano fillers with the host material homogeneously and in nano scale is very important, high speed mixer and ultrasonic device were used simultaneously for a definite time. Then the homogeneous distribution of them was checked by means of transmission electron microcopy .

2 TEST CONDITION

To apply necessary thermal shock cycles, the specimens were cooled down and heated according to the Figure 1, which shows each defined thermal shock cycle including three times temperature changing. Maximum temperature was considered about 15% above glass transition temperature or 130°C. The minimum temperature -25°C. So after numbering the specimens, they were firstly cooled down up to -25°C for one hour. Then they were immediately put in a ready oven to be heated at 130°C for one hour.

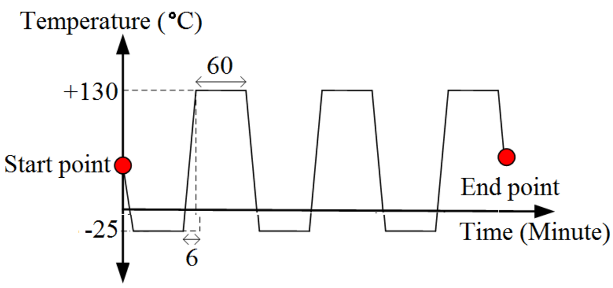
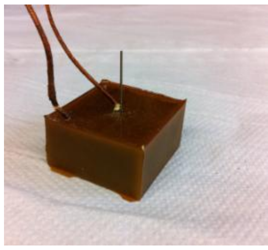
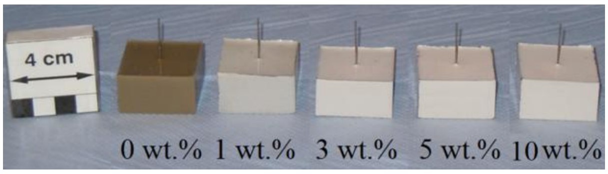


Figure 1: The one defined thermal shock cycle

To make sure, that the considered heating and cooling time is enough for the whole body of the specimens, two thermal sensors were installed during the curing process. As shown in Figure 2(a), one sensor installed in the middle of the specimen and the other one in its outside. The results show that one hour is enough for heating or cooling the whole parts of the specimen.
The specimens were taken out from the oven and put in a sealed container at room temperature for one week. This process repeated four times for all specimens and after each time their partial discharges were evaluated.
To study the partial discharge behavior of the specimens at different temperatures, the partial discharge of the specimens were measured at 90°C, 150°C and also 180°C, after they were stressed by four thermal shock cycles.
Although the specimens were produced under vacuum, it is difficult to omit cavities during the production completely.
In this condition, nano fillers can fill the cavities, when the nano fillers are mixed correctly. So it is to emphasize that mixing nano fillers with the host material homogeneously is the most important point in order to reach good results.



(a)



(b)

Figure 2: (a) A Specimen with two thermal sensors, (b) Specimens with different nano filler concentrations

2.1 Epoxy resin system

In this study, indoor epoxy resin system including CY228 as resin, HY918 as hardener, DY062 as accelerator and Quarz Millisil W12 as micro filler was used. The amount of the total micro and nano fillers should not exceed the maximum defined value by the manufacturer after adding the nano fillers, otherwise all properties can be changed negatively.

2.2 Nano filler

Unmodified TiO_2 nano fillers was selected as nano filler, because it is the conventional nano filler and also economic approximately. The specimens were produced considering maximum 10% by weight.

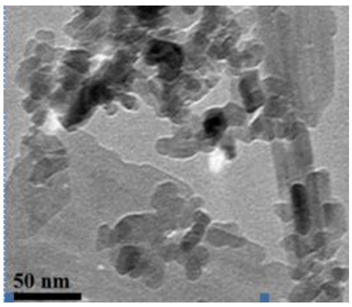


Figure 3: TiO_2 nano fillers (21±5 nm)

The mentioned percentages by weight are valid for the final specimens and not only for resin or hardener.
Some features of the TiO_2 nano filler are as follow:
- Photocatalytic
- Dry nanopowder. Mixed rutile/ anatase phase
- Average primary particle size: 21±5 nm

- Specific surface: 50±10 m2/g
- Purity: >99.5 %

2.3 Electrode configuration

Needle-plate electrode configuration was considered to create strong inhomogeneous field. The used needles have all a tip radius of 5 μm . To produce the specimens, 2 mm distance between both electrodes was considered and finally five specimens per measurement point was measured [5,6].
Regarding to the sensibility of the hardener to humidity, the nano fillers were firstly mixed with the preheated resin. Because during the mixing, the air will be also mixed with the solvent and considering hardener as a solvent is not a good idea. It was said that the resin should be already preheated, because the warm resin has much lower viscosity and makes the mixing easier. Both materials were mixed for 15 minutes by high speed mixer and ultrasonic device simultaneously, after all the nano fillers were poured in the resin. Of course the nano fillers should be distributed homogeneously and in nano scale. Otherwise they play the role of micro fillers and will not let evaluate their influence on the based material. The mentioned mixing time is not constant for each nano filler concentration, but more nano filler needs more mixing time. An easy way to check, if the particles are mixed correctly in resin is that the mixture be left for a couple of days. If the particles are mixed in nano scale, they will not sediment. But it does not give any information about the homogeneous distribution of the nano fillers in resin. Although this method can not be trusted, it can be used as a very first check, when no electronic microscope is in hand.

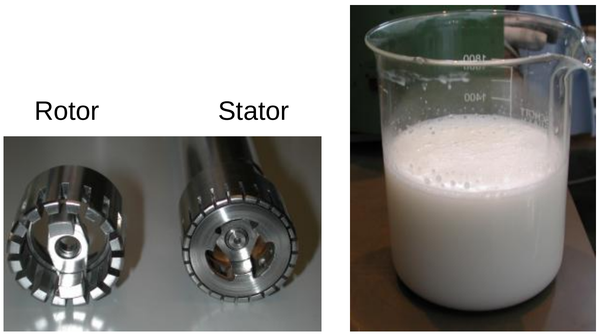
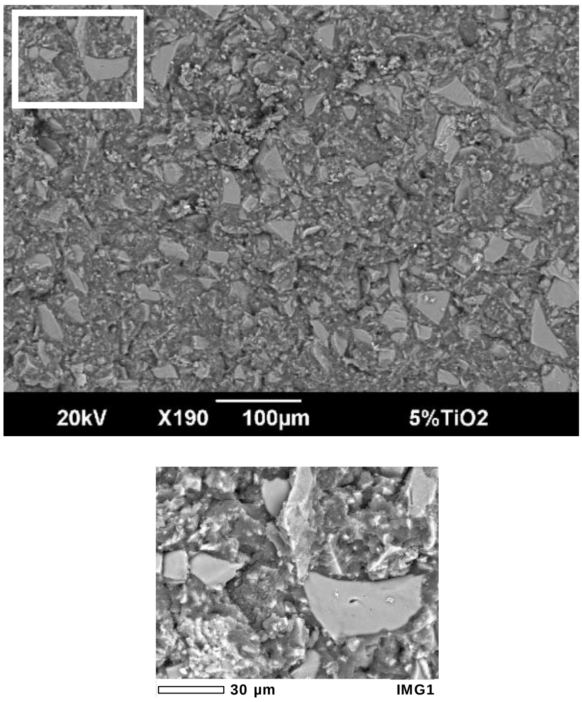
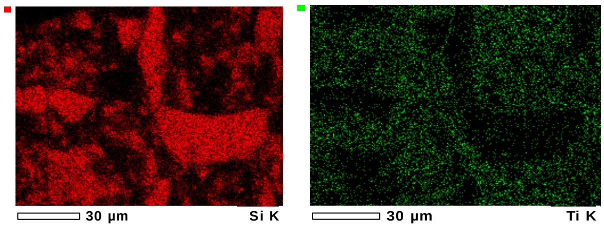


Figure 4: The especial head of the mechanical mixer for dispersing nano filler in a liquid (left) and mixture of TiO_2 nano fillers with resin (right)

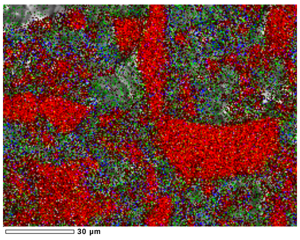
The above mentioned mixing behavior was used up to 5% by weight. For 10% by weight, mixing all the nano fillers with resin is impossible. So 60% of the nano fillers were mixed with resin and the rest with hardener, instead. To avoid mixing humidity with the hardener, the mixing can be done under vacuum existing the possibility of cooling the mixture during mixing permanently, because the mixture becomes too hot using high speed mixer and can influence the chemical structure of the hardener negatively.
In general, size, shape and type of a filler effect the mixing performance.
As the next stage, the mixture of nano fillers and resin was mixed with hardener, micro fillers and accelerator under vacuum, and temperature was controlled in three intervals within 45 minutes. Finally the mixture was casted into the moulds with needle electrodes and cured for 4 hours at 80°C and 8 hours at 140°C in an oven. Regarding to the fact that internal mechanical forces influence the electrical and dielectric properties of an epoxy resin, they should be minimized during the production. To reduce these forces, the moulds were cooled down very slowly within 8 hours.
After curing, the polymer molecules are not still in a stable condition and for example measuring the breakdown voltage, one day and one week after curing process, results different values, so that the measured breakdown voltages after one week are higher than the ones after one day. So, In order to make the molecules of the specimens relax and stabilize sufficiently, the measurements were done 4 weeks after the curing process.
To check if the nano fillers were distributed homogeneously and in nano scale, a proper specimen of each material with about 1mm thickness was prepared and TEM images of them were taken.
Figure 5 shows that the nano fillers were distributed among the micro fillers. It illustrates the micro and nano fillers separately and also a combination of them, so that the green points show the distribution of Titanium atoms which are the representatives of TiO_2 nano fillers and the red areas are the distribution of Silicium atoms which are the representatives of SiO_2 micro fillers.



(a) Area selected for applying overlay method



(b) View of micro fillers View of 5% TiO_2 nano fillers



(c) Overlay view of micro and nano fillers

Figure 5: TEM images of a specimen with 5% TiO_2 as nano filler and 65% W12 as micro filler

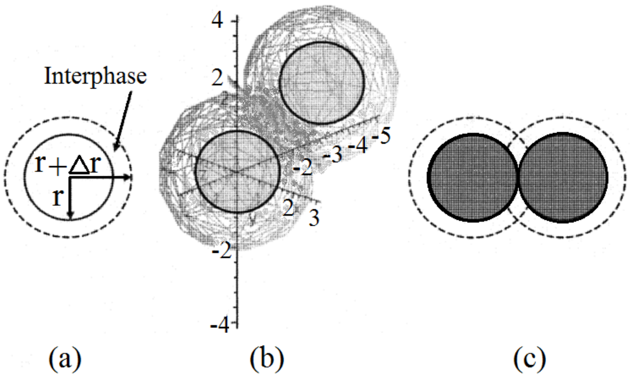


Figure 6: An example of the chemical formation of an interphase region

if we consider a specimen with nano filler and another one with micro filler, so that both specimens have the same volume fraction of the filler, the Interphases built up by using nano fillers are much more. Figure 6 shows an example of the interphase. Figure 6(a) illustrates a particle with its interphase. Figure 6(b) shows two particles surrounded by many polymer molecular chains. There are more molecular chains in the area between the particles, which can result better electrical, dielectric, mechanical and thermal properties. The reason is that the interphases trap the polymer molecular chains around the particles and do not let the ions and charge careers to move in electrical filed easily. In addition, the trapped polymer molecular chains between the particles create much better molecular network and result better mechanical features. But as shown in Figure 6(c), if a high concentration of the nano fillers be used in epoxy resin, there will be so many nano fillers in the matrix and they would be located side by side consequently. In this condition, the interphases would decrease and the influence of nano filler is not optimal. Vice versa, If a low concentration of nano filler be used, there will be a few interphases. Besides the effect of the interphases, any poor composition of the interphases with polymer molecules can result worse electrical and dielectric properties. For example, this problem leads to surface polarization and partial discharge in the area of connecting polymer matrix to the nano fillers. In brief, the interphases play the main role for the explanation of the influence of the nano fillers on an epoxy resin system.

3 SETUP FOR PARTIAL DISCHARGE INCEPTION VOLTAGE MEASUREMENTS

PD Measurements were performed using the PD measuring system of the company ICM Diagnostix Power Systems GmbH in a shield measurement cabin to prevent any external noises. Before each PD measurement, the measuring system was calibrated with a charge of 10 pC.
Increasing rate of the applied voltage was considered 0.5kV/s till the discharges appeared. Partial discharges were recorded during 60 seconds after appearing the first discharges. In order to prevent any surface discharge, the specimens were put in insulation oil and then high voltage applied.

4 RESULTS

4.1 Partial discharge inception voltage under inhomogeneous field

The measurements of PD inception voltage under inhomogeneous filed were limited up to 25 kV, because the specimens were needed for the next thermal shock cycles. As shown in Figure 7, the PD inception voltage of the specimens with nano filler is higher than the others before applying any thermal shock, especially at 3%, 5% and 10% nano filler concentrations. After applying the first thermal shock cycle, the PD inception voltage starts reducing. But the curve related to the specimens including 10% nano filler remains higher than the other curves. after the 2^{nd}., 3^{rd}. and 4^{th}. thermal shock cycle, the PD inception voltage of the specimens with 10% nano filler is much better than the other ones, so that from the 2^{nd}. cycle, the PD inception voltage is even a little bit higher than its value before applying any thermal shock cycle. It is to mention that the specimens were heated up to 130°C or 15% above T_g. So at this temperature, the insulation material is not in hard form anymore and it could be expected that during several thermal shock cycles, a gap could be created between the electrode and insulation material, what is a start point of the degradation of the insulation material by PD. This problem happened to all the specimens than the ones with 10% nano filler.
In addition, Figure 8 shows that at 10% nano filler concentration, there is no significant PD impulse during the tests up to 25 kV.

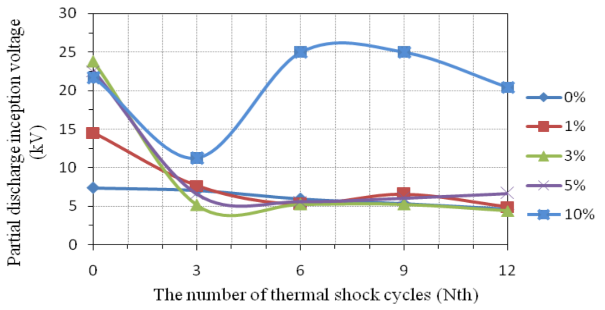


Figure 7: PD inception voltage under homogeneous field after several thermal shock cycles at different concentrations of nano filler

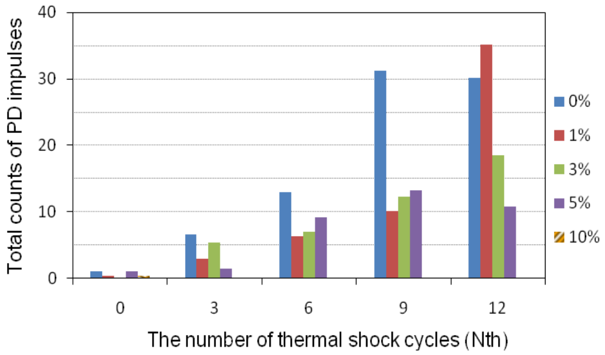


Figure 8: Total counts of PD impulses after several thermal shock cycles at different concentrations of nano filler

To evaluate the condition of the specimens after 4 thermal shock cycles at higher temperatures, the measurements were done at 90°C, 150°C and 180°C. Figure 9 illustrates that the specimens with 10% nano filler have still better condition.

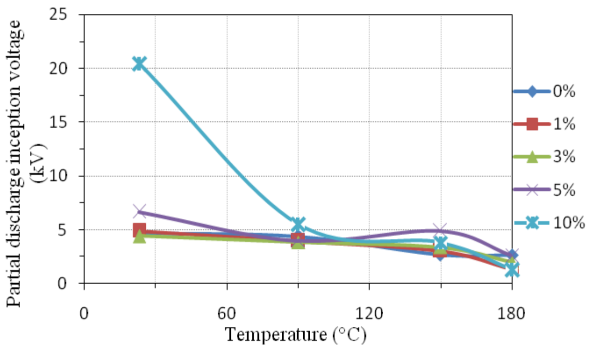


Figure 9: PD inception voltage of the specimens after 4 thermal shock cycles at different temperatures and different concentrations of nano filler

At 10% concentration in Figure 10, the values of the total counts of PD impulses are the lowest.

4.2 Tensile and flexural modulus

Tensile test was carried out by "Santam" (model: STM-20) with crosshead movement of 2 mm/min. 5 specimens were tested for each specimen with 120 mm length, 8 mm width and 2 mm thickness.

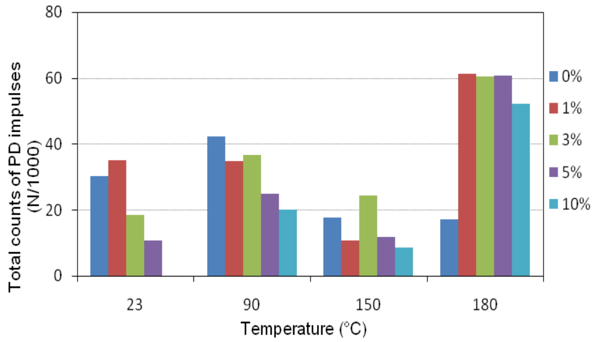


Figure 10: Total counts of PD impulses after 4 thermal shock cycles at different temperatures and different concentrations of nano filler

To measure flexural properties of specimens, the test was done by Santam device (model: STM-20) according to ASTM D-790 in mode of three points and in cross-head movement of 0.853 mm/min. 5 specimens were tested for each parameter with dimension of 38×12×1.9 mm^3.

The mentioned improvements in last section can be explained in combination with the results of the mechanical tests. As shown in Figure 11 and 12, the values of the tensile modulus and flexural modulus both confirm that adding 10% nano filler can improve these parameters. These two parameters should be evaluated simultaneously.

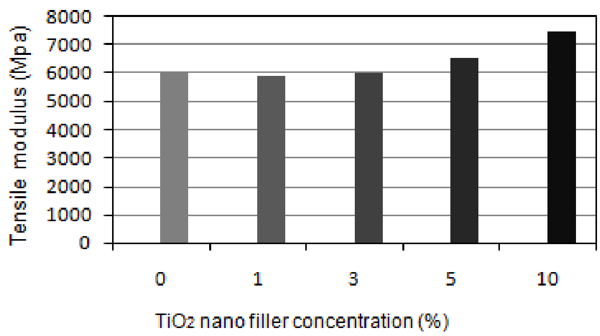


Figure 11: Tensile modulus of the specimens

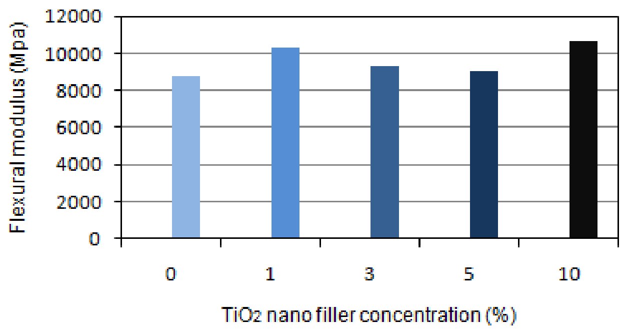


Figure 12: Flexural modulus of the specimens

Therefore, the results of the mechanical tests show that, adding nano filler makes the insulation material more flexible against the bending and tensile strengths during the thermal shock cycles and keep the adhesion forces between the electrode and insulation matrix in proper condition. It can be also so explained, that the joints, created in the areas among the fillers in matrix by overlapping the trapped polymer molecular chains with each other (the darker area of the space between two particles in Figure 6-b), make the matrix optimal mechanically.

5 CONCLUSION

- PD inception voltage of the specimens can be held in proper condition after several thermal shock cycles adding 10% by weight nano
- Adding 10% by weight nano filler can improve the mechanical parameters and consequently improve the electrical conditions.
- Adding less than 10% by weight can not keep the PD inception voltage of the specimens in good condition in this case.
- The improvement depends on the features of nano filler and epoxy resin and their compatibility with each other.

6 ACKNOLEDGMENT

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