Investigation of a Cycloaliphatic Epoxy Resin System Considering Al₂O₃ and TiO₂ Nanofillers

M. M. Saei Shirazi, H. Borsi, E. Gockenbach
Leibniz Universität Hannover, Schering-Institut, Callinstr. 25 A, 30167 Hannover
m.saei@si.uni-hannover.de

Abstract- Inorganic nanofillers combined with organic polymers have been used for several years in order to enhance the electrical and dielectric properties of insulation materials. The advantages of using nanofillers can be explained by very large interface area of them in comparison with microfillers. To evaluate the influence of Al₂O₃ and also γ-TiO₂ nanofillers separately on a cycloaliphatic epoxy resin system as an outdoor insulation system, specific DC volume resistivity, loss factor and permittivity were investigated. In this regard, several specimens with 2 mm thickness were produced containing 0%, 1%, 3%, 5% and 7% per weight under especial condition to have the most possible homogeneous distribution of nanofillers. Then the behavior of the mentioned parameters was investigated from 23 °C up to 170 °C at different frequencies. According to the results, DC volume resistivity of the specimens with Al₂O₃ shows higher resistance between 80 °C and 140 °C than the specimens without nanofiller. Adding TiO₂ does not cause considerable changes in volume resistivity. Loss factor has no significant change up to glass transition temperature (Tg), but it reduces at the temperatures above Tg, when Al₂O₃ or TiO₂ was added. Relative permittivity of the specimens containing Al₂O₃ and TiO₂ were increased up to 110 °C. After this temperature, relative permittivity of all nanocomposites decreases in comparison to 0 wt. %.

Keywords-component; nanofiller; nanocomposite; high voltage insulation system

I. INTRODUCTION

Some property changes like relative permittivity, treeing growth, partial discharge, dielectric losses, space charge, resistance, glass transition temperature and thermal conductivity are related to nanofiller in nanocomposites [1, 2].

For the enhancement of electrical insulation reliability and compact design in electric power apparatus, the electrical properties of polymer composites filled with metal oxide particles play an important role. Recently, it has been recognized that the introduction of metal oxide nanofillers to polymer has unique dielectric behavior and advantages when compared to the base polymer and the polymer filled with conventional micrometric particles. These properties would be mainly attributed to the large interfacial area of nanofillers with homogeneous dispersibility and the specific interfacial region between a nanofiller and polymer [3].

Volume resistivity can be used as an aid in the choice of an insulating material for a specific application. The change of resistivity with temperature and humidity may be great and must be known when designing for operating conditions. Volume resistivity measurements are often used in checking the uniformity of an insulating material, either with regard to processing or to detect conductive impurities that affect the quality of the material and that may not be readily detectable by other means [4].

Regarding to dielectric properties, many insulating substances have dielectric constant greater than unity and have dielectric loss when subjected to A.C. voltages. These two quantities, namely the dielectric constant and the loss, depend on the magnitude and the frequency of the applied voltage. When a dielectric is used in electrical equipment such as a cable or a capacitor, the variation of these quantities with frequency is of importance. The microscopic properties of the dielectric are described by combining the variation of the above two quantities into one "complex permittivity" known as "complex permittivity" and determining them at various frequencies [5].

In this study, the influence of nanofillers Al₂O₃ and TiO₂ was studied at different concentrations including 0%, 1%, 3%, 5% and 7% by weight. As key parameters, DC volume resistivity, loss factor and permittivity were taken into consideration.

II. SAMPLE PREPARATION

A. Solid Insulation System

To study the matter, an outdoor epoxy resin system was used containing CY184 (100) as resin, HY1235 (90) as hardener, DY062 (0.6) as accelerator and QuarzSilbond W12 EST (370) as micro filler.

The mixing process of the components should be done very well, because a good dispersion of the nanofillers plays a big role in the results. To produce specimens with the dimension of 120*120*2 mm, the material was finally casted into the moulds and cured for 16 hours at 140 °C[6].

For any outdoor application, it's recommended to use silanised silica flour for outdoor usage [7]. W12 EST is a silanized microfiller. Silanes react chemically with silanol groups, which are on the surface of the filler, by elimination of alcohol. After this coating, the surface of the filler becomes hydrophob and water can not accumulate more. The other advantage of the silanization is a strong adhesive force between the polymer matrix and the silanes[8].

B. Measurement

To make the specimens ready for measurements, they were heated from 20 °C with the steps of 30 °C up to 170 °C.
According to IEC 60250, loss factor and permittivity were measured considering 200 V, 50 Hz in a shielded measurement system with an Omicron measuring device named DIRANA. Furthermore, DC volume resistivity measurement was carried out according to VDE 0303 part 30 considering current-voltage measurement. The applied DC voltage was 2000 V in one[6].

III. EXPERIMENTAL RESULTS

A. DC Volume Resistivity

The results show, that as the nanofiller loading increases beyond 1 wt.% the volume fraction of the extended loose polymer starts to decrease (increases the volume of immobile nanolayers). An increase in the fraction of immobile nanolayers in epoxy at slightly higher nanofiller loadings probably acts as ion traps which inhibit ion mobility resulting in the dc conductivity in the nanocomposite bulk to decrease [9]. According to the description of Coulomb blockade effect, when one electron falls into a tunneling junction formed by metal particles, the barrier (about 80 meV) will be much stronger than the thermal motion energy at room temperature kBT (about 26 meV) of electron. So the movement restricting of other electrons appears, and the resistivity of composite increases. In fact, nano metal can form capacitor network in base polymer, and restrict the movement of charges by Coulomb blockade effect. But when the size or the amount of this nanofillers is not small, this increment may be very small and in such cases that contain more nanofiller, it leads to decrement of volume resistivity [10].When the filler’s loading increases, there is a subsequent increase in the volume fraction of the entire interface region coupled with an enhancement in the availability of free ionic charge carriers [11].

As shown in Fig. 1&2, at the temperatures between 110 °C and 140°C, the resistivity of the nanocomposites is higher than the conventional composite (non filled). It may be because of the interfaces between nano-layer forms on the nanofiller surface and interactions between polymer chains and the nanofillers at these temperatures, which are around Tg and the behavior of different nanofiller concentrations is different.

Although there is a simultaneous reduction in the internanofiller distance also in the nanocomposite at low filler loading, the charge carriers can still have a path which facilitates their unhindered transport between the electrodes. This can result a further reduction of the DC resistivity of the nanocomposite. By increment of filler loadings, the interparticle distances continue reducing, there will be more free charge carriers and the fraction of interface region in the material will be high [12].

As shown in Fig.3, decreasing the volume resistivity at higher temperatures is inevitable. These changes are because of the easy movement of carriers by increasing the temperature. Also by increasing the amount of the nanofiller, the results show an improvement in specific volume resistivity at higher temperatures especially at 3 wt. % concentration, but it shows a light reduction for 5 wt.% & 7 wt.% amount of nanofiller at above 80°C, which could be because of the agglomeration of nanofiller inside the epoxy. Fig.4 shows also a similar behavior but with very small changes, so that it can be said, there is no significant changes using TiO2.

B. Tan Delta

Fig.3&8 show tan delta variations with respect to different concentrations of Al2O3 & TiO2 at 23 °C & 140 °C.

Fig. 3 and 4 show that, loss factors of nanocomposites are lower than 0 wt.% at very low frequencies from 23 °C up to 140°C. This behavior continues up to 170 °C.
ical conductivity and Th is behavior continues up to 110 °C (Al2O3) and the structure of polymer, which in turn leads to entanglements inhibit the motion of charges in the system, which in turn causes a reduction in the electrical conductivity (hence a lower tan delta value) [15].

The values of the tan delta at 50 Hz and different nanofiller concentrations and temperatures show no significant changes and differences among different concentrations up to above Tg, which the values of tan delta of nanocomposites are lower than in comparison with the values of 0 wt.%.

C. Permittivity

The variations of $\varepsilon_r$ for the nanocomposites containing Al2O3 and TiO2 nanofiller with respect to the frequency at different filler concentrations and temperatures were investigated. $\varepsilon_r$ of conventional composites and nanocomposites increases as the frequency decreases. $\varepsilon_r$ of the specimens is governed by the number of oriented dipoles and their ability to be oriented under an applied electrical field. At lower frequencies of applied voltage, all the free dipolar functional groups in the epoxy system can orient themselves resulting in a higher $\varepsilon_r$ values. As the electrical field frequency increases, the bigger dipolar groups find it difficult to orient at the same pace as the alternating field, so the contributions of these dipolar groups to $\varepsilon_r$ goes on reducing resulting in a continuously decreasing $\varepsilon_r$ of the epoxy system at higher frequencies. Similarly, $\varepsilon_r$ in Al2O3 and TiO2 nanocomposites also decreases with increasing the frequencies of the applied field [16].

Fig.7&8 show, that by increasing Al2O3 concentration, the $\varepsilon_r$ increases up to Tg compared to 0 wt.%. This can be explained by the influence of the incorporated surface unmodified nanofillers at these temperatures, which changes the structure of polymer, which in turn leads to higher $\varepsilon_r$ of nanocomposites [17]. At 140 °C up to 170 °C, there is a decrease of $\varepsilon_r$.

![Figure 4.Tan delta at 140 °C (Al2O3)](image)

![Figure 5.Tan delta at 23 °C (TiO2)](image)

![Figure 6.Tan delta at 140 °C (TiO2)](image)

![Figure 7.Relative permittivity at 110 °C (Al2O3)](image)

Fig.5&6 show that, loss factors of nanocomposites with TiO2 are higher than 0% at very low frequencies at 23°C and this behavior continues up to 110 °C. At 140 °C up to 170 °C, there is reduction of loss factor.

The difference at low frequencies was attributed to interface polarization [13]. It is observed from these figures, that there is a continuous decreasing in tan delta values with increasing frequency at all filler concentrations.

The occurrence of a lower tan delta value in nanocomposites can be due to lower electrical conductivity at those frequencies. At high frequencies, the motion of charge carriers contributing to the conductivity primarily occur along polymer chains [14]. A barrier to the charge transport in polymers (causing reduction in electrical conductivity) can occur due to defects, inter-chain charge transport and transport through interfaces. Probably, in nanocomposites, the presence of a large number of interfaces and polymer chain entanglements inhibit the motion of charges in the system, which in turn causes a reduction in the electrical conductivity (hence a lower tan delta value) [15].
Furthermore, increasing $\epsilon_r$ is probably due to a major contribution of the interfacial polarization, determined by the increased number of charges (impurities & small ions) introduced in the nanocomposites. The results of $\epsilon_r$ at different Al$_2$O$_3$ and TiO$_2$ concentrations with respect to different temperatures at 50 Hz show an improvement above $T_g$. The behavior of $\epsilon_r$, which was explained for Al$_2$O$_3$ can be seen for TiO$_2$ and shown in Fig. 9 & 10.

- Al$_2$O$_3$ nanofillers decrease the tan delta up to higher temperatures.
- TiO$_2$ nanofillers increase the tan delta up to higher temperatures.
- Relative permittivity of the specimens containing Al$_2$O$_3$ or TiO$_2$ increases up to 110 °C. After this temperature, relative permittivity of all nanocomposites decrease in comparison to 0 wt. %.
- Selecting a proper type of nanofiller is very important for achieving positive results.

**REFERENCES**


**IV. CONCLUSION**

- Used nanofillers increase the DC volume resistivity of epoxy resin system especially at higher temperatures.