Volume Resistivity of Epoxy containing Nano-sized Al$_2$O$_3$ fillers

R. R. Patel, Student Member, IEEE and Nandini Gupta, Member, IEEE

Abstract—Recent research has shown that dielectric properties of epoxy-resin specimens can be improved (e.g. resistance to surface degradation) by the use of nano-sized alumina fillers. The improvement was seen to be even more marked if the nanometric fillers were pre-processed before use. In this paper, volume resistivity of nano-filled epoxy specimens is measured. The dielectric material used is epoxy resin, while nano-sized alumina (Al$_2$O$_3$) is used as filler. Polarisation current measurements are used to determine an optimum electrification time for computation of volume resistivity, such that the effect of transient currents is minimized. The effect of pre-processing the nano-particles before use is studied. Additionally the effect of temperature on the dc conductivity of the various specimens is also studied.

Index Terms—Volume resistivity, epoxy nanocomposites, polarization current, temperature, nanofillers, dc conductivity

I. INTRODUCTION

Nano fillers are used in polymeric dielectric materials for improving electrical and other properties. Recent research has shown that composite dielectrics with nano-sized fillers may exhibit better electrical characteristics [1-6]. According to a recent study, the improvement is more prominent when nano-fillers are preprocessed before adding to base polymer [4]. In this paper, we investigate the effect of using nano-sized alumina on the volume resistivity of epoxy resin. Further, the effect of using variously pre-processed alumina nano-particles is also studied. Since dc conductivity of a material is a temperature dependent parameter, measurements are made at various temperatures.

II. EXPERIMENTAL

A. Materials:

Bisphenol-A type epoxy resin is used as the polymer matrix; specifically Araldite LY556 (density 1.17 gm/cm$^3$ at 25°C) and Hardener LY951 (density 0.98 gm/cm$^3$ at 25°C) is used. The filler material used in the dielectric composite is spherical Aluminium Oxide (Al$_2$O$_3$) nanopowder (size 40 to 47 nm, density 3.97 g/cm$^3$ at 25°C and melting point 2040°C). These fillers were supplied by Sigma-Aldrich, USA. Additionally, high aspect ratio particles of submicron thickness, hereafter referred to as alumina platelets (200 nm in thickness and 5-10 μm in length, 99.8% purity, density 3.97 g/cm$^3$ at 25°C) from Advanced Nanotechnology Limited, Australia, is also used. In order to functionalize the alumina particles, 3-Glycidoxy-propyltrimethoxysilane (GPS) (Dow Corning Z- 6040, 98% purity, density 1.07 g/cm$^3$ at 25°C) is used.

B. Preparation of Nanodielectric specimens:

The following types of specimens were prepared:

1. Neat epoxy (EP)
2. Alumina platelets (MC)
3. As-received spherical nano-particles (AR)
4. Spherical nano-particles heated before use (HN)
5. Functionalizing the particles with 3-Glycidoxy-propyltrimethoxysilane (GPS) after heating (CHN)

The as-received Al$_2$O$_3$ nanoparticles (1% by volume of the composite) are dispersed in absolute ethanol using ultrasound sonicator (750W, 20 KHz, Vibra Cell USA). After addition of epoxy resin, the mixture is further sonicated. The mixture is heated to remove the solvent and desiccated in vacuum. After addition of hardener, the composite is cured in an acrylic mould. The cured specimens (AR) are further heated in the oven at 100°C for 24 h and left to cool. Alumina platelets are directly added to epoxy resin and dispersed for 1 h under sonication, for preparation of MC specimens. The mixture is degassed in vacuum and cured as mentioned above.

As-received alumina nanoparticles are first heated up to 200°C in an oven for 15 h. For preparation of HN nanocomposites with the heated particles, the same procedure as for AR specimens described above is then followed.

For preparation of CHN samples, the particles are first heated to 200°C for 15 h. Silane in the form of 3-Glycidoxypropyltrimethoxysilane (GPS) is used to functionalize the nanoparticles. The required amount of the Silane coating agent i.e. GPS is slowly introduced under sonication into a solvent comprised of 95% absolute ethanol. The silane is allowed to completely hydrolyse by sonicating for 10 to 15 minutes. As-received alumina nanoparticles are added to the hydrolyzed GPS solution at regular intervals to obtain homogeneous dispersion and proper coating of the nanoparticles. The mixture is further sonicated for 2 h. After evaporation of the solvent, the functionalized nanoparticles are washed with solvents to remove the excess GPS and completely dried in the desiccator. Next, the composite is prepared as described above. Specimens of size 100mm X 100mm X 3mm are used for the measurements. Uniform dispersion of the particles in the base resin has been verified using Transmission Electron Microscope (TEM) [1].
C. Measurements:

The experimental setup is a closed test fixture. The sample is conditioned in an oven (climatic cell) capable of controlling temperatures up to 250°C with an accuracy of 0.1°C. The internal volume of the cell is 40 X 40 X 40 cm$^3$. An electrometer with a built-in voltage source, which can measure resistances between 10 to 210 T$\Omega$ is used for the measurements. The currents are acquired by means of a General Purpose Interface Bus (GPIB) to a computer equipped with LabView. The experimental setup is shown in Fig 1. For measurement of volume resistivity, it is necessary to avoid the currents flowing from one electrode to the other via a surface path. This is accomplished by means of the guard electrode which is so placed with reference to one of the main electrodes, that any surface leakage current is collected and shunted around the measuring instrument. A standard three-electrode system is therefore used. The electrodes are made of brass and proper contact is ensured with a spring loaded terminal system. The diameter of the middle electrode (main electrode) is 54mm. The maximum applied field is 0.3 MV/m and measurements are made at several temperatures. The field level is so chosen as to be not too high to cause spurious effects within the material, but sufficient to cause discernible current flow.

Before measurement, each sample is held between grounded electrodes for at least 1 hr so that any residual charge can dissipate. Between consecutive measurements at different temperatures and voltages, the sample is again held between grounded electrodes until the short circuit current falls to a negligible level.

III. RESULTS AND DISCUSSION

A. Measurements at 50 °C :

The first measurements are made at 50°C, since the current levels are significant at this temperature. This makes it possible to discriminate between measurements by two different methods.

1) Method 1: Volume resistivity (direct) measurement

The volume resistivity values for various specimens measured with alternating polarity method are shown in Fig. 2. In this method, the voltage source alternates between ±V at timed intervals. Current measurements are taken at the end of each alternation, and resistance values are computed after calculation of $I_{av}$, $I_{av}$ is the weighted average of the latest four current measurements, each at the end of a separate alternation. The resistance value is converted to a resistivity value using the electrode dimensions and thickness of the specimens. The measurements are made at 500 V and an electrification time of 500 secs is used. It is important to remember that while the ohmic current might be too low at low voltages, high voltages may cause spurious current flows. Thus an optimum choice of measurement voltage is required.

Fig. 2. Volume resistivity at 50°C using alternating polarity method (direct measurement).

It can be seen that resistivity of unfilled epoxy is highest, and addition of filler particles decreases resistivity. HN specimens exhibit slightly higher values compared to AR nanocomposites, while CHN samples show lowest values.

2) Method 2: Measurement from polarization currents

Polarization currents are recorded till the current reaches steady values, indicating only dc current flow. Fig. 3 shows polarization currents measured for a period of 45 mins. The current in all specimens are seen to become stationary by this time, except for the CHN specimens.

Fig. 3. Polarization currents measured at 50 °C for 45 min(2800 sec).
So, polarization current measurements for CHN specimens are continued for a longer period of time (12 hrs). Fig. 4 shows that it takes about 11 hours to stabilize, indicating the presence of particularly high polarization currents in the functionalized samples.

The total current is due to polarization currents as well as dc conductivity current. The polarization currents die out with time, and the dc steady state current continues to flow. The steady state values of the measured currents are used to re-calculate volume resistivities. The volume resistivity $\rho_v$ is calculated based on equation (1).

$$\rho_v = \frac{K_e \times V}{t \times I} \hspace{1cm} \Omega \cdot cm$$  

(1)

where, $K_e$ is the effective area of electrode, and is given as $\pi \left( \frac{D_1}{2} \right)^2$. $D_1$ is the external diameter of the guarded electrode and $t$ denotes the thickness of the specimen.

The resistivity values thus calculated are shown in Fig. 5, while Table I shows the values of volume resistivities calculated by the two different methods. As we had seen earlier, neat epoxy has higher resistivity than nano-filled samples. HN specimens are seen to have slightly higher values than AR specimens. Interestingly, now CHN specimens also exhibit high resistivity, equal to or very slightly higher than HN. The discrepancy with Fig. 3 in case of CHN specimens, arises due to the difference in electrification time employed in the two cases. Evidently, the very low resistivity value observed at 500 secs electrification time is due to high polarization currents at that instant, and does not reflect dc conductivity values. In fact, a comparison of resistivity values for all specimens obtained by the two methods in Table I, indicates that direct resistivity measurements give lower values; obviously polarization currents do not entirely die out by 500 secs. Thus, in all future measurements, method 2 is adopted for computation of volume resistivity, as it ensures the choice of proper electrification time.

Further, we conclude that resistivity of nanocomposites increases due to pre-processing of the nano-particles before use. Pre-processing includes either heating of particles (HN) or functionalization of particles with GPS after heating (CHN).

### Table I

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Specimen</th>
<th>Direct Measurement</th>
<th>Calculated from Polarization Current</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>EP</td>
<td>$5.95 \times 10^{15}$</td>
<td>$1.08 \times 10^{16}$</td>
</tr>
<tr>
<td>2.</td>
<td>MC</td>
<td>$4.68 \times 10^{15}$</td>
<td>$7.49 \times 10^{15}$</td>
</tr>
<tr>
<td>3.</td>
<td>AR</td>
<td>$1.62 \times 10^{15}$</td>
<td>$3.23 \times 10^{15}$</td>
</tr>
<tr>
<td>4.</td>
<td>HN</td>
<td>$1.88 \times 10^{15}$</td>
<td>$4.10 \times 10^{15}$</td>
</tr>
<tr>
<td>5.</td>
<td>CHN</td>
<td>$3.16 \times 10^{14}$</td>
<td>$4.24 \times 10^{15}$</td>
</tr>
</tbody>
</table>

### B. Measurements at different temperatures:

In order to understand the effect of temperature, measurements are repeated at room temperature (26°C), 70°C and 90°C. Volume resistivities are computed using polarization currents as in method 2 outlined above. The respective values are outlined in Table II. It is important to note that polarization is a temperature-dependent phenomenon. In order to measure the dc conductivity values accurately, it is necessary to make sure that polarization currents have reached steady state values. At each temperature, the electrification time used is the maximum time required by any sample to reach steady current values at that temperature. Thus, in Table II, different electrification times are used for measurements at different temperatures.

In each case, the current values used are those after steady state is reached; this time is denoted as the electrification time. Lower temperatures require higher electrification times. As explained earlier, the very large electrification time required at 50°C is dictated by the singular behaviour of CHN samples at that temperature; other specimens attain steady values within 2500s. As temperature increases, required electrification time reduces considerably.
bond formation [4]. Though there is no direct evidence, it is likely that the increased resistivity is linked to the nature of the interfacial region, and the absence of water or unbonded hydroxyl groups on the surface of the particle which may form a conducting shell around the uncoated nanoparticles.

IV. CONCLUSION

The following conclusions may be drawn from this work:

1. Volume resistivity calculated from polarization currents is a more accurate and appropriate way to characterize the material than direct measurements, owing to the difference in the absorption and relaxation processes across materials.

2. Preprocessing techniques like heating and functionalization improve resistivity.

3. Resistivity decreases with temperature.

4. The decrement in resistivity with respect to temperature is less in CHN samples compared to other samples.

ACKNOWLEDGMENT

The work was carried out with funds received from the Department of Science and Technology, Government of India, under Project no. SR/S3/ME/29/2005-SERC-Engg.

REFERENCES


**BIOGRAPHIES**

**R. R. Patel** obtained his M. E. Degree from M. S. University, Baroda, India in electrical engineering in 2002. He is an Assistant Professor in the Electrical Engineering Department at GCET-Vallabh Vidyanagar, Anand, India, and currently enrolled in the Ph.D. program (under QIP) in Electrical Engineering Dept., Indian Institute of Technology Kanpur, India. His research interests are nanodielectrics and electrical characterization of nanocomposites for high voltage applications.

**Nandini Gupta** (M’02) obtained the Ph.D. degree from the Indian Institute of Science in 1998. She was a post-doctoral researcher at the University of Windsor, Canada and the Eindhoven University of Technology, the Netherlands. She is currently an Assistant Professor in the Indian Institute of Technology, Kanpur, India. She works in the area of dielectrics and insulating materials, partial discharges and treeing, and applications of plasma discharges.