Evaluation of Epoxy Nanocomposites for High Voltage Insulation

by

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ABSTRACT

Polymeric materials containing nanometer (nm) size particles are being introduced to provide compact shapes for low and medium voltage insulation equipment. The nanocomposites may provide superior electrical performance when compared with those available currently, such as lower dielectric losses and increased dielectric strength, tracking and erosion resistance, and surface hydrophobicity. All of the above mentioned benefits can be achieved at a lower filler concentration (< 10%) than conventional microfillers (40-60%). Also, the uniform shapes of nanofillers provide a better electrical stress distribution as compared to irregular shaped microcomposites which can have high internal electric stress, which could be a problem for devices with active electrical parts. Improvement in electrical performance due to addition of nanofillers in an epoxy matrix has been evaluated in this work.

Scanning Electron Microscopy (SEM) was done on the epoxy samples to confirm uniform dispersion of nano-sized fillers as good filler dispersion is essential to realize the above stated benefits. Dielectric spectroscopy experiments were conducted over a wide range of frequencies as a function of temperature to understand the role of space charge and interfaces in these materials. The experiment results demonstrate significant reduction in dielectric losses in samples containing nanofillers. High voltage experiments such as corona resistance tests were conducted over 500 hours to monitor degradation in the samples due to corona. These tests revealed improvements in partial discharge endurance of nanocomposite samples. These improvements could not be adequately explained using a macroscopic quantity such as thermal conductivity. Thermo gravimetric analysis (TGA) showed higher weight loss initiation temperatures for nanofilled samples which is in agreement with the corona resistance experimental results.
Theoretical models have also been developed in this work to complement the results of the corona resistance experiment and the TGA analysis. Degradation model was developed to map the erosion path using Dijkstra’s shortest path algorithm. A thermal model was developed to calculate the localized temperature distribution in the micro and nano-filled samples using the PDE toolbox in MATLAB. Both the models highlight the fact that improvement in nanocomposites is not limited to the filler concentrations that were tested experimentally.
DEDICATION

To

my parents Mr. G. Vijay kumar and Mrs. Hema kumar,

whose contributions cannot be mentioned in words.
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NOMENCLATURE

$\alpha$ - scale parameter
$\alpha_1$ - thermal diffusivity
$\beta$ - shape parameter
$C_p$ - Specific heat of the material
d - diameter of the particle
$\varepsilon'$ - real permittivity
$\varepsilon''$ - imaginary permittivity
$\varepsilon_1$ - real permittivity of the base resin
$\varepsilon_2$ - real permittivity of the filler
$\varepsilon_c$ - real permittivity of the composite
$\varepsilon_d''$ - dielectric loss
E - electric field
f - frequency
k - thermal conductivity
l - inter-particle distance
Lc - correlation length
LSD - Least Significant Difference
$\rho$ - density
Q - heat flux
r - radius of the particle
$\sigma_{dc}$ - DC conductivity
StV - Surface Area to volume ratio
tan$\delta$ - loss tangent
T - Temperature
\( \nu \)- volume fraction of the particles

\( \omega \)- frequency

\( \omega_c \)- cross-over frequency

\( y_1 \)- volume fraction of the base resin

\( y_2 \)- volume fraction of the filler
Chapter 1: INTRODUCTION

1.1 Introduction

Cycloaliphatic family of epoxy resins has been used for high voltage applications for indoor, outdoor and enclosed apparatus for around 50 years. Epoxies are typically used for devices such as pin and post type insulators, instrument transformers, bus support assemblies, switching and protection equipment for low and medium voltage applications [1, 2]. Their formulations and manufacturing processes have evolved continuously to the present state, where they are considered attractive replacements for porcelain for such applications. They have several advantages over conventional porcelain such as: superior impact, seismic resistance and light weight [3]. They can be easily molded into complicated shapes and have the advantage that the same material fulfills the electrical and mechanical functions, which would eliminate interface issues that are commonly the origin of problems in devices that employ separate materials (fiber glass core and elastomer housing) [4].

The epoxy used for high voltage applications is cycloaliphatic type (CEP) compared to the bisphenol epoxy variety that is used for the manufacture of fiber glass solid rods and hollow cores. The cycloaliphatic epoxy is characterized by saturated (no double or triple bonds) molecular structure that results in better tracking and erosion resistance. The tracking and erosion resistance property is inferior for bisphenol epoxy due to the unsaturated molecular structure, which otherwise has very good mechanical and electrical properties. Material formulation of cycloaliphatic epoxies can be tailored to impart surface hydrophobicity, thereby providing superior high voltage performance under contaminated conditions [5]. All the samples tested during the course of this work are made of cycloaliphatic epoxy. Figures 1.1, 1.2 and 1.3 show pictures of epoxy insulated post type insulators, current and potential transformers.
Figure 1.1: Post type insulator

Figure 1.2: Current Transformer
However, in high voltage applications, electrical insulation often experience stresses that can be withstood by only a few materials. The electrical stresses give rise to partial discharge, dry band arcing, and corona discharge on the insulation surface, which leads to the physical erosion of the material, and insulation failure. Inorganic fillers such as silica are used in epoxies for these purposes. The role of these fillers is to reduce the surface electrical stress to a level whereby discharges such as partial discharge, corona or dry band arcing does not occur [6].
1.2 Inorganic fillers

The use of inorganic fillers such as alumina trihydrate (ATH), silica etc. in polymeric insulation materials has been conducted for many years [7, 8, 9]. Addition of these fillers in the polymer formulation reduces cost and also improves mechanical and electrical properties [10]. The fillers added in all these samples are micro-sized fillers with sizes in the range of 1-100 µm. However, the micro-sized fillers are found to be needle-shaped and have pointed edges. These act as localized stress enhancement sites which reduce the dielectric strength of the material. Extensive research has been conducted to study the influence of filler size, concentration and type on the aging performance of epoxy insulators and other outdoor equipment [11]. However, the addition of these micro-sized fillers into a polymer rarely improves the electrical

Figure1.4: Sample showing micro-fillers
breakdown strength of the system. In fact, pointed edges (Figure 1.4), high aspect ratios, agglomeration (Figure 1.5), and bad interfaces (Figure 1.6) of micro-fillers with the base resin increases localized electrical stresses in these samples which can result in reduced breakdown voltage [12]. Reduction of size into the nano range and spherical shape of the filler particles may overcome such problems. It could also potentially influence the properties of the micro/nanofiller combined resin in a complex manner.

Figure 1.5: Sample showing agglomeration of micro-fillers. Base resin-epoxy with 62.5% micro-sized silica filler and 2.5% nano-sized filler
Figure 1.6: Sample showing bad interface of the micro-filler with the base resin

1.3 Nanodielectrics

The first credible mention of nanodielectrics in the high voltage industry was made in 1994 [13]. The development of nanocomposites represents a very attractive route to upgrade and diversify properties of polymers without changing their compositions and processing [14]. In contrast to conventional filled polymers, nanocomposites are composed of nanometer sized fillers which are homogeneously distributed within the polymer matrix. A nanocomposite may be defined as a dielectric material into which filler particles of nanometers in size have been introduced to form a well dispersed homogeneous liquid. Addition of these particles results in conversion of the bulk polymer into an interfacial polymer which gives rise to diversified polymer properties [15]. The full advantages of nanocomposites can be realized only if the distribution and dispersion
of the nano-filler is uniform. Hence, a lot of importance is given to sample preparation and filler dispersion [16, 17]. Figure 1.7 shows a 5% N sample containing nanofillers.

![Figure 1.7: 5% N sample containing nanofillers](image)

Nanofiller-added polymers or polymer nanocomposites might be differentiated from micro-filler-filled polymers in three major aspects:

- The nanocomposites contain small amounts (<10% by volume) of fillers
- The fillers are in the range of nanometers in size
- They have tremendously large specific surface area

All these characteristics would reflect on their material properties. The first thing that attracts interest arises from the difference in content. Conventional filled polymers usually contain a large concentration of the fillers, e.g., 60 wt%. Therefore, conventional micro-composites are mixtures of polymers with mineral fillers, resulting in big change
or difference in material properties from polymers [2, 7]. In the case of nano-fillers, fillers are added up to 10% concentration. Hence, some of intrinsic polymeric properties remain almost unchanged even after they become nanocomposites [18].

The other characteristic of interest is expected from the filler size difference. Nano-sized fillers are three orders of magnitude smaller than conventional micro-fillers. Hence, the distance between neighboring fillers is much smaller in nanocomposites than in conventional filled polymers. In many cases, the inter-particle distance might be in the range of nanometers, if fillers are homogeneously dispersed. Nano-filled samples have a large surface area as compared to the micro-filled samples. The specific surface is represented by the inverse size, and that is three orders larger for nanocomposites than that for conventional filled polymers. Interaction of polymers matrices with fillers is expected to be much more in nanocomposites than in the conventional filled polymers. The size of fillers and the inter-particle distance are in the range of nanometers causing chemical and physical interaction with the polymer matrix. This results in the emergence of mesoscopic properties that resemble neither the atomic nor the macroscopic frame [19].

Nano-filled epoxies can be used for low and medium voltage (≤ 100 kV) equipment such as dry type instrument transformers, re-closers, bushings and bus support insulators. The apparatus thus formulated would be more compact and can have longer life than what is available presently [20, 21]. They can be expected to provide improved performance when compared with conventional micro-filled materials, such as superior corona resistance, dielectric strength, and tracking and erosion resistance. These nanofilled epoxies would offer unique manufacturing and design advantages.

Conflicting results on the performance of nanocomposite fillers have been reported and the underlying mechanisms are not completely understood [22-24]. This is due to the
fact that sample preparation of nanocomposites is not easy. Uniform nanofiller dispersion in the polymer matrix is essential to realize the stated advantages. To understand better the distinct advantages that the nano-fillers provide over their micro-filled counterparts there is a need for a thorough study of electrical, mechanical and thermal properties of the different filled and unfilled samples. Different experiments were conducted to compare micro and nanofilled samples and theoretical models were developed to analyze the improvements due to addition of such nanofillers.

1.4 Organization of the report

Chapter 2 evaluates the filler dispersion using Scanning Electron Microscopy as well as investigates the weight loss initiation temperature of the samples using the TGA analysis. Polarization phenomenon in the samples is investigated using the dielectric spectroscopy technique in Chapter 3. Chapters 4 and 5 present the results of the breakdown and the corona resistance experiments on epoxy nanocomposites respectively. Degradation model to map the erosion path in epoxy nanocomposites is reported in Chapter 6. Reasonable agreement between the length of the degradation path and the corona resistance in samples containing both micro + nanofillers has been demonstrated. Thermal analysis of epoxy solid dielectrics containing micro and nanofillers conducted to better explain the partial discharge endurance performance is explained in Chapter 7. The chapter contains thermal conductivity and thermo gravimetric analysis (TGA) measurements and a thermal model which calculates the localized temperatures in filled samples using the PDE toolbox in MATLAB. Chapter 8 consists of the conclusions and an outline future work.
Chapter 2: SAMPLES EVALUATED: SCANNING ELECTRON MICROSCOPY (SEM) AND TENSILE STRENGTH MEASUREMENTS

2.1 Introduction

Thin sheets of epoxy samples containing micro and nano-sized fillers were provided by ABB Corporate Research. The dimensions of all samples were about 75 mm × 75 mm × 1 mm. Dispersion of fillers is essential in nanofilled samples to realize the improvements in the electrical and mechanical properties of epoxy resin and this was confirmed by conducting Scanning Electron Microscopy (SEM) on the samples. The filler confirmation was done using EDAX (Energy Dispersive X-ray Analysis) results. Tensile strength measurements were conducted to test the mechanical strength of the filled and the unfilled samples.

2.2 Samples Provided

In order to avoid the agglomeration of nano-fillers, ABB Corporate Research used liquid dispersions (master-batches) provided by nanofiller suppliers. The different samples that were evaluated are listed in Table 2.1. Anhydride curing cycloaliphatic epoxy resin system was used as the base polymeric matrix. The micro-sized silica was irregularly shaped, epoxy silane treated and of an average size of 16 micrometers. The filler was dried overnight at 80°C before casting. Nano-sized silica filler was of spherical shape with a diameter of about 20 nanometers and was supplied as a 40%wt master-batch by Nano-resins AG, Germany. Standard mixing, degassing, casting, curing and post-curing procedures were used to manufacture the samples. Prior to any testing at Arizona State University, the samples were heated in an oven for 20 hours at 160°C to remove the absorbed moisture from the samples. It should be noted that even longer times (several days) may be needed to remove the excess moisture in some samples.
Table 2.1: List of Samples

<table>
<thead>
<tr>
<th>Filler concentration (wt %)</th>
<th>Identification in figures</th>
</tr>
</thead>
<tbody>
<tr>
<td>65% Micro</td>
<td>65% M</td>
</tr>
<tr>
<td>62.5% Micro + 2.5% Nano</td>
<td>62.5% M + 2.5% N</td>
</tr>
<tr>
<td>60% Micro + 5% Nano</td>
<td>60% M + 5% N</td>
</tr>
<tr>
<td>65% Micro + 5% Nano</td>
<td>65% M + 5% N</td>
</tr>
<tr>
<td>5% Nano</td>
<td>5% N</td>
</tr>
<tr>
<td>0% (Unfilled)</td>
<td>0%</td>
</tr>
<tr>
<td>2.5% Nano</td>
<td>2.5% N</td>
</tr>
</tbody>
</table>

2.3 Scanning electron microscopy (SEM)

Figure 2.1: Regular SEM image of a 65% M + 5% N sample
SEM was conducted on the sample surface after applying gold coating on the sample surface in order to avoid charging of the sample. However, nothing could be seen on the sample surface except a few dust particles and cracks. So, SEM using a focused ion beam (FIB) was carried out. Figure 2.1 shows the regular SEM on the sample surface while Figure 2.2 shows the SEM image using the FIB. The procedure for getting SEM images using the FIB instrument is discussed in Section 2.3.1.

![SEM image using the FIB instrument, 65% M + 5% N sample](image)

**Figure 2.2: SEM image using the FIB instrument, 65% M + 5% N sample**

2.3.1 Procedure

The following steps were carried out to get the SEM images using the FIB setup:
1. A small piece of the sample was mounted on a stub and gold coated. Figure 2.3 shows the figure of a sample holder for the SEM.

![Figure 2.3: Sample holder with a gold coated sample](image)

2. The sample was mounted on the FIB instrument. Focusing was done on the sample surface to set-up the working distance (distance between the beam and the sample) before platinum coating was done on the surface using the electron beam. The electron beam can be used to deposit a thin protective coating of carbon-rich platinum that grows relatively slowly and conforms to high-aspect ratio structures as it is deposited. Electron beam deposition of platinum is useful for samples that are sensitive to the ion beam. The platinum deposition using the electron beam is done at 5 kV. Figure 2.4 shows an image of the sample with the platinum electron beam.
3. After the electron beam deposition, the stage is tilted to $52^\circ$ so that the sample surface is parallel to the gallium ion beam gun. Then, a platinum coating on the surface of the existing e beam coating is done using the ion beam. This is done prior to milling the sample using the ion beam as it tends to damage the sample. The ion beam coating and milling is done at 30 kV and the current is kept at 1-6 pA/µm².

4. The surface of the sample was milled (i.e. the ion beam was used to trench into the material thereby revealing the fillers and their dispersion in the matrix). Figure 2.5 shows a sample after milling. The micro sized particles can be seen in the Figure 2.5.
2.3.2 Results and Discussion

SEM images

Figure 2.6 shows the SEM picture of a nano-filled sample while Figure 2.7 shows a sample with micro + nanofillers in them. The average size of the nano-fillers was observed to be around 10-20 nm. Uniform dispersion of the nano-fillers can be seen in these images. The micro-fillers have sharp edges which can be seen from Figure 2.7 which could have high localized electrical stresses. Samples containing nanofillers are not easy to prepare as they have a tendency to agglomerate and form large clusters as shown in Figure 2.8. Agglomeration of nano-fillers occurs due to the high surface energy of the nano-particles [25]. One of the major challenges in the field of nanodielectrics is to ensure good dispersion of nanofillers in the samples. None of the samples tested in this work had agglomerated nano-fillers. Energy dispersive X-ray analysis (EDAX) was carried out at different locations on the surface confirming the filler to be silica.
Figure 2.6: SEM image showing nano-fillers

Figure 2.7: High magnification scanning electron microscopy showing nanofiller (20 nm) distribution in a sample
Figure 2.8: Sample containing agglomerated nano-sized silica fillers (10% nano)

EDAX Results

EDAX was carried out at different locations on the surface confirming the filler to be silica. Figure 2.9 shows three spots where the beam was hit and reflects the presence of silica fillers in the samples (both micro and nano). Spots 1 and 3 are micro-sized fillers and reflect peaks of Si, while spot 2 is nanofiller. The EDAX images are not as clear as the SEM images because the technique works only on lower voltages. The small gallium peaks are due to the milling done using the gallium ion beam
2.4 Tensile Strength measurements

2.4.1 Experimental setup

Epoxy filled and unfilled were tested for tensile strength using an Instron 4411, 1000 lb, 5 kN load frame, shown in Figure 2.10. was used to test the samples. The testing was conducted in SEMTE lab at Arizona State University. The samples were cut in dog bone shapes of dimensions as shown in Figure 2.11. Tensile modulus and strain-to-break
were determined on three specimens of each type at a low deformation speed (0.1 mm/min) [26].

Figure 2.10: Setup for tensile strength experiments

Figure 2.11: Dog bone shape
2.4.2 Results

![Stress vs. Strain curves of all samples](image)

**Figure 2.12: Stress vs. Strain curves of all samples**

Stress-Strain curves of all the samples are shown in Figure 2.12. The nano-filled samples (5% N and 2.5% N) have larger strain-to-break value than the unfilled sample. Longer stress curves would mean a larger tensile strength value. The improvements in tensile strength due to addition of nano-fillers could be due to restriction in the motion of polymer chain due to well-dispersed nano-fillers [27]. The micro + nanofilled samples have a higher tensile strength value than conventional microcomposites. Also, the presence of micro-fillers in these samples has not resulted in formation of voids or micro-fissures and do not have a bad interface with the base matrix which would have otherwise reflected in their tensile strength values [28]. Figure 2.13 shows the tensile strength values of all the samples.
Figure 2.13: Tensile Strength of all samples

The slope of the stress vs. strain curves (Figure 2.11) provides the Young’s modulus for the samples. The Young’s modulus is a measure of the stiffness of the material and is shown in Figure 2.13 for all the tested samples. The 5% N sample has higher tensile strength than the 65% M sample (Figure 2.12) and lower Young’s modulus than the micro-composite samples. This means that insulation equipment made out of the 5% N sample would be a lot more flexible than those available currently and still retain the tensile strength of the micro-composites.

However, the micro + nanofilled samples (60% M + 5% N and 62.5% M + 2.5% N) have a significantly larger Young’s modulus as compared to the 65% M sample. The addition of nano-fillers at the expense of micro-composites (60% M, 62.5% M as compared to 65% M) in the micro + nanofilled samples increases the tensile strength of the material, but also increases the material stiffness. Higher stiffness would result in difficulty in molding the material into varied shapes but would not make them brittle.
Figure 2.14: Young's modulus of all samples
Chapter 3: DIELECTRIC SPECTROSCOPY

3.1 Introduction

Dielectric spectroscopy is an investigative tool for the study of molecular motions of dipolar molecules in liquids and solids. The technique is a measurement of the real and imaginary permittivity, from a low frequency (e.g. 1 mHz) to high frequency (e.g. 1 MHz), as a function of temperature. Variations in temperature move the curves on the frequency scale, e.g. increasing temperature slides the curves to the right on the frequency scale. By doing temperature variations, one is able to attain permittivity values over a much broader spectrum [29].

Spectroscopic dispersion of dielectric permittivity and associated energy absorption regions may be observed due to classical electrical polarization and conduction process. The magnitude of the effects and the frequency location of the energy absorption features associated with these processes depend upon the physical and chemical nature of the material and the temperature and pressure at which it is studied.

Several dielectric mechanisms or polarization effects can happen in a material, which contributes to its overall permittivity. Charge carriers in a dielectric material can be displaced by an electric field. The charges become polarized to compensate for the electric field such that the positive and negative charges move in opposite directions. At the microscopic level, several dielectric mechanisms can contribute to dielectric behavior. The behavior of dielectric properties as a function of frequency in insulating materials is governed by polarization and relaxation effects. The polarization phenomena in a dielectric material over a wide time scale can be seen in Figure 3.1 and it can be observed that different polarization mechanisms dominate over different frequency ranges [30]. Inferences to interfacial polarization and conduction processes (low frequency) and of dipole polarization effects (high frequency) can be made from real and imaginary
permittivity values. Interfacial polarization can be related to the base resin-filler surface, while dipole polarization gives information as to how the bulk polymer is being affected [31, 32].

![Diagram](image)

**Figure 3.1**: Different polarization phenomena occurring in a solid dielectric [33]

### 3.2 Experimental Setup

The setup involves a Solartron 1260 impedance analyzer, a Novocontrol Quatro temperature controller and a sample holder. A voltage of 50 V was applied to the samples and their permittivity values were measured over a frequency range of 1 mHz to 56 kHz. Initially, all measurements were done at room temperature. Five measurements for each type of sample were carried out at room temperature. Temperature variations from 233 K (-40°C) to 393 K (120°C) at a step of 20° was also carried out for the entire frequency range as mentioned above. The results section discusses only 233 K, 333 K, and 393 K in...
addition to the room temperature measurements. Three measurements were done on each type of sample for these temperatures. Figure 3.2 shows the entire spectroscopy setup while Figure 3.3 shows the sample holder. The sample holder consists of the top and bottom electrodes and the sample was sandwiched between the two electrodes.

**Figure 3.2 Dielectric Spectroscopy setup**
As a benchmark, a teflon sheet with the same dimensions as the sample was run in the setup. Teflon has a frequency invariant relative permittivity of 2.04 [34]. All the samples were measured using the same reference measurement. The sample measurements were conducted with and without guard rings. Appendix A shows the guard ring measurements [35, 36].

3.3 Experimental Results and Discussion

The dielectric response in heterogeneous systems can contain contributions from permanent dipoles as well as mobile charge carriers namely, ions and electrons. In heterogeneous materials, the inclusion of non-conducting filler materials can restrict the overall motion of carriers. This can lead to large dielectric permittivities observed at low
frequencies. Different theories like the Logarthmic-Ritchker rule, Maxwell-Wagner-Sillars theory, and Maxwell-Wagner-Garnet theory have been proposed for calculating the real and imaginary permittivity values [15, 31]. For example, using the Logarthmic-Ritchker rule, the real permittivity of the 65% microfilled sample was calculated to be 3.68 at room temperature at 1 mHz. The Logarthmic-Ritchker rule is given by Equation 3.1 as:

\[ \log \varepsilon_c = y_1 \log \varepsilon_1 + y_2 \log \varepsilon_2 \]  

(3.1)

In Equation 3.1, \( y_1 \) and \( y_2 \) are the volume fractions, while \( \varepsilon_1 \) and \( \varepsilon_2 \) are the permittivities of the base resin and the filler respectively, while \( \varepsilon_c \) is the permittivity of the composite. The measured value was 4.75, which is significantly different from the calculated value. This is because the calculations do not take into account the filler shape, size and the possible change of matrix properties at the interface. So, it becomes imperative to measure the permittivity values to see the impact of the fillers on the overall matrix.

### 3.3.1 Room Temperature Measurements- All samples

Figures 3.4 and 3.5 show the real permittivity and the tan\( \delta \) plots of the different samples. The introduction of inorganic fillers having a permittivity value higher than the base polymer increases the effective permittivity of the composite material. The real permittivity and the tan\( \delta \) plots show that there is a significant difference in the measured values of the unfilled and nanofilled samples when compared with the micro and micro + nanofilled samples. The lower values of permittivity and tan\( \delta \) of nanofilled samples over microfilled samples, is due to their high surface-area to volume ratio which results in large interfacial areas of nanocomposites as compared to the microcomposites. This large interaction zone can have a major impact on the permittivity values of nanocomposite materials as compared to microcomposite materials.
nanofillers and the polymer chain results in reduced mobility and thus a higher surface area of the nanofillers would result in a reduction in the overall permittivity of the samples.

Figure 3.4 Real permittivity plots for studied epoxy samples at room temperature

The high real and imaginary permittivity values of the microfillers could be due to the presence of interfacial polarization due to microfillers as the base matrix in all the samples is the same. The microfillers act as charge defects in the bulk material resulting in space charge formation which leads to interfacial polarization [37]. When an electric field of high frequency is applied, the probability of these space charges to drift and accumulate at polymer-nano particle interfaces becomes very small. This is because the mean displacement of the charges is much smaller than the size of a typical nano-particle for small time durations (i.e. high frequencies: 1 kHz-56 kHz). This means that there is a certain time delay (from the time the electric field is applied) before the charge carriers
start to move. Usually, occurrences of interfacial polarizations are observed at low frequencies of dielectric measurement. This is due to the mesoscopic distances between the different microscopic fillers i.e. distances intermediate between molecular and macroscopic lengths. Since interfacial phenomena is an additional polarization mechanism apart from ionic, electronic and dipolar mechanisms, their occurrence in a system is usually associated with distinct variations in the trends of real and imaginary permittivity with respect to frequency, especially at high filler concentrations [38, 39].

![Tanδ plots for studied epoxy samples at room temperature](image)

**Figure 3.5** Tanδ plots for studied epoxy samples at room temperature

The variations in the real permittivity values may be independent of frequency, which could be due to the presence of dc conductivity, as can be seen from Figures 3.4 and 3.7. However for dc conductivity, the imaginary permittivity value is given by,
\[ \varepsilon' = \sigma_{dc} / (\varepsilon_0 \omega) \]

(3.2)

Since, \( \sigma_{dc} \) is a constant, the imaginary permittivity is inversely proportional to the frequency. However, if dc conductivity was present in these samples, the slope of the imaginary permittivity curves would be -1 on a log-log plot. Since this is not observed, any possibility of detectable dc conductivity on these samples can be ruled out. Figure 3.6 shows the imaginary permittivity plot at room temperature.

![Figure 3.6 Imaginary permittivity plots for studied epoxy samples at room temperature](image)

3.3.2 Measurements at 233K

Figure 3.7 shows the real permittivity plots of all the samples at 233 K. It can be seen that the 2.5% nanofilled sample shows a lower real relative permittivity value as compared to the unfilled sample, while the 5% nano shows the reverse phenomena. Tuncer et al. [40] reported that, for an epoxy composite system with nano-sized particles, the nanocomposite permittivity was lower than that of the base epoxy matrix up to 3%
filler concentration. Singha et al. [41] observed that epoxy nanocomposites containing ZnO nanofillers shows higher permittivity than the base resin up to 1% loading while at 5% loading the permittivity was lower. Other examples of reductions in the permittivity of epoxy nanocomposites with respect to unfilled epoxy have been reported in other literature as well [42]. This could be because of two contrasting factors affecting the overall permittivity of the samples:

a) The filler permittivity is more than that of the resin

b) The interaction between the nano particles and the polymer results in reduction in mobility of polymer chains, which can cause a reduction in the overall permittivity.

![Figure 3.7: Real permittivity of studied epoxy samples at 233 K](image)

At lower filler concentrations, the second factor plays a major role in the real permittivity value as compared to the first while at higher filler concentrations (more than 5%), the reverse seems to happen. The interaction dynamics between the two above
metioned processes is not fully understood till now. The real permittivity of the micro + nanofilled samples (sample 2(62.5% M + 2.5% N) and 3(60% M + 5% N)) was found to be lower than that of the microfilled sample (sample 1 (65% M)). In this case, the microfillers and epoxy combined can be considered as the base matrix. Figure 3.8 shows the tanδ plots for the samples. Secondary relaxations can be seen for the unfilled and the nano-filled samples [29]. The secondary relaxation peaks in the microfilled and the micro + nanofilled samples is overlapped by the interfacial polarization and hence is not visible.

![Figure 3.8: Tanδ plots of studied epoxy samples at 233 K](image)

3.3.3 Measurements at 333K

Comparison of the tanδ data for the three temperatures (Figures 3.5, 3.8, 3.9) shows how the frequency variation scales with temperature. For the tanδ plots at 333 K in Figure 3.9, the nanocomposites with 5% nanofillers shows higher tanδ values as compared to the unfilled epoxy and nanocomposites with 2.5% nanofillers. At 5% filler concentration, nano particles are more in number, the inter-particle distances are smaller and this could result in overlapping of the interfacial zones in the nanocomposites leading
to the percolation of charge carriers. This results in enhancement of charge transfer, which causes an increase in the electrical conductivity [43]. Singha et al. [41] found a similar behavior at 10% nanofiller concentration for TiO$_2$-epoxy nanocomposites. In the micro + nanofilled samples, the nanofillers act as barriers restricting the motion of charge carriers and thus causing a reduction in the tanδ values. The differences in the tanδ values for the micro-filled and the micro + nano-filled samples was found to be significant while significant differences in the tanδ values were also found between the nano-filled and the unfilled samples. The test for significance was done using Fisher’s LSD test; the results of which are included in Appendix B [44].

![Figure 3.9: Tanδ plots of studied epoxy samples at 333 K](image_url)

Figure 3.9: Tanδ plots of studied epoxy samples at 333 K
Figure 3.10: Real permittivity of studied epoxy samples at 333 K

Figure 3.10 shows the real permittivity plots at 333 K. The real permittivity plots show a much larger variation at 333 K as compared to the room temperature (Figure 3.4) and the 233 K plots (Figure 3.7). This confirms that the measurements do not show variations due to the presence of dc conductivity.

3.3.4 Measurements at 393 K

The permittivity plots at 393 K (120°C) for the samples showed intersection of real and imaginary permittivity plots for the 5% N sample, 65% M sample and the micro+nanofilled samples. This phenomenon was not seen in the 2.5% N sample and the unfilled sample. Figures 3.11, 3.12 and 3.13 show the real and imaginary permittivity plots for the 5% N; 65% M sample; micro + nano sample; unfilled and 2.5% N sample respectively. The response seen in the 5% N, 65% M and the micro + nano samples is the ‘Quasi-DC’ (QDC) behavior explained by Dissado and Hill [45] or the ‘low frequency dispersion’ (LFD) responses mentioned by A.K. Jonscher [29].
LFD responses show large variations observed in the real permittivity plots and the slope of the real and imaginary permittivities are proportional to the same powers of frequencies beyond the cross-over frequency (ω_c). In Figure 3.11, the real and imaginary permittivity plots of both the micro and the nano sample intersect at a particular frequency (crossover frequency-ω_c) beyond which there is a change in the slope of the real permittivity values. Figure 3.12 shows the same behavior for the micro+ nanofilled samples.

![Figure 3.11: Real and imaginary permittivity plots for sample 1 at 393K](image)

Low frequency dispersion is due to the presence of inter-cluster and intra-cluster charge transport in the samples. A heterogeneous macroscopic sample may be considered as an array of “clusters”. Clusters are not physically isolated but are characterized by a correlation length scale, Lc. Their structural regularity over this correlation length scale is overridden. At high frequencies, the motion of the charge carriers is localized (intra-cluster) while at low frequencies and high temperature; the charge carrier motion is...
between different clusters (inter-cluster) as they gain sufficient energies. At $\omega_c$, there is a continuous crossover from intra-cluster hopping at higher frequencies to inter-cluster hopping at lower frequencies. When $\omega < \omega_c$, there is an incoherent transfer of charge between clusters which allows charge separation to occur over a range greater than the correlation length $L_c$. This leads to large polarizability and hence high permittivity. For the 65% M sample, the cross-over frequency is say about 0.1 Hz and for the 5% N sample it is about 0.01 Hz.

![Figure 3.12: Real and imaginary permittivity of micro+ nanofilled sample](image)

The real and imaginary permittivities of the unfilled sample and the 2.5% N sample do not intersect. The unfilled sample is a homogenous material and so no LFD behavior is visible in these samples. In the 2.5% N sample, the quantity of nano-particles might not be enough to demonstrate inter-cluster charge transport, which can very easily
be seen in the 5% N sample. Comparing Figure 4.16 with Figures 4.14 and 4.15, confirms that the cross-over phenomena is depends on heterogeneous samples with larger filler concentrations. The plots at 393 K in case of the unfilled and the nano-filled samples is an extension of the 333 K temperature, where in the tan δ plots the 2.5% N sample did not seem to behave too differently from the unfilled sample. The LFD behavior is different from dc conductivity as in this case the real permittivity value increases with decrease in frequency unlike dc conductivity in which the real permittivity is independent of frequency. In all these systems heterogeneity on a certain length scale appears to be a key feature for observing the LFD response [46].

![Real permittivity- all samples](image)

**Figure 3.13: Real and imaginary permittivity of 2.5% N and the unfilled sample**

Significant differences were seen in the permittivity plots of the micro, micro+nanofilled samples and unfilled, nanofilled samples. Significant reductions in the dielectric losses (tanδ) were seen for the micro+nanofilled samples as compared to
microfilled samples. The plots demonstrated a significantly different dielectric behavior for the 5% N sample as compared to the 2.5% N sample and the 0% (unfilled sample). Further high voltage experiments were conducted in order to examine the improvements in samples containing nano-fillers.
4.1 Breakdown in solid dielectrics

The loss of material performance of a solid insulator as a result of an electric field greater than a certain critical magnitude is called dielectric breakdown. The critical magnitude of electric field at which the breakdown of a material occurs is called dielectric strength [47]. The dielectric breakdown property gives an indication of the maximum voltage that an insulation material can sustain, i.e. its electrical performance or electrical endurance. Generally, polymeric insulation exhibit an intrinsic breakdown strength up to 8 MV/cm at room temperature, but in practice this performance drops significantly by several MV/cm due to defects or impurities [48].

Dielectric breakdown depends on a variety of parameters, which includes electrode configuration, thickness of the insulating material, electrode materials, presence of cavities and/or other defects, temperature, pressure, nature of morphology of the insulating material under test, type and conditions of test, and damage path. Solid electrical insulating materials are non-homogenous and may contain defects. Dielectric breakdown occurs in an area of the test specimen where the field intensity is the greatest. Weak spots within the volume under stress sometimes determine the test results. The dielectric strength test is conducted according to ASTM D-149 or IEC 243-1[49, 50].

The dielectric breakdown voltage or strength measurement tests depend on the sample geometry and homogeneity, the shape of electrodes and the type of voltage applied. The electrodes and the sample are dipped in transformer oil to avoid corona.
4.2 Background: Dielectric Strength for nanocomposites

Conventional composites contain micro-fillers which tend to substantially reduce the electric strength of the resulting composite. The introduction of fillers into polymers usually introduces defects in the system causing centers of charge concentrations leading to lower dielectric strength [51]. It is believed that nanocomposites do not do this because they offer a huge interfacial area and therefore tend to change the very nature of the polymer into which they are included. Because the inter-particle distances are quite small, the volume of polymer that is devoid of particles is reduced and the nano-particles act like barriers to the flow of electric current between the electrodes. The expectation of nano particles as fillers is to reduce the impact of these defects or impurities on their extrinsic short and long term electrical performance [41].

However, contrasting results have been observed in the dielectric strength test of the samples containing nanofillers. Imai et al. [52] showed that with 5% by weight of fillers in an epoxy nanocomposite, the ac dielectric strengths of layered silicate and TiO₂ fillers are marginally lower (considering the median value of the data) than that of unfilled epoxy whereas with SiO₂ fillers it is higher. Hu et al. [51] showed that the 60 Hz AC electric strength in nanocomposites is marginally higher than base epoxy and significantly higher than microcomposites. Reading et al. [53] found insignificant differences in the scale parameters for the filled samples as compared to the unfilled samples. The impact of nanofillers in the breakdown strengths of the samples is still unclear. Hence, breakdown tests were conducted on the filled and the unfilled samples to investigate the behavior of the samples containing nano-fillers.
4.3 Experimental details

The schematic of the experimental set-up is shown in Figure 4.1. The samples used were sheets of dimensions 25 mm $\times$ 25 mm $\times$ 1 mm. The electrodes were stainless steel spheres of 10 mm diameter. The test apparatus was immersed in transformer oil to avoid surface flashover. The power supply is a 10 kVA, 69 kV/120 V transformer.

The voltage applied was increased at a rate of 1 kV/s until breakdown. Measurements were made at the high voltage side using a resistance voltage divider. The oil was stirred after every breakdown measurement and replaced after every 10 measurements so as to ensure that the readings were not affected due to the by-products of degradation. Also, the electrodes were cleaned after every measurement and replaced after 10 measurements.

![Figure 4.1 Schematic for breakdown experiment](image)

4.4 Results

Table 4.1 shows the breakdown strength values of all the samples. Ten replicate measurements were done for each sample type. Only small differences were observed in
the breakdown values of different samples. Figure 4.2 shows an SEM image of the punctured sample.

Table 4.1: Breakdown values for the samples (kV/mm)

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<th></th>
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<th>2.5% N</th>
<th>5% N</th>
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<td>31.7</td>
<td>33.24</td>
<td>32.68</td>
<td>32.95</td>
<td>25.69</td>
<td></td>
</tr>
<tr>
<td>31.54</td>
<td>32.07</td>
<td>30.28</td>
<td>31.19</td>
<td>29.89</td>
<td>32.76</td>
<td>34.02</td>
<td></td>
</tr>
<tr>
<td>30.48</td>
<td>30.86</td>
<td>33.64</td>
<td>32.03</td>
<td>29.93</td>
<td>29.4</td>
<td>31.71</td>
<td></td>
</tr>
<tr>
<td>29.02</td>
<td>28.19</td>
<td>36.97</td>
<td>33.68</td>
<td>31.07</td>
<td>30.8</td>
<td>29.25</td>
<td></td>
</tr>
</tbody>
</table>
Different distributions such as the Normal Distribution, Lognormal Distribution and Weibull Distribution were tried for the data. All samples satisfied the fat-pencil test for all the three Distributions for a 95% confidence interval limit [54, 55]. The Distribution curves for all the samples had a $p$ value greater than 0.05 and almost all of them had a $p$ value between 0.15 and 0.85. The individual probability plots for all Distributions for all the samples are given in Appendix C. IEEE standard 4 states that for probability values between 0.15 and 0.85, any of the Weibull, Normal or Lognormal Distribution can be used [54]. For the breakdown data, Weibull Distribution was chosen as it is commonly used for breakdown in nanodielectrics and it is the recommended Distribution for breakdown analysis conducted using ASTM D-149 [41, 52, 55].

The Weibull Distribution plot of the micro and the micro + nanofilled samples are shown in Figure 4.3. Figure 4.4 shows the same data for the unfilled and nanofilled samples.
Figure 4.3: Weibull Distribution plot (95% confidence interval) for the microfilled and micro+nanofilled samples

Table 4.2 shows the scale and shape parameters for all the samples. No significant difference was observed in the scale parameters of the different samples. The shape parameter is indicative of the scatter of the data i.e. a higher $\beta$ value indicates that the individual data points of a particular sample are closer to each other. This means that a higher shape parameter would mean that the breakdown phenomenon is more stable. Different authors [41, 53] have observed a more stable breakdown voltage performance for the filled samples as compared to the unfilled sample. However, from Table 4.2, it can be seen that the 65% M + 5% N sample had the lowest $\beta$ value. No conclusion about the performance of the filled samples can be made from the breakdown test.
Figure 4.4: Weibull Distribution plot (95% confidence interval) for the unfilled and nanofilled samples

Table 4.2: Shape and scale parameters of the results using Weibull Distribution

<table>
<thead>
<tr>
<th>Filler details</th>
<th>Scale parameter ((\alpha)) (kV/mm)</th>
<th>Shape parameter ((\beta))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unfilled (0%)</td>
<td>36.86</td>
<td>6.974</td>
</tr>
<tr>
<td>2.5% N</td>
<td>37.07</td>
<td>10.06</td>
</tr>
<tr>
<td>5% N</td>
<td>36.59</td>
<td>10.22</td>
</tr>
<tr>
<td>65% M</td>
<td>34.01</td>
<td>13.18</td>
</tr>
<tr>
<td>62.5% M + 2.5% N</td>
<td>35.87</td>
<td>8.218</td>
</tr>
<tr>
<td>60% M + 5% N</td>
<td>36.37</td>
<td>7.529</td>
</tr>
<tr>
<td>65% M + 5% N</td>
<td>35.25</td>
<td>6.945</td>
</tr>
</tbody>
</table>
4.5 Discussion

Figures 4.5 and 4.6 show voids formed in the sample bulk due to the electrical breakdown tests conducted on the samples. No voids were present in the sample before the tests were conducted as can be seen from the SEM pictures in Chapter 2.

The inclusion of the filler particles with high dielectric permittivity values increases the average dielectric constant of a composite. But, they also produce a highly non-homogeneous electric field resulting in local hot spots of increased electric field concentration and reduced dielectric strength, thus reducing the effective breakdown strength of the composite. The presence of voids in the sample bulk means that particles constituting those voids are in the sample bulk as well. Figure 4.7 shows a 2.5% N sample with voids and particles from the voids in the sample bulk.

![Figure 4.5: Breakdown channels in the micro-nano sample (bulk)](image)
Figure 4.6: Breakdown channels in the nano sample (bulk)

Figure 4.7: Voids in the 2.5% N sample

The breakdown test conducted on these samples used spherical electrodes at both ends (high voltage and ground end). In the sphere–sphere configuration, a quasi-homogeneous field exists at the electrode-dielectric interfaces. Flandin et al. [56]
suggested the concept of ‘global weakest link’ (GWL) occurring in the samples for the sphere-sphere configuration. The concept suggests that the damage can initiate anywhere between the two contacting electrodes. Because of the quasi-homogenous field, it is not possible in this electrode configuration to identify a unique starting point and an end to the damage propagation. Application of a high voltage over a very small duration could also be a factor due to which there was no significant difference in the dielectric strength of the samples. The micro-filled samples tested in this case had good interfaces with the base matrix. Some of the other micro-filled samples were seen to have poor interfaces with the base matrix as shown in Figure 1.6 in Chapter 1. The samples with poor interfaces used a different epoxy matrix composition and hence their breakdown performances cannot be compared.

The dielectric strength measurements did not reveal any significant differences between the samples containing the fillers as compared to the unfilled sample. Hence, the dielectric strength test does not seem to be a good test for evaluating the performance of the samples containing nanofillers or micro + nanofillers. A possible alternative method worth exploring is resistance to corona where the electrodes create a non-uniform electric field, and a smaller voltage is applied over a longer duration of time [57]. Corona (partial discharge) experiments were therefore performed to determine if they could discriminate between unfilled, micro and nanofilled materials. The test was conducted for a longer duration (500 hours) using point-plane (divergent field) geometry as opposed to the breakdown strength test (short duration, quasi-homogenous field) discussed in Chapter 5.
Chapter 5: CORONA RESISTANCE EXPERIMENT AND RESULTS

5.1 Introduction

Corona discharges originate in the place of maximal inhomogeneity of electrical field while increasing of applied voltage. There are discharges on surface of insulation. Corona increases with increase in voltage and at certain voltage breakdown occurs [58]. Corona can be a significant threat to the performance of polymeric insulating equipment due to the organic nature of the housing material. In practical high-voltage systems, it is difficult to avoid corona discharges in the field, especially under wet and contaminated conditions. Hence, knowledge of the corona discharge magnitude on the housing material is essential [59].

Corona resistance experiments are conducted using the rod-plane geometry. Corona discharges cause electrical stresses just exceeding the discharge inception value, slow erosion of the dielectric, at a rate corresponding either to thermal degradation by the energy of the discharge or to disruption of the carbon-hydrogen bonds by bombardment. The rate of erosion increases rapidly with voltage, and the discharges concentrate to form deep pits. The energy liberated by each discharge increases with its length, and the erosion propagates with increasing rapidity until the pits attain a critical length, when narrow semi-carbonized channels develop at their ends and often trigger complete breakdown. The ultimate breakdown channels are propagated when the stress exceeds the intrinsic electric strength over some minimum distance. If the applied stress is sufficient these channels may propagate immediately, without preliminary erosion, and this second mechanism occurs in short-time industrial electric-strength tests [60].

This chapter investigates the corona resistance of the filled samples as compared to the unfilled sample when exposed to high voltage using rod-plane geometry. The experimental results in the chapter measure the erosion depth over a period of time (500
hours), while the degradation model results developed in Chapter 6 map the path of erosion occurring through the sample. Figure 5.1 shows the impact of corona on the sample surface.

![Figure 5.1: Schematic showing the impact of corona discharge on the sample [61]](image)

### 5.2 Background

Epoxy based insulating materials are widely used in several high voltage applications and under actual operating conditions; it is possible that these materials are exposed to electrical discharges. These discharges in turn can cause degradation of the insulating material over a period of time thereby reducing the life of the equipment [62].

Preliminary research by various authors shows an improved corona resistance by the nano-filled composites as compared to the micro-filled counterparts [63, 64]. It was confirmed for different materials and electrodes that there is a similar positive effect of nano fillers on PD resistance [64]. Nanofilled particles, if well dispersed provide larger interfacial areas and reduced inter-particle distances. The result is a reduction in erosion depth of the samples containing filler particles in them or improvement in corona resistance.

### 5.3 Corona Resistance Experimental Setup

Figure 5.2 shows a schematic of the setup used for the corona resistance experiment. The samples used were sheets of dimensions 10 mm × 10 mm × 1 mm. The
point electrodes were tungsten rods of 1 mm diameter. The point electrodes were kept at a distance of 0.1 mm from the top of the sample. This distance was measured using standard gauge blocks. The geometry and the electrodes used in this experiment are similar to the setup used by CIGRE Working Group [48].

![Schematic for corona resistance experiment](image)

**Figure 5.2 : Schematic for corona resistance experiment**

Six measurements on each type of sample (Table 3.1) were conducted with the same voltage applied to all the samples. A metal plate was kept underneath the surface of the samples and it served the purpose of a ground electrode. Figure 5.3 shows a picture of the setup used for the experiment. The voltage applied was 5 kV for 500 hours on the sample surface. The degradation was measured after every 100 hours using a surface profilometer. The power supply is a 10 kVA, 69 kV/120 V transformer.
Figure 5.3: Picture showing the corona resistance experimental setup

5.4 Observations and Results
Figure 5.4 shows the microscopic image of a 5% N and the 0% (unfilled) sample after 500 hours of exposure to corona. The resistance to corona was assessed by measuring the erosion depth on the sample surface. Lower erosion depth is suggestive of higher corona resistance. The erosion was cone-shaped and spread over the upper surface of the micro and the micro+nanofilled samples. In the 5% N sample, the erosion was concentrated under the needle electrode. The 0% (unfilled) sample showed degradation along the surface while there was hardly any subsurface degradation.

5.4.1 Degradation after 500 hours

The erosion depth of the unfilled sample was found to be the greatest while that of the micro+nanofilled samples was found to be the least. Figure 5.5 shows the average value of surface degradation of all the samples after every 100 h using the profilometer. The 0% (unfilled) sample has the maximum degradation after about 300 h. The 65% M sample has the greatest degradation for the initial 200 h of about 13 μm but it increases
by only 2 μm over the next 300 h. The unfilled sample in contrast, has less degradation at the end of 200 h but is the most degraded sample at the end of 500 h. The 60% M + 5% N, 62.5% M + 2.5% N and 65% M + 5% N samples exhibit the least degradation levels from start to end. The rate of increase in surface degradation on the unfilled sample and the 2.5% N sample is rapid with time while on all the other samples, the rate of increase in surface degradation remains nearly constant over time. Figure 5.6 shows a bar graph with the mean and the standard deviation of surface roughness measured on the samples at the end of the 500 h duration. The 5% nanofilled sample has a significantly lesser degradation as compared to the base resin. The degradation of the 65% microfilled sample is comparable to the 5% N sample. However, the micro+nanofilled samples have the least degradation among all the samples. Samples 62.5% M + 2.5% N and 60% M + 5% N have significantly reduced degradation values as compared to the 65% M sample.

Figure 5.5: Erosion depth of the samples after every 100 hour duration measured with the surface profilometer
Figure 5.6: Erosion depth of all the samples at the end of 500 h duration measured with the profilometer (bars: mean, brackets: standard deviation)
Chapter 6: DEGRADATION MODEL

6.1 Introduction

A theoretical model is developed which explains the degradation occurring in the samples when exposed to corona. The model is based on Dijkstra’s algorithm to find the shortest path through the sample in the presence of fillers in them. The model uses Dijkstra’s shortest path algorithm to calculate the degradation path for different concentrations of micro and nano-fillers in the sample [65]. Dijkstra’s algorithm is a graph search algorithm that solves the single-source shortest path problem for a graph with nonnegative edges, producing a shortest path [66].

Figure 6.1 shows a schematic of a sample containing fillers in them. P. Maity et.al [64] has shown that erosion patterns in the filled samples happen in two stages.

![Figure 6.1: Schematic of a filled sample](image)

In stage-I, the epoxy resin present between nano particles starts to erode, and degradation channels are formed. With further exposure to discharge, the channels get deeper and wider; however growth of the channel in any direction is restricted due to a
filler particle. So channels are contained in the inter-particle regions. Paths of erosion in filled samples are zigzag as they avoid the filler particles. Possible erosion patterns include: propagation through the base resin or through the interfaces between the particle and the resin. Addition of nano fillers would create an obstruction to degradation as the nano fillers are more discharge resistant as compared to the resin. Figure 6.2 shows an erosion pattern in a filled sample.

![Figure 6.2: Stage- I: Erosion occurring through the base resin](image)

Further, as the channel grows deeper, nano particles emerge from the volume of the material, and degradation is arrested. The second stage involves some of the particles sitting on top of the sample being displaced which can result in the emergence of new fillers. Figure 6.3 shows a schematic of Stage- II of the filled sample.
A degradation model, based on stage-I, is developed in this section. The model tries to map the path of erosion from the top surface of the sample to the ground end through the material. This erosion path would be longer in case of a well-dispersed filled sample as it moves in a zigzag fashion by avoiding the filler particles.

The model formulates a matrix of 100 rows and 100 columns with each cell in the matrix equal to 100 nm. The matrix consists of 1’s and 0’s only. The 1’s denote the filler particles while the 0’s denote the base resin. A nano-sized particle is denoted by one cell containing a 1 (a particle size of 100 nm) while a micro-sized particle is denoted by 400 cells containing 1’s (particle size of 2 µm). A longer erosion path in the model reflects a higher resistance to corona. Figure 6.4 shows the 2D matrix of a 45% M + 5%N sample.
Figure 6.4: A 2D matrix representing 45% M + 5% N sample

6.2 Model Assumptions

The distribution of particles in the matrix is completely random, which means that for the same filler concentrations, one can get different distribution of particles each time the program is run. MATLAB function `randi` is used in order to get random distribution of particles. Once the particle distribution was achieved, a graph search algorithm was used to calculate the shortest path. Different filler concentrations for both the micro-sized fillers and the nano-sized fillers were tested. 100 batch runs for the different filler percentages were carried out.

Some of the assumptions made in the model are:

- Micro particles and nano particles are 2 µm and 100 nm in size respectively, while the actual sample has micro particles of sizes varying from 0.5 µm to 5 µm while nano-particles are about 10-20 nm. For simplicity, the model assumes the particles to be square in shape as they represent a cell in the matrix while the actual nano particles are spherical and micro particles can have different shapes. Since, the internal electric field is not calculated in the samples, the differences in shapes do not affect the results.
• In actual samples, the weight fractions of the filler are given which can be converted to equivalent volume fractions. The model, however being 2D considers the filler fractions in terms of area. For the microfilled samples, the model allows concentrations only up to 50%. This is because uniform sized micro-fillers are filled in the model sample while in actual cases the filler sizes of the micro-filled samples vary.

• The actual samples are believed to have interfacial thickness around the particles [67]. However, no particle interfaces are assumed in the model. Again, since internal electric fields are not calculated, the model results are not affected by the lack of interfaces.

6.2.1 Dijkstra’s Algorithm

Since Dijkstra’s shortest path calculation is a standard algorithm, only the steps of the algorithm are provided in this section.

Steps of the algorithm

1) Let the starting node be called an initial node. Let a distance of a node Y be the distance from the initial node to it. Dijkstra’s algorithm will assign some initial distance values and will try to improve them step-by-step.

2) For current node, consider all its unvisited neighbors and calculate their distance (from the initial node). If this distance is less than the previously recorded distance (infinity in the beginning, zero for the initial node), overwrite the distance.

3) Once all neighbors of the current node are considered, mark it as visited. A visited node will not be checked ever again; its distance recorded now is final and minimal.
4) Set the unvisited node with the smallest distance (from the initial node) as the next “current node” and continue from step 3).

5) With these steps, the shortest path from the starting point to the destination can be effectively achieved. In this case, the shortest distance to all the nodes in the bottom row is achieved from which the shortest distance to the node closest to the initial one is calculated.

6.2.2 Summarizing the code

The entire code was summarized in a flowchart which is an indication of all the steps which were carried out in order to implement the model. The flowchart is shown in Figure 6.5.

Figure 6.5: Flowchart representing the degradation model
6.3 Model Results

Figure 6.6: Model generated 2D matrix representing a 50% micro-filled sample (left) and 100 batch runs of the sample (right)

Figure 6.7: Model generated 2D matrix representing a 5% nano-filled sample (left) and 100 batch runs of the sample (right)

Figure 6.8: Model generated 2D matrix representing a 45% micro and 5% nano-filled sample (left) and 100 batch runs of the sample (right)
The unfilled sample has the shortest path of 9.9 µm. This path is attained when the degradation channel traverses a straight line from the center cell of the top electrode to the ground end. If there are fillers in the sample, then degradation circumvents the particles resulting in longer paths as compared to the unfilled sample. The model helps to calculate the erosion paths for a much wider range of micro and nano-filler concentrations as compared to the range of actual samples that are available.
Figure 6.11: Schematic showing the PD erosion pattern for a 5% nano-filled sample

Figure 6.12: Erosion path of all samples (bars: mean, brackets: standard deviation)
Figures 6.6-6.10 show some of the filler concentrations and their results for 100 batch runs for those concentrations. Figure 6.11 shows a possible erosion pattern for a 5% nano-filled sample.

Figure 6.12 shows the mean and standard deviation of all the different runs conducted. The bars show the mean, while the brackets show the standard deviation of the samples. The micro+ nano samples had the longest erosion path. It can be seen that for the same filler concentration, the nano-filled samples have a longer erosion path as compared to the micro-filled sample. A 15% nano-filled sample has a longer erosion path as compared to a 15% micro-filled sample. The longer erosion path for the nanofilled samples is due to the smaller size of nanofillers (three orders of magnitude smaller than conventional fillers) and small interparticle distances between the fillers.

Table 6.1 shows the correlation between the erosion depth measurements and the degradation model.

**Table 6.1: Correlation between degradation model and corona resistance experiment**

<table>
<thead>
<tr>
<th>Sr. no</th>
<th>Corona resistance experiment results</th>
<th>Degradation Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Unfilled sample had the largest erosion depth</td>
<td>Unfilled sample had the shortest path (“straight line”)</td>
</tr>
<tr>
<td>2</td>
<td>Nano filled samples (2.5% N and 5% N) had smaller erosion depths than unfilled sample</td>
<td>Nanofilled samples had longer short distance paths as compared to the unfilled sample</td>
</tr>
<tr>
<td>3</td>
<td>Micro filled sample had lower erosion depth than the unfilled sample</td>
<td>Microfilled samples had longer erosion paths as compared to the</td>
</tr>
<tr>
<td>4</td>
<td>Micro + nanofilled samples had the lowest erosion depth as compared to the microfilled sample for the same filler concentration (65% M, 62.5% M + 2.5% N and 60% M + 5% N)</td>
<td>Unfilled sample</td>
</tr>
</tbody>
</table>
Chapter 7: THERMAL ANALYSIS AND MODEL

7.1 Introduction

Thermal analysis of epoxy solid dielectrics containing micro and nano particles of silica was done to better understand their electrical discharge endurance. Measurements of thermal conductivity and thermo gravimetric analysis (TGA) were conducted and their results are presented in this chapter. A thermal model to calculate the local temperatures in the samples was developed in section 7.3 using the partial differential equation (PDE) toolbox in MATLAB.

The model emphasizes the importance of well-dispersed nanofillers which improves the local temperature distribution, resulting in higher discharge endurance. This was supported by TGA analysis which showed higher weight loss initiation temperatures for samples containing nanofillers as compared to conventional microcomposites and unfilled samples.

7.2 Thermal conductivity measurements

Microcomposites showed a very high corona resistance (reduced erosion depth) at the end of 500 hours. This is due to the high thermal conductivity and increasing heat dissipation from the sample surface achieved due to the higher concentration of conventional sized fillers. Published literature shows that conventional fillers are filled in the weight fraction from about 40-60% in the samples to attain improved high voltage performance [7, 68].

Samples with just the smaller nano-concentration might not have such high thermal conductivities but still show equivalent erosion performance (5% N). Also, the micro+ nanofilled samples show improvements in the erosion depth values as compared
to their microfilled counterparts for the same combined filler concentration (65%). Thermal conductivity of the samples was calculated using the rule of mixtures and this is shown in Table 7.2 [69]. The calculated value simply depends on the weight fraction of the filler and resin, and becomes higher for samples with increasing filler concentrations. Also, the rule of mixtures does not consider the different sizes of particles. It is important to confirm this with actual thermal conductivity measurement which is done in this section.

7.2.1 Experimental details

Thermal conductivity of the samples was measured according to the ASTM E 1461 at room temperature (25°C) [70]. The measuring instrument used is a NETZSCH LFA 447 nanoflash instrument. The experimental setup is shown in Figure 7.1. The sample is a disk with a diameter of 12.7 mm and a thickness of 1 mm. The samples were coated with a graphite film of 5µm thickness as they do not have a very high emissivity or absorptivity.
Figure 7.1: Experimental setup for the thermal diffusivity measurement using the Laser Flash Method

The sample is aligned in a holder between a reflector assembly and a detector in a furnace. The flash lamp at the base of the reflector assembly is a xenon flash tube with wavelengths close to the infrared (IR) range and approximately 170, 280 and 500 µs pulse widths. The detector is an indium antimonide (InSb) IR detector. The instrument is fully automated and provides value of thermal diffusivity ($\alpha$) and specific heat ($C_p$), from which the thermal conductivity ($k$) of the sample with density $\rho$ is calculated using Equation (7.1)

$$k = \alpha \times \rho \times C_p$$  \hspace{1cm} (7.1)

Once the sample has been stabilized at the desired temperature, the flash lamp is fired several times over few minute durations and the necessary data is recorded for each of those shots. The flash energy strikes and is absorbed by the front surface of the sample,
causing a heat pulse or temperature wave to travel through the sample thickness. The resulting back surface temperature rise is fairly small, ranging from about 0.5ºC to 2ºC. This temperature rise is kept in the optimum range by adjustable filters between the flash lamp and the furnace. The sample lies in the field of view of the IR detector. The temperature rise signal vs. time is amplified and recorded with a high speed A/D converter.

7.2.2 Experimental results

Two samples of each type were used and on each sample, five measurements were obtained. Table 7.1 shows the average of the measurements conducted on the samples. Table 7.2 shows the thermal conductivity determined experimentally as well using a parallel rule of mixture model. It can be seen the calculated values of thermal conductivity shown in Table 7.2 were not significantly different from the experimentally determined values.

Table 7.1: Thermal measurements conducted on the samples

<table>
<thead>
<tr>
<th>Sr. no</th>
<th>Sample</th>
<th>Bulk density (g/cc)</th>
<th>Specific heat Cp (J/g°C)</th>
<th>Diffusivity (mm²/s)</th>
<th>Thermal conductivity (W/m-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0%</td>
<td>1.21</td>
<td>1.35</td>
<td>0.106</td>
<td>0.173</td>
</tr>
<tr>
<td>2</td>
<td>2.5% N</td>
<td>1.22</td>
<td>1.37</td>
<td>0.110</td>
<td>0.184</td>
</tr>
<tr>
<td>3</td>
<td>5% N</td>
<td>1.24</td>
<td>1.27</td>
<td>0.106</td>
<td>0.167</td>
</tr>
<tr>
<td>4</td>
<td>65% M</td>
<td>1.86</td>
<td>0.941</td>
<td>0.519</td>
<td>0.892</td>
</tr>
<tr>
<td>5</td>
<td>62.5% M + 2.5% N</td>
<td>1.90</td>
<td>0.924</td>
<td>0.484</td>
<td>0.933</td>
</tr>
<tr>
<td>6</td>
<td>60% M + 5% N</td>
<td>1.82</td>
<td>0.957</td>
<td>0.557</td>
<td>0.798</td>
</tr>
<tr>
<td>7</td>
<td>65% m + 5% N</td>
<td>1.82</td>
<td>0.907</td>
<td>0.489</td>
<td>0.832</td>
</tr>
</tbody>
</table>
The microfilled and the micro + nanofilled samples had higher thermal conductivity while the nano and the unfilled samples had lower values. There was no significant difference in the thermal conductivity values among the microcomposites and the micro+nanocomposites. The thermal conductivity values of the unfilled and the nanofilled samples were also found to be similar. The experimental results demonstrate that the measured thermal conductivity, which represents an average value, cannot adequately explain the superior electrical discharge endurance characteristics in samples containing nanofillers.

**Table 7.2: Thermal Conductivity Values**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thermal conductivity (W/m-K) (experiment)</th>
<th>Thermal conductivity (W/m-K) (calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>0.168</td>
<td>0.168</td>
</tr>
<tr>
<td>2.5% N</td>
<td>0.173</td>
<td>0.183</td>
</tr>
<tr>
<td>5% N</td>
<td>0.169</td>
<td>0.199</td>
</tr>
<tr>
<td>65% M</td>
<td>0.892</td>
<td>0.781</td>
</tr>
<tr>
<td>62.5% M + 2.5% N</td>
<td>0.933</td>
<td>0.781</td>
</tr>
<tr>
<td>60% M + 5% N</td>
<td>0.798</td>
<td>0.781</td>
</tr>
<tr>
<td>65% M + 5% N</td>
<td>0.832</td>
<td>0.852</td>
</tr>
</tbody>
</table>

Improvements due to addition of nano-fillers arise from their small size, small inter-particle distances and surface area to volume ratio. High surface area to volume ratio or small interparticle distances result in heat being distributed across the entire sample and also reduce the amount of organic material exposed to high temperatures and
thus reduce the erosion depth. For this reason, a thermal model on similar lines as the degradation model was developed and is explained in the next section.

7.3 Thermal Model

7.3.1 Model Concept

A thermal model to calculate the localized temperature of the samples has been developed using the PDE Toolbox in MATLAB. The program uses the finite element method (FEM) to calculate the temperature distribution across the surface [71]. Triangular elements were used to model the surface. The filler particles are modeled with a higher density of triangular elements when compared to the base resin, as shown in Figure 7.2. The distribution and number of these triangular elements are key factors that determine the accuracy of the solution. Generally, the accuracy improves with the number of elements although this might cause an unreasonable increase in the computation time. Therefore, a trade-off between accuracy and computation time is required.

The fundamental equation for calculating temperature on the surface is shown in Equation 7.2, and is derived from Maxwell’s equations.

\[ \rho C_p \frac{\partial T}{\partial t} + \Delta(-k\Delta T) = Q \] (7.2)

The values of the parameters used for the filler and the resin in the thermal model are shown in Table 7.3. All boundaries were set at 300°C. The value of Q used for the calculations was 5 W/cc, and this is based on the laser ablation experiments performed earlier for evaluating the discharge endurance of filled polymer materials [59].
Figure 7.2: Finite Element Method showing the formulation of triangular elements in a nano-filled sample. Figure on the right shows a zoomed in image of a nano-particle highlighting the larger number of triangles inside a particle

Table 7.3: Sample properties

<table>
<thead>
<tr>
<th>Thermal property</th>
<th>Filler (SiO₂) [72]</th>
<th>Base resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (ρ) (g/cc)</td>
<td>2.65</td>
<td>1.2</td>
</tr>
<tr>
<td>Specific heat(Cₚ) (J/ gK)</td>
<td>0.74</td>
<td>1.35</td>
</tr>
<tr>
<td>Thermal conductivity (W/ mK)</td>
<td>1.5</td>
<td>0.168</td>
</tr>
</tbody>
</table>

The nano and microfillers were assumed to be spherical in shape with diameter of 40 nm and 1 µm, respectively. It was also assumed that the interface of the filler with the resin was perfect (no voids). Since the model is two-dimensional, the relative areas occupied by the filler were made to correspond with their weight fractions in the resin matrix.

Nanofillers because of their smaller size occupy a much larger area even at small weight concentrations as compared to conventional micro-fillers. Surface area to volume
ratio is considered to be a major factor in improving the corona resistance of the samples [15]. Considering all the particles as spheres, surface area to volume ratio is calculated as follows:

\[ \frac{S}{V} = \frac{3\rho}{r} \]

(7.3)

From the experimental sample, the 5% (weight fraction) nano-filled sample had a surface area to volume ratio of 15 km²/m³ while that of the 65% (weight fraction) micro-filled sample was 0.24 km²/m³.

The high surface area to volume ratio results in reducing the temperature of the samples locally around the organic material in the samples. Also, higher thermal conductivity of the filler material results in better heat dissipation which keeps the local temperatures low and thus brings about a reduction in the erosion depth of the samples.

7.3.2 Model results

Figures 7.3 and 7.4 show the localized temperatures for a 1% and 2.5% N sample. It can be seen that the filler particles are at a lower temperature than the base resin. Higher filler thermal conductivity results in better heat dissipation and lowers the temperature locally of the sample. Smaller concentrations of nano-filled samples occupy large areas in the base matrix. This is because nano particles are three orders of magnitude smaller than conventional microfillers. So, for the same filler concentration, the number of nano-particles is larger than micro-fillers. Their small inter-particle distance also reduces the amount of organic material available for erosion.
Good dispersion of nanofillers is essential for improved heat dissipation. Nanoparticles have a tendency to agglomerate due to surface energy effects. Figure 7.5 shows the localized temperatures for a material where the fillers are poorly dispersed (agglomerated). Agglomerated particles result in exposing large areas of organic material that can degrade. Thus, the advantage of using nanofillers is lost in such materials.
Hence, great care must be exercised during sample preparation to avoid agglomeration of the particles. It might also explain why it is difficult to make samples with high concentration of nano-fillers that have good dispersion.

Figures 7.6 and 7.7 show the localized temperatures for samples with relative low levels of microfillers (17% and 30%). As will be shown in Table 7.5, the local temperature for such levels of microfillers is higher than for nanofillers. This is because of the low surface area to volume ratio and large inter-particle distances between the particles.

![Figure 7.5: Temperature distribution of a 2.5% N sample (agglomerated)](image)
Figure 7.6: Temperature distribution of a 17% M sample
Figure 7.7: Temperature distribution of a 30% M sample

Figure 7.8 show the temperature distribution of samples containing 50% micro-sized fillers. However, actual micro-filled samples have agglomerated micro-fillers as shown in Figure 1.5. So, the temperature distribution shown in Figure 7.8 for 50% M sample is an over-estimation. The erosion performance of the micro-fillers can be matched by a small concentration of the nanofillers (Figure 5.6), but the exact concentration of the nano-fillers needed to achieve this performance is not known at this point.

The advantages of well-dispersed nanofillers which help to reduce the local temperatures can be significantly achieved if they are sprinkled in between the big micro-sized particles. In conventional microcomposites, as shown in Figure 7.8, the spaces between the fillers are occupied by the base resin, while in micro+nanocomposites; these
spaces are occupied by nanofillers leaving even lesser organic material to be exposed to erosion.

![Temperature distribution of a 50% M sample](image)

**Figure 7.8: Temperature distribution of a 50% M sample**

Figures 7.9 and 7.10 show the temperature distribution of a micro+ nanocomposite sample. The erosion depth is the least for samples containing both micro + nanocomposites as compared to microcomposites for the same total filler concentration could also be due to the improved local temperature distribution due to addition of nanofillers as shown in Figure 5.6.
Figure 7.9: Temperature distribution of a 40% M + 2.5% N sample

Figure 7.10: Temperature distribution of a 40% M + 5% N sample
Polymeric materials containing nanometer (nm) size particles are being introduced to provide compact shapes for low and medium voltage insulation equipment. The nanocomposites may provide superior electrical performance when compared with those available currently, such as lower dielectric losses and increased dielectric strength, tracking and erosion resistance, and surface hydrophobicity. All of the above mentioned benefits can be achieved at a lower filler concentration (< 10%) than conventional microfillers (40-60%). Also, the uniform shapes of nanofillers provide a better electrical stress distribution as compared to irregular shaped microcomposites which can have high internal electric stress, which could be a problem for devices with active electrical parts. Improvement in electrical performance due to addition of nanofillers in an epoxy matrix has been evaluated in this work.

Scanning Electron Microscopy (SEM) was done on the epoxy samples to confirm uniform dispersion of nano-sized fillers as good filler dispersion is essential to realize the above stated benefits. Dielectric spectroscopy experiments were conducted over a wide range of frequencies as a function of temperature to understand the role of space charge and interfaces in these materials. The experiment results demonstrate significant reduction in dielectric losses in samples containing nanofillers. High voltage experiments such as corona resistance tests were conducted over 500 hours to monitor degradation in the samples due to corona. These tests revealed improvements in partial discharge endurance of nanocomposite samples. These improvements could not be adequately explained using a macroscopic quantity such as thermal conductivity. Thermo gravimetric analysis (TGA) showed higher weight loss initiation temperatures for nanofilled samples which is in agreement with the corona resistance experimental results. Theoretical models have also been developed in this work to complement the results of the corona resistance experiment and the TGA analysis. Degradation model was
developed to map the erosion path using Dijkstra’s shortest path algorithm. A thermal model was developed to calculate the localized temperature distribution in the micro and nano-filled samples using the PDE toolbox in MATLAB. Both the models highlight the fact that improvement in nanocomposites is not limited to the filler concentrations that were tested experimentally.

7.3.3 Discussion

The temperature distribution was quantified over a small distance to show the improvements local temperatures due to well dispersed nanofillers. The inter-particle distance between the fillers can be calculated using the Equation 7.2 [73]. The equation is formulated for spherical particles.

\[ l = \frac{1}{3} \left( \frac{\pi \sqrt{2} / 6v}{d} \right)^{3/2} - 1 \]

Table 7.4 contains the calculated inter-particle distances for all the samples. For samples containing micro and nanofillers, the inter-particle distance cannot be calculated because they contain both micro and nanofillers at varying concentrations.

Table 7.4: Interparticle distance calculations for different filler concentrations

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Micro</th>
<th>Nano</th>
<th>Interparticle distance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>0</td>
<td>1094</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>0</td>
<td>703</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>0</td>
<td>456</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>0</td>
<td>280</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td></td>
<td>128</td>
</tr>
<tr>
<td>6</td>
<td>2.5</td>
<td></td>
<td>84</td>
</tr>
</tbody>
</table>
Consider a 1 µm span within any filled sample. Since, the particle diameter and the interparticle distances are known, the number of particles lying within this length can be easily calculated. Figure 7.11 shows a schematic with particles being separated over such a span. Now, the average temperature within this span is calculated depending on the length covered by the particle and that by the interparticle distance. For the micro+ nanofilled samples, although the inter-particle distance cannot be calculated, the average temperature is calculated by combining the inter-particle distances from the respective micro and nanofiller concentrations.

![Schematic](image)

**Figure 7.11: Schematic calculating the temperature over a span of 1 µm**

For example, for a 1% N sample, the interparticle distance was calculated to be 128 nm. So, over a length of 1 um, there would be 6 nano particles approximately of diameter 40 nm and the average temperature is calculated as 264°C. Table 7.5 contains the temperatures for the samples calculated over this distance.
The average temperature of the 1% N and the 2.5% N samples are comparable to the 30% M sample. The 10% N sample has an average temperature equivalent to the 40% M sample. Also, the micro+nano-filled samples have a marginally lower average temperature as compared to the 50% M sample, even though their combined concentrations are lower than 50% (42.5% and 45% respectively).

As mentioned before, the model results of the microcomposites samples are over-estimated because of their good dispersion which doesn’t happen in the actual samples. So, the average temperatures of the samples containing nanofillers will be even better than the numbers that are reflected in Table 7.5. This is also vindicated by the erosion depths and the TGA results of the micro+nanocomposites.

**Table 7.5: Average Temperature over a length of 1 µm**

<table>
<thead>
<tr>
<th>Sr.no</th>
<th>Sample</th>
<th>Length covered by filler</th>
<th>Length covered by the matrix</th>
<th>Average Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0%</td>
<td>-</td>
<td>-</td>
<td>300</td>
</tr>
<tr>
<td>2</td>
<td>20% M</td>
<td>-</td>
<td>1000</td>
<td>300</td>
</tr>
<tr>
<td>3</td>
<td>30% M</td>
<td>297</td>
<td>703</td>
<td>255.4</td>
</tr>
<tr>
<td>4</td>
<td>40% M</td>
<td>544</td>
<td>456</td>
<td>218.4</td>
</tr>
<tr>
<td>5</td>
<td>50% M</td>
<td>720</td>
<td>280</td>
<td>192</td>
</tr>
<tr>
<td>6</td>
<td>1% N</td>
<td>240</td>
<td>760</td>
<td>264</td>
</tr>
<tr>
<td>7</td>
<td>2.5% N</td>
<td>320</td>
<td>680</td>
<td>252</td>
</tr>
<tr>
<td>8</td>
<td>5% N</td>
<td>440</td>
<td>560</td>
<td>234</td>
</tr>
<tr>
<td>9</td>
<td>10% N</td>
<td>520</td>
<td>480</td>
<td>222</td>
</tr>
</tbody>
</table>
Thermo gravimetric analysis

Thermo gravimetric Analysis (TGA) measurements are conducted on unfilled nanofilled, microfilled and micro+nanofilled samples. The TGA monitors the temperature at which weight loss is initiated in the samples. The weight loss plot is shown in Figure 7.12. The TGA measurement system is a Setaram TG92 capable of reaching 1600°C. All the samples had an initial weight of about 25 mg. The mass loss sensitivity is 1 µg. The system uses a helium (He) atmosphere at a flow rate of 30 ml/min. The sample is held in a platinum (Pt) crucible. The ramp rate to temperature was 2°C/m.

The maximum weight loss was observed in 2.5% N sample, although the difference in the weight losses between the 2.5% N and the unfilled sample cannot be considered to be significant. The 5% N sample had a significantly lower weight loss as compared to the 2.5% N and the unfilled sample. This indicates that for very low levels of filler loading there may not be any improvement when compared to the unfilled material [47]. The weight loss pattern of the 65% M sample was better than the 5% N sample, but the micro + nanofilled samples had the lowest weight loss. Also, the temperatures at which the weight loss was initiated for the 65% M sample was not significantly different from the 5% N sample but was significantly lesser than the micro + nanofilled samples. The temperature at which this weight loss was initiated for all the samples is shown in Table 7.6.
Figure 7.12: Weight loss graphs for the different filled and unfilled samples using TGA

Table 7.6: Temperature at which weight loss was initiated

<table>
<thead>
<tr>
<th>Sr. no</th>
<th>Sample Type</th>
<th>Temperature for weight loss initiation (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>65% M</td>
<td>259</td>
</tr>
<tr>
<td>2</td>
<td>62.5% M + 2.5% N</td>
<td>285.5</td>
</tr>
<tr>
<td>3</td>
<td>60% M + 5% N</td>
<td>290</td>
</tr>
<tr>
<td>4</td>
<td>65% M + 5% N</td>
<td>280</td>
</tr>
<tr>
<td>5</td>
<td>5% N</td>
<td>214</td>
</tr>
</tbody>
</table>
The weight loss initiation temperatures seem to be in agreement with the erosion depth of the samples shown in Fig. 5.6. Both TGA and corona measurements show the benefits of adding nano-fillers to the base epoxy resin. Stronger chemical bonding between the nano-fillers and resin is a possibility suggested by the TGA data. Interfaces between the filler and resin could also play a role in improving the discharge endurance, as covalent and ionic bonds, Van der Waals forces, hydrogen bonding could exist between the matrix and filler components. The role of the interface in nanocomposites is still being analyzed by different researchers from around the world [33, 59].

<table>
<thead>
<tr>
<th></th>
<th>2.5% N</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td></td>
<td>85.8</td>
</tr>
<tr>
<td>7</td>
<td>0%</td>
<td>87.6</td>
</tr>
</tbody>
</table>
8.1 Conclusions

1. Nano filled epoxies show superior performance when compared with unfilled and micro filled samples (of the same filler concentration). Significant reduction in dielectric losses ($\tan \delta$) for the micro+ nanofilled samples as compared to microfilled samples due to space charge mitigation because of well-dispersed nanofillers.

2. Uniform filler dispersion is the key to good electrical performance. Scanning electron microscopy results concluded that the nano-fillers in the tested samples were well-dispersed. Quite difficult to achieve in large samples.

3. Mixture of micro and nanofillers can provide improvement in electrical performance when compared with micro fillers only. Degradation measurements of samples containing micro+ nanofillers showed 50% improvement in the erosion performance due to corona as compared to conventional micro composites for the same total filler concentration of 65%.

4. Extensive experimentation required to establish superior performance of nanocomposites. Traditional short term experiments may not be adequate. No significant differences in dielectric strength measurements for the filled and unfilled samples due to a quasi-homogeneous electric field and the short duration of the test. Corona resistance experiments using a rod plane geometry and for duration of 500 hours showed clear distinctions in erosion depths for samples with nanofillers.
5. Macroscopic quantities such as thermal conductivity do not seem to adequately explain improvements in corona resistance and TGA measurements in the nano-filled samples.

6. Significant improvements in spectroscopy, corona resistance, TGA and tensile strength experiments were observed only in the 5% N sample and not in the 2.5% N as compared to the unfilled sample. This showed that 5% by weight of nanofiller is required to get improved electrical, thermal and mechanical properties.

7. Theoretical models have been developed to complement experimental results. Degradation model was developed to map the erosion path, while a thermal model was developed to calculate the localized temperature distribution in the micro and nano-filled samples. Both the models highlight the fact that improvement due to addition of nanofillers is not limited to the filler concentrations that were tested experimentally.

8.2 Future Work

1. Improvements due to addition of nanofillers need to be tested on thicker samples used for inclined plane tracking test. The inclined plane test will help to understand the tracking and erosion performance of the samples.

2. Theoretical calculations and modeling can be done to determine the exact concentration of micro and nanofillers to electrical performance in medium and high voltage equipment.

3. Chemical analysis needs to be conducted to better understand the role of the interface in nanocomposite samples.
REFERENCES


[50] IEC 243-1, Methods of Test for Electrical Strength of Solid Insulating Materials—Part 1: Tests at Power Frequencies,


P. H.F. Morshuis, “Degradation of solid dielectrics due to internal partial discharge: some thoughts on the progress made and where to go now”, IEEE Transactions on Dielectrics and Electrical Insulation, vol. 12, no. 5, October 2005.


IEEE Transactions on Dielectrics and Electrical Insulation, Vol. 12, No. 4, August 2005.


[73] T. Tanaka, M. Kozako, N. Fuse and Y Ohki, “Proposal of a Multi-Core for Polymer Nanocomposite Dielectrics”, IEEE Transactions on Dielectrics and Electrical Insulation, vol. 12, no 4, August 2005.
APPENDIX A: MEASUREMENTS WITH GUARD RINGS
Guard rings are used in spectroscopy measurements to avoid the effect of fringe capacitances on the actual measurement. Figure A.1 shows a schematic of the guard ring setup.

![Figure A.1: Schematic of the guard ring setup](image)

If the upper surface consisted of only the control electrode, fringing fields would exist in the dielectric which would enhance the geometrical capacitance under the electrode. A dielectric determination that ignored fringing effects would result in erroneous measurements. Connecting the guard electrodes to a source at the same potential as the control electrode shifts the fringing field to the edge of the guard ring. Since, the permittivity values associated with the control electrode is measured; the error due to fringe capacitance is eliminated by use of guard rings. The control and guard electrode are maintained electronically at the same potential; this voltage is divided by the current supplied by the control electrode to evaluate the permittivity.

Factors that must be considered while designing guard rings are:

1. Errors in mechanical dimensions;
2. Co-planarity of the guarded electrode and the guard-ring;
3. Eccentricity of the guarded electrode with respect to the guard-ring;
4. Flatness of the guarded and the high voltage electrodes;

5. Parallelism of guarded electrode and the high-voltage electrode;

6. Effect of the width of the gap between the guarded electrode and the guard-ring;

7. Sufficient width of the guard-ring to avoid fringing.

Figure A.2: Imaginary permittivity of 65% M sample with and without guard ring

From the samples tested in this section, a 65% M sample was tested with and without the guard ring. Figure A.2 shows the imaginary permittivity plot of the 65% M sample with and without the guard ring. The top surface of the sample was coated with gold. A circular ring was carved around on the top surface. The ring constituted the sample width between the control and the guard electrode. The gold coating thus formulated control and the guard rings. All the factors mentioned above were taken care of. However, the width of the ring between the guard and the control ring was wider than desired. This is because of the fact that the samples were 1 mm thick, which meant that
the ring needed to be 100 µm wide. The ring that was carved out on the gold coated sample was wider than 100 µm. Spectroscopy measurements were conducted on this sample at room temperature. No difference in the imaginary permittivity of the samples was observed.
APPENDIX B: ANALYSIS FOR SIGNIFICANT DIFFERENCES IN TAN θ VALUES
Samples 2, 3 and 4 (62.5% M + 2.5% N, 60% M + 5% N and 65% M + 5% N) show a significant reduction in the tanδ values as compared to sample 1 (65% M), especially at lower frequencies. This was verified by using Fisher’s Least Significant Difference (LSD) test. Before conducting the LSD test, the normality assumption for the tan delta values (micro, micro+ nanofilled samples upto 0.0316 Hz) was checked using the fat-pencil test and is shown in Figure B.1.

![Figure B.1: Normality plot for log (tan delta)](image)

Fisher’s LSD was carried out on the samples and the results are shown in Figure B.2. Since the p value is very small (0.001), the null hypothesis (all samples have equal tan delta values) is rejected. Pair wise comparison for the different samples was then investigated. The fisher intervals of the samples were checked and they don’t include 0 in their limits which means that the difference between the micro samples and the micro + nano samples is significant.
One-way ANOVA: log(tan) versus nano

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
<th>R = 0.091</th>
</tr>
</thead>
<tbody>
<tr>
<td>nano</td>
<td>2</td>
<td>0.4199</td>
<td>0.2099</td>
<td>6.76</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td>Error</td>
<td>211</td>
<td>6.0678</td>
<td>0.0311</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>222</td>
<td>6.4877</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$S = 0.1762; \ \text{R-sq} = 5.70\%; \ \text{R-sq(adj)} = 4.91\%$

Individual 95% CIs for Mean Based on Pooled StDev

<table>
<thead>
<tr>
<th>Level</th>
<th>N</th>
<th>Mean</th>
<th>StDev</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>61</td>
<td>-0.0228</td>
<td>0.1040</td>
</tr>
<tr>
<td>2.5</td>
<td>54</td>
<td>-0.0129</td>
<td>0.1666</td>
</tr>
<tr>
<td>5.0</td>
<td>117</td>
<td>-0.0346</td>
<td>0.1747</td>
</tr>
</tbody>
</table>

Pooled StDev = 0.1762

Fisher 95% Individual Confidence Intervals

All pairwise comparisons among levels of nano

Simultaneous confidence level = 87.81%

nano = 0.0 subtracted from:

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
<th>Center</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>-0.1234</td>
<td>-0.1452</td>
<td>-0.0081</td>
</tr>
<tr>
<td>5.0</td>
<td>-0.0228</td>
<td>-0.0658</td>
<td>-0.0082</td>
</tr>
</tbody>
</table>

Interval does not include 0

nano = 2.5 subtracted from:

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
<th>Center</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>0.0023</td>
<td>0.0595</td>
<td>0.1166</td>
</tr>
</tbody>
</table>

Interval does not include 0

Figure B. 2: Fisher's LSD test
Figure C.1: a) Weibull Distribution b) Normal Distribution c) Lognormal Distribution

2.5% N
Figure C.2: a) Weibull Distribution b) Normal Distribution c) Lognormal Distribution

5% nano
Figure C. 3: a) Weibull Distribution b) Normal Distribution c) Lognormal Distribution
Figure C.4: a) Weibull Distribution  b) Normal Distribution  c) Lognormal Distribution

62.5% micro and 2.5% nano
Figure C. 5: a) Weibull Distribution b) Normal Distribution c) Lognormal Distribution

60% micro and 5% nano
Figure C.6: a) Weibull Distribution b) Normal Distribution c) Lognormal Distribution

65% micro and 5% nano
Figure C. 7: a) Weibull Distribution b) Normal Distribution c) Lognormal Distribution
APPENDIX D: DEGRADATION MEASUREMENTS AND ERROR CORRECTION
D.1 Degradation Measurement

A surface profilometer and an interferometer were the instruments used to measure the surface degradation of the samples. The profilometer uses a needle to scan the surface and gives the erosion depth. The needle of the profilometer encompasses a length of 2 mm to measure the depth. The interferometer uses a laser beam to scan the area of the sample and gives an erosion depth. While, the profilometer gave localized peaks on the sample surface, one can infer the average degradation depth using the interferometer.

![Graph](image)

**Figure D. 1: Surface degradation of 62.5% M + 2.5% N sample measured after 500 hours. Localized erosion depth: 10 µm**

The area (205 µm × 275 µm) scanned by the interferometer is a smaller than the length encompassed by the profilometer needle. The entire area of degradation in some samples (Unfilled and 2.5 % N sample) is not covered by the interferometer. Hence, all degradation measurements were done using the profilometer. Figure D.1 shows the
degradation on a 62.5% M + 2.5% N sample measured after 500 hours using a profilometer, while Figure D.2 shows the degradation measured using an interferometer.

![Surface degradation of 62.5% M + 2.5% N sample after 500 hours using the interferometer. Average erosion depth: 5 µm](image)

**Figure D.2:** Surface degradation of 62.5% M + 2.5% N sample after 500 hours using the interferometer. Average erosion depth: 5 µm

### D.2 Error Correction

All samples were kept on top of a glass slide (7.5 mm × 5 mm, degradation - 0 µm) and their degradation was measured using the profilometer. Figure D.3 shows the surface degradation of the glass sample measured with a profilometer.

![Surface degradation of the glass slide. Erosion depth: 0 µm](image)

**Figure D.3:** Surface degradation of the glass slide. Erosion depth: 0 µm
Figure D.4: Initial degradation depth of 65% M sample. Average erosion depth: 1.5 μm

The samples were also not perfectly flat, displaying a drift in the reading when the degradation was measured. By measuring the localized depths, the error due to the drift was compensated. Initial roughness of the surface of all samples before exposure to corona was measured in order to get rid of any error in the measurements. For the initial roughness, the average degradation depth of the overall sample was considered. Figure D.4 shows the initial degradation of a 65% M sample before exposing it to corona.
APPENDIX E: DEGRADATION MODEL PSEUDO CODE
This section provides the pseudo code for the model. The entire code is divided into several subroutines. Each subsection is a subroutine which was a part of the entire code. Pseudo codes are provided for each subsection.

E.1 Particle Insertion

This is the main routine. The type of sample is chosen in this section. All the other programs are called in this program. Each program called in this section is run 100 times to get 100 runs of short distances for each type of sample chosen.

Pseudo code
Insert the option of the choice of sample
0. Unfilled sample
1. Microfilled sample
2. Nanofilled sample
3. Micro+nanofilled sample
If choice is Unfilled sample
{}
Perform 100 runs for getting 100 shortest paths
{}
Grid_formulation
Adjacent_matrix_creation
Dijkstra code
{}
If choice is Microfilled sample
{}
Perform 100 runs for getting 100 shortest paths
{}
Grid_formulation
MicroFillingParticles
Adjacent_matrix_creation
Dijkstra code
{}
If choice is Nanofilled sample
{}
Perform 100 runs for getting 100 shortest paths
{}
Grid_formulation
NanoFillingParticles
Adjacent_matrix_creation
Dijkstra code
{
If choice is Microfilled sample
{ Perform 100 runs for getting 100 shortest paths
{ Grid_formulation
   MicroFillingParticles
   NanoFillingParticles
   Adjacent_matrix_creation
   Dijkstra code
   }
}

E.1.1 Grid Formulation

This is the first called function in the main routine. As, the name suggests the program formulates the grid and initializes the original matrix with 0’s.

Pseudo code
Initialize matrix length- 10 µm
Calculate the area of the square- 10 µm × 10 µm
Initialize cell size- 10 nm
Calculate cell area- 10 nm × 10 nm
Formulate a 100 × 100 matrix with each cell of 10 nm size.
Initialize the formulated matrix with 0’s.

E.1.2 Microfillingparticles

This routine is used for inserting micro-sized particles in the grid. As mentioned earlier, the micro-sized particles used in the model are 2 µm in size. The filler particles are denoted by 1’s in the matrix.

Pseudo code
Initialize micro-sized particle size as 2 µm
Calculate the area of a micro-particle: 2 µm × 2 µm
Initialize the filler concentration of the micro-filler
Calculate the number of particles which cover the entire matrix
Calculate the number of cells filled with 1’s to calculate the entire area
Calculate the number of rows (rspP) and columns (cspP) needed to be filled with 1’s for one micro particle (each cell is 100 nm)

For loop = 1: number of particles
{ Row and column position to insert the micro-filled particle.
Position decided using \textit{randi} function

Initialize while loop for particle overlapping
{
    If particles don’t overlap
    {
        For loop = 1: rspP
        {
            For loop= 1: cspP
            {
                Fill all the cell positions with 1’s
            }
        }
    }
    If particles overlap
    {
        Choose new row and column positions to insert the micro-filled particle.
        Position decided using \textit{randi} function
    }
}

\textbf{E.1 3 Nanofilling particles}

This routine is used for inserting nano-sized particles in the grid. As mentioned earlier, the nano-sized particles used in the model are 100 nm in size. The filler particles are denoted by 1’s in the matrix.

\textit{Pseudo code}

Initialize nano-sized particle size as 100 nm
Calculate the area of a micro-particle: 2 µm × 2 µm
Initialize the filler concentration of the micro-filler
Calculate the number of particles which cover the entire matrix
Calculate the number of cells filled with 1’s to calculate the entire area

For loop = 1: number of particles
{
    Row and column position to insert the nano-filled particle.
    Position decided using \textit{randi} function
}

Initialize while loop for particle overlapping
{
    If particles don’t overlap
    {
        Fill the cell positions with 1’s
    }
}
If particles overlap
{
    Choose new row and column positions to insert the nanofilled particle.
    Position decided using \texttt{randi} function
}

E.1.4 \textit{AdjacentMatrixFormulation}

Adjacent matrix is formulated to assign weights to all the connecting cells in the
original matrix only if the cells are filled with the base resin (i.e. contain 0).

\textit{Pseudo code}

Initialize adjacent matrix which is a square matrix to the original grid

For loop=1: number of rows in the grid
{
    For loop=1: number of columns in the grid
    {
        If an element in the matrix is the base resin
        {
            Assign all its diagonal elements with weights = $\sqrt{2}$
            provided they are also the base resin
            Assign all the other elements with weights = 1 provided
            they are also the base resin
        }
    }
}
APPENDIX F: SUBMITTED AND PUBLISHED PAPERS
Evaluation of Epoxy based Nanodielectrics for High Voltage Outdoor Insulation

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School of Electrical, Computer and Energy Engineering¹
Department of Chemistry²
¹Arizona State University, USA
²ABB Corporate Research, Switzerland

Abstract- Nano and micro based epoxy samples have been evaluated for predicting their electrical performance in outdoor high voltage insulation application. Scanning electron microscopy (SEM) is used to evaluate the shape and the dispersion of the filler material. Space charge characterization and the role of the interface in these materials is evaluated using dielectric spectroscopy on these samples. The results of dielectric spectroscopy reveal the potential of improved electrical performance in terms of dielectric strength and tracking and erosion performance of the nano-filled samples as compared to the micro-filled counterparts. The uniform filler dispersion and the low loss tangent values have been used to theorize the improvement that can be expected from nano-composites in the field of outdoor insulation.

I. INTRODUCTION

The use of inorganic fillers like aluminum nitride (AlN), silica etc. in polymeric insulation materials has been done for many years. Addition of these fillers in the polymer formulation reduces cost, improves resistance to dry band aging and also improves mechanical properties. The fillers added in all these samples are micro-sized fillers with sizes in the range of 50-100 µm. Extensive research has been conducted to study the influence of filler size, concentration and type on the aging performance of epoxy insulators and other outdoor equipment [1]. However, the addition of these micro-sized fillers into a polymer rarely improves the electrical breakdown strength of the system. In fact, pointed edges (Figure 1), high aspect ratios and agglomeration of micro-fillers (Figure 2) increases localized electrical stresses in these samples which can result in reduced breakdown voltage [2].

Reduction of the size of the filler particles into the nano range can overcome such problems and influence combinations of properties in a complex and often non-intuitive manner. Over the last few years, the use of nano-sized particles has shown a lot of promise.

Fig. 1: Sample with different shapes of micro-filler

Fig. 2: Sample showing agglomeration of micro-filler

Electrical apparatus using nanocomposites can provide improved performance when compared with conventional micro-filled materials, like superior dielectric strength, tracking and erosion resistance, and surface hydrophobicity. Such improvements can be achieved without any increase, and possibly even with a reduction, in size. This can create apparatus that are more compact and last longer than what is available presently [3, 4]. However, it is not easy to prepare samples containing nano-sized fillers. The nano-fillers when added to the base resin have a tendency to agglomerate and form large clusters which then would be no different from micro-filled samples. So, it is important to ensure uniform dispersion of the nano-fillers in order to avoid such cluster formations. Hence, it is essential to analyze their bulk properties like permittivity, conductivity, dielectric strength etc. to understand the distinct advantages that the nano-fillers provide over their micro-filled counterparts.

II. SAMPLES EVALUATED

The different samples that were evaluated are listed in Table 1. The base resin used was epoxy and silica was used as filler, with their concentrations varied over a range. The samples
were post cured for approx 20 hours at 160°C. The samples (75 mm x 3 mm x 1 mm) were prepared by ABB Corporate Research.

<table>
<thead>
<tr>
<th>Table I: Samples Evaluated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Number</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
</tbody>
</table>

III. Scanning Electron Microscopy

Scanning Electron Microscopy was performed on the samples to check the dispersion of the filler material in the samples. The samples were cut into small pieces and were mounted on a stub. A thin coating (20 nm) of platinum was deposited on the surface and then a gold layer was used to bond the material therewithout revealing the fillers and their dispersion in the matrix. The platinum coating was done to protect the surface from damage while cutting into the sample. Figure 3 shows the SEM picture of a nano-filled sample. The average size of the nano-filler was observed to be around 10-20 nm. Energy dispersive X-ray analysis (EDAX) was carried out at different locations on the surface confirming the filler to be silica.

IV. Dielectric Spectroscopy

A. Experimental Setup

Dielectric spectroscopy is a measurement of the real and imaginary permittivity, from a low frequency (1 MHz) to relatively high frequency (1 MHz), as a function of temperature. The technique enables assessments on the samples of interfacial polarization and conduction processes (low frequency) and of dipole polarization effects (high frequency). The former can be related to the matrix-filler surface, while the latter gives information as to how the bulk polymer is being affected [1, 2]. This technique can be used to compare the performance of nano-materials with the base resin and their micro-filled counterparts and could also help in determining the filler types and filler concentrations needed to optimize their outdoor performance.

The setup involves a Solartron 1250 impedance analyzer, Novocontrol Quatro temperature controller and a sample holder. Two electrodes (20 mm and 10 mm in diameter) were used for the measurements. The sample was sandwiched between the electrodes. Before the measurements were done, a Teflon sheet with the same dimensions as the sample was run in the setup so as to get a reference measurement (Teflon has a frequency invariant relative permittivity of 2). All the samples were measured using the same reference measurement.

A voltage of 50 V was applied to these samples and their permittivity values were measured over a frequency range of 1 MHz to 1 mHz. Different samples of 25 mm x 5 mm from each sheet of sample were cut and their real and imaginary permittivity values were measured. The sample measurements were carried out at different temperatures: 253 K, 293 K, 333 K and 393 K. The different temperature ranges were attained by using liquid nitrogen for cooling down the samples to those low temperatures.

B. Experimental Results and Discussion

The dielectric properties of heterogeneous systems cannot be described by the sum of those of the individual components since one of the components may adopt a structure not realizable in the bulk. The dielectric response in heterogeneous systems can contain contributions from permanent dipoles as well as mobile charge carriers, ions and electrons. The motion of carriers in condensed media is a cooperative phenomena and consequently, if the heterogeneity of the material constraints coherent displacement of charge, large dielectric permittivities may be observed at low frequencies [4]. Different theories like the Logarithmic-Brilson rule, Maxwell Wagner Sillars theory, and Maxwell Wagner Garnett theory [7] have been proposed for theoretically calculating the real and imaginary permittivity values which can be compared to the measured values. But these theories do not take into account the possible change of matrix properties at the interface. Hence, variations were observed in the measured and the calculated values of real and imaginary permittivities.

Figures 4 and 5 show the real and imaginary permittivity plots of the different samples measured at room temperature. Sample 5 has lower real and imaginary permittivity values as compared to all the other micro-filled samples. The effectiveness of nano-filled samples over their micro-filled counterparts is due to their high surface area to volume ratio which results in large interfacial areas of nano-composites as compared to the micro-composites. This large interfacial zone
can have a major impact on the bulk properties of nano-composite material as compared to micro-composite materials [1]. Also, uniform dispersion of the nano-fillers leads to the formation of charge traps on the samples, which will be explained in detail later.

![Image](image1.png)

Figure 4: Real permittivity plots at room temperature

The high real and imaginary permittivity values of the micro-fillers could be due to the presence of interfacial polarization in the micro-fillers as the base matrix in all the samples is the same. The micro-composite samples act as charge defects in the bulk material resulting in the formation of space charge builds up which lead to interfacial polarization. Built up space charges from charge carriers which cover distances in the bulk matrix resulting in charge of sample properties like imaginary permittivity. Samples 2, 3 and 4 consists nano-fillers as well, but the high percentage of micro-fillers in these samples seems to dominate the performance of these samples which is reflected in their real and imaginary permittivity plots at room temperature.

Interfacial polarization occurs because of space charge build-up occurring at the interfaces between the base matrix and the filler [9,10]. When an electric field of high frequency is applied, the probability of these space charges to drift and accumulate at polymer-nano particle interfaces become highly probable as well. Also, a large time lag for charge carriers of most of these space charges makes it even more difficult for them to drift at high frequencies. Usually, occurrences of interfacial polarization are observed at low frequencies of dielectric measurements. This is due to the macroscopic distances between the different microscopic fillers. Since interfacial phenomenon is an additional polarization mechanism apart from ionic, electronic, and dipolar mechanisms, their occurrence in a system is usually associated with distinct variations in the trends of real and imaginary permittivity with respect to frequency, especially at high filler concentration [11,12,13].

The nano-sized fillers mitigate space charge buildup due to their uniform dispersion as can be seen in Fig. 5 in the frequency range from 0.2 Hz-56 kHz. The presence of these fillers results in the formation of traps in the interface and also in scattering of charge carriers which gives them lower real and imaginary permittivity values. The imaginary permittivity plot at 333 K highlights the difference between the micro-filled and the nano-filled samples. The presence of charge traps in the nano-sample can be seen in the in the samples at medium frequency range (0.01 Hz-1 kHz). In the lower frequency range (1μHz-0.1 Hz), the nano-filled sample and the micro-sample have the same imaginary permittivity value. This could be because of the release of the charges from these charge traps which results in a higher imaginary permittivity value [14, 15].

![Image](image2.png)

Fig. 5: Imaginary permittivity plots for 0.1 Hz to 1 MHz

The imaginary permittivity plots at 333K are shown in Fig. 7. Low temperature high frequency plots of the micro and the nano samples demonstrate β relaxations which have been observed in other samples containing epoxy as well as well. The relaxation phenomenon in the nano-composite occurs at a lower frequency and is sharper as compared to the micro-sample. In sample 1, there is a phase shift in the relaxation process and it is also over-run by interfacial polarization at the lower frequencies making the β relaxation difficult to observe.
This demonstrates that these high frequency relaxations are a characteristic of the epoxy resin and not the filler characteristic [12].

The cluster model of Dissado and Hill provides an intuitively appealing mechanism for the LFD response [16]. A heterogeneous macroscopic sample may be considered as an array of “clusters.” Clusters are not physically isolated but are characterized by a correlation length scale, $L_c$, over which the structural regularity of the cluster is overridden. In the absence of an applied field the cluster array will be neutral and unpolarized. An applied field will polarize the system usually by the hopping tunneling of ions to sites at a lower potential. Ion hopping over a range less than $L_c$ constitutes a displacement of charge within the cluster which thereby becomes a polarized entity. At $\omega_L$ there is a continuous crossover from intra-cluster hopping at higher frequencies to intercluster hopping at lower frequencies. When $\omega < \omega_L$ incoherent transfer of charge between clusters allows charge separation to occur over ranges greater than the characteristic cluster length $L_c$, leading to large polarizability and hence the observed high permittivity.

The high temperature plots for the samples shown in Fig 8, demonstrated the presence of low frequency dispersion (LFD) in the samples. LFD responses show large variations observed in the real permittivity plots and the slope of the real and imaginary permittivities are proportional to the same powers of frequencies beyond the cross-over frequency ($\omega_L$). In Fig. 8, the real and imaginary permittivity plots of both the micro and the nano sample intersect at a particular frequency (cross-over frequency, $\omega_L$), beyond which there is a change in the slope of the real permittivity values. This response seen in the samples is the “Quasi-DC” (QDC) behavior explained by Dissado and Hill [16] or the “low frequency dispersion” (LFD) responses mentioned by A.K. Jonscher [4]. Low frequency dispersion is due to the presence of inter-cluster and intra-cluster charge transport in the samples.

At higher frequencies, the motion of the charge carriers is localized (intra-cluster) while at low frequencies and high temperature, the charge carrier motion is between different clusters (inter-cluster) as they gain sufficient energies. The low frequency dispersion behavior is different from dc conductivity as in this case the real permittivity values increase with decrease in frequency unlike dc conductivity in which the real permittivity is independent of frequency.

The variations in the real permittivity values are very small as can be seen from Figures 5 and 6. So, there is an inclination to believe that the real permittivity plot are independent of frequency which is probably due to the presence of dc conductivity. However for dc conductivity, the imaginary permittivity value is given by,

$$\varepsilon'' = \frac{\Delta \varepsilon}{\omega}$$

Since, $\Delta \varepsilon$ is a constant, the imaginary permittivity is inversely proportional to the frequency. Hence, the slope of the imaginary permittivity curves in these samples should be
equal to (1), which is not observed in any of these imaginary permittivity plots. Also, the minor variations in the real permittivity plots were consistent throughout all the sample measurements and cannot be attributed to experimental error. So, any possibility of detectable dc conductivity on these samples is ruled out.

V. CONVENTIONAL MICRO-FILLED EPOXY SAMPLE

Flat slabs of the epoxy filled with 33% micro-filled silica (HCEP) samples used for medium voltage outdoor equipment were machined down to 1mm thickness. Real and imaginary permittivity measurements for the same frequency range (1MHz to 1MHz) at room temperature were carried out for these samples. The imaginary permittivity plots of the hydrophobic cyclosiloxane (HCEP) samples along with sample 5 (5% nano) is shown in Fig. 9.

![Imaginary permittivity plot for HCEP sample and sample 5 at room temperature](image)

The imaginary permittivity plot of the HCEP sample follows the trend of the different micro-composite samples (sample 1-4) measured before. The nano-sample shows lower imaginary permittivity values as compared to the HCEP sample which could be an indication towards the expected improved performance of these nano-filled samples in outdoor performance.

VI. CONCLUSION

The presence of the nano-fillers mitigates space charge build-up in the samples which is reflected in the dielectric permittivity plots. The SEM pictures reveal a good dispersion of these nano-fillers which along with the low losses demonstrated in the permittivity plots point towards an improved breakdown and insulation performance of the nano-composites. There is a considerable difference in the performance of the material containing nano-fillers as compared to the samples containing micro-fillers. Dielectric spectroscopy results of the different micro- and nano-composites and the HCEP sample indicates towards an improved outdoor performance of the nano-filled samples.

Further tests on breakdown, tracking and erosion performance, partial discharge resistance would be done to analyze the improvements in the nano-filled material as compared to the micro-filled samples.

ACKNOWLEDGMENT

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REFERENCES

Dielectric Properties of Epoxy based Nanocomposites for High Voltage Insulation

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ABSTRACT

Epoxy polymer with micro, nano and micro + nano silica fillers have been evaluated for their electrical performance in high voltage insulation applications. The dielectric strength of these samples was measured in accordance with the ASTM D-149 standard. Dielectric spectroscopy was used to understand the role of space charge and interfaces in these materials. The results of dielectric spectroscopy suggest that significant improvement in the electrical performance can be expected by using samples containing nanofillers and micro + nanofillers compared to materials containing only microfillers. However, the dielectric strength measurement showed no statistically significant improvement for the nanofilled samples. Techniques other than dielectric breakdown may be required to adequately characterize differences in the electrical performance of the dielectrics. For example, a partial discharge test using a highly non-uniform field may be more useful as it would correspond to simulate actual service conditions.

INDEX TERMS — Epoxy nanocomposites, nanofillers, nanodielectrics, microcomposites, permittivity, loss tangent, dielectric strength, breakdown.

1 INTRODUCTION

CYCLOALIPHATIC epoxy resins have been used for indoor, outdoor and enclosed apparatus. They are mainly used for low and medium voltage (LV and MV) applications such as pin and post type insulators, bushings, instrument transformers for current and voltage measurement, bus support assemblies, switching and protection equipment applications [1, 2, 3]. They were first introduced in the 1950’s and their formulations and manufacturing processes have evolved continuously to the present state where high quality products can be cost economically. They have several advantages over porcelain such as light weight, easy to mold into complicated shapes, superior impact and seismic resistance. They also have the advantage that the same material (epoxy) fulfills the electrical and mechanical functions. Thus, interfacial issues that are common due to the origin of problems in devices that employ different materials like in composite insulators (fiber glass core and elastomer housing) are eliminated. Epoxy insulated devices also eliminate oil and problems associated with leakage and maintenance.

The use of inorganic fillers such as silica, alumina, etc., in polymeric materials has been done for many years. Addition of these fillers in the formulation reduces cost, improves fire resistance and mechanical properties like tensile strength. For outdoor applications, they enhance resistance to dry band arcing and surface discharges. The size of the fillers is in the range of 1-100 nm. Extensive research has been conducted to study the influence of micro-sized fillers on the electrical performance of epoxy materials for HV equipment [3, 4, 5, 6].

Over the last few years, there has been increased interest in the use of micro-sized fillers as additives in polymer materials (nanocomposites) [1, 2, 7]. Electrical insulation using nanocomposites may provide superior performance when compared with conventional microfillled materials, such as lower dielectric losses and increased dielectric strength, tracking and erosion resistance, and surface hydrophobicity [8-10]. Such improvements can create apparatus that are more compact and last longer than what is available presently. Conflicting results on the performance of nanocomposite fillers have been reported and the underlying mechanisms are not adequately understood [11-14]. This is due to the fact that it is not easy to prepare samples containing nano-sized fillers. Uniform dispersion of the nanofillers in the polymer matrix is essential to realize the above stated benefits. For all of the above mentioned reasons, experiments were conducted on epoxy samples containing different concentrations of nano and micro-sized fillers.
2 SAMPLES EVALUATED

The samples that were evaluated are listed in Table 1. They were prepared by ABB Corporate Research, Switzerland. The samples were in the form of flat sheets of dimensions 75 mm × 75 mm × 1 mm thick. Anhydride curing cycloaliphatic epoxy resin system was used as the base. The micro-sized silica filler was irregularly shaped, spongy silane treated and of an average size of 16 μm. The filler was dried overnight at 80 °C before casting. Nano-sized silica filler was of spherical shape with a diameter of about 20 nm and was supplied as a 40% wt master-batch by Nanorims AG, Germany. Standard mixing, degassing, casting, curing and post-curing procedures were used to manufacture the samples. Prior to any testing at Arizona State University, the samples were heated in an oven for 20 hours at 160°C to remove the absorbed moisture from the samples. It should be noted that even longer times (several days) may be needed to remove the excess moisture in some samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Filler Composition (wt%)</th>
<th>Identification in Fig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>65% Micro</td>
<td>6.5 N</td>
</tr>
<tr>
<td>2</td>
<td>62.5% Micro + 2.5% Nano</td>
<td>62.5% N + 25% N</td>
</tr>
<tr>
<td>3</td>
<td>60% Micro + 5% Nano</td>
<td>60% N + 5% N</td>
</tr>
<tr>
<td>4</td>
<td>65% Micro + 5% Nano</td>
<td>65% N + 5% N</td>
</tr>
<tr>
<td>5</td>
<td>3% Nano</td>
<td>3% N</td>
</tr>
<tr>
<td>6</td>
<td>9% (Grinded)</td>
<td>9%</td>
</tr>
<tr>
<td>7</td>
<td>2.5% Nano</td>
<td>2.5% N</td>
</tr>
</tbody>
</table>

3 SCANNING ELECTRON MICROSCOPY (SEM)

Scanning Electron Microscopy was performed to check the dispersion of the filler material. The samples were cut into small pieces and mounted on a stub. A thin coating (20 μm × 1 μm × 1 μm) of platinum was deposited on the surface. The platinum coating was done to protect the surface from damage while cutting into the sample. A gallium ion beam was used to etch into the material thereby revealing the fillers and their dispersion in the matrix. Figure 1 shows the micro-sized fillers of different shapes. Energy dispersive X-ray analysis (EDAX) was carried out at different locations on the surface confirming the filler to be silica.

![Figure 1: Sample with different shapes of microfillers. Epoxy-epoxy with 65% micro-sized silica filler.](image1)

![Figure 2: Sample containing agglomerated nano-sized silica fillers (10% nano). This sample was manufactured from a different kind of epoxy than all the other samples evaluated.](image2)

![Figure 3: Sample showing uniformly dispersed nanofillers. Epoxy-epoxy with 65% micro-sized silica fillers and 3% nano-sized silica fillers.](image3)

Samples containing nanofillers are not easy to prepare as they have a tendency to agglomerate and form large clusters as shown in Figure 2. So, it is important to ensure uniform dispersion of the nanofillers in order to avoid such cluster formulation. This problem can be solved by using liquid dispersion (master-batches) provided by nanofiller suppliers. Figure 3 shows a picture of a well dispersed nanofilled sample. All the samples that are reported in this
paper had well dispersed nanofillers. To understand the advantages that the nanofillers may provide over their microfilled counterparts, it is essential to analyze their properties such as dielectric permittivity and strength, electric and thermal conductivity and mechanical properties of these materials.

4 AC BREAKDOWN TEST

4.1 EXPERIMENTAL DETAILS

To assess the dielectric breakdown strength, testing was conducted in accordance with ASTM D149 using the setup shown in Figure 4. The samples used were sheets of dimensions 25 mm × 25 mm × 1 mm. The electrodes were stainless steel spheres of 10 mm diameter. The test apparatus was immersed in transformer oil to avoid surface flashover. The power supply was a 10 kVA, 69 kV/120 V transformer.

The voltage applied was increased at a rate of 1 kV/s until breakdown. Measurements were made at the high voltage side using a resistance voltage divider. The oil was stirred after every breakdown measurement and replaced after every 10 measurements to avoid degradation. Also, the electrodes were cleaned after every measurement and replaced after 10 measurements.

![Figure 4: Schematic for breakdown experiment](image)

4.2 RESULTS

The breakdown data was plotted using different distributions such as the Normal Distribution, Lognormal Distribution and the Weibull Distribution. The data points in all three distributions were within the 95% confidence interval limits. However, Weibull Distribution was chosen as it is commonly used for breakdowns in nanodielectrics [11, 13]. The Weibull distribution plot of the micro and the micro/nanofilled samples are shown in Figure 5. Figure 5 shows the same data for the unfilled and nanofilled samples. Table 1 shows the scale and shape parameters for all the samples [15]. Although a small difference can be seen in the shape and scale parameters of the different samples (Table 2), these differences were not found to be statistically significant. The replicate measurements were done for each sample type.

![Figure 5: Weibull distribution plot (95% confidence interval) for the microfilled and nanofilled samples](image)

![Figure 6: Weibull distribution plot (95% confidence interval) for the unfilled and nanofilled samples](image)

<table>
<thead>
<tr>
<th>Filled details</th>
<th>Scale parameter (kV/mm)</th>
<th>Shape parameter (β)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unfilled (0%)</td>
<td>36 36</td>
<td>6.974</td>
</tr>
<tr>
<td>2.5% nano</td>
<td>37 07</td>
<td>10.98</td>
</tr>
<tr>
<td>5% nano</td>
<td>36 59</td>
<td>10.22</td>
</tr>
<tr>
<td>65% micro</td>
<td>34 01</td>
<td>12.13</td>
</tr>
<tr>
<td>62.5% micro+2.5% nano</td>
<td>33 87</td>
<td>8.218</td>
</tr>
<tr>
<td>60% micro+5% nano</td>
<td>36 37</td>
<td>7.229</td>
</tr>
<tr>
<td>65% micro+5% nano</td>
<td>35 25</td>
<td>6.945</td>
</tr>
</tbody>
</table>
5 DIELECTRIC SPECTROSCOPY

5.1 EXPERIMENTAL SET-UP

Dielectric spectroscopy is a technique for real and imaginary permittivity measurements, over a frequency range (e.g. 1 mHz - 1 MHz), as a function of temperature [16]. Variations in temperature move the curves on the frequency scale, e.g. increasing temperature slides the curves to the left on the frequency scale. By doing temperature variations, one is able to attain permittivity values over a much wider range. Reference to interfacial polarization and conduction processes (low frequency) and of dipole polarization effects (high frequency) can be made from real and imaginary permittivity values. Interfacial polarization can be related to the matrix-filler surface, while dipole polarization gives information as to how the bulk polymer is being affected [17, 18]. This technique is used in the paper to compare the electrical performance of nanofilled materials with the base resin and their microfilled counterparts.

The setup involves a Solartron 1260 impedance analyzer, a Novocontrol Quatro temperature controller and a sample holder. No difference was observed in the sample measurements, when done with and without using guard rings [19]. A voltage of 50 V was applied to the samples and their permittivity values were measured over a frequency range of 1 mHz to 50 kHz.

As a benchmark, a Teflon sheet with the same dimensions as the sample was run in the setup. Teflon has a frequency-invariant relative permittivity of 2.04 [20]. All the samples were measured using the same reference measurement.

5.2 RESULTS

The dielectric response in heterogeneous systems can contain contributions from permanent dipoles as well as mobile charge carriers namely, ions and electrons. In heterogeneous materials, the inclusion of non-conducting filler materials can restrict the overall motion of carriers. This can lead to large dielectric permittivities observed at low frequencies [6]. Different theories like the Logarithmic-Rachcker rule, Maxwell-Wagner-Sillars theory, and Maxwell-Wagner-Garnett theory have been proposed for calculating the real and imaginary permittivity values [21]. For example, using the Logarithmic-Rachcker rule, the real permittivity of the 65% microfilled sample was calculated to be 3.68 at room temperature at 1 mHz. The Logarithmic-Rachcker rule is given by equation (1) as:

\[
\log \varepsilon_\alpha = y_1 \log \varepsilon_1 + y_2 \log \varepsilon_2
\]

(1)

In equation (1), \(y_1\) and \(y_2\) are the volume fractions, while \(\varepsilon_1\) and \(\varepsilon_2\) are the permittivities of the base resin and the filler respectively, while \(\varepsilon_\alpha\) is the permittivity of the composite. The measured value was 4.75, which is significantly different from the calculated value. This is because the calculations do not take into account the filler shape, size and the possible change of matrix properties at the interface. So, it becomes imperative to measure the permittivity values to see the impact of the fillers on the overall matrix.

5.2.1 ROOM TEMPERATURE MEASUREMENTS

Figures 7 and 8 show the real permittivity and the tan\(\delta\) plots of the different samples. The introduction of inorganic fillers having a permittivity value higher than the base polymer increases the effective permittivity of the composite material [16]. The real permittivity and the tan\(\delta\) plots show that there is a significant difference in the measured values of the unfilled and nanofilled samples when compared with the micro and micro + nanofilled samples. The lower values of permittivity and tan\(\delta\) of nanofilled samples over microfilled samples, is due to their high surface-area to volume ratio which results in large interfacial areas of nanocomposites as compared to the microcomposites. This large interaction zone can have a major impact on the permittivity values of nanocomposite materials as compared to microcomposite materials [22]. The interaction between the silica nanofillers and the polymer chains results in reduced mobility and thus a higher surface area of the nanofillers would result in a reduction in the overall permittivity of the samples.

![Figure 7. Real permittivity plots for studied epoxy samples at room temperature.](image-url)

![Figure 8. Tan\(\delta\) plots for studied epoxy samples at room temperature.](image-url)
The high real and imaginary permittivity values of the microfillers could be due to the presence of interfacial polarization due to microfillers as the base matrix in all the samples is the same. The microfillers act as charge defects in the bulk material resulting in space charge formation which leads to interfacial polarization [23, 24]. When an electric field of high frequency is applied, the probability of these space charges to drift and accumulate at polymer-nano particle interfaces becomes very small. This is because the charges have low mobility and their mean displacement is much smaller than the typical nano-particle size for small time durations (i.e. high frequencies: 1 kHz-50 kHz). This means that there is a certain time delay (from the time the electric field is applied) before the charge can reorient to move. Usually, occurrences of interfacial polarizations are observed at low frequencies of dielectric measurement. This is due to the mesoscopic distances between the different microscopic fillers i.e. distances intermediate between molecular and macroscopic lengths. Since interfacial phenomena is an additional polarization mechanism apart from ion, electronic and dipolar mechanisms, their occurrence in a system is usually associated with distinct variations in the trends of real and imaginary permittivity with respect to frequency, especially at high filler concentrations [25, 26].

![Graph](image)

Figure 9. Imaginary permittivity plots for studied epoxy samples at room temperature.

The variations in the real permittivity values may be independent of frequency, which could be due to the presence of dc conductivity, as has been seen from Figures 7 and 10. However, for dc conductivity, the imaginary permittivity value is given by:

$$
\varepsilon'' = \varepsilon_{\infty} \left( \frac{\varepsilon - \varepsilon_{\infty}}{\varepsilon_{\infty}} \right)
$$

Since, $\varepsilon_{\infty}$ is a constant, the imaginary permittivity is inversely proportional to the frequency. However, if dc conductivity was present in these samples, the slope of the imaginary permittivity curves would be -1 on a log-log plot.

Since this is not observed, any possibility of detectable dc conductivity on these samples can be ruled out. Figure 9 shows the imaginary permittivity plot at room temperature.

5.2.1 233 K (-40°C) MEASUREMENTS

Figure 10 shows the real permittivity plots of all the samples at 233 K. It can be seen that the 2.5% nanofilled sample shows a lower real relative permittivity value as compared to the unfilled sample, while the 5% nano shows the reverse phenomena. Tuncer et al. [27] reported that, for an epoxy composite system with nano-sized particles, the nanocomposite permittivity was lower than that of the base epoxy matrix up to 3% filler concentration. Singh et al. [28] observed that epoxy nanocomposites containing ZnO nanofillers shows higher permittivity than the base resin up to 1% loading while at 5% loading the permittivity was lower. Other examples of reductions in the permittivity of epoxy nanocomposites with respect to unfilled epoxy have been reported in other literature as well [29]. This could be because of two contrasting factors affecting the overall permittivity of the samples which are shown below:

a) The filler permittivity is more than that of the resin
b) The interaction between the nano particles and the polymer results in a reduced mobility of polymer chains, which can cause a reduction in the overall permittivity.

![Graph](image)

Figure 10. Real permittivity of studied epoxy samples at 233 K.

![Graph](image)

Figure 11. Tanδ plot of studied epoxy samples at 233 K.

At lower filler concentrations, the second factor plays a major role in the real permittivity value as compared to the first while at higher filler concentrations (more than 5%), the reverse seems to happen. The interaction dynamics
between these two processes which happen in nanocomposites is not fully understood at this point. The real permittivity of the micro - nanofilled samples (sample 2(61.5% M = 2.5% N) and 3(60% M = 5% N)) was found to be lower than that of the microfilled sample (sample 1 (65% M)). In this case, the microfilled and epoxy combined can be considered as the base matrix.

Figure 11 shows the tanδ plots for the samples at 233 K. In the microfilled samples, the β relaxation is over-run by interfacial polarization at the lower frequencies making it difficult to observe, while this can be easily seen in the base resin and the nanofilled samples [16]. This demonstrates that these high frequency relaxations are a characteristic of the epoxy and not the filler.

5.2.3 333 K (60°C) MEASUREMENTS

---

6 DISCUSSION

Figure 12 gives the tanδ data for 333 K (60°C). Comparison of the tanδ data for the three temperatures (Figures 6, 11, 12) shows how the frequency variation scales with temperature. For the tanδ plot at 333 K in Figure 12, the nanocomposites with 5% nanofillers shows higher tanδ values as compared to the unfilled epoxy and nanocomposites with 2.5% nanofillers. At 5% filler concentration, nano particles are more in number, the interparticulate distances are smaller and this could result in overlapping of the interfacial zones in the nanocomposites leading to the percolation of charge carriers. This results in enhancement of charge transfer, which causes an increase in the electrical conductivity [29, 30]. Singh et al [22] found a similar behavior at 10% nanofiller concentration for TiO2-epoxy nanocomposites. In the micro + nanofilled samples, the nanofillers act as barriers restricting the motion of charge carriers and thus causing a reduction in the tanδ values. Samples 2, 3 and 4 (62.5% M = 2.5% N, 60% M = 5% N and 65% M = 5% N) show a significant reduction in the tanδ values as compared to sample 1 (65% M), especially at lower frequencies.

Figure 13 shows the real permittivity plots at 333 K. The real permittivity plots show a much larger variation at 333 K as compared to the room temperature (Figure 7) and the 233 K plots (Figure 10). This confirms that the measurements do not show variations due to the presence of dc conductivity (See end of section 5.2, 1).

---

Figure 14. (a) Breakdown channel in micro-nano sample (bulk). (b) Nanofilled sample with cut out volume and voids due to dielectric breakdown in the bulk.

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Figure 14 shows voids formed in the sample built due to the electrical breakdown tests conducted on the samples, as described in Section 4.2. In the sphere-sphere configuration, a quasi-homogeneous field exists at the electrode-dielectric interfaces. At a result of this, it is not possible in this electrode configuration to identify a unique starting point and an end to the damage propagation. The damage then can initiate anywhere between the two contacts. Pandia et al. [31] suggested the concept of 'global weakest link' (GWL) occurring in the samples for the sphere-sphere configuration. The inclusion of the filler particles with high dielectric permittivity values increases the average dielectric constant of a composite. But, they also produce a highly non-homogeneous electric field resulting in local hot spots of increased electric field concentration and reduced dielectric strength, thus reducing the effective breakdown strength of the composite. Hence, the puncture test does not seem to be a good test for evaluating the performance of the samples containing nanofillers or micro-nanofillers. A possible alternative method worth exploring is resistance to partial discharges within the composite, which is non-conformal to an electric field and therefore a better fit to the in-service condition [32].

7 CONCLUSIONS

The presence of the nanofillers mitigates space charge build-up in the samples which is reflected in the dielectric permittivity plots. Significant differences in dielectric losses were noted in nanofilled epoxy materials when compared to the samples containing microfillers. However, the differences in the dielectric strength measurements as observed from breakdown experiments were not significant. The reasons for this lack of correlation have been attributed to fillers acting as defects thereby initiating breakdown at very high electric stress. Since the electric stresses encountered in practical equipment is significantly lower, it is suggested that alternative methods such as partial discharges may be required to better correlate electrical results with physical mechanisms.

ACKNOWLEDGMENT

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Copied from text:

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Ernst Nickel is a professor of Chemistry and Biochemistry at Arizona State University (ASU). The experimental research in his group addresses the physical chemistry of soft condensed matter by optical spectroscopy (visible, near-infrared, and high resolution confocal spectrometry) and by single molecule detection experiments in the 10 MHz to 10 MHz range. We are interested in understanding the relaxation and transport phenomena in disordered materials and how they relate to the structure, length scale, dynamics, and interactions. Our research topics cover the phenomena associated with glass transitions, interfacial effects, geometric confinement, relaxation and retardation processes, details of the molecular dynamics, spatial heterogeneities, nanoionic behavior, and the relation between microscopic and macroscopic properties. He has published more than 100 papers in these fields.
Corona Resistance of Epoxy Nanocomposites

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Abstract: Epoxy composites with micro, nano and micro-nano silica fillers have been evaluated for their resistance to corona using point plane electrodes. The experiments were conducted for 400 hours and the surface erosion was measured after every 100 hours using a surface profilometer. The results show significant improvement in corona resistance of micro-silicon filled samples and sand filled samples when compared with the microfilled samples and unmodified materials respectively. The results emphasize the importance of good filler dispersion.

I. INTRODUCTION

The use of inorganic fillers such as silica, alumina, etc. in polymeric materials improves key properties such as fire resistance, tensile strength and resistance to surface discharges. The size of the fillers is in the range of 10-150 μm. Extensive research has been conducted to study the influence of micro-sized fillers on the electrical performance of epoxy materials for HV equipment [1, 2].

Over the last few years, there has been increased interest in the use of nano-sized fillers as additives to polymers [3, 4]. Electrical insulation using nanocomposites may provide superior performance when compared with conventional microfilled materials, such as lower dielectric losses and increased dielectric strength, tracking and erosion resistance, and surface hydrophobicity [5-7]. Such improvements can create apparatus that are more compact and last longer than what is available presently.

At Arizona State University, experiments like dielectric spectroscopy and dielectric strength were conducted on the microfilled nanocomposites and the micro-silicon filled samples. The dielectric strength measurement did not reveal any significant differences between the samples containing the fillers as compared to the base resin [8]. Corona (partial discharge) experiments were therefore performed to determine if they could discriminate between unfilled, micro and nanocomposites materials.

II. Samples Evaluated

The samples that were evaluated are listed in Table 1. They were prepared by ABB Corporate Research, Switzerland. The samples were in the form of flat sheets of dimensions 75 mm x 75 mm x 1 mm thick. Anhydride curing cycloaliphatic epoxy resin system was used as the base. The micro-sized silica filler was irregularly shaped, spongy silicate treated and of an average size of 16 μm. The filler was dried overnight at 80 °C before casting. Nano-sized silica filler of spherical shape with a diameter of about 20 nm was supplied as a 40% weight master-batch by Nanoremes AG, Germany. Standard mixing, degassing, casting, curing and post-curing procedures were used to manufacture the samples. Prior to any testing, the samples were heated in an oven for 20 hours at 160°C to remove the absorbed moisture from the samples. It should be noted that even longer times (several days) may be needed to remove the excess moisture in some samples.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Filler Composition (wt%)</th>
<th>Identification in Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>85% Micro</td>
<td>85% M</td>
</tr>
<tr>
<td>2</td>
<td>62.5% Micro + 2.5% Nano</td>
<td>62.5% M + 2.5% N</td>
</tr>
<tr>
<td>3</td>
<td>60% Micro + 5% Nano</td>
<td>60% M + 5% N</td>
</tr>
<tr>
<td>4</td>
<td>65% Micro + 5% Nano</td>
<td>65% M + 5% N</td>
</tr>
<tr>
<td>5</td>
<td>5% Nano</td>
<td>5%</td>
</tr>
<tr>
<td>6</td>
<td>0% (Grilled)</td>
<td>0%</td>
</tr>
<tr>
<td>7</td>
<td>25% Nano</td>
<td>25% N</td>
</tr>
</tbody>
</table>

TABLE 1: Samples evaluated

All the samples that are reported in this paper had well dispersed nanofiller as shown in Figure 1.

Figure 1: SEM picture of sample 7 (25% N)
III. EXPERIMENTAL SET-UP

The samples used were sheets of dimensions 10 mm × 10 mm × 1 mm. Tungsten rods of 1 mm diameter were used as electrodes and placed 0.1 mm from the sample surface. The geometry and the electrodes used in this experiment are similar to the setup used at the CIGRE Working Group [9]. Figure 2 shows the schematic of the setup used for the experiment.

Seven types of samples (Table I) were kept under seven different tungsten rods in parallel and the same voltage was applied to all the samples. A metal plate was kept underneath the surface of the samples and it served the purpose of a ground electrode. Six replicate measurements were carried out for each type of samples.

The voltage applied was 5 kV for 500 hours on the sample surface. The surface degradation was measured after every 100 hours using a surface profilometer. An interferometer was also used to measure the degradation on the sample surfaces. The profilometer gave localized peaks on the sample surface, while the interferometer was used to get the average degradation depth in the scanned area of the samples. The power supply is a 10 kVA, 45 kV/120 V transformer.

IV. RESULTS

The resistance to corona was assessed by measuring the erosion depth on the sample surface. The erosion was cone-shaped and spread over the upper surface of the micro and the micro-nanofilled samples. In the 5% N sample the erosion was concentrated under the needle electrode. The 0% (unfilled) sample showed degradation along the surface and there was hardly any subsurface degradation. Figure 3 shows the microscopic image of a 5% N and the 0% (unfilled) sample after 500 hours of exposure to corona.

The erosion depth is represented by the maximum height of the cone. It was measured after every 100 hours using the surface profilometer. The needle of the profilometer encompassed a distance of 2 mm over the sample surface. For all samples the localized peaks were measured and the maximum localized peak was considered as the erosion depth of the samples. Figure 4 shows the surface degradation of a 65% M sample measured after 200 hrs.
The erosion depth of the unfilled sample was found to be the highest while that of the micro-nanofilled samples was the lowest. Figure 6 shows the surface degradation measurement of all the samples after every 100 hours. The base resin has the maximum degradation after about 300 hours. The micro-filled sample has the highest degradation for the initial 200 hours of about 13 μm but it rises by only 2 μm over the next 300 hours. The 0% (unfilled) sample in contrast has low degradation at the end of 200 hours but is the most degraded sample at the end of 500 hours. The micro-nanofilled samples exhibit the lowest degradation levels from start to end. Surface degradation on the 0% sample and the 2.5% N sample increases with time while on all other samples, the surface degradation saturates with time.

![Graph showing surface degradation over time](image)

Figure 6. Erosion depth of the samples after every 100 hour duration measured with the profilometer

65% M sample is comparable to the 5% N sample. However, the micro-nanofilled samples have the lowest degradation among all the samples. Samples 62.5% M + 2.5% N and 65% M + 5% N have significantly lower degradation values as compared to the 65% M sample. The total filler weight concentration in all these is the same (65%) but samples 62.5% M + 2.5% N and 60% M + 5% N contain some portion of the weight concentration in the form of nano particles which brings about a significant reduction in the surface degradation of these samples as compared to 65% M.

II. Discussion

Degradation of surface erosion in the samples occurs in the base resin and not through the filler. The concentration of conventional (micro-sized) filler is important in mitigating against excessive erosion of polymeric materials, because the filler improves the thermal conductivity and the heat dissipation [10]. Conventional fillers are filled in the weight fraction from about 40-60% in the samples to attain improved high voltage performance. Higher filler concentrations are more likely to provide greater uniformity [11].

However, from Figure 7, 5% N sample has an erosion depth equivalent to 65% M sample. This is due to the smaller size of nanofillers (three orders of magnitude smaller than conventional fillers), small interparticle distances between the fillers and large surface area to volume ratio of nano-sized fillers. The last two factors are dependent on good dispersion of nanofillers.

Considering all the particles as spheres, surface area to volume ratio is calculated as follows:

\[ \frac{A}{V} = 3 \cdot \frac{\varphi}{r} \]  

where

- \( A \) = surface area
- \( V \) = volume
- \( \varphi \) = volume fraction of the particles
- \( r \) = radius of the particle

For the 5% (weight fraction) nano-filled sample, the surface area to volume ratio was calculated to be 12 km²/m³ while that of the 65% (weight fraction) micro-filled was calculated to be 0.24 km²/m³. The smaller inter-particle distances in case of nano-sized samples is also an important reason for the samples having low erosion depths. Possible surface erosion patterns include: propagation through the polymer without contacting the nano particles, through the polymer contacting the nano particles, but not penetrating them. Well dispersed nano particles act like barriers so that degradation does not penetrate the barriers, but rather, go around them. Multiple nano particles can act as multiple barriers which offer a greater resistance to corona [12].

But only well dispersed nano-fillers can have low inter-particle distances and a high surface area to volume ratio.

Particles sticking together or agglomerated ones will not have a high surface area to volume ratio and hence a high corona resistance from not well dispersed samples cannot be
expected. Figure 8 show a two samples with 5% nanofillers in them, one agglomerated and one well-dispersed. It can be easily seen that the sample with agglomerated fillers has larger inter-particle distances as compared to the one with well-dispersed fillers.

![Image](image1.jpg)

Figure 8. Samples with 5% nanofillers – agglomerated (top), dispersed (bottom)

Figure 7 shows that 2.5% N sample have higher erosion depths while the 5% N sample has depths equivalent to the 65% M filled sample. So, higher concentrations of nanofillers could be needed to achieve improvements in the performance of composites that are available in the market today. However, dispersion of nanofillers could be a major cause of concern at higher concentrations.

Hence, the desired solution to this problem lies in the combination of micro – nanofilled samples. It is the combination of micro-nanofillers which has the highest resistance to corona (Figure 7). Micro – nano filled samples contain both the above mentioned advantages i.e. higher thermal conductivity and heat dissipation due to large filler concentration of the micro particles as well as high surface area to volume ratio and small inter-particle distances due to nano particles. So, having both sized fillers could be the way forward in preparing samples for high voltage insulation. Other research groups have also shown that the mixture composites of nano and micro fillers represented much better resistance to corona than single nano-composites or micro-composites [13].

IV. CONCLUSION

Corona experiments show significant improvement in the samples containing nano-fillers as compared to the micro-filled samples and the unfilled sample. The micro – nanofilled samples had the lowest surface degradation depth as compared to all other samples. The reduction in the erosion depth of these samples can be attributed to the uniform dispersion of the nano-fillers which translates to a higher surface area to volume ratio for them and higher heat dissipation and thermal conductivity of the filler as compared to the unfilled sample. Micro-nanofilled samples have well dispersed nano-fillers and a high concentration of micro- fillers both of which expectedly translate into an improvement in partial discharge resistance.

REFERENCES

Corona Resistance of Epoxy Nanocomposites: Experimental Results and Modeling

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ABSTRACT

Epoxy composites with micro, nano and micro + nano silica fillers have been evaluated for their resistance to corona using point plane electrodes. The experiments were conducted for 500 hours and the surface erosion was measured after every 100 hours using a surface profilometer. The results show significant improvement in corona resistance of micro+nano filled samples and nano filled samples when compared with the microfilled samples and unfilled materials respectively. The results emphasize the importance of good filler dispersion. A model to map the degradation path in the filled and unfilled samples was developed using Dijkstra's shortest path algorithm. The experimental and model results show improvements in corona resistance in samples containing both micro + nano fillers.

Index Terms — Epoxy nanocomposites, nano fillers, nanodielectrics, microcomposites, corona resistance, erosion depth.

1 INTRODUCTION

The epoxy family of polymeric materials occupies a unique position in the field of electrical insulation. It is rigid; therefore it cannot be classified as elastomeric, which includes families such as silicone rubber and ethylene propylene rubber. Epoxy composites (due to the rigidity) also serve as the strength bearing member; hence there is no need for a central fibre glass core (rod or tube) that is integral to polymeric line and apparatus insulators. Epoxy insulated devices are used extensively in low and medium voltage utility applications, such as bus support insulators, enclosures for protective devices (vacuum reclosers, circuit breakers), transformer, instrument transformers (for current and voltage measuring devices in stations), bushings and pin and post type insulators. They offer several advantages over conventional porcelain. They are lighter and non-brittle when compared with porcelain, therefore they are easy to handle and will not chip or break easily. They can be cast in a variety of shapes. Since the same material serves the electrical and mechanical functions, they eliminate a major interface which can be the source of concern during manufacture and also in service (no bonding issues). They eliminate the need for oil and the obvious maintenance issues with leaks [1, 2]. They can be installed in any orientation and this is an advantage where clearances are tight. In order to realize these benefits, it is imperative that the material withstand all stresses imposed on the outside just like composite insulators.

The use of inorganic fillers such as silica, alumina, etc in polymeric materials improves key properties such as fire resistance, tensile strength and resistance to surface discharges. The size of the fillers is in the range of 15-100 μm. Extensive research has been conducted to study the influence of micro-sized fillers on the electrical performance of epoxy materials for HV equipment [3, 4].

Over the last few years, there has been increased interest in the use of nano-sized fillers as additives to polymers [5, 6]. Electrical insulation using nanocomposites can provide superior performance when compared with conventional microfilled materials, such as lower dielectric losses and increased dielectric strength, tracking and erosion resistance, and surface hydrophobicity [7-9]. Such improvements can create apparatus that are more compact and last longer than what is available presently.

At Arizona State University, experiments like dielectric spectroscopy and dielectric strength were conducted on the microfilled, nanofilled and the micro-nanofilled samples. The dielectric strength measurements did not reveal any significant differences between the samples containing the fillers as compared to the base resin [10]. Corona (partial discharge) experiments were therefore performed to determine if they could discriminate between unfilled, micro and nanofilled materials.

A degradation model is presented which calculates the degradation path through the material. The model and the experimental results show improvements in samples...
containing nano-fillers as compared to the unfilled sample and the microcomposites.

1 SAMPLES EVALUATED

<table>
<thead>
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<th>Sample Number</th>
<th>Filler concentration (wt %)</th>
<th>Identification in figure</th>
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<tr>
<td>1</td>
<td>65% Micro</td>
<td>65% M</td>
</tr>
<tr>
<td>2</td>
<td>62% Nano + 23% N</td>
<td>62% M + 23% N</td>
</tr>
<tr>
<td>3</td>
<td>65% Micro + 5% Nano</td>
<td>65% M + 5% N</td>
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<tr>
<td>4</td>
<td>65% Micro + 5% Nano</td>
<td>65% M + 5% N</td>
</tr>
<tr>
<td>5</td>
<td>0% Nano</td>
<td>0%</td>
</tr>
<tr>
<td>6</td>
<td>0% (Unfilled)</td>
<td>0%</td>
</tr>
<tr>
<td>7</td>
<td>1.5% Nano</td>
<td>1.5% N</td>
</tr>
</tbody>
</table>

The samples that were evaluated are listed in Table 1. They were prepared by ABB Corporate Research, Switzerland. The samples were in the form of flat sheets of dimensions 75 mm x 75 mm x 1 mm thick. Anhydride curing cycloaliphatic epoxy resin system was used as the base. The micro-sized silica filler was irregularly shaped, epoxy slurry mixed, and of an average size of 16 μm. The filler was dried overnight at 10 °C before casting. Nano-sized silica filler was of spherical shape with a diameter of about 30 nm and was supplied as a 40% wet master-batch by Nacoreins AG, Germany. Standard mixing, degassing, casting, curing, and post-curing procedures were used to manufacture the samples. Prior to any testing at Arizona State University, the samples were heated in an oven for 20 hours at 100°C to remove the absorbed moisture from the samples. It should be noted that even longer times (several days) may be needed to remove the excess moisture in some samples.

![SEM picture of sample](image)

All the samples containing nanofillers had good filler dispersion. Figure 1 shows the 2.5% N sample with well-dispersed nano-fillers. Once the filler dispersion was validated, corona resistance experiments were conducted on the samples to measure their degradation depth due to corona.

3 CORONA RESISTANCE EXPERIMENTS

3.1 EXPERIMENTAL DETAILS

Figure 2 shows a picture of the setup used for the corona resistance experiment. The samples used were sheets of dimensions 10 mm x 10 mm x 1 mm. The point electrodes were tungsten rods of 1 mm diameter. The point electrodes were kept at a distance of 0.1 mm from the top of the sample. This distance was measured using standard gauge blocks. The geometry and the electrodes used in this experiment are similar to the setup used by CIGRE Working Group [1]. Figure 3 shows the schematic of the setup used for the experiment.

![Schematic of the experimental setup](image)

Six measurements on each sample (Table 1) were conducted at the same voltage and spacing. A metal plate was kept underneath the surface of the samples and it served the purpose of a ground electrode.

The voltage applied was 5 kV for 500 hours. The degradation was measured after every 100 hours using a surface profilometer. An interferometer was also used to measure the degradation on the sample surfaces. The profilometer gave localized peaks on the sample surface, while the interferometer was used to get the average degradation depth in the scanned area of the samples. The power supply is a 10 kVA, 69 kV/120 V transformer.
3.2 RESULTS

The resistance to corona was assessed by measuring the erosion depth on the sample surface. Lower erosion depth is suggestive of higher corona resistance. The erosion was cone-shaped and spread over the surface of the samples. In the 5% N sample, the erosion was concentrated under the needle electrode. The 0% (unfilled) sample showed degradation along the surface while there was hardly any subsurface degradation. Figure 4 shows the microscopic image of a 5% N and the 0% (unfilled) sample after 500 hours of exposure to corona.

![Microscopic Images](image1.png)

**Figure 4:** a) 5% nanofilled sample b) 0% (unfilled) sample

The erosion depth is represented by the maximum height of the cone. It was measured after every 100 hours using the surface profilometer. For all samples the localized peaks were measured and the maximum localized peak was considered as the erosion depth of the samples. Figure 5 shows the surface degradation of a 65% M sample measured after 500 hours. The profilometer needle encompassed a length of 2 mm on the sample surface.

Figure 6 shows the degradation measurement using the interferometer. The interferometer scans a smaller area as compared to the profilometer and gives an average of degradation measured over that area.

![Surface Degradation](image2.png)

**Figure 6:** Surface degradation of 65% M sample after 500 hours using the interferometer. Average erosion depth - 10 µm

![Graphical Data](image3.png)

**Figure 7:** Erosion depth of the samples after every 100 hours duration measured with the surface profilometer.

The erosion depth of the unfilled sample was found to be the highest while that of the micro-nanofilled samples was found to be the lowest. Figure 7 shows the average value of surface degradation of all the samples after every 100 hours using the profilometer. The 0% (unfilled) sample has the maximum degradation after about 300 hours. The 65% M sample has the highest degradation for the initial 200 hours of about 13 µm but it rises by only 2 µm over the next 300 hours. The unfilled sample in contrast, has low degradation at the end of 300 hours but is the most degraded sample at the end of 500 hours. The 65% M + 5% N, 62.5% M + 2.5% N and 65% M + 5% N samples exhibit the lowest degradation levels from start to end. Surface degradation on
the unfilled sample and the 2.5% N sample increases with time. While on all the other samples, the surface degradation does not seem to rise significantly after 400 hours.

Figure 8 shows the bar graph with the mean and the standard deviation of surface roughness measured on the samples at the end of the 500-hour duration. The 5% nanofilled sample has a significantly lower degradation as compared to the base resin. The degradation of the 65% microfilled sample is comparable to the 5% N sample. However, the micro-nanofilled samples have the lowest degradation among all the samples. Samples 62.5% N, 2.5% N and 60% M + 5% N have significantly lower degradation values as compared to the 65% N sample.

Surface area to volume ratio is considered to be a major factor in improving the corona resistance of the samples. Considering all the particles as spheres, surface area to volume ratio is calculated as follows:

\[
SV = \frac{2 \cdot \pi \cdot r}{d}
\]

where

- \(SV\) = surface area to volume ratio,
- \(d\) = volume fraction of the particles,
- \(r\) = radius of the particle.

From the experimental sample, the 4% (weight fraction) nano-filled sample had a surface area to volume ratio of \(158 \text{ mm}^2/\text{mm}^3\) while that of the 65% (weight fraction) micro-filled sample was \(0.24 \text{ mm}^2/\text{mm}^3\). Although, the surface area to volume ratio is higher for the nanofilled sample as compared to the microfilled sample, their erosion depths at the end of 500 hours were found to be equivalent. There could be other reasons for higher corona resistance than the surface area to volume ratio. This is discussed in further detail in Section 5.

4 DEGRADATION MODEL

A) Model Concept

P. Marli et al. [12] have shown that erosion patterns in the filled samples happen in two stages. In stage-I, the epoxy resin present between nano-particles starts to erode, and very fine degradation channels are formed. With further exposure to discharge, the channels get deeper and wider. However, growth of the channel in any direction is arrested when it encounters a filler particle. So channels are contained in the inter-particle regions. Paths of erosion in filled samples are zigzag as they avoid the filler particles. Possible erosion patterns include propagation through the base resin or through the interfacial layer between the particles and the base resin. Addition of nano fillers would create an obstruction to degradation as the nano fillers are more discharge resistant as compared to the resin. Further, as the channel grows deeper, nano-particles emerge from the volume of the material, and degradation is arrested. The second stage involves some of the particles sitting on top being displaced which can result in the emergence of new samples.

A degradation model, based on stage-I, is developed in this paper. The model tries to map the path of erosion from the surface of the sample to the ground end through the material. This erosion path would be longer in case of a well-dispersed filled sample as it moves in a zigzag fashion by avoiding the filler particles. The model uses Dijkstra's shortest path algorithm to calculate the degradation path for different concentrations of micro and nano-fillers in the sample [13]. Dijkstra's algorithm is a graph search algorithm that solves the single-source shortest path problem for a graph with nonnegative edge path costs, producing a shortest path [14].

Figure 9 shows an SEM picture of a sample containing 60% micro-fillers and 5% nano-fillers. The micro-particles are of multiple sizes and shapes while nano-particles are mainly spherical. The dimensions of the area shown in the above images would be about 5 \(\mu\text{m} \times 10 \mu\text{m}\). A 2D model of 10 \(\mu\text{m} \times 10 \mu\text{m}\) was developed in MATLAB. The model formulates a matrix of 100 rows and 100 columns with each cell in the matrix equal to 100 \(\mu\text{m}\). The matrix consists of 1’s and 0’s only. The 1’s denote the filler particles while the 0’s denote the base resin. A nano-sized particle is denoted by one cell containing a 1 (particle size of 100 \(\mu\text{m}\)) while a micro-sized particle is denoted by 400 cells containing 1’s (particle size of 2 \(\mu\text{m}\)). A model schematic containing both micro-nanofillers is shown in Figure 10.

\[\text{Figure 9. Sample with 60% micro + 5% nano fillers}\]
The model is a good reflection of the particle distribution in actual samples, if the distribution is assumed to be the same throughout. A longer degradation path in the model reflects a higher resistance to corrosion.

**A) Model Assumptions**

The distribution of particles in the matrix is completely random, which means that for the same filler concentration, one can get different distribution of particles each time the program is run. MATLAB function `randi` is used in order to get random distribution of particles. Once the particle distribution was achieved, a graph search algorithm was used to calculate the shortest path. Different filler concentrations for both the micro-sized fillers and the nano-sized fillers were tested. 100 batch runs for the different filler percentages were carried out.

Some of the assumptions made in the model are:

- Micro particles and nano particles are 2 μm and 100 nm in size respectively, while the actual sample has micro particles of sizes varying from 0.5 μm to 5 μm while nano-particles are about 10-20 nm. For simplicity, the model assumes the particles to be square in shape as they represent a cell in the matrix while the actual nano particles are spherical and micro-particles can have different shapes. Since, the internal electric field is not calculated in the samples, the differences in shapes do not affect the results.

- In actual samples, the weight fractions of the filler are given which can be converted to equivalent volume fractions. The model, however being 2D considers the filler fractions in terms of area. For the microfilled samples, the model allows concentrations only up to 50%. This is because uniform sized micro-fillers are filled in the model sample while in actual cases the filler sizes of the micro-filled samples vary.

- The actual samples are believed to have interfacial thickness around the particles [15]. However, no particle interfaces are assumed in the model. Again, since internal electric fields are not calculated, the model results are not affected by the lack of interfaces.

**B) Model Algorithm**

The flowchart for the degradation model is shown in Figure 11.

- Start
- Matrix of 30 μm x 10 μm. Each cell of 300 nm. Filler denoted with 'F'. base matrix with '0's
- Adjacent matrix formulated by swapping distances to the different nodes.
- Distance of initial Node=0, All other nodes=inf
- Calculate Distance of neighboring nodes from the initial node, if the distance is less than the prev distance, overwrite the distance. If the is a filler, distance=inf
- All neighbors of the node considered, it is marked as visited
- Set unvisited node with smallest distance (from initial node) as new 'current' node
- Algorithm ends when all nodes are visited. The shortest distance among all the calculated distances for all the nodes in the last row is considered

![Figure 11: Flowchart for the degradation model](image)

**C) Model Results**

The unfilled sample has the shortest path of 99 μm. This path is attained when the degradation channel traverses a straight line from the center cell of the top electrode to the ground end. If there are fillers in the sample, then degradation circumvents the particles resulting in longer paths as compared to the unfilled sample.

Table 2 provides the mean and standard deviation of all the different runs conducted. It also provides information about the shortest distance runs (9.9 μm) in each of the filled samples. Figures 12-16 show some of the filler concentrations and their results for 100 batch runs for those concentrations. Figure 17 shows a possible erosion pattern for a 5% nano-filled sample.
4 DISCUSSION

Degradation in the samples occurs through the base resin and not through the filler because of better thermal stability of the filler. In the model, the erosion path is a ‘straight line’ from the top cell to the bottom cell in an unfilled sample as there are no fillers to deflect its path. So, the shortest path in the case of an unfilled sample is 9.9 μm. Different concentrations of micro-filled samples were modeled, and their shortest paths were calculated. All the micro-filled samples had longer shortest paths than the unfilled sample. The small concentrations of micro-filled samples (<30%) had more than 10% ‘straight line’ runs in them. Samples greater than 40% micro-sized fillers had longer shortest paths and only one or two ‘straight line’ runs.

All the nano-filled samples have their shortest path longer than that of the unfilled sample. The model results showed significant differences in the erosion paths even at 1% filler concentration. Even the ‘straight line’ runs were not present in the nano-filled samples beyond 5% filler concentration. Corona resistance experiment results showed significant differences in the erosion depth of the samples at 5% concentration as compared to the base resin. The experimental results though did not highlight a significant difference in the erosion depth at the 2.5% filler concentration.

From Table 2, it can be seen that for the same filler concentration, the nano-filled samples have a longer erosion path as compared to the micro-filled sample. A 15% nano-filled sample has a longer erosion path as compared to a 15% micro-filled sample. The longer erosion path for the nanofilled samples is due to the smaller size of nanofillers (three orders of magnitude smaller than conventional fillers) and small interparticle distances between the fillers [18].

The model results also show that smaller concentrations of nano-fillers are not better than larger concentrations of microfillers in the sample. This can be seen from the erosion paths shown in Table 2 where the erosion path of 40% and 50% M sample is longer than the 5% and 10% N sample. Even from the experimental results it can be seen that the erosion depth of the 65% M sample is lesser than the 2.5% N sample and only marginally greater than the 5% N sample. Published literature shows that conventional fillers are filled in the weight fraction from about 40-60% in the samples to attain improved high voltage performance. Their high concentration helps in increasing the thermal conductivity and heat dissipation from the surface which reduces the degradation in the samples [17, 18]. Smaller concentrations of nano-fillers might give an equivalent performance as compared to higher concentrations of micro-filled samples. However, the exact filler concentration for the nanocomposites to achieve this performance is still not clear [19]. Higher concentrations of nano-fillers should yield a better performance but agglomeration of fillers is a major cause of concern. So, the real benefit of nanofillers arises by incorporating both micro and nanofillers in the samples.

The erosion path of a micro-nano-filled sample is longer than that of the micro-filled sample as can be seen from Table 2. The experimental results also showed significant improvements in erosion depths of samples containing both micro-nano-sized fillers as compared to the microcomposite. The nano-filler weight concentration is all these in the same (65%) but samples 65% M = 2.5% N and 60% M = 5% N contain some portions of that weight concentration in the form of nano particles which brings about a significant reduction in the degradation of these samples as compared to 65% M.

6 CONCLUSIONS

Corona experiments show significant improvement in the samples containing nano-fillers as compared to the micro-filled samples and the unfilled sample. A model was developed to map the degradation path in the samples using Dijkstra’s shortest path algorithm. The results showed that
the smaller concentration of nanofilled samples did not have better erosion results than higher concentration of conventional fillers.

Both the experimental and the model results showed significant improvement in the performance of micro - nanofilled samples as compared to the microfilled samples. The improvements in the concomitant resistance performance of these samples can be attributed to the uniform dispersion of the nano-fillers which result in smaller interparticle distances between the microfillers. Therefore, it appears that a combination of micro - nanofillers can give the best HV insulation performance.

REFERENCES


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Understanding Electrical Discharge Endurance of Epoxy Micro and Nano-composites through Thermal Analysis

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ABSTRACT

Thermal analysis of epoxy solid dielectrics containing micro and nano-particles of silica was performed to better understand their electrical discharge endurance. Measurements of thermal conductivity and thermogravimetric analysis (TGA) were conducted. A thermal model to calculate the local temperature in the sample was developed using the partial differential equation (PDE) toolbox in MATLAB. The experimental results demonstrate that the measured thermal conductivity, which represents an average value, cannot adequately explain the superior electrical discharge endurance characteristics as samples containing nanofillers. The model emphasizes the importance of real-temperature, which improves the local temperature distribution, resulting in higher discharge endurance. This was supported by TGA analysis which showed higher weight loss at increased temperature for samples containing nanofillers as compared to conventional micro-composites and unfilled samples.

INDEX TERMS — Epoxy nanocomposites, nanofillers, nanodielectrics, microcomposites, corona resistance, erosion depth, thermal model.

1 INTRODUCTION

Conventional micro-fillers such as silica, alumina, etc. with sizes in the range of 1-100 µm are added to polymers for electrical equipment to improve properties such as resistance to corona, arcing, UV and tensile strength. Electrical performance of polymers containing conventional micro-fillers has been extensively studied over the past 30 years [1, 2]. Published literatures shows that polymers filled with 40-60% by weight of microfillers have reduced degradation from electrical discharges due to improved heat dissipation from the sample [1, 4].

Over the past decade, polymeric materials containing nano-sized fillers have been introduced for various power apparatus in the low and medium voltage range [3, 5, 6]. It has been shown that the addition of nano-fillers improves certain aspects of electrical performance such as corona resistance, partial discharge inception and breakdown strength and lowers dielectric losses when compared with micro-filled materials [7-11].

Oversized, the nanofiller loading is less than 10% by weight [12]. It was been shown in a recent paper that nanofilled epoxy with filler concentration of 5% exhibited significant improvement in the corona discharge endurance [13]. Figure 1 shows the erosion depth measurements of the samples with various loadings of micro (designated by M) and nano (designated by N) fillers, as well as the unfilled samples.

![Figure 1: Erosion depth of all the samples at the end of 500 h duration measured with the profilometer, bars indicate mean values and brackets indicate standard deviation. M represents micro fillers and N represents Nano fillers.](image)

The 5% N sample had erosion depth comparable to the 65% M sample at the end of 500 h duration. The 62.5% M = 2.5% N and the 50% M = 5% N samples had significantly better discharge endurance than compared to the conventional 65% M sample even though the total filler concentration were the same in these samples (O3% [14]).

Thermal conductivity of the sample was calculated using the rule of mixtures and this is shown in Table 1 [11]. It can be seen that the increase in thermal conductivity for samples with low filler concentrations over the unfilled materials is significant. The calculated value simply depends on the
weight fraction of the filler and resin, and becomes higher for samples with increasing filler concentrations. Also, the rule of mixture does not consider the different sizes of particles.

This suggests that macroscopic parameter such as thermal conductivity cannot adequately explain the differences in discharge resistance of the samples evaluated. It is important to confirm this with actual measurement.

1 THERMAL CONDUCTIVITY MEASUREMENTS

Thermal conductivity of the samples was measured according to the ASTM E 1461 at room temperature (25°C) [15]. The experimental setup is shown in Figure 2. The sample is in a disk with a diameter of 12.7 mm and a thickness of 1.5 mm. The samples were coated with a layer of thermal adhesive to ensure good thermal contact. The samples were not very high emissivity or absorptivity.

![Figure 2: Experimental setup for the thermal conductivity measurement using the flash method.](image)

The sample is illuminated by a flash lamp, and the temperature rise is recorded. The thermal conductivity is calculated using the following equation:

\[
k = \frac{q}{A \Delta T}
\]

(1)

where \(k\) is the thermal conductivity, \(q\) is the heat flux, \(A\) is the cross-sectional area, and \(\Delta T\) is the temperature rise.

The microfilled and the micro-nanocomposites had higher thermal conductivity while the neat and the unmodified samples had lower values. There was no significant difference between the thermal conductivity values among the microcomposites and the micro-nanocomposites. The thermal conductivity values of the unmodified and the microfilled samples were also found to be similar.

2 THERMOGRAVIMETRIC ANALYSIS

Thermo gravimetric Analysis (TGA) measurements were conducted on all samples listed in Table 1. The TGA measurement system is a PerkinElmer TGA-7 capable of reaching 1000°C. The sample is placed in a platinum crucible. The weight loss was monitored over the temperature range of 20-900°C. The ramp rate temperature was 2°C/min. The weight loss sensitivity of the system was 1 μg. The system uses a helium (He) atmosphere with a flow rate of 50 ml/min.

TGA measurements were performed to determine the temperature at which degradation starts, and the temperature at which the degradation is complete. These results are compared to the experimental thermal conductivity results.

The weight loss as a function of temperature is shown in Figure 3.

In the temperature range of 25-300°C, the 2.5% N and the unmodified sample have similar weight loss while the 2% N sample has lower weight loss. This indicates that for very low levels of fillers, leading there may be no significant improvement compared to the unfilled material [17].

The 5% N sample had weight loss comparable to the 5% M sample. The weight loss in the micro – nanocomposites was not significantly different from the 5% M sample. However, the temperature at which the weight loss is initiated in the micro – nanocomposites is higher than that of the 5% M sample. TGA 2 loses the different temperatures at which the weight loss is initiated in the different samples.
The weight loss initiation temperatures seem to be in agreement with the erosion depth of the samples shown in Fig. 1. Both TGA and corona measurements show the benefits of adding nano-fillers to the base epoxy resin. Stronger chemical bonding between the nano-fillers and resin is a possibility suggested by the TGA data. Interfaces between the filler and resin could also play a role in improving the discharge endurance, as covalent and ionic bonds, Vander Waals forces, hydrogen bonding could exist between the matrix and filler components. The role of the interface in nanocomposites is still being analyzed by different researchers from around the world [18, 19].

4 THERMAL MODEL

A. Model Concept

A thermal model to calculate the localized temperature of the samples has been developed using the PDE Toolbox in MATLAB. The program uses the finite element method (FEM) to calculate the temperature distribution across the surface [20]. Triangular elements were used to model the surface. The filler particles are modeled with a higher density of triangular elements when compared to the base resin, as shown in Figure 4. The distribution and number of these triangular elements are key factors that determine the accuracy of the solution. Generally, the accuracy improves with the number of elements although this might cause an unreasonable increase in the computation time. Therefore, a trade-off between accuracy and computation time is required.

The fundamental equation for calculating temperature on the surface is shown in Equation 1, and is derived from Maxwell's equations.

\[
\frac{\partial T}{\partial t} + \nabla \cdot (-k \nabla T) = q
\]

The values of the parameters used for the filler and the resin in the thermal model are shown in Table 3. All boundaries were set at 300°C. The value of \( q \) used for the calculations was 5 W/m², and this is based on the laser ablation experiments performed earlier for evaluating the discharge endurance of filled polymer materials [21].

B. Model results

![Figure 5: Localized temperature for 1% N sample](image)
Figures 5 and 6 show the localized temperatures for a 1% and 2.5% N sample. It can be seen that the filler particles are at a lower temperature than the base matrix. Higher filler thermal conductivity results in better heat dissipation and lowers the temperature locally of the sample. Smaller concentrations of nano-filled samples occupy large areas in the base matrix. This is because nano particles are three orders of magnitude smaller than conventional microfillers. So, for the same filler concentration, the number of nanoparticles is larger than micro-filler. Their small inter-particle distance also reduces the amount of organic material available for emission.

![Figure 6: Localized temperatures for 2.5% N sample](image)

Figure 6. Localized temperatures for 2.5% N sample

![Figure 7: Localized temperatures for 2.5% N sample with agglomerated filler](image)

Figure 7: Localized temperatures for 2.5% N sample with agglomerated filler

Good dispersion of nanofillers is essential for improved heat dissipation. Nanoparticles have a tendency to agglomerate due to their high surface energies. Figure 7 shows the localized temperatures for a material where the fillers are poorly dispersed (agglomerated). Agglomerated particles result in exposing large areas of organic material that can degrade. Thus, the advantage of using nanofillers is lost in such materials. Hence, great care must be exercised during sample preparation to avoid agglomeration of the particles. It might also explain why it is difficult to make samples with high concentration of nanofillers that have good dispersion.

![Figure 8: Localized temperatures for 17% M sample](image)

Figure 8. Localized temperatures for 17% M sample

![Figure 9: Localized temperatures for 30% M sample](image)

Figure 9. Localized temperatures for 30% M sample

Figures 8 and 9 show the localized temperatures for samples with relative low levels of microfillers (17% and 30%). As will be shown in Table 5, the local temperature for such levels of microfillers is higher than for nanofillers. This is because of the low surface area to volume ratio and large inter-particle distances between the particles.
Figure 10 shows the localized temperatures of a 50% M sample. However, actual micro-filled samples can have agglomerated micro-fillers as shown in Figure 11. So, the temperature distribution in actual samples may not be as good as calculated in the model.

Mixing micro and nanofillers can be advantageous as the well-dispersed nanofillers help reduce the local temperature. In conventional micro-composites, as shown in Figure 10, the space between the fillers is occupied by the base resin, while in micro-nanocomposites, this space is occupied by nanofillers leaving even lesser organic material exposed to erosion.

4 DISCUSSION

The temperature distribution was calculated over a small distance to show the improvements in local temperatures due to well dispersed nanofillers. The inter-particle distance between the fillers can be determined using Equation 3 [22]. L represents the inter-particle distance, while \( v \) and \( d \) stand for volume fraction and particle diameter, respectively. The equation is formulated for spherical particles.

\[
L = \left( \frac{v}{(2v)} \right)^{\frac{1}{3}} \left( \frac{d}{d} \right) - 1 \cdot d
\]

Table 4 contains the calculated inter-particle distances for all the samples. For samples containing micro and nanofillers, the inter-particle distance cannot be calculated because they contain both micro and nanofillers at varying concentrations.

Table 4: Interparticle distance calculations for different filler concentrations

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Micro</th>
<th>Nano</th>
<th>Interparticle distance (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>0</td>
<td>1064</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>0</td>
<td>703</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>0</td>
<td>455</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>0</td>
<td>220</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>1</td>
<td>128</td>
</tr>
<tr>
<td>6</td>
<td>70</td>
<td>2.5</td>
<td>84</td>
</tr>
<tr>
<td>7</td>
<td>80</td>
<td>3</td>
<td>23.3</td>
</tr>
<tr>
<td>8</td>
<td>90</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>9</td>
<td>100</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>40</td>
<td>5</td>
<td>-</td>
</tr>
</tbody>
</table>

Consider a 1 µm span within any filled sample. Since the particle diameter and the interparticle distances are known, the number of particles lying within this length can be calculated. Figure 14 shows a schematic with particles being separated over such a span. The average temperature within this span is calculated depending on the length covered by the particle and the interparticle distance. For the micro-nanofilled samples, although the interparticle distance cannot be calculated, the average temperature is calculated by combining the intra-particle distances from the respective micro and nanofiller concentrations.
For example, for a 1N sample, the interparticle distance was calculated to be 1.28 nm. So, over a length of 1 μm, there would be 8 nano particles approximately of diameter 40 nm and the average temperature is calculated at 284°C. Table 5 contains the results for the parameters calculated over this distance.

Table 5: Average Temperature over a length of 1 μm

<table>
<thead>
<tr>
<th>Sample</th>
<th>Length covered by filler (μm)</th>
<th>Length covered by matrix (μm)</th>
<th>Average Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>-</td>
<td>-</td>
<td>200</td>
</tr>
<tr>
<td>20% M</td>
<td>22</td>
<td>38</td>
<td>215.4</td>
</tr>
<tr>
<td>30% M</td>
<td>297</td>
<td>703</td>
<td>215.4</td>
</tr>
<tr>
<td>40% M</td>
<td>444</td>
<td>456</td>
<td>218.4</td>
</tr>
<tr>
<td>50% M</td>
<td>220</td>
<td>230</td>
<td>192</td>
</tr>
<tr>
<td>1% N</td>
<td>540</td>
<td>70</td>
<td>583</td>
</tr>
<tr>
<td>2.5% N</td>
<td>320</td>
<td>680</td>
<td>252</td>
</tr>
<tr>
<td>5% N</td>
<td>440</td>
<td>560</td>
<td>204</td>
</tr>
<tr>
<td>10% N</td>
<td>420</td>
<td>480</td>
<td>222</td>
</tr>
<tr>
<td>10% M</td>
<td>420</td>
<td>480</td>
<td>222</td>
</tr>
<tr>
<td>15% M</td>
<td>440</td>
<td>560</td>
<td>197.8</td>
</tr>
<tr>
<td>20% M</td>
<td>475</td>
<td>525</td>
<td>182</td>
</tr>
</tbody>
</table>

The average temperature of the 1N and the 2.5N samples are comparable to the 10% M sample. The 1% N sample has an average temperature equivalent to the 10% M sample. Also, the micro-nanofilled samples have a marginally lower average temperature as compared to the 50% M sample, even though their combined concentrations are lower than 50% (42.5% and 45% respectively).

4 CONCLUSIONS

The presence of well dispersed nano-filler reduces the velocity within the samples and also raises the temperature at which weight loss is initiated. A macroscopic quantity such as thermal conductivity is not adequate to explain the discharge endurance satisfactorily. The thermal model for calculating the localized temperatures in the samples was developed and this along with TGA measurements was found to provide better understanding of the superior discharge endurance exhibited by the nano filled epoxies. The role of the interphases and the chemical bonding between the base resins and the nanofiller need to be studied further as it may provide additional information to explain the differences between materials containing micro and nanofillers.

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