Evaluation of Epoxy Nanocomposites for High Voltage Insulation

Final Project Report

Power Systems Engineering Research Center

Empowering Minds to Engineer the Future Electric Energy System
Evaluation of Epoxy Nanocomposites for High Voltage Insulation

Final Project Report

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Power Systems Engineering Research Center

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Executive Summary

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 experiment was conducted over a wide range of frequency 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 nano-filled 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.

Porcelain insulator bells that were in service for over 30 years were provided by EPRI and their microstructure was analyzed. New porcelain insulators were obtained from SRP We could not find any discernible differences in the microstructure between the aged and the new units. As the number of aged insulators was limited and we had adequate supply of nanodielectric samples, the focus of the project was shifted to the nano-filled epoxy samples.

A numerical model was developed that solves a sparse system of equations using the preconditioned conjugate gradient iterative method. This model was used to solve for the electric field in a material consisting of a periodic distribution of micro- and nano-dielectric particles. The simulations included a void region adjacent to the particles. The computational domain was discretized using 700 points along each of the three dimensions. The electric field was then used to predict the corona onset condition for different particle sizes and also for different locations of
the void. Results show that smaller particle sizes have higher corona onset electric field. These results could be used as a guideline for the design of future high-voltage periodic material.

The project also evaluated porcelain insulators which can be classified as microfilled dielectric materials. Few field aged insulators were provided by EPRI and new samples were provided by SRP. There was no noticeable change in the microstructure between the new and aged units that could be attributed to time in service. As the field aged samples available was limited, it was not possible to arrive at any reasonable conclusion.
Table of Contents

1 Introduction .................................................................................................................................... 1
   1.1 Inorganic fillers .................................................................................................................. 3
   1.2 Nanodielectrics .................................................................................................................. 4
   1.3 Organization of the report ................................................................................................. 6

2 Samples evaluated: scanning electron microscopy (SEM) and tensile strength measurements ................................................................................................................................. 7
   2.1 Introduction .......................................................................................................................... 7
   2.2 Samples provided ................................................................................................................ 7
   2.3 Scanning electron microscopy (SEM) ................................................................................ 8
       2.3.1 Procedure ................................................................................................................ 9
       2.3.2 Results and discussion ............................................................................................ 11
   2.4 Tensile strength measurements ....................................................................................... 13
       2.4.1 Experimental setup ............................................................................................... 13
       2.4.2 Results .................................................................................................................... 14

3 Dielectric spectroscopy ............................................................................................................ 17
   3.1 Introduction ........................................................................................................................ 17
   3.2 Experimental setup .......................................................................................................... 18
   3.3 Experimental results and discussion ............................................................................... 20
       3.3.1 Room temperature measurements - all samples .................................................... 20
       3.3.2 Measurements at 233K ......................................................................................... 23
       3.3.3 Measurements at 333K ......................................................................................... 24
       3.3.4 Measurements at 393K ......................................................................................... 26

4 Dielectric breakdown experiments ............................................................................................ 29
   4.1 Breakdown in solid dielectrics ........................................................................................... 29
   4.2 Background: dielectric strength for nanocomposites ....................................................... 29
   4.3 Experimental details ......................................................................................................... 30
   4.4 Results ............................................................................................................................... 30
   4.5 Discussion ......................................................................................................................... 33
Table of Contents (continued)

5  Corona resistance experiment and results ........................................................................36
    5.1  Introduction .................................................................................................................. 36
    5.2  Background ............................................................................................................... 37
    5.3  Corona resistance experimental setup ...................................................................... 37
    5.4  Observations and results .......................................................................................... 39
        5.4.1  Degradation after 500 hours ............................................................................. 40
6  Degradation model ............................................................................................................ 42
    6.1  Introduction ............................................................................................................... 42
    6.2  Model assumptions .................................................................................................... 44
        6.2.1  Dijkstra’s algorithm ......................................................................................... 45
        6.2.2  Summarizing the code ..................................................................................... 46
    6.3  Model results ............................................................................................................ 47
7  Thermal analysis and model ............................................................................................. 51
    7.1  Introduction ............................................................................................................... 51
    7.2  Thermal conductivity measurements ........................................................................ 51
        7.2.1  Experimental details ......................................................................................... 51
        7.2.2  Experimental results ......................................................................................... 53
    7.3  Thermal model .......................................................................................................... 54
        7.3.1  Model concept .................................................................................................... 54
        7.3.2  Model results .................................................................................................... 55
        7.3.3  Discussion .......................................................................................................... 60
    7.4  Thermo gravimetric analysis ..................................................................................... 62
8  Internal electric field calculations .................................................................................... 64
    8.1  Numerical approach .................................................................................................. 65
    8.2  Simulation results ..................................................................................................... 68
        8.2.1  Validation of iterative method ............................................................................ 68
        8.2.2  Finite to infinite approximation ....................................................................... 69
    8.3  Electric field distribution .......................................................................................... 73
    8.4  Corona onset condition analysis .............................................................................. 75
    8.5  Summary ................................................................................................................... 78
### Table of Contents (continued)

9 Conclusions and future work ................................................................. 79  
  9.1 Conclusions ...................................................................................... 79  
  9.2 Future work .................................................................................... 79  

References ............................................................................................. 81  

Appendix A: Measurements with guard rings .................................... 87  

Appendix B: Analysis for significant differences in tan δ values .......... 89  

Appendix C: Degradation measurements and error corrections ............. 91  
  C.1: Degradation measuring equipments .............................................. 91  
  C.2: Error correction ........................................................................... 93
List of Figures

Figure 1.1: Post type insulator ....................................................................................................... 1
Figure 1.2: Current Transformer .................................................................................................... 2
Figure 1.3: Potential Transformer .................................................................................................. 2
Figure 1.4: Sample showing micro-fillers ..................................................................................... 3
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 ................................................................. 3
Figure 1.6: Sample showing bad interface of the micro-filler with the base resin ......................... 4
Figure 1.7: 5% N sample containing nanofillers ........................................................................... 5
Figure 2.1: Regular SEM image of a 65% M + 5% N sample ...................................................... 8
Figure 2.2: SEM image on the FIB instrument. 65% M + 5% N sample ...................................... 8
Figure 2.3: Sample holder with a gold coated sample ................................................................. 9
Figure 2.4: Platinum coating on the surface of the sample .......................................................... 10
Figure 2.5: Sample with visible fillers after milling ................................................................. 10
Figure 2.6: SEM image showing nanofillers ............................................................................... 11
Figure 2.7: High magnification scanning electron microscopy showing nanofiller (20 nm) distribution in a sample ................................................................. 12
Figure 2.8: Sample containing agglomerated nano-sized silica fillers (10% nano) .................... 12
Figure 2.9: EDAX results of a micro+nano-filled sample .......................................................... 13
Figure 2.10: Setup for tensile strength experiments .................................................................... 14
Figure 2.11: Dog bone shape ....................................................................................................... 14
Figure 2.12: Stress vs. Strain curves of all samples ..................................................................... 15
Figure 2.13: Tensile Strength of all samples (bars: mean, brackets: standard deviation) .......... 15
Figure 2.14: Young's modulus of all samples (bars: mean, brackets: standard deviation) ...... 16
Figure 3.1: Different polarization phenomena occurring in a solid dielectric [33] ................. 18
Figure 3.2: Dielectric Spectroscopy setup ................................................................................... 19
Figure 3.3: Sample holder for dielectric spectroscopy setup .................................................... 19
Figure 3.4: Real permittivity plots for studied epoxy samples at room temperature .......... 21
Figure 3.5 Tanδ plots for studied epoxy samples at room temperature .................................... 21
Figure 3.6: Imaginary permittivity plots for studied epoxy samples at room temperature ..... 22
Figure 3.7: Real permittivity of studied epoxy samples at 233 K ........................................... 23
Figure 3.8: Tanδ plots of studied epoxy samples at 233 K ..................................................... 24
List of Figures (continued)

Figure 3.9:  Tanδ plots of studied epoxy samples at 333 K .......................................................... 25
Figure 3.10:  Real permittivity of studied epoxy samples at 333 K .................................................. 25
Figure 3.11:  Real and imaginary permittivity plots for sample 1 at 393K ........................................ 26
Figure 3.12:  Real and imaginary permittivity of micro+ nano-filled sample .................................. 27
Figure 3.13:  Real and imaginary permittivity of 2.5% N and the unfilled sample .......................... 27
Figure 4.1:  Schematic for breakdown experiment ....................................................................... 30
Figure 4.2:  SEM image of the surface of a punctured sample ........................................................ 31
Figure 4.3:  Weibull Distribution plot (95% confidence interval) for the microfilled and micro+nano-filled samples ........................................................................................ 32
Figure 4.4:  Weibull Distribution plot (95% confidence interval) for the unfilled and nano-filled samples ...................................................................................................................... 32
Figure 4.5:  Breakdown channels in the micro-nano sample (bulk) ............................................... 33
Figure 4.6:  Breakdown channels in the nano sample (bulk) ............................................................ 34
Figure 4.7:  Voids in the 2.5% N sample .......................................................................................... 34
Figure 5.1:  Schematic showing the impact of corona discharge on the sample [61] ...................... 36
Figure 5.2:  Schematic for corona resistance experiment .............................................................. 37
Figure 5.3:  Picture showing the corona resistance experimental setup ......................................... 38
Figure 5.4:  a) 5% nano-filled sample b) 0% unfilled sample ....................................................... 39
Figure 5.5:  Erosion depth of the samples after every 100 hour duration measured with the surface profilometer ........................................................................................................... 40
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) ........................................ 41
Figure 6.1:  Schematic of a filled sample ....................................................................................... 42
Figure 6.2:  Stage- I: Erosion occurring through the base resin .................................................... 43
Figure 6.3:  Stage-II: Fillers displaced from the top of the sample .............................................. 43
Figure 6.4:  A 2D matrix representing 45% M + 5% N sample .................................................... 44
Figure 6.5:  Flowchart representing the degradation model ........................................................ 46
Figure 6.6:  Model generated 2D matrix representing a 50% micro-filled sample (left) and 100 batch runs of the sample (right) .................................................. 47
Figure 6.7:  Model generated 2D matrix representing a 5% nano-filled sample (left) and 100 batch runs of the sample (right) ........................................... Error! Bookmark not defined.
List of Figures (continued)

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) ................................................................. 47

Figure 6.9: Model generated 2D matrix representing a 15% nano-filled sample (left) and 100 batch runs of the sample (right) ............................................................................... 48

Figure 6.10: Model generated 2D matrix representing a 15% nano-filled sample (left) and 100 batch runs of the sample (right).................................................................................. 48

Figure 6.11: Schematic showing the PD erosion pattern for a 5% nano-filled sample ............... 48

Figure 6.12: Erosion path of all samples (bars: mean, brackets: standard deviation) ............... 49

Figure 7.1: Experimental setup for the thermal diffusivity measurement using the Laser Flash Method ....................................................................................................................... 52

Figure 7.2: Finite Element Method showing the formulation of triangular elements in a nano-filled sample ........................................................................................................................................ 54

Figure 7.3: Temperature distribution of a 1% N sample ........................................................................ 56

Figure 7.4: Temperature distribution of a 2.5% N sample ........................................................................ 56

Figure 7.5: Temperature distribution of a 2.5% N sample (agglomerated) ........................................ 57

Figure 7.6: Temperature distribution of a 17% M sample ........................................................................ 57

Figure 7.7: Temperature distribution of a 30% M sample ........................................................................ 58

Figure 7.8: Temperature distribution of a 50% M sample ........................................................................ 58

Figure 7.9: Temperature distribution of a 40% M + 2.5% N sample .................................................. 59

Figure 7.10: Temperature distribution of a 40% M + 5% N sample .................................................. 59

Figure 7.11: Schematic calculating the temperature over a span of 1 μm ........................................ 61

Figure 7.12: Weight loss graphs for the different filled and unfilled samples using TGA ............ 62

Figure 8.1: Array of particles in a periodic dielectric material ........................................................................ 65

Figure 8.2: Three dimensional finite different grid node (i,j,k) and its neighbors. ......................... 66

Figure 8.3: Results obtained using Matlab and the PCG method .................................................. 69

Figure 8.4: Voltage along a z-oriented line through the center of the grid ...................................... 70

Figure 8.5: The z component of the electric field along a z-oriented line through the center of the grid. These points correspond to those of Fig. 3.2 ........................................................................ 71

Figure 8.6: The z component of the electric field in each of the ten cells in a 10-cell simulation. The void is on the top. ........................................................................................................ 72

Figure 8.7: The z component of the electric field in each of the ten cells in a 10-cell simulation. The void is on the side. ........................................................................................................ 73

Figure 8.8: The z component of the electric field over a yz-plane with the void on the top. ........ 74
List of Figures (continued)

Figure 8.9: The z component of the electric field over a yz-plane with the void on the side..... 75
Figure 8.10: Corona onset electric field for different void sizes (and thus different cell sizes).. 77
Figure A.1: Schematic of the guard ring setup ............................................................................. 87
Figure A.2: Imaginary permittivity of 65% M sample with and without guard ring................... 88
Figure B.1: Normality plot for log (tan delta) .............................................................................. 89
Figure B.2: Fisher's LSD test ....................................................................................................... 89
Figure C.1: Surface degradation of 62.5% M + 2.5% N sample measured after 500 hours.        
Localized erosion depth: 10 µm................................................................................................. 91
Figure C.2: Surface degradation of 62.5% M + 2.5% N sample after 500 hours using the     
interferometer. Average erosion depth: 5 µm........................................................................... 92
Figure C.3: Surface degradation of the glass slide. Erosion depth: 0 µm.................................... 93
Figure C.4: Initial degradation depth of 65% M sample. Average erosion depth: 1.5 µm........ 94
List of Tables

Table 2.1: List of Samples ........................................................................................................ 7
Table 4.1: Breakdown values for the samples (kV/mm) ..................................................... 31
Table 4.3: Shape and scale parameters of the results using Weibull Distribution......... 33
Table 6.1: Correlation between degradation model and corona resistance experiment .. 50
Table 7.1: Thermal measurements conducted on the samples......................................... 53
Table 7.2: Thermal Conductivity Values......................................................................... 53
Table 7.3: Sample properties ........................................................................................... 55
Table 7.4: Interparticle distance calculations for different filler concentrations .......... 60
Table 7.5: Average Temperature over a length of 1 µm............................................... 61
Table 7.6: Temperature at which weight loss was initiated............................................. 63
Table 8.1: Corona onset condition for different void lengths......................................... 77
Nomenclature

α - scale parameter
α₁ - thermal diffusivity
α - Ionization coefficient
β - shape parameter
Cₚ - Specific heat of the material
d - diameter of the particle
D - Electric flux density
ε' - real permittivity
ε" - imaginary permittivity
ε₁ - real permittivity of the base resin
ε₂ - real permittivity of the filler
ε₉ - real permittivity of the composite
εᵈ'' - dielectric loss
εᵥar - Average dielectric constant
η - Attachment coefficient
E - electric field
f - frequency
k - thermal conductivity
l - inter-particle distance
Lc - correlation length
ρ - density
p - Pressure in pascals
Q - heat flux
r - radius of the particle
σₑ - DC conductivity
StV - Surface Area to volume ratio
tanδ - loss tangent
T - Temperature
ν - volume fraction of the particles
ω - frequency
ωₑ - cross-over frequency
y₁ - volume fraction of the base resin
y₂ - volume fraction of the filler
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 voltage 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 porcelain such as: light weight, superior impact and seismic resistance [3]. They can be easily molded into complicated shapes and have the advantage that the same material fulfills the electrical and mechanical functions, thereby eliminating 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) as opposed 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. This particular property is inferior for bisphenol epoxy owing 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 outdoor 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.

![Post type insulator](image_url)
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, and/or to modify the material to impart resistance to the effects of discharges [6].

1.1 Inorganic fillers

Figure 1.4: Sample showing micro-fillers

The use of inorganic fillers such as alumina trihydrate (ATH), silica etc. in polymeric insulation materials has been done 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 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 1.6: Sample showing bad interface of the micro-filler with the base resin

1.2 Nanodielectrics

The first credible mention of nanodielectrics for the power 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 conventional dielectric material into which filler particles of few tens of nanometers in size have been introduced to form a well dispersed homogenous 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 nanofiller 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

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 nanofillers, 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. Nanofilled 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 intermediate or mesoscopic properties that belong neither to atomic nor macroscopic frame [19].

Nanofilled 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 last longer than what is available presently [20, 21]. They can be expected to provide improved performance when compared with conventional micro-filled materials, like superior dielectric strength, corona resistance and tracking and erosion resistance. These nano-filled 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 adequately understood [22-24]. 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. To understand better the distinct advantages that the nanofillers 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 nano-filled samples and theoretical models were developed to analyze the improvements due to addition of such nanofillers.

1.3 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 future work.
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 nano-filled 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 nanofillers, 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>
<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

Figure 2.2: SEM image on the FIB instrument. 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.

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.

![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 52º 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.

Figure 2.5: Sample with visible fillers after milling

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

2.3.2.1 SEM images

Figure 2.6: SEM image showing nanofillers

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 nanofillers was observed to be around 10-20 nm. Uniform dispersion of the nanofillers 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 nanofillers 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 nanofillers. Energy dispersive X-ray analysis (EDAX) was carried out at different locations on the surface confirming the filler to be silica.
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)
2.3.2.2 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.

![EDAX results](image)

Figure 2.9: EDAX results of a micro+nano-filled sample

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-Strain curves of all the samples are shown in Figure 2.12. The nano-filled samples (5% N and 2.5% N) have longer stress curves than the unfilled sample. Longer stress curves would mean a larger tensile strength value. The improvements in tensile strength due to addition of nanofillers could be due to restriction in the motion of polymer chain due to well-dispersed nanofillers [27]. The micro + nano-filled 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 2.12: Stress vs. Strain curves 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 + nano-filled 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 + nano-filled 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 (bars: mean, brackets: standard deviation)
3 Dielectric spectroscopy

3.1 Introduction

Dielectric spectroscopy is used as 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 relatively 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 left on the frequency scale. By doing temperature variations, one is able to attain permittivity values over a much wider range [29].

Spectroscopic dispersion of dielectric permittivity and associated energy absorption regions may be observed in a material over the frequency range 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 will depend markedly 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 dielectric 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 matrix-filler surface, while dipole polarization gives information as to how the bulk polymer is being affected [31, 32].
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.
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)

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 tanδ 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 tanδ plots show that there is a significant difference in the measured values of the unfilled and nano-filled samples when compared with the micro and micro + nano-filled samples. The lower values of permittivity and tanδ of nano-filled 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. The interaction between the silica 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.
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 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-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].

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
### 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% nano-filled 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 upto 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 a reduced 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 these two processes which happen in nanocomposites is not fully understood at this point. The real permittivity of the
micro + nano-filled 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 + nano-filled samples is overlapped by the interfacial polarization and hence is not visible.

Figure 3.8: Tanδ plots of studied epoxy samples at 233 K

### 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 TiO2-epoxy nanocomposites. In the micro + nano-filled 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 tan delta values for the micro-filled and the micro + nano-filled samples was found to be significant while significant differences in the tan delta 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

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 393K

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+nano-filled 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 ($\omega_c$). 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-$\omega_c$) beyond which there is a change in the slope of the real permittivity values. Figure 3.12 shows the same behavior for the micro+ nano-filled samples.

![Figure 3.11: Real and imaginary permittivity plots for sample 1 at 393K](image-url)
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, $L_c$, over which the cluster’s structural regularity 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 $L_c$, leading 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.

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 (Unfilled and 2.5% N sample do not demonstrate cross-over phenomena). 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 $\tan\delta$ 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].

Significant differences were seen in the permittivity plots of the micro, micro+nano-filled samples and unfilled, nano-filled samples. Significant reductions in the dielectric losses ($\tan\delta$) were seen for the micro+nano-filled 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 nanofillers.
4 Dielectric breakdown experiments

4.1 Breakdown in solid dielectrics

The loss of the dielectric property 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 of 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 formed using particulates of micron scale 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 obey this rule. This is because nano-particles 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] shows 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. In another result, Hu et al [51] shows that the 60 Hz AC electric strength in nanocomposites is marginally higher than base epoxy and significantly higher than
microcomposites. Reading et al [53] also 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 nanofillers.

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 × 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 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

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)

<table>
<thead>
<tr>
<th>0% filled</th>
<th>65% M</th>
<th>2.5% N</th>
<th>5% N</th>
<th>62.5% M + 2.5% N</th>
<th>60% M + 5% N</th>
<th>65% M + 5% N</th>
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<td>33.6</td>
<td>35</td>
<td>37.17</td>
<td>34.3</td>
<td>34.3</td>
<td>36.4</td>
<td>34.3</td>
</tr>
<tr>
<td>35.9</td>
<td>33.95</td>
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<td>43.4</td>
<td>32.9</td>
<td>37.9</td>
</tr>
<tr>
<td>32.55</td>
<td>37.8</td>
<td>38.35</td>
<td>38.15</td>
<td>36.4</td>
<td>33.6</td>
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<td>32.95</td>
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<td>28.19</td>
<td>36.97</td>
<td>33.68</td>
<td>31.07</td>
<td>30.8</td>
<td>29.25</td>
</tr>
</tbody>
</table>

Figure 4.2: SEM image of the surface of a punctured sample

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. 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 + nano-filled samples are shown in Figure 4.3. Figure 4.4 shows the same data for the unfilled and nano-filled 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 β value. No conclusion about the performance of the filled samples can be made from the breakdown test.

<table>
<thead>
<tr>
<th>Filler details</th>
<th>Scale parameter (α) (kV/mm)</th>
<th>Shape parameter (β)</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

Figure 4.5: Breakdown channels in the micro-nano sample (bulk)

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.
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 nano-filled 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.
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

![Schematic for corona resistance experiment](image)

Figure 5.2: Schematic for corona resistance experiment

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 gage blocks. The geometry and the electrodes used in this experiment are similar to the setup used by CIGRE Working Group [48].
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.
5.4 Observations and results

Figure 5.4: a) 5% nano-filled sample b) 0% unfilled sample

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+nano-filled 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

Figure 5.5: Erosion depth of the samples after every 100 hour duration measured with the surface profilometer

The erosion depth of the unfilled sample was found to be the greatest while that of the micro+nano-filled 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% nano-filled 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+nano-filled 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 5.6: Erosion depth of all the samples at the end of 500 h duration measured with the profilometer (bars: mean, brackets: standard deviation)
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 nanofillers 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 edge paths, 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 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 interfaces between the particle and the base resin. Addition of nano fillers would create an obstruction to degradation as the nanofillers are more discharge resistant as compared to the resin. Figure 6.2 shows an erosion pattern in a filled sample.
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 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 2 D 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.

6.2.1.1 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.

![Flowchart](image)

Figure 6.5: Flowchart representing the degradation model
6.3 Model results

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 nanofiller concentrations as compared to the range of actual samples that are available.

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 6.6: 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 45% micro and 5% nano-filled sample (left) and 100 batch runs of the sample (right)
Figure 6.8: Model generated 2D matrix representing a 15% nano-filled sample (left) and 100 batch runs of the sample (right).

Figure 6.9: Model generated 2D matrix representing a 15% nano-filled sample (left) and 100 batch runs of the sample (right).

Figure 6.10: Schematic showing the PD 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 nano-filled samples is due to the smaller size of nanofillers (three orders of magnitude smaller than conventional fillers) and small interparticle distances between the fillers.

Figure 6.11: Erosion path of all samples (bars: mean, brackets: standard deviation)
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 unfilled sample</td>
</tr>
<tr>
<td>4</td>
<td>Micro + nano-filled 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>Micro + nano-filled samples had longer erosion paths as compared to the microfilled sample for the same filler concentration (50% M, 45% M + 5% N, 40% M + 10% N and 35% M + 15% N)</td>
</tr>
</tbody>
</table>
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 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+ nano-filled 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 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 Infra-red (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 ($\alpha_1$) and specific heat ($C_p$), from which the thermal conductivity ($k$) of the sample with density $\rho$ is calculated using Equation (7.1)

$$k = \alpha_1 \times \rho \times C_p$$  \hspace{1cm} (7.1)

Once the sample has been stabilized at the desired temperature, the flash lamp is fired several times over a span of few minutes 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 0.5°C to 2°C. 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>
<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>

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>
<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>

The microfilled and the micro + nano-filled 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 nano-filled 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.
Improvements due to addition of nanofillers 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.

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

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].

<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 (k) (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:

\[ S/V = 3 \pi r^2 / (4 \pi r^3) \]

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 their high surface energies. 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 nanofillers that have good dispersion.
Figures 7.5 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 7.7: Temperature distribution of a 30% M sample

Figure 7.8: Temperature distribution of a 50% 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 nanofillers 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.

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
7.3.3 Discussion

The temperature distribution was quantified 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 calculated using the Equation 7.2 [73]. The equation is formulated for spherical particles.

\[ l = \left( \frac{\pi \sqrt{2}}{6v} \right)^{1/3} - 1 \]  \hspace{1cm} (7.2)

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>
<tr>
<td>7</td>
<td>5</td>
<td></td>
<td>58.3</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td></td>
<td>38</td>
</tr>
<tr>
<td>9</td>
<td>40</td>
<td>2.5</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>40</td>
<td>5</td>
<td>-</td>
</tr>
</tbody>
</table>

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.

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+ nano-filled 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.
For example, for a 1% N sample, the interparticle distance was calculated to be 128 nm. So, over a length of 1 µm, 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>
<tr>
<td>10</td>
<td>40% M + 2.5% N</td>
<td>748</td>
<td>252</td>
<td>187.8</td>
</tr>
<tr>
<td>11</td>
<td>40% M + 5% N</td>
<td>767</td>
<td>233</td>
<td>185</td>
</tr>
</tbody>
</table>
7.4 Thermo gravimetric analysis

Thermo gravimetric Analysis (TGA) measurements are conducted on unfilled nano-filled, microfilled and micro+nano-filled 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. The mass loss sensitivity is 1 microgram. The system uses a helium (He) atmosphere at a flow rate of 30 ml/min. The sample is held in a 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 + nano-filled 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 + nano-filled 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>
<tr>
<td>6</td>
<td>2.5% N</td>
<td>85.8</td>
</tr>
<tr>
<td>7</td>
<td>0%</td>
<td>87.6</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 nanofillers to the base epoxy resin. Stronger chemical bonding between the nanofillers 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 [33, 59].
8 Internal electric field calculations

Corona, which can cause electromagnetic interference, audible noise and physical deterioration of some insulating materials, can limit the performance of any configuration of electrical conductors and limit the voltage to which the line can be energized [74, 75, 76]. Thus, one of the primary principles of high-voltage hardware design is ensuring the system is corona-free under operating voltage.

With the development of new technologies, manufacturers have many more new materials from which to choose when addressing applications of interest to power utilities. For example, polymers and porcelains containing micron- to nanometer-sized elements can be used in the manufacture of various components such as insulators, bushings, instrument transformers, etc. These micro- and nano-materials promise significant improvement over other materials in terms of resisting corona.

Nano-particles provide a greater surface to volume ratio compared to micron-sized particles. However, the precise mechanism by which this enhances performance is still unclear. For nano-materials that are well dispersed in a background medium, the presence of nano-particles reduces the space available for the ionized electrons to accelerate and collide with other neutral molecules. This reduced space leads to fewer ionizing collisions, and thus may yield a higher breakdown voltage. However, a complete theory of this performance has not yet been developed.

The goal of this work is to develop a numerical model to calculate the electric field inside periodic array of cells. The cells themselves are inhomogeneous (but the in homogeneity is assumed to be the same from one cell to the next). The model attempts to incorporate the presences of nano-dielectrics in porcelain. Instead of calculating the field associated with the entire insulator (including the nano-materials), we calculate the field in a “column” of one or more cells. The “top” and “bottom” of the column are assumed to be at fixed potentials. The sides of the column are modeled using periodic boundary conditions. In this way, the horizontal periodicity of the structure can be modeled using a single line of cells, i.e., a column.
Figure 8.1: Array of particles in a periodic dielectric material. The top and bottom of the structure are assumed to be at fixed potentials. The periodicity is assumed to be infinite in the horizontal directions. A single cell of the array is shown to the side. Cells are inhomogeneous, but all cells are assumed to have the same inhomogeneities. In this report we assume a background material. Cells contain a spherical dielectric (red circle) which has an air-filled void adjacent to it. This void is indicated by the smaller circle that extends beyond the top of the red circle.

Figure 8.1 depicts the periodic array. Shown to the side is a single cell. Given the electric field, predictions can be made concerning the onset of partial discharges, a precursor to breakdown, using the theory described in [77] and [78]. Thus, it may be possible to introduce a theory regarding the effect of different particle size.

8.1 Numerical approach

We assume the fields are static and calculate them using the finite difference method (FDM) [79]. Finite difference techniques are based upon approximations that replace differential equations by finite difference equations. These finite difference approximations yield algebraic equations that relate the value of the dependent variable at a point to the values at neighboring points. The entire solution space is discretized into a grid of nodes where, in a three-dimensional space, every node is specified by a triplet of indices (i, j, k).

In a charge-free region, the integral form of Gauss’s law is

\[ \iiint_{S} \mathbf{D} \cdot d\mathbf{s} = \iiint_{S} \varepsilon \mathbf{E} \cdot d\mathbf{s} = 0 \]  

8.1
where $D$ is electric flux density, $E$ is electric field, $\varepsilon$ is the permittivity, and $S$ is the surface that bounds the region. Substituting $\mathbf{E} = -\nabla V$ into Eq. (2.1) gives

$$0 = \oiint_S \mathbf{E} \cdot \mathbf{ds} = \oiint_S \varepsilon \frac{\partial V}{\partial n} \mathbf{\hat{n}} \cdot \mathbf{ds} \tag{8.2}$$

where $\mathbf{\hat{n}}$ is a unit vector normal to $S$.

Turning now to a discretized world, let us assume the surface $S$ is a cube as depicted in Fig. 8.1. Each face of the cube is half way between a pair of nodes. The nodes are separated by a distance $\Delta$. If one assumes the fields are constant over each of the six faces, a suitable approximation of Eq. (8.2) is

Figure 8.2: Three dimensional finite difference grid node $(i,j,k)$ and its neighbors.
where \( \epsilon_{\text{var}} \) is the average dielectric constant over a face of the cube where \( \text{var} \in \{\text{left}, \text{right}, \text{front}, \text{back}, \text{top}, \text{bottom}\} \). Rearranging terms yields

\[
0 = \epsilon_{\text{left}} \frac{V(i - 1, j, k) - V(i, j, k)}{\Delta} \Delta^2 + \epsilon_{\text{right}} \frac{V(i + 1, j, k) - V(i, j, k)}{\Delta} \Delta^2 + \\
\epsilon_{\text{front}} \frac{V(i, j - 1, k) - V(i, j, k)}{\Delta} \Delta^2 + \epsilon_{\text{back}} \frac{V(i, j + 1, k) - V(i, j, k)}{\Delta} \Delta^2 + \\
\epsilon_{\text{bottom}} \frac{V(i, j, k - 1) - V(i, j, k)}{\Delta} \Delta^2 + \epsilon_{\text{top}} \frac{V(i, j, k + 1) - V(i, j, k)}{\Delta} \Delta^2 
\]

where \( \epsilon_{\text{self}} = \sum_S \epsilon_{\text{var}} \).

The domain is assumed to have a fixed potential at the “top” and “bottom” boundaries. For nodes adjacent to these boundaries, one of the voltages in Eq. (8.4) will be a known (given) value. For nodes at the side of the computational domain, the periodic boundary condition allow one to specify that the voltage associated with a node that is actually outside of the domain is given by the voltage at a node at the other side of the interior.

Combining Eq. (8.4) for all free nodes \((i, j, k)\) in the grid results in a set of simultaneous equations of the form

\[
[A][x] = [b] 
\]

where \([A]\) is a sparse matrix, \([x]\) is a column matrix consisting of the unknown values of \(V(i, j, k)\) at the free nodes, and \([b]\) is a column matrix containing the known values at the top and bottom boundaries of the domain. The sparse matrix \([A]\) is banded in that its nonzero terms appear clustered near the main diagonal. Matrix \([x]\), representing the voltage distribution of the grid, is obtained from

\[
[x] = [A]^{-1}[b]. 
\]
There are several methods to invert the matrix \([A]\). One of the most popular software packages for working with sparse matrices is SuiteSparse by Tim Davis [80]. However, many of the direct inversion methods in this package require excessive memory even for grids with a relatively modest size of \(100 \times 100 \times 100\) nodes. Instead of directly inverting \([A]\), an iterative approach can be used that avoids the memory problems associated with direct inversion. The conjugate gradient technique is an iterative approach that is applicable to symmetric positive definite systems. The method proceeds by generating vector sequences of iterates (i.e., successive approximations to the solution), residuals corresponding to the iterates, and search directions used to update the iterates and residuals [81]. Though in our system \([A]\) is symmetric, but not necessarily positive definite, this method converges to the correct solution.

### 8.2 Simulation results

Using the numerical model discussed above, periodic material is initialized with background material corresponding to an epoxy resin with \(\epsilon_0 = 4.0\), the red spheres shown in Fig. 1.1 correspond to silicon dioxide (nano-fiber) with \(\epsilon_1 = 3.9\), and the void has \(\epsilon_2 = 1.0\). Simulation results are obtained with various resolutions (points per cell). We also consider two different locations of the void: either on the top of the silicon dioxide sphere or on the side, where the silicon dioxide sphere resides in the center of the periodic cell.

#### 8.2.1 Validation of iterative method

In Matlab (version 7.9 and above), when matrix \([A]\) is sparse and rectangular, SuiteSparseQR is the default method for calculating \([x] = [A]\backslash[b]\) [7] (the Matlab backslash operator is such that \([A]\backslash[b]\) is functionally equivalent to \([A]^{-1}[b]\) but the inverse of \([A]\) is never explicitly obtained). We compared the results obtained from our preconditioned conjugate gradient (PCG) iterative method [81] with those obtained from Matlab using \([A] / [b]\).

The calculation corresponded to an overall grid size of \(101 \times 101 \times 101\) (with indices from 0 to 100). The silicon dioxide sphere was centered at \((50, 50, 50)\) with a radius of 30 points. The void corresponded to the portion of a sphere that was outside of the silicon when the sphere was centered at \((50, 50, 75)\) with a radius of 15 points. The voltage at the top of the cell is set to 1 V and is fixed at 0 V at the bottom of the cell. As will be discussed, the potentials used at the boundaries are unimportant since the results can be scaled in accordance with whatever the true boundary values are. Similarly, the spacing between the nodes (\(\Delta\)) can be scaled to any desired value.
Figure 8.3: Results obtained using Matlab and the PCG method.

Figure 8.3 shows a plot of the results obtained from Matlab and from the iterative PCG approach. The results appear identical. The maximum difference between these results is on the order of $10^{-6}$. This demonstrates the PCG method can be used to solve for these fields (and can be used to solve much larger problems than can be obtained with direct matrix inversion).

### 8.2.2 Finite to infinite approximation

We previously mentioned that a column of cells can be used to model the fields within the periodic material. To prove this point, a series of simulations is conducted with 1, 2, 3, 4, 5, and 10 cells stacked together along the z direction. The resulting voltage is shown in Fig. 8.4 and the corresponding z component of the electric field is shown in Figure 8.5.
Figure 8.4: Voltage along a z-oriented line through the center of the grid.
Figure 8.5: The z component of the electric field along a z-oriented line through the center of the grid. These points correspond to those of Fig. 3.2.

Each cell is discretized using $401 \times 401 \times 401$ nodes. Interestingly, for multi-cell simulations (i.e., models of columns of cells with two or more cells), the electric field associated with the first cell is nearly independent of the total number of cells. More generally, for an n-cell simulation (where n is 2, 3, 4, or 5), the electric field for the first $n - 1$ cells coincided with the field found in the first $n - 1$ cells of the 10-cell simulation. The one-cell simulation is unique because it is bound by fixed voltages at both the top and bottom of the cell. Nevertheless, regardless of how many cells are used, the field in the void is nearly the same in all the simulations. (In terms of corona onset [highest electric fields], the worst-case scenario corresponds to the fields in the bottom cell of a two-cell column).

The similarity of the fields in the various cells is demonstrated by the plots shown in Figs. 8.6 and 8.7. Figures 8.6 and 8.7 show the z component of the electric field along a z-oriented line from the bottom to the top of each cell. In this case the bottom of each cell is assigned an index of zero. Thus there are 10 separate plots, each of which spans from the bottom to the top of its respective cell. In Fig. 8.6, where the void is at the top of the sphere, we see that, other than at the bottom of the first cell and near the top of the tenth cell, all the cells have nearly the same field. In Fig. 8.7, where the void is on the side of the sphere, essentially all the cells have the same electric field.
Figure 8.6: The z component of the electric field in each of the ten cells in a 10-cell simulation. The void is on the top.
8.3 Electric field distribution

The previous analysis shows we can use the first cell of a 2-cell simulation to approximate an infinite periodical material. From this, we can determine the corona onset condition. Due to limits on the available memory, each cell has at most 701 points in each dimension. Figure 8.8 shows the z component of the electric field in the yz-plane when the x index is held at 350 (i.e., this is a vertically oriented plane that slices through the center of the domain). The void starts at a z-index of 561 and ends at 630, with a total length of 69 points in the z direction.
Another scenario worth considering is when the void is on the side of the silicon sphere. As indicated in Fig. 8.9, it appears electrons have a longer free path in this void than when the void is at the top of the sphere. (Assuming the electric field is held fixed, a longer free path leads to corona.)
8.4 Corona onset condition analysis

After determining the potential throughout the computational domain, we use the voltage in the first cell \((V(i, j, k) \text{ where } 0 \leq i, j, k \leq 700)\) to analyze the corona onset condition. In particular, the electric field \(E_z(i, j, k) = (V(i, j, k+1) - V(i, j, k)) / z\) is obtained, where \(z\) is the distance between two adjacent nodes in the \(z\) direction. Note that \(V(i, j, k)\) and \(E_z(i, j, k)\) are the “normalized” voltage and electric field because the voltage between the top and the bottom boundaries of the two-cell simulation is set to 2 V (0 V on the bottom boundary and 2 V on the top boundary). Because the simulation involves the solution of a linear system of equations, we can scale \(V(i, j, k)\) (and hence \(E(i, j, k)\)) by an arbitrary constant \(C_s\) in order to simulate the domain being bound by any voltage. Correspondingly, the dimension associated with the distance between nodes can be scaled to any value.
The ionization coefficient and attachment coefficient developed by Sarma and Janischewskyj [82] are continuous approximations to the work of Mauch [83], Sander [84], and Harrison and Geballe [85]. The resulting expressions are

\[
\frac{\alpha}{\delta} = \begin{cases} 
3632 \exp \left(-168.0 \frac{\delta}{E}\right) & 1.9 < \frac{E}{\delta} < 45.6, \\
7385 \exp \left(-200.8 \frac{\delta}{E}\right) & 45.6 < \frac{E}{\delta} < 182.4, 
\end{cases} \tag{8.7}
\]

\[
\frac{\eta}{\delta} = 9.9865 - 0.541 \times 10^{-3} \frac{E}{\delta} + 1.118 \times 10^{-8} \left(\frac{E}{\delta}\right)^2, \tag{8.8}
\]

where

\[
\delta = \frac{p}{101.3 \times 10^3 \cdot 273 + T}, \tag{8.9}
\]

\(p\) is pressure in Pascals, and \(T\) is temperature in Celsius. We can also find the ratio of the number of free electrons at the end of the void to the number at the start of the void via [78]:

\[
K^* = \exp \left(\int (\alpha - \eta) ds\right) = \exp \left(\sum_{\text{void, end}} (\alpha(i, j, k) - \eta(i, j, k)) \Delta z_j\right) \tag{8.10}
\]

A value of \(K_*\) of 3500 is considered to correspond to the onset of corona. This value was found to give the best agreement with experimental ac corona onset data reported by [86, 87] over the range of 0.05 cm to 2 cm for a coaxial geometry. Using Eqs. 8.7 – 8.10, where we assume the maximum value for \(\alpha\) and the minimum value for \(\eta\) for which these equations remain valid, the minimum length of the void necessary for corona is approximately 30 \(\mu\)m. Thus we consider the amount of field necessary for corona onset for voids on the top that have lengths of 50, 100, 150, 200, 250, and 300 \(\mu\)m. Additionally, we consider the same voids when they are on the side of the spheres instead of on the top.
Based on the results shown in Fig. 8.10 and Table 8.1, we can conclude that, regardless of whether the void is on the top or the side, the smaller the cell size, the higher the corona onset electric field. This is because the larger cells provide a greater void length for electrons to avalanche. However, when the void is on the side, the corona onset is typically at a higher electric field (compared to when the void on the top) even though this geometry has a longer free path. The reason is the electric field inside the void on the side is lower than the void on the top. However, at the smallest dimension considered, the void on side has the lower fields associated with corona onset. Thus, as the dimension is further reduced, the void along the side may be the more important one.
8.5 Summary

A numerical model was developed that solves a sparse system of equations using the preconditioned conjugate gradient iterative method. This model was used to solve for the electric field in a material consisting of a periodic distribution of micro- and nano-dielectric particles. The simulations included a void region adjacent to the particles. The computational domain was discretized using 700 points along each of the three dimensions. The electric field was then used to predict the corona onset condition for different particle sizes and also for different locations of the void. Results show that smaller particle sizes have higher corona onset electric field. These results could be used as a guideline for the design of future high-voltage periodic material.
9 Conclusions and future work

9.1 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 (tanδ) for the micro+ nano-filled 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 nanofillers 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.

9.2 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


[61] Morshuis, P. H. F. 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.


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.

![Diagram of guard ring setup](image)

Figure A.1: Schematic of the guard ring setup

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 the fringing would be in error. 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 the guard rings are:

1. Errors in the 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 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 guard-ring to avoid fringing.
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 δ 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 tan δ 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+ nano-filled samples up to 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)

Figure B.2: Fisher's LSD test
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.
Appendix C: Degradation measurements and error corrections

C.1: Degradation measuring equipments

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.

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 6.4 shows the degradation on a 62.5% M + 2.5% N sample measured after 500 hours using a profilometer, while Figure C.1 shows the degradation measured using an interferometer.

![Figure C.0.1: Surface degradation of 62.5% M + 2.5% N sample measured after 500 hours. Localized erosion depth: 10 µm](image)

Figure C.0.1: Surface degradation of 62.5% M + 2.5% N sample measured after 500 hours. Localized erosion depth: 10 µm
Figure C.0.2: Surface degradation of 62.5% M + 2.5% N sample after 500 hours using the interferometer. Average erosion depth: 5 µm
C.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 6.6 shows the surface degradation of the glass sample measured with a profilometer.

Figure C.3: Surface degradation of the glass slide. Erosion depth: 0 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 C.4 shows the initial degradation of a 65% M sample before exposing it to corona.
Figure C.4: Initial degradation depth of 65% M sample. Average erosion depth: 1.5 μm