INFLUENCE OF SURFACE MODIFICATION OF BaTiO₃ NANO-
PARTICLES ON THE DIELECTRIC PROPERTIES OF Ba-
TiO₃/EPOXY COMPOSITE FILMS

By

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ABSTRACT OF THE DISSERTATION


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Polymer-Ceramic nanocomposite dielectric films have received a lot of attention recently due to the flexibility and the ease of processing of polymers coupled with the functional properties of the ceramic nanoparticles. However, a common problem associated with inorganic-organic composites is the inherent incompatibility of the two materials. BaTiO$_3$, which is the ceramic nanoparticle of interest is hydrophilic, that is it has an affinity to water due to the presence of hydroxyl groups on its surface. On the other hand the epoxy matrix and organic solvent are hydrophobic, that is they repel water. This leads to the separation of the BaTiO$_3$ nanoparticles and the epoxy matrix creating an inhomogeneous dispersion, which is not ideal. In addition, the ceramic nanoparticles tend to agglomerate due to van der Waals attractive forces resulting in the formation of particle clusters within the epoxy matrix and leading to inhomogeneous distribution. Two methods used to overcome this attractive force are electrostatic stabilization, which involves developing a
charge on the surface of the particle so that they begin to repel each other and steric stabilization, which reduces the surface energy of the particle by bonding with a surfactant or coupling agent.

This work seeks to understand the influence of surface modification of the BaTiO$_3$ nanoparticles in composite dielectrics where the dielectric permittivity, leakage current and dissipation are studied to achieve optimal dielectric performance of these composites. The BaTiO$_3$ nanoparticles were surface treated using (i) ethanol and (ii) silane coupling agent to aid in uniform distribution of the particles within the epoxy matrix. The Ba-TiO$_3$/epoxy composite films were fabricated using a modified sol-gel method and were spin-coated onto stainless steel substrates followed by curing at 75°C for 8 hours in air. The samples were then corona poled at 30 kV/mm for 30 mins. The piezoelectric strain coefficients $d_{33}$ and $d_{31}$ were measured for all the samples, along with the real and imaginary permittivity, electrical resistivity and conductivity and dielectric breakdown strength and leakage current. Energy Dispersive X-Ray Spectroscopy (EDS) and Scanning Electron Microscopy (SEM) micrograph images were taken to investigate the surface morphology and particle distribution, respectively.

This work identified that the ideal volume fraction of the coupling agent for the surface treatment of the BaTiO$_3$ nanoparticles was determined to be 0.020. The volume fraction of BaTiO$_3$ that yielded the highest dielectric and piezoelectric properties was 50%. The piezoelectric strain coefficients $d_{33}$ and $d_{31}$ for the samples that were prepared using SCA 0.02 for 0.5 volume fraction of BaTiO$_3$ was found to be 1.16 pC/N and 2.65 pC/N, respectively. The dielectric constant was recorded to be 48.03 at 20 MHz, a low
conductivity value of $2.38 \times 10^{-4}$ S/m and a high breakdown strength of 85 kV/Cm was recorded for this composite type.
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Dedication

This dissertation is dedicated to my beloved parents, Sundar and Usha, and my lovely sister, Uthra for this would not have been possible without their love and support. This dedication also goes out to the newest member of the family, my dearest niece, Dyuti.
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SCA. The maximum value is 1.89 pC/N and occurs at 0.4 volume fraction of BaTiO$_3$.

**Figure 5.72:** The piezoelectric strain coefficient, $d_{31}$, for the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.020 SCA. The maximum value is 3.11 pC/N and occurs at 0.6 volume fraction of BaTiO$_3$.

**Figure 5.73:** The piezoelectric strain coefficient, $d_{31}$, for the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.025 SCA. The maximum value is 2.38 pC/N and occurs at 0.4 volume fraction of BaTiO$_3$.

**Figure 5.74:** The piezoelectric strain coefficient, $d_{31}$, for the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were untreated, surface modified by 0.01 SCA, 0.015 SCA, 0.02 SCA and 0.025% SCA. The maximum $d_{31}$ values are 0.86, 2.18, 1.89, 3.11 and 2.38 pC/N at volume fractions of 0.6, 0.6, 0.5, 0.5 and 0.4, respectively.

**Figure 5.75:** The real permittivity of the BaTiO$_3$-epoxy composite that were fabricated using untreated BaTiO$_3$ nanoparticles is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 10% to 60%. This value at 20 MHz attains a maximum of 28.70 at 60% volume fraction of BaTiO$_3$.

**Figure 5.76:** The dielectric loss of the BaTiO$_3$-epoxy composite that were fabricated using untreated BaTiO$_3$ nanoparticles is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6. The maximum dielectric loss at 20 MHz was recorded to be 11.06 at a volume fraction of 0.6 of BaTiO$_3$.

**Figure 5.77:** The dissipation factor of the BaTiO$_3$-epoxy composite that were fabricated using untreated BaTiO$_3$ nanoparticles is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6. The maximum dissipation factor at 20 MHz was recorded to be 0.3836 at a volume fraction of 0.6 of BaTiO$_3$.

**Figure 5.78:** The real permittivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.010 SCA is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6.

**Figure 5.79:** The dielectric loss of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.010 SCA is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6. The maximum value is 2.05 for BaTiO$_3$ at 0.5 volume fraction. The imaginary permittivity increases with increasing volume fraction of BaTiO$_3$ nanoparticles and increases with increasing frequency. With increasing frequency, there are less contributing factors to the real permittivity do the delayed response of these orientations.

**Figure 5.80:** The dissipation factor of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.010 SCA is plotted as a
function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6. The maximum value is 0.1106 for BaTiO$_3$ at 0.5 volume fraction.

**Figure 5.81:** The real permittivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6.

**Figure 5.82:** The dielectric loss of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6. The maximum value is 1.60 for BaTiO$_3$ at 0.6 volume fraction.

**Figure 5.83:** The dissipation factor of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6. The maximum value is 0.087 for BaTiO$_3$ at 0.6 volume fraction. The imaginary permittivity increases with increasing volume fraction of BaTiO$_3$ nanoparticles and increases with increasing frequency. With increasing frequency, there are less contributing factors to the real permittivity do the delayed response of these orientations.

**Figure 5.84:** The real permittivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.020 SCA is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6.

**Figure 5.85:** The dielectric loss of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.020 SCA is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6. The maximum value is 5.89 for BaTiO$_3$ at 0.6 volume fraction.

**Figure 5.86:** The dissipation factor of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.020 SCA is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6. The maximum value is 0.136 for BaTiO$_3$ at 0.6 volume fraction.

**Figure 5.87:** The real permittivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.025 SCA is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6.

**Figure 5.88:** The dissipation factor of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.025 SCA is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6. The maximum value is 3.26 for BaTiO$_3$ at 0.6 volume fraction.

**Figure 5.89:** The dissipation factor of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.025 SCA is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6. The maximum value is 0.119 for BaTiO$_3$ at 0.6 volume fraction.
Figure 5.90: Comparison of the relative permittivity of the theoretical models with different experimental results, where the readings were taken at 20MHz for the composites that were prepared using 0.5 volume fraction of BaTiO$_3$.

Figure 5.91: The resistivity of the BaTiO$_3$-epoxy composites that were fabricated using BaTiO$_3$ nanoparticles which were not surface treated (pristine) is plotted as a function of frequency. The maximum resistivity recorded at 20MHz was 4.20 ohm-m which corresponds to the composites containing 10% of BaTiO$_3$.

Figure 5.92: The resistivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.010 SCA is plotted as a function of frequency. The maximum resistivity recorded at 20MHz was 22.08 ohm-m which corresponds to the composites containing 0.1 of BaTiO$_3$.

Figure 5.93: The resistivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA is plotted as a function of frequency. The maximum resistivity recorded at 20MHz was 24.26 ohm-m which corresponds to the composites containing 0.5 of BaTiO$_3$.

Figure 5.94: The resistivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.02 SCA is plotted as a function of frequency. The maximum resistivity recorded at 20MHz was 39.76 ohm-m which corresponds to the composites containing 0.5 of BaTiO$_3$.

Figure 5.95: The resistivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.02 SCA is plotted as a function of frequency. The maximum resistivity recorded at 20MHz was 58.22 ohm-m which corresponds to the composites containing 0.4 of BaTiO$_3$.

Figure 5.96: The conductivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were not surface treated (pristine) is plotted as a function of frequency. The maximum value of conductivity at 20 MHz is $7.84 \times 10^{-4}$ S/m and occurs at BT 0.6.

Figure 5.97: The conductivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.010 SCA is plotted as a function of frequency. The maximum value of conductivity at 20 MHz is $4.63 \times 10^{-4}$ S/m and occurs at BT 0.6.

Figure 5.98: The conductivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA is plotted as a function of frequency. The maximum value of conductivity at 20 MHz is $4.36 \times 10^{-4}$ S/m and occurs at BT 0.6.

Figure 5.99: The conductivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.020 SCA is plotted as a function of frequency. The maximum value of conductivity at 20 MHz is $2.38 \times 10^{-4}$ S/m and occurs at BT 0.6.
**Figure 5.100:** The conductivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.025 SCA is plotted as a function of frequency. The maximum value of conductivity at 20 MHz is $2.58 \times 10^{-4}$ S/m and occurs at BT 0.6. 

**Figure 5.101:** Substitution of the hydroxyl groups due to the surface modification with the silane coupling agent. This leads to a decrease in conductivity as there is no more water adsorbed on the surface of the BaTiO$_3$ nanoparticle.

**Figure 5.102:** The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.1 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.010 SCA is plotted as a function of increasing electric field. The maximum polarization at 30 kV/cm value was recorded to be 0.01 µC/cm$^2$.

**Figure 5.103:** The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.2 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.010 SCA is plotted as a function of increasing electric field. The polarization value increases with increasing electric field, where the highest polarization value was recorded to be 0.05 µC/cm$^2$ for the sample at 70 kV/cm.

**Figure 5.104:** The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.3 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.010 SCA is plotted as a function of increasing electric field. The polarization increases with increasing electric field as a result of more number of dipoles being reoriented. The maximum recorded polarization value is 0.02 µC/cm$^2$ and occurs at 40 kV/cm.

**Figure 5.105:** The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.4 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.010 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.05 µC/cm$^2$ and occurs at 50 kV/cm.

**Figure 5.106:** The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.5 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.010 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.02 µC/cm$^2$ and occurs at 40 kV/cm.

**Figure 5.107:** The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.6 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.010 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.02 µC/cm$^2$ and occurs at 35 kV/cm.

**Figure 5.108:** The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.1-0.6 volume fraction of BaTiO$_3$ nanoparticles, which were surface modified using 0.010 SCA is plotted as a function of increasing electric field. The maximum permissible electric field is 69.80 kV/cm and the corresponding polarization was 0.05 µC/cm$^2$. 

xxv
Figure 5.109: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.1 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.014 µC/cm$^2$ and occurs at 45 kV/cm.

Figure 5.110: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.2 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA is plotted as a function of increasing electric field. The maximum electric polarization is 0.09 µC/cm$^2$ corresponding to a field of 69.91 kV/cm.

Figure 5.111: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.3 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.04 µC/cm$^2$ and occurs at 50 kV/cm.

Figure 5.112: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.4 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.2 µC/cm$^2$ and occurs at 70 kV/cm.

Figure 5.113: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.5 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.13 µC/cm$^2$ and occurs at 80 kV/cm.

Figure 5.114: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.6 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.03 µC/cm$^2$ and occurs at 50 kV/cm.

Figure 5.115: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.1-0.6 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA is plotted as a function of increasing electric field. The maximum permissible electric field is 80.19 kV/cm with a corresponding polarization of 0.14 µC/cm$^2$.

Figure 5.116: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.1 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.020 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.1326 µC/cm$^2$ and occurs at 80 kV/cm.

Figure 5.117: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.2 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.020 SCA is plotted as a function of increasing electric field. The maximum electric polarization is 0.09817 µC/cm$^2$ corresponding to a field of 79.74 kV/cm.

Figure 5.118: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.3 volume fraction of BaTiO$_3$ nanoparticles which were surface modified
using 0.020 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.109 µC/cm\(^2\) and occurs at 70 kV/cm.

**Figure 5.119:** The electric polarization of the BaTiO\(_3\)-epoxy composite that were fabricated using 0.4 volume fraction of BaTiO\(_3\) nanoparticles which were surface modified using 0.020 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.3562 µC/cm\(^2\) and occurs at 85 kV/cm.

**Figure 5.120:** The electric polarization of the BaTiO\(_3\)-epoxy composite that were fabricated using 0.5 volume fraction of BaTiO\(_3\) nanoparticles which were surface modified using 0.020 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.1456 µC/cm\(^2\) and occurs at 70 kV/cm.

**Figure 5.121:** The electric polarization of the BaTiO\(_3\)-epoxy composite that were fabricated using 0.6 volume fraction of BaTiO\(_3\) nanoparticles which were surface modified using 0.020 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.096 µC/cm\(^2\) and occurs at 85 kV/cm.

**Figure 5.122:** The electric polarization of the BaTiO\(_3\)-epoxy composite that were fabricated using 0.1-0.6 volume fraction of BaTiO\(_3\) nanoparticles which were surface modified using 0.020 SCA is plotted as a function of increasing electric field. The maximum permissible electric field is 84.92 kV/cm and the corresponding polarization value is 0.356 µC/cm\(^2\).

**Figure 5.123:** The electric polarization of the BaTiO\(_3\)-epoxy composite that were fabricated using 0.1 volume fraction of BaTiO\(_3\) nanoparticles which were surface modified using 0.025 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.09 µC/cm\(^2\) and occurs at 90 kV/cm.

**Figure 5.124:** The electric polarization of the BaTiO\(_3\)-epoxy composite that were fabricated using 0.2 volume fraction of BaTiO\(_3\) nanoparticles which were surface modified using 0.025 SCA is plotted as a function of increasing electric field. The maximum electric polarization is 0.25504 µC/cm\(^2\) corresponding to a field of 89.93 kV/cm.

**Figure 5.125:** The electric polarization of the BaTiO\(_3\)-epoxy composite that were fabricated using 0.3 volume fraction of BaTiO\(_3\) nanoparticles which were surface modified using 0.025 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.114 µC/cm\(^2\) and occurs at 80 kV/cm.

**Figure 5.126:** The electric polarization of the BaTiO\(_3\)-epoxy composite that were fabricated using 0.4 volume fraction of BaTiO\(_3\) nanoparticles which were surface modified using 0.025 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.1402 µC/cm\(^2\) and occurs at 80 kV/cm.

**Figure 5.127:** Cross-sectional images of the BaTiO\(_3\)/epoxy composite prepared using 0.025 SCA and at 0.5 volume fraction of BaTiO\(_3\). It is interesting to note that the delamination occurs for the entire film from the substrate i.e. the film in itself remains cohesive and crack-free. However this makes it difficult to successfully pole the composite.
Figure 5.128: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.5 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.025 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.023 µC/cm$^2$ and occurs at 60 kV/cm.

Figure 5.129: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.6 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.025 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.022 µC/cm$^2$ and occurs at 50 kV/cm.

Figure 5.130: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.1-0.6 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.025 SCA is plotted as a function of increasing electric field. The maximum permissible electric field is 89.93 kV/cm and the corresponding polarization value was 0.255 µC/cm$^2$.

Figure 5.131: Leakage current measurements of the composite prepared using 0.5 volume fraction of untreated or pristine BaTiO$_3$ nanoparticles that were taken at a constant electric field of 10 kV/cm for 1000 ms. The steady state current after 1000ms was recorded to be 3.37E-7 Amps.

Figure 5.132: Leakage current measurements of the composite prepared using 0.5 volume fraction of ethanol surface treated (4 hours) BaTiO$_3$ nanoparticles that were taken at a constant electric field of 10 kV/cm for 1000 ms. The steady state current after 1000ms was recorded to be 5.40E-7 Amps.

Figure 5.133: Leakage current measurements of the composite prepared using 0.5 volume fraction of 0.010 silane coupling agent BaTiO$_3$ nanoparticles that were taken at a constant electric field of 10 kV/cm for 1000 ms. The steady state current after 1000ms was recorded to be 3.54E-8 Amps.

Figure 5.134: Leakage current measurements of the composite prepared using 0.5 volume fraction of 0.015 silane coupling agent BaTiO$_3$ nanoparticles that were taken at a constant electric field of 10 kV/cm for 1000 ms. The steady state current after 1000ms was recorded to be 9.14E-11 Amps.

Figure 5.135: Leakage current measurements of the composite prepared using 0.5 volume fraction of 0.020 silane coupling agent BaTiO$_3$ nanoparticles that were taken at a constant electric field of 10 kV/cm for 1000 ms. The steady state current after 1000ms was recorded to be 1.02E-12 Amps.

Figure 5.136: Leakage current measurements of the composite prepared using 0.5 volume fraction of 0.025 silane coupling agent BaTiO$_3$ nanoparticles that were taken at a constant electric field of 10 kV/cm for 1000 ms. The steady state current after 1000ms was recorded to be 1.79E-9 Amps.

Figure 5.137: A comparison of the leakage current characteristics of the BaTiO$_3$ (0.5)-epoxy composite using untreated, ethanol surface treated (4 hours), SCA 0.01, SCA 0.015, SCA 0.020 and SCA 0.025 BaTiO$_3$ nanoparticles. It was observed that the leakage current
reduced with surface treatment using ethanol and silane coupling agent. This reduction in leakage current can be attributed to reduced conductivity at the interface due to the substitution of hydroxyl groups on the surface of the BaTiO₃ nanoparticle.

**Figure 5.138:** SCA 0.020 BT(0.5)/epoxy composites fabricated at different viscosities starting **A)** from 148 mPas up to 282 mPas; **B)** Composites fabricated between 200 mPas and 282 mPas, it can be seen that with increasing viscosities sample begins to curve, making it inflexible and prone to delamination. The increase in viscosity led to an increase in thermal mismatch between the composite film and the substrate i.e. between the BaTiO₃ ceramic and stainless steel.

**Figure 5.139:** SEM micrograph images showing the fractured cross section of the SCA 0.020 BT(0.5)/epoxy composite at different viscosities; **A)** sample viscosity is 282 mPas, showing signs of delamination at the electrode-composite interface, **B)** sample viscosity is 220 mPas, showing brief signs of voids existing at the interface and **C)** 180 mPas – good adhesion at the interface.

**Figure 5.140:** Piezoelectric strain coefficient, d₃₃ of the BaTiO₃-epoxy composite fabricated using BaTiO₃ nanoparticles that were surface treated at 0.020 SCA plotted as a function of sol viscosity. The piezoelectric strain coefficient was recorded to be 1.3 pC/N at optimum viscosity i.e. 180 mPas.

**Figure 5.141:** Relative permittivity of the BaTiO₃-epoxy composite fabricated using BaTiO₃ nanoparticles that were surface treated at 0.020 SCA plotted as function of sol viscosity. The value of permittivity was recorded to be 50.02 at optimum viscosity i.e. 180 mPas.

**Figure 6.1:** A schematic diagram representing a capacitor network comprised of multiple arrays of two-phase BaTiO₃-epoxy nanocomposites sandwiched by stainless steel electrodes. These composites are made using silane coupling agent treated (0.02 v/v) BaTiO₃ nanoparticles. These formed capacitors can then be tested by charging and discharging the capacitors.

**Figure 6.2:** The charging and discharging of the capacitor using a DC voltage source and the voltage readings recorded using an Agilent Technologies Oscilloscope DSC 1004A. This circuit includes a breadboard for the circuitry and two switches that can independently charge and discharge the capacitor.

**Figure 6.3:** The voltage during charging of the capacitor was recorded using an Agilent Technologies Oscilloscope DSC 1004A and was found to be 5.44V.
# Nomenclature

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Chapter 1

Introduction

1.1 Research Goal

Ferroelectric-polymer composites with high permittivity have attracted attention because they are relatively easy to process and can be applied as dielectric energy storage materials in capacitors [1]. In order to attain high permittivity, researchers have investigated adding electrically conductive particles into polymer matrices to form percolating networks and adding micron-sized ferroelectric ceramic fillers such as barium titanate (BaTiO$_3$) and PZT into polymer matrices [1]. According to percolation theory [2], high permittivity can be obtained in the composite when the electrically conductive filler volume fraction reaches a critical or threshold. However, this method of achieving high permittivity is has limitations because it is difficult to control the dispersion of the electrically conductive fillers within the polymer matrix. Composites such as these also suffer from high dielectric loss and very low dielectric breakdown strength due to the high electrical conductivity of the fillers [1, 2], which influences the effective properties of the composite. The addition of micron-sized ceramic fillers such as BaTiO$_3$ and PZT into polymer matrices can also lead to very high permittivity values (BaTiO$_3$ ~ 100 [3], and PZT ~ 134 [4] and 95 [5]) however, in order to realize such values, high filler loading is required. This leads to difficulty in processing the composite due to agglomeration of the filler particles and deterioration in the mechanical and dielectric properties [1].
A possible solution to both problems would be to explore polymer-based nanocomposites, wherein nanoparticles are dispersed into polymer matrices. This type of nano-composite is amongst the most attractive of materials because it combines the benefits of the polymer with the functional properties of the nanoparticles. Nano-sized inorganic particles can exhibit fascinating size-controlled electrical and mechanical properties [6-8]. By incorporating nanoparticles into a polymer matrix there can be several advantages namely, (i) increased breakdown strength, (ii) enhanced voltage endurance and (iii) suppression of the space charges associated with contact of the film with the electrode lead to accumulation of trapped charges in the dielectric medium [9-11] (which is more pronounced in micron sized particles) and (iv) enhancement of the partial discharge resistance of dielectric polymer [12-16].

Some of the disadvantages associated with nanoparticles are that a high filler loading (>50%) is required to achieve high permittivity values [17-21] whereas researchers have found that micron-sized BaTiO$_3$ can exhibit similar permittivity values at lower volume fractions [22-24]. Nanoparticles also have the proclivity to agglomerate within the polymer matrix. These clusters lead to the formation of voids and pores within the composite, thereby lowering permittivity and increasing the dielectric loss of the composite. Hence, an optimum amount of polymer is necessary to completely wet the particles. Low polymer volume fractions result in a low dielectric constant that may be attributed to residual porosity of the composites [25-27]. The tendency of nanoparticles to form clusters may be due to the high surface area to volume ratio of nanoparticles that can lead to high surface energy and attractive van der Waals forces between like particles [25, 28]. The surface energy is defined as the sum of all intermolecular forces that are on the surface of a material [28, 29], the degree of attraction or repulsion force of a material surface
exerts on another material, i.e. it is the excess amount of energy at the surface of a material compared to the bulk. Atoms at the surface are less tightly bound and hence possess higher surface energy, and because breaking bonds costs energy, surface atoms always have higher energy than atoms in the bulk, where nanoparticles have a fraction of their atoms on the surface [25, 30]. In order to diminish the high surface energy, particles tend to form bonds with neighboring particles, therefore leading to the formation of agglomerates [28].

Therefore, to make an effective polymer nano-composite it is imperative to achieve uniform particle distribution by overcoming the agglomeration problem. Another significant stumbling block is the incompatibility of the inorganic ceramic particles that are hydrophilic and the organic matrix that is hydrophobic [31, 32]. The incompatibility of inorganic particles and organic polymer matrices leads to the separation of the particles from the polymer the non-uniform distribution of particles within the matrix and weak bonds at the particle–matrix interface. Weak bonds at the particle-matrix interface can lead to voids in the composite. However, by employing suitable surface modification of the nanoparticles, the dual-natured problem of nanoparticle agglomeration and the inorganic-organic incompatibility may be overcome [25, 31, 32]. While there have been reports on using dispersants [33-36] and coupling agents [37-40] to solve this problem, there has been (to our knowledge) little work that aims to understand the influence of varying concentrations of these surface modifiers on the effective dielectric and mechanical properties of the composite. There have been reports of improved permittivity values at a particular concentration, however there hasn’t been a study that understands the permittivity as a function of varying concentration of the coupling agent, which influences the particle-matrix interface. This goal of this work is to understand the mechanisms
governing the interfacial relationship between the coupling agent, particle and matrix as a function of coupling agent concentration. To achieve this goal, imaging techniques will be used to observe the influence of surface modification of inorganic ceramic nanoparticles was conducted. The particle-matrix interface and permittivity values were examined as a function of surface modification of the active material. The surface of BaTiO$_3$ will be modified with ethanol and by a silane coupling agent to aid in the disassociation of the formed agglomerates.

1.2 Research motivation and background

Piezoelectricity can be defined as the electric polarization produced by mechanical strain in crystals belonging to certain classes (21 non-centrosymmetric point groups out of which 20 are piezoelectric viz. in the tetragonal phase, 4mm, 42m), where the polarization is proportional to the strain and changes sign with it. In other words, if the pressure is replaced by a stretch (i.e. a reversal in sign of the pressure) the sign of the electric polarity reverses too [41]. Piezoelectric materials exhibit a non-centrosymmetric structure in the tetragonal phase, i.e., there is no crystalline inversion symmetry. As such, these materials have a linear relationship between the mechanical and electrical energy of the material [42].

Piezoelectric materials are primarily used as transducers to convert mechanical energy into electrical energy, or vice versa. To this end, they are employed in structural health monitoring applications for civil structures [43-46] and as industrial sensors and actuators [47-49]. Materials such as these are also used in passive devices such as embedded capacitors [50-53] and vibration based energy harvesting applications due to their ability to convert mechanical energy to electrical energy [47, 54, 55].
Research and innovation in piezoelectric and dielectric materials is currently motivated by the Internet of Things (IoT) [47, 54, 56] - namely devices, vehicles, buildings, etc. that are wirelessly connected via electronics, software, sensors and network connectivity. The realization of devices such as these that can transmit information, communicate wirelessly, and self-power themselves requires the development and optimization of advanced piezoelectric and dielectric materials. Also, systems such as these that employ sensors are powered using conventional batteries; which limit their operation cycle. Replacement of the batteries can prove problematic in cases where the batteries are in remote locations, such as structural sensors on a bridge or as tracking devices on moving objects [57]. Hence, it is desirable to use self-powered sensors in such applications. Piezoelectric energy harvesting devices provide an alternative to traditional battery powered systems, where they can be used to self-power themselves and other components within micro-electromechanical systems (MES), where they can be integrated into hybrid power systems [47, 58, 59].

There are several materials that exhibit the piezoelectric effect, like ceramic materials such as lead zirconate titante (PZT) (strain coefficient, $d_{33} \sim 630$ pC/N) [60] and barium titanate (BaTiO$_3$) (strain coefficient, $d_{33} \sim 191$ pC/N) [61]. Materials such as these are widely used commercially. These materials have also been used as dielectric materials for capacitor applications ($\varepsilon$ of PZT $\sim 3300$ [62], $\varepsilon$ of BaTiO$_3$ $\sim 2100$ [63]). For this current work, BaTiO$_3$ was used as the dielectric ceramic material because it is less toxic than PZT. The other goal of this work is to couple the BaTiO$_3$ with a polymer to create a dielectric composite to develop a touch-based capacitor [64] as the test bed for the proposed material.
The goal of this work is to understand how surface modification of the active nanoparticle can influence the particle-matrix interface. Hence, the effect of the surface modification of the BaTiO$_3$ nanoparticles using ethanol and a silane coupling agent will be studied and the optimum concentration of silane coupling agent will be identified. The composite interfacial properties and morphology will be studied with the aid of scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy, (EDS) micrograph images and Fourier transform infrared spectroscopy (FTIR). In order to understand the influence of surface modification of BaTiO$_3$ on interfacial properties formed in the composite, the dielectric and piezoelectric properties of the BaTiO$_3$/epoxy composite will be determined. The optimal surface concentration modification technique and concentration of coupling agent will be determined and correlated to the dielectric permittivity and interfacial properties observed with the SEM and EDS micrograph images.

1.3 Research Hypotheses

The research hypotheses of this work focus on understanding how to fabricate the most effective dielectric composite to be used in capacitors.

(i) Hypothesis I: The dielectric permittivity of the composite will increase with increasing concentration of the silane coupling agent. The permittivity of the composite will be measured for samples that are surface treated with ethanol and the silane coupling agent, 3-glycidoxypropyltrimethoxysilane. The permittivity is expected to increase with increasing concentration of the coupling agent. The surface morphology and distribution of particles will be observed using SEM and EDS micrograph images.
(ii) Hypothesis II: Composites fabricated using surface modified BaTiO$_3$ particles will exhibit lower conductivity values compared to composites prepared using the non-surface treated BaTiO$_3$. Lowering the conductivity of the composite will make the dielectric material less lossy. It is expected that the surface modification with the silane coupling agent will lead to the replacement of the hydroxyl groups on the surface of the BaTiO$_3$ nanoparticle with the (O-Si-O) of the coupling agent. The surface modification with ethanol, which acts as a dispersant does not react chemically with the particle surface. Instead, ethanol breaks down the particle aggregates. This could result in creating more BT-OH particle networks in the ethanol surface treated composites thereby increasing the electrical conductivity as compared to the composites fabricated using non-surface treated BaTiO$_3$.

(iii) Hypothesis III: Improved particle-polymer interfacial bonding of the silane coupling agent surface modified composites will exhibit lower dielectric losses compared to the composites prepared using non-surface treated BaTiO$_3$. Surface modification of the BaTiO$_3$ should reduce the amount of agglomerates within the polymer matrix, which in theory should result in stronger adhesion at the particle-polymer interfaces thereby leading to increased polarization in the composite. Interface or space charge polarization will occur at two different interfaces within a material or at the interface between two different materials [65]. Breaking up the agglomerates leads to a larger network of BaTiO$_3$-polymer networks within the composite material. As a result of this there will be an
enhanced interface or space charge type polarization occurring at the 
Ba-TiO$_3$-polymer interfaces. Steric stabilization involves modifying the sur-
face of the nanoparticle by a surfactant monolayer or a coupling agent. The 
nanoparticle surface atoms form bonds with the coupling agent thereby 
diminishing their inherent surface energy creating aggregate-free disper-
sions. The surface treated BaTiO$_3$ should reduce the dielectric loss of the 
overall composite.

(iv) Hypothesis IV: Composites fabricated using surface modified BaTiO$_3$ par-
ticles will have enhanced dielectric breakdown strength compared to com-
posites prepared using non-surface treated BaTiO$_3$. By reducing the ag-
gglomerates within the polymer matrix we can achieve more uniform dis-
ersion of the particles, this leads to more effective poling.

(v) Hypothesis V: Optimum viscosity of the sol that is deposited on the sub-
strate will enhance the permittivity of the surface modified BaTiO$_3$-epoxy 
composite. Optimum viscosity can be determined by observing cross-sec-
tion SEM micrograph images which indicate the adhesion of the composite 
with the substrate, dielectric and piezoelectric properties of the fabricated 
BaTiO$_3$/epoxy composites at different viscosities between 150-300 mPas. 
Prior to spin-coating if optimal viscosity of the sol will lead to a more uni-
form spread. Incorporation of a vacuum desiccation step should lead to a 
reduction in the density of air voids in the sol, as shown in Figure 1.1.
1.4 Research Objectives

The goals of this thesis are to fabricate a polymer nano-composite thick film to be used as a dielectric material for a touch-based capacitor and to enhance the critical parameters that can help in achieving the most effective dielectric material. In order to achieve the goals of this thesis, several objectives were proposed.

Objective 1: Surface treat the BaTiO$_3$ nanoparticles with ethanol and the silane coupling agent, KH-560. The surface morphology and the distribution of the particles were investigated using SEM and EDS micrograph images. Two-phase BaTiO$_3$/epoxy composites were prepared where the volume fraction of BaTiO$_3$ was varied from 0.10 to 0.60. The piezoelectric coefficients $d_{33}$ and $d_{31}$ were measured for each sample (minimum of three samples), and the permittivity value was calculated by measuring capacitance over a frequency range from 2000 Hz to 40 MHz. The piezoelectric and dielectric permittivity values of the composites prepared using the surface modified BaTiO$_3$ were compared to non-surface treated BaTiO$_3$, nano-composites. The nano-composites that incorporated non-surface treated BaTiO$_3$, will serve as the datum.

Objective 2: The conductivity values will be calculated from the conductance measurements obtained as a function of frequency i.e. from 2000 Hz to 40 MHz for each
sample set. This measurement will be taken for different coupling agent concentrations 0.015, 0.02 and 0.025 (v/v) and compared with composites that were prepared using non-surface treated BaTiO$_3$ nanoparticles show that conductivity does decrease.

Objective 3: The dissipation factor will be measured for the BaTiO$_3$/epoxy composites prepared using 0.10 – 0.60 volume fraction of BaTiO$_3$ and will be plotted as a function of frequency. The dissipation factor will then be measured for different coupling agent concentrations, 0.015, 0.02 and 0.025 and compared with the composites prepared using non-surface treated BaTiO$_3$ nanoparticles.

Objective 4: The dielectric breakdown strength will be measured by plotting hysteresis loops for the BaTiO$_3$/epoxy composites prepared using 0.10 to 0.60 volume fraction of BaTiO$_3$. The hysteresis loops will be plotted my ramping up the electric field until breakdown occurs which is indicative of the dielectric breakdown strength. This will be measured for different coupling agent concentrations, 0.015, 0.02 and 0.025 and compared with the composite prepared using 0.01 coupling agent.

Objective 5: The viscosity of the sol prior to spin coating will be measured using a Brookfield DV-E Viscometer and the values of permittivity at different viscosities, between 150-300 mPas will be compared with each other. SEM micrograph images will be used to observe the cross-section of the composite to gain an understanding of the interfacial adhesion between the composite and the electrode. Recent investigations have shown that the viscosity of the sol has direct influence on the final properties of the film [66, 67]. The viscosity of the sol reflects the intermolecular interactions between the polymer chains, and therefore can affect the integrity of the surface of the composite on the substrate [68, 69]. High sol viscosity results in insufficient wetting of the particles in
the polymer can lead to formation of cracked and porous surfaces \[^{25, 26}\]. In addition to that, the piezoelectric strain coefficient \(d_{33}\) and the permittivity of the composite will be measured. The results at different viscosities will compared.

A summary of the research hypotheses are shown as a schematic in Figure 1.2.

![Figure 1.2: Summary of the various research hypotheses in the thesis, each one aimed at solving a particular problem related to developing the dielectric medium between the parallel-plate capacitor](image)

1.4 Overview of the structure of the thesis

The structure of the thesis is as follows; Chapter 1 opens with a brief background, research goal and research motivation. It provides the research hypotheses and the research objectives. Chapter 2 introduces the concept of dielectric, ferroelectric and piezoelectric materials whilst also providing a historical background of these materials, from their discovery to their evolution and their current state. Chapter 2 briefly discusses the
basics of composite piezoelectric/dielectric materials and the different connectivity patterns of such materials. Chapter 3 covers the current state of the literature and the evolution of this subject, from simple pristine materials to more sophisticated surface modification procedures to functionalize the materials. It also provides the current challenges that need to be addressed. Chapter 4 described the different materials used and their physical properties, followed by the different processing techniques involved in fabricating these composites. It also describes the different characterization techniques such as measuring the piezoelectric coefficients, complex permittivity, resistivity, conductivity and the composite surface morphology that will be carried out with the goal of understanding these materials better. Chapter 5 discusses the results from the experimental work and their significance. It aims to provide an understanding of the different mechanisms and physiological effects and their interplay by connecting it with the data. Chapter 6 concludes the work and provides some insight into possible future work.
Chapter 2

Definitions and History of Dielectric Materials, Complex Permittivity and Introduction to Composite Processing

2.1 Overview of the Chapter

This chapter begins with the concepts of dielectric, ferroelectric and piezoelectric materials and explores some of the related physical phenomena such as polarization mechanisms and complex permittivity. It also provides a brief historical background of these materials from their discovery through to the current state of knowledge. The chapter also describes the various procedures and processes needed to fabricate dielectric composite materials and the different connectivity patterns between constituent phases. The chapter concludes by providing the relevance of these materials and the type of processing techniques currently being employed in industrial applications.

2.2 Dielectric Materials

A dielectric material is an electrically insulating (nonmetallic) material that exhibits or may be processed to exhibit an electric dipole structure. An electric dipole structure occurs when there is a separation of positive and negative electrically charged particles on a molecular or atomic level. Dielectric materials exhibit one of the following types of polarization: electronic, ionic and dipolar or orientation. The process of dipole formation, or alignment of already existing permanent or induced dipoles under the influence of an external electric field is called polarization [70]. Dielectric materials can also exhibit
interface or space charge polarization. The various polarization mechanisms are explained in Sections 2.2.1 Electronic Polarization through 2.2.5 Polar and Non-Polar Dielectrics) of this chapter.

2.2.1 Electronic Polarization

Within each atom or ion there is a positively charged nucleus surrounded by a negative electron cloud. The application of an electric field causes the electron cloud to distort in one direction while the nucleus moves in the other direction. Since the center of the electron cloud no longer coincides with the nucleus, a dipole moment develops. This polarization mechanism is known as electronic polarization as shown in Figure 2.3 [65].

![Figure 2.3: Schematic of an A) atom or ion that has a positively charged nucleus surrounded by a negative electron cloud. B) The application of an electric field, E causes the electron cloud to distort in one direction while the nucleus moves in the other direction.](image)
2.2.2 Ionic Polarization

Ionic polarization occurs in materials that exhibit an ionic structure because they are composed of cations and anions, as shown in Figure 2.4.

Consider a cation and anion pair that possess equal and opposite charges that are held together by an ionic bond. This ion pair already possesses a dipole moment before the application of an electric field. However, the net polarization, which is the sum of dipole moments over the entire material, may still be equal to zero. The application of an electric field causes the ionic bond between these two ions to stretch, i.e. increasing $r$, which is the distance between the cation and anion. If the material possesses spontaneous polarization before the application of the field, the application of an external electric field will increase the magnitude of the individual dipole moments, a dipole moment is the cross product of the charge, $q$, multiplied by the distance, $r$. Similarly, if the direction of the electric field is reversed, the bond will compress, i.e. $r$, the distance between the cation
and anion will reduce), which results in a decrease in the magnitude of the dipole moment. This mechanism of ionic polarization is shown in Figure 2.5 [65].

![Figure 2.5](image)

**Figure 2.5:** A) A simple case of a cation and an anion of equal and opposite charges, held together by an ionic bond, with a distance \( r \) between them. B) The application of an electric field causes the ionic bond to stretch thereby increasing the value of \( r \). Here \( +q \) and \( -q \) represent the equal and opposite charges of the ionic bond.

### 2.2.3 Orientation Polarization

Some molecules, such as \( \text{H}_2\text{O} \) possess a permanent dipole moment. A permanent dipole moment exists in molecules when there is an inherent separation of charge within the molecule, even in the absence of an electric field. This type of polarization is depicted in Figure 2.6. Permanent dipoles also exist within ionic structures, such as crystals in which the cations are off-centered within the unit cell and do not coincide with the center of the negative charge [65]. These dipoles may be randomly oriented and therefore the dipole moments from different molecules may end up canceling each other out resulting
in a net polarization equal to zero. One possible reason for the random orientation of dipoles could be the result of thermal motion amongst molecules.

**Figure 2.6**: An example of H$_2$O, a molecule that possesses a permanent dipole moment i.e. there is always a separation of charges within the molecule even in the absence of an electric field. The permanent dipole is represented by an arrow for convenience. Here $\delta^-$ is the oxygen ion O and the two $\delta^+$ represent the hydrogen H$^+$ ions. The arrow represents the direction of the dipole moment, which is a vector that goes from the negative charge to the positive charge.

**Figure 2.7**: Molecules of water containing many dipoles randomly oriented resulting in the cancelation of the dipole moments leading to zero net polarization.
If an electric field is applied in a particular direction, the dipoles will rotate parallel to the vector that describes the direction of the electric field. The application of an external electric field results in the dipoles being aligned with each other and amplifies the net polarization value of the entire system of molecules. This mechanism is shown in Figure 2.8.

Figure 2.8: The dipoles rotate to align with the direction of the applied electric field. As a result, the dipoles align with each other. In this scenario, the dipole moments no longer cancel each other out, which can lead to a net polarization that is not equal to zero.
2.2.4 Interface or Space Charge Polarization

Interface or space charge polarization involves limited movement of charges that result in the alignment of charge dipoles under an applied electric field. This usually happens at the grain boundaries in a material or any other interface such as an electrode-material interface \([71]\). This type of polarization occurs when there is an accumulation of charge at an interface between two materials or between two regions within a material because of an external electric field. This type of polarization can occur when there is a composite dielectric, or when there are two electrodes connected to a dielectric material. This type of polarization is different from orientation or dipolar and ionic polarization because instead of affecting bound positive and negative charges i.e. ionic and covalent bonding, interfacial polarization affects free charges as well.

Maxwell-Wagner-Sillars (MWS) interfacial polarization is related to the reorganization of interfacial charges e.g. electrons and holes accumulated at interfaces in heterogeneous systems \([72]\). It exists in all multi-component dielectric systems such as semi-crystalline polymers, polymer blends, and nano-composites consisting of high permittivity ceramic nanoparticles. When an electric field is applied across composites with more than one material, and hence interfaces between the different materials, charges can accumulate at the interfaces between the two materials \([73, 74]\). Therefore, a large contrast in dielectric constant between filler and polymer matrix is highly desirable for interfacial polarization and leads to a higher overall permittivity of the composite.

A bound charge is one that cannot move macroscopically in response to an external electric field, charges on a surface of a material are an example of these. Free charges on the other hand, are not subject to these constraints e.g. electrons in a conductor or charges
formed on a capacitor plate \footnote{75}. The bound charges are the charges that are in contact with the capacitor plates, while the free charges usually float around in the material, but in this case, they are aligned with the bound charges \footnote{76}. As a result, interfacial polarization is usually observed in amorphous or polycrystalline solids. This polarization mechanism is shown in Figure 2.9 \footnote{71}.
2.2.5 Polar and Non-Polar Dielectrics

There are two types of dielectrics: polar and non-polar dielectrics. Polar dielectrics have a permanent electric dipole moment, where the centers of the positive and negative
charges are not overlapped. When an electric field, $E$, is applied to a polar dielectric substance, a torque is created, which causes the molecules to align in the direction of the externally applied electric field. A depiction of two examples of polar substances, hydrogen chloride and water are shown in Figure 2.10 [70].

![Diagram showing molecular alignment under electric field](image)

**Figure 2.10:** Molecules of **A)** HCl and **B)** H$_2$O both polar dielectrics, i.e. they exhibit permanent dipole moments. Upon application of an electric field a torque is created causing the molecules to align in the direction of the applied field. In **C)** an ionic bond stretches due to an applied electric field. In **D)** an applied electric field creates a torque and the molecule rotates to align with it.

Non-polar dielectrics are dielectrics that do not possess a permanent dipole moment. In other words, non-polar dielectrics are substances where the centers of the positive and negative charges overlap as shown in Figure 2.11. Dipole moments can be induced in non-polar dielectrics when they are subjected to an external electric field as shown in
Figure 2.11. The ability to polarize dielectric materials with the application of an electric field makes these materials useful for application in the capacitor industry because of their ability to increase charge storage capabilities [70].

![Diagram of two molecules: H₂ and CO₂](image)

**Figure 2.11**: Two molecules A) H₂ and B) CO₂ both represent non-polar dielectrics, i.e. they do not possess a permanent dipole moment because the centers of the positive and negative charges overlap each other.

### 2.3 Complex Relative Permittivity

An expression for the relative permittivity is provided in Equations (2.1), (2.2). The relative complex permittivity ($\varepsilon_r$) is a dimensionless vector quantity, which is the ratio of complex permittivity of a material ($\varepsilon$) to the permittivity of the free space ($\varepsilon_0 = 8.854 \times 10^{-12}$). It describes the interaction of a material with an applied electric field and consists of a real part $\varepsilon_r'$, which represents the charge storage, and an imaginary part $\varepsilon_r''$, which represents the losses (mainly heat loss and conduction loss) [77]. The real part of the permittivity ($\varepsilon_r'$) is a measure of how much energy from an external electric field can be stored by the material. The real part of the permittivity is referred to as the dielectric constant at a specific frequency. The imaginary part of the relative permittivity ($\varepsilon_r''$) is called the loss factor, which is a measure of the energy dissipated per cycle, which can be
either heat dissipation or ohmic conduction losses. When the relative complex permittivity is drawn as a vector diagram, the real and imaginary components are 90° out of phase, as can be seen in Figure 2.12. The vector sum, $\varepsilon_r$, forms an angle $\delta$ with the real axis $\varepsilon_r'$. Two expressions for the relative permittivity are presented in (2.1) and (2.2).

$$\varepsilon_r = \varepsilon_r' - j\varepsilon_r'' \quad (2.1)$$

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0} \quad (2.2)$$

![Figure 2.12: The complex relative permittivity vector diagram. The real part of permittivity, $\varepsilon_r'$, and the imaginary part of permittivity, $\varepsilon_r''$, are 90° out of phase. The vector sum forms an angle $\delta$ with the real axis.](image)

The $\tan \delta$, for a ceramic material is the tangent of the dielectric loss angle $\delta$, and is determined by the ratio of effective conductance to effective susceptance as depicted in an equivalent parallel circuit in Figure 2.13 and in Equation (2.3).
\[
tan \delta = \frac{1}{R_p \omega C_p} \quad (2.3)
\]

In Equation (2.3), \( R_p \) is the resistance, \( C_p \) is the capacitance and \( \omega \) is the frequency.

The dielectric loss, \( tan \delta \), represents the electrical damping capacity of the material, i.e. the material’s inherent ability to dispel electromagnetic energy. Dielectric loss, also describes the ability of the material to convert mechanical energy into electrical and heat energy, when subjected to an external load. It can be represented in the form of an equation,
\[
\tan \delta = \frac{|E| \sin(\delta)}{|E| \cos(\delta)} = \frac{E''}{E'}, \tag{2.4}
\]

where \(\delta\) is the phase angle between the stress and strain, while \(E'\) and \(E''\) are the elastic storage modulus and elastic loss modulus, respectively [48]. The storage modulus represents the amount of mechanical energy stored during deformation, while the loss modulus denotes energy lost as heat during the same deformation cycle.

Dielectric constants range over four orders of magnitude in insulator materials (\(\varepsilon'_r\) of silicon dioxide, \(\text{SiO}_2 \sim 3.9\) [78] up to \(\varepsilon'_r\) of calcium copper titanate, \(\text{CaCu}_3\text{Ti}_4\text{O}_{12} \sim 250,000\) [79][80]). Gases, have dielectric constants that are nominally equal to one (\(\varepsilon'_r\) for propane \(\sim 1.00992\) at pressure and temperature equal to 472.392 kPa and 22.5 °C, respectively [81][80]) due to their low density. At one atmosphere, the dielectric constant of air is 1.0006 [80]. Most common ceramics and polymers have dielectric constants in the range between 2 and 10. Polyethylene is 2.3 and silica glass is 3.8. More ionic materials like sodium chloride (NaCl) and aluminum oxide (Al\(_2\)O\(_3\)) have slightly higher real relative permittivity (\(\varepsilon'_r\)) values in that range from 6 to 10 [80].

### 2.4 Ferroelectric Materials

Ferroelectric ceramics were discovered in the 1940s in barium titanate (BaTiO\(_3\)) ceramics, which have a perovskite. Barium titanate possess an unusually high permittivity value (\(>1100\)). The high permittivity values were attributed to the phenomenon of
Ferroelectricity \[82, 83\]. The idea that BaTiO$_3$ exhibited ferroelectric behavior proved invaluable when Gray \textit{et al.} \[84\] discovered that an external electric field could orient the domains within the grains, thus resulting in a ceramic material that acted very similar to a single crystal possessing both ferroelectric and piezoelectric properties. This electrical alignment of dipoles is called polarization \[85\]. The polarization process converts an inert ceramic into an electromechanically active material. This discovery led to the end of the notion that ceramics could not be piezoelectrically active because the randomly oriented crystallites would cancel out each other \[85\].

Ferroelectrics are a class of dielectrics that exhibit spontaneous polarization i.e. polarization in the absence of an electric field. The spontaneous polarization of ferroelectric materials can be switched or reversed by applying an electric field in the opposite direction, which is known as ferroelectric switching. Ferroelectric materials undergo a structural phase transition to the cubic phase at their Curie temperature, thereby becoming paraelectric. Both paraelectric and ferroelectric materials exhibit electronic, atomic, and ionic polarization but the distinguishing factor is that ferroelectric materials do not lose their ionic polarization when the field is removed and paraelectric materials do \[86\]. Paraelectric materials are materials that do not possess a residual polarization once the electric field is removed since they do not have a mobile charged atom with more than one stable lattice position \[86\].

All ferroelectric materials exhibit a P-E hysteresis loop as shown in Figure 2.14 \[85\], where \(P\) represents the net polarization within a material and \(E\) represents the applied electric field. In Figure 2.14, a plot of the polarization versus the applied electric
field is depicted. As this figure indicates, an increase in the applied electric field initially leads to a corresponding increase in polarization. Upon further application of an electric field, the polarization starts to become nonlinear and eventually saturate, $P_{sat}$ at a particular value of electric field, $E$. The point at saturation polarization represents the point where increasing the electric filed beyond this point yields no greater polarization value in the material. The polarization of the material eventually drops to a value known as $P_r$ or remnant polarization (beyond $P_{sat}$). This happens because some of the aligned dipoles return to their original orientation when the applied electric field is reduced to zero. If the field is applied in the reverse direction, the dipoles switch or reverse towards the direction of the field of the negative electric field. This is known as ferroelectric switching, as the dipoles can be aligned in the opposite direction.

![Figure 2.14: P-E Hysteresis loop i.e. electric polarization versus an applied electric field. In this figure, points a, b and c denote saturation polarization, remnant polarization and the coercive field, respectively.](image-url)
Some of the most important applications of ferroelectric ceramics are in compact multilayer capacitors in the bulk and thin film form. This is because they possess high permittivity, low dissipation and a wide frequency range response. Nonlinear hysteretic response is of interest in thin film nonvolatile semiconductor memory [87, 88] and high permittivity films are also of interest in Dynamic Random Access Memory (DRAM) and chip packaging applications [89].

2.5 Piezoelectricity

Walter Guyton Cady defines piezoelectricity as electric polarization produced by mechanical strain in crystals belonging to certain classes. In materials that possess this characteristic, the polarization is proportional to the strain and changes sign with it. In other words, if the pressure is replaced by a stretch (i.e. a reversal in sign of the pressure) the sign of the electric polarity becomes reversed too [41]. The ‘piezo’ in piezoelectricity, is derived from the Greek word, meaning ‘to press’. Hence piezoelectricity is the generation of electricity that is the direct result of the application of mechanical stress.

Piezoelectricity was discovered in 1880 by Jacques and Pierre Curie whilst studying the effect of pressure on the generation of electrical charge by crystals, such as quartz, zinc blende and tourmaline [90]. Their discovery was no mere coincidence; the Curie brothers were previously trying to study the relationship between pyroelectric phenomena and crystal symmetry. This led them to not only look for electric charges but to also know in which direction pressure needed to be applied [91]. In 1881, the converse piezoelectric effect (that is the change of crystal shape upon application of an electric field) was mathematically predicted by Lipmann using thermodynamic principles and empirical
data [92]. The converse piezoelectric effect was later experimentally verified by the Curie brothers the following year [91]. In 1972, Paul Langevin, the French physicist, made use of quartz crystal to locate German submarines by creating a depth sounding device, and then after the war the same instrument was used to locate the debris caused by the ships he was trying to find [93]. In 1954, lead zirconate titanate (Pb(Zr\textsubscript{1-x}Ti\textsubscript{x})O\textsubscript{3}, PZT) was discovered by Jaffe et al. PZT showed very strong piezoelectric activity near the morphotropic phase boundary (MPB), and to this day remains one of the most widely used piezoelectric ceramics [94].

All crystals can be classified into 32 crystal class or point groups, of which 21 are non-centrosymmetric and 20 of them are potentially piezoelectric, as shown in Figure 2.15. Of these 20 point groups, ten are polar, that is they exhibit a permanent dipole moment. Such materials have a spontaneous polarization. Thus, these materials are also pyroelectric. Ferroelectric materials are a subset of pyroelectric materials in which the spontaneous polarization can be reoriented between crystallographically defined direction by application of an electric field [95]. Non-centrosymmetric crystals lack a center of symmetry, which is critical for the presence of piezoelectricity, because when the material lacks a center of symmetry, there will be a net displacement of the positive and negative ions with respect to each other (as a result of the stress) thereby producing electric dipoles, i.e., polarization [85]. The polarization process is defined as the process that electrically aligns the internal dipoles of the crystallites within the material by applying an external field. Polarization is an important technique that makes use of the piezoelectric effect in ferroelectric ceramics that otherwise would be inactive [96].
Figure 2.15: Symmetry hierarchy for materials exhibiting piezoelectricity. All crystals can be classified into 32 point groups, of which 21 are non-centrosymmetric. Of the non-centrosymmetric groups, 20 point groups are piezoelectric. 10 of these point groups are polar, which makes their properties a function of temperature, and hence pyroelectric.

The Heckmann diagram [70] which is depicted in Figure 2.16 is a diagram that explains the relationship between different physical phenomena such as the electric field, polarization, stress and strain. Electric field, stress and strain are located at the vertices of the triangle. The phenomenon that yields an electric field upon applied stress is called piezoelectricity. When this stress leads to polarization of charges on the surface, it is the dielectric piezoelectric effect. Permittivity in materials results from the application of an electric field that yields polarization. When an applied electric field causes a material to strain, it is known as the converse piezoelectric effect.
There are primarily two effects in piezoelectricity, the direct piezoelectric effect (generator) and the converse or indirect piezoelectric effect (motor). The direct piezoelectric effect is the phenomenon where electrical charge is generated upon the application of mechanical stress. The converse piezoelectric effect is associated with the strain created upon application of an electric field \[85\]. In Equations (2.5 and (2.6, the linear piezoelectric constitutive equations are expressed.
In Equations (2.5 and 2.6, $D$ is the dielectric displacement (C/m$^2$), $T$ is the stress (Pa or N/m$^2$), $E$ is the electric field (V/m), $S$ is the strain, $d$ is a piezoelectric coefficient (pC/N), $s$ is the material compliance (1/Pa), and $\varepsilon$ the dielectric constant (relative permittivity) \[^{63}\]. The piezoelectric charge coefficient represents a tensor quantity with 27 components (eventually 18 components after accounting for material symmetry) i.e. it goes from $d_{ij}$ to $d_{ij}$. These physical properties also contain directional components and are usually followed by numerical subscripts to denote this. The piezoelectric strain coefficient $d_{31}$ represents the polarization in the perpendicular direction i.e. 3 direction and the strain is developed in the lateral direction i.e. the 1 direction.

Equations (2.7(2.8 describe the direct and converse piezoelectric effect, respectively. Equation (2.7 shows that the dielectric displacement and applied stress are directly proportional to the piezoelectric strain coefficient $d_{33}$ serving as the constant of proportionality. Similarly Equation 2.8 shows that strain can be developed in the material by applying an electric field, $E$, again with $d_{33}$ serving as the constant of proportionality.

$$D_3 = d_{33}T_3$$ (2.7)
Piezoelectric materials have garnered interest in energy harvesting applications due to their ability to withstand large amounts of strain. Large strains can potentially lead to greater mechanical energy, which in can be usable electrical energy. To convert more available energy, it is essential that an effective coupling mode is used. There are two practical coupling modes, the $-31$ and the $-33$ modes as shown in Figure 2.17. In the $-31$ mode, force is applied in a direction perpendicular to the poling directions, whilst in the $-33$ mode the force is applied in the same direction as the polarization direction. Although the $-33$ mode is more robust and has a higher coupling coefficient at lower applied stresses, the $-31$ mode can yield a higher overall power output depending on the application $[57]$. A design study was conducted by Ramsay et al. $[97]$ which investigated the feasibility of using a piezoelectric transducer as power supply for an in vivo MEMS application. The $33$- and $31$- modes of operation were analyzed and compared and it was determined that when using the $31$- mode, there existed a strong mechanical advantage in converting applied pressure to working stress. For very low-pressure sources, the $31$-mode had a greater advantage in energy conversion $[57]$. 

\[ S_3 = d_{33}E_3 \]  

(2.8)
**Figure 2.17:** Two coupling modes are shown A) -33 mode in which the force applied in the same direction as the poling direction. B) -31 mode in which the force is applied in a direction perpendicular to the poling direction.

![Diagram of coupling modes](image)

**Figure 2.18:** A) Piezoelectric material before (dotted) and after poling B) strain in material upon applied electric field C) strain upon changing polarity of applied field D) generated voltage with polarity similar to poling E) generated voltage with polarity opposite to poling voltage.

![Diagram of piezoelectric material](image)

A Venn diagram is shown in **Figure 2.19:** Venn diagram describing the interrelationship between different types of materials [84]. Venn diagrams are used to summarize the above definitions and to help in understanding the interrelationship between ferroelectric, pyroelectric piezoelectric and dielectric materials [98]. From this diagram it can be concluded that all ferroelectric materials are pyroelectric, all pyroelectric materials are piezoelectric and all piezoelectric materials are dielectrics, but the converse is not true.
2.6 Barium Titanate

Since the discovery of ferroelectricity in single-crystal materials in Rochelle salt in 1921, there has been considerable interest into exploring the realm of polycrystalline ceramics such as barium titanate \([85]\). Barium titanate has two basic structures, a perovskite form, which is ferroelectric at certain temperatures and a non-ferroelectric hexagonal form. In this thesis, the perovskite form is of primary interest. The perovskite form is shown in Figure 2.20. At high temperatures, it exhibits the paraelectric phase (non-polar phase) where there is no spontaneous polarization \((m\bar{3}m)\). On the other hand, below the transition temperature \(T_c\), the Curie temperature \((\sim 130 \, ^\circ C)\), there exists spontaneous polarization where the crystal becomes slightly elongated and becomes tetragonal \((4mm)\) \([99]\).
BaTiO$_3$ was the first piezoelectric transducer ceramic ever produced. However, most of its current applications have shifted towards its use in discrete and multilayer capacitors due to its high dielectric constant.

This shift is due to two main reasons, (i) its relatively low curie temperature of 120-130 °C, which limits its use as high-power transducers, and (ii) its low electromechanical coupling factor in comparison to PZT (0.35 vs 0.65), which limits its operational output. These two characteristics make it a more suitable material for applications as dielectric materials in capacitors.

### 2.7 Polarization Process

The aligning process discovered by Gray et al. that orients the domains within a grain by applying an external electric field is termed polarization. Polarization is the process that induces piezoelectricity in ferroelectric ceramics via the application of an electric field. The electric field is used to switch the polar axis of the crystallites to the
symmetry-allowed directions nearest to the applied field \([100]\). Polarization is the process that converts inert ceramics into electromechanically active materials \([85]\). Polarization is an important step in obtaining the desired piezoelectric properties of the material. In composites that are polymer based, polarization is carried out at its glass transition temperature, by gradually heating the material and placing it in a strong static external electric field \([101, 102]\). The temperature at which polarization takes place and the applied electric field strength are critical parameters in defining the electromechanical properties of the poled material. Both the temperature and the applied field are required to reduce the energy band gap required to orient the domains in the direction of the field. Most multiphasic composites have been traditionally polarized using the contact poling method. In this poling method, the material is in direct contact with the polarization electrode. However, there are some disadvantages with this technique. Contact polarization can cause dielectric breakdown of the composite material, especially when the composite has conductive inclusions \([101, 102]\). Also in this method, the samples must be placed inside a dielectric media, such as silicone oil for uniform heating of the sample. In order to overcome the challenges of this method, researchers \([100]\) have developed the corona discharge polarization method where a high poling voltage is applied to the air molecules above the sample, thereby eliminating physical contact. Researchers have also shown that higher voltages can be achieved by the corona poling method in comparison to traditional contact poling method \([102, 103]\).

### 2.7.1 Contact Polarization

Contact polarization is the conventional poling method by which piezoelectric ceramics and composites are polarized. In this process, a large direct current (DC) voltage
is applied to the sample. This polarization method requires physical contact of the live electrode with the sample electrode and with the application of a very large electric field. However, the application of large DC fields to polymer matrix composites often causes dielectric breakdown of the sample. The samples are usually placed in a silicone oil bath and uniformly heated up to their glass transition temperature, as shown in Figure 2.21. The samples need to be coated with a top electrode for this method in addition to a bottom electrode and polarization is usually limited to samples of smaller area $[100]$. One of the major drawbacks of this method, in addition to the dielectric breakdown, is the local breakdown at non-homogeneities within the sample, such as cracks or grain boundaries, such as pinholes, which short-circuit the electrodes and prevents further poling. In order to improve this form of polarization, the corona discharge technique was developed $[100]$.  

![Figure 2.21: Contact poling setup for electrically aligning samples. The poling electrode is in contact with the sample top electrode. The base plate on which the sample rests is grounded.](image)
2.7.2 Corona Polarization Method

In the corona polarization technique, charge from the corona point/needle is sprayed onto the surface that has no electrode, creating an electric field between the sample surfaces. Electrodes generally are not needed or used for this type of polarization process. Hence, electrical short-circuit conditions are nearly eliminated at weak points in the samples, which enables higher poling voltages to be achieved. This method also allows samples of larger surface area to be polarized and may be adapted to a continuous process for mass production. Here the live wire is connected to the corona discharge needle and the base plate upon which the sample rests, is grounded as shown in Figure 2.22. The fine tip of the corona needle ensures that nearby air molecules are ionized. The entire polarization setup is placed inside a protective casing. This ensures that the ionized air molecules do not contact any surrounding objects. The distance between the needle and sample is a critical experimental variable. Studies have shown that different distances between the corona needle and the surface of the sample can influence the corona polarization procedure significantly [100]. So, for these experiments the corona needle distance from the sample was kept constant at 10 mm to ensure experimental repeatability and eliminate experimental variability.
2.8 Composite Piezoelectric Materials

Piezoelectric ceramic/polymer composites, also known as piezo-composites have been developed over the past few decades mainly because they have shown superior properties when compared to single-phase materials [104], such as high electromechanical coupling, low impedance, low mechanical quality factor and possess an intermediate dielectric constant. In addition, their increased flexibility makes them excellent candidates for electromechanical transducer applications.\[104\]. A summary of the advantages and disadvantages of using polymer/ceramic composites is listed in Table 2.1.

The ways in which piezoelectric composite materials can be designed is described by a characteristic called connectivity. Connectivity, the microstructural arrangement of the individual components in a piezoelectric composite was first reported by Newnham et al. [105] and later modified by Pilgrim et al. [106]. It may also be defined as the number...
of dimensions in which a phase within the composite is self-connected [10+]. For a composite that contains two phases, there are a total of sixteen different connectivity patterns that can be accomplished. For example, for a 0-0 composite, neither phase is self-connected. For 3-3 connectivity composites, each phase is self-connected in three dimensions. In this representation, the first digit refers to the dimension of the piezoelectric ceramic, also known as the active phase and the second digit represents the dimension of the polymer or inactive phase. A schematic representation is shown in Figure 2. The connectivity pattern where ceramic particles are randomly distributed within a passive polymer matrix is referred to as 0-3 connectivity. A polymer matrix with ceramic fillers is an example of a 0-3 connectivity pattern. The first digit represents the number of connected dimensions of the fillers, i.e. particles, which have zero connected dimensions. The second digit, ‘3’, represents the number of connected dimensions of the polymer matrix, which is connected in all three directions.
Figure 2.23: Ten different connectivity patterns of diphasic composites, the digits represent the number of dimensions in which the phase within the composite is self-connected. In this representation, the first digit refers to the dimension of the piezoelectric ceramic, also known as the active phase and the second digit represents the dimension of the polymer or inactive phase.

Most research has been limited to the 0–3 connectivity composites, where randomly dispersed ceramic particles are embedded into a three-dimensional polymer matrix. 0-3 composites have gained popularity owing to their flexibility, ease of processing and use in embedded passive devices \cite{50, 53, 107}. Two-phase, or diphasic composites, such as metal/polymer and ceramic/polymer have been extensively investigated \cite{108-111}.

The two-phase connectivity convention of describing piezoelectric composites can be extended to accommodate a third phase by incorporating a third digit. So a 0-3-0 composite will have two phases that are particles that are assumed to not be self-connected, dispersed within a self-connected matrix material. Several researchers have looked at
introducing conductive fillers into the composite as a third phase, and have reported an increase in the conductivity of the polymer matrix [112, 113].

Table 2.1: Advantages and Disadvantages of Piezoelectric Ceramic, Polymers, and Composites [104, 114]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ceramic BaTiO$_3$</th>
<th>Polymer PVDF</th>
<th>Ceramic/polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acoustic Impedance, $Z$ 10$^6$ kg/m$^2$s</td>
<td>High 33.5 [63]</td>
<td>Low 3.9 [115]</td>
<td>Low Z &lt; 7.5 Mray [116]</td>
</tr>
<tr>
<td>Coupling Factor, $k_p$</td>
<td>High 0.68 [63]</td>
<td>Low 0.2 [115]</td>
<td>High 0.60-0.70 [116]</td>
</tr>
<tr>
<td>Piezoelectric strain coefficient $d_{33}/d_{31}$ pF</td>
<td>High 230/149 [63]</td>
<td>Low 30/18 [117]</td>
<td>Medium 23/55 [118]</td>
</tr>
<tr>
<td>Dielectric constant, $\varepsilon_r$</td>
<td>High 2100 [63]</td>
<td>Low 11.5 [117]</td>
<td>Medium $\sim$ 125 [119]</td>
</tr>
<tr>
<td>Flexibility/Brittleness Modulus of elasticity (GPa)</td>
<td>Stiff 67 [63]</td>
<td>Flexible 1.6-2.2 [117]</td>
<td>Flexible</td>
</tr>
</tbody>
</table>

2.9 Ethanol Surface Treatment

Composites offer a long-term solution to problems that prevail in stand-alone materials such as ferroelectric ceramics. These challenges include high stiffness that leads to limited flexibility as shown in Table 2.1. However, to take advantage of composite systems it is important that the ferroelectric ceramic particles are uniformly dispersed
within the polymer matrix. Uniform dispersion ensures that the composite can be processed easily, and with repeatability to ensure uniform material properties and achieve to more effective polarization.

This thesis focuses on the investigation of using various surface treatments of the ceramic filler material to explore the mechanisms that lead to the reduction of particle-to-particle agglomerations within the composite. From previous work [4], it has been shown that dispersing particles in an ethanol solution and then subjecting the solution to ultrasonic vibrations can prevent the formation of such agglomerated ceramic particles. In this case, ethanol acts as a dispersant. Researchers have made use of dispersants to ensure homogeneous distribution of filler particles into polymer matrices [24, 33, 34].

The stability of ceramic particles is based on the summation of the van der Waals attractive forces, electrostatic repulsion and steric hindrance from adsorbed surfactants or coupling agents [28, 120]. Either electrostatic repulsion or steric hindrance counteract the strong van der Waals forces. Ethanol is considered to be a weakly acidic solvent and as result of this solvent polarity a surface charge may be developed on the surface of the ceramic particle when ethanol is used as the mechanism of surface treatment. Fowkes et al. [121, 122] observed the development of a positive surface charge on the ceramic particles in ethanol which was achieved by proton exchange i.e. the acidic nature of the adsorbate results in proton transfer to the particle surface. The charged surface that forms on the particles results in electrostatic repulsion between successive particles thereby counter acting the van der Waals attractive forces leading to improved particle dispersions within the organic medium [120]. In some of our earlier work [4], we have shown that surface treatment with ethanol can break down the size of the agglomerates in multi-
walled carbon nanotubes. As shown in Figure 2.24, when micron-sized aluminum particles were surface treated with ethanol for 4 hours, the size of the agglomerates were reduced from ~ 13 µm to ~5 µm.

While dispersants have proved to be effective, they only react with the filler particles and not the polymer itself. An alternative to using dispersants is to employ coupling agents, which are typically materials that contain two different organic functional groups that can react with the filler particle and the polymer simultaneously. Coupling agents will be described in the next section.

![Particle Size of Surface treated Al](image-url)

**Figure 2.24:** Surface treatment of micron-sized Al powder dispersed in ethanol at different times, where the agglomerates were gradually broken down with increasing time i.e. from ~13 to ~5 microns [4]
2.10 Coupling Agents

Bonding of organic polymers to inorganic surfaces has been a familiar operation for some time now, but a major need remerged in the 1940s when glass fibers were first used as reinforcements in organic resins. Early glass-resin composites had higher strength-to-weight ratios compared to that of steel and aluminum. However they eventually lost their strength due to extended exposure to moisture. The loss of strength was attributed to the debonding of the resin from the hydrophilic glass surface by the intrusion of water. Coupling agents, can therefore be described as, materials that improve the chemical resistance, especially to water, of the bond across the interface. The concept that two dissimilar materials may be held together by a third intermediate material, e.g. a coupling agent was introduced by Plato [123]. In the case of the glass-resin composites, the functional groups of the coupling agent react with the silanol groups of glass. In addition, coupling agents contain at least one other different functional group that can react with the resin during curing. This leads to better bonding at the interface between the glass fibers and the epoxy resin.

2.10.1 Silane Coupling Agents

Organofunctional silicones are hybrids of silica and of organic materials (related to resins) and were first used as coupling agents to improve the bonding of organic resins to mineral surfaces [40]. Silane coupling agents are generally considered to be adhesion promoters between mineral fillers and organic matrix resins and provide improved mechanical strength and chemical resistance to the composite [40]. Silane coupling agents are easily hydrolysable and hence make them a prime candidate for bonding with inor-
ganic mineral surfaces that contain hydroxyl groups on their surface. Silanols of a hydro-
lyzed silane coupling agent, form hydrogen bonds with the hydroxyl groups of a mineral
surface. Although any polar functional group in a polymer may contribute to improved
adhesion to mineral surfaces, methylacrylate-chrome complex (Volan A) [124] and organ-
nofunctional silanes have shown the most promise as true coupling agents [40]. The
organofunctional groups are chosen based on their compatibility and reactivity with the
organic polymer that is being used. Silane coupling agents were originally designed for
thermosetting resins and their performance is best understood in this application.

Table 2.2: Various commercial coupling agents based on the type of organofunctional group. Each organo-
functional group is representative of a specific type of polymer.

<table>
<thead>
<tr>
<th>Organofunctional</th>
<th>Chemical Structure</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl</td>
<td>CH₂=CHSi(OCH₃)₃</td>
<td>Bowen et al. [125]</td>
</tr>
<tr>
<td>Chloropropyl</td>
<td>ClCH₂CH₂CH₂Si(OCH₃)₃</td>
<td>Domka et al. [126]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>CH₂OCHCH₂OCH₂CH₂CH₂Si(OCH₃)₃</td>
<td>Zeng et al. [127]</td>
</tr>
<tr>
<td>Mercapto</td>
<td>HSCH₂CH₂CH₂Si(OCH₃)₃</td>
<td>Sakamoto et al. [128]</td>
</tr>
<tr>
<td>Methacrylate</td>
<td>CH₂=C-COOCH₂CH₂CH₂Si(OCH₃)₃</td>
<td>Solnit et al. [129]</td>
</tr>
<tr>
<td>Primary Amine</td>
<td>H₂NCH₂CH₂CH₂Si(OC₂H₅)₃</td>
<td>Chen et al. [130]</td>
</tr>
<tr>
<td>Diamine</td>
<td>H₂NCH₂CH₂ NHCH₂CH₂Si(OCH₃)₃</td>
<td>Sforca et al. [131]</td>
</tr>
</tbody>
</table>

Organofunctional silane coupling agents can be represented by the formula R-Si-
X₃, where R is a short hydrocarbon chain with an organic functional group and X is a
hydrolysable alkoxy group (–OC₂H₅). The first reaction is typically the hydrolysis of the
triethoxysilane group to produce silanols (Si-OH), which has an interaction with BaTiO₃.
by hydrogen bonds as shown in Figure 2.25. Further reaction involves condensation of the hydrolyzed molecules to form siloxane bonds.

\[
\begin{align*}
X & \quad \text{OH} \\
\text{R} - \text{Si} - X + 3 \text{H}_2\text{O} & = \text{R} - \text{Si} - \text{HO} + 3 \text{HX} \\
\text{X} & \quad \text{OH}
\end{align*}
\]

\[X - \text{OC}_2\text{H}_5 \quad \text{R} - \text{Organic functional group}\]

Figure 2.25: Reaction scheme between any silane coupling agent and a hydrous solvent during surface modification process. R could be any organic functional group and X is the alkoxy group.

Therefore, the choice of R depends on the type of polymer that is being used in the composite. R can be any organic functional group listed in Table 2.2.

2.11 History of industrial application of piezoelectric materials

The number one technique for medical imaging and non-destructive evaluation (NDE) is ultrasound. There have been several innovations in ultrasound, such as stimulated elastography, magnetic resonance imaging (MRI) and ultrasound therapy [95, 114]. These techniques used in NDE (such as ultrasound, MRI etc.) can only advance in their performance and design with the realization of advanced material discovery and investigation. The performance of a transducer can be evaluated using (1) electrical input impedance, (2) electroacoustic response and (3) radiation pattern. Piezoelectric materials are the most common materials that are used to develop transducers for these applications. The geometry and size of these materials are important, since they influence all
the properties. Lead zirconate titanate (PZT) based compositions such as PZT-polymer composites are the most efficient compromise for the vibration modes used in medical diagnosis and NDE applications [95].

The design of these transducers essentially consists of an active material, i.e. the piezoelectric material and a rear face or the backing material. The backing material not only acts as a mechanical support for the active material, but also is a filter for acoustic energy to flow by the rear face and thus induces damping of the transducer, and the closer to the acoustic impedance is between the two materials the lower the efficiency. For this reason the active material is usually a PZT based material and the backing layer is a high loss polymer, such as an epoxy resin. Even today a combination of these two materials possesses the best performance trade-off that no material can achieve [95].

An electroacoustic transducer is a device that converts acoustic energy (sound) into electrical energy (voltage or current) or vice versa. When the transducer is used to generate sound, it is known as a transmitter. When it is used to detect sound, it is called a receiver. When these receivers are used to detect sound underwater, then they are known as hydrophones. The purpose of the hydrophone is to measure extremely weak hydrostatic pressure waves using large area sensors. For hydrostatic pressure, the normal stress values are all equal as shown in Equation (2.9).

\[ X_{11} = X_{22} = X_{33} = -p. \] (2.9)

The change in polarization is given by,
\[ P_3 = d_{33}(-p) + d_{31}(-p) + d_{31}(-p), \]  
\[ = (d_{33} + 2d_{31})(-p) \]  
\[ = d_h(-p). \]  

In Equation (2.12), \( d_h \) is the hydrostatic piezoelectric charge coefficient. The voltage generated by the hydrophone, is given by Equation (2.13, and the figure of merit is the product of \( d_h g_h \) and is given by Equation (2.14).

\[ g_h = \frac{(d_{33} + 2d_{31})}{\varepsilon_{33}}, \]  
\[ d_h g_h = \frac{(d_{33} + 2d_{31})^2}{\varepsilon_{33}}. \]

For a high sensitivity PZTs (PZT 5A) \([88]\), there is a near cancellation between \( d_{33} \approx -2d_{31} \), and hence the PZT alone is not a good enough hydrophone material. On the other hand, if we create a composite with dielectric constant approximately in the region of 10, we can enhance the voltage coefficient, due to the reduced overall dielectric constant. This is how industrial hydrophones are manufactured \([88]\).

### 2.12 Use of spin coat and deposition for films in industry

The spin coating technique is currently the predominant technique employed to produce uniform thin films with thickness of the order of micrometers and nanometers
The pioneering analysis of spin coating was performed over fifty years ago by Emslie et al. [133] who proposed the spreading of a thin axisymmetric film of Newtonian fluid on a planar substrate rotating with constant angular velocity. In most common scenarios, the coating material is polymeric and is applied in the form of a solution from which the solvent evaporates [132].

This process is widely used in the manufacture of integrated circuits [134], optical mirrors, television screens and as a magnetic discs for DRAM applications and data storage [135]. The centrifugal force drives the liquid radially outward, and the viscous force and surface tension causes a thin residual film to be retained on the flat substrate. Spin coating has also been widely used in the semiconductor industry [136]. Circuit designs are generally imprinted on the silicon by the process of photolithography, where circular semiconductor wafers are coated with thin polymeric photoresist films that are then exposed through masks to transfer the circuit design to the silicon. The process of layering this photoresist material onto the wafer is achieved by spin coating. Compared with other nanosurface-texturing techniques, spin coating possesses several advantages for controlling the mechanical and tribological properties such as adjustable nanotexture surfaces, size and density [137]. For this work a multi-step spin coating process was used to deposit the BaTiO$_3$/epoxy composite on to the stainless substrate. The spin-speed was ramped up gradually in steps of 100 rpm till 1000 rpm and then brought down gradually with the same 100 rpm interval.
Chapter 3

Literature Review

The ceramic capacitor market is the most widely used passive component in modern electronics and accounts for 90% of the capacitor market in part volume and 40% in value [138, 139]. Barium titanate (BaTiO$_3$) is one of the most widely used ceramic materials in the industry due to its excellent dielectric properties and as of 2008 boasts a market share ~ 80-90% [140, 141]. The most dominant form of the ceramic capacitor is the multi-layer ceramic capacitor (MLCC) due to its high capacitance and relative compactness [139].

The ceramic materials used to fabricate capacitors can be broadly divided into three types of classes. Class I dielectrics have low dielectric permittivity (low-K, 5-a few hundred) with low dissipation factor (<<0.01). They typically have a linear temperature coefficient. Class II dielectrics, such as BaTiO$_3$ are high-K materials (1,000 - >20,000) based on ferroelectric ceramics with a dissipation factor in the range of 0.01 to 0.03. This class of dielectrics has moderate-to-high temperature dependence of dielectric constant. Class III dielectrics are the basis for barrier layer capacitors [139, 142].

The specification of Class II dielectrics is based on the Electrical Industry Alliance (EIA) three-character alphanumeric code as shown in Table 3.3. The first character denotes the low temperature-operating limit, the second is the high temperature limit and the third is the maximum capacitance deviation over the specified temperature range. For example, X7R means that the variation in
Table 3.3: Electrical Industry Alliance (EIA) specification codes for Class II dielectric materials.

<table>
<thead>
<tr>
<th>First Marking</th>
<th>Second Marking</th>
<th>Third Marking</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
<td>Low Temperature Limit (°C)</td>
<td>Symbol</td>
</tr>
<tr>
<td>Z</td>
<td>+10</td>
<td>4</td>
</tr>
<tr>
<td>Y</td>
<td>-30</td>
<td>5</td>
</tr>
<tr>
<td>X</td>
<td>-55</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>+125</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>+150</td>
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</table>

Two of the most important types of BaTiO$_3$ based dielectric materials for MLCC capacitors are (i) high-K dielectrics (5-20,000) \cite{139} e.g. Z5U, Y5V specification capacitors, and (ii) moderate-K dielectrics e.g. NP0 X7R specification capacitors. The high-K Z5U and Y5V dielectrics are used in high capacitance devices that operate near room temperature. NPO dielectrics are used in low-capacitance devices applications that require precision over a wide temperature range \cite{143}. X7R dielectric materials are used in capacitors for military and automotive applications that require moderately high capacitance values over a wide temperature range. Z5U capacitors are mainly used in the US, whereas the X7R capacitors are more commonly used in Europe and Japan \cite{143}. Table 3.4 shows the different MLCC characteristics including dielectric constant, temperature
coefficient of capacitance, and relative BaTiO$_3$ content for the corresponding capacitor based on the EIA specifications [140, 14+].

Table 3.4: Classification of MLCC’s based on the Electrical Industry Alliance (EIA) specifications

<table>
<thead>
<tr>
<th>Designation</th>
<th>Class</th>
<th>Temperature Range (°C)</th>
<th>Dielectric constant</th>
<th>Temperature coefficient</th>
<th>BaTiO$_3$ content (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPO</td>
<td>1</td>
<td>-55 – 125</td>
<td>~ 100</td>
<td>± 30 (ppm)</td>
<td>10 – 50</td>
</tr>
<tr>
<td>X5R</td>
<td>2</td>
<td>-55 – 85</td>
<td>~ 4,000</td>
<td>± 15</td>
<td>90 – 98</td>
</tr>
<tr>
<td>X7R</td>
<td>2</td>
<td>-55 – 125</td>
<td>~ 4,000</td>
<td>± 15</td>
<td>90 -98</td>
</tr>
<tr>
<td>Z5U</td>
<td>2</td>
<td>10 – 85</td>
<td>~ 14,000</td>
<td>±22, -56</td>
<td>80 – 90</td>
</tr>
<tr>
<td>Y5V</td>
<td>2</td>
<td>-30 85</td>
<td>~ 18,000</td>
<td>±22, 82</td>
<td>80 – 90</td>
</tr>
</tbody>
</table>

The MLCC’s have however suffered from the brittle fracture behavior of dielectric ceramics like barium titanate from defects such as cracks to electrical degradation and mechanical failure[145, 146]. Stresses arising from the ferroelectric phase transformation in these dielectric materials have a significant role in initiating crack-growth. Calcination of pure ceramic materials leads to a thermal mismatch effect in the capacitor due to the differences in thermal expansion between the ceramic and the electrode. In addition to the above drawbacks, MLCC’s suffer from low-voltage failures and premature dielectric breakdown. Low-voltage failure is mainly used to describe two types of failures of insulation resistance at low dc voltages, i.e. (i) low impedance failures causing high heat dissipation and (ii) high impedance failures [147]. Dielectric breakdown occurs when a certain critical electric field is exceeded and a conduction path is created through the thickness of the sample, causing breakdown. Pristine BaTiO$_3$ is also sensitive to moisture-enhanced growth i.e. the crack-propagation due to the chemical reaction between the crack tip and
adsorbed water molecules [146, 148]. Table 3.5 presents the physical and mechanical properties of two of the most common BaTiO₃-based MLCC’s.
Table 3.5: Physical and Mechanical Properties and the Thermal Shock Resistance Parameters for different Dielectrics (without electrodes)

<table>
<thead>
<tr>
<th>Dielectric Material</th>
<th>Young’s Modulus of Elasticity, E (GPa)</th>
<th>Poisson’s Ratio, ν</th>
<th>Coefficient Of Thermal Expansion, α</th>
<th>Thermal Diffusivity, D M²/s (×10⁻⁸)</th>
<th>Thermal Conductivity, K W/M °K at 300 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>X7R</td>
<td>106.7</td>
<td>0.35</td>
<td>10.14</td>
<td>59.2</td>
<td>1.66</td>
</tr>
<tr>
<td>Z5U</td>
<td>85.3</td>
<td>0.35</td>
<td>10.73</td>
<td>63.8</td>
<td>1.79</td>
</tr>
</tbody>
</table>
The high permittivity ferroelectric ceramics suffer from poor mechanical strength i.e. they are brittle due to high stiffness (51-59 GPa) \cite{62}, have very high processing temperatures and they suffer from inferior dielectric strength \cite{149}. Polymers on the other hand are flexible, easy to process and have high dielectric breakdown strength but exhibit small dielectric constant values (i.e. <10). Therefore, a lot of effort has gone towards developing polymer-ceramic composites \cite{3, 52, 150-154}, which combine the dielectric and electrical properties of the ceramic fillers with the advantages of a polymer matrix, e.g. low temperature (<250 °C), relative ease of processing and flexibility (modulus of elasticity ~ 1.6-2.2 GPa) \cite{117, 155-157}.

Embedded capacitor technology is an important technique for extensive miniaturization and high performance of electronic packaging systems. High dielectric constant polymer-ceramic composites have been of great interest as embedded capacitor materials because of their ease of fabrication, compatibility with printed wiring boards (PWB), and high relative permittivity (5-20,000) \cite{31, 32, 139, 158}. To design more effective capacitors it is essential to achieve high permittivity of the composite. Researchers have worked towards achieving this goal in two ways. One strategy is to add conductive particles in insulating polymers as a third phase. This enhances the overall permittivity of the composite by forming conductive networks. However, these composites suffer from high dielectric losses due to increased dielectric loss, and low breakdown strengths, which makes them less amenable to electrical polarization \cite{2, 37, 159}.

Composites that contain high filler loadings (vol% > 50) exhibit high overall permittivity values. Nanoparticles in polymer matrices have several advantages such as increased dielectric breakdown strength, improved voltage endurance over the life of the
sample and by suppressing space charge and enhancing the partial discharge resistance of dielectric polymers \([12]\). A minor stumbling block is the proclivity of nanoparticles to agglomerate by forming aggregates within the matrix \([28, 160]\). This agglomeration can typically be attributed to two main factors. The first factor is the surface area to volume ratios, which have high surface energy, which causes them to form bonds with one another to diminish this energy. The second factor is the van der Waals forces that arise between all molecules and particles. Uncoated nanoparticles of metals, metal oxides and ceramic materials have strong van der Waals forces \([28, 160]\). Surfactants and coupling agents can reduce this surface energy by forming covalent bonds with the nanoparticles, thereby reducing the inter-particle agglomeration.

Surface energy is a direct result of intermolecular forces. The molecules at the surface of a liquid or a solid are influenced by unbalanced forces and therefore possess additional energy, in contrast with the molecules inside the liquid or solid \([161]\). In liquids the surface energy manifests itself as an internal force, which tends to reduce the surface area to a minimum. Just like in the liquid, the surface of the solid too possesses additional free energy. The additional free energy at the interface between two phases is known as interfacial energy \([161]\).

Van der Waals forces exist between all molecules and particles, be it in air, vacuum or in liquid. Typically, between identical materials they are attractive and can be repulsive between dissimilar materials in a third medium \([28]\). Agglomeration of these materials results in the formation of nanorods or nanowires. The formation of aggregates can be prevented by steric or electrostatic stabilization. Steric stabilization usually involves coat-
ing the nanoparticles with a tightly bound polymer or surfactant monolayer. Electrostatic stabilization can be used in aqueous solutions where the particles become charged and/or encapsulated by a hydration layer, which further prevents their agglomeration \[28\].

In addition to the agglomerations of nanoparticles, the inherent incompatibility of inorganic-organic constituent materials that make up a composite creates further difficulties in processing \[31, 32, 162-165\]. In BaTiO$_3$/epoxy composites, the surface of BaTiO$_3$ particles have residual hydroxyl groups, which are hydrophilic in nature, while the epoxy resin and organic solvent are hydrophobic. Hence, BaTiO$_3$ tends to agglomerate and separate from the organic solvent or resin, resulting in processing difficulties, as discussed before \[25, 31, 32\]. As a result, dielectric polymer nano-composites comprised of high volume fractions of ceramic filler have only received limited attention due to the difficulties in processing and particle dispersion.

Identification of a suitable surface modification method could address both of the aforementioned problems. Researchers have looked at modifying BaTiO$_3$ by treating it with hydrogen peroxide (H$_2$O$_2$) to further hydroxylate the surface \[166-170\]. To improve compatibility between inorganic fillers and polymer materials, surface modifiers have been used such as macromolecular surface modifiers \[39, 171\] and small-molecular weight ones, such as surface active agents, e.g. silane coupling agents and titanate coupling agents \[172-175\]. By surface modification with a coupling agent, which has two functional groups, with one reacting with either BaTiO$_3$ or epoxy by forming covalent bonds. Silane coupling agents were studied in dielectric polymer composites that did not include BaTiO$_3$ such as epoxy/aluminum \[176\] and epoxy/fosterite (Mg$_2$SiO$_4$) \[177\].
Zhou et al. [176] investigated the influence of coupling agents by modifying the surface of aluminum (Al) particles by examining their microstructure and dielectric properties. In this study, four kinds of coupling agents were used i.e., silane KH550, silane KH560, titanate NXT-102, titanate NXT-201. The coupling agents were used to improve the interfacial bond strength between the aluminum and epoxy in Al/epoxy composites. The polymer matrix used in this study was a diglycidyl ether of bisphenol A-type epoxy resin (D.E.R-331). The Al particles were surface treated in an aqueous solution of 95% ethanol. Silane coupling agent as added to this mixture and stirred for 15 minutes, followed by further stirring and ultrasonication for 60 minutes. The mixture was heated at 80 C for 6 hours. The surface modified Al was mixed with epoxy to form a mixture. This liquid mixture was poured into a clean glass plate mold kept at 80 C, and was cured in an oven at 100 C for 1 h and 150 C for 5 h. The epoxy-based composites with Al powder concentrations ranging from 0 to 70 wt% were prepared. The dielectric analysis of the composites at 70 wt% of Al particles yielded increased permittivity values, 34 for the treated particles, as opposed to the pristine ones, which had permittivity equal 19.6. Surface treated particles also exhibited reduced dielectric loss values. The use of coupling agents improved the interfacial bonding strength between the aluminum particles and the epoxy resin, and decreased the voids and defects at the phase interfaces. The KH-560 silane coupling agent, had an epoxide as one of its end groups, and three hydroxyls at its other end after reacting with the Al particles. Therefore, it reacted with the Al particle and epoxy resin.
Table 3.6: Summary of literature review of surface modification of BaTiO$_3$ that employed a silane coupling agent

<table>
<thead>
<tr>
<th>Type of composite</th>
<th>Surface modification</th>
<th>Fabrication Procedure</th>
<th>Surface morphology</th>
<th>Dielectric permittivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO$_3$ – epoxy composite: thin film capacitors [31]</td>
<td>N-phenyl aminopropyltrimethoxysilane</td>
<td>40g BaTiO$_3$ + 0.2g of coupling agent + 95ml ethanol + 5ml water and ultrasonication for 5min then stirred at 70C for 1h</td>
<td>BaTiO$_3$ – epoxy films were spin-coated on metallized Cu-polyimide substrates between 2000-5000rpm for 30s, followed by curing at 100C</td>
<td>Increased permittivity values after surface modification i.e. 40 @ 1kHz</td>
</tr>
<tr>
<td>BaTiO$_3$ – epoxy composite [178]</td>
<td>3-aminopropyltriethoxysilane (KH-550)</td>
<td>BaTiO$_3$ powder, KH-550 and solvent were prepared in a beaker. Ultrasonic vibrations were applied. Heating at 75C for 1h.</td>
<td>Films were hot-pressed between 150-160C</td>
<td>Formation of voids above 70%. Increased permittivity values for all vol. fraction &lt; 70%. ~ 35 @ 10$^5$ Hz</td>
</tr>
<tr>
<td>BaTiO$_3$/epoxy composites [37]</td>
<td>3-glycidoxypropyltrimethoxysilane</td>
<td>40g of BaTiO$_3$ in 100ml solvent, then 12.8 mol/m2 GPTMS, stirred for 24h at 80C, then dried for 24h at 50C Solvents: (i) water, (ii) 95% ethanol solution and (iii) xylen</td>
<td>Suspension was spin-coated at 5000rpm on Cu plate for 30s and dried at 75C for 24h</td>
<td>Improved compatibility between particle surface and epoxy resin. Reduced slightly when modified with GPTMS in water and ethanol, but increased when modified in xylene.~28 @10$^5$Hz</td>
</tr>
<tr>
<td>BaTiO$_3$/(EVM) copolymer elastomer [1]</td>
<td>$\gamma$-aminopropyl triethoxysilane (Silquest A-1100)</td>
<td>BaTiO$_3$ dispersed by sonication in ethanol/water (95/5) 30 min. A-1100 was added slowly + stirred for 2h at 70C</td>
<td>Composites were obtained using compression molding at 175C for 15min under 10MPa pressure Composite thickness was 500 +/- 50μm</td>
<td>BaTiO$_3$ (&gt;50% vol.) are uniformly dispersed in EVM matrix. Increasing permittivity with BaTiO$_3$ loading. ~ 25 @ 70 wt% of BaTiO$_3$</td>
</tr>
<tr>
<td>System</td>
<td>Composition</td>
<td>Preparation</td>
<td>Properties</td>
<td></td>
</tr>
<tr>
<td>-------------------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------------------------------------------------------------------------------</td>
<td>----------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>BTresin/BaTiO$_3$ [127]</td>
<td>3-glycidoxypropyl trimethoxysilane (KH-560)</td>
<td>5 g of BaTiO$_3$ + 50 ml of 95% ethanol solution + 0.5 g of KH-560. Stirred for 12 h at 70°C, then 50 °C for 24 h</td>
<td>BaTiO$_3$/BT suspension was roll-coated on Cu plate + 80°C for 30 min + curing at 150-240°C for 2h</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>BaTiO$_3$ nanoparticles are homogeneously dispersed</td>
<td>Permittivity increased with loading. ~ 5 at 0% - ~ 25 at 70%</td>
</tr>
<tr>
<td>BaTiO$_3$/epoxy: Integral thin film capacitors [25]</td>
<td>N-phenyl aminopropyltrimethoxysilane, glycidoxy, mercapto, cyclohexyl</td>
<td>40 g of BaTiO$_3$ powder (120 nm diameter) + 2g of organic silane + 95ml ethanol + 5ml water. Ultrasoundicated 5min + 70°C for 1h</td>
<td>BaTiO$_3$ – epoxy films were spin-coated on metallized Cu-polyimide substrates between 2000-5000rpm for 30s, followed by curing at 100°C</td>
<td>Better particle dispersion</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>~ 40 @ 10$^5$ Hz</td>
</tr>
<tr>
<td>BaTiO$_3$-epoxy composites [27]</td>
<td>Glycidoxymethoxysilane Z-6040</td>
<td>Coupling agent + acetic acid + stirring 15min then dried 110C</td>
<td>BaTiO$_3$ + solvent (THF), epoxy and curing agent mixed. Agitation at 2000rpm followed by dc sputtering. Cured at 100°C for 2h</td>
<td>Not homogeneous particle dispersion</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Increases with particles that were surface modified ~ 40 at 100 Hz</td>
</tr>
<tr>
<td>DGEBA-forsterite composites [177]</td>
<td>Aminopropyltriethoxy silane (APTS)</td>
<td>APTS at 2% concentration added to 95/5 ethanol/water. 5 mins to allow reaction, then 6h of stirring. Followed by heating for 5-6 hours at 110°C</td>
<td>The filler was dispersed properly in the resin and the curing agent was added (mix ratio by weight 100:10). It was then degassed and poured into Teflon. Samples were first pre-cured at 70 °C for 2 h and then</td>
<td>Better distribution and improved micro-structure of composite.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Dielectric permittivity increased from 3.7 to 3.9 after surface treating.</td>
</tr>
<tr>
<td>BaTiO₃-P(VDF-TrFE) [38]</td>
<td>3-aminopropyltriethoxysilane (APTES)</td>
<td>Three BaTiO₃ powders were used &lt; 2 µm (average particle size 1.1 µm), 0.7 µm and 0.2 µm. The powders were surface modified in APTES in a 95% ethanol/water solution.</td>
<td>The mixture was first sonicated for 5 minutes, then magnetically stirred at 70 °C for 1 hour. The composite films were obtained using compression molding at a pressure of 5 MPa and heated from 25 to 200 °C for 20 minutes.</td>
<td>Improved dispersion and reduce particle agglomerates.</td>
</tr>
</tbody>
</table>
The influence of silane coupling agent on the microstructure, dielectric and thermal properties were studied by Sasikala et al. [177] for epoxy-forsterite (Mg$_2$SiO$_4$) composites. The surface treatment of forsterite was carried out using aminopropyltriethoxysilane (APTS) in a solution containing 95/5 ethanol/water solution for 5 minutes to allow hydrolysis leading to the formation of silanol. The mixture is then stirred for 6 hours. The resin was heated to 50°C to reduce the viscosity and the ceramic filler was added at different concentrations (10, 20, 30, 40 vol%). The composite was fabricated by pouring the solution into Teflon molds and allowing them to cure at 70°C for 2 hours, followed by 120°C for another 2 hours. The dielectric permittivity was found to increase with the composite fabricated using silane coupling agent due to uniform dispersion of the filler within the matrix leading to enhanced polarization from the increased dipole-dipole interaction. [179]. The dielectric permittivity was found to be ~3.7 and ~3.9 at 7 GHz for untreated composites and for composites that were treated with silence coupling agent, respectively. It was also reported that surface treated samples had more homogeneous distribution and better microstructure.

Iijima et al. [37] modified the surface of BaTiO$_3$ particles using 3-glycidoxypropyltrimethoxysilane (GPTMS) to attach epoxy groups on them and to improve their compatibility with epoxy resin. To analyze the effects of solvents, the particles were modified in water, ethanol and xylene. They took 40 g of BaTiO$_3$ nanoparticles were suspended in 100 ml of solvent. Then, 12.8µmol/m$^2$ of GPTMS were slowly added to the prepared BaTiO$_3$ suspension, and further stirred for 24 h at 80 °C. After stirring, the BaTiO$_3$ nanoparticles were collected by centrifugation. Then, 6.5 g of the surface-modified BaTiO$_3$ nanoparticles were dispersed into 2.6 g of NMP with 0.84g of epoxy resin. Then, the BaTiO$_3$/epoxy/NMP suspension was mixed using a planetary ball mill for 5
minutes. The 60% volume fraction BaTiO$_3$/epoxy/NMP suspension was then spin-coated at 5000 rpm on a Cu plate for 30 seconds and dried under vacuum at 75 °C for 24 h. The resulting BaTiO$_3$/epoxy composite was cured at 160 °C for 1.5 h. At 1 kHz the dielectric constant for BaTiO$_3$ nanoparticles that were untreated was 37 and those treated in water, ethanol and xylene were 31, 30 and 52 respectively. The surfaces of the BaTiO$_3$ nanoparticles were surface treated by using GPTMS in various solvents, in order to improve the properties of BaTiO$_3$/epoxy composites. They were effected by the solvent that was used. The composites that were surface modified in xylene showed the most improved properties. The surface modified samples showed reduced surface roughness and less voids compared with the non-surface treated composites.

Huang et al. [1] investigated the influence of the surface modified BaTiO$_3$ nanoparticles on the electrical, thermophysical and micromechanical properties of ethylene-vinyl acetate (EVM) vulcanizates. The nanoparticles were surface modified using gamma-aminopropyltriethoxysilane. BaTiO$_3$ nanoparticles were ultrasonicated in ethanol/water (95/5) for 30 minutes to ensure uniform dispersion. Mixture was subsequently placed in an oil bath at 343K. The resulting mixture was centrifuged at 12000 rpm for 10 minutes. Even at high concentrations ~ 50% volume fraction of BaTiO$_3$, the particles were uniformly dispersed. This could mainly be attributed to the substitution of hydroxyl groups of the BaTiO$_3$ nanoparticles, which has two effects, one, it lowers the interfacial tension between the separated phases and two, it prevents coalescence of the nanoparticle during processing. The dielectric constant of 50% BT-EVM was 15 at 1 kHz. It was reported that the incorporation of surface modified BaTiO$_3$ nanoparticles into the EVM matrix increased the permittivity, thermal conductivity (from 0.295 Wm$^{-1}$K$^{-1}$ for pure EVM matrix to 0.87 Wm$^{-1}$K$^{-1}$ for EVM-BaTiO$_3$ (0.5)) and the mechanical strength and showed
comparable dielectric loss tangent with pure EVM vulcanizes. They reported that the high dielectric strength of the nanocomposites even at high BaTiO$_3$ loading levels is attributed to the good dispersion state of BaTiO$_3$ particles in EVM matrix and also due to the excellent interfacial adhesion between the EVM and BaTiO$_3$ nanoparticles. The improved interfacial adhesion can also lead to decreased possibility of void and pores \cite{180, 181}.

Zeng \textit{et al.} \cite{127} fabricated bismaleimide-triazine resin/barium titanate (BT/ Ba-TiO$_3$) nanocomposite films by mixing BaTiO$_3$ nanoparticles into BT resin. The nanoparticles were surface treated using gamma-glycidoxypropyl trimethoxysilane (KH-560). BaTiO$_3$ nanoparticles were suspended in 50 ml of 95% ethanol solution to which 0.5g of KH-560 was added. The mixture was stirred for 12 hours at 70 C, followed by drying the powder at 50 C for 24 hours. The BaTiO$_3$/BT suspension was then roll-coated on a Cu plate and dried at 80 °C for 30 min to evaporate the solvent for weight fractions from 10-70wt%. The films were then cured for 2 hours at 150-240 C. It was reported that for the composite with 70 wt% of BaTiO$_3$, the effective dielectric constant at room temperature reaches 23.63, and with a dielectric loss of 0.0212 at 100 Hz. The dielectric properties of the nanocomposite films were nearly frequency-independent, which is attributed to the excellent dispersion of BaTiO$_3$ nanoparticles in the BT matrix. The surface modification of BaTiO$_3$ nanoparticles with silane coupling agent resulted in excellent dispersion and enhanced the interaction between BaTiO$_3$ and the BT matrix. The derived nanocomposite films exhibited improved dielectric constant values (\sim 20 for BaTiO$_3$ at 50% volume fraction), while the dielectric loss remained at a low level (<0.05).
The surface of BaTiO$_3$ particle was chemically modified by Dang et al. \cite{39} using a silane coupling agent gamma-aminopropyltriethoxy silane (KH550) in order to improve its compatibility with polyvinylidene fluoride (PVDF) matrix. BaTiO$_3$ particles were treated in ethanol media with KH550 at concentrations of 0.5, 1.0, 1.5, 2.0, 3.0, and 5.0 wt% in comparison. Then the dry BaTiO$_3$ powders modified were dispersed into an organic solvent of N, N-dimethylformamide (DMF) with PVDF. The mixture was subsequently heated to 80 C to completely evaporate the solvent and then molded by hot pressing at 200 C and 15 MPa. The sample were ~ 12 mm in diameter and 1 mm in thickness. The volume fraction of BaTiO$_3$ in BaTiO$_3$/PVDF composites was 40%. The dielectric constant was ~ 48 for the BaTiO$_3$/PVDF composite modified in KH 500 while the dielectric constant of the untreated BaTiO$_3$ composite was 40 at 10 kHz.

BaTiO$_3$/epoxy composites were fabricated by Ramajo et al. \cite{182} using low concentrations of silane coupling agent to improve the microstructure and dielectric properties. Epoxy (DER 325) was used as the polymer matrix. The BaTiO$_3$ particles were surface modified using glycidoxy methoxy silane (Z-6040) and dried at 110 C. Surface modified BaTiO$_3$ powder (volume fractions 45-70%) was mixed with epoxy in a glass container. The resulting mixture was agitated at 2000 rpm for 3-5 minutes to avoid agglomerations and ensure uniform dispersion. The composites were fabricated using drip technique onto glass substrates with gold electrodes. The dielectric permittivity of 60% volume fraction of BaTiO$_3$ was 48, 43, 34 at 60wt%, 75wt% and 85wt% of THF solvent at 100 Hz, respectively. Increasing the solvent reduced the matrix viscosity and enabled wetting of the particles thereby leading to improved interface contact. Surface treating the BaTiO$_3$ lead to improved dielectric properties (~47 for untreated samples and ~ 50
Dang et al. [178] studied high dielectric permittivity BaTiO$_3$/epoxy composites with different size BaTiO$_3$ particles i.e. 0.7 µm and 0.1 µm. The epoxy resin (DER 661) was used as the polymer matrix. Gamma-aminopropyltriethoxysilane (KH550) was used as the coupling agent to surface treat the BaTiO$_3$ particles. BaTiO$_3$ powders and KH550 were mixed in a container and subjected to ultrasonic agitation to prohibit the agglomeration of the particles. The mixture was then grinded using a planetary ball mill. The mixture was then molded by hot-press at 150-160 °C. The resulting composites were electrode with gold on both sides. It was reported that KH550 improved the interaction between the epoxy resin and BaTiO$_3$ particles and therefore lead to homogeneous dispersion. This also led to increased dielectric permittivity (~ 26 for the untreated composite to ~ 28 for the surface treated composite at 10 kHz) and decreased dielectric loss values (from 0.08 for the untreated composite to 0.06 for the surface treated composite). It is evident that the size of BaTiO$_3$ has an effect on the dielectric property of the composites. As a result, the dielectric property of the composite with BT-07 (0.7 µm) was reported to be better than that with BT-01 (0.1 µm). The BaTiO$_3$/EPR composites with good miscibility can be prepared by employing the optimum amount of silane coupling agent and subsequently induce a high dielectric permittivity and a low loss tangent.

Liang et al. [31] looked at investigating a thin film technology based on BaTiO$_3$/epoxy composites, whose advantages in terms of ease of processing, low processing temperature, and versatility make it quite promising. In order to improve the dispersion of the BaTiO$_3$ powder into the epoxy matrix, the particles were surface modified using a
silane coupling agent (N-phenylaminopropyltrimethoxysilane). BaTiO$_3$ powders (average particle size $\sim$100-200 nm) were mixed with N-phenylaminopropyltrimethoxysilane, ethanol and water. The resulting mixture was subsequently ultrasonicated for 5 minutes and then stirred at 70 °C for 1 hour. Epoxy resin (EPON 828) was used as the polymer matrix. The powders were mixed with the polymer and stirred for 3 minutes under ultrasonication. The BaTiO$_3$/epoxy composite thin films were fabricated by spin coating the mixture on to polyimide substrates with electroplated Cu metallization at 2000-5000 rpm for 30-60 seconds. The films were then dried at 100 °C for 10 minutes. A dielectric constant of $\sim$ 40 was recorded at 1 kHz and a breakdown strength of $> 0.5$ MV/cm was obtained in BaTiO$_3$/epoxy (60/40, v/v). The dielectric loss was less than 0.035 over a wide frequency range. These researchers also developed promising integrated capacitors by surface modification of BaTiO$_3$ in BaTiO$_3$/epoxy composite. It was reported that homogeneous dispersion of the inorganic particles in the organic polymer matrix was achieved by observing SEM micrograph images of the fractured surface of the composite.

Dalle Vacche et al. [38] investigated the influence of varying size BaTiO$_3$ particles which were surface modified with aminopropyl triethoxy silane, and incorporated into poly(vinylidene fluoride–trifluoroethylene) P(VDF-TrFE) up to 60% volume fraction. Three BaTiO$_3$ powders were used < 2 µm (average particle size 1.1 µm), 0.7 µm and 0.2 µm. The powders were surface modified using 3-aminopropyltriethoxysilane (APTES) in a 95% ethanol/ water solution. The mixture was first sonicated for 5 minutes, then magnetically stirred at 70 °C for 1 hour. The composite films were obtained using compression molding at a pressure of 5 MPa and heated from 25 to 200 °C for 20 minutes. The resulting films were $\sim$ 120 – 180 µm thick. The dielectric permittivity for the composites containing 60% volume fraction of BaTiO$_3$ was $\sim$ 113 (1.1 µm) for surface treated and $\sim$ 100 for non-
surface treated composites and, $\sim 100$ (0.7 µm) for the surface treated samples and $\sim 80$ for the untreated samples and $\sim 85$ (0.2 µm) for the surface treated samples and $\sim 75$ for the untreated samples at 1 kHz, respectively. The dissipation factor was recorded to be $\sim 0.1$ for the untreated sample and $\sim 0.05$ for the surface treated samples. Surface modification was found to be effective for improving the dispersion of the ceramic in the matrix therefore reducing particle aggregates and enhancing the compatibility and adhesion of the P (VDF–TrFE) matrix to the inorganic filler. The composites also showed lower dielectric losses.

Organically modified BaTiO$_3$ nanoparticles were mixed with epoxy resin matrix (EPON 828) by Ramesh et al. [25] to form composites that would serves as dielectrics for integrated capacitors. The influence of type of silane coupling agent was also studied. $40$ g of BaTiO$_3$ powder were suspended in a solution containing $2$ g of the organic silane, $95$ mL of ethanol and $5$ mL of water. The mixture was ultrasonicated for $5$ minutes and then stirred on a hot plate at $70$ C for $1$ hour. The composites were fabricated at $60\%$ volume fraction of modified BaTiO$_3$ by casting them into molding discs at $75$ C for $72$ hours followed by curing at $175$ C for $15$ hours. The dielectric permittivity of the composites surface modified with glycidoxy silanes, mercapto, N-phenylamino and cyclohexyl epoxy silanes was $42$, $45$, $45$ and $45$, respectively at $10$ kHz.

Chao et al. [183] looked to investigate the effects of silane coupling agent, c-aminopropyl triethoxy silane (KH-550), on the preparation and dielectric properties of (Ba-TiO$_3$)/Bisphenol-A dicyanate (2,2'-bis (4-cyanatophenyl) isopropylidene)(BADCy) composites for embedded passive applications. BaTiO$_3$ particles were mixed with acetone solution and KH-550. The mixture was stirred for $10$ minutes to evaporate the solvent.
Subsequently the resulting mixture was placed in an oven at 110 C. The surface modified 
BaTiO$_3$ was then mixed with the BADCy and cast into a glass mold at 150 C, then was 
cured at 160 C – 200 C. The composite was then post treated at 230 C for 4 hours. The 
dielectric permittivity was ~ 8 for powders treated with 1.5% mass fraction of KH550. 
KH-550 improved the compatibility between BaTiO$_3$ inorganic filler and BADCy matrix. 
With the addition of KH550, the dielectric permittivity increased.

In order to understand the role of interface in highly filled polymer nanocompo-
sites due to a current lack of comprehensive research work Huang et al. [12] conducted 
the surface modification of BaTiO$_3$ with 6 different types of surface chemistry was carried 
out. Epoxy resin (DGEBA) was used as the overlaying polymer matrix. Silane coupling 
agents (3-mercaptopropyltrimethoxysilane (KBM 803), 3-aminopropyltrimethoxysilane 
(KBM 903) and 2-(3, 4-epoxycyclohexyl) ethyltrimethoxysilane (KBM 303) were used to 
surface modify BaTiO$_3$ nanoparticles. The BaTiO$_3$ nanoparticles were first hydroxylated 
using an aqueous solution of H$_2$O$_2$. Then silane coupling agent was added to it and stirred 
at 135 C for 24h under a N$_2$ atmosphere, followed by washing with ethanol. The samples 
were prepared using an injection of epoxy/ BaTiO$_3$ mixture into a mold and pressed under 
30 MPA for 10 minutes. Further pressing of 30 MPa was carried out at 70 C for 3 hours 
and then heated to 150 C for curing. All the nanocomposites contain 50 vol% BaTiO$_3$ 
nanoparticles. The dielectric permittivity of pristine BaTiO$_3$, BaTiO$_3$ treated with H$_2$O$_2$, 
BaTiO$_3$ treated with KBM 803, BaTiO$_3$ treated with KBM 903 and BaTiO$_3$ treated with 
KBM 303 were found to be 30, 31, 25, 28 and 28 respectively at 1 kHz. They also reported 
that surface modification of BaTiO$_3$ with silane coupling agents resulted in decreased di-
electric loss tangent and weak dielectric dispersion.
The choice of coupling agent chiefly depends on the type of polymer that is being used in the composite. For example, Dang et al. [178] and Dalle Vacche et al. [38] both made use of PVDF as their polymer, and as a result had to choose one that is compatible, and in this case they both incorporated 3-aminopropyltriethoxysilane as the coupling agent. This thesis work makes use of epoxy as the matrix and incorporates γ-glycidyloxypropyltrimethoxysilane as the coupling agent.

The literature however does not provide any insight regarding the influence of concentration of the coupling agent as a function of permittivity, both real and imaginary. As a result there is a limited understanding on how the variability of the concentration of the coupling agent impacts the properties of the dielectric composite namely, piezoelectric coefficients $d_{33}$ and $d_{31}$, electrical resistivity and conductivity, dielectric breakdown strength. This thesis work aims to understand how concentration of the coupling agent influences these parameters to develop an effective dielectric composite.
Chapter 4

Experimental Methods

4.1 Materials and Methodology

BaTiO$_3$/epoxy thick film composites were fabricated where the volume fractions of BaTiO$_3$ were varied from 0.10 to 0.60. A minimum of four samples of each volume fraction was fabricated for the studies described herein. Nano-sized barium titanate (Ba-TiO$_3$) powder was surface modified using ethanol (3 ml per unit gram of BaTiO$_3$) and varying concentrations (in terms of volume fraction of the combined mixture) of silane coupling agent (0.01, 0.015, 0.020 and 0.025). In this chapter, the materials used are described along with their mechanical, piezoelectric and dielectric properties. In addition, the experimental methods used for the fabrication of the composite dielectrics and procedures for the characterization of the materials are described in detail.

4.1.1 Materials

The materials used in all experiments were BaTiO$_3$ (Sigma-Aldrich, <100 nm particle size, >= 99%), Epofix Cold-Setting embedding resin (Bisphenol-A-Diglycidylether, Electron Microscopy Sciences) $^{[184]}$ and 3-Glycidoxypropyltrimethoxysilane (Sigma-Aldrich, >= 98%, KH-560). The piezoelectric and physical properties of the BaTiO$_3$, DGEBA epoxy and KH-560 are presented in Table 4.7, Table 4.8 and Table 4.9, respectively.
### Table 4.7: Physical properties of BaTiO$_3$\textsuperscript{[63]}

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm$^3$)</td>
<td>6.08</td>
</tr>
<tr>
<td>Mean Diameter*</td>
<td>~ 100 nm</td>
</tr>
<tr>
<td>Curie Point (°C)</td>
<td>130 C</td>
</tr>
<tr>
<td>Dielectric Constant</td>
<td>150 \textsuperscript{[185]}</td>
</tr>
<tr>
<td>$d_{33}$ (pC/N)</td>
<td>230</td>
</tr>
</tbody>
</table>

* As received from the manufacturer.

### Table 4.8: Physical, dielectric and piezoelectric properties of DGEBA epoxy \textsuperscript{[184]}

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric Constant</td>
<td>2.9 – 3.2*</td>
</tr>
<tr>
<td>Dielectric dissipation</td>
<td>~ 0.02-0.04</td>
</tr>
<tr>
<td>Electromechanical coupling factor, $k_{33}$</td>
<td>--</td>
</tr>
<tr>
<td>Piezoelectric strain coefficient, $d_{33}$</td>
<td></td>
</tr>
<tr>
<td>Young’s Modulus</td>
<td>0.15-0.20 $10^{10}$ N/m$^2$</td>
</tr>
<tr>
<td>Density</td>
<td>1.16 g/cm$^3$</td>
</tr>
<tr>
<td>Electrical Resistivity</td>
<td>0.15 @ 1 kHz</td>
</tr>
</tbody>
</table>

* Experimental values
Table 4.9: Physical properties of 3-glycidoxypropyltrimethoxysilane

<table>
<thead>
<tr>
<th>Silane Coupling Agent – KH 560</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Property</strong></td>
</tr>
<tr>
<td>Density</td>
</tr>
<tr>
<td>Boiling point</td>
</tr>
</tbody>
</table>

4.2 Sample Fabrication Methodology

4.2.1 Surface Modification of BaTiO₃ Nanoparticles

Polymer-based nanocomposite materials in which nanoparticles are dispersed into polymer have gained a lot of attention as attractive materials because they have the potential to combine the benefits of polymeric materials with the functional properties of nanoparticles [1, 20, 37, 39, 172, 186-190]. BaTiO₃/epoxy composites are used as dielectric materials for capacitor applications because they combine the high permittivity of the BaTiO₃ nanoparticle and the easy processing of the epoxy resin. To develop a composite that serves as an effective capacitor it is essential to control the dispersion of the nanoparticles within the epoxy matrix. It is paramount that there is homogeneous distribution of nanoparticles within the matrix to enhance the dielectric properties of the composite. However, particle-polymer systems have two main processing challenges: (i) organic-inorganic polymer composites inherently repel each other during processing [25, 31, 32] and (ii) nanoparticle agglomeration arises due to high surface energy [28].

The primary drawback of inorganic-organic composite systems is the incompatibility of the two materials. In the case of BaTiO₃/epoxy composites, the surface of the
BaTiO$_3$ nanoparticle contains residual hydroxyl groups, which make it hydrophilic i.e. has an affinity to water, whereas the surface of the epoxy matrix and organic solvent are hydrophobic. So when these two materials are mixed with each other, the BaTiO$_3$ nanoparticles tend to repel the epoxy matrix. When the powder particles repel from the matrix, the particle-to-matrix interface is sacrificed and the particles begin to aggregate and form into clusters. The agglomeration of the particles causes inhomogeneous distribution of nanoparticles and processing difficulties. Employing a suitable surface modification procedure may make it is possible for the two dissimilar materials to be mixed together to form a homogeneous composite as shown in Figure 4.26.

Figure 4.26: A) BaTiO$_3$ particle with hydrophilic hydroxyl groups on its surface. B) Conceptual diagram highlighting the effect of surface treatment.

Another drawback is the innate behavior of the BaTiO$_3$ nanoparticles to form agglomerates due their high surface area – volume ratio leading to high surface energy. In order to diminish this energy, they tend to form bonds with neighboring particles and hence agglomerate. Van der Waals forces arise between all molecules and particles be it in air, vacuum or in liquids [28]. Between identical materials they are attractive, but can be repulsive between dissimilar materials in a third medium. Uncoated nanoparticles of metals, metal oxides, ceramic materials and chalcogenides have strong van der Waals
forces and tend to aggregate when in inert non-polar liquids as shown in Figure 4.27. However, these types of aggregations can be prevented in two ways via *steric* or *electrostatic* stabilization. Steric stabilization involves coating of the nanoparticle with a polymer or surfactant to reduce its surface energy \([160]\). Electrostatic stabilization occurs when the particle becomes charged and/or surrounded by a hydration layer which prevents aggregation \([28, 160]\).

![Figure 4.27: A) conceptual diagram outlining the effects of van der Waals forces, and a visual diagram outlining the B) van der Waals forces pulling molecules together. Van der Waals forces are attractive between identical materials, and bare uncoated oxides or ceramic particles have strong such forces and tend to aggregate [28].](image)

Therefore, by incorporating a suitable surface modification procedure both drawbacks associated with the agglomeration of nanoparticles can be minimized. Two surface modification procedures were explored in this work: (i) surface modification of \(\text{BaTiO}_3\) nanoparticles in ethanol and (ii) surface modification of \(\text{BaTiO}_3\) nanoparticles using a silane coupling agent i.e. \(\gamma\)-glycidyloxypropyltrimethoxysilane. This work is novel in that there isn’t sufficient literature that tries to simultaneously evaluate the influence of the coupling agent on the dielectric permittivity, electrical conductivity and electrical resistivity of the surface treated composite material. The literature also does not indicate the behavior of the dielectric breakdown of the surface treated composite.
4.2.2 Surface Modification with Ethanol

The surface modification of the BaTiO$_3$ nanoparticle using ethanol provides the baseline datum for the subsequent studies. Ethanol has been used in the past as a dispersant to aid in breaking down the particle-particle agglomerations [44]. This study was aimed at identifying the minimum amount of time required to break down most of the agglomerations. As in previous investigations [44], a time study was carried out, wherein the mixture containing BaTiO$_3$ and ethanol was be placed in an ultrasonicator between 1 and 5 hours, for every hour. A paraffin film was placed at the top of the beaker to prevent evaporation of the ethanol into the air. The BaTiO$_3$ particle morphology and distribution were observed with the aid of a Zeiss Sigma Field Emission scanning electron microscope (SEM) and an Oxford INCA PentaFET x3 8100 energy dispersive X-ray spectroscopy (EDS). The SEM micrograph images were captured of the BaTiO$_3$ as received, and after surface modification at each of the time increments described in the table. These images will be in the Results section of the thesis.

Table 4.10: Ethanol surface treatment of BaTiO$_3$ at various time intervals between 1 and 5 hours

<table>
<thead>
<tr>
<th>Ethanol</th>
<th>Set 1</th>
<th>Set 2</th>
<th>Set 3</th>
<th>Set 4</th>
<th>Set 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
<td>1 hour(s)</td>
<td>2 hour(s)</td>
<td>3 hour(s)</td>
<td>4 hour(s)</td>
<td>5 hour(s)</td>
</tr>
</tbody>
</table>

4.2.3 Surface Modification Using a Silane Coupling Agent

Use of coupling agents improves the adhesion between mineral fillers and organic resin matrices [40]. Coupling agents improve the chemical resistance of the bond across
the interface. Coupling agents essentially comprise of two different functional groups, one that can react with each part of the repulsive system, thereby acting as an adhesion promoter [40]. Silane coupling agents consist of two functional groups, one which can react with the surface of the BaTiO$_3$ nanoparticle by forming a covalent bond with the residual hydroxyl groups on its surface, and the other which can react with the epoxy chain of the resin as shown in Figure 4.28.

![Figure 4.28: General structure of a silane coupling agent, where R is an organic functional group](image)

A list of some of the different organic functional groups (the choice of which typically depend on the type of organic polymer being employed) that can be used to form silane coupling agents is shown in Table 4.11.
The *glycidyloxypropyl* type silane was chosen as the type of organic functional group given that a glycidylfunctional epoxy resin was being employed i.e. dyglycidyl ether of bisphenol A (DGEBA) is the type of epoxy being used in our composites [40, 127]. Silane coupling agents were originally designed for these resins and their performance is best understood in this application. *γ*-glycidyloxypropyltrimethoxysilane i.e. KH-560 was selected as the silane coupling agent that would be used to modify the surface of the BaTiO$_3$ nanoparticles. Four different concentrations, in terms of volume fraction of the entire mixture, of coupling agent were used namely, 0.01, 0.015, 0.020 and 0.025 (v/v i.e. volume fraction percentage) to modify the BaTiO$_3$ nanoparticles, so that one can study the effect of varying the concentration on the dielectric properties of the final composite.

For the 0.01 KH-560 treatment, 5g of BaTiO$_3$, 50 ml of ethanol and 0.5g of KH-560 were mixed in a beaker (amount of KH-560 was varied accordingly for the 0.015, 0.020 and 0.025 treated samples). The mixture was subsequently magnetically stirred for 12 hours and 70 °C. The powders were then dried at 50 °C for an additional 12h in air for

<table>
<thead>
<tr>
<th>Organofunctional Group</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Vinyl</td>
<td>CH$_2$=CH</td>
</tr>
<tr>
<td>B. Chloropropyl</td>
<td>ClCH$_2$CH$_2$</td>
</tr>
<tr>
<td>C. Epoxy</td>
<td>CH$_2$-CH=CH$_2$-O-CH$_2$-CH$_2$</td>
</tr>
<tr>
<td>D. Methacrylate</td>
<td>CH$_2$=C-COOCH$_2$CH$_2$</td>
</tr>
<tr>
<td>E. Mercapto</td>
<td>HSCH$_2$CH$_2$</td>
</tr>
</tbody>
</table>

Table 4.11: A list of different organic functional groups for silane coupling agents
the residual ethanol to evaporate. Once the powders were surface treated they were then used for sample preparation. The surface modification procedure is shown in Figure 4.29.

![Surface treatment of BaTiO$_3$ nanoparticles with KH-560](image)

**Figure 4.29**: Surface treatment of BaTiO$_3$ nanoparticles with KH-560. The mixture was magnetically stirred for 12 hours and 70 °C followed by drying in air at 50 °C for an additional 12h.

**Table 4.12**: Varying concentration of silane coupling agent for surface treatment of BaTiO$_3$ nanoparticle

<table>
<thead>
<tr>
<th>KH-560</th>
<th>Set 1</th>
<th>Set 2</th>
<th>Set 3</th>
<th>Set 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>0.01</td>
<td>0.015</td>
<td>0.020</td>
<td>0.025</td>
</tr>
</tbody>
</table>

### 4.2.4 Composite Film Fabrication

BaTiO$_3$/epoxy thick film composites were deposited on to stainless steel substrates using a multi-step spin coat and deposition technique. The stainless-steel substrates were 20 mm by 20 mm squares and 0.0254 mm thick. An overview of the fabrication process for the two-phase or diphasic composites is provided in Figure 4.30. The volume fractions of the BaTiO$_3$ were varied from 0.10 to 0.60 (v/v). The nanoparticle which was surface modified (either by ethanol alone or silane coupling agent) are allowed
to dry. The dried powder was then weighed to achieve the desired volume fraction and transferred to a beaker. The appropriate amount (based on desired volume fraction) of DGEBA epoxy resin was then added to this beaker by means of a measuring syringe. The subsequently formed mixture was ultra-sonicated for 1 hour, whilst being hand-stirred every 15 mins.

![Figure 4](image1.png)

**Figure 4.30:** A) Schematic diagram of the composite preparation. The contents i.e. surface treated-BaTiO$_3$, epoxy was mixed in a beaker and ultra-sonicated for 1 hour, B) the subsequent mixture is spin-coated using a multi-step method to ensure uniform dispersion by accelerating and decelerating gradually.

Finally, the epoxy hardener was added to this mixture. The contents of this combined mixture were transferred via a dropper to the stainless steel substrate, which sits on the spin-coater as shown in Figure 4.31. The multi-step spin coating method comprised of 17 steps to ensure that the final speed was achieved in a step-wise manner. The initial speed was set to 200 rpm and increased by 100 rpm every 5 seconds until it reached 1000 rpm. The substrate spun at 1000 rpm for 30 seconds before the speed was reduced
to 200 rpm in the same way, to ensure that there was no sudden cessation. This spin-coat process was designed to reduce any inertia that may act on the substrate.

Figure 4.31: A) Fixture that holds the sample in the spin coater, with a vacuum suction that holds the sample in place, B) the sample placed on top of the fixture whilst spin coating.

Once the samples were coated, they were removed and placed on a hot plate in air for 8 hours at 75 °C as shown in Figure 4.32. The samples were then cooled for 24 hours. The BaTiO3/epoxy composites were corona polarized (contactless) at 30 kV/mm in air at 75°C for 30 minutes using a Spellman SL 1200 high voltage power source. The samples were then wrapped in aluminum foil for 24 hours to rid them of any remnant charges on the surface of the sample.
4.3 Materials Characterization

4.3.1 Piezoelectric Coefficients

The piezoelectric strain coefficient, $d_{33}$, was measured using PIEZOTEST’s PiezoMeter PM 300 System. This PiezoTest system can piezoelectric strain coefficients $d_{33}$, $d_{31}$ as well as capacitance and tan $d$. The system works by clamping the sample, and subjecting it to a low frequency force of 0.25 N at 110 Hz. Based on this oscillating mechanical vibration, the sample, being piezoelectric creates an equivalent electrical signal.
Figure 4.33: Two measuring configurations for different coefficients, A) the $d_{33}$ measurement showing the longitudinal piezoelectric strain coefficient and B) $d_{31}$ which measures the strain in the axial direction. Each measuring configuration uses different probes and fixtures.

The electrical signal that is received from the sample is then compared with a built-in reference and thereby enabling the system to provide a direct reading of the $d_{33}$, which is one of the most useful parameters in determining the piezoelectric properties, i.e. it is a material coefficient representing charge per unit force in the direction of the polarization. The units for $d_{33}$ are pC/N, i.e. Pico Coulomb per Newton, which is the amount of charge generated on the surface of the sample per unit of applied force. This method of operation in this system is often called the quasi-static or Berlincourt method.

A key reason of recording the measurements at a low frequency is to avoid any likely system or sample resonances, yet it is high enough to demonstrate a conclusive measurement. This system also provides useful material metrics such as the capacitance in pF and tan $\delta$. 
4.3.2 Dielectric Permittivity, Resistivity and Conductivity

The capacitance, resistance and conductance were measured using a Hewlett Packard 4194A Impedance/Gain-Phase Analyzer as shown in Figure 4.34. The HP 4194A impedance/gain-phase analyzer is an integrated solution for efficient measurement and analysis of components and circuits. It features a wide test frequency range, 100 Hz to 40 MHz for impedance measurement, it also boasts a high degree of measurement accuracy i.e. 0.17% for impedance measurements. The sample is clamped between the probes that are connected to the test equipment. In order to transfer the electrical signals generated, the sample is typically has electrodes on both sides before testing.

![Image](image_url)

**Figure 4.34:** The HP4194A impedance/gain-phase analyzer was used to measure the capacitance, resistance and conductance as a function of frequency. The frequency range for measurement is between 2000 Hz up to 40 MHz

For these measurements namely the capacitance, resistance and conductance the frequency was varied between 2000 Hz and 40 MHz. This large frequency sweep provides insight into the electromechanical behavior of the sample with increasing frequency. The complex dielectric permittivity consists of the real and imaginary part. The real part of
the complex permittivity is known as the dielectric constant and it is a measure of the charge storage abilities of the material. The imaginary part is the loss component i.e. dielectric loss or dissipation. This loss could originate from heat or from ohmic conduction of the material. The dielectric constant was calculated using the expression,

\[
\varepsilon_r = \frac{Ct}{A\varepsilon_o},
\]

where, \( C \) is the capacitance in Farads, \( A \) is the area of the sample, \( \varepsilon_o \) is the permittivity of free space \( \sim 8.854 \times 10^{-12} \text{ F m}^{-1} \) and \( t \) is the thickness of the sample. The HP 4194A impedance analyzer was used to measure the impedance, \( Z \). The real part of impedance is resistance, \( R \) and the imaginary part is reactance, \( X \). The imaginary part physically represents the phase angle between voltage and current, in an ideal capacitor, where the voltage lags behind the current by 90°.

\[
Z = R + jX.
\]
The real part of impedance, i.e. resistance was then used to calculate resistivity, so as to normalize it for units of length as can be seen in Equation (4.17),

\[
\rho = \frac{RA}{t}. \tag{4.17}
\]

Similarly, the admittance, Y, is also measured by the HP 4194A impedance analyzer which like impedance is also a complex quantity as shown in (4.18),

\[
Y = G + jB, \tag{4.18}
\]

where, \(G\) is conductance and \(B\) is susceptance. Conductivity is calculated using the equation to normalize it for units of length,
4.3.3 Theoretical Models for Predicting Effective Permittivity of Polymer Nanocomposites

The effective permittivity of a polymer nanocomposite can be calculated by knowing the individual permittivity of the ceramic fillers and polymer matrix along with filler loading level i.e. volume fraction of the filler in the polymer matrix. There are several models that can be used to determine the effective permittivity of the composite.

(i) Maxwell-Garnett Equation

This model is typically applicable to composites composed of continuous media filled with spherical particles [191, 192]. Consider an isotropic medium i.e. polymer matrix of dielectric permittivity $\varepsilon_m$ filled with spheroids of permittivity $\varepsilon_f$. The volume fraction of filler particles is designated as $\phi_f$ and the resulting volume fraction of the matrix is $\phi_m = 1 - \phi_f$. Here the assumption is that the filler and matrix components have no dielectric loss. It also assumes that the separation distances between the randomly oriented inclusions are greater than their characteristic sizes [10, 193, 194]. This model is not limited by the resistivity of the filler or the polymer matrix.

$$\varepsilon_{eff} = \varepsilon_m \left[ 1 + \frac{3\phi_f(\varepsilon_f - \varepsilon_m)}{\phi_m(\varepsilon_f - \varepsilon_m) + 3\varepsilon_m} \right].$$  \hfill (4.20)

(ii) Bruggeman Self-Consistent Effective Medium Approximation
This model is more applicable for composites that contain slightly larger filler concentrations in comparison to the Maxwell-Garnett equation (which is more effective for lower filler loadings). This model also yields better results when the fillers particles are very close to one another and even agglomerate \cite{10, 192}. The formula of this model for spherical fillers is,

\[
(1 - \phi_f) \frac{\varepsilon_m - \varepsilon_{\text{eff}}}{\varepsilon_m + 2\varepsilon_{\text{eff}}} + \phi_f \frac{\varepsilon_f - \varepsilon_{\text{eff}}}{\varepsilon_f + 2\varepsilon_{\text{eff}}} = 0. \tag{4.21}
\]

This can be further solved for the final Bruggeman’s formula \cite{195, 196},

\[
\frac{\varepsilon_f - \varepsilon_{\text{eff}}}{\varepsilon_{\text{eff}}} = \left(1 - \phi_f\right) \frac{\varepsilon_f - \varepsilon_m}{\varepsilon_m} \tag{4.22}
\]

This equation is expected to hold for \(\phi_f\) values up to 0.5, with the constraint that the dispersed spheres do not form a percolative path throughout the medium.

(iii) Lichtenker’s Formula

This is a logarithmic mixture formula and is effective in calculating the permittivity of the polymer composite. The Lichtenker’s formula is shown in (4. 23 \cite{197-199}.

\[
\varepsilon_{\text{eff}}^\alpha = \phi_m \varepsilon_m^\alpha + \phi_f \varepsilon_f^\alpha \tag{4.23}
\]

In Equation (4. 23), \(\varepsilon_{\text{eff}}\) is the effective permittivity of the composite, and \(\varepsilon_m\) and \(\varepsilon_f\) are the permittivities of the polymer matrix and ceramic filler, and \(\phi_f\) and \(\phi_m\) are the volume
fraction of fillers and matrix, respectively. The parameter $\alpha$ varies from -1 to +1 and is considered to describe the transition from anisotropy ($\alpha= -1$) to isotropy ($\alpha= +1$) [192].

(iv) Jaysundere-Smith Equation

Maxwell-Garnett equation is typically only valid for lower concentration of fillers since the interaction between filler particles is relatively weak, and at higher volume fractions the interaction between the fillers becomes significant because the distance between them reduces [10, 192]. Jayasundere and Smith [200] proposed a more realistic mixing rule. They calculated the electric field with a dielectric sphere embedded in a continuous dielectric medium by taking into account polarization of adjacent particles and arrived at the following equation:

$$
\varepsilon_{eff} = \frac{\phi_m \varepsilon_m + \phi_f \varepsilon_f}{\phi_m + \phi_f} \left[ 1 + \frac{3 \phi_f (\varepsilon_f - \varepsilon_m)}{2 \varepsilon_m + \varepsilon_f} \right] 
$$

4.3.4 Hysteresis Loop Measurements

The hysteresis measuring set-up consists of three separate pieces of equipment, the Radiant Technologies, Inc. (i) Precision LC II Ferroelectric Tester, (ii) the Precision Single Channel High Voltage Interface (10kV HVI-SC), which is an attachment for the aforementioned Precision Test System and (iii) the Trek Model 609B High Voltage Power Amplifier as shown in Figure 4.36. The Precision Test System can be used to test thin films and bulk ceramics. The Precision LC II tester has a frequency rating of 5 kHz.
at +/- 200V built-in to the system. This system can execute hysteresis loops, pulse, leakage, IV and CV measurements. Based on the type of fixture, it can also detect pyroelectric properties, magnetoelastic properties, transistor characteristics, cryogenic properties, bulk and/or thin film piezoelectric properties. The Trek 609 B is a DC stable, high voltage power source amplifier that used along with the Precision Test system.

The type of fixture that was used is a High Voltage Test Fixture (HVTF) with an added capability that allows the test system to monitor the piezoelectric displacement of the sample (High Voltage Displacement Meter – HVDM). The HVTF, rated at 250 °C, is a unique Teflon sample holder for bulk and/or thin film ceramic devices, and the sample holder is meant to be operated at room temperature. The HVTF is made up of high temperature Teflon and is able to withstand exposures of up to 180 °C continuous or 250 °C for short periods, making it ideal for both high-temperature and high-voltage testing. The HVTF separates into two parts. The fixture is shown in Figure 4.37.
The sample is placed in a chamber in bottom half of the fixture. A copper electrode fixed in the bottom of the chamber contacts the electrode on the bottom of the sample. A 25KV cable connects the copper contact to an external 25 KV electrical connector. The bottom chamber is sealed so it may be filled with insulating oil to protect the sample from the arcing that may occur in open air. The top half of the fixture fits over the bottom half, sealing the chamber. The top half of the fixture has an unclamped copper electrode that is held in place against the top sample electrode by gravity. This contact is free to move up or down to allow for varying thicknesses of sample.

![Sample fixture](image)

**Figure 4.37: A) High Voltage Test Fixture (HVTF), B) Sample is sandwiched between copper electrodes**

### 4.3.5 Leakage Current Measurements

The Leakage Task is a vision measurement task that samples the steady state current through the test element connected to the Precision tester. Sampling is done by placing a constant DC bias voltage across the sample. A programmable delay or ‘soak’ time period passes before the measurement begins. This is intended to allow any polarization...
switching current or other currents induced by the application of the voltage to settle so that the sample is in steady state. After the delay period, a measurement period begins in which the current through the device under test is regularly sampled and recorded.

![Diagram of Leakage Test Stimulus and Measurement Profile](image)

**Figure 4.38:** Leakage test stimulus and measurement profile. Initial soak time is to ensure the sample is in steady state before measurement begins, i.e. this is intended to allow any polarization switching current previously induced to settle.

The current is sampled as frequently as possible i.e. 510 data points but only the final 90% of the measurement is plotted by the Radiant Technologies Inc. software.

### 4.3.6 Viscosity Measurements

The viscosity measurements were taken using a Brookfield digital viscometer model DV-E. This DV-E viscometer measures fluid viscosity at given shear rates. Viscosity can be defined as a measure of a fluid’s resistance to flow. The principle of operation of the DV-E is to rotate a spindle (which is fully immersed into the fluid) through a calibrated spring. The viscous drag of the fluid against the spindle is measured by the spring
deflection. Spring deflection is measured with a rotary transducer which provides a torque signal. For these measurements, spindle s64 was used to conduct the viscosity measurements. The measurement range of the DV-E (milliPascal seconds, mPas) is determined by the rotational speed of the spindle (100 rpm for these measurements), the size and shape of the spindle (s64, cylindrical), the container in which the spindle is rotating, and the full-scale torque of the calibrated spring.

The DV-E Viscometer employs an optical signal pick-up inside the equipment to determine the torque value of the calibrated spring. This optical signal pick-up is measured four times per revolution of the spindle. When the spindle begins to rotate at a preset speed, four torque values are recorded during the first full revolution of the spindle and then averaged. The display reports the average value for both torque (%) and viscosity (cP or mPas). Thereafter, the next torque value recorded by the optical signal pick-up is averaged together with the three preceding torque values and the newly calculated torque (%) and viscosity (cP or mPas) values are then displayed. This 4x revolution pick-up and display continues as long as the motor is on.
4.3.7 Viscosity Study

Once the ideal concentration of coupling agent was determined it was followed by carrying out a viscosity study. The viscosity study was aimed at further enhancing the overall dielectric composite. In order to be able to develop the most effective composite, it was imperative to identify the concentration of the coupling agent prior to the viscosity study.

This study was carried out to determine the optimum viscosity that corresponded to the optimal dielectric permittivity. In addition, different qualitative properties were also taken into account, such as possible delamination and sample curvature as a function of viscosity. The viscosity was varied between 150 - 300 mPas. This range would observed determine the optimal value for adequate adhesion of the solution onto the substrate and optimal dielectric constant values. The Brookfield DV-E viscometer (with s64 spindle) was used for these studies. Eight samples were fabricated between 150 - 300 mPas in increments of 10 mPas.
Table 4.13: The samples were fabricated at eight different viscosities between 150 and 300 mPas in order to determine the ideal viscosity to be used for future fabrication.

<table>
<thead>
<tr>
<th>Sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (mPas)</td>
<td>148</td>
<td>160</td>
<td>170</td>
<td>180</td>
<td>200</td>
<td>220</td>
<td>230</td>
<td>282</td>
</tr>
</tbody>
</table>

4.3.8 Vacuum Desiccation

A vacuum desiccation procedure was incorporated in the study in order to get rid of the air voids present in the precursor solution. The desiccation process was carried out just before spin coating for 4 hours, as shown in Figure 4.40. The beaker containing the different composite constituent materials such as the surface-modified BaTiO$_3$ nanoparticles, ethanol and epoxy is placed inside the vacuum chamber. The vacuum chamber is connected to a pump to its right, which creates a suction inside the chamber, removing the air bubbles from the solution.

Figure 4.40: Vacuum desiccation process, with the vacuum chamber on the left and the vacuum pump to the right. The sol prior to spin coating was vacuum desiccated for 4 hours.
4.3.9 Material Morphology and Surface Characterization

4.3.9.1 SEM and EDS

The surface morphology of the individual phases and the surface of the overall composite was examined using a Zeiss Sigma Field Emission scanning electron microscope (SEM) and an Oxford INCA PentaFETx3 8100 energy dispersive X-ray spectroscopy (EDS). Two types of SEM micrograph images were captured for these composite materials. One image was captured from the top surface of the sample to provide information about the distribution of the individual phases within the polymer matrix, and the other image capture was the cross-sectional along the thickness of the sample. The cross-sectional image represents how the particles are distributed along the thickness whilst also providing a macroscopic view of the composite-substrate interface, which is a critical identifier of qualitative nature of the composite.

The EDS micrograph images are used to obtain elemental analysis of the composite, which help in obtaining the distribution of the particles within the polymer matrix, by isolating them.
Chapter 5

Results and Discussion

5.1 Overview of the Chapter

This chapter presents the qualitative observations from the SEM and EDS micrograph images, particle mean diameter of the datum (non-surface treated) samples, ethanol treated and silane coupling agent treated BaTiO$_3$ nanoparticles. The EDS micrograph images were taken for samples with 0.5 volume fraction of BaTiO$_3$ as the reference because for our measurements, they represent the best properties. The next part of this chapter describes the quantitative observations such as the piezoelectric strain coefficients $d_{33}$ and $d_{31}$, the permittivity values, electrical conductivity and resistivity and dielectric breakdown strength of the datum samples, ethanol treated and silane coupling agent treated composites.

5.2 Surface Treatment of Barium Titanate with Ethanol

5.2.1 Morphological Characterization

The non-surface treated BaTiO$_3$ composites were used as the datum for this work and compared with the composites that were prepared using ethanol surface treated and silane coupling agent treated BaTiO$_3$ nanoparticles. The BaTiO$_3$ nanoparticles were surface modified in ethanol at different durations, 1, 2, 3, 4 and 5 hours and the dispersion of the particles were studied using EDS micrograph images, as shown in Figure 5.41. From the images it can see that with prolonged duration, the dispersion of the nanoparticles
improve. The different colors in Figure 5.41 represent the distribution of the BaTiO$_3$ nanoparticles in an ethanol solvent. (Note: the colors are different as they are on different SEM studs and hence the machine treats them as different samples.

Figure 5.41: EDS micrograph images of the BT powder surface treated using ethanol for A) 1 hour, B) 2 hours, C) 3 hours, D) 4 hours and E) 5 hours. It is evident that there is better particle dispersion with
longer sonication time in ethanol. However, the optimal sonication time based on the images is for four hours. (Note: The different colors all represent BT nanoparticles, but since they are on different SEM studs, the machine treats them as different sample sets, and hence the change in color.)

The EDS images also indicate that the exposure of the BaTiO₃ nanoparticles to ethanol over extended periods of time diminished the agglomeration and particle-particle clusters. From these results, 4 hours was chosen as the ideal surface treatment time for the BaTiO₃ nanoparticles. From the SEM micrograph images in Figure 5.42 we can see charging of the samples even after applying a gold coating of 30 nm, which could be attributed to the surface charges produced on the BaTiO₃ nanoparticle due to its reaction with ethanol. This electrostatic charge keeps the BaTiO₃ nanoparticles from agglomerating as can be seen by the reduction in mean particle size compared with the untreated nanoparticles (from ~60 µm to 40 µm).

![Figure 5.42: SEM micrograph images of BaTiO₃ nanoparticles that were surface treated in ethanol for 4 hours A) at a scale of 100 µm and B) at a scale of 20 µm. From the images we can see charging of the samples even after applying a gold coating of 30 nm, which could be attributed to the surface charges produced on the BaTiO₃ nanoparticle due to its reaction with ethanol. This electrostatic charge keeps the BaTiO₃ nanoparticles from agglomerating as can be seen by the reduction in mean particle size i.e. from ~60 µm to 40 µm.](image-url)
The stability of ceramic particles is based on the summation of the van der Waals attractive forces, electrostatic repulsion and possible steric hindrance from adsorbed surfactants or coupling agents [63, 64]. Either electrostatic repulsion or steric hindrance counter acts the strong van der Waals forces to reduce the formation of particle clusters. Ethanol is considered to be a weakly acidic solvent (pKₐ ~16 and pH ~<7 [201]). As result of this solvent’s polarity a surface charge may be developed on the surface of the ceramic particle (Silica fillers and Calcium Carbonate, CaCO₃) [120, 202] as they are exposed to the solvent over time. Fowkes et al. [121, 122] observed the development of a positive surface charge on ceramic particles after they were mixed with ethanol. The surface charge was achieved by proton exchange, i.e. the acidic nature of the adsorbate results in proton transfer to the particle surface. This charged surface that forms on the particles results in electrostatic repulsion between successive particles thereby counter acting the van der Waals attractive forces leading to improved particle dispersions within the organic medium [63].

5.2.2 Piezoelectric and Dielectric Characterization of Ethanol Surface Treated BT-Epoxy Composites

The BaTiO₃-epoxy composites were fabricated using BaTiO₃ nanoparticles that were surface modified using ethanol for 4 hours. The sonication of these particles in ethanol improved their dispersion and led to improved piezoelectric strain coefficient values compared to pristine BaTiO₃-epoxy composites, as can be seen in Figure 5.43 and Figure 5.44. The relative permittivity or dielectric constant was measured at 20 MHz and plotted as function of increasing volume fraction of the nanoparticle fillers, as shown in Figure 5.45.
Figure 5.43: The piezoelectric strain coefficient, $d_{33}$ for the BaTiO$_3$-epoxy composite fabricated using BaTiO$_3$ nanoparticles that were surface modified using ethanol for 4 hours is plotted as a function of volume fraction of BaTiO$_3$. The maximum value is 0.58 pC/N at 0.6 vol. fraction of BaTiO$_3$.

Figure 5.44: The piezoelectric strain coefficient, $d_{31}$ for the BaTiO$_3$-epoxy composite fabricated using BaTiO$_3$ nanoparticles that were surface modified using ethanol for 4 hours is plotted as a function of volume fraction of BaTiO$_3$. The maximum value is 1.49 pC/N at 0.6 volume fraction of BaTiO$_3$. 
It can be seen in Figure 5.43 and Figure 5.44 that the piezoelectric properties $d_{33}$ and $d_{31}$ and the relative permittivity increase with increasing volume fraction of the Ba-TiO$_3$ nanoparticles within the composite. Ethanol only acts as a dispersant, i.e. it can only improve dispersion of the fillers and not act as a binding or molecular bridge between fillers and polymers \[33, 34, 36, 39\], however the ethanol does aid in better dispersion of the particles within the composite, and as previously mentioned is due to electrostatic stabilization.

\textbf{Figure 5.45}: The relative permittivity of the BaTiO$_3$-epoxy composite fabricated using BaTiO$_3$ nanoparticles that were surface modified using ethanol for 4 hours is plotted as a function of vol. fraction. The measurements were taken at 20 MHz.
5.3 Surface Treatment of Barium Titanate with Silane Coupling Agent

5.3.1 Reaction Mechanism

The silane coupling agent, KH-560, contains an organic functional group that resembles an epoxy chain and three alkoxide groups viz. (Si-OCH₃). During the surface modification procedure, which involves mixing KH-560, ethanol and BaTiO₃, the alkoxide groups are hydrolyzed by water generating Si-OH groups and alcohols, as can be seen in Figure 5.46. The water that reacts with the alkoxide groups can come from two sources namely, (i) the solvent, in this case ethanol (95/5; ethanol/water) or (ii) water adsorbed on particle surface when an anhydrous solvent is used.

![Figure 5.46: The alkoxide groups (Si-OCH₃) of KH-560 are hydrolyzed by water thereby leading to the formation of Si-OH groups and methanol.](image)

The hydrolysis reaction is followed by a condensation reaction between the newly formed Si-OH groups of the coupling agent and the hydroxyl groups on the surface of the BaTiO₃ nanoparticle, as shown in Figure 5.47. This causes BaTiO₃ to rid itself of the hydroxyl group on its surface with a coupling agent that can bond easily with epoxy as can be seen in Figure 5.48. The condensation reaction leads to the formation of water and BaTiO₃ particles with a modified surface chemistry. This reaction makes the BT nanoparticle surface more compatible with the epoxy matrix.
Figure 5.47: A condensation reaction occurs between the newly formed Si-OH groups of the coupling agent and the hydroxyl groups adsorbed on the surface of the BaTiO$_3$ nanoparticle.

If multiple such reactions occur, then more hydroxyl groups are available to react with the coupling agent, leading to the formation a modified BaTiO$_3$ particle as shown in Figure 5.48.

Figure 5.48: The surface of the BaTiO$_3$ nanoparticle, which previously contained hydroxyl groups now is replaced by a coupling agent which can bond easily with epoxy resin.
The results above indicate that for a single particle surface the hydroxyl (−OH−) groups have been substituted with that of the coupling agent after the condensation of the silanol groups. This implies that the BaTiO$_3$ can bond easily with the epoxy (Bisphenol A diglycidyl ether) matrix due to the ‘glycidyl’ functional group of the coupling agent (γ-glycidoxytrimethoxysilane).

**5.3.2 Morphological Characterization**

The SEM micrograph images shown in Figure 5.49 represent the cluster size of pristine and surface treated BaTiO$_3$ particles, respectively. From the distribution plots shown in Figure 5.50 it can be seen that the cluster size reduces after surface modification with a silane coupling agent, i.e. from ~60 µm to around ~ 30 µm. The image in Figure 5.49 B did undergo some charging due to the adsorbed insulative organofunctional silane layer and as result had to be taken at lower EHT voltage < 5kV (i.e. lower gun voltage). Figure 5.49 A however contains no such insulative layer and hence could be observed at higher EHT voltage > 7kV.

![Figure 5.49: SEM micrograph images of A) pristine BaTiO$_3$ particles and B) BaTiO$_3$ particles surface treated using SCA 0.01. The images represent the cluster sizes of the of BaTiO$_3$ nanoparticles on a carbon tape. The average cluster size of the pristine BaTiO$_3$ particles is ~60 µm and that of the BaTiO$_3$ particles surface treated using SCA 0.01 is ~ 30 µm.](image-url)
A) Untreated BaTiO$_3$

Size Distribution of Nano-clusters

B) Surface Treated BaTiO$_3$ - Ethanol 4h

Size Distribution of Nano-clusters
C) 

Surface Treated BaTiO$_3$ - SCA 0.010
Size Distribution of Nano-clusters

D) 

Surface Treated BaTiO$_3$ - SCA 0.015
Size Distribution of Nano-clusters
Figure 5.50: Particle distributions of A) pristine BaTiO$_3$ which shows an average cluster size of ~ 60 µm and B) ethanol surface treated for 4h with an average cluster size of ~ 40 µm C) 0.01 silane coupling agent treated BaTiO$_3$ with an average cluster size of ~ 30 µm. It can observed that the agglomerates reduce with surface treatment. D) 0.015 silane coupling agent with an average cluster size of <~ 30 µm E) 0.020 silane
coupling agent with an average cluster size of <~ 25 µm, F) 0.025 silane coupling agent with an average cluster size of ~ 25-30 µm.

**Table 5.14:** Table summarizing the average particle size diameter of the nano-clusters. Surface treatment helps in reducing the cluster size, and improves with increasing concentration of coupling agent.

<table>
<thead>
<tr>
<th>Sample Set</th>
<th>Average Particle Diameter (nano-clusters)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-surface Treated BaTiO$_3$</td>
<td>~ 60 µm</td>
</tr>
<tr>
<td>Ethanol Surface Treated (4h)</td>
<td>~ 40 µm</td>
</tr>
<tr>
<td>Silane Coupling Agent – 0.010</td>
<td>~ 30 µm</td>
</tr>
<tr>
<td>Silane Coupling Agent – 0.015</td>
<td>~ &lt; 30 µm</td>
</tr>
<tr>
<td>Silane Coupling Agent – 0.020</td>
<td>~ 25 µm</td>
</tr>
<tr>
<td>Silane Coupling Agent – 0.025</td>
<td>~ 28 µm</td>
</tr>
</tbody>
</table>
Figure 5.51: EDS micrograph images of the fractured surface of the pristine (not surface treated) BT(0.5)/epoxy composite film where A) overall surface of the composite, B) distribution of Ba and C) Ti within the overlaying epoxy matrix.

The EDS micrograph images were taken for samples with 0.5 volume fraction of BaTiO$_3$ as the reference because for our measurements, they represent the best properties. The EDS micrographs showing the fractured surface of the BT (0.5) – epoxy composite that were not surface treated is shown in Figure 5.51. From the images one can see that there are regions of aggregations of the BaTiO$_3$ particles caused by one of two reasons or both, i) the nanoparticles themselves formed clusters to reduce their surface energy and/or ii) the incompatibility between the inorganic ceramic filler BaTiO$_3$ and the organic
polymer epoxy resin. It is quite evident that agglomerations are undesirable due to increased difficulty in processing, formation of voids and thereby leading to ineffective poling. Surface modification of these composites with a silane coupling agent can greatly improve the overall distribution of the inorganic filler particles as can be seen from the EDS micrograph images in Figure 5.52. Compared to the composites that were not surface treated in Figure 5.51, there is a greater ‘density’ of particles, which coincidentally increases the total surface area creating more interfacial regions between $\text{BaTiO}_3$ and the epoxy matrix. The enhanced dispersion leads to more effective poling as the applied electric field will have influenced more ferroelectric particles within the matrix.

Figure 5.52: EDS micrograph images of the fractured surface of the SCA 0.010 surface treated BT (0.5) – Epoxy composite film where A) is the overall surface of the composite, B) distribution of Ba and C) Ti particles within the overlaying epoxy matrix.
From the EDS micrograph images shown in Figure 5.53 for the 0.020 silane coupling agent surface modified BaTiO$_3$ powders one can see that the particle distribution of Ba, Ti and Si are almost identical. Also from the EDS layered image shown in Figure 5.53A, one can see that Si sits on the surface of the BaTiO$_3$ particles, indicating that successful surface modification occurred.

**Figure 5.53**: EDS micrograph images of SCA 0.015 surface modified BaTiO$_3$ powder showing A) the EDS layered image and the distribution of B) Ti, C) Ba and D) Si particles. It is interesting to note that Si has the same particle distribution as Ba and Ti, which is indicative of the successful modification of the surface of the BaTiO$_3$ nanoparticle. While there is a 1:1 correspondence between B) and C) as they from the same compound i.e. BaTiO$_3$, we see that the Si atoms do not share the same 1:1 correspondence. This could be
attributed to the fact that the volume fraction of silane coupling agent i.e. 0.015 was not sufficient to generate maximum number of reactions.

Figure 5.54: EDS micrograph images of BaTiO$_3$ nanoparticles that were surface treated using SCA 0.020 taken at a scale of 100 µm. It can be seen that Si was successfully coated on to the surface of the BaTiO$_3$ nanoparticles. The images in B), C) and D) represent the particle distributions of Ti, Si and Ba, respectively. Compared to the samples surface treated using SCA 0.015, we notice that there is a greater correspondence between the Ba atoms in B) and the Si atoms in D).
Figure 5.55: EDS micrograph images of the BaTiO$_3$ nanoparticles that were surface treated using SCA 0.025. The green color depicts the B) particle distribution of silicon atoms and the red denotes C) the barium atoms. For composites prepared using SCA 0.025 volume fraction of coupling agent we see a greater correspondence with the Ba and Si atoms, which can be attributed to the increased number of reactions between the BaTiO$_3$ nanoparticle and the silane coupling agent. This almost represents a case of saturated reactions wherein further increases in concentration will yield no further results.
Figure 5.56: SEM micrograph images of the cross-section of the fractured surface of the composite that was prepared using 0.5 volume fraction of non-surface treated or pristine BaTiO$_3$ nanoparticles. Images A) and B) taken at slightly different magnifications of 127X and 245X, respectively. The images show that there is delamination and cracking of the film from the stainless steel substrate. This cracking occurs due to excessive agglomeration of the BaTiO$_3$ nanoparticles within the polymer matrix, leading to a poor quality film. The presence of localized aggregated of BaTiO$_3$ also lead to cracking and poor substrate adhesion.

Figure 5.57: SEM micrograph images of the cross-section of the fractured surface of the composite that was prepared using 0.5 volume fraction of ethanol surface treated (4 hours) BaTiO$_3$ nanoparticles at A) 147X and B) 174X. The images show that overall there is good adhesion between the composite film and the stainless substrate despite observing a minor local delamination.
Figure 5.58: SEM micrograph images of the cross-section of the fractured surface of the composite that was prepared using 0.5 volume fraction of 0.01 silane coupling agent BaTiO$_3$ nanoparticles at A) 1.77 KX and B) 761 X. The images show that surface treating the composite with a coupling agent results in good adhesion between the composite film and the stainless steel substrate.

Figure 5.59: SEM micrograph images of the cross-section of the fractured surface of the composite that was prepared using 0.5 volume fraction 0.015 silane coupling agent BaTiO$_3$ nanoparticles at A) 518 X and B) 753 X. The images show that surface treating the composite with a coupling agent results in good adhesion between the composite film and the stainless steel substrate.
Figure 5.60: SEM micrograph images of the cross-section of the fractured surface of the composite that was prepared using 0.5 volume fraction 0.020 silane coupling agent BaTiO$_3$ nanoparticles at A) 129 X and B) 93 X. The images show that surface treating the composite with a coupling agent results in good adhesion between the composite film and the stainless steel substrate.

From the cross-section images shown in Figure 5.61, for the BaTiO$_3$/epoxy composites fabricated using 0.025 SCA at 50% volume fraction of BaTiO$_3$ the observations indicate severe delamination of the film from the substrate. It is important to note that this delamination is not caused by cracking of the film, instead the film is intact, and peels off as a whole.

Figure 5.61: SEM micrograph images of A) SCA 0.025 BT (0.5)/epoxy composite at 280 X and B) SCA 0.025 BT (0.6)/epoxy at 151 X; both showing significant delamination of the film from the composite. It is interesting to note that there is no cracking on the composite film, it delaminates as a whole.
Table 5.15: Table summarizing the interfacial adhesion between the composite films (at 0.5 volume fraction of BaTiO₃) and the stainless steel substrate. All the sample sets show enhanced adhesion except the 0.025 silane coupling agent where there was complete delamination from the substrate.

<table>
<thead>
<tr>
<th>Sample Set</th>
<th>Composite Film – Substrate Adhesion</th>
<th>Figure Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-surface Treated BaTiO₃</td>
<td>Partial delamination and cracking</td>
<td>Figure 5.56</td>
</tr>
<tr>
<td>Ethanol Surface Treated (4h)</td>
<td>Good adhesion despite minor crack</td>
<td>Figure 5.57</td>
</tr>
<tr>
<td>Silane Coupling Agent – 0.010%</td>
<td>Very good adhesion – no delamination</td>
<td>Figure 5.58</td>
</tr>
<tr>
<td>Silane Coupling Agent – 0.015%</td>
<td>Very good adhesion – no delamination</td>
<td>Figure 5.59</td>
</tr>
<tr>
<td>Silane Coupling Agent – 0.020%</td>
<td>Excellent adhesion – no delamination</td>
<td>Figure 5.60</td>
</tr>
<tr>
<td>Silane Coupling Agent – 0.025%</td>
<td>Complete Delamination</td>
<td>Figure 5.61</td>
</tr>
</tbody>
</table>

There is a noticeable difference when comparing two composite thick films, one is SCA 0.020 BT (0.5)/epoxy and the other is SCA 0.025 BT (0.5)/epoxy as shown in Figure 5.62 A. The observations indicate that the SCA 0.025 sample is showing signs of delamination from the stainless steel substrate. Increasing the coupling agent concentration leads to improved sample cohesiveness and can be seen from the crack-free surface, however this leads to it peeling of the surface of the stainless steel as can be seen in Figure 5.62 B, C. Here the entire film delaminates from the substrate. The complete delamination occurs prior to polarization of the material. Table 5.15 provides a summary of the interfacial adhesion between the composite films at 0.5 volume fraction of BaTiO₃ and the stainless steel substrate. There is good adhesion between most of the surface treated composites as there are presence of no cracks or delaminating partition, however at higher concentrations of silane coupling agent i.e. 0.025, due to enhanced cohesion of the composite, the
adhesion with stainless steel weakens, thereby leading to complete delamination of the film.

**Figure 5.62:** A) Comparison of two composite thick films. The one on the left is SCA 0.020 BT (0.5)/epoxy and the one on the right is SCA 0.025 BT (0.5)/epoxy. There is significant delamination of the composite on the right. In B), the sample has suffered complete delamination, where the 0.025 BT (0.6)/epoxy composite film has separated from the substrate. In C) the composite is remarkably flexible without the substrate.
5.4 Piezoelectric and Dielectric Characterization

5.4.1 Piezoelectric Properties

The longitudinal piezoelectric strain coefficient, i.e. $d_{33}$ was measured using a Piezo Meter System manufactured by Piezo Test, Piezoelectric Materials & Device Testing Company. For the BaTiO$_3$-epoxy composites that were not surface treated, the volume fraction of BaTiO$_3$ was varied from 0.1 to 0.6. As can be observed from Figure 5.63, the piezoelectric strain coefficient, $d_{33}$ increases with increasing volume fraction of BaTiO$_3$ nanoparticles, which is consistent with the observations of several researchers [4, 109, 203-209]. This is expected with increasing the concentration of ferroelectric materials within the composite, thereby leading to enhanced poling and hence greater piezoelectric values. The maximum value of $d_{33}$ is observed at 60% volume fraction of BaTiO$_3$ and is ~ 0.42 pC/N which is comparable to that reported by Yamamoto et al [118].
The BaTiO$_3$ nanoparticles were then surface modified using silane coupling agent, KH-560 at a volume fraction of 0.01. As can be seen from Figure 5.52 this created more number of interfacial regions between BaTiO$_3$ and epoxy creating a more uniform and homogeneous dispersion of nanoparticles within the matrix. The volume fraction of BaTiO$_3$ for these composites was also varied from 0.1 through 0.6. From Figure 5.64 it is evident that the piezoelectric strain coefficient $d_{33}$ increases with increasing concentration of BaTiO$_3$ culminating at 0.6 volume fraction to a value of $\sim 0.7$. Followed by initially surface treating these composites with KH-560 at 0.01 the concentration was subsequently increased to SCA 0.015, SCA 0.020 and SCA 0.025. By varying the concentration
of the coupling agent during surface treatment it enables us to gain a broader understanding of its interaction with BaTiO$_3$ nanoparticles.

The piezoelectric strain coefficient for sample surface treated using SCA 0.015, SCA 0.020 and SCA 0.025 is shown in Figure 5.64, Figure 5.65 and Figure 5.66, respectively. The observations shown in these figures exhibit a similar trend where the value of $d_{33}$ increase with increasing concentration of BaTiO$_3$. This increase in $d_{33}$ values as volume of the ferroelectric particle is increased is consistent with the observations of several researchers [4, 109, 203-209]. However in these composites there seems to be a drop in the value at 0.6 volume fraction. This drop in value could be due to the formation of voids at higher volume fractions thereby increasing the overall porosity of the composite and making them more difficult to pole. Or, the decrease in longitudinal piezoelectric strain coefficient could be due to the delamination of the composite from the substrate, leading to ineffective poling thereby weakening its form and function.
Figure 5.64: The piezoelectric strain coefficient, $d_{33}$, for the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.010 SCA. The maximum $d_{33}$ value is 0.71 pC/N and occurs at a volume fraction of 0.6.

Figure 5.65: The piezoelectric strain coefficient, $d_{33}$, for the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA. The maximum $d_{33}$ value is 0.87 pC/N and occurs at a volume fraction of 0.5.
The piezoelectric strain coefficient, $d_{33}$, for the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.02 SCA. The maximum $d_{33}$ value is 1.16 pC/N and occurs at a volume fraction of 0.5.

The composites that were surface modified using SCA 0.025 suffered from delamination at higher volume fractions viz. 50% and 60%. In these composite, quite unusually, the composites were peeling off of the substrate. At higher concentrations of coupling agent i.e. 0.025, there are more number of covalent bonds formed especially at higher volume fraction of BaTiO$_3$ nanoparticles i.e. 0.5 or higher. As a result there are increased number of BaTiO$_3$-epoxy-silane coupling agent bonds as can be seen from the EDS images above, which lead to improved cohesion of the composite but at the cost of weakened substrate adhesion, i.e. the cohesive strength of the composite outweighs the adhesive strength resulting in complete delamination of the composite but remarkably no cracking of the composite occurs.
Figure 5.67: The piezoelectric strain coefficient, $d_{33}$, for the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.025 SCA. The maximum $d_{33}$ value is 0.84 pC/N and occurs at a volume fraction of 0.4.

A comparison plot showing the variation in the $d_{33}$ across all the composites is shown in Figure 5.68. Largely, the $d_{33}$ shows a similar trend culminating at 50% BaTiO$_3$ except for the composites surface treated using SCA 0.01 where it peaks at 60%.

For the composites that were untreated, the $d_{33}$ at 50% volume fraction of BaTiO$_3$ was recorded to be 0.86 pC/N and the $d_{31}$ is 0.42 pC/N, which is more than double as shown in Figure 5.69. The magnitude of the $d_{31}$ values is considerably higher than the $d_{33}$ values owing to the higher strain in the direction along the 1-axis as compared to the strain in the 3-axis which is consistent with other reports\cite{111, 210}. The general trend
is as expected, the $d_3$ value increases with increasing volume fraction of the BaTiO$_3$ nanoparticle.

Similarly for the SCA 0.01 surface treated samples, at 60% volume fraction of Ba-TiO$_3$ the $d_3$ is 0.71 pC/N while the $d_{31}$ is 2.18 pC/N as shown in Figure 5.70, which is almost 4 times in magnitude.

![Figure 5.68: The piezoelectric strain coefficient, $d_{33}$, for the BaTiO3-epoxy composite that were fabricated using BaTiO3 nanoparticles which were untreated, surface modified by 0.01 SCA, 0.015 SCA, 0.02 SCA and 0.025 SCA. The maximum $d_{33}$ values are 0.44, 0.71, 0.87, 1.16 and 0.84 pC/N at volume fractions of 0.6, 0.6, 0.5, 0.5 and 0.4, respectively.](image-url)
Figure 5.69: The piezoelectric strain coefficient, $d_{31}$, for the BaTiO$_3$-epoxy composite that were prepared using untreated/pristine BaTiO$_3$ nanoparticles. The maximum value is 0.86 pC/N and occurs at 0.5 volume fraction of BaTiO$_3$.

Figure 5.70: The piezoelectric strain coefficient, $d_{31}$, for the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.010 SCA. The maximum value is 2.18 pC/N and occurs at 0.6 volume fraction of BaTiO$_3$. 
Figure 5.71: The piezoelectric strain coefficient, $d_{31}$, for the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA. The maximum value is 1.89 pC/N and occurs at 0.4 volume fraction of BaTiO$_3$.

Figure 5.72: The piezoelectric strain coefficient, $d_{31}$, for the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.020 SCA. The maximum value is 3.11 pC/N and occurs at 0.6 volume fraction of BaTiO$_3$. 
Figure 5.73: The piezoelectric strain coefficient, $d_{31}$, for the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.025 SCA. The maximum value is 2.38 pC/N and occurs at 0.4 volume fraction of BaTiO$_3$.

A comparison of all the $d_{31}$ values for untreated and surface treated composites using 0.01, 0.015, 0.02 and 0.025 is shown in Figure 5.74.
Figure 5.74: The piezoelectric strain coefficient, $d_{31}$, for the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were untreated, surface modified by 0.01 SCA, 0.015 SCA, 0.02 SCA and 0.025% SCA. The maximum $d_{31}$ values are 0.86, 2.18, 1.89, 3.11 and 2.38 pC/N at volume fractions of 0.6, 0.6, 0.5, 0.5 and 0.4, respectively.

The $d_{31}$ values increase once they have been surface treated, which could be ascribed to better particle distribution leading to more homogeneous dispersion \cite{31, 127}. Ramesh et al. \cite{25} reported that the surface modified BaTiO$_3$ composites demonstrate enhanced mechanical response due to increased cross link density in the epoxy network resulting in the closer connectivity of particle and the matrix network which could also be attributed to the increased piezoelectric coefficient. The maximum $d_{31}$ value occurs for the BaTiO$_3$/epoxy composite that were surface treated using a 0.020 concentration of silane coupling agent KH-560.
Table 5.16: A summary of results of the piezoelectric strain coefficients $d_{33}$ and $d_{31}$ for all the composites that were prepared using untreated and surface treated BaTiO$_3$. The surface treated samples include ethanol treatment at 4 hours and different concentration of silane coupling agent.

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<th>Standard Deviation</th>
<th>$d_{31}$ pC/N</th>
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5.4.2 Dielectric Permittivity

The dielectric permittivity was measured using a HP 4194A impedance analyzer. These measurements were taken at a broad frequency range between 2000 Hz and 40 MHz. This enabled us to observe the behavior of the permittivity values with increasing frequency and to understand the effect or lack thereof of different polarization mechanisms. Here too, the BaTiO₃ volume fraction was varied from 0.1 to 0.6 for each concentration of surface modification. All the composites were corona poled at 30 kV/mm to ensure consistency of data. Figure 5.75 shows the real part of permittivity of the untreated or pristine BaTiO₃/epoxy composites plotted against increasing frequency. As expected, one can see that the permittivity of the entire composite increases with increasing volume fraction of BaTiO₃.

Frequency dependence of permittivity shows a decrease in permittivity with increasing frequency for composites and resins [211]. The dielectric relaxations in Figure 5.75, Figure 5.78, Figure 5.81, Figure 5.84 and Figure 5.87 can be explained by polarization mode changes. The polarization of dielectrics in alternating current fields has mode changes as frequency changes. Initially, at low frequencies, the total polarization manifests itself completely [161, 212]. However, at high frequencies the internal space charges can no longer react (this is because the space charges cannot keep up with fast switching polarity of the electric field i.e. the electric field switches rapidly and the space charges cannot react to it thereby negating its effect) and therefore has no effect on the net polarization. Furthermore, the orientation of the polar groups is relatively slow and once the
frequency increases, tends to lag behind. A further increase in frequency manifests in the inactivity of the dipole contributions towards polarization, i.e. only random orientations are left and these do not contribute to the resultant polarization. Of the total polarization, now only the atomic and electronic polarization remain. At even further frequencies the stretching and bending of the bonds start to slacken, thereby negating the effect of the ionic polarization. Finally at much higher frequencies ~ $10^{15}$ Hz the distortion of electronic clouds from the nuclei begins to lag behind.

The real permittivity value at 20 MHz attains a maximum values of 28.70 for the untreated BaTiO$_3$/epoxy composite where the volume fraction of BaTiO$_3$ was 60%. The dissipation factor is defined as the ratio of imaginary part of permittivity i.e. dielectric loss with the real part of permittivity i.e. relative permittivity or dielectric constant. Therefore the dielectric loss can be calculated my multiplying the dissipation factor and the relative permittivity. The maximum dissipation factor at 20 MHz was recorded to be 0.3836 at a volume fraction of 60% of BaTiO which is comparable to that reported by Dalle Vacche et al. (~0.4)$^{38}$. It is important to note that the dissipation factor increases quite significantly at 60% of BaTiO$_3$, as can be seen in Figure 5.77, and this could be attributed to the increase in agglomerations due to lack of wettability of the powders, and hence causing inhomogeneous dispersion of particles. This creates more air voids within the sample, increasing its porosity and making it difficult to pole, as the air voids are prone to increase in electric conduction.
Figure 5.75: The real permittivity of the BaTiO$_3$-epoxy composite that were fabricated using untreated Ba-TiO$_3$ nanoparticles is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 10% to 60%. This value at 20 MHz attains a maximum of 28.70 at 60% volume fraction of BaTiO$_3$.

The dielectric loss for the composite that were prepared using untreated BaTiO$_3$ nanoparticles are plotted as a function of increasing frequency as shown in Figure 5.76 where the volume fraction of BaTiO$_3$ was varied from 0.1 to 0.6. The maximum dielectric loss at 20 MHz was recorded to be 11.06 at a volume fraction of 0.6 of BaTiO$_3$. 
Figure 5.76: The dielectric loss of the BaTiO$_3$-epoxy composite that were fabricated using untreated BaTiO$_3$ nanoparticles is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6. The maximum dielectric loss at 20 MHz was recorded to be 11.06 at a volume fraction of 0.6 of BaTiO$_3$.

Figure 5.77: The dissipation factor of the BaTiO$_3$-epoxy composite that were fabricated using untreated BaTiO$_3$ nanoparticles is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied.
from 0.1 to 0.6. The maximum dissipation factor at 20 MHz was recorded to be 0.3836 at a volume fraction of 0.6 of BaTiO₃.

The permittivity of the 0.01 surface treated samples also show an increase in value with increasing volume fraction of BaTiO₃ as shown in Figure 5.78. The maximum value of real permittivity at 20 MHz was recorded to be 32.80 at 60% volume fraction of Ba-TiO₃. This is approximately 14.28% increase compared to the untreated samples. It was also found that at even high concentrations of BaTiO₃ the composite did not crack or delaminate due to the improved dispersion, this observation has been made by several researchers [1, 12, 19, 31, 37, 127]. With the addition of the coupling agent, a more homogeneous and uniform dispersion can be obtained. The enhanced dispensability of the nanoparticles can mainly be attributed to the substitution of the hydroxyl groups, which has a dual effect, (i) lowering interfacial tension between the separated phases and (ii) preventing coalescence of the nanoparticles during processing [1].
Figure 5.78: The real permittivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.010 SCA is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6.

From Figure 5.80, one can see that the dissipation factor for the SCA 0.01 samples behaves similar to that of the untreated ones, wherein the dissipation factor begins to increase with increasing frequency. This is synonymous with the decrease in permittivity over the same frequency range. A relaxation process of the polymer matrix leads to a decrease in the permittivity values from low frequency to high frequency values. The dissipation factor at 20 MHz attains a maximum value of 0.1106, which is significantly lower compared to the untreated samples; 0.3836. For composite systems, the dielectric loss factor might originate from the contributions of dipole orientation, conduction loss and interfacial polarization [1, 213]. The loss factor could be expressed as a sum of three distinct effects [214] namely, conduction loss contribution, interfacial polarization and the dipole orientation or Debye loss factor. Surface treatment of the BaTiO$_3$ nanoparticles
minimizes the conduction losses due to substitution of the hydroxyl groups, which would have been present at the BaTiO$_3$-epoxy interface.

**Figure 5.79**: The dielectric loss of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.010 SCA is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6. The maximum value is 2.05 for BaTiO$_3$ at 0.5 volume fraction. The imaginary permittivity increases with increasing volume fraction of BaTiO$_3$ nanoparticles and increases with increasing frequency. With increasing frequency, there are less contributing factors to the real permittivity do the delayed response of these orientations.
Figure 5.80: The dissipation factor of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.010 SCA is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6. The maximum value is 0.1106 for BaTiO$_3$ at 0.5 volume fraction.

For the samples that were surface treated using 0.015 concentration of silane coupling agent, the relative permittivity shows an increasing tendency with the loading levels of the nanoparticles. The maximum permittivity values at 20 MHz was found to be 41.76 at 50% volume fraction of BaTiO$_3$. This value is a 27% increase compared to the permittivity of the SCA 0.015 sample.

The loss factor begins to increase with increasing frequency and can be attributed to the decrease in reorientation of dipoles and polar entities, it may also originate from the contributions of conduction loss and interfacial polarization $[^1, 213]$. 
Figure 5.81: The real permittivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6.

The maximum dissipation factor for BaTiO$_3$/epoxy composites prepared using SCA 0.015 occurs at 60% volume fraction of BaTiO$_3$ and was recorded to be 0.088 as shown in Figure 5.83. The trend observed for the dissipation factor shows an increase in value with increasing volume fraction of BaTiO$_3$. This increase in dissipation factor can be attributed to the increased conduction losses associated with increasing amount of Ba-TiO$_3$. 
Figure 5.82: The dielectric loss of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6. The maximum value is 1.60 for BaTiO$_3$ at 0.6 volume fraction.

Figure 5.83: The dissipation factor of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA is plotted as a function of frequency where the vol-
ume fraction of BaTiO$_3$ is varied from 0.1 to 0.6. The maximum value is 0.087 for BaTiO$_3$ at 0.6 volume fraction. The imaginary permittivity increases with increasing volume fraction of BaTiO$_3$ nanoparticles and increases with increasing frequency. With increasing frequency, there are less contributing factors to the real permittivity do the delayed response of these orientations.

This is an almost 21% decrease in dissipation compared to the maximum value exhibited by the composites prepared using SCA 0.01. The decrease in dissipation factor, as previously mentioned, could be attributed to better interfacial bonding between the BaTiO$_3$ nanoparticles and the epoxy matrix because the coupling agent acts as a molecular bridge between the two, and therefore contributes to lower conduction losses [215, 216].

![Figure 5.84](image-url)

**Figure 5.84:** The real permittivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.020 SCA is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6.
There is a further decrease in dissipation factor for the composite that were surface modified using SCA 0.020. For these composites prepared using 0.5 volume fraction of BaTiO$_3$ the dissipation factor exhibits a value of 0.033 as shown in Figure 5.86.

**Figure 5.85**: The dielectric loss of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.020 SCA is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6. The maximum value is 5.89 for BaTiO$_3$ at 0.6 volume fraction.
Figure 5.86: The dissipation factor of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.020 SCA is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6. The maximum value is 0.136 for BaTiO$_3$ at 0.6 volume fraction.

When the concentration of coupling agent is increased to 0.025 and for higher BaTiO$_3$ volume fractions, the dissipation factor began to increase again slowly. From Figure 5.89 the maximum dissipation factor was found to be 0.119 at 0.6 volume fraction of BaTiO$_3$. 
Figure 5.87: The real permittivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.025 SCA is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6.

Figure 5.88: The dissipation factor of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.025 SCA is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6. The maximum value is 3.26 for BaTiO$_3$ at 0.6 volume fraction.
Figure 5.89: The dissipation factor of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.025 SCA is plotted as a function of frequency where the volume fraction of BaTiO$_3$ is varied from 0.1 to 0.6. The maximum value is 0.119 for BaTiO$_3$ at 0.6 volume fraction.

A comparison of the experimental relative permittivity values and theoretical models is plotted in Figure 5.90. The mathematical models used were the Maxwell-Garnett equation, Bruggeman self-consistent effective medium approximation, the Jaysundere-Smith equation and Lichtenker rule. Table 5.17 lists the values of the values obtained from the mathematical models and the experimental values obtained at 20MHz.
Figure 5.90: Comparison of the relative permittivity of the theoretical models with different experimental results, where the readings were taken at 20MHz for the composites that were prepared using 0.5 volume fraction of BaTiO$_3$.

Table 5.17: Comparison of the relative permittivity of the theoretical models with different experimental results, where the readings were taken at 20MHz for the composites that were prepared using 0.5 volume fraction of BaTiO$_3$.

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#### 5.5 Resistivity and Conductivity

The resistivity and conductivity measurements were recorded using an HP 4194A Impedance Analyzer over a wide frequency spectrum i.e. between 2000 Hz and 40 MHz to gather insight into the resistive behavior of these composites.
Figure 5.91: The resistivity of the BaTiO$_3$-epoxy composites that were fabricated using BaTiO$_3$ nanoparticles which were not surface treated (pristine) is plotted as a function of frequency. The maximum resistivity recorded at 20MHz was 4.20 ohm-m which corresponds to the composites containing 10% of BaTiO$_3$.

The resistivity measurements as a function of frequency is shown in Figure 5.91 for composites that were fabricated with pristine or non-surface treated BaTiO$_3$. At 20 MHz the maximum resistivity was recorded to be 4.20 ohm-m at 0.1 volume fraction of BaTiO$_3$. With increasing volume fraction of BaTiO$_3$ the value of resistivity began to decrease, and the lowest recorded resistivity at 20MHz was found to be 1.02 ohm-m at 0.6 volume fraction.
Figure 5.92: The resistivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.010 SCA is plotted as a function of frequency. The maximum resistivity recorded at 20MHz was 22.08 ohm-m which corresponds to the composites containing 0.1 of BaTiO$_3$. 
Figure 5.93: The resistivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA is plotted as a function of frequency. The maximum resistivity recorded at 20MHz was 24.26 ohm-m which corresponds to the composites containing 0.5 of BaTiO$_3$.

At 20 MHz, the maximum resistivity was recorded to be 24.26 ohm-m for the sample containing 0.5 of BaTiO$_3$ and surface treated using SCA 0.015 as shown in Figure 5.93. For the same volume fraction of BaTiO$_3$ but for the samples surface treated at SCA 0.020 and 0.025, the resistivity was recorded to be 39.76 ohm-m and 16.81 ohm-m, respectively. The initial increase in resistivity can be attributed to the better particle-polymer adhesion, thereby reducing conduction losses. Surface treating the sample substitutes the hydroxyl groups present on the surface of the BaTiO$_3$ nanoparticle with that of an organofunctional silane, i.e. it replaces conductive hydroxyl groups with an insulating polymer, leading to improved adhesion with the epoxy matrix and thereby also reducing
the electrical conductivity at the interface. However, when the coupling agent concentration is increased to 0.025, there is an increase in film delamination, leading to inefficient poling and increased conduction losses.

![Graph showing resistivity vs. frequency for different BaTiO$_3$ concentrations.]

**Figure 5.94:** The resistivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.02 SCA is plotted as a function of frequency. The maximum resistivity recorded at 20MHz was 39.76 ohm-m which corresponds to the composites containing 0.5 of BaTiO$_3$. 
Figure 5.95: The resistivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.02 SCA is plotted as a function of frequency. The maximum resistivity recorded at 20MHz was 58.22 ohm-m which corresponds to the composites containing 0.4 of BaTiO$_3$.

The conductivity measurements, as expected, showed a similar trend to that of the resistivity observations. For the composites prepared with 0.5 volume fraction of BaTiO$_3$ and surface modified using SCA 0.015, SCA 0.0 and SCA 0.025 the conductivity values were 2.61e-4 S/m, 7.02e-5 S/m and 7.3e-5 S/m, respectively.
Figure 5.96: The conductivity of the BaTiO$_3$-epoxy composite that were BaTiO$_3$ nanoparticles which were not surface treated (pristine) is plotted as a function of frequency. The maximum value of conductivity at 20 MHz is 7.84*10$^{-4}$ S/m and occurs at BT 0.6.

Figure 5.97: The conductivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.010 SCA is plotted as a function of frequency. The maximum value of conductivity at 20 MHz is 4.63*10$^{-4}$ S/m and occurs at BT 0.6.
Figure 5.98: The conductivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA is plotted as a function of frequency. The maximum value of conductivity at 20 MHz is $4.36 \times 10^{-4}$ S/m and occurs at BT 0.6.

There is a drop of \sim 73\% in the conductivity at 20 MHz between the composites prepared using SCA 0.015 and SCA 0.02 at 0.5 volume fraction of BaTiO$_3$ as shown in Figure 5.98 and Figure 5.99. There is a 4\% increase in the conductivity of the composite for the SCA 0.025 samples.

The pristine or untreated BaTiO$_3$ due to its hydrophilic nature tends to adsorb water onto its surface [$31, 32$]. The surface modification leads to the substitution of the hydroxyl (−OH−) groups on the surface of the BaTiO$_3$ with a modified surface chemistry (O-Si-) as shown in Figure 5.101. Therefore when the concentration of coupling agent is increased more such reactions may occur, thereby lowering the conductivity values [$19, 37$].
**Figure 5.99**: The conductivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.020 SCA is plotted as a function of frequency. The maximum value of conductivity at 20 MHz is $2.38 \times 10^{-4}$ S/m and occurs at BT 0.6.

**Figure 5.100**: The conductivity of the BaTiO$_3$-epoxy composite that were fabricated using BaTiO$_3$ nanoparticles which were surface modified using 0.025 SCA is plotted as a function of frequency. The maximum value of conductivity at 20 MHz is $2.58 \times 10^{-4}$ S/m and occurs at BT 0.6.
Figure 5.101: Substitution of the hydroxyl groups due to the surface modification with the silane coupling agent. This leads to a decrease in conductivity as there is no more water adsorbed on the surface of the BaTiO$_3$ nanoparticle.

5.6 Hysteresis Loop Measurement

Dielectric breakdown could be due to one of the following factors, (i) intrinsic breakdown, (ii) electron avalanche breakdown, (iii) thermal breakdown and (iv) electromechanical breakdown [72]. Intrinsic breakdown occurs when electron-electron interactions are strong. This type of breakdown will take place in amorphous or non-crystalline dielectrics when interactions of electrons with impurity levels exceed those with phonons. This results in electron temperature increase and is considered to explain the nature of high-temperature breakdown. Electron avalanche breakdown occurs when successive electron multiplication like an avalanche takes place due to the ionization by collision process which gives large energy to phonons to cause dielectric breakdown [72]. Thermal breakdown is when there is a temperature rise due to Joule heating by dielectric dissipation loss will melt the insulation to cause dielectric failure. This type of breakdown is not only material specific, but also depends on heat radiation conditions like electrode sizes and structures. Soft insulating materials can be reduced in thickness due to Maxwell stress when they are subjected to voltage. In that case, the electric stress is enhanced and
then the thickness is further reduced. This causes a positive feedback process to lead to the insulation to electric failure. This is called electromechanical breakdown \[72\].

The breakdown strength of a composite with a specific filler and at different loadings can be considered to be mainly determined by the physical properties of the filler viz. dielectric constant, electrical conductivity etc., the particle dispersion and the type and number of defects within the sample \[19\]. For any two or more epoxy/BaTiO\(_3\) nanocomposites prepared using the same nanoparticles at the same filler loading levels, the difference in their breakdown strength boils down to the defects and/or more importantly, the nanoparticle dispersion within the polymer matrix.

The hysteresis loop measurements were taken using a Radiant Technologies, Inc. Precision LC II Ferroelectric Tester. The hysteresis loop plots provide us with two critical data sets, the polarization and the coercive field of the composite material. These studies elucidate the dielectric breakdown strength of these materials. By making use of the high voltage test fixture (HVTF), the electric field is gradually increased across the composite until dielectric breakdown is observed.

Energy storage density in a linear dielectric is proportional to the product of the dielectric constant and square of the dielectric breakdown strength as shown in equation \((5.25)\) \[215\]. Where \(U\) is the electrical energy density, \(\varepsilon_r\) is the dielectric permittivity of the material and \(E_b\) is the dielectric breakdown strength.

\[
U = \frac{1}{2} \varepsilon_r E_b^2
\]  \((5.25)\)
One approach to increase this value is to increase the overall dielectric constant of the composite \([215, 217]\). This can be achieved by increasing the volume fraction of the ceramic nanoparticle filler, typically to around 50%, while volume fractions greater than 50% could lead diminished values because of growing sample porosity \([170, 215]\). High filler loadings could also create Maxwell-Wagner relaxation losses, conduction losses due to local enhancement of electric field \([2, 170, 215, 218-220]\). Higher volume fractions could also lead to weaker composite adhesion and inflexibility.

On the other hand, since energy density increases with the square of the dielectric breakdown, \(E_b\), it is paramount that the material possesses a high value. As previously mentioned, dielectric breakdown strength depends on intrinsic and extrinsic factors, but one of the dominating factors is the presence of defects within the composite, e.g. free charge carriers within the dielectric is a common defect that needs to be controlled \([215]\). It has also been observed that in addition to the presence of defects, poor particle dispersion exacerbates the weakening of the breakdown strength. This can be overcome by particle surface modification \([215, 216]\).

### 5.6.1 Silane Coupling Agent - 0.010

To determine the dielectric breakdown of these sets of composites, the voltage was gradually ramped up to increase the electric field across the composite. At a certain critical electric field value it was noted that no hysteresis loop was observed, rather there were a set of incoherent lines which denotes dielectric breakdown has been achieved. For the samples that were surface modified using 0.010 SCA the maximum dielectric breakdown strength was 69.79 kV/cm at 0.2 \(\text{BaTiO}_3\) volume fraction, and coincidentally also had the highest polarization value of 0.05024 \(\mu\text{C/cm}^2\).
Figure 5.102: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.1 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.010 SCA is plotted as a function of increasing electric field. The maximum polarization at 30 kV/cm value was recorded to be 0.01 µC/cm$^2$.

The dielectric breakdown strength as expected began to reduce with increasing filler volume fraction 49.82 kV/cm, 39.93 kV/cm, and 34.95 kV/cm for the samples at 0.4, 0.5 and 0.6 volume fraction of BaTiO$_3$, respectively. In Figure 5.103 the polarization value increases with increasing electric field, where the highest polarization value is recorded for the sample at 70 kV/cm. The hysteresis loops for the plots at lower electric fields, i.e. at 30 kV/cm and 50 kV/cm we see an almost linear behavior and this straight line is a typical loop for an ideal capacitor [221].
Figure 5.103: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.2 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.010 SCA is plotted as a function of increasing electric field. The polarization value increases with increasing electric field, where the highest polarization value was recorded to be 0.05 µC/cm$^2$ for the sample at 70 kV/cm.

Figure 5.104: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.3 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.010 SCA is plotted as a function of
increasing electric field. The polarization increases with increasing electric field as a result of more number of dipoles being reoriented. The maximum recorded polarization value is 0.02 µC/cm² and occurs at 40 kV/cm.

![Graph showing polarization vs electric field for different fractions of BaTiO₃ nanoparticles](image)

**Figure 5.105**: The electric polarization of the BaTiO₃-epoxy composite that were fabricated using 0.4 volume fraction of BaTiO₃ nanoparticles which were surface modified using 0.010 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.05 µC/cm² and occurs at 50 kV/cm.

Quite similarly, there is a decline in the polarization values 0.04959 µC/cm², 0.01787 µC/cm² and 0.02111 µC/cm² for the samples at 0.4, 0.5 and 0.6 volume fraction of BaTiO₃, respectively.
Figure 5.106: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.5 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.010 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.02 µC/cm$^2$ and occurs at 40 kV/cm.
Figure 5.107: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.6 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.010 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.02 µC/cm$^2$ and occurs at 35 kV/cm.

A summary of the dielectric breakdown strengths of the BaTiO$_3$/epoxy composites at different volume fractions of BaTiO$_3$ ranging from 0.1 to 0.6 is presented in Figure 5.108. The P-E hysteresis loop for an ideal capacitor is a straight line whose gradient is proportional to the capacitance. This is because for an ideal capacitor the current leads the voltage by 90 degrees, and therefore the charge (the integral of the current with time) is in phase with the voltage \([221]\). If however, the P-E hysteresis loop is not a straight line, this represents a lossy capacitor, where the area within the loop is proportional to the loss tangent of the device, and the slope is proportional to the capacitance \([221]\).
Figure 5.108: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.1-0.6 volume fraction of BaTiO$_3$ nanoparticles, which were surface modified using 0.010 SCA is plotted as a function of increasing electric field. The maximum permissible electric field is 69.80 kV/cm and the corresponding polarization was 0.05 µC/cm$^2$.

5.6.2 Silane Coupling Agent - 0.015

For the BaTiO$_3$/epoxy composites that were surface modified using 0.015 SCA, the dielectric breakdown strength was determined by gradually ramping up the voltage to increase the electric field across the sample until breakdown occurred.

The maximum breakdown strength was recorded to be 80.19 kV/cm for the sample prepared using 0.5 volume fraction of BaTiO$_3$. However, the maximum electric polarization was 0.2011 µC/cm$^2$ for the sample prepared using 0.4 volume fraction of BaTiO$_3$. The dielectric breakdown strength and the electric polarization plummeted at 49.89 kV/cm and 0.03518 µC/cm$^2$ respectively, for the sample prepared using 0.6 volume fraction of BaTiO$_3$. This could possibly be attributed to the increased sample porosity [215].
Figure 5.109: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.1 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.014 µC/cm$^2$ and occurs at 45 kV/cm.
Figure 5.110: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.2 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA is plotted as a function of increasing electric field. The maximum electric polarization is 0.09 µC/cm$^2$ corresponding to a field of 69.91 kV/cm.

Figure 5.111: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.3 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.04 µC/cm$^2$ and occurs at 50 kV/cm.
Figure 5.112: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.4 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.2 µC/cm$^2$ and occurs at 70 kV/cm.

The BaTiO$_3$/epoxy composites that were fabricated at 0.1, 0.2 and 0.3 volume fractions of BaTiO$_3$ recorded breakdown strengths of 49.81 kV/cm, 69.91 kV/cm and 49.95 kV/cm respectively. And their corresponding electric polarizations were 0.01475 µC/cm$^2$, 0.19099 µC/cm$^2$ and 0.04863 µC/cm$^2$. 
Figure 5.113: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.5 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.13 $\mu$C/cm$^2$ and occurs at 80 kV/cm.
A summary of the dielectric breakdown strengths of the BaTiO$_3$/epoxy composites prepared using 0.015 SCA at different volume fractions of BaTiO$_3$ ranging from 0.1 to 0.6 is presented in Figure 5.115. The P-E hysteresis loop for an ideal capacitor is a straight line whose gradient is proportional to the capacitance. This is because for an ideal capacitor the current leads the voltage by 90 degrees, and therefore the charge (the integral of the current with time) is in phase with the voltage [221]. If however, the P-E hysteresis loop is not a straight line, this represents a lossy capacitor, where the area within the loop is proportional to the loss tangent of the device, and the slope is proportional to the capacitance [221].
Figure 5.115: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.1-0.6 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.015 SCA is plotted as a function of increasing electric field. The maximum permissible electric field is 80.19 kV/cm with a corresponding polarization of 0.14 µC/cm$^2$.

5.6.3 Silane Coupling Agent - 0.020

The maximum dielectric breakdown strength for the BaTiO$_3$/epoxy composite prepared using 0.020% SCA was found to be 84.92 kV/cm and which corresponded to the sample at 0.4 volume fraction of BaTiO$_3$. This breakdown strength is an almost 6% increase compared to the composites that were prepared using 0.015 SCA.
Figure 5.116: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.1 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.020 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.1326 µC/cm$^2$ and occurs at 80 kV/cm.
Figure 5.117: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.2 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.020 SCA is plotted as a function of increasing electric field. The maximum electric polarization is 0.09817 µC/cm$^2$ corresponding to a field of 79.74 kV/cm.

Figure 5.118: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.3 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.020 SCA is plotted as a function of
increasing electric field. The maximum recorded polarization value was 0.109 $\mu$C/cm$^2$ and occurs at 70 kV/cm.

\textbf{Figure 5.119}: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.4 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.020 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.3562 $\mu$C/cm$^2$ and occurs at 85 kV/cm.
Figure 5.120: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.5 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.020 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.1456 µC/cm$^2$ and occurs at 70 kV/cm.
Figure 5.121: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.6 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.020 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.096 µC/cm$^2$ and occurs at 85 kV/cm.

A summary of the dielectric breakdown strengths of the BaTiO$_3$/epoxy composites prepared using 0.020 SCA at different volume fractions of BaTiO$_3$ ranging from 0.1 to 0.6 is presented in Figure 5.122. In contrast to the composite before, the dielectric breakdown strength remained relatively stable and reliable with increasing volume fraction of BaTiO$_3$ nanoparticles, i.e. there was no apparent plummet in values. To substantiate that claim the estimated fluctuation was calculated to be 20% over the entire breadth of samples. For the BaTiO$_3$/epoxy composites prepared using 0.1, 0.2, 0.3, 0.5 and 0.6 volume fractions of BaTiO$_3$ the dielectric breakdown strength was recorded to be 79.75 kV/cm, 79.74 kV/cm, 69.73 kV/cm, 69.73 kV/cm and 84.92 kV/cm respectively.
Figure 5.122: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.1-0.6 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.020 SCA is plotted as a function of increasing electric field. The maximum permissible electric field is 84.92 kV/cm and the corresponding polarization value is 0.356 µC/cm$^2$.

5.6.4 Silane Coupling Agent at 0.025

The maximum dielectric breakdown strength for the BaTiO$_3$/epoxy composite prepared using 0.025 SCA was found to be 89.93 kV/cm and which corresponded to the sample at 0.2 volume fraction of BaTiO$_3$. This breakdown strength is an almost 5.89% increase compared to the composites that were prepared using 0.020 SCA.
Figure 5.123: The electric polarization of the BaTiO₃-epoxy composite that were fabricated using 0.1 volume fraction of BaTiO₃ nanoparticles which were surface modified using 0.025 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.09 μC/cm² and occurs at 90 kV/cm.

Figure 5.124: The electric polarization of the BaTiO₃-epoxy composite that were fabricated using 0.2 volume fraction of BaTiO₃ nanoparticles which were surface modified using 0.025 SCA is plotted as a function of...
increasing electric field. The maximum electric polarization is 0.25504 \( \mu \text{C/cm}^2 \) corresponding to a field of 89.93 kV/cm.

![Diagram](image.png)

**Figure 5.125:** The electric polarization of the BaTiO\(_3\)-epoxy composite that were fabricated using 0.3 volume fraction of BaTiO\(_3\) nanoparticles which were surface modified using 0.025 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.114 \( \mu \text{C/cm}^2 \) and occurs at 80 kV/cm.

However it is important to note that this improved dielectric breakdown strength is only exhibited at low volume fractions after which premature breakdown occurs at higher volume fractions of BaTiO\(_3\). The dielectric breakdown strength for the Ba-TiO\(_3\)/epoxy samples at 0.5 and 0.6 volume fractions falls to 60.04 kV/cm and 49.80 kV/cm respectively. This steep decline in breakdown strength could be attributed to delamination of the entire composite at elevated volume fractions. It is interesting to observe that the delamination is of the entire film as a whole and not a case of the composite cracking as can be seen in Figure 5.127. This perhaps is the cause of the premature breakdown.
Figure 5.126: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.4 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.025 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.1402 µC/cm$^2$ and occurs at 80 kV/cm.

Figure 5.127: Cross-sectional images of the BaTiO$_3$/epoxy composite prepared using 0.025 SCA and at 0.5 volume fraction of BaTiO$_3$. It is interesting to note that the delamination occurs for the entire film from the substrate i.e. the film in itself remains cohesive and crack-free. However this makes it difficult to successfully pole the composite.
Figure 5.128: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.5 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.025 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.023 µC/cm$^2$ and occurs at 60 kV/cm.
Figure 5.129: The electric polarization of the BaTiO₃-epoxy composite that were fabricated using 0.6 volume fraction of BaTiO₃ nanoparticles which were surface modified using 0.025 SCA is plotted as a function of increasing electric field. The maximum recorded polarization value was 0.022 µC/cm² and occurs at 50 kV/cm.

A summary of the dielectric breakdown strengths of the BaTiO₃/epoxy composites prepared using 0.025 SCA at different volume fractions of BaTiO₃ ranging from 0.1 to 0.6 is presented in Figure 5.130. Despite possessing a higher dielectric breakdown strength at low volume fractions, the composite suffers from reduced values due to composite film delamination.
Figure 5.130: The electric polarization of the BaTiO$_3$-epoxy composite that were fabricated using 0.1-0.6 volume fraction of BaTiO$_3$ nanoparticles which were surface modified using 0.025 SCA is plotted as a function of increasing electric field. The maximum permissible electric field is 89.93 kV/cm and the corresponding polarization value was 0.255 µC/cm$^2$.

5.7 Leakage Current Measurement

The leakage current measured by applying a constant DC bias voltage across the sample thickness and simultaneously measures the current through the composite material. An electric field of 10 kV/cm was applied across all the composites (0.5 volume fraction of BaTiO$_3$) for 1000 ms and the corresponding current through the sample was recorded.
For the composites that were prepared using untreated or pristine BaTiO$_3$ nanoparticles the steady state leakage current was measured to be $3.37 \times 10^{-7}$ A as shown in Figure 5.131.

The composites that were prepared using 4 hour ethanol surface treated BaTiO$_3$ nanoparticles showed a steady state leakage current of $5.40 \times 10^{-7}$ A as shown in Figure 5.132. This increase in leakage current could be attributed to the presence of surface charges that are present on the surface of the BaTiO$_3$ nanoparticles that were developed due to the acidic nature of ethanol.
Figure 5.132: Leakage current measurements of the composite prepared using 0.5 volume fraction of ethanol surface treated (4 hours) BaTiO$_3$ nanoparticles that were taken at a constant electric field of 10 kV/cm for 1000 ms. The steady state current after 1000ms was recorded to be 5.40E-7 Amps.

A steady state leakage current of $3.54 \times 10^{-8}$ A and $9.14 \times 10^{-11}$ A were recorded for the samples that were prepared using 0.01% and 0.015% silane coupling agent surface treated BaTiO$_3$ nanoparticles, respectively. We can see that the leakage current begins to reduce with increasing concentration of coupling agent which can be attributed to the steric stabilization achieved due to adsorbed layer of coupling agent, thereby reducing the overall current through the sample.
Figure 5.133: Leakage current measurements of the composite prepared using 0.5 volume fraction of 0.010 silane coupling agent BaTiO$_3$ nanoparticles that were taken at a constant electric field of 10 kV/cm for 1000 ms. The steady state current after 1000ms was recorded to be 3.54E-8 Amps.

Figure 5.134: Leakage current measurements of the composite prepared using 0.5 volume fraction of 0.015 silane coupling agent BaTiO$_3$ nanoparticles that were taken at a constant electric field of 10 kV/cm for 1000 ms. The steady state current after 1000ms was recorded to be 9.14E-11 Amps.
Leakage currents of $1.02 \times 10^{-12}$ A and $1.79 \times 10^{-9}$ A were recorded for samples that were surface treated using 0.020 and 0.025 of silane coupling agent. We can see a further decrease in values for the samples that were prepared using SCA 0.020 compared with the samples that were surface treated using 0.015 of coupling agent.

**Figure 5.135**: Leakage current measurements of the composite prepared using 0.5 volume fraction of 0.020 silane coupling agent BaTiO$_3$ nanoparticles that were taken at a constant electric field of 10 kV/cm for 1000 ms. The steady state current after 1000ms was recorded to be 1.02E-12 Amps.

There is an increase in conductivity for the samples that were surface treated using SCA 0.025 compared with the samples that were prepared using SCA 0.020.
Figure 5.136: Leakage current measurements of the composite prepared using 0.5 volume fraction of 0.025 silane coupling agent BaTiO$_3$ nanoparticles that were taken at a constant electric field of 10 kV/cm for 1000 ms. The steady state current after 1000ms was recorded to be 1.79E-9 Amps.
Figure 5.137: A comparison of the leakage current characteristics of the BaTiO$_3$ (0.5)-epoxy composite using untreated, ethanol surface treated (4 hours), SCA 0.01, SCA 0.015, SCA 0.020 and SCA 0.025 BaTiO$_3$ nanoparticles. It was observed that the leakage current reduced with surface treatment using ethanol and silane coupling agent. This reduction in leakage current can be attributed to reduced conductivity at the interface due to the substitution of hydroxyl groups on the surface of the BaTiO$_3$ nanoparticle.

5.8 Results from Viscosity Studies

5.8.1 Morphological Characterization

The viscosity study was carried out for BaTiO$_3$-epoxy composites that were fabricated using BaTiO$_3$ nanoparticles that were surface treated using 0.020 KH-560 and at 0.5 volume fraction of BaTiO$_3$. From the results above, it has been shown that 0.020 of silane coupling agent proved to be the optimum amount for surface modification of the nanoparticle ceramic filler as it exhibited the highest permittivity value 48.03 and the lowest dissipation factor of 0.033 at 20 MHz. In order to further improve the composite it was imperative to conduct an investigation to identify the ideal viscosity required to fabricate these composites.
Eight BaTiO$_3$-epoxy composites were fabricated via the spin-coating deposition method at different viscosities of the sol, ranging from 148 mPas up to 282 mPas, as can be seen in Figure 5.138. From these images one can see that with increasing viscosity of the sol, the composite thus prepared, leads to an increase in the curvature of the sample i.e. the sample with a viscosity of 282 mPas possesses the highest value of curvature. This poses problems such as weaker interfacial adhesion between the composite and the stainless-steel substrate thereby causing premature delamination.

SEM micrograph images of the composite cross-section were utilized in order to understand the interface adhesion between the composite and the stainless-steel substrate, as can be seen in Figure 5.139. There are signs of a large crack i.e. a sign of noticeable delamination on the sample that was fabricated using a sol viscosity of 282 mPas as shown in Figure 5.139 A. For the 220 mPas sample, despite not having a significant cracks at the interface, however it is evident that there are growing signs of disconnect between the substrate and the composite, and perhaps will eventually start delaminating with cyclic loading. The last image, Figure 5.139 C, shows a sample that was fabricated with a sol viscosity of 180 mPas where it is clear that there is good interface adhesion between the composite and the substrate throughout the thickness of the sample, with no signs of cracking.
Figure 5.138: SCA 0.020 BT(0.5)/epoxy composites fabricated at different viscosities starting **A)** from 148 mPas up to 282 mPas; **B)** Composites fabricated between 200 mPas and 282 mPas, it can be seen that with increasing viscosities sample begins to curve, making it inflexible and prone to delamination. The increase in viscosity led to an increase in thermal mismatch between the composite film and the substrate i.e. between the BaTiO$_3$ ceramic and stainless steel.

Figure 5.139: SEM micrograph images showing the fractured cross section of the SCA 0.020 BT(0.5)/epoxy composite at different viscosities; **A)** sample viscosity is 282 mPas, showing signs of delamination at the electrode-composite interface, **B)** sample viscosity is 220 mPas, showing brief signs of voids existing at the interface and **C)** 180 mPas – good adhesion at the interface.
5.8.2 Piezoelectric and Dielectric Characterization

The piezoelectric strain coefficient, $d_{33}$ was recorded for each sample set at varying sol viscosities as shown in Figure 5. The piezoelectric strain coefficient, $d_{33}$ was recorded for each sample set at varying sol viscosities as shown in Figure 5.140. It can be seen that as the viscosity increases there is an increase in the $d_{33}$ attributed to the decrease in the presence of ethanol in the overall composite. This value attains a maximum at a viscosity of ~ 200 mPas, and then there is a decline. This decline could be due to the delamination of the composite from the substrate caused by the increase in sample curvature. Although the maximum value occurs at 200 mPas the qualitative nature of the sample begins to decline, owing to the presence of isolated weaker interface adhesion zones across the thickness of the sample. Whereas for the sample prepared at 180 mPas despite possessing a slightly lower $d_{33}$ value still shows much improved composite-substrate adhesion throughout the thickness.

![Figure 5.140](image-url)

*Figure 5.140*: Piezoelectric strain coefficient, $d_{33}$ of the BaTiO$_3$-epoxy composite fabricated using BaTiO$_3$ nanoparticles that were surface treated at 0.020 SCA plotted as a function of sol viscosity. The piezoelectric strain coefficient was recorded to be 1.3 pC/N at optimum viscosity i.e. 180 mPas.
The relative permittivity at different viscosities was plotted at 20 MHz as shown in Figure 5. The real part of permittivity begins to increase with increasing viscosity content peaks and 200 mPas but then drops very quickly at higher viscosities. This can be correlated with cross-section images in Figure 5.19 where one begins to see the composite delaminating from the substrate. The maximum permittivity value was recorded to be 51.14 at 200 mPas. However, from the cross-section images there are signs of premature cracking. Increasing sol viscosity leads to insufficient wetting of the BaTiO$_3$ nanoparticle. There exists a high thermal expansion mismatch between ceramic materials and metals \cite{222}. This leads to thermal stresses arising at the interface between the two materials and thus leads to premature cracking \cite{222}. As a result of this 180 mPas proved to be the most effective viscosity for the sol, because it retained sample quality i.e. good adhesion to the substrate and represented high permittivity and piezoelectric strain coefficients compared to any other viscosity value.
Figure 5.141: Relative permittivity of the BaTiO$_3$-epoxy composite fabricated using BaTiO$_3$ nanoparticles that were surface treated at 0.020 SCA plotted as function of sol viscosity. The value of permittivity was recorded to be 50.02 at optimum viscosity i.e. 180 mPas.
Chapter 6

Conclusions and Future Work

6.1 Conclusions

Two-phase BaTiO$_3$/epoxy composite films were fabricated for its application as dielectric materials in capacitors where the volume fraction of the BaTiO$_3$ nanoparticle was varied from 0.1 to 0.6. In order to ensure uniform dispersion of the filler nanoparticles within the epoxy matrix the BaTiO$_3$ was surface treated using (i) ethanol and (ii) silane coupling agent, KH-560. The piezoelectric strain coefficients and the dielectric permittivity were measured and calculated, respectively. Different concentrations (v/v) of the coupling agent were used for the surface modification of BaTiO$_3$: 0.01, 0.015, 0.02 and 0.025.

Hypotheses I: When the concentration of the coupling agent was increased, an increase in the dielectric permittivity values of the BaTiO$_3$/epoxy composite was observed. This could be attributed to better dispersion of the BaTiO$_3$ nanoparticles as observed using the EDS, SEM micrograph images. The SEM micrograph images helped in providing a particle size analysis that showed that the mean diameter of the nano-clusters reduced in size with increasing concentration of silane coupling agent. The presence of silicon molecules that were adsorbed on to the surface of the BaTiO$_3$ nanoparticle were observed using the EDS micrograph images, which also showed the reduction in the aggregate size, which led to better particle distribution. The highest value of permittivity (~ 48.03)
and the lowest value of loss (~0.136) were observed for the samples that were fabricated using 0.5 volume fraction of BaTiO$_3$ and that were surface treated with 0.02 volume fraction of silane coupling agent. The improved adhesion between the polymer-ceramic interface led to higher interfacial polarization within the composite material, and as result led to increased permittivity values. Due the insulating adsorption layer of the organo-functional silane the localized conductivity of the interface was reduced leading to enhanced permittivity values.

**Hypothesis II:** The conductivity values were measured for each concentration of the silane coupling agent, and it was found that the conductivity began to decrease. The maximum conductivity values for the BaTiO$_3$-epoxy composites that were prepared using untreated, SCA 0.01, SCA 0.015, SCA 0.020 and SCA 0.025 treated BaTiO$_3$ nanoparticles at 20MHz were found to be 7.84*10$^{-4}$ S/m, 4.63*10$^{-4}$ S/m, 4.36*10$^{-4}$ S/m, 2.38*10$^{-4}$ S/m and 2.58*10$^{-4}$ S/m, respectively. This could be ascribed to the substitution of the hydroxyl (-OH-) groups on the surface of the BaTiO$_3$ nanoparticle with that of the coupling agent. By eliminating the formation of adsorbed water on the surface of the particle, the conductivity of the system was gradually reduced by increasing the amount of the coupling agent.

**Hypothesis III:** The dielectric loss or dissipation factor was measured for the Ba-TiO$_3$/epoxy composites that were surface treated by the silane coupling agent. Surface treatment of the samples led to better particle distribution within the polymer matrix therefore minimizing the formation of particle-particle clusters and aggregations. As a result, the dielectric loss began to decrease with increasing concentration of the coupling
agent. The maximum dissipation factor for the BaTiO$_3$-epoxy composites that were prepared using untreated, SCA 0.01, SCA 0.015, SCA 0.020 and SCA 0.025 treated BaTiO$_3$ nanoparticles at 20MHz were found to be 0.3836, 0.1106, 0.087, 0.136 and 0.119, respectively.

**Hypothesis IV:** The dielectric breakdown strength was calculated by increasing the electric field across the sample until breakdown occurred. The dielectric breakdown measurements were recorded for BaTiO$_3$-epoxy composites that were fabricated using 0.1-0.6 volume fraction of BaTiO$_3$ nanoparticles using untreated, SCA 0.01, SCA 0.015, SCA 0.02 and SCA 0.025 surface treated particles. The composites that were prepared using SCA 0.020 and SCA 0.025 showed the most promising results, however for the latter only at lower volume fractions i.e. 0.1, 0.2 and 0.3. The maximum breakdown strength for the samples prepared using SCA 0.02 and SCA 0.025 were recorded to be 85 kV/cm (at 0.4, 0.6 BaTiO$_3$) and 90 kV/cm (at 0.2 BaTiO$_3$), respectively. These results along with SEM and EDS micrograph images showed that the dielectric breakdown strength began to increase with increasing concentration of the coupling agent owing to enhanced interfacial adhesion.

**Hypothesis V:** The viscosity study was conducted between a range of 150-300 mPas for the SCA 0.020 BaTiO$_3$/epoxy samples at 50% volume fraction of BaTiO$_3$. The optimum viscosity was found to be 180 mPas and by optimizing the viscosity we were able to achieve not only higher permittivity values but also improved film-substrate interfacial adhesion. The value of permittivity at the optimum viscosity i.e. 180 mPas was recorded to be 50.02 and the maximum value of piezoelectric strain coefficient, $d_{33}$ at 180 mPas was found to be 1.30.
### 6.2 Future Work

After the completed two-phase BaTiO$_3$-epoxy composites have been fabricated we can then begin to develop them into capacitors. Multiple arrays of such composites can be connected electrically and sandwiched between two stainless steel electrodes to form a set of capacitors. These capacitors can then be insulated from each other by an insulating material as shown in Figure 6.

![Figure 6.1: A schematic diagram representing a capacitor network comprised of multiple arrays of two-phase BaTiO$_3$-epoxy nanocomposites sandwiched by stainless steel electrodes. These composites are made using silane coupling agent treated (0.02 v/v) BaTiO$_3$ nanoparticles. These formed capacitors can then be tested by charging and discharging the capacitors.](image)
Figure 6.2: The charging and discharging of the capacitor using a DC voltage source and the voltage readings recorded using an Agilent Technologies Oscilloscope DSC 1004A. This circuit includes a breadboard for the circuitry and two switches that can independently charge and discharge the capacitor.

Figure 6.3: The voltage during charging of the capacitor was recorded using an Agilent Technologies Oscilloscope DSC 1004A and was found to be 5.44V.
References


[75] W. Lewin. (2002). *Dielectrics and Polarization*


