Piezoelectric and dielectric characterization of corona and contact poled PZT-epoxy-MWCNT bulk composites

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Piezoelectric and dielectric characterization of corona and contact poled PZT-epoxy-MWCNT bulk composites

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Abstract
Three-phase lead zirconate titanate (PZT, PbZr0.52Ti0.48O3)-epoxy-multi-walled carbon nanotube (MWCNT) bulk composites were prepared, where the volume fraction of PZT was held constant at 30%, while the volume fraction of the MWCNTs was varied from 1.0%–10%. The samples were poled using either a parallel plate contact or contactless (corona) poling technique. The piezoelectric strain coefficient ($d_{33}$), dielectric constant ($\varepsilon$), and dielectric loss tangent ($\tan \delta$) of the samples were measured at 110 Hz, and compared as a function of poling technique and volume fraction of MWCNTs. The highest values for dielectric constant and piezoelectric strain coefficients were 465.82 and 18.87 pC/N for MWCNT volume fractions of 10% and 6%, respectively. These values were obtained for samples that were poled using the corona contactless method. The impedance and dielectric spectra of the composites were recorded over a frequency range of 100 Hz–20 MHz. The impedance values observed for parallel-plate contact poled samples are higher than that of corona poled composites. The fractured surface morphology and distribution of the PZT particles and MWCNTs were observed with the aid of electron dispersion spectroscopy and a scanning electron microscope. The surface morphology of the MWCNTs was observed with the aid of a field emission transmission electron microscope.

Keywords: piezoelectric composite, dielectric, MWCNT, impedance spectra

(Some figures may appear in colour only in the online journal)

1. Introduction

Though piezoelectric ceramics such as lead zirconate titanate (PZT, Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$), 0 ≤ x ≤ 1) and barium titanate (BaTiO$_3$) are used ubiquitously in sensor and electromechanical applications [1–5], their application to advanced sensor/actuator, electromechanical, and electrical/energy storage and harvesting devices is limited because they possess poor mechanical properties, are difficult to process; and suffer from impedance mismatch with host structures. Development of composite piezoelectric materials could increase the number of available material and design degrees of freedom, which would enable these materials to be tailored to address some of the aforementioned challenges [6, 7].

Two-phase composite piezoelectric materials, so-called 0–3 composites comprised of piezoelectric particles embedded within a continuous polymer matrix, have attracted much attention due to their flexibility, ease of processing and use in embedded passive devices [8, 9], such as capacitors. Two-phase composites: metal-polymer [10, 11] and ceramic-polymer have been extensively studied [7, 12, 13] for application in coupling or by-pass capacitor technology and are promising materials because of their excellent tailored properties [6, 14]. Piezo-polymer materials have many advantages including high electro-mechanical coupling factors [15–17], low acoustic impedance [18, 19], mechanical flexibility [20, 21], and broad bandwidths [22, 23] in combination with low mechanical quality factors [24, 25]. The mechanical,
electrical and acoustic properties of these materials can also be tailored to meet desired applications [12, 26].

The enhancement of properties observed in piezopolymer composites [5, 27] is because the properties of the constituent phases combine to improve the mechanical properties and range of applicability of the composite [28, 29]. The effective piezoelectric and dielectric properties of two-phase composites are not comparable to their single phased counterparts due to the polymer matrix, which has lower dielectric constants and piezoelectric coefficients in comparison to the embedded piezoelectric ceramic [30, 31]. Hence, several researchers have demonstrated that the inclusion of electrically conductive particles within the polymer matrix [32, 33] will enhance the polarization of the embedded piezoelectric fillers within the matrix, thereby enhancing their electrical properties [18, 34, 35]. Recently, carbon nanotubes (CNTs) have emerged as attractive fillers [18, 33, 36] due to their electrically conductive nature [37, 38]. However, less is known about the interrelationship between the composite processing technique, morphology and properties of the electrically conductive particles, which dictate the piezoelectric and dielectric properties of the materials [6, 36].

Multi-walled carbon nanotubes (MWCNTs) have been investigated for inclusion within polymer matrices to enhance electron transport and mechanical strength of the composite structure [18, 33, 36–38, 40] and have been extensively studied due to their unique electrical and mechanical properties as shown in Table 1 [24, 39]. MWCNTs have high electrical conductivity due to their unidirectional structure and the ballistic transport of electrons over long nanotube lengths. MWCNTs also have higher Young’s moduli (~0.64 TPa [41]) than other materials such as stainless steel (0.203 GPa [13, 42, 43]).

Polymers composite with CNT inclusions possess higher dielectric properties (in comparison to polymers without carbon fillers) because the CNTs increase the number of charge carriers within the polymer matrix material. However when the volume fraction of the CNTs reaches the percolation threshold, the dielectric properties diminish due to the formation of electrically conductive pathways in the composite [44]. On the other hand, the insulating properties of the polymer matrix diminish electron transport in polymer-based composites. The low electron transport causes low dielectric constants in these materials [28, 30, 40, 45, 46].

Ma and Wang [13] compared the microstructure and dielectric properties of epoxy-based composites that contained CNTs and lead magnesium niobate-lead zirconate titanate (PMN-PZT) piezo-ceramics. These composites exhibited a percolation threshold in the range of 1.0–1.5 g CNTs per 100 g epoxy, wherein in the region of the percolation threshold, a continuous electro-conductive network was formed. These materials demonstrated dynamic mechanical loss factors that were higher than materials below the percolation threshold, and without semi-conductive inclusions. Tian and Wang [47] examined the performance of MWCNT-piezoelectric ceramic composites as rigid damping materials. Their results were similar to Ma and Wang [13], where the percolation threshold was found to be in the range of 1.0–1.5 g CNTs per 100 g epoxy. They concluded that loss factors were higher with the incorporation of CNT and PZT, when the amount of CNT was above the critical electrical percolation threshold. Researchers have found that increases in the volume fraction of the electrically conductive inclusion phase within polymeric composites can lead to increases in electrical conductivity [27, 48]. Changes in the percolation threshold due to variations of the aspect ratio of the conductive inclusions have also been studied [49–51] as shown in Table 2. Due to their enhanced dielectric and piezoelectric properties [33, 36] and multifunctional nature [39], multiphasic piezoelectric composites have a high potential for applications as sensors, transducers and energy harvesting devices.

Multiphase piezoelectric composite materials have been traditionally poled using the parallel plate-contact polarization method where the material is in contact with the poling electrodes [35, 52]. This method can cause dielectric breakdown in the presence of conductive inclusions [52, 53]. To overcome this drawback, corona discharge polarization was developed where a high poling voltage is applied to two asymmetric electrodes such as a point and a plate [52]. Researchers have shown that higher voltages can be achieved with corona polarization, in comparison to the parallel plate contact polarization method [35, 53]. The method of polarization plays a key role in the piezoelectric and dielectric properties of piezo-composites.

In this work, the mechanisms that influence the piezoelectric, dielectric and impedance properties of the PZT-epoxy-MWCNT composites are investigated as a function of

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific density</th>
<th>Young’s modulus (TPa)</th>
<th>Strength (GPa)</th>
<th>Electrical conductivity (S m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single walled carbon nanotube</td>
<td>1.3–2</td>
<td>0.9–1.1 (variation due to tube diameter)</td>
<td>3–25 (variation due to tube diameter)</td>
<td>10⁶–10⁷</td>
</tr>
<tr>
<td>(bundles)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Multi-walled carbon nanotubes</td>
<td>1.3–2</td>
<td>0.8–1.5 (variation due to number of tubes)</td>
<td>20–60 (variation due to number of tubes)</td>
<td>10⁶–10⁷</td>
</tr>
<tr>
<td>(bundles)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silver</td>
<td>10.4</td>
<td>0.083</td>
<td>0.054</td>
<td>6.3 × 10⁷</td>
</tr>
<tr>
<td>Copper</td>
<td>8.9</td>
<td>0.125</td>
<td>0.069</td>
<td>5.96 × 10⁷</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>7.8</td>
<td>0.2</td>
<td>4.1</td>
<td>2–8.5 × 10⁶</td>
</tr>
<tr>
<td>Carbon fiber</td>
<td>1.7–2</td>
<td>0.2–0.6</td>
<td>1.7–5</td>
<td>1.45 × 10⁶</td>
</tr>
</tbody>
</table>
the volume fraction of the conductive phase and poling technique. The distribution of the phases in the matrix, and phase interaction have been studied with the aid of a scanning electron microscopy (SEM), electron dispersion spectroscopy (EDS) and transmission electron microscopy (TEM) to ascertain the degree of separation of particles, particle morphology, composite porosity and agglomeration.

2. Methodology and procedure

The three-phase piezoelectric composites that were fabricated, were comprised of MWCNTs from stream chemicals, CAS—1333-86-4, lead zirconate titanate (PZT, APC International 855, Navy VI) and a two-part epoxy resin (Electron micro-scopy sciences, DGEBA, EMS 1232). The piezoelectric and dielectric properties of the PZT, MWCNTs and epoxy used in the fabrication of the composite are provided in table 3. The volume fraction of PZT was held constant at 30%, while the volume fraction of the MWCNTs was varied from 1%–10%. The volume fraction range of the MWCNTs was chosen to identify the percolation threshold of the MWCNTs within the composite. A flow diagram of the procedure for fabrication of the composites is provided in (figure 1).

2.1. Surface treatment of the MWCNTs and PZT

The MWCNTs were surface treated in ethanol prior to inclusion within the composite mixture. The raw MWCNTs (stream chemicals) were in the form of pellets, which consisted of agglomerated clusters of MWCNTs bound together due to van der Wall’s forces. The MWCNTs were dispersed in ethanol (200 proof, Sigma-Aldrich) and sonicated for four hours in an ultra-sonicator. The sonication method used is a non-covalent dispersion method where the sonication energy provides surface energy to the nanotubes to overcome the van der Walls forces between nanotubes [59, 60]. The degree of agglomeration of the MWCNTs post sonication treatment was observed with the aid of a TEM.

The PZT particles (from APC International) were received with poly vinyl alcohol (PVA) as a surface coating. The PZT powder was sintered at 500 °C to remove the PVA coating and subsequently ball milled for 24 h prior to incorporation within the mixture. The microstructure and morphology of the PZT particles (binder removed) were observed with the aid of a SEM.

2.2. Composite preparation

A schematic that depicts an overview of the composite fabrication process is provided in figure 2. MWCNTs were sonicated in ethanol for 4 h. PZT and epoxy were combined with the MWCNTs in ethanol. The mixture has both the components of a sol (non-macroscopic particles in solution) and a gel (bushy structures as clusters and agglomeration pockets of PZT epoxy and MWCNTs). The organic residues left behind by the gradual evaporation of the ethanol from the sol–gel bind the different phases in the mixture forming the gel-like structures. The suspension of the three-phase mixture was desiccated for an additional 4 h to eliminate air pockets. The resulting mixture was then sonicated again for a half an hour after the epoxy binder (Epofix hardener, EMS 1232) was added.

The three-phase PZT-epoxy-MWCNT mixture was cast into disks, 7 mm in radius and 6 mm thick. The disks were cured at 750 °C for 8 h. After the disks were cured, the samples were polished using a 2000 grit sand paper and colloidal silver electrodes were painted on both the surfaces of the disks. All samples were poled using a Spellman SL Series high voltage generator. The samples were poled at 2.2 kV mm⁻¹ (@ 75 °C) using either the parallel plate contact polarization method or the corona discharge poling method.

2.3. Sample poling

Bulk samples were either contact or corona poled. Schematics of contact and corona processes are provided in figure 3. The samples were poled for 60 min at a polarization voltage of 2.2 kV mm⁻¹. The parallel plate contact polarization method, depicted in figure 3(A)), was achieved by placing the composite material in between the top electrode and the ground base plate in a dielectric medium (silicone oil). The beaker containing the composite and silicone oil was heated to 75 °C, which is below the glass transition temperature of the epoxy.

The Corona discharge polarization method depicted in figure 3(B)), was performed by applying 2.2 kV mm⁻¹ to a needle suspended above the composite material, while the

<table>
<thead>
<tr>
<th>Electrically conductive filler</th>
<th>Composite/fabrication method</th>
<th>Percolation (volume fraction %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT (aspect ratio = 400) [54]</td>
<td>MWCNT-PVDF/sol–gel and hot molding</td>
<td>1.0%</td>
</tr>
<tr>
<td>MWCNT (aspect ratio ~100) [54]</td>
<td>MWCNT-PMMMA/compression molding</td>
<td>2.4%</td>
</tr>
<tr>
<td>SWCNT (aspect ratio ~100) [54]</td>
<td>SWCNT-PMMMA/compression molding</td>
<td>3.4%</td>
</tr>
<tr>
<td>SWCNT (aspect ratio ~1000) [38]</td>
<td>SWCNT-PZT-PMMMA/solution casting</td>
<td>0.8%</td>
</tr>
<tr>
<td>CNT (aspect ratio ~100) [55]</td>
<td>CNT-alumina/colloidal processing</td>
<td>2.2%</td>
</tr>
<tr>
<td>MWCNT (aspect ratio ~100) [47]</td>
<td>MWCNT-epoxy/sol–gel sintering</td>
<td>2.0%–2.75%</td>
</tr>
<tr>
<td>Double Walled CNTs (aspect ratio &gt;1000) [56]</td>
<td>MWCNT-epoxy/ vacuum sintering</td>
<td>0.25%</td>
</tr>
<tr>
<td>MWCNT (aspect ratio &gt;100) [57]</td>
<td>MWCNT-epoxy/ sol–gel sintering</td>
<td>2.5%</td>
</tr>
<tr>
<td>CNT (aspect ratio = 200–1000) [48]</td>
<td>CNT-epoxy/ sol–gel sintering</td>
<td>0.5%–1.5%</td>
</tr>
<tr>
<td>MWCNT (aspect ratio ~1000) [58]</td>
<td>MWCNT-epoxy/sol–gel sintering</td>
<td>0.8%</td>
</tr>
</tbody>
</table>
Table 3. Piezoelectric and dielectric properties of the PZT and epoxy resin.

<table>
<thead>
<tr>
<th>Material</th>
<th>Dielectric constant ($\varepsilon$)</th>
<th>Piezoelectric strain coefficient, $d_{33}$ (pC N$^{-1}$)</th>
<th>Piezoelectric strain coefficient, $d_{31}$ (pC N$^{-1}$)</th>
<th>Dielectric loss (tan $\delta$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT (APC International, 855, Navy VI)</td>
<td>3300 (at 1 kHz)—from manufacturer</td>
<td>400</td>
<td>175</td>
<td>$\leq 2.50$</td>
</tr>
<tr>
<td></td>
<td>(606.70— from measurement in the lab at the same frequency)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Epoxy (Electron Microscopy Sciences, DGEBA, EMS 1232)</td>
<td>8.239 (at 1 kHz)—from the (manufacturer. 12.23 from measurement in the lab at the same frequency)</td>
<td>NA</td>
<td>NA</td>
<td>$&lt; 1$</td>
</tr>
</tbody>
</table>
Surface treatment of MWCNTs by dispersion in Ethanol (MWCNTs are sonicated for 4 hours).

PZT and Epoxy (Bisphenol A diglycidyl ether) were added and the mixture sonicated for 4 hours.

Mixture desiccated for 4 hours. The epoxy binder was added to the mixture and sonicated for 1/2 hour.

Curing of the epoxy matrix. (at 75°C)

Polishing of bulk composite surface and deposition of electrode.

Alignment of dipoles in PZT by contact/contactless poling. (Applied voltage of 2.2 kV/mm at 75°C.)

**Figure 1.** Flow diagram depicting the fabrication procedure for PZT-epoxy-MWCNT, three-phase bulk composites.

The composite temperature was held at 75 °C [15, 61]. When the needle reached the ionizing potential of the surrounding air, ionic species were generated. These ionic species were attracted towards the ground base plate. When a sufficient surface charge density was reached on the surface of the top electrode, the ions flowed toward the base plate through the thickness of the composite material and aligned the dipoles of the PZT phase.

After the polarization step, the samples were wrapped in aluminum foil for 24 h to remove any residual charges on either surface. A piezometer (PM300 from PiezoTest) was used to measure the dielectric constant, dielectric loss tangent and the piezoelectric strain coefficients ($d_{33}$ and $d_{31}$) at a frequency of 110 Hz. Impedance and dielectric spectroscopy of the bulk composites were performed using the HP4194A Impedance Analyzer over a frequency range of 100 Hz–20 MHz. The fractured surface morphology and distribution of the particles within the matrix were observed with the aid of an EDS, scanning electron microscope (FESEM ZEISS 982) and the field emission transmission electron microscope (TEM JEOL 2010F).

**3. Results and discussion**

**3.1. MWCNT and PZT characterization**

The surface morphology and distribution of MWCNTs within ethanol after 4 h of sonication were observed with the aid of TEM images in figure 4. In addition, the Raman spectrum of the MWCNTs was obtained to ascertain the composition and defects in MWCNTs. The diffraction pattern shown in figure 4(A)) shows the presence of 4 rings, which can be attributed to the two-dimensional graphite sheets rolled up to form MWCNTs. The structure of the MWCNTs found in figure 4(B) are consistent with the literature [59, 60]. The Raman spectrum of the MWCNTs (in figure 5) shows the presence of D, G and G’ peaks, which indicate the presence of sp2 hybridized MWCNTs.

The PZT powder (as received) was coated with PVA. The polyvinyl alcohol (PVA) binder coating on the PZT was removed and the PZT powder was subsequently ball milled for 24 h. SEM images of the PZT powder prior to PVA binder removal, post PVA binder removal and after ball milling are provided in figures 6(A)–(C).

The average particle size of the PZT was determined by use of SEM micrograph image analysis by software packages Imagej and Photoshop CS5.1. The particles coated with PVA had an average particle size of $\sim\text{4.6} \pm \text{1.5}\ \mu\text{m}$. After PVA coating was removed, the particle size reduced to $\sim\text{3.0} \pm \text{0.5}\ \mu\text{m}$. The ball milled PZT particles had a mean particle size of $\sim\text{1.5} \pm \text{0.3}\ \mu\text{m}$. The uniformity of the particle size increased and the standard deviation decreased with the use of ball milling. The particle size distribution from the SEM micrograph analysis of the PZT (post PVA removal) and (post ball milling) are shown in figures 7(A) and 7(B), where the sample sizes were of 1330 and 400 particles respectively. The particle size was averaged over three different sample regions. The XRD and Raman Spectrum of PVA coated PZT and sintered PZT are shown in figure 8.

**3.2. SEM and TEM micrograph analysis of PZT-epoxy-MWCNT bulk composites**

SEM and TEM micrographs, and EDS spectra were analyzed for the different volume fractions of MWCNTs in the bulk composites ranging from 1.0%–10% to ascertain the morphology structure and distribution of MWCNTs and PZT within the composite. The SEM micrographs show the morphology of the fractured surface of the composite. The EDS spectrum shows the distribution of the different phases in the epoxy matrix by use of selective elemental analysis, wherein the elements of the different phases are mapped on the bulk composite surface. In particular, the selected area diffraction patterns of the composite with MWCNT volume fractions of 0.06 (6%) and 0.02 (2%) were studied to compare the distribution of MWCNTs and the formation of clusters and agglomerations. In figure 9(A) the selected area diffraction pattern of the three phase bulk composite with a MWCNT volume fraction of 6% is depicted. The white spots correspond to the polycrystalline PZT and the rings correspond to the cylindrical tubes of the MWCNTs in the epoxy matrix. The TEM micrograph in figure 9(B) shows three MWCNTs embedded in the epoxy matrix. The PZT particle clusters are not visible in the TEM due to their average particle size $\sim\text{1.5}\ \mu\text{m} \pm \text{0.3}\ \mu\text{m}$, which is much larger than the scope of the micrograph.

Similarly, the TEM electron diffraction surface area images in figures 10(A) and (B) depict the composite that is comprised of 2% volume fraction of MWCNTs, where less
rings are apparent, thus indicating a smaller volume fraction of MWCNTs in the composite. The distribution and agglomeration of PZT and MWCNTs are depicted in SEM micrographs (figures 11(A) and (B)) of the composites with MWCNT volume fractions of 0.01 (1%) and 0.03 (3%).

The SEM micrograph, EDS spectrum (corresponding selective elemental analysis) and layered image of the fractured surface of the bulk PZT-epoxy-MWCNT composite with a MWCNT volume fraction of 0.01 (1%), are depicted in figures 12(A)–(C), respectively. The larger particle clusters in the SEM micrograph shown in figure 12(A) are PZT particles. The evidence of PZT particle clusters is also verified in figures 12(B) and (C), layered image and elemental analysis. The smaller clusters seen in figure 12(A), are the MWCNT agglomerations that are distributed in the epoxy matrix. The carbon element in the elemental analysis represents both the MWCNT and the epoxy matrix.
3.3 Piezoelectric and dielectric characteristics of bulk PZT-epoxy-MWCNT composites

The piezoelectric and dielectric characteristics of the bulk three-phase PZT-epoxy-MWCNT composites were measured using a Piezometer (PM300 from PiezoTest) and a HP4194A impedance analyzer. The properties of composites that were either the parallel plate contact or the corona polarization method were compared.

3.3.1 Contact poled bulk PZT-epoxy-MWCNT composites

The strain coefficient ($d_{33}$), loss factor ($\tan(\delta)$) and capacitance ($C$) were measured using a Piezo Meter System manufactured by Piezo Test, Piezoelectric Materials & Device Testing Company (at 110 Hz) and HP4194A impedance analysis system. The dielectric constant, $\varepsilon$, was calculated from $C$ and the geometry of the composite. The volume fraction of the PZT was held constant at 30%, while the volume fraction of MWCNTs was varied from 1% to 6% for the contact poled samples. In Figure 13, $\varepsilon$ and $\tan(\delta)$ are plotted as a function of volume fraction of MWCNTs. Both $\varepsilon$ and $\tan(\delta)$ of the composite increase with the volume fraction of the MWCNT inclusions. For example, for an increase in MWCNT volume fraction from 2% to 5% the $\varepsilon$ and $\tan(\delta)$ increase from $\sim 40$ to $\sim 70$ and $\sim 0.07$ to $\sim 0.22$, respectively.

A similar trend is observed for the piezoelectric strain coefficient ($d_{33}$) of the composite as shown in Figure 14. Hence, as expected, $d_{33}$ increases as the volume fraction MWCNT increases. For example, $d_{33}$ increases from $\sim 0.7$ to $\sim 5.3$ pC/N for volume fractions equal to 2% to 5%, respectively. The piezoelectric strain coefficient, $d_{33}$ is a function of the effective dipole moment in the direction of the energy generation under an applied mechanical deformation. The enhanced values of $d_{33}$, $\varepsilon$ and $\tan(\delta)$ as a function of volume fraction of the MWCNT inclusions are consistent with the observations of others [36, 58, 62].

On the other hand, a decrease in the $d_{33}$ values from $\sim 5.3$ to $\sim 5.08$ pC/N was observed for MWCNT volume fractions equal to 5% and 6%, respectively. The decrease in $d_{33}$ values was coupled with a sharp rise in the $\varepsilon$ and $\tan(\delta)$; e.g. from $\sim 84$ to $\sim 138$ and from 0.22 to 0.28, respectively (for...
Figure 6. SEM micrographs of distribution of (A) PZT particles with PVA coating at a magnification of \(\sim 300 \times\), (B) PZT particles without PVA coating at a magnification of \(\sim 300 \times\) and (C) ball milled PZT particles at a magnification of \(\sim 900 \times\). The images show an increase in the uniformity of particle size due to ball milling.

Figure 7. Particle size distributions of (A) PZT particles without the PVA coating with a sample size of 1300 particles and averaged over three sample regions, (B) PZT particles ball milled for 24 h with a sample size of 400 particles and averaged over three sample regions. As expected, the variability in particle size diminished with the ball milling process.
MWCNT volume fractions of 5% and 6%, respectively. In theory, this piezoelectric and dielectric behavior can be attributed to the formation of MWCNT clusters within the composite. The formation of MWCNT clusters promotes conductive pathways, which result in electrical percolation above a specific volume fraction of electrically conductive inclusion. Also, $\varepsilon$ for ALL of the three-phase composites are higher than the 0% MWCNT (two-phase) composites. Specifically, for a contact poled PZT-epoxy composite (0% volume fraction of MWCNT) that was prepared under the same conditions, $\varepsilon \sim 8.64$. Also, the dielectric loss of samples containing 0% volume fraction of MWCNT composite was less ($\tan(\delta) \sim 0.0060$) than all of the three-phase bulk composites. The $d_{33}$ for a three phase PZT-epoxy-MWCNT composite ($d_{33} \sim 0.60 \text{ pC/N}$ for a MWCNT volume fraction of 1%) is also enhanced when compared to a two phase composite ($d_{33} \sim 0.2 \text{ pC/N}$). The increase in the $\varepsilon$ and the $d_{33}$ values can be attributed to the increase in charge carriers due to the addition of MWCNTs. The evidenced higher values of $\varepsilon$ can be attributed to several mechanisms; hopping charge transport, metal–insulator transitions, and interfacial effects. Hence, the addition of MWCNT inclusions also resulted in increased conductivity of the composite (shown in figure 15), which lead to higher dielectric loss [5] observed in figure 13.

The increase in electrical conductivity as a function of MWCNT volume fraction shown in figure 15 is due to the increase in the formation of conductive pathways in the composite and electron transport through electron tunneling in the composites. For example, in figure 15 the conductivity increases sharply from 0.10–0.25 $\mu \text{S m}^{-1}$ for volume fractions of 5% and 6% MWCNTs, respectively. A similar increase in the conductivity values are also seen for the contactless (corona) poled composites.

### 3.3.2. Corona poled bulk PZT-epoxy-MWCNT composites.

In $\varepsilon$ and $\tan(\delta)$ for the composites poled using the corona discharge poling method are plotted as a function of MWCNT volume fraction. The volume fraction in this case was varied from 0% to 10%. The values of $\varepsilon$ and $\tan(\delta)$ increase with volume fraction of MWCNTs in a manner similar to the observed trend for the contact poled samples shown in
For example, \( \varepsilon \) increased from \( \sim 54 \) to \( \sim 249 \) for MWCNT volume fractions of 2\% and 6\%, respectively in the corona poled samples. This trend was also observed for composites that had MWCNT volume fractions lower than 1\%. Similarly, the dielectric loss of the composites, increased as a function of MWCNT volume fraction and \( \tan(\delta) \) increased from \( \sim 0.09 \) to \( \sim 0.20 \) for a change in MWCNT volume fraction from 2\% to 5\%, respectively.

The \( d_{33} \) values of the three-phase composite are plotted as a function of the MWCNT volume fraction in figure 17. For a change in MWCNT volume fraction from 2\% to 5\%, the \( d_{33} \) coefficients increased from \( \sim 12 \) to \( \sim 18 \) pC/N.
respectively. In addition, for MWCNT volume fractions below 1%, the $d_{33}$ changes from $\sim 2$ to $\sim 10$ pC/N, for MWCNT volume fractions of 0.1% and 0.9%, respectively.

The trends observed in figures 16–18 seem to indicate multiple percolation thresholds that correspond to regimes and transitions that are related to MWCNT network contact as noted by [63, 64]. In these figures three different regimes are depicted. For example, at low volume fractions of MWCNTs from 0.0 to 0.01, $d_{33}$ increases linearly with volume fraction of MWCNTs. This linear regime adheres to the effective medium theory model [65]. Two subsequent transitions are observed in all three figures at volume fractions equal to 0.02 and 0.05. The other percolation thresholds have been observed by others who have concluded that for thicker samples subjected to strain, compression perturbs the CNTs into bundles linked through van der Waals bonds that are perpendicular to the strain [63]. These inter tube van der Waals potentials are so strong as to render the CNTs irreversibly bonded on contact, which can lead to marked changes in the percolation threshold at increased filler volume fractions. Also, interfacial effects and tunnel-assisted interfacial conductivity are enhanced with increased in CNT volume fractions [65, 66].

Similar to the samples that were contact poled, the transition to the final percolation region was observed to occur at MWCNT volume fractions between 5% and 6%. For example, a sharp decrease in the $d_{33}$ and a sharp increase in $\varepsilon$ and tan ($\delta$) values were observed at a MWCNT volume fraction change from 5% to 6%. In particular, the $d_{33}$ values decreased from $\sim 18$ pC/N to $\sim 4$ pC/N, and the $\varepsilon$ and tan ($\delta$) values increase from $\sim 128$ to $\sim 248$, and 0.02 to $\sim 0.06$ for MWCNT volume fractions of 5% and 6%, respectively. Further, the $d_{33}$ values also decrease from 3 to 0.97 and 0.62 pC/N for MWCNT volume fractions of 7%, 8% and 9%, respectively. This change in the dielectric and piezoelectric coefficients correspond to the sharp rise in conductivity due to the increase in the number of localized MWCNT percolation clusters that lead to formations of electrically conductive pathways due to electron tunneling and direct contact [67]. This change in the material properties takes place at a MWCNT volume fraction of $\sim 5\%–6\%$. As expected, the number of electrically conductive pathways increases with the increase in MWCNT volume fraction within the composite.

The conductivity measurements for the corona poled composites are presented in figure 18. Similar to the trend observed for the contact poled composites, the conductivity increases as a function of MWCNT volume fraction. For example, the conductivity increases from 0.17 to 0.69 $\mu$S m$^{-1}$ for volume fractions of 5% and 6% MWCNTs, respectively. This sharp rise in the conductivity values indicates that the bulk composites reach the percolation threshold around a MWCNT volume fraction of 5%–6%.

3.4. Impedance spectroscopy of three phase PZT-epoxy-MWCNT bulk composites characterized by corona and contact poling methods

In this work, the complex impedance spectra was measured (from 2.5 to 20 MHz) and correlated to the volume fraction and poling technique, to observe the relationship between the microstructure and electrical properties of the material. Variation of electrical impedance over the frequency range and as a function of the volume fraction of MWCNTs elucidates the mechanisms of electron transport and conductivity, which influences their overall dielectric properties.

In figures 19 and 20, the impedance spectra (frequency range from 100 Hz to 20 MHz) for the three-phase parallel plate contact and corona poled composites are presented, respectively. As expected, the magnitude of the impedance (in both cases) decreases as the frequency increases due to the frequency dependence of the relaxation phenomenon in cross-linked composites. The chemical and physical interactions of the viscoelastic polymeric phase and solid fillers, e.g. PZT and MWCNTs, influence the relaxation phenomenon in the
crosslinked and reinforced polymers. The aforementioned interactions result in the formation of interphase regions between the filler and polymer. MWCNTs possess high surface areas, which enhance the polymer-filler interfacial interactions, which cause the stiffness at these interphases to be higher than those of the bulk polymer due to hindered molecular mobility. Decreased electrical impedance at higher frequency values is attributed to enhanced mobility of the conductive species at higher frequencies. Also, the impedance values decrease as the volume fraction of MWCNTs increases due to electron hopping, a mode of conduction, which is more significant at microwave frequencies. There is a sharp drop in the impedance values when the MWCNT volume fraction in the composite changes from 5% to 6%, indicating a sharp rise in conductivity (decrease in resistance) of the composite. This trend is seen over the entire range of the frequencies. For example, at a frequency of 2.5 kHz the impedance drops from \( \sim 1852 \, \text{k\Omega} \) to \( 1631 \, \text{k\Omega} \) for a change in the MWCNT volume
fraction from 5% to 6% as compared to a drop of $\sim 1990$ k\(\Omega\) to $1852$ k\(\Omega\) for a MWCNT volume fraction change of 4% to 5% (contact poled samples). This phenomenon is consistent with the sharp drop in the piezoelectric strain coefficients and the sharp increase in the dielectric constants at the percolation threshold. The impedance values provide evidence that the percolation threshold is present around this region, where lower values of impedance are also indicative of percolation through the conductive network formed from aggregated and agglomerated conductive fillers within the insulative matrix and electron tunneling through the isolated piezoelectric sites.

Figure 13. PZT-epoxy-MWCNT bulk composites (contact poled), where the volume fraction of PZT was held constant at 30%, while the volume fraction of MWCNTs was varied from 0.01 to 0.06. The bulk samples were poled using the contact—parallel electrode process. As expected the, both the dielectric constant and loss increased with increasing volume fraction of MWCNTs.

Figure 14. Variation of the piezoelectric strain coefficient, $d_{33}$ of three phase PZT-epoxy-MWCNT bulk composites with contact poling, as a function of the MWCNT volume fraction measured at a frequency of 110 Hz and an applied force of 0.25 N. The $d_{33}$ coefficient increases with an increase in the MWCNT volume fraction from 1% to 5%, below the percolation threshold.

Figure 15. Conductivity measurements at 2 kHz for contact-parallel plate poled bulk composites. There is a sharp rise in the values around a MWCNT volume fraction change from 5%–6%, which indicates the transition to the percolation threshold of the composite.

Figure 16. The dielectric constant and dielectric loss ($\tan(\delta)$) are plotted as a function of MWCNT volume fraction for the PZT-epoxy-MWCNT bulk composites (corona poled). The volume fraction of PZT was held constant at 30%, while the volume fraction of MWCNTs was varied from 0.01 to 0.10. The bulk samples were poled using the corona poling process. As expected the, both the dielectric constant and loss increased with increasing volume fraction of MWCNTs.

In figure 21, the impedance values (at a frequency of 2 kHz) for the contact and corona poled three phase bulk PZT-epoxy-MWCNT composites are plotted as a function of MWCNT volume fraction. The impedance of the contact poled samples is higher than those of the corona poled composites. For example, for a MWCNT volume fraction of 3%, the impedance of the contact poled composite $\sim 2377$ k\(\Omega\), in comparison to $\sim 2042$ k\(\Omega\) for the corona poled composite. This trend is followed for all volume fractions of the composite. This difference in impedance indicates the higher resistance of contact poled composites, which is most likely due to the larger number of dipoles being aligned along the
poling direction by the corona poling method in comparison to the contact poling method. In other words, the corona poling processing method enables a higher polarization density. In the contact poling technique, the electrons flow through the path of least resistance (through hopping and electron tunneling) from one surface to another, while in the corona poling technique, the polarized ions are distributed over the entire cross-sectional area of the sample geometry and flows from the top to the bottom surface. This is also demonstrated by the higher piezoelectric strain coefficients of the corona poled samples shown in figure.

3.5. Dielectric spectroscopy of three phase PZT-epoxy-MWCNT bulk composites

In figure 22, the effective dielectric spectrum (frequency range from 100 Hz–20 MHz) of the corona and contact poled composites are presented, respectively. The MWCNT volume fraction was varied from 1% to 10% for the corona poled samples, and from 1% to 6% for the contact poled composites. Higher volume fractions of MWCNTs (greater than 6% volume fraction) could not be processed using the contact poling method.
poling technique, due to the occurrence of short circuiting observed in the samples. An increase in the dielectric constant with an increase in the MWCNT volume fraction is observed for composites fabricated using both poling techniques. The transition of the composites to the percolation threshold is observed when there is a jump in the dielectric constant above a MWCNT volume fraction of 5%. For example, below the percolation threshold and for a MWCNT volume fraction change from 3%–4% the dielectric constant changed from ∼88 to 98 for the corona polied composites and ∼32 to 37 for the contact polied composites at a frequency of 2 kHz. However, when the volume fraction changed from 5–6%, the dielectric constant increased from ∼124 to 241 and ∼48 to 67 for Corona and contact poling, respectively. This increase in the dielectric constant was coupled with the increase in the impedance as seen in figures 19–21. The evidenced transition into the percolation region was most likely due to the sharp rise in electron hopping and tunneling in the composites, which resulted in higher conductivity within the composite as indicated in figures 15 and 18.

For lower volume fractions of the composite below the percolation threshold (below 6% of MWCNTs), the dielectric performance of the composites show very little frequency dependence below 15 MHz. Above 15 MHz the dielectric constant values increase with increasing frequency indicating a frequency dependence due to the presence of the MWCNT inclusions which causes an increase in the mobility of the conductive species at higher frequencies. In the case of the composite with MWCNT volume fractions greater than or equal to 6%, the frequency dependence is observed over the entire range of frequencies from 100 Hz–20 MHz indicating a system with percolation, similar to the results shown by Yao et al and Dang et al [18].

\[
\log(\varepsilon) = \nu_f \cdot \log(\varepsilon_f) + (1 - \nu_f) \cdot \log(\varepsilon_m),
\]

\[
\varepsilon = \nu_f \cdot \log(\varepsilon_f) + (1 - \nu_f) \cdot \log(\varepsilon_m).
\]

As expected, the data follows the trends of both models however, the Lichteneck model over estimates the values for the dielectric constant. The Lichteneck model gives values that are in general over estimates because is applied the mixing rule to approximate the dielectric constant. The dielectric value for the PZT used in this model is 3300, which is for bulk, sintered PZT. It is well known that the dielectric constant for piezoelectric powder is less than for its bulk counterpart. The difference in the values predicted by this model would be more exaggerated if the volume fraction of PZT were higher than 0.30 as in this study. On the other hand, the Maxwell–Garnett model underestimates the values for the dielectric constant of the composite. This model does not take into account the polygonal-shaped morphology of the PZT or the aspect ratios of the MWCNTs. This model is best suited for composites that incorporate spherical-shaped particles that are uniformly coated by the polymer matrix.

The frequency based behavior of the dielectric constant for the corona polied samples is plotted for a MWCNT volume fractions of 0.01 and 0.06 against the Debye relaxation law prediction for the dielectric constant (figure 24), which is expressed as

\[
\varepsilon' = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_{\infty}}{1 + \omega^2 \tau^2},
\]

In equation (3), \(\varepsilon_s\) and \(\varepsilon_{\infty}\) are the low and high frequency limits of \(\varepsilon'(\omega)\), respectively, \(\omega = 2\pi f\) and \(\tau\) is the relaxation time. The data for volume fractions of 0.01 and 0.06 follow the Debye law for frequencies up to ∼12 000 kHz. The difference in the predicted values beyond 12 000 kHz may be

![Figure 21. The impedance is plotted for contact and corona polied composites as a function of volume fraction of MWCNTs. The impedance values are for a frequency of 2 kHz. The contact polied composites show a higher impedance juxtapose the corona polied composites for all MWCNT volume fractions of the composite, which could indicate that a higher poling density achieved in the corona polied samples.](image-url)
attributed to the distribution and differences in relaxation times between the constituent material, which can arise due to the distribution of grain sizes in ceramic samples, different interfacial regions in the samples and hopping conductivity from the MWCNTs.

4. Conclusions

In this work, two poling techniques were examined, the contact parallel-plate and corona poling methods. The corona poling technique provides a higher density of polarized dipoles within the composite, as evidenced by the higher piezoelectric strain coefficients and dielectric constants, and lower dielectric loss (tan δ) values obtained for the corona poling method juxtaposed the contact poled technique. For example, for a MWCNT volume fraction of 5% the $d_{33}$ coefficients for contact and corona poling were $\sim5$ and $\sim18$ pC/N, respectively. The effective dielectric constant and tan δ for (for a MWCNT volume fraction of 5%) the contact and corona poled composites were $\sim84$ and 0.2, and $\sim128$ and 0.02, respectively. This trend is similar for all volume fractions of the MWCNTs. The enhanced values of the $d_{33}$ and $\varepsilon$, and lower values of tan δ can be attributed to formation of localized spots and regions of dielectric breakdown in the three phase composites. These localized regions increase the conductivity of the composites, which leads to high dielectric loss as indicated by the higher values of tan δ for the contact poled composites [8, 35].
References


[17] Zhao P and Li J 2009 Investigation of orientation effects on the electro-mechanical coupling behavior of 1–3 piezoelectric composites under compression Smart Mater. Struct. 18 104011


[26] Li Z, Dong B and Zhang D 2005 Influence of polarization on properties of 0–3 cement-based PZT composites Cement Conc. Compos. 27 27–32


[38] Ounaida Z et al 2008 Evidence of piezoelectricity in SWNT-polyimide and SWNT–PZT-polyimide composites J. Thermoplastic Compos. Mater. 21 393–409


[46] Romasanta L et al 2011 Functionalised graphene sheets as effective high dielectric constant fillers Nanoscale Res. Lett. 6 1–6


[50] Hermant M C 2009 Manipulating the percolation threshold of carbon nanotubes in polymeric compositesTechnische Universiteit Eindhoven


[54] Hermant M C 2009 Manipulating the percolation threshold of carbon nanotubes in polymeric composites Technische Universiteit Eindhoven p 166


