Characterization of Piezoelectric PDMS-Nanoparticle Composites

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Abstract. In this work, the novel fabrication and characterization of elastomeric piezoelectric nanocomposites are explored. Fabrication methods explored herein utilize ball milled barium titanate powder dispersions, along with double walled carbon nanotubes which are dispersed in toluene though the use of an ultrasonic probe. Test devices are then constructed with electrodes made from evaporated gold on polyimide foils and protective dielectrics of pristine PDMS. Two different device construction methods are explored utilizing both direct contact bonding and plasma bonding of the active composite layers to the dielectric/electrode. Test samples are evaluated through the use of a dedicated Berlincourt type piezoelectric $d_{33}$ meter.

1. Introduction
With the ever shrinking power consumption of modern electric devices and sensors, the feasibility of autonomous sensor nodes powered exclusively from renewable energy harvesters is ever increasing. For powering sensor nodes for use in concealed environments such as in textiles or on the skin, piezoelectric generators that utilize kinetic energy are advantageous as they do not require direct sunlight or thermal differentials needed for thermoelectric or photovoltaic generation methods. One of the challenges in traditional resonant piezoelectric generators is that they optimally produce power at frequencies in the range of hundreds of Hertz\textsuperscript{[1]}. While there are many strategies for frequency down converters, researchers are now looking towards the new paradigm of composite piezoelectric energy harvesters that are capable of low frequency power generation.

While there have been many advances in piezoelectric composite development over the past several years, most authors reported generator outputs generators of different areas, and under different strain conditions. Herein we synthesize piezoelectric elastomeric composites composed of polysiloxane (PDMS), double walled carbon nanotubes (DWCNT) and barium titanate (BaTiO$_3$) and characterize test structures using a Berlincourt type $d_{33}$ meter for which the static and dynamic clamping forces can be precisely controlled. Utilizing a controlled characterization method as described above, we compare the differences that can be seen by directly adhering vs plasma bonding of the active piezoelectric layer to foil electrodes comprised of gold evaporated on polyimide.
2. Fabrication

When synthesising the piezoelectric active layer, the following stock materials are utilized. Barium titanate particles consisting of a tetragonal crystal structure and a nominal diameter of 200nm were purchased from US Research Nanomaterials Inc, DWCNT’s with an average diameter of 3.5nm’s and length of 1-10 microns were purchased from Nanocyl S.A., Dow Sylgard 184 was utilized as a matrix material. Fabrication begins with the de-agglomeration of the BaTiO$_3$ particles. De-agglomeration is carried out through attrition milling for one and a half hours in ethanol with a phosphoric ester dispersant (BYK W – 9010). The size distribution of the nanoparticles before and after ball milling was characterized using a Malvern Mastersizer laser diffraction instrument, and it can be seen on Figure 1 that the majority of the bulk micron sized agglomerates can be reduced within 1.5 hours of milling.

Figure 1. a) Frequency and cumulative size distribution of BaTiO$_3$ in ethanol before and after ball milling. b) Schematic overview of piezoelectric nanocomposite test sample.

After milling a solvent exchange to toluene was performed by ultracentrifugation of the BaTiO$_3$/ethanol mixture, then removal of the supernatant and addition of toluene, this mixture was then added to uncured PDMS resin. Separately, DWCNT’s in toluene were given a 10 minute ultrasonic treatment, the BaTiO$_3$/PDMS mixture was then added to the DWCNT/toluene mixture while stirring. Throughout the piezoelectric composite literature it is common to use carbon allotropes around 1 wt%, whereas pristine CNT composites we expect appreciable changes in electrical conductivity and Young’s modulus at ranges of 0.0025 wt% [2]. With this in mind it was decided to use 0.001 wt% DWCNT’s and 10 wt% BaTiO$_3$ to explore compositions with smaller inert carbon loading.

Assembly of the piezoelectric test structures begins with the addition of PDMS curing agent followed by bar casting of 250µm piezoelectric composites membranes on a PET foil. The electrodes were fabricated by first evaporating titanium/gold (10nm/100nm) on 125µm polyimide foil. Dielectric layers of 15µm pristine PDMS were then directly cast over the gold electrodes, these dielectrics protect the piezoelectric nanocomposite layer from electric breakdown while poling. Finally assembly of the test samples were then carried out by both contact adhesion, and O$_2$ plasma bonding of the active layers to the PDMS dielectrics. Bonding of PDMS layers by first exposing both surfaces to O$_2$ plasma before contact leads to the formation of highly reactive silanol groups at the PDMS surface [3]. These silanol groups subsequently form permanent bonds when brought into contact with oxides or neighboring PDMS molecules. After assembly, all samples are poled at a voltage of 2500V and a temperature of 150°C for three hours.
3. Characterization

As the development of composite piezoelectric energy harvesters is still in its early phases, standardized testing procedures have yet to be adopted. In order to address the issue of a standardized test we utilize a Berlincourt type piezoelectric d_{33} meter which can precisely deliver both static and dynamic forces to the test sample that is seen in Figure 4. The piezoelectric d_{33} coefficient can be calculated by dividing the output charge signal created from the piezoelectric sample by the dynamic force that was applied. Initial piezoelectric characterization was carried out on a piezoelectric composite containing 1 wt% CNT’s, and 10 wt% BaTiO\textsubscript{3} and with a 0.25N dynamic force. After measuring the initial response seen in Figure 2, the leads from the sample to the charge amplifier used to measure the piezoelectric output signal were switched, and an otherwise identical measurement was carried out. As can be seen in Figure 3, the polarity of the piezoelectric response was reversed. Such behavior is indicative piezoelectric materials, which will have distinct positive and negative poles. Similar “Switching Polarity Tests” are widely used to confirm the presence of a piezoelectric behavior in experimental materials\textsuperscript{[4]}.

It has been known that increasing the static preloading will lower the charge output in soft materials and thus the d_{33} coefficient\textsuperscript{[5]}. Such behaviour was seen during initial testing of piezoelectric composite samples and dynamic and static loading of 5 and 3 Newton’s were selected as such setting provided the clearest output charge signals. PVDF control samples with a known d_{33} of 22 pC/N were first measured in order to compare experimental outputs to known piezoelectric materials.

![Figure 2. Initial piezoelectric response.](image1)

![Figure 3. Piezoelectric response with opposite leads connected.](image2)

![Figure 4. Custom built d_{33} meter.](image3)

![Figure 5. Piezoelectric composite test sample complete with gold/polyimide electrodes and wire leads.](image4)
Figure 6 shows both the average piezoelectric coefficients the signal to noise ratios for both the test samples which utilize plasma bonding and contact bonding assembly methods, as well as the PVDF control sample. It is immediately evident that the plasma bonding the active layer to the dielectric/electrodes hinders charge generation when compared to the simply utilizing direct contact methods. At present, it is difficult to pinpoint the exact cause as to why the plasma bonded samples provide less charges, but one could speculate that the cracking and increased surface roughness known to be induced from oxygen plasma treatment\cite{6} ultimately serves to resist charge flow more than direct contact adhesion to the electrodes.

4. Conclusion
In the following work we illustrate the raw materials processing, device fabrication and characterization of a piezoelectric BaTiO$_3$/DWCNT/PDMS nanocomposite. Utilizing traditional Berlincourt piezoelectric characterization methods we can conclude that the use of O$_2$ plasma bonding in device fabrication hinders charge generation when compared to non-permanent contact bonding of the active nanocomposite layer to the protective dielectric and electrode.

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