MULTIFUNCTIONAL BORON NITRIDE NANOTUBE (BNNT) POLYIMIDES AND COMPOSITES FOR DEVICES IN EXTREME AEROSPACE ENVIROMENTS

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Abstract

An investigation into boron nitride nanotubes (BNNTs) for potential usage in extreme space environment devices was performed on both polyimide and epoxy composite structures. By preforming fundamental ferroelectric and piezoelectric tests, a level of efficacy in BNNTs can be ascertained. The research performed to date for this project has mainly focused on the fundamental electrical properties of the BNNT composites and polyimides. These samples were run through many testing procedures, including, direct d_{33} testing, polarization loops, impedance analysis, and more to try find consistent data. Under current testing, it's still too early to draw conclusions about increased wt% of BNNTs causing increased piezoelectric properties, however we can see clear differences between pure epoxy samples and the BNNT samples in terms of inherent piezoelectric values. This paper will mainly discuss challenges faced while preforming these tests, observations on the testing to get more repeatable data, and some potential use cases for the materials. Our goal is to provide an alternative material with enhanced mechanical properties when compared to traditional piezoelectric materials, while still being able to perform comparably in piezoelectric devices such as surface acoustic wave devices, sensors, energy harvesters, and actuators.

1. Introduction

Nanotubes are a relatively new field of scientific exploration, dating back to 1991 [1] with the discovery and experimental setup for carbon nanotubes (CNTs). Nanotubes typically are interspersed throughout bulk materials to alter the base materials structure and provided enhanced material properties for different end user purposes. Shortly after the discovery of CNTs, BNNTs in 1995 [2] were discovered and synthesized using laser ablation to vaporize boron nitride, which was thee condensed onto a substrate sitting in a high temperature gas chamber, the then condensed vapor was collected forming BNNTs. Since the early stages of these nanotube structures many teams of scientists have attempted different synthesis techniques, aimed for different material properties, and preformed various testing procedures to try and fully unlock the potential of BNNTs and BNNT hybrid materials. Many researchers have reported BNNTs as having high thermal conductivity, high mechanical strength, great electrical insulant, useable temperature ranges of -250 °C to 900 °C, radiation shielding and what we are investigating, piezoelectric properties [3-13]. These properties can be attributed to many things, such as the morphology of the BNNTs causing a strong bond between boron and nitrogen atoms, or the lattice structure causing dipole moments upon deformation, lending the material to be piezoelectric in nature.

In our case, the team at LaRC has developed a novel way of creating and manufacturing both the raw BNNT and the subsequent composite or polyimide with a weight percentage (wt%) of BNNTs [7,15]. Under the mentorship of Dr. Cheol Park at LaRC we have been investigating the base material properties of these BNNT

composites/polyimides to provide future space missions with reliable and robust materials capable of maintaining operational status in space.

2. Experimental Setup

To investigate these materials, they must first be setup to properly run experimental procedures. This setup is as follows:

- Synthesize bulk material-either in a composite epoxy or polyimide structure
- Cut bulk material into workable samples, in our case, circular samples with set diameters (12.5mm for composites, 20mm for polyimides)
- Samples are then to be coated with some form of conductive electrode.
    - Initial electrode was just a silver conductive ink.
    - Sputter deposition with a gold 99.9% purity sputter source (seen in figure 2) established after silver ink.
        - Electrode thickness has changed three times, different sputtering times.

With the samples cut, coated, and cleaned an iterative testing procedure was performed using two separate ferroelectric testing stations (one at LaRC, and one at ODU) to test for piezoelectric properties.

Figure 1: Example of a bulk composite epoxy disk with 5 wt% BNNTs. Sample was rough cut with a bandsaw and then polished to a uniform diameter of 12.5mm by a lathe.

The two separate ferroelectric testing stations that were used for a bulk of material testing were purchased from Radiant Technologies, a R 66 Precision test located at LaRC, and the Precision LC II located at ODU. The purpose of these systems is to apply electrical fields to our prepared samples and get a PE-loop (Polarization versus Electrical field) that can directly be attributed to inherent piezoelectric values.

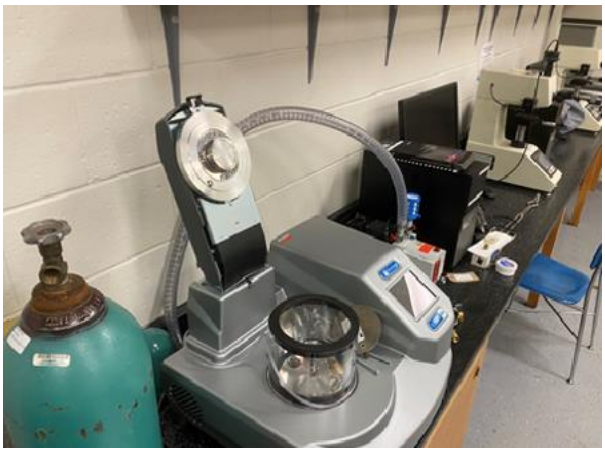

Figure 2: Quorum 150R Rotary Sputter deposition setup

It's important to note that this process needs to be consistent, any alterations in time spent in the sputter chamber will inherently cause a non-uniform coating for each sample, making the data less repeatable and dependable.

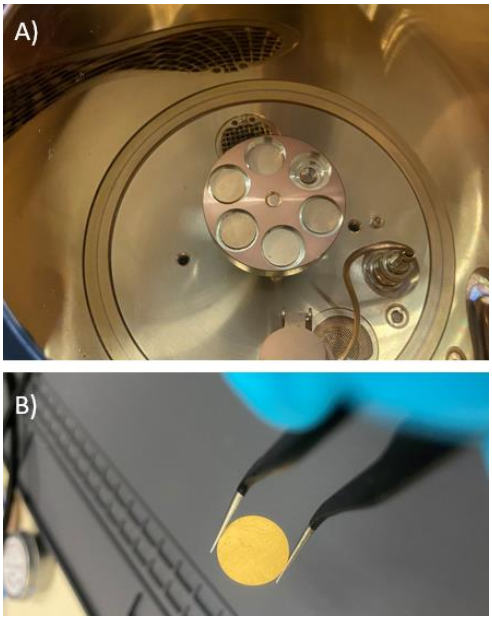

Figure 3: A) Inside of sputtering machine, on sample stage B) After sputtering, coated sample.

3. Issues with Testing and Their Solutions

Throughout the course of this project, we have run into many roadblocks and uncertainties, to certify that BNNTs can be used as an alternative piezoelectric material these issues must be resolved. Currently we have worked through many of these issues such as: electrode thickness, edge effect, voltage limitations, and various others that have since been addressed.

What we have learned from these initial problems has given us a new plan which will eliminate most of these issues and hopefully lead to more consistent data, which will be discussed in further sections. And while none of these problems are new in terms of know scientific experimentation and thoery, their interactions with one another in the case of this project we believe may have caused issues with getting consistent data. Due to the relatively new research field, this is too be expected and correcting these mistakes while limiting the number of variables when it comes to assessing these complex nanostructures are a part of this projects fundamental approach.

3.1 Edge Effect

To properly evaluate these samples inside an electrical field without damaging the samples or causing extra spatial charge something called the "Edge effect" must be considered. In essence this is the capability for the electrical charge from two parallel plates (electrodes) to carry the electrical field around the outside edge of a sample, instead of through the thickness of the sample. Seen in figure 4 is an example of this process, and to protect from this arcing or shorting, a distance from the edge of the sample must be made clear of the electrode, as to not encourage the flow of electricity to go anywhere but through the thickness of a material, this is also called the "capacitor edge effect" [14]. This is generally accounted for by the thickness of a sample, but because our samples are thinner then most, this must be considered or damage, as seen in figure 5, will occur. There are two main approaches to solving this issue, maximizing the ratio between Surface area (A) and sample thickness (t), and removing some of the applied electrode from the edges of the sample. Our new approach plans to do both.

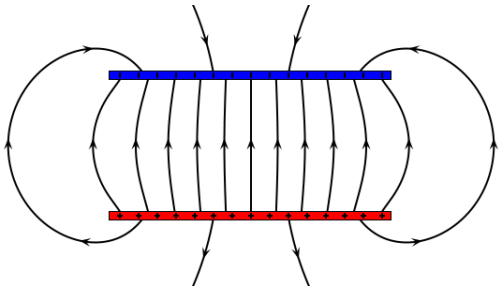

Figure 4: Showing two parallel "plates" or electrodes and the Edge effect when applying an electric field.

Without the removal of some of the electrode from the sides of a sample (how much depends on a multitude of factors, mainly how large the surface area of the sample is), the arcing electrical field of the edge of the plates seen in figure 3 can cause a short in the sample, scorching it and causing carbon buildup, making it more susceptible to damage from that point forward.

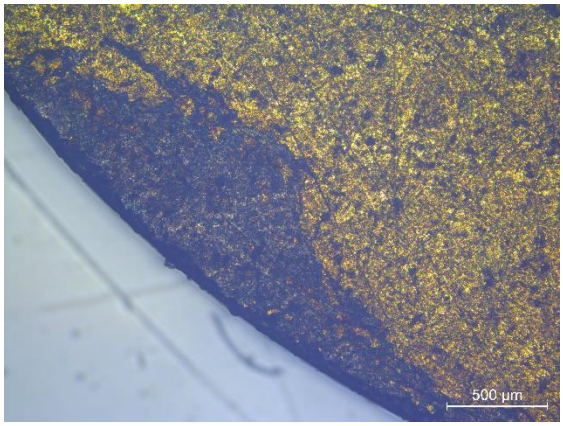

Figure 5: Optical microscope image showing damage caused by edge effect: Darker area is where the short occurred on the edge, gold area is the gold electrode.

Our initial assumption was that our composite samples were thick enough to avoid the edge effect (800-1400 microns thick), but after testing this has been proven incorrect. Because of this mutiple "shadow masks" were designed to ensure that during the coating process enough of the edge of the sample would not have the same issue of shorting occur. They do this by adding a counterbore to a circular cutout with an outer diameter equal to that of the samples, the counterbore is then set to a desired level of offset which will block that portion of the material from being coated. For example: In figure 6 is an AutoCAD design of a shadow mask aimed at coating our composite samples with an outer

diameter of 20mm, and an inner diameter of 16mm. This provides a 4mm gap between edge and electrode, making it harder for the electrical field to flow through the edges instead of the thickness.

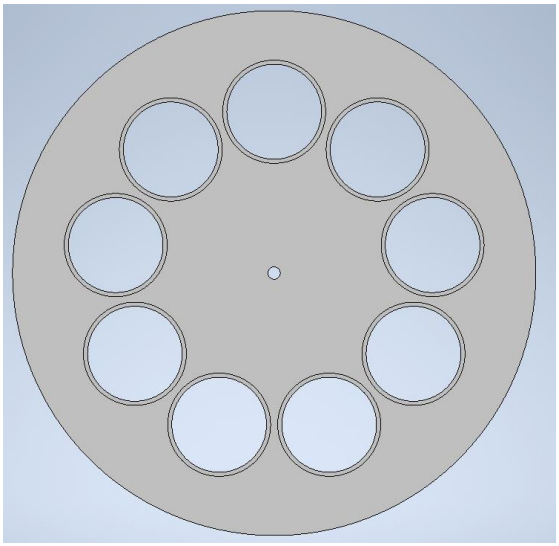

Figure 6: Shadow Mask for sputter deposition to allow for edge effect to be considered.

Therefore, by limiting the electrode to a portion of the sample surface area and increasing the sample surface area itself this should decrease the chances of a short occurring and make testing more consistent.

3.2 Electrode Thickness

Initially the thickness of the electrode of the sample wasn't considered because the Q150R Sputtering machine we had purchased came with a "Film Thickness Monitor", so we had assumed we knew the value of the electrode to be between 100-200 nm conservatively. But do to suspicions that the electrode was too thick, mainly caused by concern of limiting electrostriction, a cross sectional SEM image was taken of one of the various samples that were originally sputtered. This SEM image seen in figure 7 clearly shows that the electrode is much larger then anticipated, and research has shown that when applying electrical fields to a sample with large electrode thickness, the results can lead to data errors depending on the electrical tests being ran [16-17].

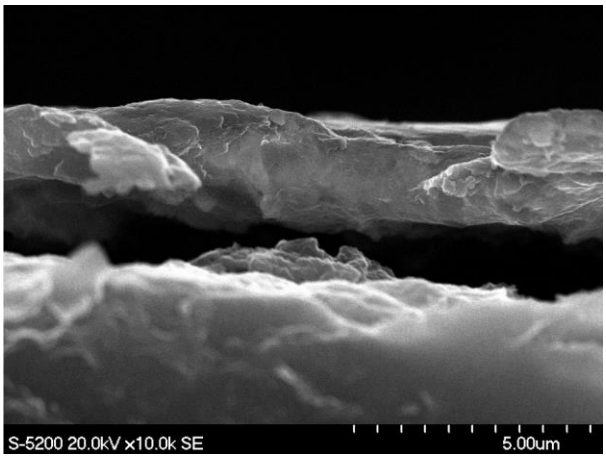

Figure 7: SEM cross section of a cut sample, showing electrode thickness ranging between 4-5 um.

To get an accurate reading of where the sputter machines rate of deposition was at a series of silicon wafers were coated at time intervals ranging from 5-30 minutes and then cut with a diamond blade to try and get clean cross-sectional images. Upon SEM imaging it was determined that for the next round of coating samples would be coated at 10 minutes each side, resulting in electrode thickness of around 125 nm. It's important to note that the uniformity of sputter deposition when in the nanometer scale will not be exactly 125nm.

With this information the second round of samples were retested for the values of the PE-Loop, which indicated an increase in polarization, as well as a widening of the curve more typical of a piezoelectric. We believe this was due to the limitation of electrostriction considering that piezoelectric generate their electrical signal from deformation, therefore the less allowable deformation the less electrical response.

After discussing these trials with industry experts and based on the results from the second group of samples it was determined that the new set of samples will be coated as follows: 2 minutes of deposition, 5 minutes to cool down, followed by 3 more minutes of deposition. This was deemed to be optimal not only to cut down on temperature related effects of sputter deposition, but also because a thinner electrode should allow for less discrepancy in data.

3.3 Combined Effect of Solutions

Between the edge effect and the electrode thickness problems, alongside the other issues that we had such as voltage limitations for our equipment at ODU, and dimensional limitations created from our original sized samples of 12.5mm, a full picture of an idealized run of samples was created from many months of trial and error.

- New testing procedure:
  - Larger sample sizes, to allow for better distribution of electrical field.
    - From 12.5mm to 20mm sample diameter
  - Considering edge effect
    - New shadow masks for coating allowing for 3-4mm of the sample nearest to the edge to not be coated in gold, decreasing the odds of a short
  - Electrode thickness
    - From the iterative thickness testing, the updated sputter procedure should allow for thin as allowable electrodes, which should provide less errors in results.

With these combined solutions we should limit the amount of variability in testing data, allow for less damage to be caused by an over-voltage of the sample, and lastly a better baseline to compared to commercial piezoelectric materials.

4. Methodology and Current Results

Now that our new testing procedure is in effect, we will be retesting the 22 (and including three more samples between the 12-25 wt% BNNT gap) samples under the same PE-Loop station at LaRC, the R66 Precision Tester. With that being said, we have many iterations of previous data that seems too inconclusive to report on here. We are currently in the process of implementing the new testing procedure for samples ranging from 0-25 wt% BNNT in both polyimide (thin, flexible polymer) and composite (thicker, more rigid) structures and will be comparing those directly to commercial samples like the PZT sample provided by Radiant Technologies seen in figure 8.

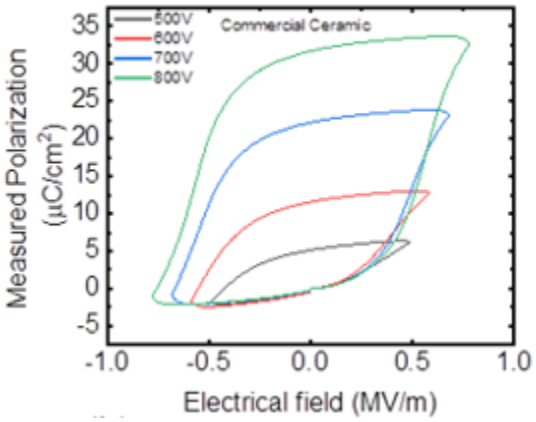

Figure 8: Commercial PZT results from the R66 Tester preformed at LaRC.

The next sections will discuss previous results, showcasing a good proof of concept for the BNNT samples, but as stated before the data isn't repeatable enough to state with full confidence the effect increasing wt% has on the BNNT samples. Testing procedures for d_{33} direct testing, PE-Loops, and some miscellaneous testing procedures will also be discussed in the following sections as well as future testing plans to follow in the next few months.

4.1 D_{33} Measurements

Direct d_{33} measurements were taken at LaRC using a piece of equipment made by PolyK. The system works by applying a force of 0.25N at a frequency of 115 Hz to the sample that is secured on the testing fixture. The load is applied to both the top and bottom of the system and the corresponding electrical response is recorded on the monitor. For reference the system is calibrated using a piece of commercial PVDF that is rated at around 27 pC/um for its d_{33} value. After calibration was confirmed, the second round of 10-minute coated samples were assessed both before and after the PE-Loop experiments.

Figure 9: PolyK d_{33} Measurement system

It's important to note that when the "updated" testing procedure will be performed, that all previous twenty-two samples will be polished and recoated and then compared to a new set of the same twenty-two samples to ascertain if a years' worth of electrical testing has damaged the samples when compared to the pristine samples. As stated previously, the data hasn't been dependable enough to fully draw conclusions.

4.2 PE-Loop

The main testing fixture that has been used to quantify these samples has been the ferroelectric testing stations that allow for out circular samples to have an electrical field applied to them, and have their stimulated response recorded. The main tests being ran on both the LC II and the R66 has been a hysteresis loop monitoring polarization vs electrical field. As stated previously these samples have undergone three different testing timeframes, which we classify based on the electrode applied to all the samples at that given time. The first being the silver conductive ink, the second being the gold sputter electrode that was too thick, and the last section to date was the run of samples coated at 10-minute intervals. The results of our last round of testing were the most consistent and promising so far but cannot be discussed due to the uncertainties discussed in section three.

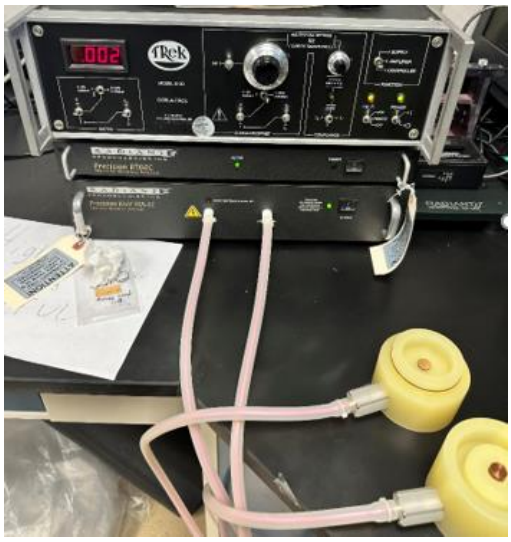

Figure 10: R66 testing station at LaRC, showcasing both the high voltage amplifier (Trek 610D) and the sample holder.

4.3 Miscellaneous Testing and Future Testing Plans

As previously stated in section 3.3, all our current samples will have copies made of them, with larger diameter and coated to ensure no electrode deposition occurs near the edge of the samples. This will provide us with a pristine new set and the old already tested set to really narrow down any lingering variables or issues that may be causing discrepancies in the data. There are also various other testing fixtures that we would like to utilize, aiming more towards our initial investigation into what devices we could use the BNNT materials for.

For starters, we already have a cantilever beam setup which will test directly for energy harvesting capabilities alongside a direct measurement of d_{33}. This is done by placing a cantilever beam (in our case a 3D printed design) with the sample secured either via epoxy or doubled sided tape on top of the shaker system at ODU and applying a vibrational force to the beam through the shaker. Previously we ran a test with a 2wt% BNNT polyimide and compared it directly to a PVDF coated in aluminum. Unfortunately, the sample had sustained some damage while reaching its resonance peak (around 22 Hz), so we only received limited data to compare too. The issue occurred due to the 3D printer cantilever beam warping around the base where it was secured by an M3 screw. To combat this issue, we have since

started using a M3-M5 adapter and heat pressing it into the base of the beam to give it a secure fit. The first trial run when compared to the PVDF film went as such: Both beams were run through a frequency sweep from 50Hz-1Hz, data was collected on the Vrms and monitored on channel 2 of our signal analyzer. The PVDF Beam was able to produce 3.7V at its natural frequency of around 21.5 Hz.

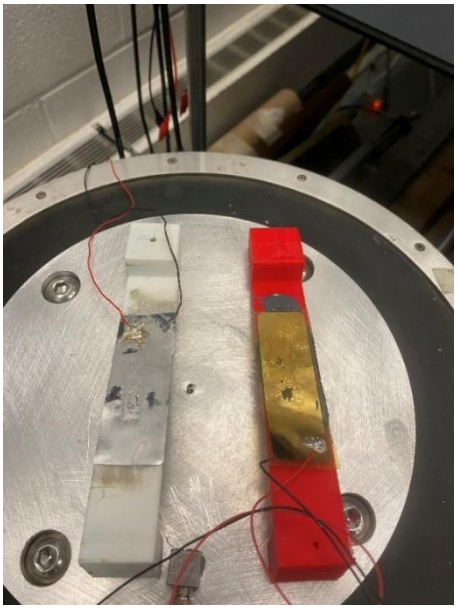

Figure 11: Cantilever beam with PVDF (Left side, white beam) and BNNT polyimide (Right side, red beam) and the Shaker underneath the two samples.

Also, at ODU we recently acquired a means of setting up a Pyroelectric testing station, which will essentially heat up a sample and monitor both the temperature change and the electrical output caused by the change in temperature. This combined with the cantilever beam will give a good understanding of the materials energy harvesting capabilities, while also allowing us to record and test for some fundamental values.

Outside of these two ideas, we have more fundamental, less device driven, experiments planned as well if the new sample procedure will go over smoothly and take care of the shorting issue. These include transverse strain displacement (TSD) using a LDV (Laser-doppler vibrometer) to evaluate for d_{31}, thermally stimulated current spectroscopy (TSC) to assess for dielectric fundamentals, and others.

5. Conclusion

Overall, we have learned a lot from the trial and error done over the last year. All the work that has been completed will only help us reach our end goal of creating devices for space exploration that can survive the extreme temperature changes, radiation, and debris that one finds when exploring space. With the great mechanical properties of BNNTs, these nanotubes should be able to provide excellent resiliency to space systems and devices such as sensors, actuators, SAW devices, and energy harvesters. The continuation of advanced synthesis methods, polling, aligning, and stretching these materials to increase their inherent electrical properties will also improve the devices. If we can make BNNTs into a comparable piezoelectric material, while maintaining its structural bonuses, space exploration devices can be improved upon. The initial proof of concept is there, now it just needs to be expanded upon in greater detail with more consistent data.

6. Acknowledgements

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