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Use of polydicyclopentadiene as a matrix in composite structural capacitors

by

Diana Gottschalk

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

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Major: Materials Science and Engineering

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Abstract

In this work the dielectric and mechanical properties of neat polydicyclopentadiene (polyDCPD) as well as polyDCPD-polyaniline and polyDCPD-BaTiO$_3$ composites were investigated. Neat matrix properties were tested extensively to probe the effects that the reaction retardant triphenylphosphine (PPh$_3$) may have on the desired macroscopic properties. The addition of PPh$_3$ was necessary for processing of ceramic filled composites to successfully suspend nanoparticles in the polymerizing solution. In order to achieve this level of kinetic control, switching catalysts from the 1$^{st}$ generation Grubbs (which was used during the polyDCPD-PANI investigation) to 2$^{nd}$ generation was required because of its affinity towards PPh$_3$. According to the acquired data there is no detrimental difference between the three catalytic systems therefore 2$^{nd}$ generation and PPh$_3$ was adopted without incurring any foreseeable drawbacks.

Mechanically, neat polyDCPD samples that were polymerized with 2$^{nd}$ generation and PPh$_3$ show from dynamic mechanical analysis (DMA) that the system has an average glassy modulus around 1 GPa with slight variations but show even smaller differences in the $T_g$. Across the concentration range studied (.05 - .3 wt. %) there was no visible trend in the dielectric permittivity data. There is however a reasonably systematic rise in tan $\delta$ with concentration, suggesting possibly that catalyst concentration has an effect on the relaxation mechanisms. Dielectric breakdown strength characterization has also been employed and is portrayed here using Weibull distributions. Steep slopes in a Weibull plot correspond to small error bars on a single averaged point. Values on the y-axis will give the percent likelihood of failure at that specific voltage. In terms of the current system, variation is again minimal.
Upon the introduction of conducting organic polyaniline (PANI) particles or inorganic BaTiO$_3$ (BTO) particles to the system it was possible to get significant increases in the permittivity at low frequencies and relatively low volume percents. The main concern about these two systems is that of their already remarkably high tan $\delta$, which can be at least partially attributed to the particle size and weak particle-matrix interfaces in the PANI and BTO systems respectively.
Introduction

Miniaturization has been the driving force of advanced electronics since the proclamation of Moore’s law over 50 years ago. Since then the majority of success in this field has been with advancements in transistors and their printing. In general, devices were made smaller by making their components smaller and more economically packed. Functional components and their packaging were advanced towards miniaturization separately. Another possible approach to this goal is to prevent required components from taking up space at all, while still maintaining the reliability and computing power of current non-active components.

Exploration of integral passive components has been going on since the late 1990s and according to the National Electronics Manufacturing Initiative are defined by “functionality embedded or incorporated on the surface of the interconnection substrate” \(^{(1)}\). If passive components such as resistors, inductors or, in this case, capacitors, were designed to be embedded or better yet, completely structural, then their current weight and circuit board real estate could be effectively removed. Accomplishing this task would be a large step in the way of optimized electronics since as it stands now, over 80% of board surface area is taken up by passive components.\(^{(2)}\) Integration of this type can be done successfully either into the printed wire board directly (Figure 1) or as the dielectric layers between chips on a multichip module.\(^{(3)}\)

While embedding capacitors into circuit boards can help the performance of everyday electronics, other industries can benefit greatly from advancements in capacitor technology. By integrating circuit elements into load bearing assemblies, the weight and volume of passive components can be removed from large vessels like space ships and hybrid ground
vehicles.\(^{(4)}\) Indirectly this integration would also make the whole vessel smaller saving on construction material costs as well. This overall smaller ship should be able to run on less energy from capacitors and give unmanned crafts longer possible mission times.\(^{(5)}\) A possible example of a structural component that could be made to store electricity would be something akin to a car floorboard.\(^{(6)}\) Substantial amounts of fuel can be saved after seemingly insignificant losses of materials because, on the scale of space travel, every pound removed means thousands of dollars saved.

![Image of capacitors embedded into the printed wire board](image)

**Figure 1. Capacitors embedded into the printed wire board\(^{(7)}\)**

Capacitors are a prime target for pioneering the way to structural integration of passives. They take up more space than most other elements on a circuit board (in both numbers and in individual size) but are necessary for signal decoupling, switching noise suppression, filtering and tuning in almost all devices. Decoupling for instance is a required function because it reduces inductance that causes delta-I noise in current pathways which if left alone would result in erroneous switching.\(^{(8)}\) There is also something to be said for capacitors’ advantages over present day battery technology. Energy storage capacity of a battery is still ahead of a capacitor’s by 2000:1\(^{(9)}\) but capacitors’ ability to charge
instantaneously cannot be overlooked. Their respective speeds are a result of where the
down is coming from. In a battery, energy is a product of a chemical reaction that needs to
be reversed and the corresponding high energy barriers overcome just to be refueled again.
Capacitors simply need to store the charges given by the circuit which will occur at the rate
of current flow. If a new dielectric material could be developed with higher energy densities
and structural capabilities, some batteries may even be phased out.

Secondary benefits can be realized through the integration of embedded and structural
capacitors. If capacitors were to become part of the printed circuit board then total device
inductance could be minimized via shortening of the connections between the capacitor and
voltage source. Less inductance means less noise and impedance at high frequencies while
simultaneously enhancing signal intensity. Removing large quantities of closely packed and
unprotected circuit elements reduces the losses that result from parasitic capacitance
occurring between components due to their unhindered interference with one another.
Embedded capacitors would also not need to be physically attached to the board, eliminating
a step in manufacturing thereby improving construction reliability and reducing assembly
costs. Capacitors used as structural elements would extend mission times through efficient
use of mass and volume without sacrificing safety, performance or power.

Something else to keep in mind while designing an embedded thin film capacitor is;
what will it take to put one into use. To avoid complications in the final assembly of a
product it was only natural to use polymer matrix composites as the new dielectric material
since printed circuit boards are already epoxy or polyimide based. In addition, most
polymers qualified for structural implementation are resistant to the diffusion of metal
electrode material into the bulk of the sample thereby maintaining high breakdown strengths.
Even a remotely porous dielectric as a thin film would rapidly begin conducting between the
two electrodes as metal atoms migrated through the sample shorting the circuit.

As signal frequency of mainstream devices increases the need for thin, tough and
flexible alternatives grows. The requirement of both a tough and flexible material exists
because of the structural nature of the final part combined with the current printed circuit
board manufacturing process. As a consequence, the bulk ceramic dielectrics that encompass
90 vol.% of the entire capacitor market\(^\text{(10)}\) can no longer be relied on. They can’t accomplish
the tasks required for the next generation of dielectric materials due to their brittle nature and
high temperature processing. Low leakage capacitors have already been made using
homopolymers like polypropylene for their high breakdown strength and simple
maintenance. The downside being that such nonpolar polymers have a dielectric constant on
the order of only \(\sim 2\).\(^\text{(11)}\) The final goal of dielectric nanocomposite research is to fabricate a
polymer matrix composite using 0-dimensional fillers (0-3 composite) which will have
synergistically combined properties of the constituents. It is expected that a high dielectric
constant from the filler can be achieved while maintaining the toughness of a lightweight
structural material like polydicyclopentadiene (polyDCPD). Initial attempts at fabricating
integrated capacitors were done using simple sputtering, sol-gel techniques, chemical vapor
deposition, anodization and ceramic greensheet processes. Unfortunately none of these
methods have the potential for industrial use because of high cost or high temperature
processing.\(^\text{(1)}\)

Presently, the structural capacitor concepts discussed in the literature can be classified
under one of two categories. They are either based on woven fiber reinforced polymers or
concentric cylinder capacitors formed off a single fiber. That makes the particle filled
composite materials described here both novel and hard to compare with previous examples. There is no reason to refrain from adding reinforcing fibers to these 0-3 composites but they are not developed enough to take that step. Data found in this research will be placed against similarly structured composites instead of similarly applied composites.

![Figure 2. Concentric cylinder capacitor fiber](image1)

![Figure 3. Multilayer fiber weave composite](image2)

**Dielectric Materials and Capacitors**

The electrical properties and potential for wide spread use of a capacitor can be summed up by the magnitude of its energy density (W) which in a parallel plate capacitor is a function of its ability to store that energy (or capacitance; C) and the voltage potential between the plates (V) in the following way:

\[ W = 0.5CV^2 \]

In turn, the value of its capacitance is a measure of how much charge is able to build up (Q) on a single plate per unit of applied field

\[ C = \frac{Q}{V} \]

Capacitance can also be expanded upon based on the properties and dimensions of internal components, in the case of parallel plate capacitors; capacitance depends on plate area (S), distance between the plates (d) and the permittivity of the insulating material (\( \varepsilon_r \)): 
\[ C = \varepsilon_r \varepsilon_0 \frac{S}{d} \]

where \( \varepsilon_0 \) is the permittivity of free space which is at a constant \( 8.85418782 \times 10^{-12} \text{ F/m} \). As a benchmark, decoupling capacitors need materials with a permittivity between 25 and 170.\(^{(13)}\)

Even though the voltage going across the plates isn’t dependent on the capacitor’s material properties it is still an important aspect to be wary of while trying to achieving high energy densities because of a sample’s dielectric strength \( (E_{ds}) \).

\[ V_{bd} = E_{ds} d \]

If the material’s dielectric (or breakdown) strength is too low the material will experience an insulator-to-conductor transition during routine uses, ceasing to hold charges. This becomes the limiting factor on how high of a voltage can be placed across the plates and therefore affecting the overall energy density. In other words miniaturization of the entire system can’t be achieved simply by reducing \( d \). If the material is too thin or generally likely to breakdown for compositional reasons, the voltage range and possible applications are limited.

Alternate reasons that a composite might breakdown at low voltages include factors stemming from deficiencies in sample preparation, for instance particle dispersion or incomplete polymerization. Increasing the volume fraction of nanoparticles decreases the dielectric strength due to accompanying defects and an enhancement of the electric field centered at the particle within the polymer matrix.\(^{(14)}\) As particles get closer to one another, their fields begin to overlap and enhance the field concentration making initiation points for local breakdown channels more abundant.\(^{(15)}\) Highly loaded samples will also begin to approach hard and soft percolation thresholds.

Soft percolation refers to the loss in breakdown strength due to the creation of long sequences of connected weak points that form direct pathways across the thickness of the
film allowing for easy breakdown (Figure 4).\(^{14, 16}\) In a nanocomposite of randomly placed particles, each element will have an average of about ten neighboring particles and, if any of them break down it will start a cascade among those nearest neighbors.\(^{17}\) There is a widely accepted volume fraction at which point these pathways begin forming. It occurs at around 10 – 20 vol.% \(^{18}\) in practice and is predicted to be 16 vol.% by percolation theory.

![Figure 4. Soft percolation and the ceramic path that current can take through the defects in the sample](image)

Hard percolation represents the particle three dimensional packing limit\(^{14}\), when the local particle density in a sample can’t increase any more even if the volume fraction of the composite increases (Figure 5). At that point other extrinsic aspects begin to influence and carry out the decrease in breakdown strength, most importantly air, along with particles of dust or trapped solvent. These highly packed particles inevitably create air voids, which will increase in density if particle volume fraction continues to increase beyond hard percolation. Formation of such air voids is unavoidable; there is no way, even from a strictly geometrical perspective that any normal filler type (i.e. spheroid, rod or whisker) can pack perfectly. As a consequence, since air is a much worse insulator than the composite materials, the breakdown strength becomes the property most strongly affected by these voids. Also the addition of air increases the variability in the breakdown strength between measurements and
samples because the air voids will be randomly distributed as well, assuming complete mixing. There are significant mechanical threats resulting from such pores as well; if a crack were to start it would redirect through these defects leaving less material to be penetrated before failure.

![Figure 5. Hard percolation, the addition of more particles does not affect local packing around the red particle](image)

Breakdown will always occur along the easiest, most direct path through the sample. In the majority of cases this is the path containing the most voids, conductive regions or other defects within the volume between the electrodes. That means when predicting failure, it is best simply to determine the least amount of insulating material that could reasonably be encountered. For such a scenario it has been determined that the size of the vacancies isn’t nearly as critical as their concentration$^{19}$ Increasing void diameter will increase volume fraction of the overall void space, but doesn’t promote breakdown as easily as an equivalent volume of smaller particles lined up. Another basic statistical conclusion that can be drawn is the bigger the electrode area the more likely it is that an easy discharge path exists.

Failure can’t be completely eliminated from the system even with neat polymer samples because there is a finite probability for carrier generation inside the matrix material itself that will lead to breakdown. That having been said, the addition of nanoparticles with high permittivity (at loadings below the soft percolation threshold) can act like sinks for these charges and in the end scatter them throughout the sample, thereby keeping the breakdown
strength up. A final optimized volume fraction should be chosen with both breakdown strength and permittivity in mind in order to reach the highest energy density possible.

Permittivity is a complex function whose real part (dielectric constant, $\varepsilon'$) is commonly represented as the relative permittivity; a unitless quantity calculated from the sample’s capacitance over the capacitance of a vacuum. Its imaginary part (dielectric loss, $\varepsilon''$) is manifested physically as heat generated during use from charges stored under alternating currents. Besides simply wasting the stored energy, dielectric loss is detrimental to a capacitor because it can cause thermally facilitated breakdown. Under direct current or in an ideal dielectric material there would be no loss. A perfect dielectric during alternations would have the current and voltage out of phase by 90° but realistically there will be a phase difference of 90° - $\delta$ and $\tan\delta$ is the standard measurement of loss.

The permittivity of a material is a measure of how much charge can be kept segregated per unit of area and thickness. When an electric field is placed across a single component homogeneous insulating material the area closest to the electrodes will be poled to the best of the material’s ability to the charge opposite of the plate. The strength of the opposing field is determined by the insulating materials polarizability. With the addition of filler there are more sources of polarization, both the filler itself and the interfaces (Figure 6). Unfortunately, only the interfaces and particles near the sample surface really contribute to the overall charge storage, giving more reason to make thinner film or layered capacitors. This is also one of the advantages of using nanoscale fillers; the more area to interact with the matrix the more enhanced the polarization effects become because there are more points of polarization at the surface.
Polydicyclopentadiene

Dicyclopentadiene (DCPD) can be polymerized by either cationic polymerization or ring opening metathesis polymerization (ROMP), monomer and polymer structures are shown in Figure 7. ROMP is a form of living polymerization, ensuring consistency in structure and properties. Samples made using ROMP, throughout the literature have more desirable mechanical properties and a lower polydispersity index than the cationic alternative.\(^{(21)}\) A comparison of mechanical properties between the standard high dielectric polymer; poly(vinylidene fluoride) (PVDF) and polyDCPD shows higher tensile strength (43 to 31 MPa) and elastic modulus (1.8 to 1.1 GPa) for polyDCPD which are both crucial considerations for a structural application. In contrast to unmodified epoxy, another thermoset which has historically been the matrix for dielectric composite studies, polyDCPD
has significantly higher toughness. Filling relatively brittle epoxy with a brittle ceramic in a similar application would be self-defeating. PolyDCPD has already found a place in industry; it is currently used as a material to make semi-truck hoods and similar large parts of construction equipment by reaction injection molding\textsuperscript{(21)}.

![Structural formulas of DCPD and crosslinked polyDCPD](image)

Figure 7. Structural formulas of DCPD and crosslinked polyDCPD

In order to perform ROMP an organometallic alkylidene species is required for initiation. In the past, when the original ROMP catalysts came out it was only possible to polymerize completely nonpolar molecules. With a firm knowledge that DCPD is in fact highly nonpolar it was nevertheless decided to use a more recently established series of Ru catalysts. These new organometallics have a tolerance for polar group functionality but also better environmental stability and therefore a longer shelf life. The ROMP reaction itself is highly exothermic due to the energy released upon removal of ring strain, making the reaction self-sustaining following initiation. As is typical of living polymerizations the chain propagation rate is much larger than that of initiation, ensuring high molecular weight chains. In ROMP of the highly strained DCPD molecules rate divergence is a result of steric effects.
caused by the large tricyclohexylphosphine groups coordinated to the Ru atom along with the active alkylidene. Lower hindrance associated with the propagating species compared to that of the original catalyst drives the addition of monomers onto existing chains over initiation of new ones. Propagation is also aided by the existing chain’s ability to easily remove the phosphine through chelation into a stable form. The final polymer product after curing is a highly crosslinked amorphous network of pentanes and double bonds.

Grubbs’ catalyst is the organometallic initiator of ROMP in DCPD for each sample in the current work and has been developed into several possible molecular forms called generations used for different applications. In this work, 1st generation was used for its simple preparation and rapid polymerization. While in other samples 2nd generation was used for its tunable kinetics. Grubbs’ catalyst of the same generation can exist in a variety of different crystal structures depending on the manufacturer and preparation methods. Manufacturing differences are no longer an issue because now there is only one source for the compound. Prior to addition of the catalyst to monomer it should be treated to optimize dissolution. It can be prepared by grinding, freeze drying, and recrystallization in either a solvent or non-solvent. As received Grubbs’ catalyst, from Sigma Aldrich comes in the form of large (150 µm long) prism shaped crystals. Having such sized crystals makes it impossible to quickly dissolve in monomer, simply because only what’s in contact with the liquid can dissolve in it, so if the majority of the molecules are in the bulk it will have to be reached before it can be dissolved and by that point a substantial amount of polymerization will have already taken place. The purpose of catalyst pretreatment is to create smaller crystals before to the introduction of monomer. Grinding is the easiest but also the most variable between samples and the least effective. Some smaller crystals are achieved but not
all of the initial particles will be broken down uniformly and a sizeable percentage of the crystals will still be on the scale of hundreds of microns. Recrystallization with methylene chloride is decidedly the most economical method for reducing particle size based on the amount of time and energy it takes. The resulting morphology is similar to that of the original but approximately half the size (Figure 8). It is possible to get smaller crystals by freeze drying or recrystallization using a non-solvent\(^{(22)}\) but they are longer procedures that turn out not to be necessary for the practical use of 1\(^{st}\) generation considering the speed and efficiency of dissolution.

![Figure 8. ESEM images of Grubbs' catalyst a) as received and b) after recrystallization in methylene chloride](image)

**Conductive Filler Composites**

In MacDiarmid’s Nobel Prize winning work\(^{(23)}\) he discovered that some polymers have the capability to conduct electricity when doped, which is very different from the well-established “conducting polymers” that have no chemical interactions between the insulating polymer and the source of conduction (eg. metals or graphite). In these synthetic metals current can be carried over large distances by extensive systems of conjugated double bonds. The electrons in a conjugated \(\pi\) system are free to move across the extent of the conjugated area with relative ease which is comparable to the delocalization of electrons in metallic bonding. This allows for the polymer to have the long range movement of charge carriers
inherent to conduction. Depending on the molecular structure of the polymer and conjugated sections the conduction may be more or less pronounced. If conjugation runs along the polymer backbone as in poly(3-hexylthiophene) then conductivity will be limited to essentially one direction. In network polymers made of such monomers as phthalocyanines\(^{(24)}\) there is freedom of motion in two directions across the plane. Application of an electric field to a doped synthetic metal is an acceptable way of polarizing a composite.

In order to make a more environmentally compatible and significantly lighter composite it was decided to use the conducting polymer polyaniline (PANI). There are three possible forms of PANI, the completely oxidized form (pernigraniline, Figure 9a), completely reduced form (leucoemeraldine, Figure 9b) or an alternating half and half mixture of imine and amine mers, (emeraldine base, Figure 9c) which as synthesized is a semiconductor. The most useful molecular make-up for the current work is the half and half emeraldine base. During the initial years of synthetic metals research all doping was done by redox chemistry, since then a charge neutral method that rearranges energy levels\(^{(23)}\) has been developed for PANI. The polymer can be protonated in an acidic environment and will be converted into the emeraldine salt. While in contact with an acid the imine group nitrogens will react to form a stable semiquinone radical cation at each monomer unit, introducing charges into the delocalized pi system giving the emeraldine salt a higher conductivity than either of the other two forms, even if they were doped.
Between the three possible forms of PANI the macroscale degree of protonation can be tuned by changing the polymer’s degree of oxidation and pH of the acidic environment used. Even though there are only three possible oxidations; completely reduced, completely oxidized or alternating it is possible to have multiple segments of each form in a block copolymer type assembly in order to vary oxidation more smoothly.

High dielectric constants are obtained in a conductive filler system because in the ideal case all the conducting particles are separated, but only by a very thin layer of insulating matrix, forming a large series of microcapacitors. As is true with fractals the capacitor can be seen as one whole or as increasing amounts of smaller capacitors as the field of view decreases. When an electric field is then applied to the composite nomadic polarization will be induced and the dielectric constant will be increased by the strength of the opposing field. This effect continues to get stronger up until the percolation threshold has been reached. There is a consistent critical volume after which the dielectric constant spikes,
which makes the percolation threshold visible upon characterization (i.e. dielectric spectroscopy). For most possible conductive fillers, such as metals, there is a metal-insulator transition at percolation where despite the insulating matrix, the composite will conduct. An unfortunate downside to conducting filler dielectric composites is the electrical properties will be very temperature dependent. As the sample heats up there will be more and more available charge carriers to affect polarization.

Mechanically, doped PANI is very brittle; but again, polyDCPD has a high toughness that should counteract enough embrittlement to still obtain a composite with a high dielectric constant and acceptable structural potential. It is also well known that the solubility of PANI is very poor, especially when doped. This aspect could be overlooked considering a simple suspension in polyDCPD to embed the PANI during *in situ* polymerization of DCPD will meet all expectations.

**Nanocomposites**

In the field of materials science, and more specifically composites, nanocomposites have a very unique set of attributes stemming from the high surface area to volume ratio of the particles. Such a large amount of interfaces gives the particles an optimal opportunity to interact with the matrix imparting the composite with the maximum benefit of the filler material. At the size scale of less than 100 nm the particles themselves begin to have vastly different properties than that of their bulk counterpart. Effects from phenomena like friction and surface tension begin to increase exponentially. High van der Waals forces between particles will cause them to significantly prefer to form agglomerations over homogenous dispersions.\(^{(25)}\) For every nanocomposite combination with fillers of any shape there will
exist a maximum loading after which point the filler’s benefits will no longer increase. Loading the system beyond this point will cause the introduction of stress concentration points leading to an overall brittle material and lower tensile strength.

When a nanocomposite is fabricated, the high surface area of the particles creates a much greater percentage of interfaces throughout the composite than with conventional micron scale particles. The matrix and filler communicate at the interface and transfer loads between one another, determining toughness and tensile strength of the sample. In nanocomposites the interface itself has to then be taken into account as a completely separate entity having its own properties that work either against or in concert with the other materials in the system, directly dictating macroscopic behavior. Molecular motion at the interfaces can lend a lot of insight into these interactions. On modified particle surfaces the matrix dynamics will be slower, indicating higher activation energies. In some cases the activation energy jumps three orders of magnitude. Surface tension arises from incompatibilities between the matrix and filler. If both components were to have similar degrees of hydrophilicity, hydrogen bonding and wettability to adequately coat each particle with matrix material would increase. Particles assemble in whatever formation will lead to the lowest total energy, therefore if the polymer-particle interfaces are undesirable, particles will agglomerate to reduce the overall system energy despite the fact that it’s not being beneficial for the composite’s functionality. For more reasons than just enhanced contact with the matrix, it is beneficial to have nanoscale particles to ensure the capability of creating thin films.
Ceramic Nanocomposites

Ceramics have many different crystal structures giving metal oxides the capability for catalysis, magnetoresistance and luminescence. Barium titanate (BTO) alone has five possible crystal structures, each with different properties. Even a sample of one single crystal type could have multiple crystals within each particle, introducing grain boundaries which greatly affect dielectric capabilities. A large amount of variation is introduced with the formation of grain boundaries, as well as high temperature dependence and non-linearity. For this reason it is important to understand the atomic structure of the particles being used. As described in greater detail in the materials systems section, the BTO used here is 62 nm, single phase with a cubic crystal structure.

High surface energy of insulating nanoparticles and, therefore, the drive to bring external surfaces into part of the bulk, usually leads to agglomeration and micron scale phase separation from the polymer matrix. Segregated phases make processing difficult and leaves the resulting composites with a high defect density.\(^{(17, 27, 28)}\) The vast majority of polymer-ceramic nanocomposites were made with the ferroelectric thermoplastic poly(vinylidene fluoride) (PVDF) and its copolymers as the matrix.\(^{(9, 11, 14, 29-34)}\) PVDF, being a thermoplastic means that it can be melt processed and more readily dissolved allowing for much easier film casting but resulting in a much poorer microstructure. By heavily mixing the DCPD monomer with ceramic powder at high shear rates during polymerization, agglomerations could be avoided without directly confronting the problem of surface tension. The microstructure of the resulting composite can be maintained to temperatures beyond that of metal-filled systems despite thermal expansions. Terminal hydroxyl functionality, on metal oxide nanoparticles is the reason for such hindering amounts of surface tension. It was
possible to prove the existence of hydroxyl functionality through infrared spectroscopy (FT-IR). After drying BTO overnight the characteristic –OH stretch at 3400 cm\(^{-1}\) was still visible (Figure 10). It is expected that after an extended shelf life the nanoparticles will have adsorbed a certain amount of water. Thermal gravimetric analysis (TGA) was performed on the particles alone to quantify their affinity towards moisture. Weight loss accrued below 300 °C can be attributed to the presence of water, beyond that temperature is the bound hydroxyl groups. It will be assumed that the loss below 300 °C was all due to adsorbed water and not trapped molecular water (Figure 11).

![Figure 10. FTIR of dried BTO showing -OH stretch at 3443 cm\(^{-1}\)](image)

It has been modeled and proven that there is a certain threshold of about 30 vol.% filler that needs to be passed before significant increases in dielectric constant of the composite can be realized.\(^{(35, 36)}\) That increase can be continued up to 90 vol.% with proper processing adjustments.\(^{(37)}\) Simple solution casting methods don’t maintain a steady increase beyond 60 vol.%; instead the permittivity reaches a maximum, when air voids start forming
and permittivity drops rapidly. Experimentally determined loadings where this drop begins to occur deviate greatly from those predicted because the predictions don’t take physical relaxations (i.e. kinetic and thermal) into account if the model system is built as a simple statistical packing of particles. Percolation theory also suggests that upon approaching the percolation threshold the permittivity should come to an asymptote and rise to infinity. Instead, the limit as volume fraction approaches percolation will be the permittivity of the filler.

![Figure 11. TGA of as received BTO particles](image)

**Material Systems**

*Polydicyclopentadiene*

In each capacitor material sample the matrix was polydicyclopentadiene (polyDCPD) containing 5 wt.% of a reactive diluent, 5-ethylidene-2-norbornene (ENB). This loading was just enough to ensure that the monomer solution remained a liquid at room temperature.

Polymerization of this monomer mixture was always carried out by ring opening metathesis...
polymerization (ROMP) initiated by a ruthenium catalyst, either benzylidene-
bis(tricyclohexylphosphine)dichlororuthenium (1st generation Grubbs’ catalyst, Figure 12) or
benzylidene[1,3- bis(2,4,6-trimethylphenyl)-2-
imidazolidinyldene]dichloro(tricyclohexylphosphine) ruthenium (2nd generation Grubbs’
catalyst, Figure 13).

![Figure 12. 1st Generation Grubbs' Catalyst](image1)
![Figure 13. 2nd Generation Grubbs' Catalyst](image2)

Depending on the catalyst generation to be used, pretreatment varied. It is very
beneficial for catalyst dissolution and therefore reactivity to have crystal sizes of Grubb’s
reduced significantly. For 1\textsuperscript{st} generation small crystals were achieved by simply dissolving
the desired amount of catalyst in methylene chloride and letting the solvent evaporate off
under flowing N\textsubscript{2}. In order to successfully implement 2\textsuperscript{nd} generation it had to be freeze dried
in benzene. Freeze drying was done by dissolving 50mg of as received 2\textsuperscript{nd} generation per
every 1ml of benzene in a small vial. Once well dissolved the solution was flash frozen in
liquid nitrogen and placed in a vacuum flask to allow the benzene to sublime over several
hours.
Significant processing complications arose while working with precise quantities of either generation of Grubbs’ catalyst. Exact weights and strong confidence in those values was necessary during neat polymer tests to determine effects of catalyst concentration. Despite having the advantage of rapid gellation, it makes transferring and molding of the polymer in the allotted time difficult. Polymerization gets even faster as catalyst concentration increases, even over the range of .05 to .3 wt.% that was tested. At higher loadings it takes less energy to reach the peak of the reaction, as proven by Kessler and White\(^{(38)}\), and shown graphically in Figure 14. The weight percent range of .05 -.3% and incrimination of .05% that was studied was decided upon based on the standard .2 wt.% regularly used in preparation of the composite samples and determined to be reasonable in accordance with evidence given by Wu \textit{et al.} who varied the monomer catalyst ratio a tenth as much as in the current study and still found polymer molecular weights’ increased by \(~5000\) g/mol at each ratio increment.\(^{(39)}\) The monomer used in Wu’s study is more readily approached by the propagating alkylidene than that of a norbornene based monomer like DCPD which again unlike bicycle[3.2.1]heptane is a diene so the parallel is not quite exact.
However, other studies show a noticeable effect on dielectric properties with increased crosslinking (Figure 15).

Figure 14. DSC scans of curing DCPD showing exothermic peak positions shifting to lower temperatures as catalyst concentration goes from low (a) to high (c) \(^{(38)}\)
In order to overcome the inconsistencies introduced by unknown catalyst variations a new sample preparation method had to be developed. For neat 1\textsuperscript{st} generation samples bulk amounts of catalyst were recrystallized together and then weighed out for their specific purpose. A vial of weighed DCPD-ENB was then flash frozen in liquid nitrogen. Once all the monomer solidified the preweighed catalyst was poured on top. The whole mixture was then sonicated together until all the monomer melted. By this point the catalyst was always completely dissolved with enough time remaining before gellation that processing could continue. For samples made with 2\textsuperscript{nd} generation the catalyst was ground up after freeze drying and the monomer was simply frozen in the freezer. Once melted it was injected forcefully into the catalyst to prevent polymerization and encapsulation against the walls.

Specific sample shapes were required for each characterization method and these molding procedures hold true for the subsequent composites as well. Dielectric spectroscopy samples were cut from cylinders polymerized in vials. Dynamic mechanical analysis (DMA)
samples were made by injecting the polymerizing mixture into culture tubes. Breakdown strength samples were made using a mold constructed of two sheets of glass sprayed with PTFE release agent and pressed around shaped rubber.

In an attempt to limit capacitance variations caused by surface roughness, each sample to be tested in the Novocontrol dielectric spectrometer for this and subsequent systems was cut parallel and polished flat down to 1mm in thickness. Samples were cut using a Buehler ISOMET® Low Speed Saw with diamond wafering blades. Saw blades were of the 15 high concentration series and had dimensions of 5” x 0.015” (127 x 0.4) and a central mounting hole 1/2” (12.7mm) in diameter. Part of maintaining the blades is to make sure that they are kept in a lubricating oil (IsoCut® Fluid) at all times during use. Polishing was done on polishing wheels with sandpaper grits of 320, 600, and 1200, in that order. At this point silver electrodes less than a micron in depth were sputtered on with an Edwards Scancoat Six, Pirani 501.

The most common applications for high energy density capacitors involve pulsed power so it is important to understand how the system reacts under high frequencies. That having been said, the best way to determine a sample’s maximum possible permittivity is to test it under direct current so for all dielectric measurements a frequency sweep from 1 to $10^6$Hz was implemented using a Novocontrol dielectric spectrometer with brass electrodes at room temperature.

All measurements of dielectric strength were done on a CEAST Dielectric Rigidity instrument with brass electrodes. For each test a current of .1 Ohms and voltage ramp of .5kV/second was used. It is known that partial discharges will occur in the surrounding medium, at the edge of the electrode; leading to inaccuracies and eventually arcing around
the sample. This made it necessary to implement a high dielectric constant environment which was provided by a natural ester based transformer oil called Envirotex® FR3® fluid.

The DMA (Q800), TGA (Q50) and DSC (Q2000) were all provided by TA instruments. All DMAs were done under tension mode for cylindrical samples with 0.01 N preload force, 10 μm amplitude and at a heating rate of 5 °C/min. TGAs were done in air at 20 °C/min. Finally, DSCs were done in Al pans with different cycles described later depending on the goal of the data.

All organic composites

In order to maximize weight savings, an all organic capacitor system was proposed, using the conductive polymer polyaniline (PANI) as the filler. The emeraldine base form of PANI was positively doped in 1M HCl aqueous solution after purchase at 70 °C for 24hrs under constant stirring and then dried in air at 80 °C for 4hrs. These steps fully protonated the polymer and created charge carriers to facilitate the chain’s conductivity. After the PANI was doped it was broken down into smaller particles by ball milling and running through a sieve to ensure no particle was larger than 32 μm.

Composite samples were made by adding the doped PANI to DCPD-ENB and sonicating by horn for 1 min and in a bath for 1 hr. During this time 1st generation Grubbs’ catalyst was recrystallized at room temperature in a glass vial which would be used as the mold and broken after curing at to release the sample.

When the PANI mixture was removed from the sonication bath and all the methylene chloride had evaporated the suspension was added to the catalyst and stirred manually until it
began to gel at which point it was set down and allowed to polymerize until the system was no longer giving off heat. The sample was then post-cured at 80 °C for an hour.

By using predoped and prepolymerized PANI it was not possible to form a single phase with the matrix material. However, when comparing work done on macromolecular acid doped PANI that was formed by a dual in situ polymerization of both the acid and aniline monomer (Figure 16 left) it is apparent that the resulting single phase is more porous than the current system (Figure 16 right). The image on the right was taken using an Olympus BX51TRF polarized optical microscope (POM) with a PAXcam mounted on it. When considering the crippling effects that air has on a film’s dielectric properties and the inherent compatibility between polymers, it is more important to be homogeneous relative to air pockets than the polymer phases.

![Figure 16. Comparison of dispersion between SEM of in situ polymerized PANI (left) and POM image of dispersed PANI (right)]
Ceramic 0-3 Composites

Barium titanate (BTO) nanoparticles with an average size of 62 nm were used as received from TPL Inc. and were shown to have a cubic crystal structure (paraelectric, see Figure 17). It has been taken into consideration that at room temperature the BTO should be tetragonal and ferroelectric but as the particles shrink beyond 100 nm surface defects distort the tetragonal characteristics of the material. Nothing but the best X-ray Defractometers (XRD) can truly sense the difference on the nanometer scale. Whether the crystal structure is tetragonal or cubic isn’t nearly as important as how it will behave, which in this case is as that of a paraelectric material.

Spherical particles were chosen for this investigation despite the mechanical advantages to high aspect ratio particles because of dielectric considerations. Whiskers or carbon nanotubes are more likely to align in a way that conducts and breaks down across a thin sample. As a result the composites would have lower critical volume fractions for the percolation threshold and they will also create higher local electric fields. If it were possible to have high aspect ratio particles align perpendicular to the applied field then they
could act as a space charge dissipation layer. Attempting to introduce a degree of isotropy adds another layer of complexity to fabrication, especially if the filling particles are not magnetic at all.

Poor interaction between the polymer matrix and filler can be overcome by either changing the surface functionality of the filler, \(^{(3, 26, 43, 44)}\) to make it less likely to aggregate, or physically forcing high degrees of wettability. Forcing better dispersion will in the process, remove air bubbles thereby improving the composite density. Brute force application of monomer can be done using a hot press, vacuum or a planetary mixer. Implementing a planetary mixer will not only degas but actively break up agglomerates. Substituting this step into the processing instead of sonication is what made it necessary to find an alternative polymerization method. Using a small enough amount of 1\(^{st}\) generation Grubbs’ to extend gelation time to the point where there is an adequate processing window means there won’t be enough catalyst available in the system to properly polymerize the sample. This called for the addition of an inhibitor. Triphenylphosphine (PPh\(_3\)) when added
to the monomer solution, will substitute for the phosphine group already on Grubbs’ instead of a double bond on DCPD cyclically deactivate 2nd generation and imparting a variable processing time depending on the catalyst to PPh₃ ratio. While this gave the system time to process is also gave the BTO time to settle. Before implementation of the planetary mixer it was necessary to watch the slurry mixing in an overhead mixer until viscosity was high enough to suspend the BTO for long enough to degas in the vacuum oven without settling before gellation. This process was further complicated by the fact that with increased amounts of filler the gel time decreased.

Even during curing, viscosity will work against homogeneity. When curing begins thermal effects dominate and the currently linear polymer will lose viscosity until enough crosslinking has occurred to counteract the increased flow at higher temperatures. At higher loadings of filler viscosity will also vary by causing wall slip, flow instabilities, yield stresses and dilatancy.

The internal morphology of the planetary mixed sample was shown to have no voids based on SEM images from multiple different depths within the sample (Figure 18). It is worth mentioning that these BTO particles did not have any surface modifications which is highly regarded as the best method to improve dispersion, increase continuity in crosslinking and generally form a more homogeneous composite with a higher T_g. It is also obvious from the same literature that it does not improve permittivity or relaxation time which could be important depending on the frequency range of the eventual application. As well, by doing in situ polymerization, many of the benefits are maintained.
Dispersion across a sample’s surface is also important since that is the area in contact with the electrode and is where the field is strongest, so any considerable defect would without question initiate a breakdown event. Although the surfaces in the SEM images were cross sections those surfaces were prepared in the same way as those sputtered with silver and are assumed to be the same structure.

Thermogravimetric analysis is reasonable method for determining inorganic content in a sample. The final weight percent will be that of the total weight percent of the composite made up of constituents with degradation temperatures above 800 °C. It is safe to say that the only substances falling into that category would be inorganics and since there was only one inorganic component in these samples it can be assumed that the final weight
percent is the actual loading of BTO in the sample. In each of the three samples shown in Figure 19 the intended weight percent and resulting weight percent match within 1%.

![Figure 19. TGA of polyDCPD and BTO composites showing experimental weight percent loadings](image)

**Dielectric and Mechanical Properties of Polydicyclopentadiene**

As an insulator, the dielectric constants and dielectric loss of polyDCPD are quite low, which is true for most unmodified polymers but to rely on a material in a dielectric application without knowing its dielectric contributions would leave this study incomplete. There is also the possibility that a significant percentage of entrapped metal (specifically Grubbs’ catalyst) might have noticeable effects on the polarizability of the system. Referring back to Figure 12 & 13 there are noticeable conjugated regions in the catalyst structure. Ruthenium being coordinated to two chlorines as well, in both generations gives the necessary charge to distribute across the $\pi$ system. It is also already understood that the rate constant has a 1st order dependence on the catalyst concentration and the effects that kinetic variations may have on mechanical and dielectric properties are not fully understood.
Commencing this avenue of research was admittedly an afterthought to that of the polyDCPD composite fabrication. It was necessary to begin this investigation when it was determined that triphenylphosphine would be required for successful processing. Mauldin and Kessler found that while increasing peak reaction temperature, adding PPh$_3$ also significantly reduced $T_g$ (Figure 20) therefore it was imperative to understand what other influences it may have on the polymer and subsequent composites.

![Figure 20. Effect of PPh3 on reaction rate](45)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2$^{nd}$</td>
<td>160.3</td>
</tr>
<tr>
<td>2nd + 30 eq. PPh3</td>
<td>145.3</td>
</tr>
<tr>
<td>2nd + 60 eq. PPh3</td>
<td>139.7</td>
</tr>
<tr>
<td>2nd + 120 eq. PPh3</td>
<td>121.2</td>
</tr>
</tbody>
</table>

*Table 1. Effect of PPh3 on $T_g$*
PolyDCPD and ENB both have completely hydrocarbon based structures and are highly nonpolar, leaving little to no dipoles or charge mobility. This explains the high breakdown strength but also the low permittivity values. During current oscillation the only things in a perfect sample of polyDCPD that can pole are the electron clouds and nuclei of individual atoms. This process is instantaneous (on the order of $10^{-12}$ seconds) resulting in very low frequency dependence but the effectiveness is minimal. Nothing can be stored with such shallow polarization, leaving the polymer with a minuscule permittivity. Based on Figure 23 it is apparent that the introduction of catalytic amounts of ruthenium does not affect the dielectric constant to any significant degree.

It must be accepted that even homopolymer systems are heterogeneous. It is a practical impossibility to have a sample free of defects, solvent, monomer or general packing inconsistencies. By virtue of this fact and the weakness of electron cloud polarization, dielectric properties of polyDCPD are dominated by interfacial polarization (formerly known as Maxwell-Wagner-Sillars polarization)\(^{(24)}\). In areas of irregularities and defects charge will be able to travel, but once the matrix is approached all charge will be trapped there unable to continue poling but also unable to discharge causing a small opposing field.

Statistical irregularities in polyDCPD don’t deviate far from the norm, its permittivity with different generations of catalyst all fall close to the standard unmodified polymer value of $3^{(9, 15, 47)}$ as shown in Figure 21 through Figure 23. At room temperature permittivity is determined by this single mechanism at higher temperatures (above the glass transition) the polymer will exhibit some ionic conduction at very low frequencies (.01 Hz), that are then possibly falsely enhanced by the electrode polarization effect. This minimal ionic conduction will still increase permittivity 8% but as might be expected, at the cost of
higher losses. Ionic effects will change with the induced potential as well; beyond a certain voltage the electrodes are able to inject electrons into the material. The current study did not probe these affects; each dielectric test was done at a single applied voltage.

Figure 21. Permittivity and loss of neat polyDCPD polymerized by 1st generation

Figure 22. Permittivity (left) and tan δ (right) of neat polyDCPD polymerized with 2nd generation
The tan δ in these samples is consistently low across generations (Figure 24) and catalyst loading at ~1 x 10^{-3} which is expected from the polymer’s purely olefin based structure. Groups with low polarity and the high degree of polymerization associated with living polymerizations both help keep the loss down. However, it is important to note for the sake of the following composite samples that literature claims .5 to be an acceptable tan δ value for use in certain devices. \(^{(32)}\)
Based on a simple TGA of neat polymer (Figure 25) the degradation temperature and moisture content can be determined. For polyDCPD the main degradation step onset occurs at ~450 °C, but it should be stated that the main degradation mechanism begins before the actual onset of rate change, while the minor degradations like water evaporation will continue on beyond the primary drop point. When trying to determine the amount of absorbed water it’s hard to differentiate loss of moisture from loss of absorbed gases\(^{(48)}\) but the loss prior to 100 °C in total is negligible.
Not all of polyDCPD’s mechanical properties have been studied here so it seems worthwhile to review properties relevant to the current study and application that were found in the literature. Fracture toughness ($K_{IC}$) is a measure of the stress required to grow cracks to failure from existing flaws, polyDCPD has an accepted value of 3.3 MPa·√m compared to epoxy or polyester’s 1.5 MPa·√m. In most polymer-inorganic composites one major benefit is the reduction of the polymer’s coefficient of thermal expansion which neat is 70 μm/μm/°C and can be easily reduced to below 60 μm/μm/°C with minimal amounts of silica particles\(^{(21)}\).

Dynamic mechanical analysis was used to determine $T_g$ and Young’s modulus of each sample. In both series of neat polyDCPD polymerized without triphenylphosphine there was a very interesting trend observed among the glass transition temperatures while the glassy and rubbery moduli were completely disordered (Table 2). Each sample consistently had an increase in $T_g$ with increasing catalyst concentration as would be expected from a higher crosslink density but increasing the crosslinker in epoxy only raises the $T_g$ to 138 °C.
The extent to which the $T_g$ increased at high catalyst loadings of .3 wt.% was by 60 °C from that of the .05 wt.% to 180 °C (Figure 26). All these samples were cured at the same time, in the same way at 120 °C so a $T_g$ that high goes against the time temperature transformation theory. This phenomenon can be at least partially explained by exothermic effects. The polymerization that occurs at room temperature is very exothermic as a result of removal of ring strain. Those same types of rings are opened during curing so it stands to reason that the temperature of reaction would be higher than that of the temperature that the oven was set at. If this is true, it stands to reason that the reaction temperature would increase with higher catalyst amounts. This trend will not continue on indefinitely, there exists a concentration at which excess catalyst will begin to build up which will simply start to get in the way and bring the $T_g$ back down again through the formation of mobile chain segments. Glass transition temperatures determined here do not fall within the bounds of the commonly considered ‘high temperature’ polymers such as bisphenol-E cyanate ester or polyimides which are usually the first choice for applications putting capacitors in a heat generating environment. However, polyDCPD has a resistance to moisture that polyimides don’t.

Water will react with mers in the middle of a chain creating ionic ends that compromise its insulating ability through increased charge transport. These stiffness results obtained from neat polyDCPD studies should make a good reliable baseline for the possible variations of the composites because there should be no variation caused by inhomogeneous filler dispersion in the neat polymer samples.
Table 2. Averages and standard deviations of $T_g$ and moduli of each catalytic system

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$T_g$ Avg</th>
<th>$T_g$ Stdev</th>
<th>$E_{\text{glassy}}$ Avg</th>
<th>$E_{\text{glassy}}$ Stdev</th>
<th>$E_{\text{rubbery}}$ Avg</th>
<th>$E_{\text{rubbery}}$ Stdev</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>128.66</td>
<td>33.29</td>
<td>1271.92</td>
<td>55.835</td>
<td>10.92</td>
<td>3.166</td>
</tr>
<tr>
<td>2nd</td>
<td>159.17</td>
<td>24.00</td>
<td>993.353</td>
<td>89.209</td>
<td>7.437</td>
<td>2.070</td>
</tr>
<tr>
<td>2nd + PPh$_3$</td>
<td>127.76</td>
<td>3.21</td>
<td>967.563</td>
<td>73.549</td>
<td>7.177</td>
<td>1.541</td>
</tr>
</tbody>
</table>

Figure 26. DMA of neat polyDCPD with 1$^{\text{st}}$ (left) and 2$^{\text{nd}}$ (right) generation catalyst concentration from 0.05-.3 wt.%

It is understood that reducing the crosslink density will directly reduce the $T_g$ but how this affects the electrical properties is a little less intuitive. By changing curing times of epoxy, Tomer et al. was able to detect a decided loss in breakdown strength with lower crosslink densities.\(^{(15)}\) In the polyDCPD system changing catalyst amount should be equivalent to varying curing times in terms of the resulting crosslinking. Molecular weight and crosslink density can have a considerable effect on breakdown strength\(^{(49)}\) further validating the study of dielectric properties in the polyDCPD matrix at different catalyst
loadings. The effect of crosslink density is more pronounced at high temperatures because of the increase in $T_g$ that results.\textsuperscript{(50)} Molecular conformation has also shown to change a material’s dielectric strength. As an example, atactic PP has a higher breakdown strength at room temperature than isotactic but above the glass transition the opposite is true. The random and amorphous nature of atactic PP makes it harder for electrons to accelerate because of structural irregularities which should also hold true in an amorphous polymer like polyDCPD.\textsuperscript{(51)}

There is also a strong dependence of breakdown strength on film thickness. As stated in the introduction, thickness and dielectric strength will determine the maximum operating voltage, but more often than not, the operating voltage is fixed, leaving the breakdown strength to increase with reduced thickness (Figure 27). Thickness can decrease down to a practical limit where the breakdown voltage is a safe minimum amount higher than the operating voltage. Dielectric strength isn’t an intrinsic material property so this size dependence shouldn’t be out of the realm of possibility. This means that even though the breakdown voltages of different samples or different areas may have been normalized to a per-unit-of-thickness value, that doesn’t mean they can be compared to one another if the actual sample’s thickness varied even tenths of a millimeter because the breakdown strength is dependent on the thickness by an inverse power law.\textsuperscript{(21)}

![Figure 27. Thickness dependence on breakdown strength](image-url)
When performing dielectric breakdown tests the sample and instrument geometry beyond that of just the thickness has a significant influence on the resulting values. Under perfect circumstances, most nonpolar polymers will have breakdown strengths between 1-9 MV/cm. As of yet no sample in this investigation has been able to reach even 1 MV/cm. One possible explanation is that of edge effects. All measurements were done completely submerged in high strength oil but partial discharges are still likely to occur in the immediate external environment around the electrode prior to the actual breakdown event if there isn’t perfect contact. Partial discharges will obviously aid in an early complete breakdown event.

Wagner introduced a breakdown mechanism where evolved heat from current flow is created faster than it can be dissipated throughout the material and eventually the area between electrodes has a large amount of free flowing accelerated electrons. However, at room temperature these contributions are negligible. Another possibility is that electrons made mobile by the voltage potential will interact and exchange energy with phonons or impurity related space charges present in the sample in a similar way to how current multiplies in a gas when there is ionization during high speed collisions.

After performing a dielectric breakdown test it is clearly visible that mechanical damage has occurred in addition to the insulating failure. On the tested samples, along the breakdown pathway, there is a definite small hole through each point; a representative sample is shown in Figure 28. While breakdown strength is an electrical property it has mechanical components and ramifications. The voltage put on the sample’s surface if not carried away by ions or other conductive means will collect at the electrode causing mechanical deformation and eventually reach the bond energy beginning current
multiplication and leading to mechanical and dielectric failure through newly accessible charged chain ends. Without current multiplication deformation still exists and will therefore dominate the breakdown process. In addition, the existence of mobile moieties affect the breakdown strength in a similar way as it does the $T_g$. Loose chains makes it easier to form space charges and higher local polarization.

![Figure 28. Image of breakdown sample after testing](image)

Weibull describes a statistical distribution function that can be applied to a wide range of scenarios; he lists yield strength, size distribution, and fatigue life as examples. This function attempts to determine the weakest link in a system based on a series of experimentally acquired data.

$$P_n = 1 - e^{-n \varphi(x)}$$

The internal function $\varphi(x)$ is required to be a positive, non-decreasing function that at some $x$ value will equal zero. The simplest function of this type is:

$$\frac{(x - x_u)^m}{x_0}$$
which suits most distributions. When using Weibull statistics to manage dielectric breakdown data however it is best to use:

\[ \varphi(E) = \left( \frac{E}{\alpha} \right)^{\beta} \]

Where \( \alpha \) and \( \beta \) are the scale and shape parameters respectively and whose derivations can be found elsewhere.\(^{(54)}\) Substituting this formula back into \( \varphi(x) \) of the original function gives a dependable final form. In the case of breakdown strengths, plots of \( E_{DS} \) vs. \( \ln(\ln(1/(1-P_n))) \) give straight lines but the y-axis becomes simply a relative distribution function. The plotted y-values are not exact percent probabilities but a sample’s reliability can still be determined by the steepness. Dielectric strength for each point is given by the x-value. This kind of representation makes it possible to compare the probability of failure at which voltage of multiple samples simultaneously.

Configuring all of the breakdown data into the form of Weibull made it possible to see differences between the three systems. There are no particular trends with different loadings but the different systems do have distinct characteristics. The series of samples polymerized using 1\(^{st} \) generation have the largest amount of scatter in reliability. Each line crosses at common points of dielectric strength but none have similar slopes. Both types of 2\(^{nd} \) generation don’t necessarily have better reliability but it is consistent throughout the six samples in each plot. Adding PPh\(_3\) seems to anchor both the scatter and the strength except for in the case of the lowest loading.

Since there is no systematic variation of breakdown strength with catalyst loading it is safe to say that the catalyst isn’t directly affecting breakdown. That leads to the hypothesis that it has something to do with the molecular structure of the resulting polymer which would require a stronger understanding of the ROMP mechanism than was studied here.
Judging by the Weibull plots of each different catalytic system (Figure 29-Figure 31) it is clear that polyDCPD doesn’t come close to that of the values obtained from epoxies (~4MV/cm\(^{15}\)). One of epoxy’s advantages over polyDCPD in terms of breakdown strength is the polar groups present in epoxy monomers.\(^{(52)}\) Polar groups, like those in epoxies or even nitrogens and flourines will act as scattering points for the accelerated electrons accrued during an electron avalanche to increase the dielectric strength. However this is only true at temperatures below the glass transition.\(^{(55)}\) Above the glass transition electro-mechanical breakdown dominates. Amorphous regions have similar yet milder scattering effects that have been observed to be enhanced with decreases in percent crystallinity. Increases of this type are more of a relative effect, having an amorphous structure isn’t incredibly beneficial on its own. If there were no crystalline regions to begin with that doesn’t make the whole material inherently better. When an amorphous section is approached by traveling charge through a crystal the disorder will scatter it. If the molecular structure is not tightly bound, chain rearrangement may move free volume to facilitate electron transport leading to breakdown.
Figure 29. Distribution of breakdown strengths in neat polyDCPD polymerized by 1st generation

Figure 30. Distribution of breakdown strengths of neat polyDCPD polymerized by 2nd generation
Dielectric Properties of All Organic Composites

There is great potential in the market for an all organic capacitor material. So much of the weight saved and portability achieved is lost when adding large amounts of dense ceramics to a polymer. Before the dielectric capabilities of such a system can be explored though, the physical limitations incurred by this sort of combination must be revealed. Any doped synthetic metal can be successfully undoped with relative ease, so during fabrication of the all organic composites it was necessary to maintain all processing temperatures below
100 °C. At temperatures any higher there would have been significant removal of dopant as seen in Figure 32. Extended exposure times during curing would understandably exasperate dopant removal, as proved by the weight drop at 250 °C where the TGA was held for a 2hr long isothermal.

Looking at the side by side TGA thermograms of doped and neat PANI in Figure 32 there is a 15% weight loss beginning at 100 °C present only in the curve of doped PANI. Removal of dopant eliminates charges from the chains rendering the polymer
nonconductive and ineffective as filler. Also judging by this plot and the doping method there was significant water absorption in PANI during the doping process. Such a conclusion implies that water was introduced during the fabrication of composites. It can also be assumed that polyDCPD being nonpolar would not absorb any water on its own.

In an effort to minimize dopant losses the curing time and temperature were kept low and as a result the matrix was not completely polymerized. A small sample of neat DCPD was allowed to polymerize with 1\textsuperscript{st} generation Grubbs’ at room temperature then was put through the typical curing cycle of 1 hr. at 80 °C in the DSC. Afterwards, the same sample was run a second run a second time at 15 °C/ minute up to 200 (Figure 33) where an exotherm corresponding to 7% of total heat of reaction occurs immediately after the isothermal temperature representing the incomplete cure and marking the first complication with this system.
There is a strong correlation between polymerization kinetics and properties of the final product. If the extent of polymerization and crosslinking is hindered by a slow reaction then it will be at the cost of the sample’s chemical resistivity, mechanical and electrical properties. DSC is an effective method for determining percent completion of cure. Equations have been developed to relate the heat generation with the extent of a reaction $\alpha$, leading the amount of heat given off the second time to be a good estimate of how close the cure cycle gets the sample to completion.

$$\frac{dQ}{dt} \propto \frac{d\alpha}{dt}$$

It is understood that curing will occur before the DSC has heated to the desired temperature but the oven used for curing is not an instantaneous process either, so this effect was determined to be negligible.
According to the DSC data presented in Figure 34 the addition of PANI to the composite system increases the $T_g$ from 148 °C to 160 °C systematically with increased amounts of filler. This proves that despite the incomplete cure there is still a very compatible interface between the polyDCPD and PANI. A strong interface in the case of these micron sized particles of polymer could be from their jagged surfaces left over from being milled. Rising $T_g$ also plants the initial idea that the composites at as high a loading as 20 wt.% are not at percolation.

![Figure 34. Dielectric scanning calorimetry illustrating the $T_g$ of composites with increasing PANI content](image-url)
It is expected that at the percolation threshold there will be a large increase in both dielectric constant and loss during the metal-insulator transition. Higher losses are obtained and explained below, but there is no drastic increase in permittivity (Figure 35). Theory dictates that increases of several orders of magnitude should be achievable. Pecharroman and Moya\(^{(56)}\) were able to obtain a four order of magnitude increase, which is nothing like what is seen here. The metal-insulator transition will occur at percolation, when the thin layers of matrix separating particles ceases to exist. Right before that happens, at the point of finest compartmentalization, there will be the highest dielectric constant. As one might imagine, reliably making composites with such accuracy that close to the percolation threshold is a tremendous challenge. Near the critical loading percent, electric properties

![Figure 35. Permittivity of polyDCPD-PANI composites](image-url)
behave as an exponential function so minor divergences make all the difference. A modest increase in the wt.\% could mean large amounts of improvement in the dielectric constant.

Under these circumstances it is also necessary to minimize the probability of a conducting pathway. In order to say with confidence that there are no pathways, the loading may have to be lower than ideal. Another way of describing this would be to think of a sample as being composed of many phases of slightly different concentration all connected in parallel, summed to create the conductance spectrum. Looking at the components themselves, there is no fundamental reason why this system can’t be successful, enhancement at the percolation threshold is only a function of the composite geometry and conductivity ratio between the metal and insulator phases anyway.

Dielectric loss in a filled system is a function of losses accumulated by the matrix, filler and interface through polarizations of electronic, dipolar and interfacial nature. As a direct result of the nomadic polarization mechanism, charges collect at the surfaces of PANI particles. This build up creates space charges which will lead these composite materials to experience unavoidable high losses at low loadings (Figure 36) despite the insulating matrix of polyDCPD. It can be assumed that even at the loadings studied the particles themselves were too big to ever completely avoid one another and this phenomenon. There was no reasonable method for making smaller PANI particles; therefore the system was no longer pursued. Though not studied here, it can be assumed based on the conductive nature of the polymer as well as their particle size that composites of this specific combination would have very poor breakdown strengths.
Dielectric Properties of Ceramic Nanocomposites

When a 0-3 composite is formed the interface between phases becomes particularly important. As stated previously defining feature that makes nanocomposites different from all other materials is the amount of contact the matrix has with its filler. Almost nothing is lost in the ‘bulk’ of a particle. With that in mind, surface effects become drastically more important and influential in a composite. A significant number of models exist for what might be occurring at the interface between polymer and particle. First, it is theorized that the decrease in $T_g$ upon addition of a nanofiller points to the existence of a two layer interface between the two entities. The first layer around a particle is of tightly bound immobile chains; the layer beyond that is more unrestricted during relaxation, but still locally bound. Mobile layers like this exist because during curing the mixed particles will block and prevent crosslinking leaving a sphere around the particle of linear polymer. This theory has

Figure 36. Tan $\delta$ of polyDCPD-PANI composites
been effectively proven through the differences observed by Tomer et. al\textsuperscript{(15)} while monitoring differences in $T_g$ shifts between composite samples containing fillers of different surface areas. There was a much larger reduction of $T_g$ in samples containing flat platelets like montmorillonite (MMT) than those filled with 150 nm spherical BTO particles.

For the present composites, $T_g$ was determined by the peak in loss modulus of a DMA curve. There is a slight increase in the glass transition which points towards a moderately well established interaction at the interface. This result however is contrary to the requirements for the double layer model. Having established some binding between the two there may not have been nearly as much reduction of crosslinking by the addition of the BTO. Assuming this is true allows for the validation of the double layer model without the increase in glass transition causing concern. If a $T_g$ similar to that of the neat polymer or this single composite representative is maintained through higher loadings then this theory can be proven. In a composite environment with poor interfaces, there would be a considerably more substantial decrease in glass transition temperatures with such loading incrimination.

![DMA comparison of stiffness between polyDCPD and polyDCPD-BTO composites](image)

Figure 37. DMA comparison of stiffness between polyDCPD and polyDCPD-BTO composites
In addition to the amount of surface area created by nanoparticles a lot of inclusions or defect sites have also been introduced depending on how the particles are viewed. These pinning points can hinder the mobility of polymer chains within the matrix, which would affect the dielectric constant in PVDF matrix composites, but here merely reduces flexibility (Figure 37), which isn’t necessarily detrimental, plenty of applications can benefit from a higher Young’s modulus, especially if there is the eventual goal of structural implementation. Stiffness is also increased by the molecular structure of BTO itself. The particles, being the size they are, are a single crystal, which means any force is working against actual bond strength, not secondary forces. This is in opposition to the decrease in permittivity that comes from a lack of grain boundaries, which Kuo et al. determined was not nearly as influential as volume percent of filler. Higher stiffness is exactly what would be predicted by the rule of mixtures, but experimentally the values don’t hold tightly to theory. The rule of mixtures assumes a seamless combination of the two constituents as its upper bound (2,057 MPa) or a completely disjointed interface as the lower bound (915.8 MPa). Since the particles are unmodified some strength is certainly lost to the nonideal interfaces. Modulus will increase with added BTO until percolation has been reached. When considering particle enhanced stiffness it is only natural to be concerned about the inevitable fracture and failure. If particles are well dispersed then microcracks and other defects should be as well. This will keep mechanical failure localized and significantly postpone complete failure of the part. Moreover, when normalizing the glassy moduli it becomes apparent that the ΔT_g’s are similar, eluding to the fact that the local environments determining the T_g in the composite are similar to that of the neat polymer. Observing the rubbery modulus it is visible that the opposite of the glassy region occurs. Nanoparticles in this situation do not
help to strengthen the rubbery network; in fact they may hinder the necessary crosslinking and entanglements.

It is readily apparent from Figure 38 that as BTO loading increases, the permittivity and frequency dependence of the permittivity increases. According to a model presented by Chao et al. the permittivity at 10 vol.% should be 8. Dielectric constant is falling short but not by much. Frequency dependence can be ascribed to a combination of soft percolation and interfacial polarization.\(^{(33)}\) It has already been discussed that after a volume percent of about 10 soft percolation paths begin to form. In the case of dielectric spectroscopy and permittivity measurements this is important because prior to the actual spanning of sample thickness there are long chains in the transverse direction spanning segments of a sample’s thickness. These internal chains promote poling without actually discharging at the sample’s surface. It is reasonable to conclude that the formation of these pathways would be of a similar statistical probability as the soft percolations leading to their increased abundance at higher loadings. Poling can be best realized at lower frequencies, yielding the observed effect. Interfacial polarization is said to become negligible at .3 volume percent filler because of the formation of percolation pathways. It follows then that at low concentrations, interactions between matrix and filler are dominant and after the .03, particle-particle interactions are dominant.\(^{(3)}\)
Relaxation time becomes very important because that is what will determine the composite’s frequency running limit. If the relaxation time is slower than the frequency, the composite won’t reach its optimal state before current is switched again, resulting in a lower dielectric constant for that frequency.

There is no question about the high losses present in the current system (Figure 39). Interfaces between BTO and the matrix are unmodified cause a significant amount of interfacial polarization that will introduce high losses. As well, at higher loadings there will be increasing amounts of steric hindrance near the filler. Going back to the fact that there is water on the BTO particles means water is trapped within the sample and when current is alternated around there will be ionic impurities along with proton motion ionizing any remaining catalyst leading to greater polarization potential and loss. Water ionization effects can’t be a very substantial contributor to the overall mechanisms because then loss would be greatest at higher frequencies. Space charge formation and dissipation will change the local
electric field putting both electric and electric-mechanical stress on the samples lowering performance. These factors will peak the dielectric loss at different frequencies depending on the material nothing can be concluded from this however because the loss plots (not shown here) never peaked in the observed frequency range. Based on Das-Gupta’s observations it can be said with confidence that the polymer dominates the dielectric properties of the composite but BTO is dominant in conduction. As a result the composite will maintain resistance to leakage current and dielectric heating at high frequencies which are associated with a low permittivity, low loss polymer. Less dielectric heating means lower probabilities of the thermally induced breakdown. That unfortunately doesn’t change the fact that polymer matrix deficiencies still must be overcome when reaching for higher permittivities. Presence of moisture can ruin the low dielectric heating at high frequencies since it has a higher polarity than the matrix and will lead to conductive power loss as well as burning of the matrix depending on how much water there is.

Figure 39. Loss in polyDCPD-BTO composites
It is expected that there will be a major dielectric relaxation process across the frequency range which is really all that’s visible in the Cole-Cole plots in Figure 40. There are smaller events that must be taking place however because there is no manipulation of the Cole-Cole equation that rightly fits the data. High dielectric loss can occur at low frequencies because of conductivity or the heterogeneous nature of composites. It’s possible to separate these causes from one another by performing dielectric spectroscopy at various temperatures. If the relaxation were caused by conductivity the loss would increase along with the temperature.\(^{(30)}\) In the current composites, they are linear dielectrics and experience the major relaxation that comes from local relaxation of the crosslinked thermoset whose local environment doesn’t change with the addition of filler.\(^{(15)}\)

![Figure 40. Cole-Cole plots of polyDCPD-BTO composites of 10-40 wt.% loading](image)

It is important to note that the majority of the spectra in Figure 40 experience a jagged point near the end of test, but this can be explained by limitations of the dielectric
spectrometer. At low loadings the capacitance is practically zero and it is very hard for the instrument to measure subtle differences between one infinitesimal number and the next.

Another point worth addressing about defects in such a system is how they affect breakdown. Unlike breakdown of conducting materials, ceramics break down at defect sites (i.e. grain boundaries, impurities and porosity). Prior to complete dielectric failure there will be a partial discharge somewhere in the sample at any of these defect sites. The more weak points in a ceramic filled composite the more possible breakdown channels there are and therefore the more likely it is that one of those channels reaches from one electrode to the next, especially after preferential degradation of the matrix caused by the partial discharges.\(^{(57)}\) Since partial discharges occur predominantly in voids and impurities and more harshly effects organic matter, the addition of ceramic nanoparticles can give the composite higher partial discharge resistance. Defects outside the particles themselves will cause breakdowns in a poor interface where there could be a connected network of air through the sample.\(^{(20)}\)
Breakdown strength, even with the smallest addition of BTO decreases dramatically. When additives are introduced into a polymer matrix the breakdown strength is affected negatively by local field distortion and space charge distributions, or positively by an increase in path length to breakdown in the cases of high dielectric strength filler. All breakdown tests were done under dc conditions, if the filler and matrix had comparable permittivities and conductivities; local field distortion would only be determined by particle size. Neither of these things is true, therefore in such a situation field distortion is caused by these differences in conductivity between the matrix and filler. Size effects are still present though, larger particles cause higher field enhancements, a particle will act as the center for local field enhancement, the implication being that the use of nanoparticles should limit this effect.\(^{58}\) The effect observed in the present situation (Figure 41) can’t be simply due to percolation since the critical volume fraction is .16 and 10 wt.% is merely .02 volume fraction. Partial discharge can be at least a partial explanation of the significant drop. It has been established that there are air pockets between particles so once the partial discharge value is reached, complete breakdown is inevitable. In addition, as stated earlier there is a certain percentage of water that comes along with the nanoparticles that can be the nucleation point of partial discharge and create poor hydrophilic surfaces. However, as expected by Tuncer et. al\(^{42}\) the variation among breakdown values in the composite is much lower.

**General Conclusions and Summary**

In this work three different systems were tested for their applicability as structural capacitors (polyDCPD, and polyDCPD-PANI or –BTO composites) by characterizing their
dielectric and mechanical properties. It can be concluded from the collected data that in order for any of these systems to become viable some considerable changes need to be made in their processing and testing.

As expected, polyDCPD alone does not have a high enough permittivity to suit the energy density needs of current applications. However, it is now understood that the type of catalyst used as well as in what concentration does not significantly affect its performance as a good insulator in the sense of its high breakdown strength and negligible charge mobility, though the permittivity is not significantly improved by these changes in composition either. There were however noticeable differences in the breakdown characteristics between samples polymerized by different catalyst systems.

All organic composites show great potential for capacitor applications in theory, however implementing them has proven to be more difficult. Being able to obtain nanoscale particles of PANI, or possibly utilizing another conducting alternative like P3HT would solve some of the conductivity issues that were faced during the current study. At that point the percolation threshold could be properly probed and determined to achieve a maximum dielectric constant.

In retrospect, the literature has made it clear that functionalization of inorganic particles in organic filler results in significant benefits to the composite. Some groups have shown slight decreases in permittivity\(^\text{(15)}\), but when considering the benefits it would have on breakdown strength the decision is easily made. Most likely the best course of action would be to functionalize the BTO particles with a norbornyl silane as performed by Jeong\(^\text{(59)}\) on the surface of carbon nanotubes to be used in a similar polyDCPD matrix. If successful, voids would be greatly reduced along with interfacial polarizations. Processing may also be
simplified because of the interactions the particles would have with the monomer resulting in a homogeneous suspension that could be reached at lower viscosities while using the same dispersion method. Looking more closely at the particles themselves, with a modified surface, the use of ferroelectric particles should produce the high permittivity without the characteristic leakage current associated with it.\(^{(60)}\) Obtaining ferroelectric BTO nanoparticles may be more reasonable than previously suggested considering that the optimal particle size for a composite of this type is 100 nm and at which point will have a better chance of being ferroelectric.\(^{(61)}\)
Works Cited