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Solid-State Ultracapacitor Polymer Composite

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December 2022

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LIST OF ACRONYMS AND SYMBOLS

$BaTiO_3$	barium titanate
DC	dielectric constant
EDLC	electrochemical double layer capacitor
ESR	equivalent series resistance
La	lanthanum
LCR	inductance-capacitance-resistance
RH	relative humidity

NOMENCLATURE

A	area
C	capacitance
d	distance separating electrodes
E	energy
P	power
Q	stored positive charge
V	applied charge
ε_r	dielectric constant of insulating material
ε_0	dielectric constant of free space

TECHNICAL MEMORANDUM

SOLID-STATE ULTRACAPACITOR POLYMER COMPOSITE

1. INTRODUCTION

An ultracapacitor made from a polymer loaded with ceramic powder would have several advantages over current ultracapacitors and batteries. First is the possibility of it being printable, which would allow for printing the energy storage device along with the circuit instead of having to find a way to add one later without damaging the rest of the components. When not printed in a specific design for use on a printed wiring board, this type of ultracapacitor could still be cured via a mold to a shape suitable to specific applications. Many polymers maintain some flexibility even after curing, such as the silicone used in this study. The manufacturing process would also be far simpler than that of conventional ultracapacitors.

In this work, solid-state ultracapacitors were made by adding the dielectric powder to a two-part polymer (resin and hardener) at the same time. The mixture was then cured in the desired shape at a low temperature until completely set. The addition of the powder to the polymer increased its dielectric properties while leaving most of its physical properties unaltered. At higher powder loading percentages, there were some physical changes as the maximum loading point was approached. To determine the efficiency of these solid-state ultracapacitors, their capacitances were tested and their dielectric constants (DCs) were measured and compared.

2. BACKGROUND

2.1 Conventional Capacitors

Parallel plate capacitors consist of two electrodes separated by an insulating material. The insulating material keeps the charges separate when a voltage is applied, producing an electric field and allowing the capacitor to store energy. This process is modeled by the following equation 1, where C is the capacitance, Q is the stored positive charge, and V is the applied voltage.[1]

$$C=\frac{Q}{V} \tag{1}$$

In parallel plate capacitors, capacitance is related to the surface area of the electrodes and the distance between them. This relation is seen in the following equation 2, where A is the area, d is the distance separating the electrodes, ε_r is the DC of the insulating material, and ε_0 is the DC of free space.[1]

$$C=\varepsilon_0\varepsilon_r\frac{A}{d} \tag{2}$$

Capacitors have two properties applicable to this work, energy density, which is the amount of energy that can be stored and power density, which indicates how quickly that energy can be delivered. The energy storage of a capacitor is described by the following equation 3 for energy (E).[1]

$$E=\frac{1}{2}CV^2 \tag{3}$$

The power (P) is energy expended per unit of time. To determine power, the resistance of the capacitor's internal components is needed so that the voltage during discharge can be found. This internal resistance value is known as the equivalent series resistance (ESR) of the capacitor. The maximum power for the capacitor measured at matched impedance is calculated using the following equation 4.[1]

$$P=\frac{V^2}{4\times ESR} \tag{4}$$

The power or energy density of a capacitor is simply its power or energy in relation to its mass or volume. Conventional capacitors tend to have high power densities but low energy densities in comparison to batteries;[1] meaning that while they can delivery energy quickly, they can store less energy than batteries.

2.2 Ultracapacitors

Current ultracapacitors, sometimes called 'supercapacitors,' work using the same basic principles as parallel plate capacitors but with a higher surface area and thin electrolytic dielectrics to achieve higher capacitances than conventional capacitors.[1] This design gives ultracapacitors increased capacitance and energy compared to conventional capacitors. While there are several ways to build ultracapacitors, the most common type are electrochemical double layer capacitors (EDLCs).[2] EDLCs typically consist of carbon-based electrodes on either side of an electrolyte with a separator down the center, as seen in figure 1.

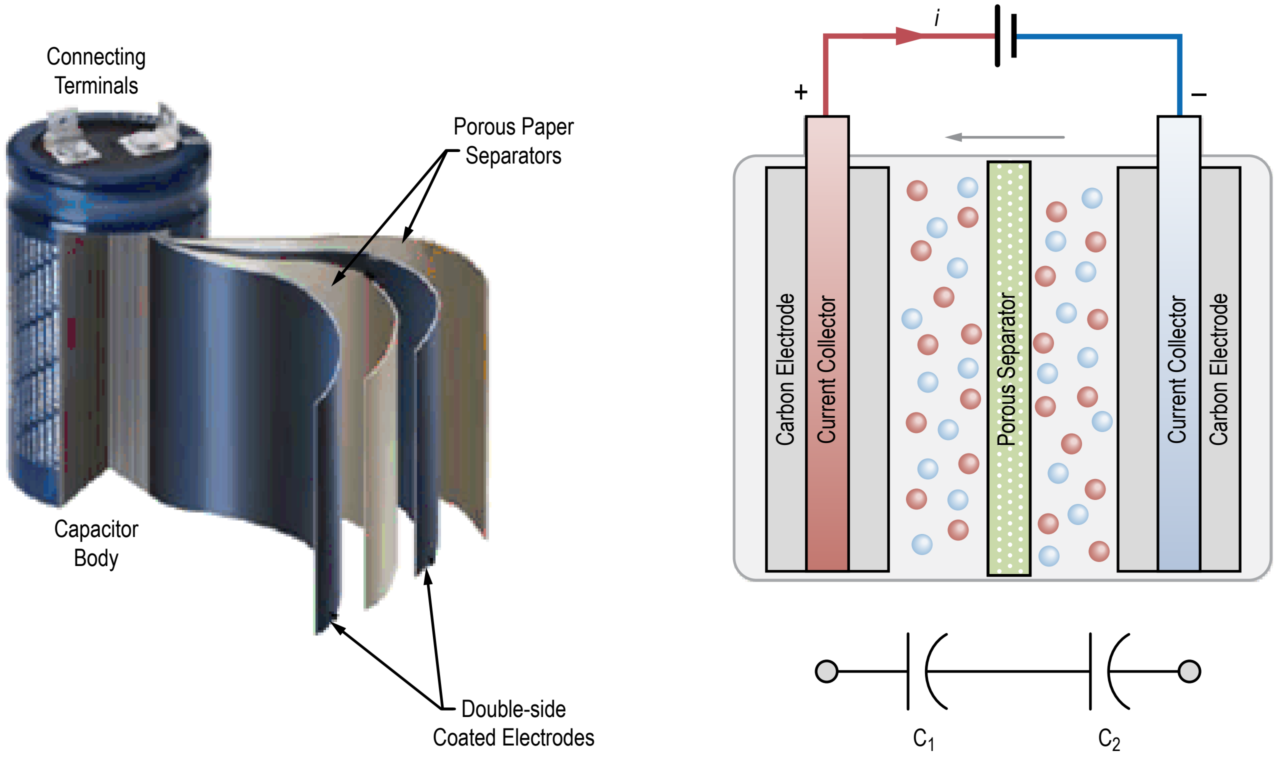

Figure 1. EDLC construction.[2]

In EDLCs, the ions in the electrolyte layer diffuse across the separator toward the electrode of opposite charge when a voltage is applied. The electrodes are designed to prevent the ions from recombining, which creates a buildup of charge at each electrode. EDLCs tend to have high cycling stabilities.

In 2017, NASA developed an internal barrier layer capacitor using novel dielectric materials to in an attempt to create solid-state ultracapacitors as a replacement for batteries.[3] They looked into various particle sizes of barium titanate ($BaTiO_3$) in coated and uncoated configurations. The powders were pressed into pellets at 300 lbf using a potassium bromide dye. The finished pellets were between 4–8 mm thick with masses of 1.5–2.5 g. Once the pellets' properties were understood, a screenprinted test cell was built from silicon dioxide-coated $BaTiO_3$ at a thickness of 50 µm. The prototype exhibited a capacitance of 125 nF at 1 kHz with an energy density of 7.96×10^{-2} J/cm^3 at 50 V. Further study of these capacitors at much higher voltages is required to fully understand their capabilities and applications since they have demonstrated breakdown as high as 500 V. Later, this work was expanded to include dopants and co-dopants in $BaTiO_3$ to mimic the properties of the coatings and preprocessed powder. The resulting material was different in that it was found to breakdown at lower voltages (<40 V) but exhibited extremely large DCs and capacitance in the milliFarads.[4] Testing showed this powder to work as both a humidity sensing material and an energy storage material, the latter independently verified to have an energy density in the 4–6 J/cm^3 range. In this research, the same basic idea of creating a novel, energy storage system using a powder with strong dielectric properties was investigated. In this case, the powder was combined with a polymer instead of pressed into pellets to achieve different physical properties.

2.3 Loaded Polymer Dielectrics

Composite materials made from polymers and ceramic powders with strong dielectric properties are now being investigated to serve as the insulating material in capacitors. This can be advantageous since the composite materials have the physical properties of the polymer (i.e., flexibility and low temperature curing) while maintaining some of the dielectric properties of the ceramic powder.

Previous studies have been conducted using lead titanate,[5] barium strontium titanate,[6] calcium copper titanate,[7] and several other ceramic powders with various polymers to create materials with greater permittivities and energy storage capabilities. In general, past studies have found that while the addition of the ceramic powder does increase the permittivity of the polymer it does not increase it to a degree that would make the new material suitable for being used in a solid-state ultracapacitor. The ceramic powder utilized in this research is a specially-formulated, lanthanum (La)-doped $BaTiO_3$ that is subsequently co-doped with potassium hydroxide.[4] The novel material was determined on its own to have excellent dielectric properties, making it a good candidate for polymer loading.

3. METHODOLOGY

3.1 Making the Pucks

The initial focus was on two polymers, a silicone and an epoxy, mixed with varying percentages of $BaTiO_3$ powder to get a basic idea of how the pucks should be made. The silicone pucks were made using Dowsil™ SE 1700 silicone (fig. 2). Dowsil SE 1700 comes as a clear base with a separate catalyst that are then mixed at a 10:1 ratio and cured at 125 °C. For the epoxy pucks, EpoThin™ two-part resin (fig. 3) was used. EpoThin is mixed at a 100:39 ratio and takes 8 h to cure at room temperature but can be cured in approximately 2 h at temperatures near 40 °C. Different weight percentages of powder were tested, starting from 0 wt.% and loading up to 70 wt.% $BaTiO_3$ powder. For the silicone test runs, 125 °C was above the desired curing temperature, so initial attempts focused on curing at room temperature. However, it was found that it took approximately 10 d to cure. To find the lowest cure temperature for the silicones, curing runs were conducted, where it was determined that the optimal cure conditions were 65 °C with a cure time between 1–3 h. Additional experiments were performed in which the ratio of the catalyst was adjusted in an attempt to speed curing, but no significant changes were observed. For the epoxy experimentation, mixtures were initially left to cure at room temperature. However, the low viscosity permitted powder settling such that the dielectric powder was stratified. To find the optimal curing conditions, curing runs for epoxy were also conducted. The runs demonstrated that if the temperature was too high, bubbles in the mixture from the initial stirring did not rise out of the puck before it set. If the temperature was too low, the powder would settle to the bottom. The optimum temperature was determined to be 45 °C with a cure time between 1–3 h. All of the mixtures were mixed by hand. Once the first round of pucks was cured, they were sanded to give them an even thickness. They were then tested using a dielectric test fixture and inductance-capacitance-resistance (LCR) meter.

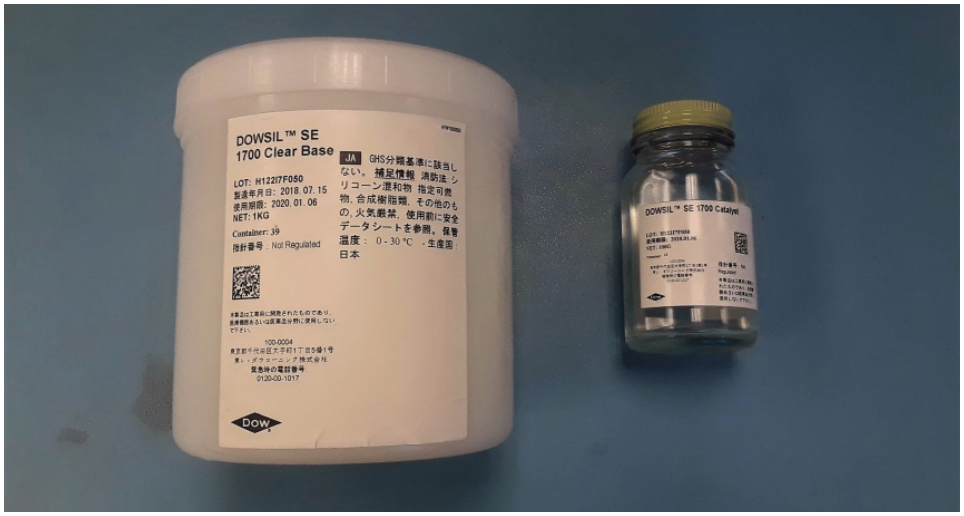

Figure 2. Dowsil SE 1700 base (left) and catalyst (right).

Figure 3. EpoThin hardener (left) and resin (right).

Once the optimal curing conditions and sizes of pucks were determined, the loading powder was shifted from $BaTiO_3$ to the La-doped material. For this second round of tests, the pucks were molded to a uniform size and shape along with adding copper disks to each side to serve as electrodes. To create these pucks, the epoxy and silicone were individually mixed in the same manner as the first round, with varying percentages of the doped powder added. The silicone pucks were made by placing one copper disk at the bottom of a cylindrical mold, adding the premixed and uncured silicone/powder formulation, and then placing another copper disk on top. Any excess silicone/powder mixture was squeezed out until the puck was the desired thickness. The epoxy samples were treated similarly, except that due to its low viscosity, the epoxy had to be partially cured before adding it to the mold so that the top disk would not sink. The epoxy/powder composite was placed in the oven, removed to re-mix every five minutes to prevent the powder from settling, and repeated for about 40 m until the epoxy had thickened sufficiently. Then it was added to the mold in the same manner as the silicone/powder mixture. After curing, the molds were cut away and any mixture that was present around the sides was removed using 240 grit paper until smooth (figs. 4–7). During this round of testing, it was discovered that the epoxy mixture would hold together when it was between 80–90 wt.% powder or less, while the silicone would only hold together up to 70 wt.% powder. The 90 wt.% powder epoxy puck was no longer adhesive enough to attach the copper electrodes, so wire leads were connected using conductive epoxy and Kapton® tape. This difference between it and the other pucks led to some difficulties during testing, so some of the data from that sample was found to be out-of-family.

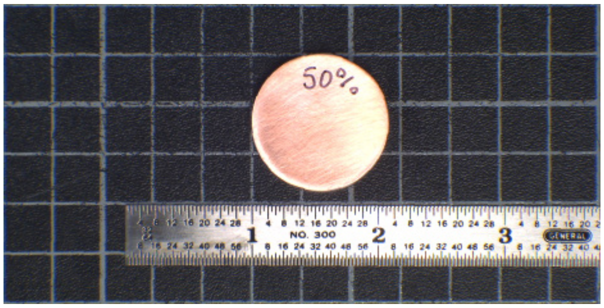

Figure 4. 50 wt.% Epoxy puck front view.

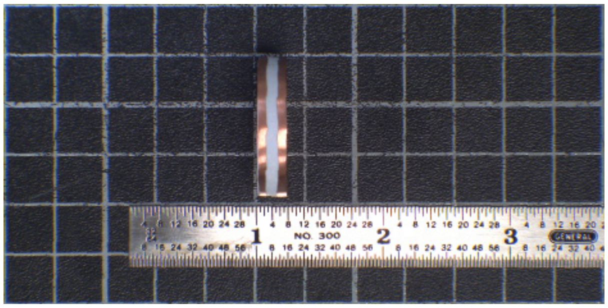

Figure 5. 50 wt.% Epoxy puck side view.

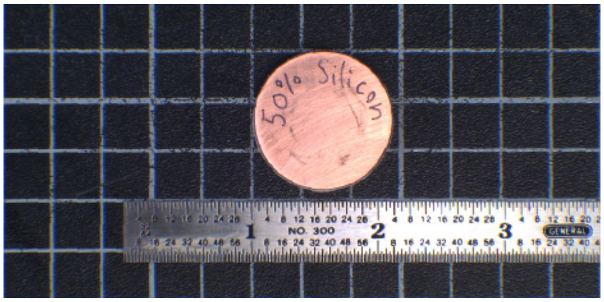

Figure 6. 50 wt.% Silicone puck front view.

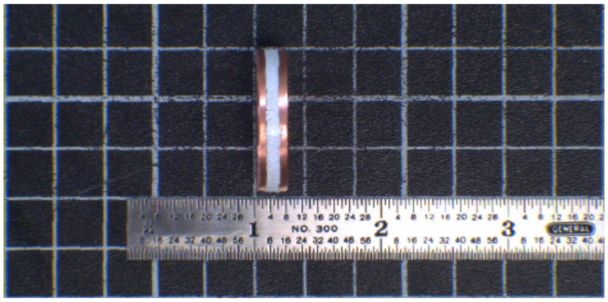

Figure 7. 50 wt.% Silicone puck side view.

After LCR testing the new pucks, the epoxy pucks were discovered to have a high sensitivity to relative humidity (RH). Due to this finding, the epoxy pucks were retested with less of their surface area being covered by copper electrodes to increase the moisture contact area. The copper disks were removed by heating slightly and prying. Then small squares of conductive epoxy were painted on the top surface to create a new electrode. The leads were embedded in the conductive epoxy for ease of measurement. The manufacturer recommended a curing temperature for the conductive epoxy that was too high for the pucks to endure, so a much slower cure was attempted at 85 °C. The slow cure hardened the thin areas of painted epoxy but failed to cure the thicker areas meant to hold the leads in place. This idea was abandoned, so the squares were scraped off and a 3D-printed clamp with metal leads on both sides was used instead. The clamp left more surface area open than the copper rounds, but not as much as originally intended when using the conductive epoxy. Two weeks after the copper electrode pucks were built and tested, three new epoxy pucks with varying weight percentages of powder (a 20 wt.%, a 50 wt.%, and a 70 wt.%) were made with the same method to determine if the results were repeatable.

3.2 Testing the Pucks

For the first batch of pucks, an Agilent/Keysight™ 16451B Dielectric Test Fixture (fig. 8) was connected to a Keysight™ E4980A Precision LCR Meter (fig. 9) to measure the capacitance of each puck and calculate some preliminary DCs. Each puck was placed into the fixture and tested once ‘dry’ (i.e., in normal room conditions) and again with added humidity. Exposing the samples to humidity was very subjective and simply consisted of breathing on the pucks. This would typically drive the instantaneous humidity to between 80–90 RH when checked against a calibrated hygrometer. The typical room temperature humidity for the dry tests ran between 30–40 RH. The puck was then removed from the test fixture and the capacitance of the air at that same distance was recorded. The puck’s dry and humid capacitances were then divided by the corresponding air capacitances to find approximate DCs. These first tests were performed in parallel mode at 1 kHz.

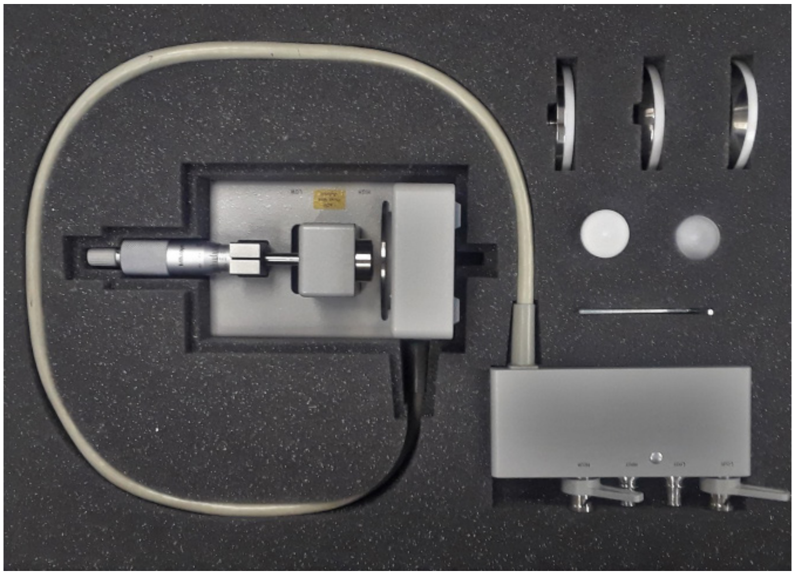

Figure 8. Agilent/Keysight dielectric test fixture.

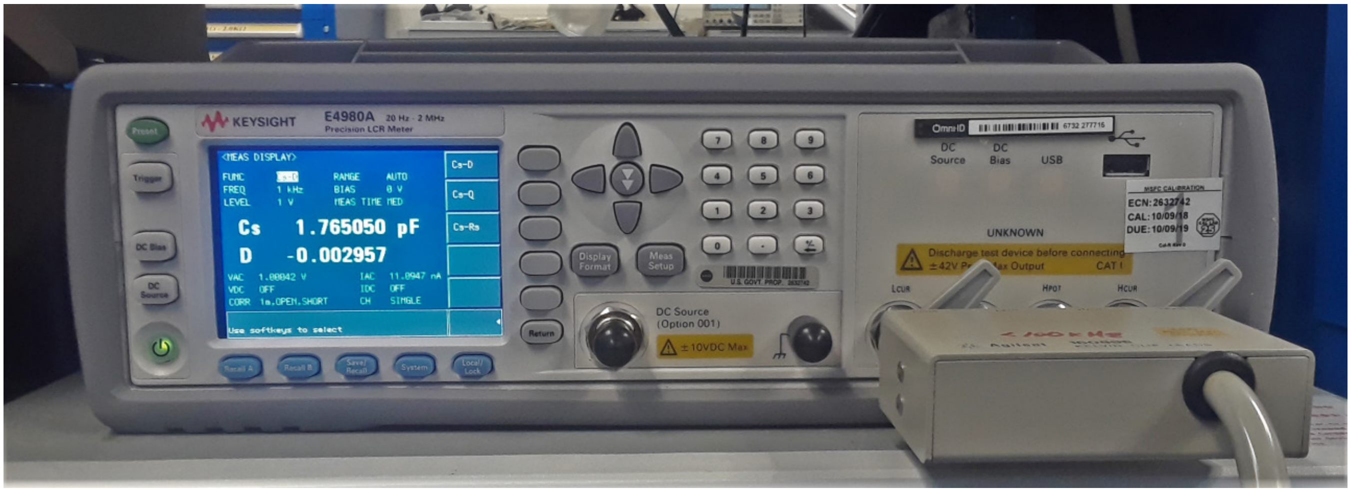

Figure 9. Keysight LCR meter used during puck testing.

Table 1. Dielectric constants of epoxy pucks.

	Test 1		Test 2	
wt.% Powder	DC Dry	DC Humid	DC Dry	DC Humid
0%	3.703704	5.714286	4.166667	6.25
10%	6.105263	8.513514	7.088235	23.27778
50%	15.58696	71.89796	17.45455	101.0417
50%	17.38	61.63462	21.12	79.18367
50%	4	8.857143	3.8	6.894737
50%	20	50.65306	19.95349	46.68
60%	23.7037	33.66667	23.65385	33.08

Table 2. Dielectric constants of silicone pucks.

	Test 1		Test 2	
wt.% Powder	DC Dry	DC Humid	DC Dry	DC Humid
0%	3.181818	3.181818	3	2.8
10%	2.909091	3.090909	4	3.3
10%	3.035714	3.214286	3.32	2.933333
50%	5.296296	6.038462	5.64	5.64
60%	5.409091	5.833333	5.9	5.047619
70%	7.894737	8.666667	8.757576	9.257143

For the second round of testing, where pucks that had copper contacts were used, the dielectric test fixture was no longer needed. The capacitance of each of the new pucks was measured so that the dielectric constants could be calculated. Tests were done in series mode both dry and with added humidity at 20 Hz, 1 kHz, 10 kHz, and 100 kHz. The area of the copper disks was calculated from their measured diameter along with the distance between each set of copper plates. Equation 2 was used to calculate the DC. The 90 wt.% powder epoxy puck tested normally under dry conditions, but due to the anomalies in its construction, it did not absorb the humidity the same as the others and thus gave unreliable data. However, the data is provided in table 3. The three pucks that were made later to verify repeatability were tested the same way.

Table 3. Puck capacitances (pF).

		Dry				**Humid**			
	Frequency (wt. % Powder)	20 Hz	1,000 Hz	10,000 Hz	100,000 Hz	20 Hz	1,000 Hz	10,000 Hz	100,000 Hz
Silicone	0%	9.15	9.19	9.17	9.161	10.21	10.05	9.43	9.31
	20%	9.49	11.96	11.9	11.85	11.33	11.65	11.63	11.64
	30%	16.57	15.98	15.86	15.78	17.49	16.87	16.59	16.43
	40%	16.55	15.78	15.64	15.53	16.43	15.58	15.41	15.32
	50%	18.07	15.78	17.75	17.59	20.35	19.19	18.05	17.74
	60%	25.64	24.88	24.57	24.29	27.19	25.58	24.69	24.49
	70%	32.34	30.68	30.19	29.76	34.42	32.36	31.08	30.73
Epoxy	0%	14.24	13.31	12.98	12.45	3,190	761	21	12
	20%	17.12	16.48	16.21	15.84	1,225,000	13,220	261.7	19.34
	30%	17.58	17.23	16.92	16.52	1,050,000	5,417	98.7863	18.225
	40%	21.71	21.08	20.65	20.13	1,040,000	3,721	80.31	21.77
	50%	31.46	29.8	29.05	28.21	1,201,840	5,576.64	118.404	29.42
	60%	46.01	43.46	42.12	40.73	1,300,000	113.82	43.09	41.28
	70%	62.43	57.58	55.55	53.63	1,101,520	3,840.6	112.966	55.16
	80%	79.32	73.25	70.73	68.55	337,309	2,648.98	112.264	70
	90%	105.11	82.293	65.46	53.53	171	95	73	58

Once the copper had been removed from the first batch of epoxy pucks, they were placed in a 3D-printed clamp (fig. 10) then tested in dry and humid conditions at the same four frequencies to check for any differences in sensitivity. This round of tests revealed similar results to the previous test, with no significant difference from the slightly larger open surface area.

Figure 10. Photograph of 3D-printed clamp.

4. ANALYSIS

Once all the measurements for the capacitances of the uniform pucks were taken, each puck's DC was calculated using each one's measured dimensions. Results of these calculations are in table 4. The DCs were calculated using equation 2, rearranged to solve for ε_r. The calculated DCs were then plotted. The humid epoxy measurements were plotted using a logarithmic scale since there were large differences between the frequencies (figs. 11–14). All of the pucks had slightly higher DCs and were more responsive in humidity at lower frequencies.

Overall, the epoxy pucks had more desirable test results than the silicone pucks. The epoxy pucks had higher DCs in room conditions and exhibited even higher DCs when exposed to humidity. A comparison of the two materials in room conditions (fig. 15) and with added humidity (fig. 16) can be seen in table 5. The data for the 90 wt.% powder epoxy pucks with added humidity was not included in these graphs due to the pucks' inconsistent construction and test results. The second batch of pucks made to confirm the results of the first batch of electrode pucks showed similar results, a comparison of which is shown in figure 17.

Table 4. Dielectric constants of silicone-filled copper electrode pucks.

	Frequency (wt.% Powder)	0%	20%	30%	40%	50%	60%	70%
Dry	20 Hz	3.457	3.427	5.984	6.253	7.262	9.308	12.998
	1 kHz	3.472	4.319	5.771	5.962	6.342	9.032	12.331
	10 kHz	3.464	4.298	5.728	5.909	7.134	8.919	12.134
	100 kHz	3.461	4.280	5.699	5.868	7.069	8.818	11.961
Humid	20 Hz	3.778	4.092	6.317	6.208	8.179	9.870	13.834
	1 kHz	3.778	4.207	6.093	5.886	7.713	9.286	13.006
	10 kHz	3.400	4.200	5.992	5.822	7.254	8.963	12.492
	100 kHz	3.400	4.204	5.934	5.788	7.130	8.890	12.351

Table 5. Dielectric constants of epoxy-filled copper electrode pucks.

	Frequency (wt.% Powder)	0%	20%	30%	40%	50%	60%	70%	80%	90%
Dry	20 Hz	4.908	5.773	5.926	7.985	10.663	14.828	21.854	27.473	43.999
	1 kHz	4.587	5.731	5.808	7.572	10.100	14.006	20.157	25.371	34.448
	10 kHz	4.473	5.633	5.703	7.424	9.846	13.574	19.446	24.498	27.401
	100 kHz	4.291	5.504	5.568	7.239	9.561	13.1267	18.774	23.743	22.407
Humid	20 Hz	1,098.997	689,460.5	476,071.5	796,265.4	577,500.6	613,875.3	486,919.2	412,462.3	116.982
	1 kHz	262.174	12,300.12	6,656.799	7,796.511	5,279.316	4,147.699	3,239.322	2,695.71	40.376
	10 kHz	7.234	379.477	158.151	144.456	104.296	79.506	71.957	70.758	30.796
	100 kHz	4.134	10.923	7.971	9.361	11.327	14.805	20.273	26.067	24.619

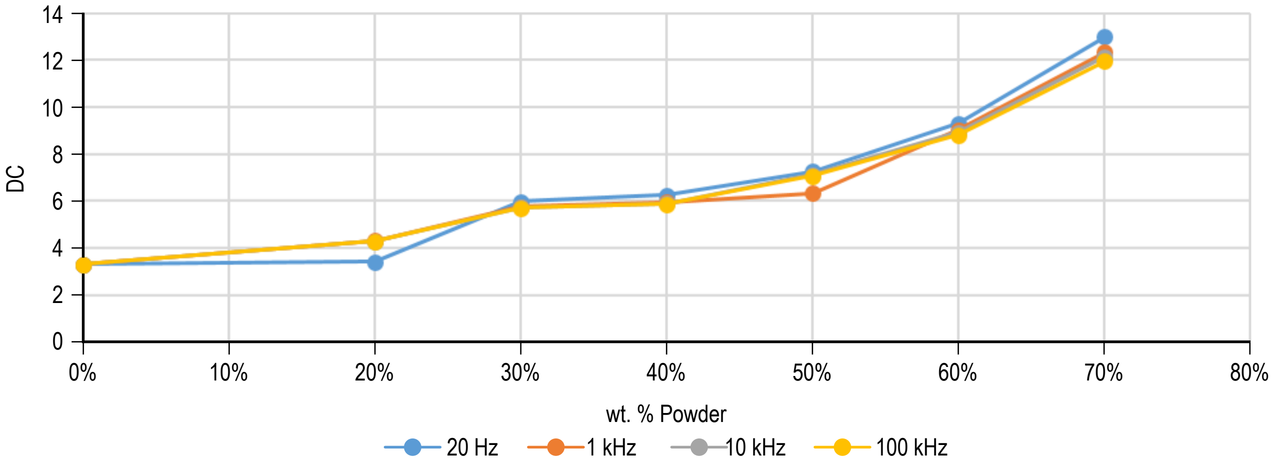

Figure 11. Silicone puck DCs in room conditions.

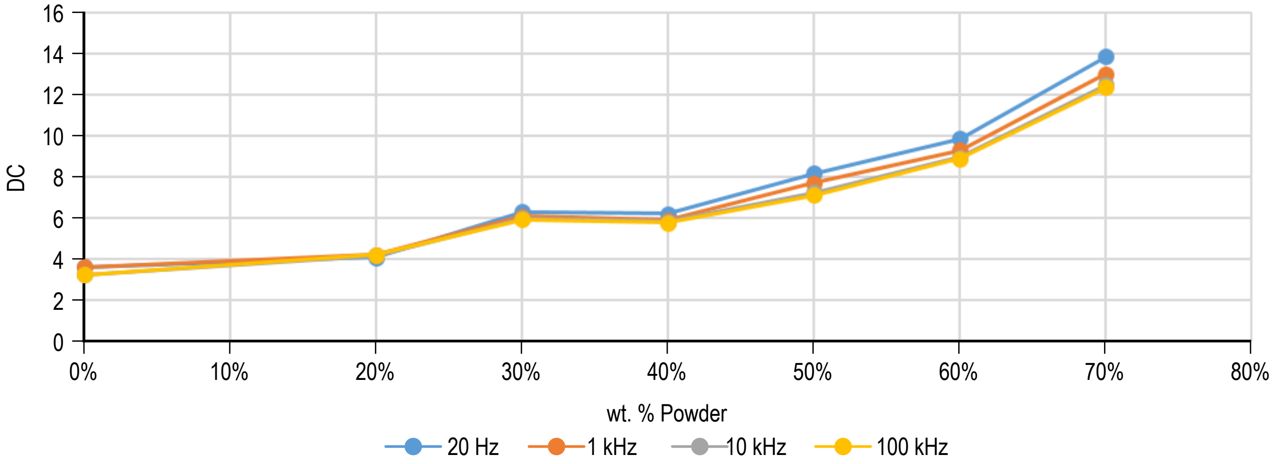

Figure 12. Silicone puck DCs with added humidity.

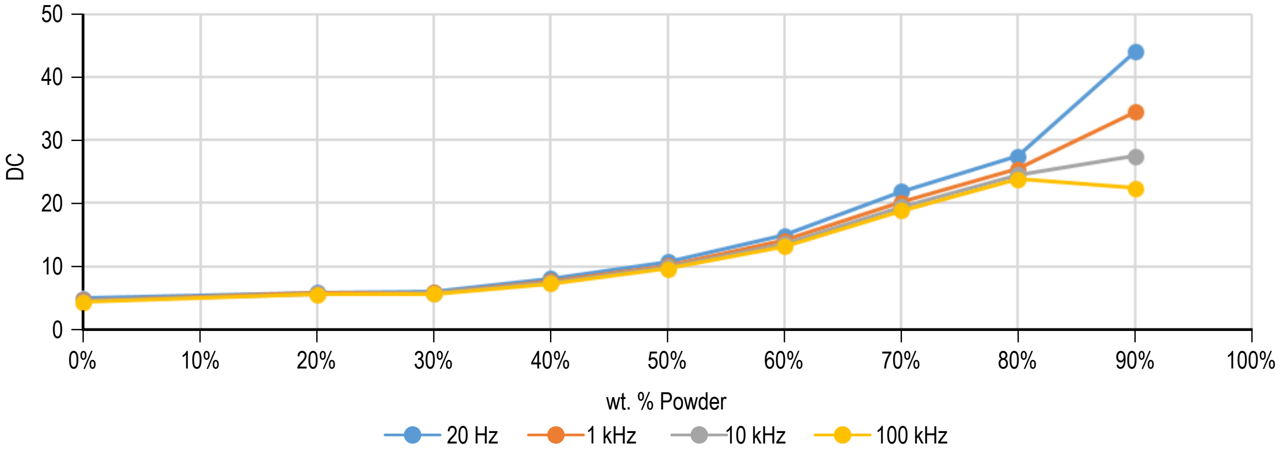

Figure 13. Epoxy puck DCs in room conditions.

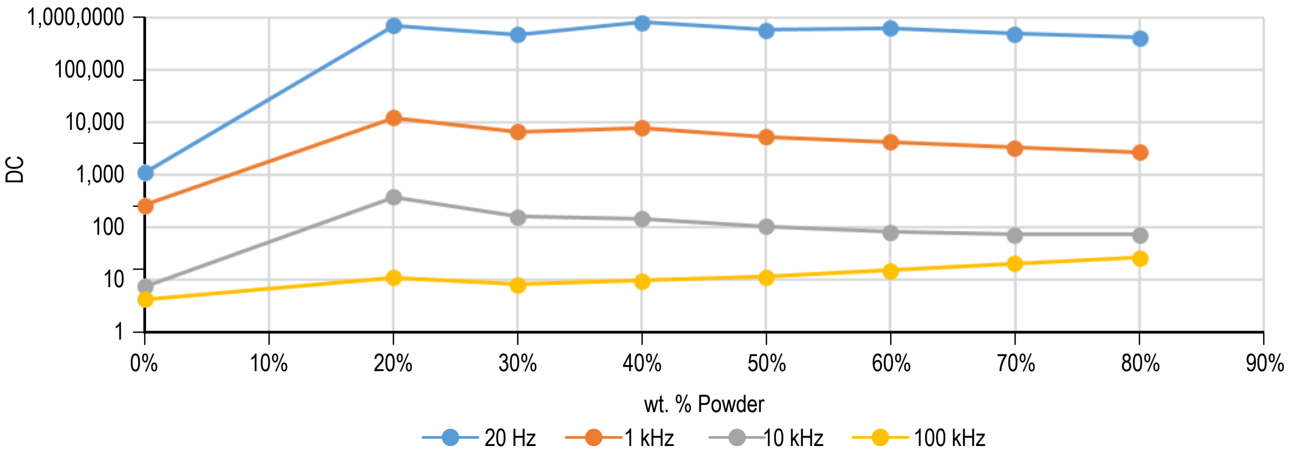

Figure 14. Epoxy puck DCs with added humidity (log scale).

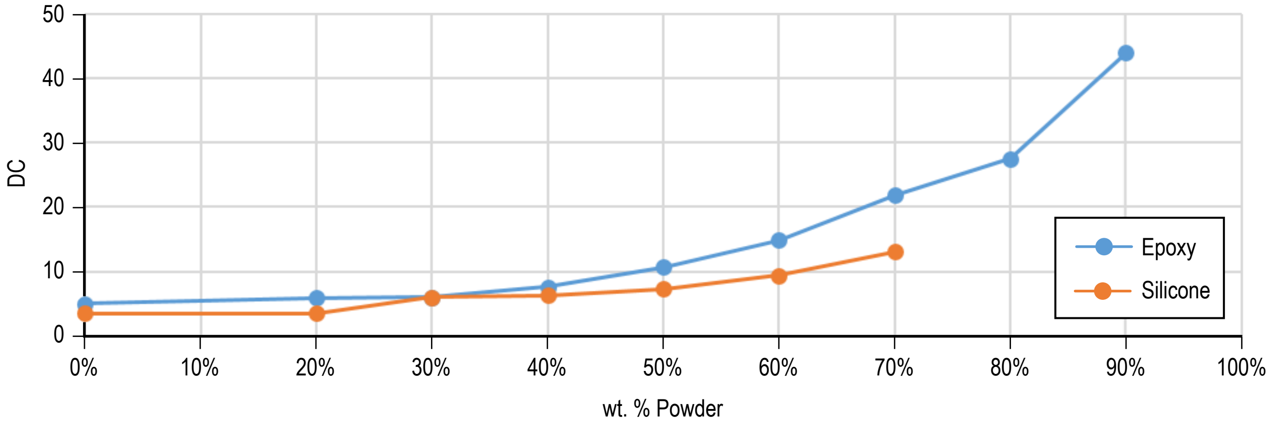

Figure 15. Comparison of epoxy and silicone DC measurements at 20Hz in room conditions.

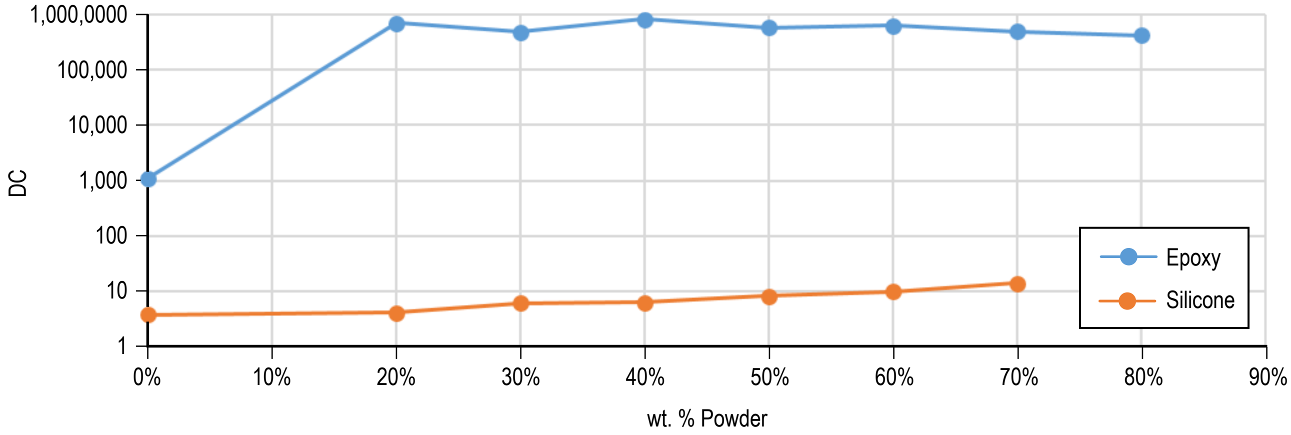

Figure 16. Comparison of epoxy and silicone DC measurements at 20Hz with added humidity (log scale).

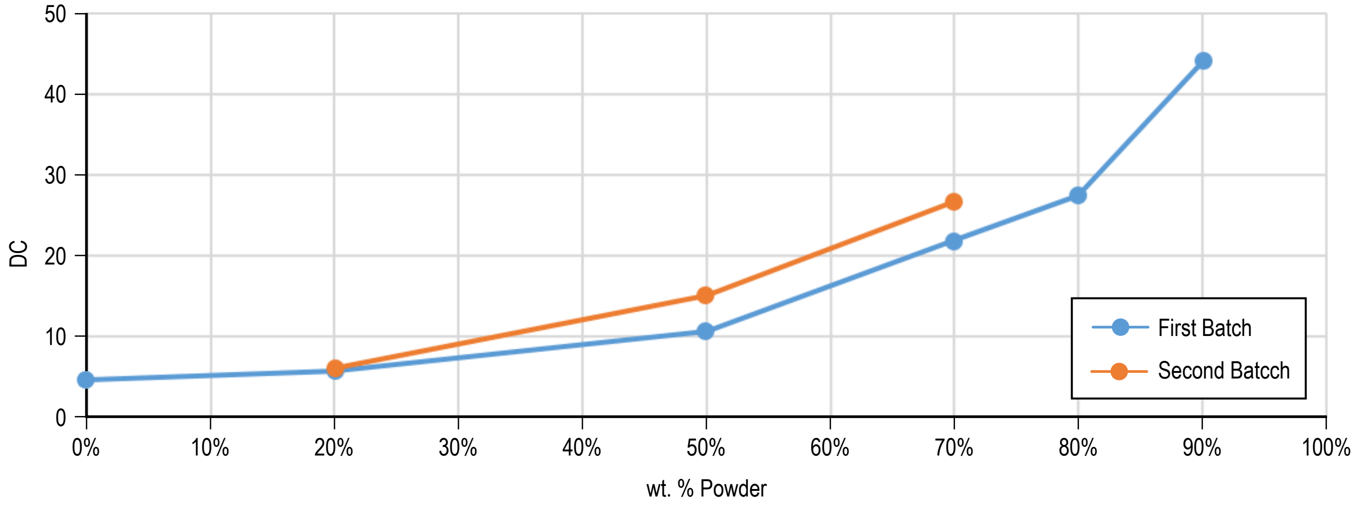

Figure 17. Comparison of DC results from first and second batches of copper electrode pucks.

5. CONCLUSION

Materials and manufacturing processes to create composite pucks via a ceramic-powder-loaded polymer were explored. The data provided new insight into how a low-temperature solid-state ultracapacitor could be constructed in future. Of the two polymers tested, the epoxy outperformed the silicone in every phase, making it appear to be a good option for future testing. Valuable information on how the doped powder works when added to a polymer was gained. New parameters that will help speed future research, such as the maximum weight percentage of powder that can be loaded into these particular polymers successfully and the effects of curing both polymers at different temperatures, were determined. Another unexpected outcome of this research was the discovery of the doped powder's sensitivity to humidity in the polymer matrix. This potentially has applications in the humidity sensing market. Finally, further study is required to determine if a polymer loaded with doped powder could possibly be used as the dielectric for a solid-state ultracapacitor. For example, charge/discharge testing needs to be conducted to determine power density performance.

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