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Effect of processing conditions and electrode characteristics on the electrical properties of structural composite capacitors

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ABSTRACT

Structural capacitors are manufactured from glass fabric/epoxy prepreg dielectrics and metalized polymer film electrodes. The electrical breakdown strengths of these multifunctional materials are investigated across a wide range of electrode constructions and processing parameters. The results show that electrode selection and materials processing have a significant impact on the energy that the device can store. Also, this careful consideration of processing parameters and electrode construction has led to the development of a structural capacitor with an energy density exceeding 0.90 J/cm^3 , the highest yet reported.

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1. Introduction

There has been significant interest in developing multifunctional materials that both store energy and support mechanical load, referred to as structural power devices [1–8]. By combining energy storage and structural functions, such materials offer the possibility to reduce platform weight and volume, resulting in performance improvements such as vehicles with increased fuel economy and range, satellites with reduced launch masses, and electronics with more compact form factors. Several researchers have pursued a variety of structural power concepts including structural capacitors [8,9], batteries [2–4,10], supercapacitors [11,12] and fuel cells [13,14]. Regardless of the energy storage mechanism, combining energy storage and structure often involves a reduction in per-mass or per-volume performance for the structural and/or energy storage functions when compared to their conventional, monofunctional counterparts. Despite this compromise, the multifunctional approach can lead to overall volume or mass savings because the same mass and volume elements are performing energy storage and mechanical functions simultaneously. The performance thresholds necessary to achieve mass or volume savings have been derived and expressed in terms of a minimum multifunctional performance metric [15].

In the present work we study how processing and environmental conditioning affect the performance of structural

capacitors, multifunctional materials that could enable mobilizing pulsed power-based technologies such as electromagnetic armor, rail guns, and high energy lasers. Earlier contributions demonstrated the feasibility of achieving system-level weight [15] and volume [16] savings with a structural capacitor made from a continuous glass fiber reinforced epoxy dielectric, sandwiched between metallized polymer film electrodes (Fig. 1). The results showed that the choice of dielectric material has a significant effect on structural capacitor energy density. It was also found that the breakdown strength decreases with increasing fiber volume fraction, a result consistent with another investigation [17]. Unfortunately, the mechanism causing this decrease was unclear. It is possible that the electric field concentration caused by the dielectric mismatch between the glass and polymer constituents results in an increased probability of a critical flaw at higher fiber volume fractions. However, an increase in void content accompanying the increased fiber volume fraction confounded the experimental results. Like reinforcing fibers, voids would also act as electric field stress raisers that could precipitate breakdown in the surrounding matrix, or directly initiate breakdown due to the relatively low dielectric strength of the gas-filled void relative to the solid polymer matrix. Also, specimens cured at higher pressures had higher breakdown strengths, possibly as a result of decreased void content. Several researchers have shown that voids can play a significant role in the performance of capacitors [18,19]. In other work Flandin et al. [20] showed that the extent of reaction plays an important role in breakdown strength of polymer composite dielectrics. Together, these results suggest that processing plays a significant role in the performance of structural capacitors.

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Fig. 1. Schematic of a structural capacitor. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In addition to processing and environmental conditions, we study the effects of electrode characteristics (metallization type, thickness, and carrier material) on the energy density of structural polymer composite capacitors. Previous work has shown that these parameters can affect performance of conventional capacitors. For example, researchers have shown that breakdown strength in solid dielectrics has a positive correlation with the electrode metal's work function, suggesting that a greater work function necessitates more energy to liberate a surface electron [21,22]. If such electrons participate in the cascade that causes the breakdown event, selecting an electrode material with a high work function (thus limiting the source of electrons) might increase breakdown strength. In another work considering electrode properties, Sato et al. studied the effect of electrode roughness and found that the breakdown strength decreased as the electrode roughness increased [23].

The sections that follow describe a series of experiments conducted on single dielectric layer capacitors. These experiments investigate the effect of a range of parameters on the breakdown strength, including processing method, processing pressure, cure cycle, humidity, electrode metallization type, metallization thickness, and electrode carrier material. The experimental techniques for manufacturing and testing the capacitor specimens are described first, followed by a presentation and interpretation of the results.

2. Experimental

2.1. Materials

For this study, sixteen sets each of at least five capacitor specimens were constructed using geometries similar to a previous study, Figs. 2a and 3a [15]. A range of processing conditions and laminate constructions, outlined in Table 1, were used in order to study their effects on capacitor performance. All capacitors consisted of layers of glass fabric-reinforced prepreg interleaved

with thin metallized films of paper, polyimide (PI), or biaxially oriented polypropylene (BOPP). The prepreg material used for most specimens consisted of an FR4-type epoxy reinforced with a style 2116 woven E-glass (N4205-6FC, Nelicote, Northfield MN). Two capacitor sets, used to study the effect of pressure on breakdown strength, were constructed from a structural epoxy prepreg reinforced with a style 120 woven E-glass (120-765, Nelicote). Both prepregs were approximately 100 μm thick. The PI electrode carrier material was 12.7 μm thick with a 100 nm layer of aluminum on one side (146454-004, Sheldahl Inc., Northfield MN). The BOPP films (Bollor Inc. Dayville, CT) had metallizations of either Al, Zn, or a Zn–Al alloy in thickness ranges from 4.3 to 12 nm (10–4 Ω/sq). While the precise composition of the Zn–Al alloy was not specified, the manufacturer indicated that the metallization is mostly Zn with a small amount of Al added to improve stability against atmospheric corrosion [24]. Rutherford backscattering spectroscopy indicated an atomic ratio of 9:1 Zn for Zn to Al. All paper carriers (Winter-Wolff International, Inc., Jericho, NY) were 8 μm thick, 1.3 g/cm^3 density, with Al metallizations ranging from 7 nm to 54 nm (4–0.5 Ω/sq). All electrode metal resistivity values were provided by the electrode manufacturers, and electrode metal thickness was calculated using the manufacturer-provided sheet resistivities along with the bulk resistivities of aluminum and zinc, 2.65 $\mu\Omega\text{-cm}$ and 5.92 $\mu\Omega\text{-cm}$, respectively [25]. Copper tape with an electrically conductive pressure-sensitive adhesive (05012D-AB, 3 M via SPI Supplies, West Chester, PA) and conductive silver paint (05002-GA, SPI Supplies) were used to enhance connectorization, as described below.

2.2. Manufacturing

2.2.1. Layup and connectorization

Prior to layup, prepregs were wiped with technical wipes (TX612, Texwipe, Mahwah NJ) that were partially soaked in 100% ethanol. Compressed nitrogen was then blown on prepregs and electrodes to help remove any remaining surface dust. A previous study showed that cleaning the constituent materials greatly improves their dielectric breakdown strength [26].

Two types of capacitors were fabricated, “unencapsulated” and “encapsulated”. All polyimide electrode capacitors, sets 1–7, were unencapsulated and consisted of one prepreg ply sandwiched between two electrode layers, as seen in Fig. 2. The metallized faces of the electrodes both faced the same direction, as this is the configuration that would be used in a capacitor with multiple dielectric layers. As such, one layer of the electrode support film was present in the dielectric layer of all capacitors. Encapsulated

Fig. 2. (a) Schematic and (b) photograph of unencapsulated capacitors, sets 1–7. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. (a) Schematic and (b) photograph of encapsulated capacitors, sets 8–16. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Construction and processing parameters for the capacitors studied in this work.

Set	Dielectric Material	Electrode			Cure cycle			
		Carrier (thick., μm)	Metal (thick., nm)	Resistivity (Ω/sq)	Method ^a	Pressure (kPa)	Temp. ^b	Pre/post-cure conditioning
1	2116-FR4	PI (12.7)	Al (100)	≤1	HP	1379	A	N/A
2	2116-FR4	PI (12.7)	Al (100)	≤1	HP	3034	A	N/A
3	2116-FR4	PI (12.7)	Al (100)	≤1	HP	5928	A	N/A
4	120-765	PI (12.7)	Al (100)	≤1	AC	345	B	N/A
5	120-765	PI (12.7)	Al (100)	≤1	AC	1379	B	N/A
6	2116-FR4	PI (12.7)	Al (100)	≤1	AC	1379	C	N/A
7	2116-FR4	PI (12.7)	Al (100)	≤1	AC	1379	C	Post-cured
8	2116-FR4	Paper (8)	Al (7–14)	2–4	AC	1379	D	Post-humid.
9	2116-FR4	Paper (8)	Al (7–14)	2–4	AC	1379	D	Post-ambient
10	2116-FR4	Paper (8)	Al (7–14)	2–4	AC	1379	D	Post-dried
11	2116-FR4	BOPP (11)	Zn (6–12)	5–10	AC	1379	E	N/A
12	2116-FR4	BOPP (6)	Zn–Al (4.3–8.7)	5–10	AC	1379	E	N/A
13	2116-FR4	BOPP (4.5)	Al (3.4–6.8)	4–8	AC	1379	E	N/A
14	2116-FR4	Paper (8)	Al (27–54)	0.5–1	AC	1379	E	N/A
15	2116-FR4	Paper (8)	Al (7–14)	2–4	AC	1379	E	N/A
16	2116-FR4	Paper (8)	Al (7–14)	2–4	AC	1379	D	No top plate

^a HP ≡ hot press, AC ≡ autoclave.

^b Temperature cycle specified as A: Ramp 3.5 °C/min to 180 °C, hold for 60 min, cool at –4 °C/min, B: Ramp 3.5 °C/min to 130 °C, hold for 90 min, cool at –3 °C/min, C: Ramp 3.5 °C/min to 180 °C, hold for 60 min, cool at –3 °C/min, D: Ramp 3.5 °C/min to 149 °C, hold for 60 min, Ramp 3.5 °C/min to 177 °C, hold for 60 min cool at –4 °C/min, E: Ramp 3.5 °C/min to 149 °C, hold for 60 min, Ramp 5 °C/min to 170 °C, hold for 60 min cool at –4 °C/min.

capacitors were constructed using one layer of prepreg between electrodes, with an additional prepreg layer placed outside each electrode layer (Fig. 3). This configuration, as compared to the unencapsulated configuration, provides a more realistic representation of a scaled structural capacitor, as all dielectric layers in a multi-layer laminated capacitor will be mechanically confined between other dielectric layers. All capacitors incorporating paper or BOPP electrodes (sets 8–16) were encapsulated.

Connectorization directly to metallized films and papers is challenging, particularly since the metallization is very thin. Direct physical connectorization, for example with a spring-tensioned alligator clip, tends to induce local breakdown at contact points, leading to rapid erosion of the metallization layer and a degradation of electrical connectivity. Industrial capacitors typically use techniques such as flame-sprayed metals to create robust connectorizations. In this study samples were connectorized by applying copper tape to the free ends of the electrode films. For the polyimide electrodes, the copper tape was applied directly to the film,

while for all other capacitor specimens, conductive silver paint (05002-GA, SPI Supplies, West Chester, PA) was applied to each electrode's free end and allowed to dry before attaching the copper tape.

2.2.2. Processing

Table 1 summarizes the cure conditions used for the sample sets reported in this study. Capacitor sets 1–3 were fabricated in a hot press (HP, C400, Hull Industries Inc., New Britain, PA). The electrode and prepreg layers were arranged as shown in Fig. 4 and placed between 2 mm thick sheets of Teflon, which were then placed between two aluminum caul plates, each 61 × 61 × 1 cm. Each set was then placed in the hot press, and the appropriate pressure was applied according to the table.

Capacitor sets 4–16 were processed in a custom-manufactured autoclave (AC), 1 × 2 m inner dimensions (Thermal Equipment Corporation, Los Angeles CA). Sets 4–7 were arranged as shown in Fig. 4, with the capacitors placed between 2 mm thick sheets

Fig. 4. Schematic of layup configuration for unencapsulated capacitors of sets 1–7. The right schematic shows the process stack prior to placement of another Teflon plate and then aluminum plate on top of the stack. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of Teflon, which were then placed between two aluminum plates, each $61 \times 61 \times 1$ cm. The assembled plates were placed inside a vacuum bag, and 711 mmHg vacuum applied. For sets 4 and 5, each set was placed in the autoclave, and either 345 or 1379 kPa of pressure was applied, respectively. After cure, all unencapsulated capacitors were cut to coupon size with dry scissors as shown in Fig. 2b.

Capacitor sets 8–16 were arranged as shown in Fig. 5, with the capacitors placed between 2 mm thick sheets of Teflon, which were then placed between two aluminum plates, each $61 \times 61 \times 1$ cm. The assembled plates were placed inside a vacuum bag, and 711 mmHg vacuum applied. After each set was placed in the autoclave, a pressure of 1379 kPa (200 psi) was applied to the assembly. Capacitor sets 8–10, used to study the effects of humidity on capacitor performance, were processed and cured simultaneously for direct comparison. Capacitor set 16 was arranged and processed identically to the other autoclaved specimens, except for changes in the supporting plates and release material. A thin brown Teflon-coated fiberglass release sheet (RE234 TFNP50, Airttech International Inc., Huntington Beach, CA) was placed on either side of the capacitors, instead of the 2-mm-thick white Teflon plates used in other samples. Additionally, the layup of set 16 did not use a top aluminum plate to cover the capacitor array. After cure, all encapsulated capacitors were cut to coupon size as shown in Fig. 3b.

For density determination three “neat” composite laminates, without electrode interlayers, were manufactured in an autoclave. The laminates were manufactured with processes similar to those of specimen sets 4, 5, and 6. One laminate was manufactured from 2116-FR4 material and cured at 1379 kPa according to cycle ‘C’ (Table 1) while the other two were manufactured from 120–765 prepreg with cycle ‘B’ at 345 kPa and 1379 kPa, respectively. After manufacture these panels, 12 plies thick and nominally 200×125 mm, were cut into 28×28 mm specimens for density measurement via displacement in water [27].

2.2.3. Post-processing

Capacitor sets 7–10 were subject to additional processing steps after initial processing. Capacitors of set 7 were post-cured by placing the samples in an oven at 185°C for 24 h, with constant nitrogen flow. Capacitors of set 8 were put in a humidity chamber (CFR-7552C-4, Blue M, White Deer, PA) for 8 days at 95% relative humidity and 30°C , while set 9 capacitors were placed in a zip-seal bag and left in the laboratory for 8 days. Relative humidity in the laboratory was measured at 53%, and temperature was measured at 21°C , although the atmosphere in the laboratory may fluctuate. Capacitors of set 10 were placed in a glovebox with constant low-flow nitrogen purge, and Dri-Rite (238988-454G, Sigma-Aldrich, St. Louis, MO) to maintain relative humidity at 2%. Temperature was the same as laboratory ambient temperature, approximately

Fig. 5. Schematic of layup configuration for encapsulated capacitors of sets 8–16. The right schematic shows the process stack prior to placement of another Teflon plate and then aluminum plate on top of the stack. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

21 °C, and may have fluctuated slightly over the 8 day treatment period.

2.3. Testing

The humidity-conditioned capacitors, sets 8–10, were tested within 5 min of removal from their respective chambers. All other specimens were kept in zip-seal bags under ambient laboratory conditions and tested within two weeks of manufacture. The capacitance of each specimen was measured with a portable LCR meter (879, B&K Precision Corp., Yorba Linda, CA) at 120 Hz, and the total thickness was measured directly using digital calipers. Dielectric breakdown testing was carried out using ASTM 3755–97 as a guideline [28]. Each capacitor was placed in mineral oil (3190K629, McMaster-Carr, Elmhurst, IL), and voltage was applied using a Glassman series FC high voltage power supply (FC60N2, Glassman High Voltage Inc., High Bridge, NJ). Voltage was ramped from 0 to 60 kV at a rate of 100 V/s.

During testing, voltage across the capacitor was recorded at 100 Hz using a LabView interface (version 2010, with modules NI 9215 and NI cDAQ-9178, National Instruments, Austin, TX). Samples typically underwent multiple voltage drops during the voltage ramp due to clearing events, short duration electrical shorts between electrodes due to localized dielectric breakdown. For electrodes with thin metallization, these events locally erode the electrode metallization and can “clear” the short by isolating the flaw from rest of the electrode, enabling continued capacitor operation in the presence of flaws [29]. After testing, the data were analyzed to identify each clearing event, registered as a drop in voltage of 500 V or more. Through this analysis, it was possible to create data sets of the voltage and time of each clearing event. Capacitor energy densities at the first and 50th clearing events are reported here as primary metrics for comparison of materials. The 50th clearing event metric was chosen to represent the capacitor's maximum operating voltage, although other failure criteria are also possible. Energy densities at the 50th clearing event are calculated based on the initial capacitance measurement. However, since clearing events erode the electrodes and reduce capacitance, the reported 50th clearing event energy densities may be somewhat higher than the true energy densities. Voltage application ended when the capacitor could be considered “failed,” typically as evidenced by the inability of the capacitor to sustain voltage. This failure mechanism is induced by the presence or formation of a flaw that cannot be cleared by local erosion of electrode metallization, resulting in a permanent short through the capacitor. Failure could

also result from isolation of the composite dielectric from the voltage supply due to excessive erosion of the electrode.

3. Results

Table 2 shows property data for each of the capacitor sets considered in this study. The capacitor densities were estimated from the thicknesses and densities of the dielectric and electrode layers, assuming electrode densities of 1.42 g/cm³ [30], 0.90 g/cm³ [31], and 1.30 g/cm³ for polyimide, BOPP and paper, respectively. The neat 120–765 laminates processed at 345 kPa and 1379 kPa, had densities of 1.89 g/cm³ and 2.01 g/cm³, respectively, while the neat 2116-FR4 laminate had a density of 1.77 g/cm³. In estimating the capacitor densities of the various 2116-FR4 sets, we assume a density of 1.77 g/cm³ for all specimens processed at 1379 kPa. For the 2116-FR4 specimens processed at higher pressure, we estimate the density by assuming that any decrease in thickness is a result of eliminating some of the epoxy, with density 1.20 g/cm³ [31]. The table also includes values for each set's volume- and mass-normalized energy densities calculated from for the 1st and 50th clearing events. Volume-normalized energy density is traditionally used to compare dielectric capacitors although, for achieving mass-savings via multifunctionality, the mass-normalized energy density is more relevant [15]. A small number of samples, approximately 12%, did not reach the 50th clearing event before failure. The data for such samples were not included in the 50th clearing event energy storage calculations shown in Table 2. However, each set consisted of at least five capacitors that survived past 50 events. Capacitance, which is primarily determined by dielectric thickness and dielectric constant, does not change significantly across the samples. However, there is a significant variation in breakdown strength, from 63 V/μm to 211 V/μm at the 50th clearing event, which leads to greater than 10× spread in energy density across all materials and conditions considered.

3.1. Electrode effects

Fig. 6 shows the energy density of capacitors made with various electrode constructions, varying surface resistivity (sets 14–15), metallization (sets 11–13), and carrier material (sets 13 and 15). Considering resistivity, there is an increase in maximum energy density at low surface resistivity, from less than 1 Ω/sq to approximately 3 Ω/sq where there are increases of both the initial and 50th clearing events. Also, the metallization type has a significant effect on performance among the metals considered, with the

Table 2
Dielectric and physical properties of capacitor specimens.

Set	Dielectric thickness (mm)	Density (g/cm ³)	Capacitance (nF)	Energy density, volume (J/cm ³)		Energy density, mass (J/g)	
				1st	50th	1st	50th
1	0.124 ± 0.013	1.74	2.12 ± 0.32	0.391 ± 0.135	0.729 ± 0.145	0.226 ± 0.078	0.420 ± 0.084
2	0.118 ± 0.015	1.76	2.01 ± 0.29	0.502 ± 0.165	0.912 ± 0.190	0.285 ± 0.094	0.518 ± 0.108
3	0.113 ± 0.018	1.79	2.04 ± 0.61	0.543 ± 0.225	0.988 ± 0.211	0.303 ± 0.125	0.552 ± 0.118
4	0.115 ± 0.006	1.84	2.51 ± 0.120	0.042 ± 0.029	0.098 ± 0.016	0.023 ± 0.016	0.053 ± 0.009
5	0.108 ± 0.009	1.95	2.71 ± 0.130	0.197 ± 0.143	0.640 ± 0.140	0.101 ± 0.073	0.328 ± 0.072
6	0.149 ± 0.004	1.74	1.65 ± 0.058	0.403 ± 0.091	0.595 ± 0.087	0.231 ± 0.053	0.341 ± 0.050
7	0.122 ± 0.004	1.73	1.80 ± 0.070	0.575 ± 0.201	0.883 ± 0.172	0.332 ± 0.116	0.509 ± 0.099
8	0.143 ± 0.002	1.74	2.15 ± 0.102	0.116 ± 0.042	0.234 ± 0.009	0.066 ± 0.024	0.134 ± 0.005
9	0.139 ± 0.002	1.74	1.71 ± 0.04	0.377 ± 0.092	0.500 ± 0.058	0.216 ± 0.053	0.287 ± 0.033
10	0.141 ± 0.006	1.74	1.81 ± 0.06	0.365 ± 0.235	0.552 ± 0.066	0.209 ± 0.135	0.316 ± 0.038
11	0.146 ± 0.006	1.73	1.09 ± 0.358	0.195 ± 0.051	0.290 ± 0.093	0.113 ± 0.030	0.166 ± 0.054
12	0.138 ± 0.004	1.73	1.47 ± 0.047	0.437 ± 0.090	1.200 ± 0.518	0.252 ± 0.052	0.690 ± 0.299
13	0.148 ± 0.003	1.74	1.44 ± 0.055	0.309 ± 0.078	0.441 ± 0.107	0.177 ± 0.045	0.253 ± 0.062
14	0.145 ± 0.007	1.75	1.94 ± 0.131	0.159 ± 0.106	0.296 ± 0.103	0.091 ± 0.061	0.170 ± 0.059
15	0.131 ± 0.005	1.74	1.80 ± 0.082	0.477 ± 0.194	0.834 ± 0.078	0.274 ± 0.111	0.479 ± 0.045
16	0.151 ± 0.003	1.74	1.66 ± 0.051	0.806 ± 0.094	0.939 ± 0.083	0.462 ± 0.054	0.538 ± 0.048

Fig. 6. Performance of structural capacitors for various electrode constructions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 7. Effect of processing and environmental conditions on capacitor performance. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

energy density of the Zn–Al specimen at least twice that of Zn, although we note the large standard deviation of the Zn–Al 50th clearing result. Finally we observe that electrodes on a paper carrier result in a higher energy density than those on BOPP.

3.2. Processing and environmental effects

Fig. 7 shows the effects of various processing and environmental conditions on structural capacitor performance. The most dramatic change is observed across the consolidation pressures considered in this study with both the 1st and 50th clearing event energy densities showing a continuous increase with consolidation

pressure. Between 345 kPa and 1379 kPa the energy density of the 50th clearing event increases by more than six times, to 0.328 J/g, for autoclaved 120–765 prepreg (sets 4 and 5). The increase is less dramatic at higher pressures for the 2116-FR4 prepreg, increasing from 0.42 J/g at 1379 kPa to 0.45 J/g at 5928 kPa in hot-pressed sets 1–3. We also note that the increase in performance with pressure persists across manufacturing method from autoclave to hot press. However, hot pressing resulted in higher performance for the two sets that were processed at 1379 kPa. Fig. 8 shows representative micrographs of polished cross-sections of autoclaved specimens cured at 345 kPa and 1379 kPa. Cross-sections of specimens cured at 1379 kPa had fewer voids than specimens cured at 345 kPa.

Post-curing the specimens resulted in an almost 50% increase in energy density from 0.34 J/g to 0.51 J/g. Finally, the humidity of the capacitor's environment after processing had a significant effect, especially when going from a moderate level (53% RH) to a wet condition (95% RH) where the energy density was measured as 0.29 J/g and 0.14 J/g, respectively.

Figs. 9 and 10 show images and cross sections of specimens that were processed identically in the autoclave at 1379 kPa except that one specimen (set 9, Fig. 9) was processed with a top aluminum plate while the other specimen (set 16, Fig. 10) was processed without the top aluminum plate. As the figures show, the paper electrode of the specimen with the aluminum plate showed extensive wrinkling, while the electrodes remained relatively flat for the specimen processed without a top plate. Comparing the micrographs of the two specimens, we see that the wrinkling results in a significant decrease in the minimum distance between electrodes, from approximately 135 μm to 110 μm, a 19% decrease. Fig. 11 shows the energy densities of the two specimen types. The specimen with wrinkled electrodes, manufactured with a caul plate, had an energy density of 0.216 J/g, while the specimens with flat electrodes and manufactured without a caul plate had an energy density of 0.462 J/g.

4. Discussion

Processing and electrode selection play significant roles in the performance of structural capacitors. Across all parameters considered in this study, the energy density based on the first clearing event ranged from 0.02 J/g to 0.46 J/g, a 23 × difference, while the energy density based on the 50th clearing event ranged from 0.05 J/g to 0.69 J/g. Performance appeared to be very sensitive to processing pressure, with energy density varying by 600% over the range considered for the 120–765 structural dielectric material. This result is consistent with previous work that showed an increase in energy density of structural capacitors with processing pressure across two different material types [15]. Higher pressures would likely lead to better consolidation and less void content through the elimination of entrapped air as well as the suppression of void growth from dissolved volatiles. Micrographic inspection of capacitor cross sections in the present study confirms lower void

Fig. 8. Cross-section of dielectric of representative samples cured at different pressures. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 9. Images of representative sample with wrinkled paper electrodes from set 9, (a) top view and (b) cross-section. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 10. Images of non-wrinkled paper electrodes of a representative sample from set 16, (a) top view and (b) cross-section. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 11. Energy density of specimens that were autoclave manufactured with (wrinkled, set 9) and without (flat, set 16) a caul plate.

content in specimens cured at higher pressure. It is also possible that higher consolidation pressure leads to straightening of the

crimp present in woven fabrics, a process that could lead to more uniform spacing between electrodes.

Post-cure increased breakdown strength by almost 50% and could be the result of densification and an increase in crosslink density. Flandin et al. also observed a 14% increase in breakdown strength for a filled epoxy after increasing the cure extent from 0.96 to 0.995, supporting the notion that breakdown strength is affected by post-cure [20]. In their work, the increase in breakdown strength was attributed to the elimination of unreacted “dead ends” in the polymer network that would serve to increase its polar nature and precipitate breakdown. Palomo et al. [32] also observed a significant effect of cure cycle on breakdown strength of an epoxy dielectric. In that work, post-curing for 8 h at a temperature well above the ultimate T_g led to a significant increase in breakdown strength, however extended post-curing resulted in a decrease in energy density.

Considering electrode effects, we observe that the paper-based electrode performed better compared to BOPP, possibly because the paper may be more capable of withstanding the temperature and pressure necessary to cure the epoxy prepreg dielectric. For structural applications, the increase in energy storage performance of the paper must be balanced against a likely decrease in the shear properties [33]. Previous work has shown that structural capacitors readily fail in shear through the paper layer,

whereas a polymer film layer could promote toughness. We also observed a correlation between metallization resistivity and energy density, observing an energy density of 0.479 J/g for Al coated paper electrodes with 2–4 Ω/sq resistivity compared to 0.274 J/g for those with electrodes 0.5–1 Ω/sq resistivity. Researchers have shown that an increase in film resistance results in a decrease in the “clearing energy”, the energy released for a given clearing event [29]. Rabbuffi and Picci suggested that a reduction in clearing energy increases breakdown strength by decreasing the probability of failure via thermal runaway [34]. One of the best performing capacitors had surface resistivity of 2–4 Ω/sq and was cured in the autoclave without a top plate. Its 1st clearing energy density was 0.462 J/g which corresponds to a volume-normalized value of 0.806 J/cm³, significantly higher than any other in the present study.

The effect of breakdown strength on electrode materials type has been observed before [21,22,35,36]. In the present research we find that Al electrodes perform better than Zn, although the work function of Zn and Al are similar, 4.3 eV and 4.2 eV respectively [37]. The difference in performance could be the result of environmental stability, as Zn electrodes have been shown to be susceptible to corrosion [24]. The Zn–Al metallization performed the best of all three. The high performance of this electrode relative to the Zn is surprising, given their similarity in composition. However, the differences could be a result of changes in the chemistry and morphology of the metal polymer interface. Chen et al. reported a significant variation in breakdown strength for the same electrode materials across several deposition conditions [21].

Comparing the energy density of the wrinkled and unwrinkled specimens suggests that waviness of the electrode plays a significant role in the capacitor's performance. While the specific mechanisms that lead to wrinkling are unknown, they appear to be related to the boundary conditions of the laminate. We observed that the capacitor processed in the autoclave without an aluminum caul plate displayed very little wrinkling while specimens cured with a caul plate showed excessive wrinkling. Several studies have shown that formation of out-of-plane wrinkles in thin layers is a complex process controlled by process variables including laminate thickness, ply thickness, interlayer thickness, ply stiffness, interlayer viscosity, as well as the thermoelastic properties and geometry of the mold [38–40]. All of these variables govern how in-plane stresses develop in a given layer as the laminate is subjected to its processing cycle. While the determination of the specific mechanism of wrinkling is beyond the scope of the present work, we expect that the thin and compliant electrode carrier materials used in this work are particularly susceptible to buckling driven by in-plane compression. The reduction in energy density of the wrinkled electrode is likely due to shorting caused by a local decrease in electrode spacing combined with a local field concentration due to the wrinkle. These results are consistent with other research that found a negative correlation between electrode surface roughness and breakdown strength [23].

Mechanical properties were not measured or reported in this study. However, the in-plane stiffnesses of the laminates are expected to be similar to those of the 2116-FR4 and 120–765 glass–epoxy dielectrics previously reported in [15]. Therefore, for the composite capacitors tested in the present study, we expect in-plane tensile stiffness of at least 12 GPa and strengths of at least 150 MPa. Assuming the mechanical properties reported in [15] and repeating the multifunctional efficiency analysis described in the same work, we find that the best-performing specimen from the present work (set 12) has a multifunctional efficiency of 1.26. As shown in [15], a value greater than one indicates system level mass savings of a hypothetical multifunctional system when compared to conventional solution in which the capacitor and structural elements are separate.

Although single layer capacitors are studied, we expect the trends to correspond well to many-layer structural capacitor laminates due to our use of consistently oriented electrodes and encapsulating dielectric layers. The scaling of energy density with size is not straightforward, since failure is triggered by critical flaws. If these critical flaws are consistent in per-volume population, then increasing capacitor volume should lead to a proportional increase in flaw population and an increase in the likelihood of a flaw event per device. The use of self-clearing electrodes may be effective at ameliorating these effects.

5. Conclusions

In this work we have investigated routes towards maximizing the electrical performance of structural composite capacitors. In particular, we manufactured structural capacitors with energy density over 0.90 J/cm³, the largest values yet reported. In general, the results show that the details associated with processing and electrode selection can have a significant effect on performance, with energy density varying by an order of magnitude across the processing and electrode parameters considered here. First, the processing method is important, with hot press-cured capacitors demonstrating superior energy density compared to those cured in the autoclave. Specifically, the results show that the energy density increases with increased pressure applied during cure, although increased pressure may also lead to more variability in performance. Also, elevated temperature post-curing can have a positive effect on capacitor performance. Conversely, conditioning capacitors in an elevated humidity environment leads to a decrease in energy density. On the other hand conditioning capacitors in a low humidity environment resulted in a slight increase in energy density to 0.32 J/g, a 10% increase over the specimen stored under ambient humidity conditions. This result suggests that steps should be taken to limit moisture ingress, perhaps through a barrier coating applied to the capacitor's surface, or by using a more hydrophobic matrix material compared to epoxy. Also, we found that thin film electrodes are prone to wrinkling which can cause a serious decrease in energy density. Therefore steps should be taken (e.g. during manufacture or through materials selections) to ensure that the electrodes remain flat with a constant gap thickness. For example an electrode material or carrier with high bending stiffness would be less prone to wrinkling.

Overall, the results support earlier studies that show that it is possible to create structural composites with high dielectric energy density via carefully controlled processing and material selection. The present study used off-the-shelf composite prepreg and electrode materials, such that the present designs are scalable and manufacturable. However, it is expected that significant gains in performance could be made by creating composites and electrodes that are customized for this application. In particular, the creation of ultra-clean prepreps with few inclusions and impurities, low-crimp reinforcement, and nano-particulate high dielectric constant additives [41,42], combined with optimized metallization on mechanically robust carriers, could be explored to further improve multifunctionality.

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References

- [1] Gibson RF. A review of recent research on mechanics of multifunctional composite materials and structures. *Compos Struct* 2010;92(12):2793–810.
- [2] Snyder JF, Carter RH, Wetzel ED. Electrochemical and mechanical behavior in mechanically robust solid polymer electrolytes for use in multifunctional structural batteries. *Chem Mater* 2007;19(15):3793–801.
- [3] Snyder JF, Wetzel ED, Watson CM. Improving multifunctional behavior in structural electrolytes through copolymerization of structure- and conductivity-promoting monomers. *Polymer* 2009;50(20):4906–16.
- [4] Thomas J, Qidwai S, Pogue W, Pham G. Multifunctional structure–battery composites for marine systems. *J Compos Mater* 2013;47(1):5–26.
- [5] Thomas JP, Qidwai MA. Mechanical design and performance of composite multifunctional materials. *Acta Mater* 2004;52(8):2155–64.
- [6] Lin Y, Zhou Z, Sodano HA. Barium titanate and barium strontium titanate coated carbon fibers for multifunctional structural capacitors. *J Compos Mater* 2013;47(12):1527–33.
- [7] Lestoquoy G, Chocat N, Wang Z, Joannopoulos JD, Fink Y. Fabrication and characterization of thermally drawn fiber capacitors. *Appl Phys Lett* 2013;102:152908.
- [8] Luo X, Chung D. Carbon-fiber/polymer-matrix composites as capacitors. *Compos Sci Technol* 2001;61(6):885–8.
- [9] Carlson T, Ordeus D, Wysocki M, Asp LE. Structural capacitor materials made from carbon fibre epoxy composites. *Compos Sci Technol* 2010;70(7):1135–40.
- [10] Snyder JF, Wong EL, Hubbard CW. Evaluation of commercially available carbon fibers, fabrics, and papers for potential use in multifunctional energy storage applications. *J Electrochem Soc* 2009;156(3):A215–24.
- [11] Qian H, Kucernak AR, Greenhalgh ES, Bismarck A, Shaffer MS. Multifunctional structural supercapacitor composites based on carbon aerogel modified high performance carbon fibre fabric. *ACS Appl Mater Interfaces* 2013.
- [12] Javaid A, Ho K, Bismarck A, Shaffer M, Steinke J, Greenhalgh E. Multifunctional structural supercapacitors for electrical energy storage applications. *J Compos Mater* 2013.
- [13] Wetzel ED, O'Brien DJ, Snyder JF, Carter RH, South JT. Multifunctional structural power and energy composites for US army applications. DTIC Document 2006.
- [14] Arisetty S, Prasad AK, Advani SG. Metal foams as flow field and gas diffusion layer in direct methanol fuel cells. *J Power Sources* 2007;165(1):49–57.
- [15] O'Brien DJ, Baechle DM, Wetzel ED. Design and performance of multifunctional structural composite capacitors. *J Compos Mater* 2011;45(26):2797–809.
- [16] O'Brien DJ, Baechle DM, Wetzel ED. *Asme. Performance Metrics for Structural Composite Capacitors*. New York: Amer Soc Mechanical Engineers; 2010.
- [17] Lovell R. The effect of specimen size on the electric breakdown of unfilled and filled epoxy polymers. *IEEE Trans Electr Insul* 1976;11(4):110–4.
- [18] Tandon S. Modeling of stresses in cylindrically wound capacitors: characterization and the influence of stress on dielectric breakdown of polymeric film [Ph.D.]. Ann Arbor: University of Massachusetts Amherst; 1997.
- [19] Chen YH, Li H, Lin FC, Lv F, Li ZW, Zhang MA. Effect of interlayer air on performance of dry-type metallized film capacitor in DC, AC and pulsed applications. *IEEE Trans Dielectr Electr Insul* 2011;18(4):1301–6.
- [20] Flandin L, Vouyovitch L, Beroual A, Bessede JLD, Alberolal N. Influences of degree of curing and presence of inorganic fillers on the ultimate electrical properties of epoxy-based composites: experiment and simulation. *J Phys D Appl Phys* 2005;38(1):144–55.
- [21] Chen Q, Chu B, Zhou X, Zhang QM. Effect of metal–polymer interface on the breakdown electric field of poly(vinylidene fluoride–trifluoroethylene–chlorofluoroethylene) terpolymer. *Appl Phys Lett* 2007;91(6).
- [22] Zhao L, Su JC, Zhang XB, Pan YF. Experimental investigation on the role of electrodes in solid dielectric breakdown under nanosecond pulses. *IEEE Trans Dielectr Electr Insul* 2012;19(4):1101–7.
- [23] Sato S, Koyama K. Relationship between electrode surface roughness and impulse breakdown voltage in vacuum gap of Cu and Cu–Cr electrodes. *IEEE Trans Dielectr Electr Insul* 2003;10(4):576–82.
- [24] Garet C. Personal communication. Dayville, CT: Bollore, Inc.; 2008.
- [25] Baucio M. *ASM metals reference book*. American Society for Metals International; 1993.
- [26] Baechle DM, O'Brien DJ, Wetzel ED. Design and processing of structural composite capacitors. Baltimore (MD): SAMPE; 2007.
- [27] ASTM International. ASTM standard D 792 – 00. Standard test methods for density and specific gravity (relative density) of plastics by displacement. West Conshohocken, PA; 2000.
- [28] Standard A. Standard test method for dielectric breakdown voltage and dielectric strength of solid electrical insulating materials under direct-voltage stress. D 3755-97. West Conshohocken (Pennsylvania): ASTM International; 2004.
- [29] Chen YH, Li H, Lin FC, Lv F, Zhang M, Li ZW, et al. Study on self-healing and lifetime characteristics of metallized-film capacitor under high electric field. *IEEE Trans Plasma Sci* 2012;40(8):2014–9.
- [30] Summary of Properties for Kapton® Polyimide Films. DuPont Inc. Available from: <http://www.dupont.com/content/dam/assets/products-and-services/membranes-films/assets/DEC-Kapton-summary-of-properties.pdf> (accessed May 2014).
- [31] Callister WD. *Materials science and engineering: an introduction*. 3rd ed. New York: John Wiley and Sons; 1994.
- [32] Palomo B, Habas-Ulloa A, Pignolet P, Quentin N, Fellmann D, Habas JP. Rheological and thermal study of the curing process of a cycloaliphatic epoxy resin: application to the optimization of the ultimate thermomechanical and electrical properties. *J Phys D Appl Phys* 2013;46(6).
- [33] Yurchak OB, O'Brien DJ, Baechle DM, Wetzel ED. Shear properties of multifunctional structural capacitors. Baltimore (MD): SAMPE; 2012.
- [34] Rabuffi M, Picci G. Status quo and future prospects for metallized polypropylene energy storage capacitors. *IEEE Trans Plasma Sci* 2002;30(5):1939–42.
- [35] Miron C, Bratescu MA, Saito N, Takai O. Effect of the electrode work function on the water plasma breakdown voltage. *Curr Appl Phys* 2011;11(5):S154–8.
- [36] Wetz D, Mankowski J, McCauley D, Dickens J, Kristiansen M. The impact of water conductivity, electrode material, and electrode surface roughness on the pulsed breakdown strength of water. In: *Proceedings of the 27th international power modulator symposium and 2006 high voltage workshops*, 2006. p. 104–7.
- [37] Carter GF, Paul DE. *Materials science and engineering*. ASM International; 1991.
- [38] Basu SK, McCormick AV, Scriven LE. Stress generation by solvent absorption and wrinkling of a cross-linked coating atop a viscous or elastic base. *Langmuir* 2006;22(13):5916–24.
- [39] Lightfoot JS, Wisnom MR, Potter K. A new mechanism for the formation of ply wrinkles due to shear between plies. *Compos A Appl Sci Manuf* 2013;49:139–47.
- [40] Pandey RK, Sun CT. Mechanisms of wrinkle formation during the processing of composite laminates. *Compos Sci Technol* 1999;59(3):405–17.
- [41] Ieda M. Dielectric breakdown process of polymers. *IEEE Trans Electr Insul* 1980;EI-15(3):206–24.
- [42] Barber P, Balasubramanian S, Anguchamy Y, Gong S, Wibowo A, Gao H, et al. Polymer composite and nanocomposite dielectric materials for pulse power energy storage. *Materials* 2009;2(4):1697–733.