Freeform additive manufacturing of carbon fiber reinforced composites using dielectric barrier discharge-assisted Joule heating

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Abstract:

We developed an out-of-oven additive manufacturing (AM) technique to rapidly print and cure thermosetting carbon fiber reinforced composites (CFRCs) using dielectric barrier discharge (DBD). Conventionally, CFRCs are produced by automated fiber placement machines (AFPs) that use molds and oven treatments to cure CFRCs in the desired shape. AM allows for on-the-fly printing and curing of CFRCs without the use of molds. AM techniques are limited to UV-curable, low viscosity, or rapid-curing resins. Here, we use DBD for in-situ heating and curing of continuous CFRCs using commercial thermosetting resins. As the partially cured composite is deposited, Joule-heating is induced via the DBD applicator, allowing the part to cure in the desired shape. DBD-manufactured composites show properties similar to conventionally manufactured (oven) composites. The method is capable of 2D and 3D multilayered structures, deposited automatically. This technology leverages AM techniques to enable printing of high-performance and lightweight materials in any desired shape.

Keywords: Thermoset, Additive Manufacturing, Joule heating, Plasma

Introduction:

Carbon fiber reinforced composites (CFRCs) are lightweight, strong, and corrosion resistant, making them desirable materials that have a wide range of applications[1] in various areas such as defense, marine, aviation, and automotive industries[2,3]. They can also be used in wind turbines to fabricate blades and structural trusses[4].

In conventional processing of thermosetting CFRCs, automated fiber placement (AFP) machines deposit partially cured CFs in molds of the desired shapes; large, time-consuming ovens, and heat guns are used to heat and completely cure the deposited composite. Creating a mold each time a new shape is designed is a labor intensive and capital-intensive process. Since AFP machines occupy large volumes of space, they are often immobile; they cannot be used locally to create composites. Therefore, there is an increasing necessity to design a compact and convenient method to manufacture CFRCs.

A relatively new development in the production of these composites is out-of-oven additive manufacturing of continuous carbon fiber composites [5-13]. In this method, a nozzle is used to deposit a carbon fiber prepreg (partially cured carbon fiber/resin tow) in the desired shape, followed by the immediate curing of the resin. However, these approaches typically require non-conventional resin chemistries or UV sensitive resins to achieve rapid curing [7,14-16]. AM techniques which use frontal polymerization enable rapid curing of the matrix at room temperatures. However, in frontal polymerization before the resin is deposited on the CF tow it is chilled to sub-zero temperatures to ensure that curing occurs only after deposition. To initiate the curing reaction the CF and resin are deposited on a heated bed[14]. Deng *et al.* created a sophisticated automatic system to use conventional thermally curing resins to fabricate CFRCs[17]. However, they use a UV curable resin to create strong interlayer adhesion. In another work, Deng et al. used a very energy efficient method where the dynamic capillary effect facilitated wicking of the resin in the carbon fibers[18]. However, this method of manufacturing is limited to resins having low viscosity. Majority of the commercially applicable resins are not UV curable, do not have low viscosity, and do not follow frontal polymerization kinetics. Thus, it is desired to create a rapid method to print and cure CFRCs thermally using commonly found commercial resins [19-23].

One promising approach for out-of-oven heating is the use of electric fields [24,25]. The electrical conductivity of carbon fibers makes them a prime candidate to undergo Joule heating when placed in the influence of external electric fields[26,27]. Our group has shown how carbon fiber prepregs can be manufactured using an electric field generated by a radio frequency applicator [28]. Recently, Joule heating was also used to recycle carbon fibers from CFRCs by degrading the surrounding matrix using the heat generated within the fibers[29]. Since the electric field induces heat in the fibers themselves, this method can be used with a range of thermosetting resins surrounding the fibers. Thus, using electric fields to induce heating in the fibers from the inside out is especially useful for processing and manufacturing thermosetting composites[30]. CFRCs can be cured rapidly using electric fields without degrading the fiber-matrix interface.

Another means of applying an electric field is using a Dielectric Barrier Discharge (DBD) applicator. The DBD-assisted Joule heating was previously used by our group in resistive composite materials. The DBD applicator ionizes the air creating a plasma. The plasma interacted with a polymer having carbon nanotubes as fillers causing them to undergo Joule heating[31]. The DBD applicator consists of a top electrode, which contains a dielectric disc. The DBD applicator generates an electric field in the 1-50 kHz (center frequency of 26 kHz typically) range. The electric field is generated between this top electrode and a bottom ground electrode. The grounded conductive sample is placed between the two electrodes. An air gap is maintained between the top electrode and the sample. The electric field ionizes the air, and plasma streamers are created in this gap between the sample and the surface of the dielectric disk which creates a path for current to flow. When the sample connects with the plasma, a discharge current travels through the sample, to the bottom electrode. This applicator can be converted into a handheld portable electric field generator. The DBD-assisted Joule heating was recently used to heat carbon fiber prepregs and use them as patching materials to repair damage in composites [32].

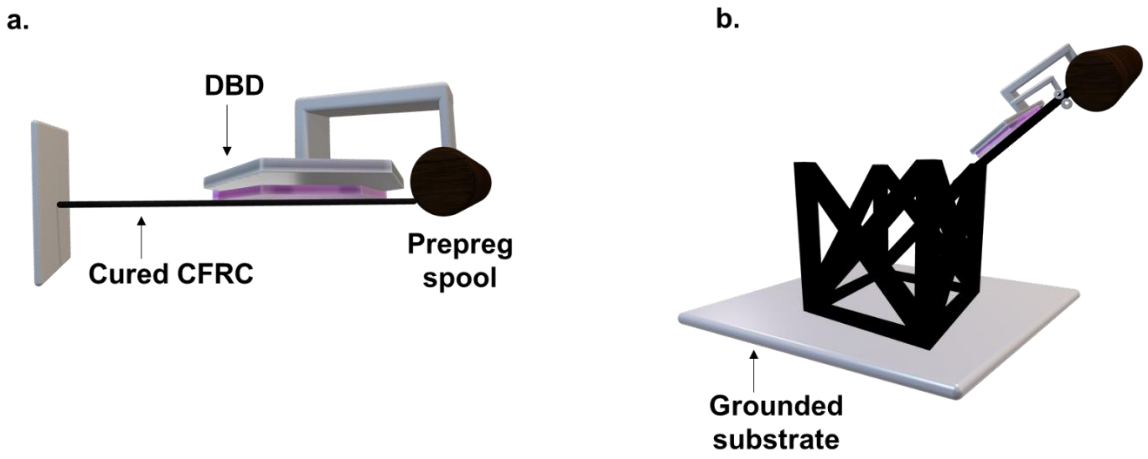

Fig. 1: Key concept: DBD can be used to heat and cure carbon fiber prepregs *in-situ* as the prepreg is deposited. Examples: (a) free-hanging carbon fiber tow that is being unspooled, printed, and cured mid-air. The wall is electrically grounded. (b) Truss structure being printed and cured using DBD. The substrate is electrically grounded.

In this work, DBD-assisted Joule heating was used to additively manufacture fully cured continuous carbon fiber composites with complex geometries. Here, suspended CFRCs (**Fig. 1a**) were created rapidly. Multilayered structures were also created using successive deposition of continuous carbon fiber prepregs on a grounded substrate (**Fig. 1b**). DBD-assisted Joule heating was used to rapidly cure the structures at the required temperature. This approach demonstrates that *in-situ* curing of CFRCs can be carried out without changing the resin chemistry; instead, the use of electric fields during deposition allows for local heating and curing. This approach is a mold-less, out-of-oven composite manufacturing technique that is not restrained by resin chemistry.

Materials & Methods:

Materials: T700S unidirectional carbon fibers (Torayca), EPON 828 + Jeffamine T403 Hardener

Preparing prepregs:

Continuous unidirectional T700S carbon fiber tows were laid down flat and impregnated with a two-part thermosetting epoxy (EPON 828 + Jeffamine T403 Hardener). They were heated in an oven at 100 °C for 6 min to produce prepregs. These prepregs were then rolled onto a spool. This is similar to the process of making prepregs done previously in our lab[28] Thus, prepregs were made using the common commercial composition of EPON 828 + Jeffamine T403. The curing kinetics of this resin system are known from our prior work, and one can predict the temperature and time needed to cure the resin completely[33]. The curing kinetics of the resin were predicted based on the Kamal-Sourour model Eq. (2). This model predicts the degree of cure achieved by exposing the resin to a given temperature for a certain time duration.

$$\frac{d\alpha}{dt} = (k\alpha^m)(1-\alpha)^n, \quad (2)$$

Here, α is the degree of cure, dα/dt is the curing rate, k is the temperature-dependent rate constant, and m and n are empirical reaction constants.

From the previous work[33] on this same resin, m = 0.402, n = 1, and k = 0.00542 s^{-1} were selected as the parameters (for curing to occur in the 100–110 °C). The simulation of the kinetic model (Eq. 2) shows that the prepreg is 60% cured after 6 min at 100 °C (**Fig. S1c**). For printing multi-layered structures, the prepreg

is exposed to the DBD plasma at 100 °C for an additional 5 min to get to ~90% cured. Thus, throughout this work, 5 min was chosen as the time to cure the first layer in a multilayer structure. The simulations show that at 100 °C, a prepreg is completely cured when it is exposed to an additional time of 8 min. This is also confirmed based on the DSC results shown in **Fig. S1a-b**. Thus, in this work, to fully cure a given layer (such as in a free-standing composite), the prepreg was exposed to the DBD plasma at 100 °C for 8 min.

DBD Experiments:

A metallic electrode is embedded in a dielectric ceramic disc in the Dielectric Barrier Discharge (DBD) applicator. The ceramic disk is approximately 3 mm thick and 70 mm in diameter. To generate plasma between the dielectric disk and a ground electrode, a 24 V Direct Current (DC) power was supplied to a frequency and power modulation device using a NICE-POWER DC Power Supply (Model: R-SPS3010). A high ratio winding transformer (286:1) receives the frequency generator's 24 V peak-to-peak 25-32 kHz modulated square wave signal, and outputs the corresponding high voltage (8-10 kV) modulated signal to the ceramic disc applicator. A thermal camera (FLIR Systems Inc., A655sc) was used to observe the maximum & average temperature of the sample from the side.

Preparing a continuous CFRC using DBD:

The prepreg is dispensed through the DBD generated plasma using a motor. For fabricating a suspended sample, the grounded copper wire was attached to the prepreg. For fabricating a part on a substrate, the prepreg was laid on a grounded aluminum plate. To completely cure a prepreg it was exposed to the plasma for 8 minutes at 100 °C. The heating zone has a length of 50 mm. The translation speed of the prepregs was 6.25 mm/min.

The distance between the grounded prepreg and the DBD applicator was varied between 0-7 mm. The heating rate of the prepreg at each 1 mm incremental distance was recorded.

Fabricating multilayered structures:

Additive manufacturing using in-situ curing: The first layer of prepreg was dispensed and laid across the ground plate. Based on the kinetics, at 107 °C the prepreg will cure completely in 7 min **(Fig. S1d)**. We want to resin to be only partially cured so that it can bond with the new layer. Thus, the first layer was cured for 5 minutes at 107 °C using the DBD applicator. The duty cycle was varied to maintain a temperature of 107 °C. A second layer of prepreg was then laid on top of the previous layer. The second layer was cured for 5 minutes as well at 107 °C, so that the third layer can bond with it. This process was repeated over many layers.

Additive manufacturing using post-cure: The first layer of prepreg was dispensed and laid across the ground plate. The second layer was then directly laid across the first layer. Similarly, the third, fourth and fifth layers were laid on top of the preceding layer. The entire structure was then exposed to the plasma for 25 minutes. The power of the DBD applicator was modulated to maintain the maximum temperature of the top layer at 107 °C.

Complex shapes: Multiple prepreg layers were moved relative to the DBD applicator by using an automated stage. The prepregs were deposited in the desired complex shapes and the layers were consolidated using rollers. The prepregs were then cured using the DBD generated plasma. For fabricating a multilayered rectangular composite, the prepreg layers were additively printed with DBD-assisted *in-situ* curing for 8 minutes each (at 100 °C) before printing the subsequent layer. For fabricating the helix, each prepreg layer was printed and *in-situ* cured using the DBD for 5 minutes each at 100 °C before printing the next layer. The next layer was offset by a slight angle (<15°). For fabricating the circle, a pressing roller was used to consolidate the prepreg that was being deposited on the automatic rotating stage.

Characterization:

Differential Scanning Calorimetry: The glass transition temperatures and degrees of cure of samples were calculated using differential scanning calorimetry (DSC). These experiments were conducted using a TA Instruments DSC Q20 (New Castle, DE). The samples contained 3-5 mg of substance total. Nitrogen was used to purge the test chamber at a rate of 50 mL/min. The temperature was ramped up from room temperature to 200 °C at a rate of 3 °C/min. For multilayered structures, a cross section cutting across all layers (5 layers) was used for testing. The samples were transported in a 0 °C container to prevent any curing at room temperature.

Mechanical Testing: Each sample for lap shear test consisted of two unidirectional T700S CF prepreg tow pieces having a length of 5 cm and width of 0.8 cm, placed one on top of the other such that the overlap area had dimensions of 0.8 cm x 0.8 cm. The 2 samples were completely cured at 100 °C for 14 minutes in oven and using the DBD applicator. An Instron load frame with a 30 kN load cell was used for these tests; the displacement rate was set at 2 mm/min for all tests.

ILSS assessment was carried out as per ASTM 2344 standards. The sample thickness was maintained at 4 mm, width at 8 mm, and length at 16 mm. A strain rate of 1 mm/min was used. The short beam strength was calculated as follows:

$$F = 0.75 * \frac{P_m}{b * h}$$

Where P_m is maximum load observed during the test, (N)

F = short-beam strength, MPa

b = measured specimen width, mm

h = measured specimen thickness, mm

Themogravimetric Analysis (TGA): TGA measurements were done in a TA Instruments TGA 5500 in air to determine the mass fraction of the composites. The sample was loaded on a Platinum pan and temperature was ramped from room temperature to 400 °C at a rate of 20 °C/min, then the temperature was held constant to observe degradation of the epoxy matrix.

Scanning Electron Microscopy (SEM): The cross-sections of 2 composites manufactured using the DBD-assisted method were polished and observed with a FEI Quanta 600 field-emission scanning electron microscope. For imaging, the cross-section image was divided into 9 sections and ImageJ software was used to calculate volume fraction and void fraction.

Results:

Our goal is to evaluate whether electric fields can cure prepregs during deposition to create freestanding CFRCs. Our general approach is as follows: To produce prepregs, continuous unidirectional carbon fiber tows were impregnated with epoxy and partially cured at 100 °C for 6 minutes in an oven. These prepregs were then rolled onto spools. These prepregs are then dispensed at a certain speed through the DBD-generated plasma. For as long as the tow is in the heating zone (residence time), the plasma couples with the CFs such that the CFs heat and the surrounding epoxy cures. The DBD power was modulated in order to achieve a target maximum temperature (100–110 °C). The curing kinetics of this resin system was studied previously, and can be used to predict the temperature and time needed to cure the resin completely[33]. As described below, we utilized several different methodologies to dispense the prepreg and build up multilayered structures. In a commercial setting, this technology would be controlled by a robotic arm that dispenses prepregs with DBD-assisted *in-situ* curing to create self-supporting structures.

The DBD-assisted Joule heating method was first used to cure a stationary prepreg at a given temperature. A prepreg was laid on a grounded aluminum plate and was exposed to the DBD generated plasma. The sample undergoes Joule heating and reaches a steady state maximum temperature of 100 °C when an input power of 35 W was applied to the DBD applicator. The prepreg sample is kept at this temperature for 8 minutes. To verify that the DBD-assisted Joule heating would completely cure the sample as expected, DSC measurements were carried out on the prepreg sample before and after exposure to DBD generated plasma. In **Fig. S1a**, the DSC data shows that the prepreg was completely cured after being heated by the plasma. Thus, this method can indeed be used to fabricate fully cured composites without post-cure.

The Kamal-Sourour model (Eq. (2)) was used to predict the curing kinetics of the resin system. This model predicts the degree of cure achieved by exposing the resin to a given temperature for a certain time duration.

$$\frac{d\alpha}{dt} = (k\alpha^m)(1-\alpha)^n, \quad (2)$$

Here, α is the degree of cure, dα/dt is the curing rate from rheology measurements, k is the temperature-dependent rate constant, and m and n are empirical reaction constants. The curing kinetics at 100 °C were modeled in **Fig. S1c**.

The DSC data (**Fig. S1a**) confirms that the kinetic model can be used successfully to predict the degree of cure of a sample, if the time and temperature are known. Throughout this work, to completely cure a composite, the prepreg was heated at or above 100 °C for 8 min or longer. To create a multilayered structure, the first layer was heated at 100 °C (wall) & 107 °C (helix) for only 5 min so that it can bond to the next layer (discussed below). TGA in air was carried out on the completely cured composite **(Fig. S7)**. The CFs make up 55wt% of the composite. This is comparable to other works in this field. The epoxy matrix burns off completely beyond 400 °C[34]. Based on the SEM images of the cross-section of the composites **(Fig. S8)**, it observed that the fiber distribution is fairly uniform, with a few voids present. Again, this is comparable to prior work[17]. The areal density calculations show that CFs have a volume fraction of 63%. The void fraction was found to be 2.4%.

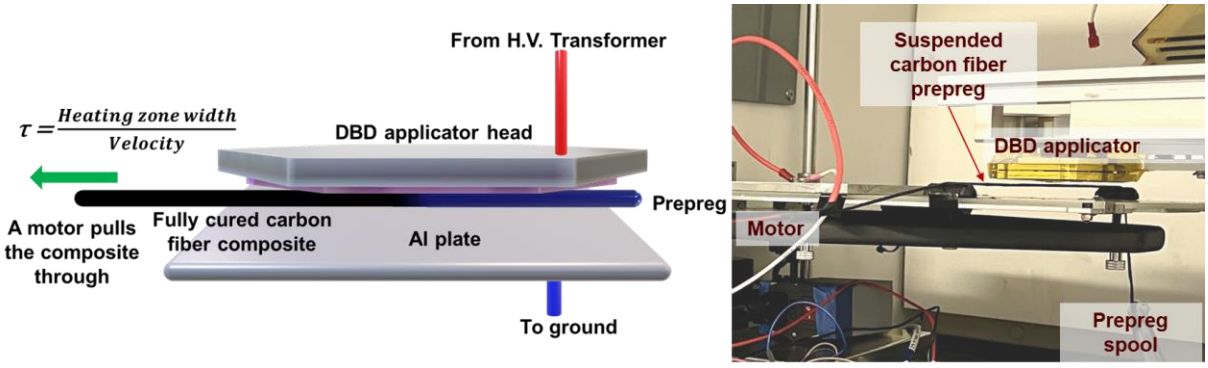

Fig. 2: (a) Schematic of the setup of DBD-assisted Joule heating and curing of continuous composites. The composite is free hanging and suspended in air. (b) Digital image of actual setup shows that the motor pulls the cured composite and unspools the prepreg.

Next, the DBD applicator was used to create composites that hold their shape in air without sagging or bending (**Fig. 2**). A suspended continuous prepreg sample was unspooled and dispensed at a constant speed (6.25 mm/min) through the DBD generated plasma to rapidly heat and cure. The heating zone has a length of 50 mm. Thus, the prepreg is exposed to the plasma for 8 minutes. The prepreg remained suspended under tension with the help of a motor. This pulling motion of the motor also unspools the prepreg in the desired direction. In this case, a grounded copper wire brush was kept in contact with one end of the prepreg. The power was modulated to maintain the sample at a steady-state maximum temperature of 100 °C (average

power 35 W). The sample cured completely to form a stiff, suspended composite (**Fig. S3b**). This demonstrates that this technique can be used to create freeform self-supporting structures.

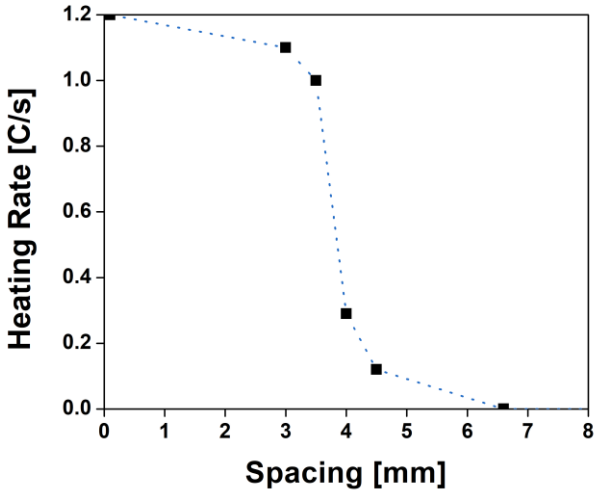

Fig. 3: The heating rate of the carbon fiber composite sample decreases with increasing spacing between the sample and DBD applicator. Beyond 5 mm spacing, no plasma formation is observed between the sample and the DBD applicator.

We next examine the effect of a practical processing parameter: the distance between the grounded sample and the DBD applicator (top electrode). This distance was varied from 0 mm to 7 mm, and the heating rates of the prepreg were recorded at each distance. **Fig. 3** shows that the heating rate is highest when the sample is closest to the top electrode, as expected. Beyond a certain spacing (5 mm), plasma is not formed between the sample and the DBD applicator, i.e., no ionization of air occurs. This implies that the applicator needs to be within 5 mm of the sample for plasma to form and the sample to heat and cure.

DBD-assisted Joule heating can also be used to produce multilayer structures. In order to do so, the degree of cure must be controlled for each layer. If a given layer is insufficiently cured, the part will not hold its shape; however, if a given layer is completely cured, it will not bond to the next deposited layer. To investigate this phenomenon, the residence time of the first layer was varied, and lap shear tests were conducted to measure interfacial shear strength **(Fig. S2)**. Note that the steady-state maximum temperature was maintained at ~100 °C during this experiment. As expected, the data shows that the longer a layer is cured before laying another prepreg layer on top, the weaker the interfacial adhesion between the two layers is. To balance these two design considerations (maintaining shape and interfacial bond strength), we selected a residence time of 5 minutes for all experiments where multilayered structures were made. The simulation of the kinetic model shows that when the prepreg is made, it is 60% cured after 6 min at 100 °C (**Fig. S1c**). When the prepreg is exposed to the DBD plasma at 100 °C for an additional 5 min it gets ~90% cured. Similarly, when the prepreg is exposed to 107 °C for an additional 5 min it gets ~92% cured.

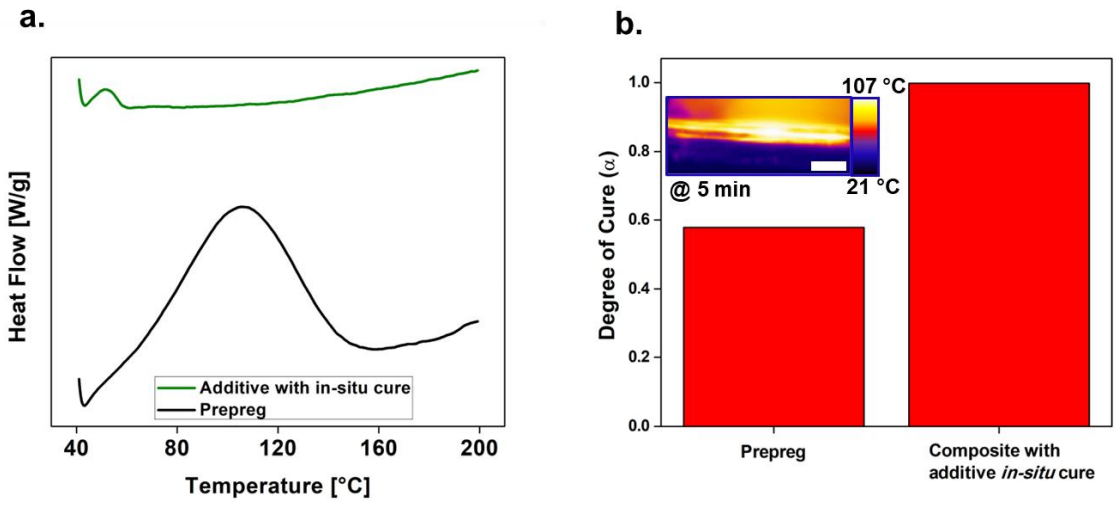

Fig. 4: (a) DSC curves and (b) degree of cure for: the prepreg, composite produced via deposition followed by *in-situ* cure cycling. The prepregs were prepared by heating the resin impregnated CF tow for 6 min at 100 °C. The cure cycles were held at ~107 °C for 5 min. The composites consist of 5 layers of CF prepreg tows. Inset: thermal image of side-view of the *in-situ* cure sample during a cure cycle. Scale bar represents 1 cm.

Fig. 4 shows the DSC data for a 5-layer wall structure that was additively manufactured with a DBD-assisted *in-situ* cure cycle where the steady-state maximum temperature was maintained at 107 °C. The area under the exotherm in the DSC plot for the samples before and after exposure to the plasma was measured and compared to the area under the exotherm of a completely uncured sample. The mathematical relation to find degree of cure using DSC is shown in Eq. (1).

$$\alpha = 1 - \frac{\Delta H_t}{\Delta H_0}, \quad (1)$$

where α is degree of cure, ΔH_t is the heat released during curing (obtained by area under the exotherm in DSC plot) of a sample with plasma exposure time *t*, and ΔH_0 is the heat released during curing of a completely uncured sample.

, (2)

In-situ curing allowed for each CF prepreg tow layer to cure for 5 minutes at 107 °C and retain its shape before a new layer was placed on top of it. **Fig. S1 (d)** shows that the kinetic model predicts that the first layer cured to an α = ~0.92 when the prepreg is exposed to 100 °C for an additional 5 min. Then the second layer was deposited on top of the first layer, followed by an additional 5 minutes of plasma exposure. While the second layer cured partially, the first layer cured completely due to heat conduction from the top layer. Similarly, a third, fourth, and fifth layer were deposited and cured. This way, a post-cure step in an oven is not needed to completely cure the entire structure. The DSC of a cross-sectional slice of the DBD-manufactured multilayered composite (consisting of all 5 layers) shows that the degree of cure is 1 (**Fig. 4**).

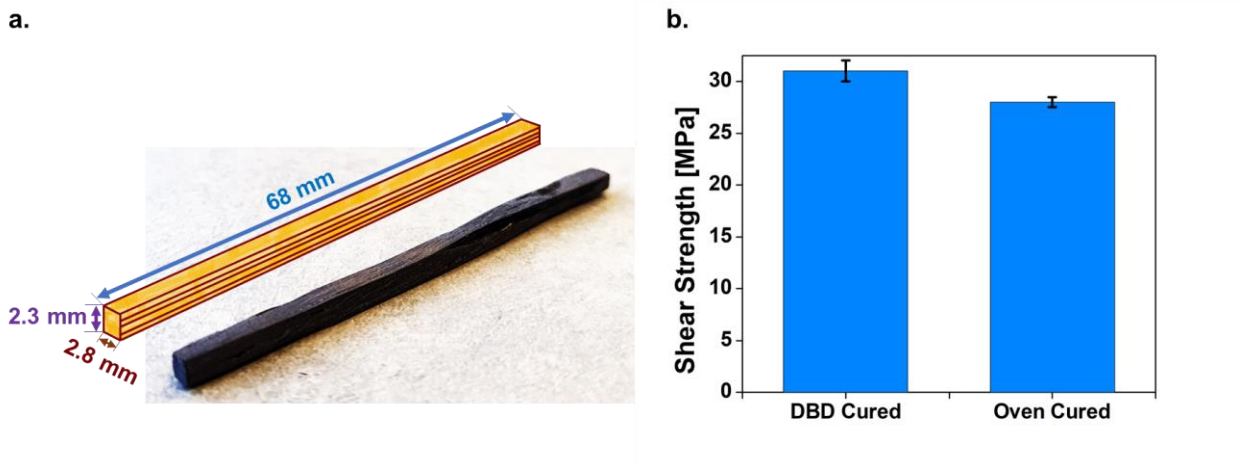

Fig. 5: (a) Multilayer sample fabricated using additive *in-situ* DBD-assisted heating and curing of carbon fiber prepregs. (b) Comparison of lap shear strength of DBD-cured and oven-cured samples. Both samples were cured at 100 °C for 14 minutes.

Next, the DBD-assisted Joule heating approach was used to produce a multilayered structure (a wall) of 20 CF tow layers **(Fig. 5a)**. The structure retained its shape, and has flat and smooth edges, and sharp corners. For this method of additive manufacturing to be incorporated in industry, the mechanical properties of the fabricated structures using the DBD have to be similar to those fabricated conventionally. Lap shear tests were conducted on 2 samples: a sample manufactured through the DBD-assisted process and a sample cured in the oven. Both samples were cured at 100 °C for 14 minutes to ensure that they are completely cured. The two samples showed comparable shear strength **(Fig. 5b)**. ILSS tests were also carried out to compare the short beam strength of the composite manufactured using oven and DBD **(Fig. S5)**. Thus, the multilayered structures fabricated using DBD-assisted Joule heating show similar mechanical strength to those fabricated in an oven.

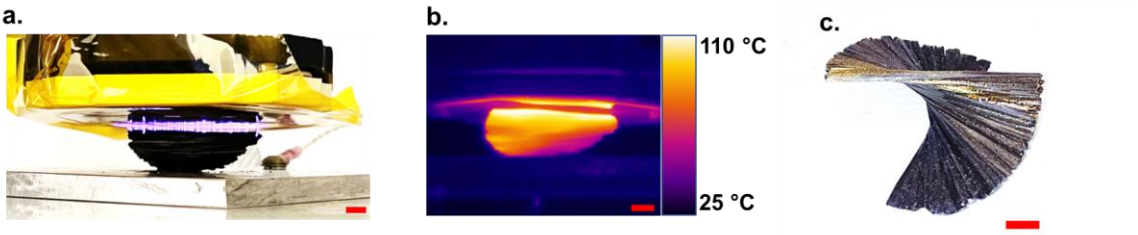

Fig. 6: (a) Helix production using DBD method (b) thermal image of helix being printed and cured using DBD method to produce (c) the final part. The scalebar represents 1 cm.

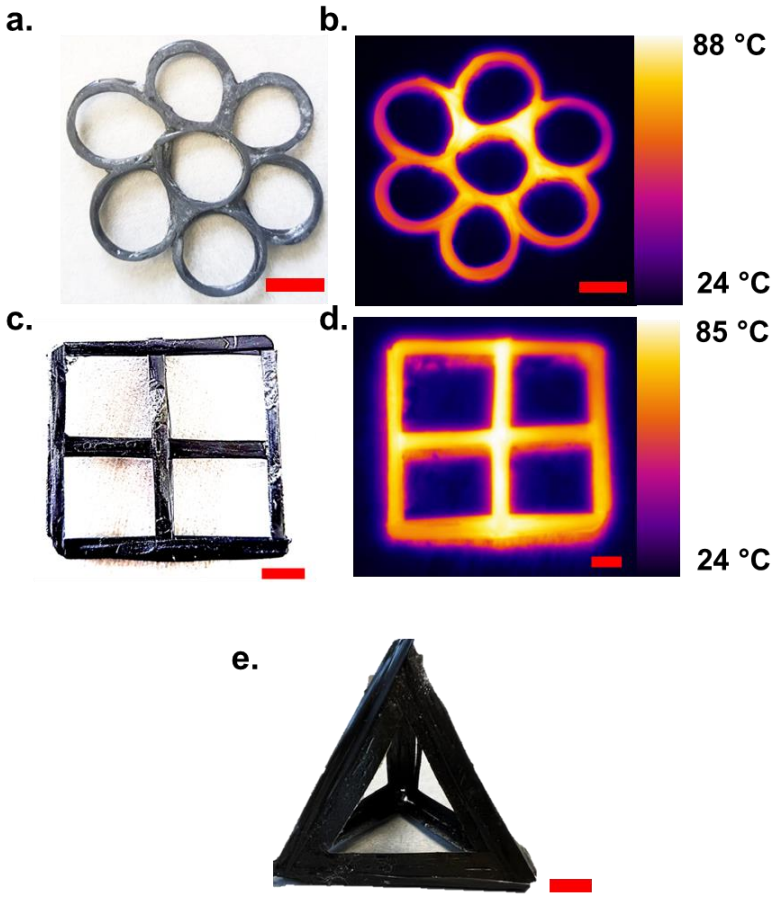

Fig. 7: (a) DBD-assisted Joule heating was used to fabricate a CFRC shaped like a flower (b) Thermal image of flower shaped CFRC after exposure to plasma (c) Multilayered CFRC grid manufactured using DBD-assisted Joule heating (d) Thermal image of CFRC multilayered grid immediately after exposure to plasma. (e) Self-supporting 3D CFRC pyramid crated using DBD-assisted Joule heating. The scalebar represents 1 cm.

Using this method, one can also create 3-dimensional self-supporting structures in air. A helical structure with overhang was fabricated using the DBD-assisted *in-situ* curing (**Fig. 6**). The helix was created by depositing layers of prepreg successively along a central axis. Each new layer was rotated at an angle of 5° before deposition. Every layer was cured for 5 minutes at 107 °C before depositing a new layer on top.

Several structures of different shapes **(Fig. 7)** were created to demonstrate the practical use of the DBD applicator. Note that in **Fig. 7**, the shapes were laid by hand and cured using the DBD-assisted Joule heating method. **Fig. 7a, b** show that this method can be used to create shapes with curved edges, while **Fig. 7c-e** show structures with straight edges. **Fig. S6** shows the temperature-time data and thermal image when the composite is being fabricated using the DBD. The symmetry and precision of creating a shape using this method depends on the accuracy with which the prepregs can be deposited.

To automate this AM process, a circular CFRC ring was fabricated using a stage that moved relative to the stationary DBD applicator (**Fig. 8**). The prepreg is deposited on the rotary stage and the stage simultaneously moves in a predetermined path to create the desired geometry. The stage had a stationary roller which pressed down on the as-deposited prepreg to guide the unspooled prepreg and consolidate the new layer onto prior layers. As the prepreg passes through the DBD applicator, the sample is heated and

cured in the desired shape. Another approach that was explored was using a robotic arm to make a hands-free setup **(Fig. S9)**. The robot can pull or deposit the prepreg in the desired shape.

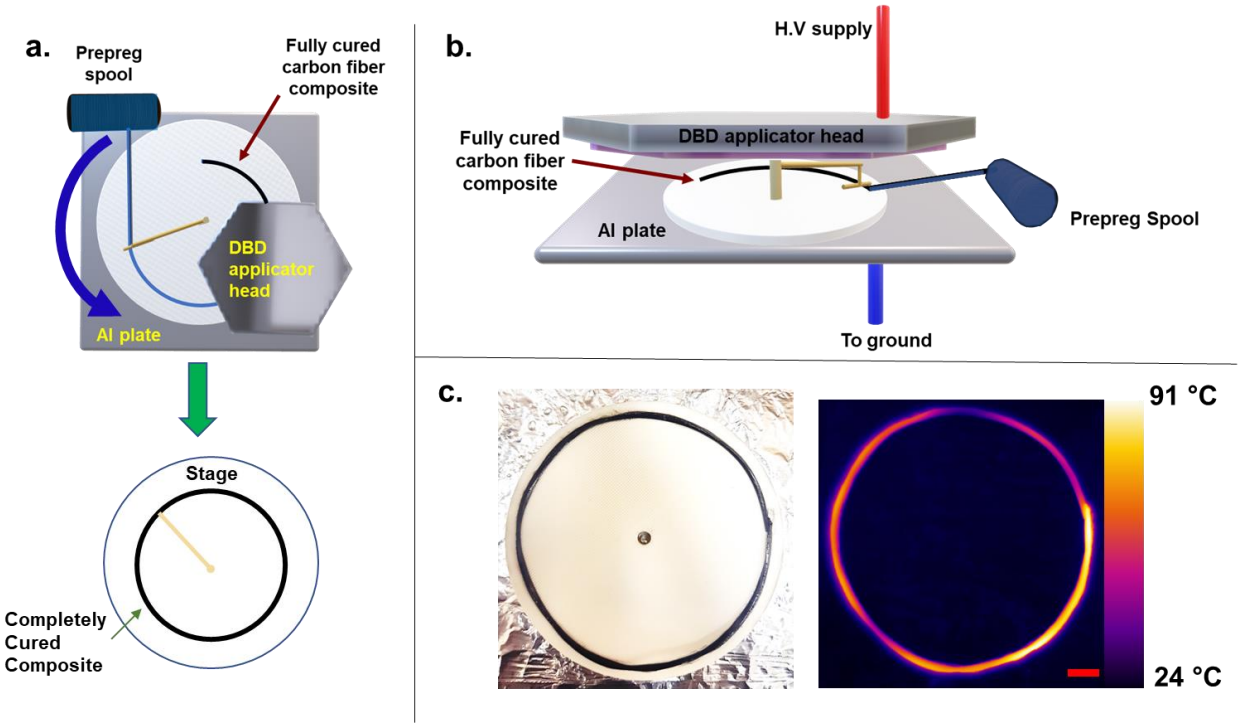

Fig. 8: Automated process for simultaneous deposition and curing of a continuous CFRC structure using DBD-assisted Joule heating. (a) Schematic of setup. The prepreg is represented by blue color. The completely cured carbon fiber composite is represented by black color. (b) Schematic of top view of setup. (c) Final product and thermal image immediately after curing. The stage rotates in the direction shown by the blue arrow. A roller (shown in yellow color) consolidates the new layer before it is exposed to the plasma. The wrinkles shown in the circular structure are caused due to the layup effects and not the heating effects.

The maximum speed at which the part is fabricated using the DBD depends on the curing kinetics and curing temperature of the resin. For instance, for the resin system we have used here, the prepreg (with a degree of cure of ~0.6) needs to be maintained at a temperature 100 °C for at least 8 min to cure completely. Since, the DBD is used to heat only the topmost layer of the composite being printed, this methodology can potentially be used to fabricate a composite of any desired height in a layer-by-layer curing manner. This method can be extended to any thermosetting resin, as long as the curing kinetics of the resin is known.

Conclusions

This work shows that it is possible to additively manufacture continuous carbon fiber composites using DBD-assisted Joule heating. One can create self-supporting and freeform composites using this technique. Prepregs can be successively deposited in the desired shape and cured to form complex three-dimensional and multilayered structures. The parts fabricated with this method show comparable strength to those manufactured in an oven. A stage that moves relative to the DBD applicator can be used to demonstrate a hands-free setup. With an automated deposition nozzle and path control methods, the DBD applicator can be moved relative to the prepreg. The DBD-assisted Joule heating approach can be extended to a range of fillers and matrices: many different grades of carbon fiber and SiC fiber act as susceptors, and the matrix

can be virtually any thermosetting resin, making this method remarkably versatile and practical. Using this method, it is possible to eliminate the need for post-curing and post-processing.

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Freeform additive manufacturing of carbon fiber reinforced composites using dielectric barrier discharge-assisted Joule heating

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Supporting Information

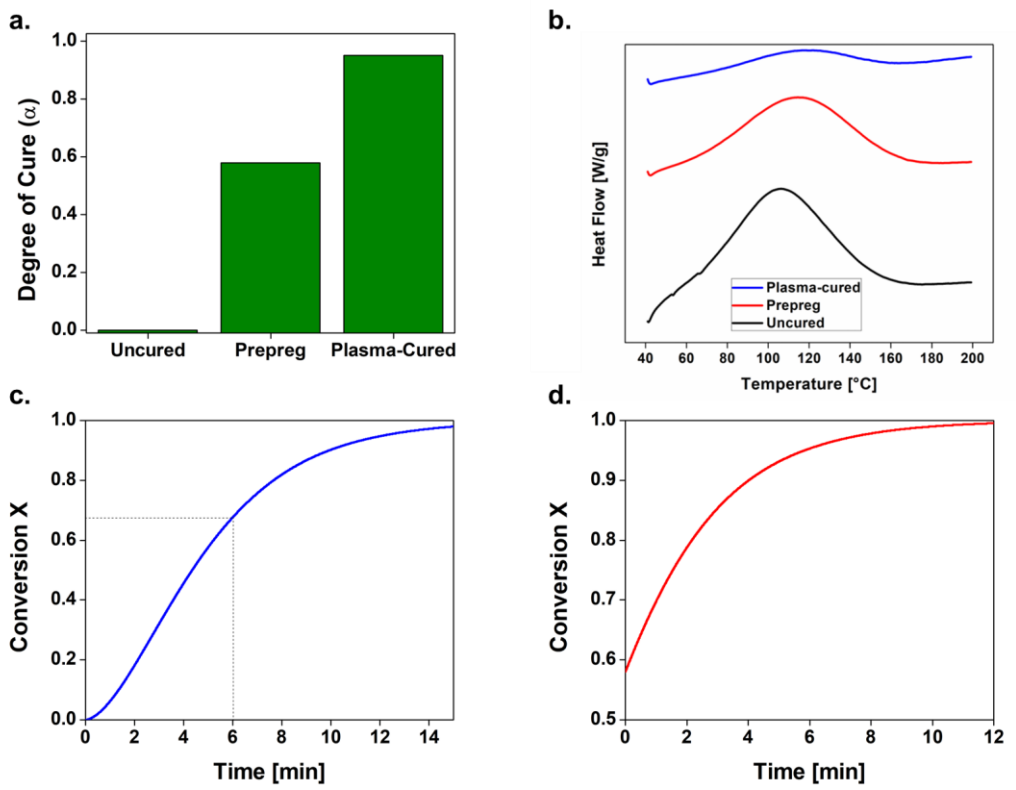

Fig. S1: (a) The degrees of cure of T700 CFs + epoxy composites were found from DSC. The prepreg was fabricated at 100 °C at 6 min, and it was cured at 100 °C for 8 min using DBD-assisted Joule heating. (b) DSC curves for T700 CFs + epoxy composites. (c) The simulation of the kinetic model (equation 2) shows that the degree of cure is estimated to be around 0.65 for the prepreg. For the model, m = 0.402, n = 1, and k = 0.00542 s^{-1}. When the resin is cured for an additional 8 min at 100 °C the model predicts that the resin should be almost completely cured. (d) Simulation of the progress of the curing reaction of the resin when it is cured for additional time at 107 °C.

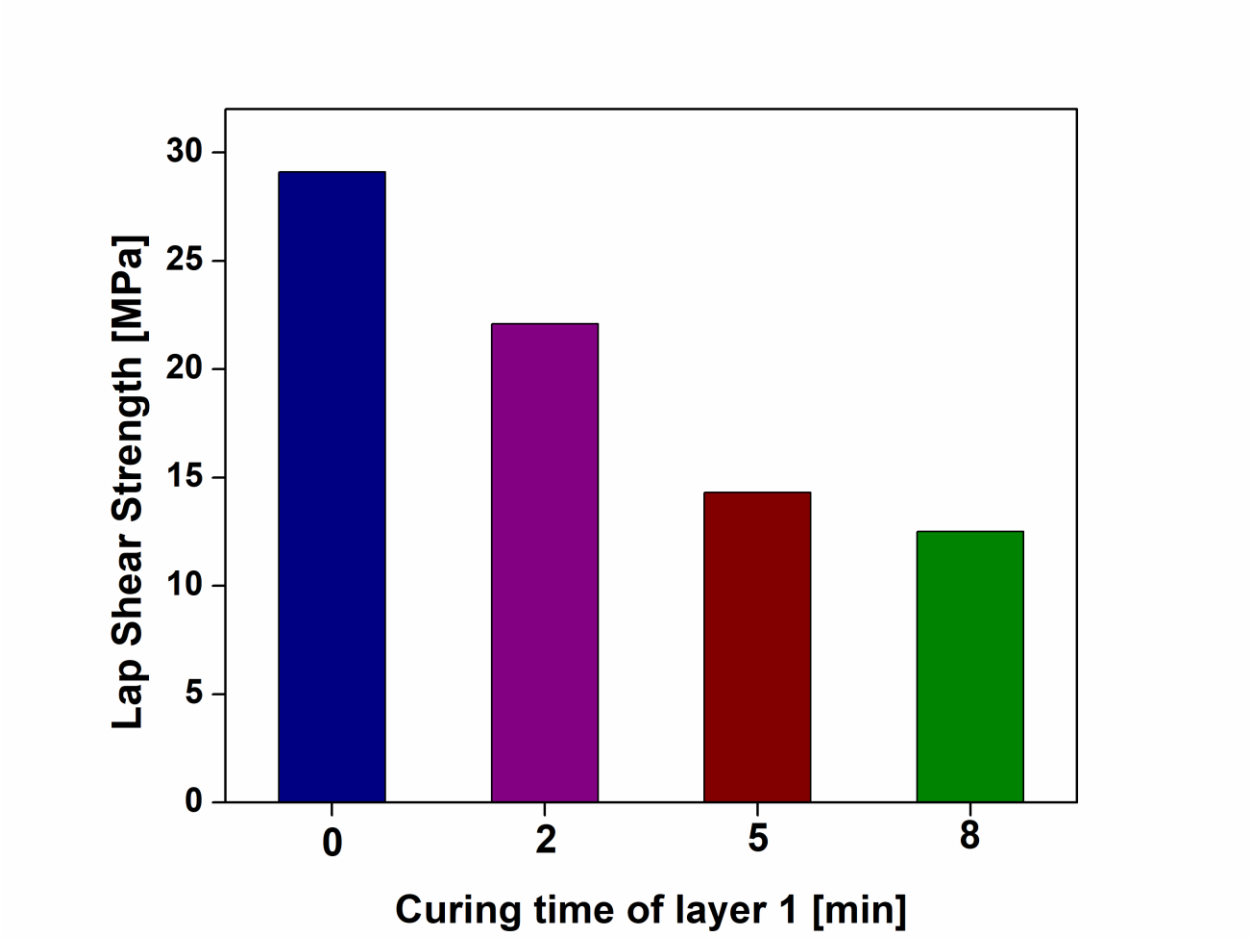

Fig. S2: Lap shear tests were conducted on samples where the first prepreg was cured using DBD-assisted Joule heating at 100°C for varying time. As the first layer gets completely cured, its bond strength with the next layer decreases.

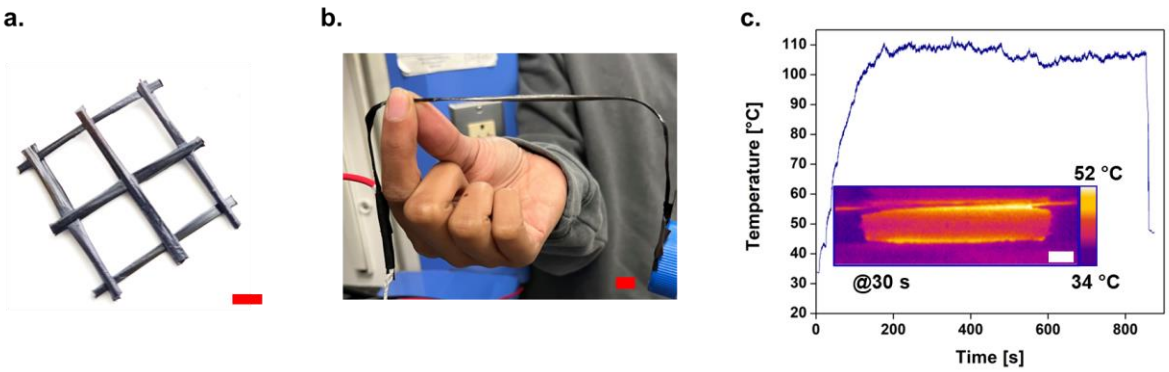

Fig. S3: (a) Single layer grid, (b) completely cured composite, (c) Temperature changing with time while manufacturing a continuous multilayered wall structure. Inset: thermal image at a time of 30s of topmost layer of prepreg being cured after deposition. Scale bars represent 1 cm length.

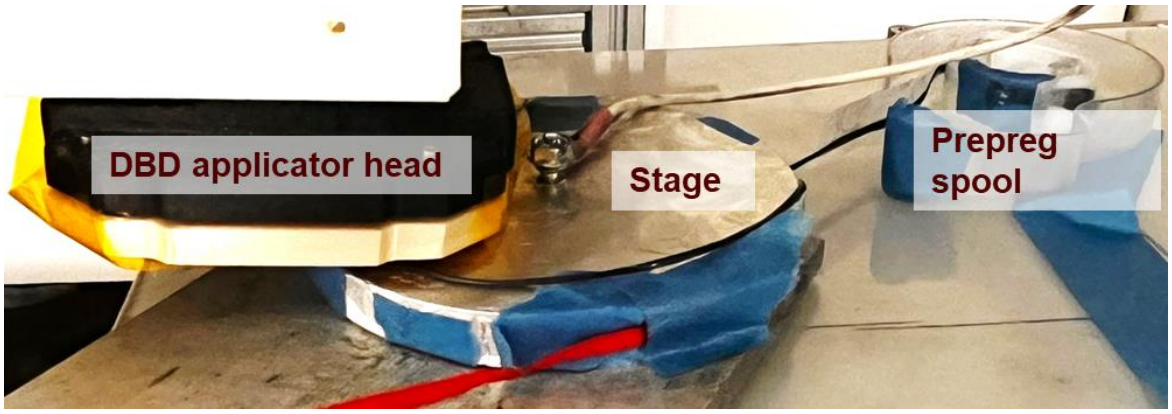

Fig. S4: Automated process for printing and curing a continuous CF circle using DBD-assisted Joule heating. A roller (behind the DBD head in this image) presses down on the prepreg and consolidates the shape before it gets cured. The stage in this case was a motor assisted rotating turn table.

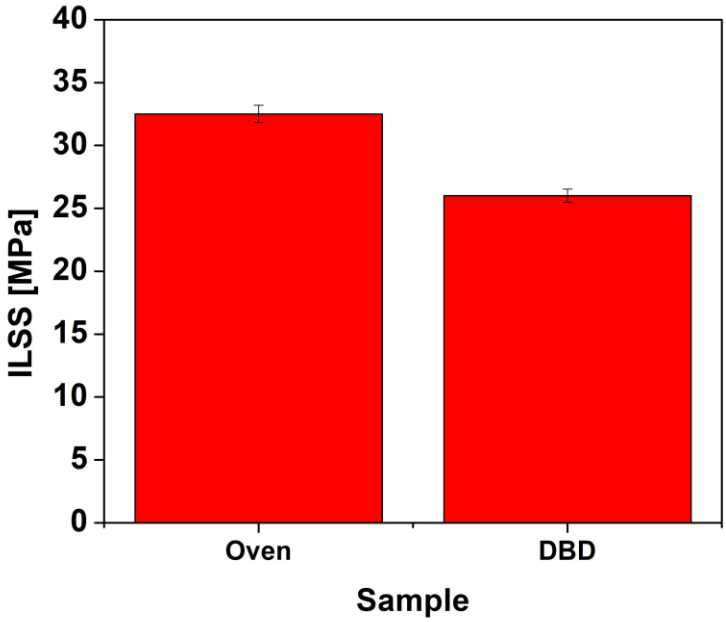

Fig. S5: ILSS was found for a composite fabricated using the oven, and for a composite fabricated using the DBD. The thickness of each sample was 4 mm, width 8 mm, and length 16 mm. The composites were cured using either method for 8 min at 107 °C.

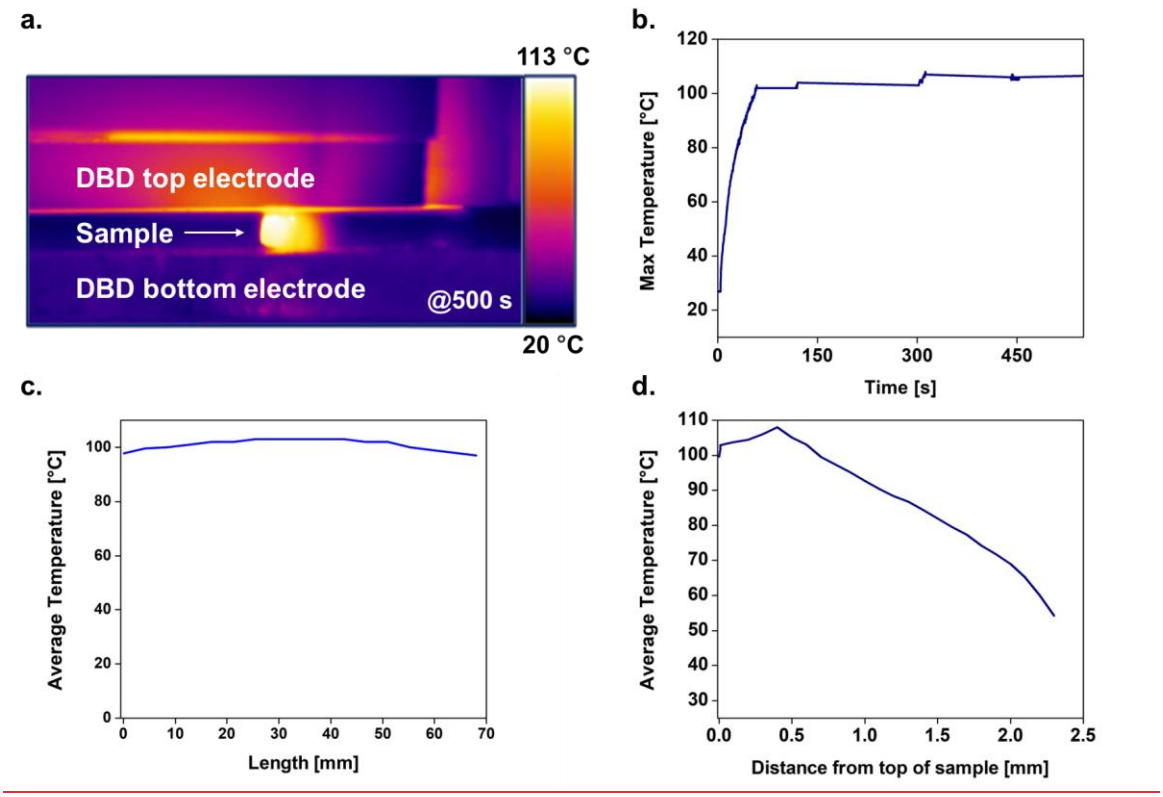

Fig. S6: Maximum temperature of the composite was recorded as it changed with time. (a) Thermal camera image (side-view) of a multilayered sample. (b) Time-Maximum temperature data of multilayered structure (from side). (c) Average temperature along horizontal length of sample at 10 s. (d) Average temperature of sample along vertical height at 10 s.

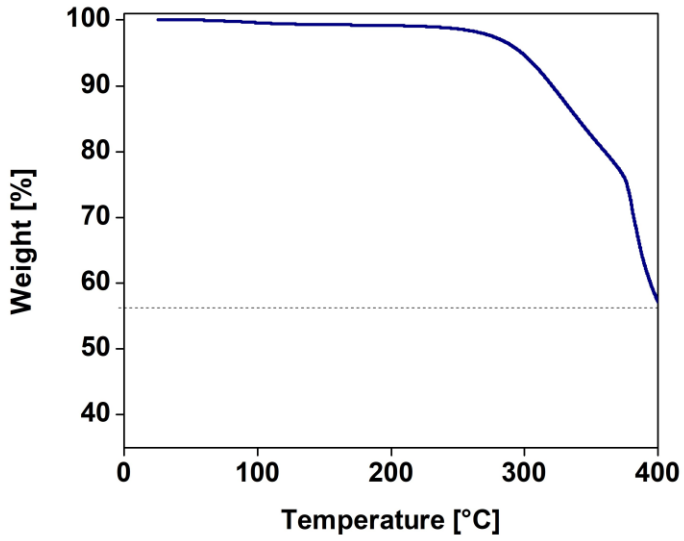

Fig. S7: TGA of the fully cured composite manufactured using the DBD-assisted Joule heating method.

TGA in air was carried out on the completely cured composite. The CFs make up 55wt% of the composite. This is comparable to other works in this field. The epoxy matrix burns off completely beyond 400 °C[1].

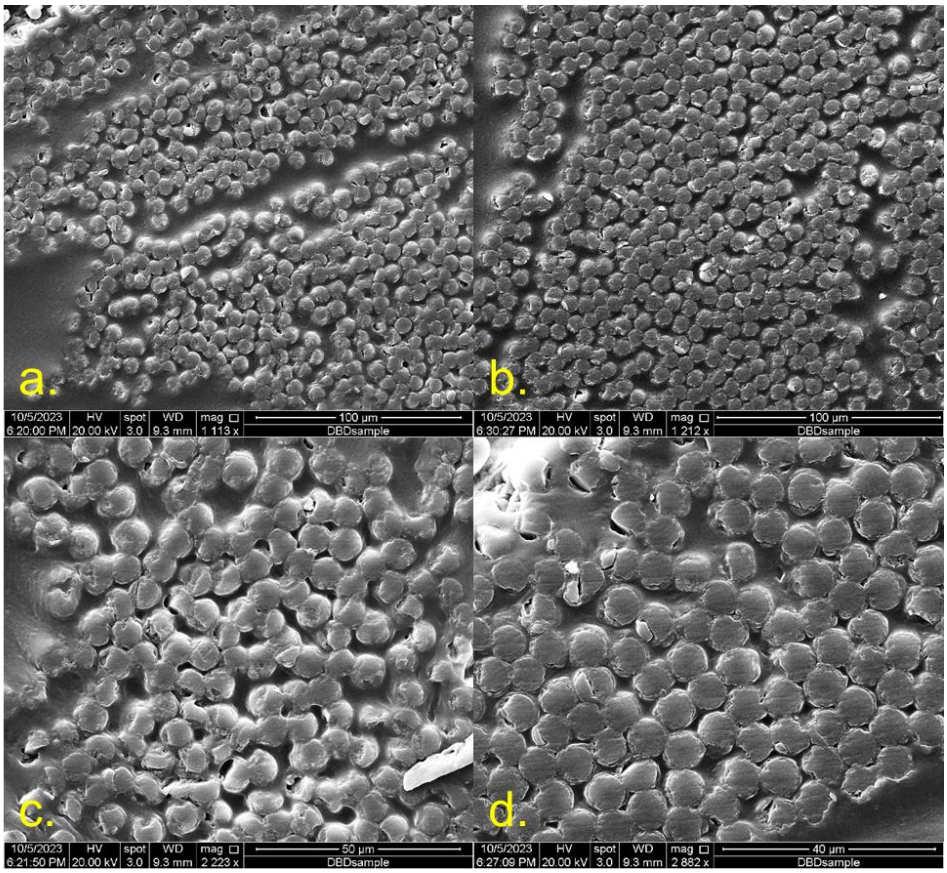

Fig. S8: SEM images of the cross-section of the fully cured composites. Note: Some portions of the composites still have a very thin layer of epoxy due to a polishing error.

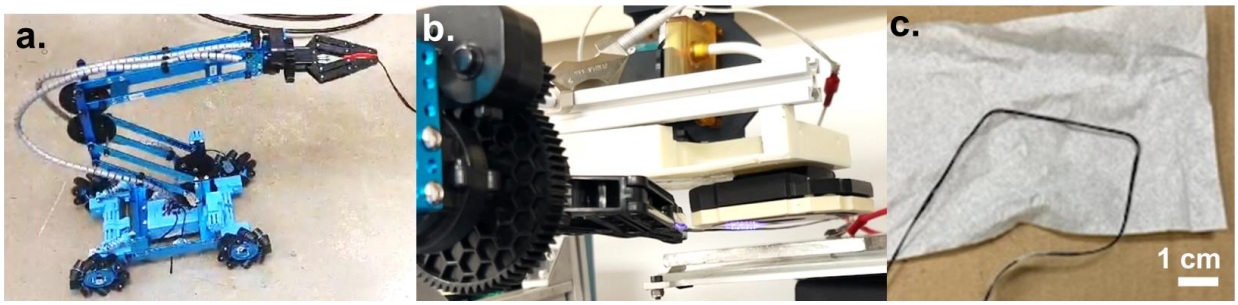

Fig. S9: A robotic arm was used to create a hands-free setup to use the DBD to cure a composite. (a) robotic arm, (b) robot pulling a prepreg through the DBD, (c) cured CFRC composite manufactured using hands-free setup.

(1) Sarmah, A.; Morales, M. A.; Srivastava, A.; Upama, S.; Nandi, A.; Henry, T. C.; Green, M. J.; Vashisth, A. Interfacial carbon fiber–matrix interactions in thermosetting composites volumetrically cured by electromagnetic fields. *Composites Part A: Applied Science and Manufacturing* **2023**, *164*, 107276.