CARBON FIBER PREPREG COMPOSITE LAMINATES CURED VIA CONDUCTIVE CURING USING NANOENGINEERED NANOCOMPOSITE HEATERS

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ABSTRACT

Next-generation composite manufacturing processes can be improved to overcome limitations from traditional manufacturing techniques such as autoclave and vacuum-bag-only oven curing. Here, we explore features of the newly-developed out-of-oven (OoO) curing that cures the composite prepreg using a resistive-heating film comprised of aligned carbon nanotubes. The OoO composite cure process using a nanoengineered nanocomposite heater consumed two orders of magnitude less electrical energy during a cure cycle, compared to vacuum bag-only oven out-of-autoclave (OoA) curing. Also, OoO curing reduces part-to-part variations through direct (and more immediate) temperature control. From a multifunctional perspective, the nanocomposite heater showed a clear change in resistance associated with infiltration of a polymer matrix into carbon nanotube network and cure shrinkage during curing, which can be utilized as a cure status monitoring technique. This out-of-oven manufacturing technique is expected to enable highly efficient curing of prepreg with *in situ* cure status monitoring ability.

1 INTRODUCTION

Carbon-fiber-reinforced plastic (CFRP) composites are widely used as structural materials because of their exceptional physical properties. Although there are several manufacturing processes for curing polymeric matrix composites using external stimuli such as heat [1–5] and light [2–4], autoclave curing remains the industrial standard technique for achieving the desired properties. In the autoclave manufacturing technique, the pre-impregnated carbon fibers (prepreg) are widely used because of their ease of use. The prepreg composite laminates are subjected to high temperatures for polymer crosslinking, and high pressure for high fiber volume fraction and low void content in the resulting components. However, manufacturing via autoclave is accompanied by high initial installation costs and expensive operating outlays of a high-temperature pressurized vessel. Most importantly, since an autoclave has geometrical constraints on composite parts, and effective energy transfer for curing is restricted by the convective heat transfer mechanism, the autoclave manufacturing technique cannot meet the increasing demand for manufacturing flexibility. Also, the amount of energy for curing composites scales with the size of the component and is limited by the capacity of the autoclave because of the fixed volume of the gas medium inside of the vessel. Thus, the autoclave manufacturing process consumes a fixed amount of energy no matter how large or small the components are. Even a newly proposed manufacturing technique using microwave heating has similar drawbacks related to the geometrical constraints due to radiation shielding [6]. Therefore, new interest has developed in novel manufacturing technologies for the prepreg process.

Recently, we reported that it is possible to eliminate the need for a heating vessel for the thermal processing by using an aligned carbon nanotube (CNT) network as a heating element directly embedded in the surface of the laminate; this new manufacturing technique is called out-of-oven curing [7]. As an in-depth study, here we address the characteristics of the out-of-oven curing to understand the thermal and energy utilization during the manufacturing process with finite element modeling, and to justify the advantages of out-of-oven process comparing with conventional composite curing processes such as autoclave and oven curing. Also, we suggest that the CNT film heater, which is the core component of the out-of-oven curing process, can additionally be used as an *in situ* cure status monitoring sensor during curing.

2 EXPERIMENTAL

2.1 Manufacturing of the CNT heater and cure status sensor

Vertically aligned CNT forests were grown in a quartz tube furnace at atmospheric pressure with a thermal chemical vapor deposition process [8, 9]. The CNTs were grown Si substrates with a catalytic layer of 10nm/1nm of alumina/iron deposited by E-beam evaporation. To obtain better electrical conductivity after densification [10] and enable more electric energy to be dissipated as thermal energy at operating voltage [11], the CNT forests were comprised of $\gtrsim$500 μm CNTs. The CNTs were composed of an average outer diameter of $\approx$7.8 nm (3-7 walls with an average inner diameter of $\approx$5.1 nm), intrinsic CNT density of $\approx$1.6 g/cm^3, the average inter-CNT spacing of $\approx$59 nm, and volume fraction of $\approx$1.6% CNTs [10, 12, 13]. To produce a film-like material, the vertically grown CNT arrays were densified and re-aligned horizontally by using a 10 mm radius rod after covering with a Guaranteed Nonporous Teflon (GNPT) film.

To utilize a CNT film as a cure status sensor as well as a resistive heater, two copper tape electrodes were attached to both ends of A-CNT film. As an adhesive substrate holding the CNT film together with the electrodes, a composite surfacing film (i.e., TC235-1SF from Tencate Advanced Composite USA, Inc.) was used. The surfacing film is co-curable with prepreg which post cure cycle is 180°C. See

Figure **1** for a scheme of aligned CNT cure status sensor.

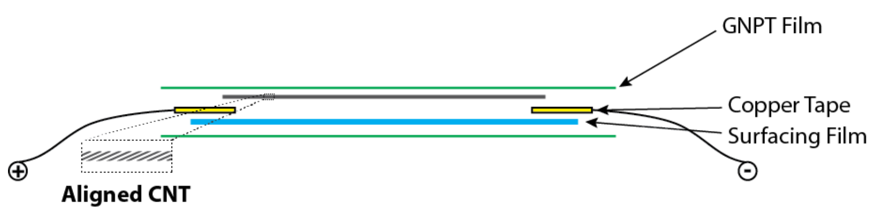

Figure 1: Side view of aligned CNT film resistive heater and cure status sensor.

2.2 Convective and out-of-oven curing experiments

The Hexply AS4/8552 prepreg was used for the laminates, and the dimension of a laminate was 100mm x 25mm. Also, 16-ply unidirectional lay-up was conducted for simplicity. In the case of convective oven process, the recommended vacuum bagging procedure from the prepreg manufacturer was followed, and a prepared vacuum bag was placed in a gravity convection oven (i.e., Lindberg/Blue M, GO1350A). During a cure cycle, the temperature of a laminate was recorded by a thermocouple directly attached on the surface of a laminate. For out-of-oven curing setup, a prepared nanocomposite component described in chapter 2.1 was attached to one side of the uncured laminate as a heater. The recommended vacuum bag scheme for the Hexply 8552 technical data sheet was followed for curing setup, and additional thermal insulating blocks were installed to minimize the heat loss to the environment. For resistive heating of the nanocomposite heater, the DC power supply was connected to the two copper tape electrodes of the heater. Input voltage and current were recorded using digital multimeters during the whole cure cycle. The temperature was measured by a thermocouple that is attached to the CNT heater. The temperature control of the CNT heater was performed by manual adjustment of the input voltage to follow the recommended cure cycle in the technical data sheet. The following cure cycle was used for all curing processes: cure temperature of 110°C with a hold time of 60min; and post cure temperature of 180°C with a hold time of 120min; ramp rate at 3°C/min.

After the curing process, the degree of cure (DoC) was acquired to compare with the results from the finite element model. To analyze DoC, differential scanning calorimetry (DSC) was conducted on the top and bottom layer of a processed laminate with TA Instruments DISCOVERY DSC. The DoC was calculated from the area of the exothermic peak of the cured laminates and uncured prepreg by heating up to 300°C at 5°C/min ramp rate.

2.3 Cure status monitoring with CNT network

As described above, the architecture of a CNT cure status sensor is exactly same to the CNT heater, and it can be used as a heater and a sensor at the same time. However, in this study, external heat (using a hot plate) was applied to a CNT sensor to minimize the effect coming from Joule heating of CNT network and to focus on understanding the phenomenon in a CNT network during the cure cycle. Also, to simulate the composite cure environment, a manufactured CNT component was cured under vacuum. The resistance was recorded using a digital multimeter (i.e., Agilent 34461A) and a 4-wire Kelvin probe during the whole cure cycle. Also, the temperature was recorded by a thermocouple that is attached to the CNT sensor.

3 FINITE ELEMENT MODEL

The modeling of the fully multi-physical composite curing process was achieved by using the ANSYS Composite Cure Simulation (ACCS) to compare the convective curing processes and the out-of-oven process. The transient thermal analysis was conducted to capture the thermal response such as temperature, directional heat flux, and degree of cure within the laminate. The Hexply AS4/8552 prepreg from Hexcel Corporation was used for finite element modeling. The quasi-isotropic laminates were composed of unidirectional 16 plies of Hexply AS4/8552 (~2mm thick). Each ply was modeled with ten meshes to acquire the results through the thickness of the laminate. For the convective curing process, a gravity convection oven (i.e., Lindberg/Blue M, GO1350A) process is assumed, and therefore the thermal analysis considered the laminate to be surrounded by the dry heated air following the manufacturers recommended cure cycle. The power and energy consumption was acquired by estimating the electrical power consumption of oven heating elements to follow the cure cycle. The convective heat transfer coefficient was set to be 15 W/m^2 ºC on the surface of the aluminum tooling plate (5mm thick). In this model, the dry air in the oven was under the lumped capacitance model. Also, the heat flux on the surfaces of a laminate and heat loss to the environment were included in this model.

For the out-of-oven curing process, the top surface of the laminate was subjected to the recommended cure cycle with conductive thermal boundary conditions because the CNT heating component is installed directly onto the top surface of the laminate. Also, it was assumed that the laminate and CNT heater is insulated with MICROSIL Microporous Insulation from ZIRCAR Ceramics, Inc. The cure cycle here matches to the cycle that is used in the experiments.

4 RESULTS AND DISCUSSION

4.1 Convective composite curing process vs. out-of-oven curing process

Figure 2 shows finite element analysis and experimental results of the convective oven and out-of-oven curing process. The composite cure simulation results present that minimum and the maximum value of temperature and DoC overlap each other. Thus, the variation of temperature and degree of cure within ~2mm laminate is negligible. Also, DoC from DSC agreed with the finite element model. Given that there is no significant difference in DoC of both processes, they are both useful for composite manufacturing. However, the convective oven process showed a transient temperature response due to convection, while the out-of-oven performed an immediate response through direct heat conduction. Considering that DoC is attributed to thermal history during curing, this result indicates that out-of-oven process may reduce the part-to-part variation of thermal and mechanical properties. Also, given that the convection coefficient varies a lot in a heating vessel due to the uncertainty of the gas flow, the gradient of temperature and degree of cure within the laminate in the case of the conventional process may be exaggerated in the practical circumstances.

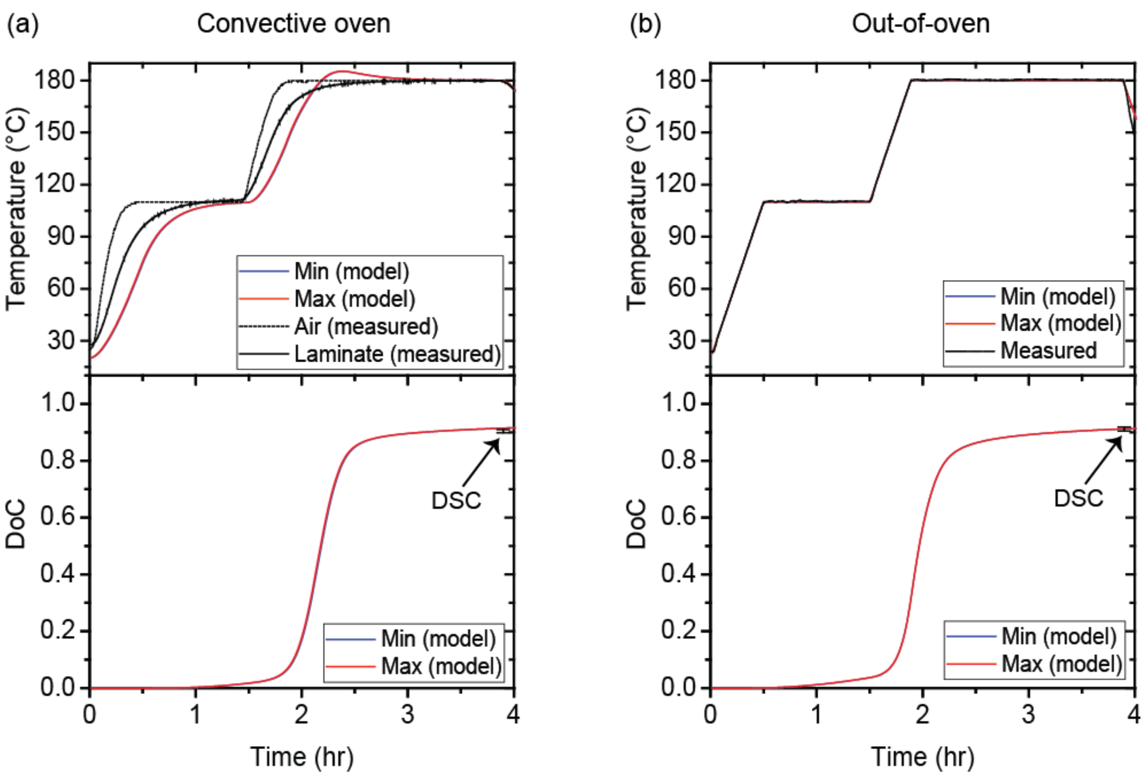

Figure 2: Finite element modeling and experimental results of composite curing. Shown here are the maximum and minimum temperature and degree of cure of the (a) Conventional process (gravity convection oven curing), and the (b) Out-of-Oven curing process.

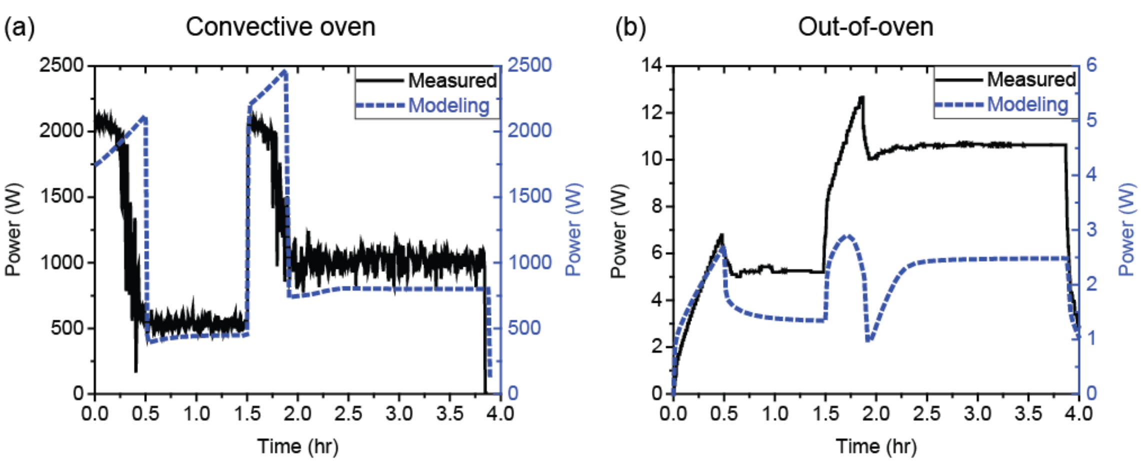

Figure 3: Power consumption of the (a) Conventional process (gravity convection oven curing), and the (b) Out-of-Oven curing process. Finite element modeling results of composite curing were included for modeling.

The distinctive difference between the convective oven and the out-of-oven process occurs in energy consumption during the cure cycle. Figure 3 represents the power consumption of each manufacturing process. In the case of a convective oven, most power consumptions were used for increasing the temperature of the heat transfer medium gas (i.e., dry air) inside of the oven, and for maintaining the temperature against heat loss to the environment. Since the amount of heat loss from the manufacturer was included in the convective oven model, power consumption of the model showed a good agreement with experimental results. The power consumption of ~2.1kW was observed during the ramp up period, and ~500W and ~1kW were consumed at the soak period 110°C and 180°C, respectively. In contrast, out-of-oven process showed the maximum power consumption of ~12.5W, which is much smaller power consumption than convective oven process. The integrated energy consumptions during the whole cure cycle were 13.7MJ for the convective oven and 118.8kJ for the out-of-oven process; approximately, a difference by two orders of magnitude in energy consumption was observed in this study. On a different note, the model of out-of-oven process underestimated the power consumption even though the trend is similar to the measurement. Future work will address the underestimation by evaluating other heat loss sources.

4.2 Cure status monitoring with CNT network

In the case of the dry CNT network, the resistance can be expressed as a function of temperature due to the fluctuation induced tunneling conduction (FITC) model [14–16]. Therefore, the resistance change of a dry CNT network and the temperature of it show a mirror image of each other. However, as presented in Figure 4, there are remarkable changes in electrical properties of CNT cure status sensor under a composite cure cycle. Specifically, the most distinct feature was the sharp resistance peak occurring at the late-stage of the first temperature ramp-up, as well as the logistic growth in resistance in the post cure cycle.

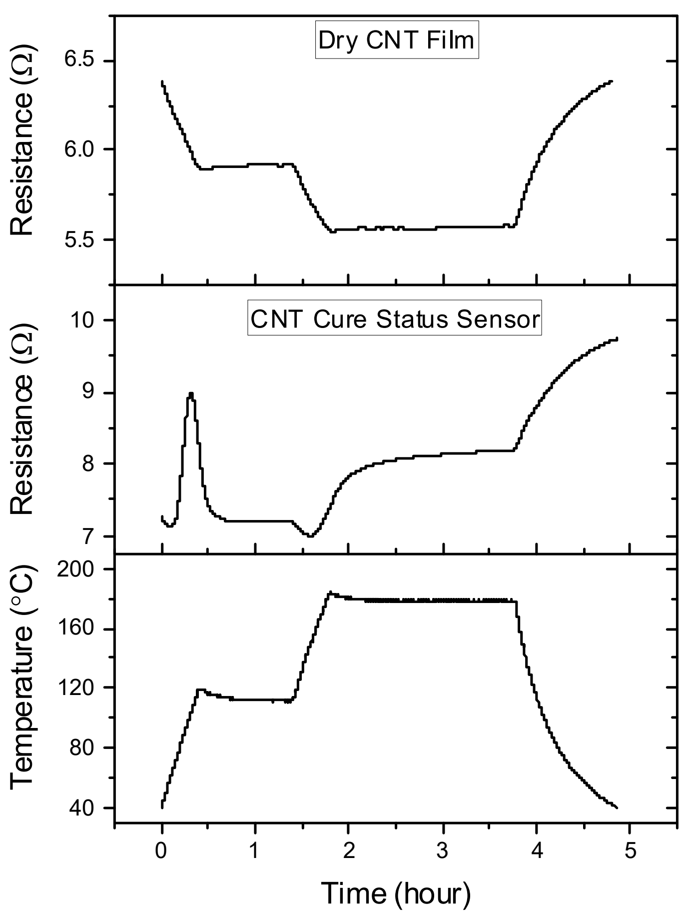

Figure 4: Resistance change of a dry aligned CNT network and a CNT cure status sensor. Both were conducted and acquired under the same cure cycle (lower image).

To explore the underlying physics of these phenomena, CNT cure status sensors were tested under different isothermal cure temperatures. Since the surfacing film (i.e., TC235SF-1) is designed to be cured in ~110°C, the temperature range from 65°C to 105°C was selected to change cure rate and the final degree of cure. The resistance of each sensor was normalized by the peak value. As presented in Figure 5, the resistance's decreasing rate after the peak increased as the isothermal soak temperature increases. Also, the amount of resistance decrease from the peak to the end of the cure was larger as the soak temperature is higher.

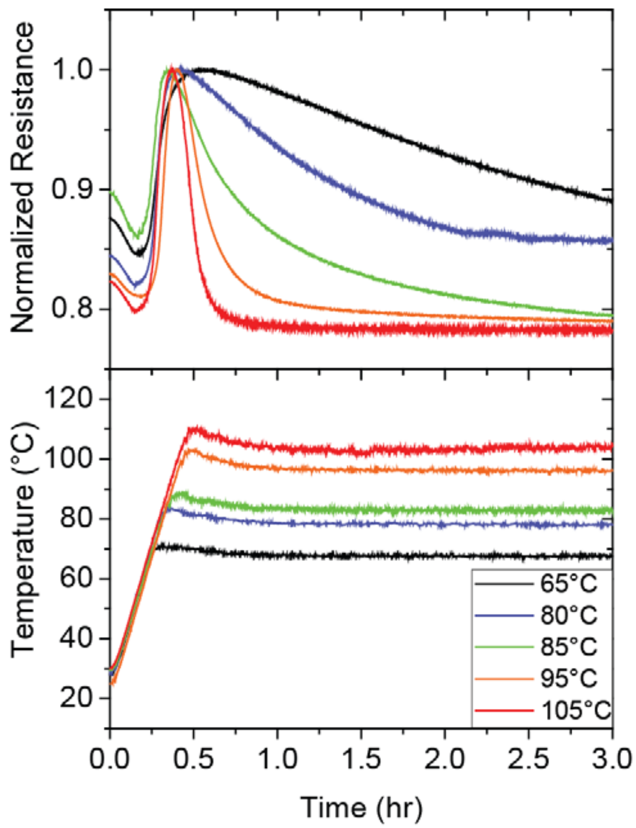

Figure 5: Resistance change of CNT cure status sensors depending on different isothermal cure cycles.

During ramping the temperature up, the viscosity of the resin decreases. Thus, the resin of the surfacing film starts to be infiltrated into CNT network due to capillary pressure. As a CNT network is wetted by the resin, there is a separation between CNT bundles, resulting in an increase in junction resistance between bundles [17]. Consequently, the total resistance of a device increases at the ramp-up process.

During the isothermal region, the crosslinking of the polymer occurs, and the crosslinking rate is dependent on the cure temperature. As the degree of cure increase, the volume of the resin decreases due to cure shrinkage, and the usual shrinkage range of epoxy resin is 2-7% [18]. As a result, the resin penetrated into CNT bundles shrinks as it is cured, and therefore the junction resistance can decrease. From the experiment of devices comprised of CNT network and the surfacing film, the cure shrinkage appears to be correlated to the observations that higher cure temperature shows faster and larger degree of decrease in resistance.

By evaluating a resistance change of CNT network during cure cycle, it will be possible to evaluate the status of the resin wetting within a composite laminate and to determine the ideal cure termination by monitoring the degree of cure. Most importantly, since carbon nanotube arrays are introduced into the interlaminar regions in a laminate for improving mechanical properties [19], these findings are expected to enable non-degradable in situ cure status sensors in the future. Also, considering that the nanocomposite heater can be used as the ice protection system on the aerosurfaces [20] after curing, the out-of-oven cure approach shows multi-functional aspects of the manufacturing process.

5 CONCLUSIONS AND FUTURE WORK

In summary, we justify the advantages of out-of-oven process comparing with conventional convective composite curing processes such as autoclave and oven curing, and further present the possibility of an efficient composite manufacturing process. The composite cure modeling and experiment indicated that out-of-oven composite cure process using a nanoengineered nanocomposite heater gives a significant reduction in energy consumption by two orders of magnitude (from 13.7MJ to 118.8kJ) as well as the quality control advantages by minimizing the part-to-part variations due to the immediate temperature control. Also, considering that the nanocomposite heater shows a distinct change in resistance associated with infiltration of a polymer matrix into CNT network and cure shrinkage during curing, the out-of-oven curing method provides multifunctionality to the composite laminates. For the future work, the further study on larger laminates will be useful to evaluate the scalability of out-of-oven curing. Also, besides the surfacing film, different kinds of the polymer should be tested as a polymer matrix to characterize the cure status sensing mechanism.

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REFERENCES

[1] R. J. Wojtecki, M. A. Meador, and S. J. Rowan, "Using the dynamic bond to access macroscopically responsive structurally dynamic polymers," *Nature Materials*, vol. 10, no. 1, pp. 14–27, 2011.

[2] S. Burattini, B. W. Greenland, D. Chappell, H. M. Colquhoun, and W. Hayes, "Healable polymeric materials: a tutorial review," *Chemical Society Reviews*, vol. 39, no. 6, p. 1973, 2010.

[3] M. D. Hager, P. Greil, C. Leyens, S. Van Der Zwaag, and U. S. Schubert, "Self-healing materials," *Advanced Materials*, vol. 22, no. 47, pp. 5424–5430, 2010.

[4] M. L. Hammock, A. Chortos, B. C. K. Tee, J. B. H. Tok, and Z. Bao, "25th anniversary article: The evolution of electronic skin (E-Skin): A brief history, design considerations, and recent progress," *Advanced Materials*, vol. 25, no. 42, pp. 5997–6038, 2013.

[5] X. Yan, F. Wang, B. Zheng, and F. Huang, "Stimuli-responsive supramolecular polymeric materials," *Chemical Society Reviews*, vol. 41, no. 18, p. 6042, 2012.

[6] E. T. Thostenson and T.-W. Chou, "Microwave processing: fundamentals and applications," *Composites Part A: Applied Science and Manufacturing*, vol. 30, no. 9, pp. 1055–1071, 1999.

[7] J. Lee, I. Y. Stein, S. S. Kessler, and B. L. Wardle, "Aligned carbon nanotube film enables thermally induced state transformations in layered polymeric materials," *ACS Applied Materials and Interfaces*, vol. 7, no. 16, pp. 8900–8905, Apr. 2015.

[8] B. L. Wardle, D. S. Saito, E. J. Garc??a, A. J. Hart, R. Guzm??n De Villoria, and E. A. Verploegen, "Fabrication and characterization of ultrahigh-volume-fraction aligned carbon nanotube-polymer composites," *Advanced Materials*, vol. 20, no. 14, pp. 2707–2714, 2008.

[9] A. M. Marconnet, N. Yamamoto, M. A. Panzer, B. L. Wardle, and K. E. Goodson, "Thermal

conduction in aligned carbon nanotube-polymer nanocomposites with high packing density," *ACS Nano*, vol. 5, no. 6, pp. 4818–4825, 2011.

[10] J. Lee *et al.*, "Impact of carbon nanotube length on electron transport in aligned carbon nanotube networks The MIT Faculty has made this article openly available . Please share Citation and Brian L . Wardle . " Impact of Carbon Nanotube Length on Publisher Version Access," *Applied Physics Letters*, vol. 106, no. 5, p. , 2015.

[11] D. Janas and K. K. Koziol, "A review of production methods of carbon nanotube and graphene thin films for electrothermal applications," *Nanoscale*, vol. 6, no. 6, p. 3037, 2014.

[12] I. Y. Stein and B. L. Wardle, "Morphology and processing of aligned carbon nanotube carbon matrix nanocomposites," *Carbon*, vol. 68, pp. 807–813, 2014.

[13] A. J. Hart and A. H. Slocum, "Rapid growth and flow-mediated nucleation of millimeter-scale aligned carbon nanotube structures from a thin-film catalyst," *Journal of Physical Chemistry B*, vol. 110, no. 16, pp. 8250–8257, 2006.

[14] M. Salvato *et al.*, "Charge transport and tunneling in single-walled carbon nanotube bundles," *Physical Review Letters*, vol. 101, no. 24, p. 246804, Dec. 2008.

[15] P. Sheng, "Fluctuation-induced tunneling conduction in disordered materials," *Physical Review B*, vol. 21, no. 6, pp. 2180–2195, 1980.

[16] P. Sheng, E. K. Sichel, and J. I. Gittleman, "Fluctuation-induced tunneling conduction in carbon-polyvinylchloride composites," *Physical Review Letters*, vol. 40, no. 18, pp. 1197–1200, May 1978.

[17] J. Qiu, J. Terrones, J. J. Vilatela, M. E. Vickers, J. A. Elliott, and A. H. Windle, "Liquid infiltration into carbon nanotube fibers: Effect on structure and electrical properties," *ACS Nano*, vol. 7, no. 10, pp. 8412–8422, Oct. 2013.

[18] L. Khoun and P. Hubert, "Cure shrinkage characterization of an epoxy resin system by two in situ measurement methods," *Polymer Composites*, vol. 31, no. 9, pp. 1603–1610, 2010.

[19] E. J. Garcia, B. L. Wardle, and A. John Hart, "Joining prepreg composite interfaces with aligned carbon nanotubes," *Composites Part A: Applied Science and Manufacturing*, vol. 39, no. 6, pp. 1065–1070, 2008.

[20] S. T. Buschhorn, N. Lachman, J. Gavin, and B. L. Wardle, "Electrothermal Icing protection of Aerosurfaces Using Conductive Polymer Nanocomposites," *54th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference, Boston, Massachusetts*, pp. 1–8, 2013.