Nanomaterial-enabled Manufacturing for Next-generation Multifunctional Advanced Composite Prepreg Laminate Architectures

by

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Abstract

Manufacturing of advanced aerospace-grade structural composites has traditionally utilized autoclaves to impart heat and pressure, in addition to vacuum, to create high-quality, void (defect)-free, reproducible structures. Carbon (micro) fiber reinforced polymer (CFRP) composites, which are pre-impregnated with a thermoset or thermoplastic polymer to form prepreg sheets, are in widespread use via autoclave processing due to their ease of use and high fiber volume fraction. However, autoclaves have high capital costs, and incur high operating costs due to the convective heating and applied pressure. Furthermore, the fixed capacity of an autoclave limits the size and design of composite parts, and the production rate is limited by autoclave availability. As a result, there has been an increasing interest in the development of alternatives, for example, out-of-autoclave (OoA) specially-formulated prepregs that only require heat and vacuum (i.e., pressure is not required). OoA prepreg processing also has drawbacks due to their specialized morphological and chemical formulation for vacuum-only conditions, as well as part quality (especially, composite interlaminar properties) that is below autoclave-processed materials. In light of the limitations described above, this dissertation (1) develops a novel prepreg processing technique, termed ‘out-of-oven’ (OoO) curing, that conductively cures OoA prepregs via nanoengineered resistive heating; (2) expands the applicability of the OoO process to conventional autoclave-formulated prepregs; and (3) introduces multifunctionality in the form of cure status sensing.

Characteristics of the OoO process using a CNT film as a heating element are first examined and compared to those of an oven curing process, focusing on an aerospace-grade OoA-formulated unidirectional aerospace-grade CFRP prepreg system. Thermophysical and mechanical property comparisons suggest that there is no difference in laminates cured via OoO and oven curing as evaluated by void content, degree of cure analysis, short beam shear interlaminar testing, dynamic mechanical analysis, and double-edge notch tensile testing. The OoO process reduces electrical energy consumption by two orders of magnitude (from 13.7 to 0.12 MJ) due to conductive vs. convective heating, under a typical industrial curing condition for a small (60 mm x 50 mm) test panel. Modeling shows that for parts beyond a meter-scale, energy savings will also be at least two orders of magnitude. Moreover, comparative finite element modeling of the OoO and oven curing shows excellent agreement with measured values, including the reduction in electrical energy and instantaneous power consumption. Altogether, these findings show that OoO curing works for OoA prepreg systems, with significant energy savings.

Given the results of the first study, the next study effectively removes the need for an autoclave by adapting the OoO process to conventional autoclave-formulated prepreg systems that currently require applied pressure of ~700 kPa in addition to vacuum. This technique entails OoO curing plus insertion of a nanoporous network (NPN, e.g., vertically aligned CNT arrays) into the inter-
laminar regions of autoclave-formulated composite laminates. Capillary pressure due to the NPN is calculated to be of the same order as the pressure applied in conventional autoclave processing. Results show that capillary-enhanced polymer wetting by the NPN enables sufficient reduction of interlaminar voids to levels commensurate with autoclave-processed composites. Thermophysical property comparisons and short beam shear interlaminar strength testing show that OoO-processed composites with NPN are equivalent to those of autoclave-cured composites, with energy and other savings similar to OoO curing with OoA prepreg in the first study. Conformability of the NPN to the micron-scale topology of the prepreg surface, and continuous vacuum channels created by the NPN, are identified as key factors underlying interlaminar void reduction.

Finally, this dissertation introduces a multifunctional aspect of the OoO manufacturing: an in situ cure status monitoring technique utilizing the nanostructured CNT-based heating element of the OoO process. The OoO heating elements are nanoporous and CNT-based, but in this study have different morphology (randomly-oriented or in-plane aligned CNTs) than the NPN (vertically aligned CNTs, A-CNTs). As OoO curing proceeds and the heating element is powered, the adjacent polymer flows into the nanoporous heater via capillary action. Based on cure status sensing experiments and theoretical models, it is found that electrical resistance changes of the heating element correspond to several mechanisms associated with different stages in the cure process, including polymer infiltration into the CNT network that causes the average CNT-CNT junction distance to increase, giving a resistance increase. Later in the manufacturing, as the polymer cross-linking occurs after infiltration into the heating element, chemical cure shrinkage decreases the CNT-CNT junction distance, leading to a decrease in resistance. Thus, the heating element is multifunctional as a cure status sensor, and is found to be highly repeatable, demonstrating a new capability to enhance both quality and productivity of composite manufacturing.

OoO curing and related processing techniques introduced here are expected to contribute to the design and manufacturing of next-generation multifunctional composite architectures. These processing techniques have several advantages, including: (1) compatibility with a wide range of composite materials, including OoA- and autoclave-formulated prepregs; (2) removal of size and shape constraints on composite components imposed by the use of a heating vessel; (3) manufacturing cost savings by efficient conductive (as opposed to convective) thermal processing; (4) production improvements via the in situ cure status monitoring by multifunctional heating elements as cure sensors; and (5) the potential for spatial heating control to accommodate structural features such as thick and thin transitions. Future work will expand the techniques to thermoplastics and other high-temperature polymers. The OoO techniques are expected to enable several systems-level production and operational savings, such as accelerated cure cycles, that require further study. Other areas of exploration include on-site composite curing and repair, and leveraging the spatial control of heat flux from the OoO technique into other OoA composite processes, such as resin infusion and resin transfer molding.

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ACCS  ANSYS advanced composite cure simulation
ANL   Argonne National Laboratory
APS   Advanced Photon Source (at ANL)
CFRP  Carbon fiber reinforced polymer (or plastic)
CNT   Carbon nanotube
DENT  Double-edge notch tensile
DMA   Dynamic mechanical analysis
DoC   Degree of cure
DSC   Differential scanning calorimetry
ESRF  European synchrotron radiation facility
EVAC  Engineered vacuum channel
FITC  Fluctuation induced tunneling conduction
FTIR  Fourier transform infrared spectroscopy
GFRP  Glass fiber reinforced polymer
GNPT  Guaranteed nonporous Teflon
ILSS  Interlaminar shear strength
NPN   Nanoporous network
OoA   Out-of-Autoclave
OoO   Out-of-Oven
PDMS  Polydimethylsiloxane
Prepreg Pre-impregnated composite fibers with thermoset or thermoplastic polymer
SBR   Sensor-to-baseline ratio
SBS   Short beam shear
SRCT  Synchrotron X-ray computed tomography
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<tr>
<td>UD</td>
<td>Unidirectional</td>
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<tr>
<td>UTS</td>
<td>Ultimate tensile strength</td>
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<td>$\alpha$</td>
<td>Degree of cure</td>
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<td>$\alpha_g$</td>
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<td>$\bar{u}$</td>
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Chapter 1

Introduction

Composite materials are of great interest as an alternative to traditional materials, because they are composed of two distinct components so that they act as a new material having advantages of each ingredient, and beyond when new mechanisms are introduced\[4,5\]. For example, carbon fibers show high tensile strength but are vulnerable to damage\[5-8\]. In contrast, most polymers are compliant with relatively weak tensile strength\[6-8\]. When combined (i.e., fiber-reinforced polymers), the fibers and polymer matrix create a material that mitigates the weaknesses of each other\[6-8\]. In particular, aerospace structural components on large new commercial aircraft are up to 50% by weight, due to their excellent stiffness- and strength-to-weight ratios\[6\]. The reinforcing fibers (e.g., glass, carbon, and aramid fibers) can be selected according to the strength and stiffness range of the final application\[6\]. In addition, fibers placed at different angles within the composite enable the structures to take full advantage of strength and stiffness, and to withstand complex load states, depending on the application\[4,5,7,8\]. Likewise, the matrix can be polymer, ceramic, or metal. The most widely used matrix in commercial and high-performance aerospace applications is thermoset polymers\[7,8\].

Aerospace structural composites are manufactured in an autoclave to achieve high fiber volume fraction and low void content. Particularly, carbon fibers, pre-impregnated with thermoset or thermoplastic polymers in a form of sheet (prepreg), are extensively processed via autoclaves, especially in advance aerospace structural applications to achieve unmatched mechanical performance. The laminate, composed of layered/stacked prepreg plies, sometimes with other layers such as honeycomb or metal foils, cured inside a vacuum bag at $\sim 100\text{ kPa}$ and at a high applied pressure of about $700\text{ kPa}$ to suppress the formation of voids. Autoclave processing is robust, and remains as
a benchmark process with considerable research and experience gained from extensive industrial use. However, manufacturing based on autoclaves is accompanied by high acquisition and operating costs due to convection heating and pressure. For example, a previous study on the composite manufacturing cost estimation reported that the cost during a curing process accounts for 26% of the total composite acquisition costs\cite{9}. In addition, the capacity of the autoclave limits the size and design of the parts, and the production rate is mainly influenced by the availability of autoclaves (e.g., commercial aerospace autoclaves for fuselage and wing sections can be the size of a multi-story building). Therefore, a faster, more cost-effective, and versatile manufacturing process is desired to overcome the limitations of traditional composite manufacturing processes.

In addition to the development of alternative manufacturing processes, there are other approaches to make the current manufacturing process more efficient, in particular monitoring the status of the curing cycle. Composite part processing converts the matrix polymer to a near-liquid state and then to a solid state. During the curing process, manufacturers may control the curing process through a thermal sensor, or simply following the prepreg manufacturer's cure recipe of applied temperature, pressure, and vacuum. That is, the curing process is controlled indirectly, and it is hard to determine the effectiveness of the recipe directly. For instance, without a direct way to monitor the progress of cross-linking of thermoset polymers, manufacturers usually impose an extra long cure cycle to avoid under-curing of the parts. Even though sufficient cross-linking can occur with this strategy, it leads to additional cure time and operating costs. There is also the risk of over-curing, which can make parts brittle. As a result, manufacturers must establish process specifications based on multiple empirical iterations to ensure acceptable cure cycles for composite production. Furthermore, during the actual cure cycle, the desired cure state may not be reached due to uncertainty about the thermal responses and thermal boundary conditions. This is particularly problematic in built-up structures with cavities and/or parts that have both thick and thin sections. Thus, despite identical parts under the same cure cycle/recipe, the curing progress can vary from part to part, and spatially within a part. The age (i.e., the amount of elapsed time from prepreg manufacture) of the prepreg, environmental conditions during the preparation of the composite laminate, and ambient temperature in an autoclave can also affect the final cured state. Consequently, yield variances can be shown in manufactured parts, and a greater safety margin is utilized during component design. Hence, manufacturers are interested in how to improve the quality and productivity of composite manufacturing by monitoring the cure state\cite{10-15}. By using a more direct and reliable method to monitor the cure status, it should be possible to adjust the cure cycle in real time according to each
batch of production, and less trial and error might improve properties of manufactured composites because of the more accurate control over the process.

In view of the above limitations, the concept of an out-of-oven (OoO) process, in which a nanostructured film comprised of a network of carbon nanotubes (CNTs) is used as a heating element integrated directly on the surface of the laminate, as proposed by the author in earlier work. Although the previous study demonstrated the concept of OoO curing with a comparison of degree of cure (DoC) only, mechanical and physical properties of OoO cured composites have not yet been comprehensively evaluated. A direct comparison of OoO with conventional curing focusing on energy consumption has also not been reported. This dissertation assesses the characteristics of OoO curing compared to conventional composite manufacturing processes using commercialized OoA prepreg systems (Chapter 3) including a significant discovery leading to an extension of OoO to curing autoclave-formulated (non-OoA) prepregs (Chapter 4). Additionally, an in situ cure status technique by utilizing the OoO CNT network elements is introduced (Chapter 5). Finally, the important findings of this dissertation are summarized, and recommendations for future studies are provided (Chapter 6).
Chapter 2

Objectives and Approach

As discussed in Chapter 1, there has been a need for a next-generation composite manufacturing technique which can address the shortcomings of the entrenched oven- and autoclave-dominated convective curing manufacturing processes. To demonstrate the out-of-oven (OoO) curing as a next-generation multifunctional composite manufacturing technique, the characteristics of OoO curing and its advantages and limitations must be understood. In addition, the physical quality of the manufactured composites via OoO curing must be evaluated relative to that of the conventionally manufactured composites.

2.1 Objectives

The objectives of this dissertation are to demonstrate novel composite prepreg laminate processing techniques which can be utilized for manufacturing next-generation multifunctional advanced composite architectures, and to gain the engineering knowledge about the associated phenomena and mechanisms.

2.2 General Approach

This dissertation can be categorized into three sections: characterization of the OoO curing process with an out-of-autoclave (OoA) prepreg; investigation on how to apply OoO curing for conventional autoclave-formulated prepreg; and development of an in situ cure status sensor to achieve multifunctionality with the OoO heaters. Both experimentation and modeling are utilized in all three major sections, and the approach employed in each section is outlined in the remainder of this Chapter.
and the results of the work can be found in subsequent Chapters.

2.2.1 Characterization of the out-of-oven (OoO) curing process with out-of-autoclave (OoA) prepreg

This section focuses on development and validation of OoO curing from a manufacturing perspective focusing on energy consumption and part quality, utilizing OoA-formulated carbon fiber reinforced polymer (CFRP). Characterization of the OoO curing is required in order to understand the underlying physics during the various process steps, and to identify future investigation approaches. This section contains experiments and finite element modeling of composite curing. The finite element modeling was performed using ANSYS advanced composite cure simulation (ACCS) to evaluate the effectiveness of the OoO curing and provide confidence in the modeling approach for future work. The major avenues of exploration and development are:

- Conceptual comparison of the OoO curing with conventional heating-vessel-based (e.g., oven) manufacturing processes
- Examination of thermal response and power consumption of OoO curing, compared to conventional heating-vessel-based manufacturing processes
- Degree of cure (DoC) analysis including differential scanning calorimetry (DSC), and finite element model in order to investigate the thermal progression within a laminate under the OoO curing, such as through-thickness DoC as introduced in Lee et al.\[16\], and evaluating the location of the heater for effective curing
- Experimental void analysis to evaluate if the laminates cured under OoO process have lower void content than acceptable levels (<1% volume fraction) as a primary structural component, using micro computed tomography (μCT) on the cured laminates
- Evaluation of thermophysical properties via dynamic mechanical analysis (DMA)
- Mechanical performance tests to evaluate if the laminate cured under OoO process shows comparable performance as equivalent oven-cured laminates, such as static failure test under a short beam shear configuration (ASTM 2344), double-edge notch tensile testing under 3-point-bending configuration, and comparison of damage progression by synchrotron X-ray computed tomography (SRCT)
Scaling-up demonstration with a 10 cm-scale heater comprised of randomly oriented carbon nanotube film to present the industrial applicability of out-of-oven curing, and to propose future scaling studies towards industrialization

2.2.2 Nano-engineered void reduction technique

The manufacturing of a void-free composite is a key objective in composite manufacturing, because voids inside the composite have a detrimental effect on the mechanical properties\(^\text{[17-22]}\). Interlaminar voids, leading to reduced interlaminar mechanical properties (strength and toughness) are a known issue even with state-of-the-art OoA prepregs\(^\text{[19-21]}\). The nano-engineered void reduction technique provides a means to cure conventional autoclave-formulated prepreg systems without using autoclave pressure. Work that contributes to developing this novel capability and understanding the underlying mechanisms includes:

- Void characterization in order to assess the intrinsic sources of void during a cure cycle and to evaluate the amount and distribution of voids within manufactured composites using \(\mu\)CT and SRCT
- Prepreg surface profile measurement (characterization of surface roughness) to understand the irregularity of the surface of prepreg using a stylus surface profiler
- Quantification of conformability of a nanoporous network (NPN) interleave (vertically aligned carbon nanotube arrays) to the prepreg surface, since this feature is expected to contribute to void extraction
- Study of void reduction mechanism via experiments including investigation of what factors (e.g., capillary wetting and porous network thoroughly linked to free edges) contribute to the enhanced void reduction phenomenon
- Mechanical performance tests to evaluate if the laminate cured under the OoO curing and nano-engineered void reduction technique shows comparable performance as equivalent autoclave-cured laminates, using short beam shear testing (ASTM 2344), which focuses on interlaminar shear strength
2.2.3 Multifunctionality of OoO curing: *in situ* cure status monitoring technique

During the development of OoO curing, we found that there are measurable and repeatable changes in electrical properties of the CNT resistive heater during composite curing, as well as the resistance change with temperature\[^{16}\]. Specifically, a sharp resistance peak occurred at the late-stage of the first temperature ramp-up in the cure cycle, and that a gradual decrease in resistance was presented during curing. Each finding is thought to be related to polymer infusion into network and increase in degree of cure, respectively. This dissertation explores the understanding of these phenomenon, and identifies the main parameters. Additionally, a theoretical model is developed to quantify such parameters as main mechanisms. The detailed topics that will be studied are summarized below:

- Understanding the correlation between cure status and change in electrical properties, via experiment and modeling; the model for tracking infusion status will be studied by adopting the capillary model into our nanoporous network (NPN)
- Correlating the change in CNT-CNT contact spacing and electrical resistance of the network
- Mapping degree of cure (DoC) into change in electrical resistance, using DSC analysis to acquire DoC as a function of post-cure cycle time; additionally, the model including cure kinetics is developed
- Developing a combined model that simulates the electrical resistance of the CNT conductive network during the entire cure cycle
- Evaluation of the applicability of the observed mechanisms to different types of CNT network morphologies
- Repeatability testing to see the efficacy of the proposed sensing technique

2.2.4 Out-of-scope of current work

There are some limitations of the current work and unexplored areas, that are not addressed by the current work:

- Complex-shaped composite manufacturing via OoO curing. The current work on OoO curing focuses on the manufacturing of flat laminates as a first step and to minimize the problems which can occur when manufacturing the complex-shaped laminate (e.g., wrinkle and warpage due to spatio-thermal gradients)
OoO curing for thermoplastics. The OoO curing is expected to be applicable to high-temperature (~ 400 °C) processed aerospace-grade thermoplastic composite materials (e.g., PEEK and PEKK CFRP) due to the temperature range of the nanostructured heater\textsuperscript{[23]}. However, this dissertation focuses solely on the OoO curing with aerospace-grade thermoset polymeric materials which are predominantly used in the aerospace industry currently.

\textit{In situ} cure status monitoring with an actual CFRP. The current work focuses on introducing the multifunctionality of OoO curing and understanding the mechanism of it; therefore, a polymer surfacing film is utilized to simplify the conditions and create a cure status sensor basic element. The application of the proposed technique in an actual CFRP or GFRP (glass fiber reinforced polymer) should be explored in the future.

Various systems-level economic impacts of the introduced OoO, OoO for autoclave-formulated prepreg, and \textit{in situ} cure monitoring technique. Two Spring 2017 MIT 2.S998 "Bench to Bucks" teams explored related topics with support of the author, specifically: (1) Cost savings due to strength variability reduction of composites by Out-of-Autoclave curing, and (2) Out-of-Oven curing of composites: commercialization & use.

The out-of-scope works are discussed in detail in Chapter 6 as recommended future work.
Chapter 3

Carbon Fiber Reinforced Polymer (CFRP) Composite Out-of-Autoclave Laminate Manufacture via OoO Curing

Next-generation composite manufacturing processes are needed to overcome several limitations of conventional manufacturing processes (e.g., high energy consumption). In this chapter, we explore, via experiments and modeling, the characteristics of the out-of-oven (OoO) curing technique that cures a composite laminate via resistive heating of a carbon nanotube film. When compared to oven curing of an aerospace-grade out-of-autoclave (OoA) carbon fiber prepreg advanced composite laminate, the OoO curing reduces energy consumption by over two orders of magnitude. Thermophysical and mechanical tests including differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), short beam shear, and ex-situ and in situ double-edge notch tension indicate that the physical and mechanical properties of OoO-cured laminates are equivalent to those of oven-cured (baseline) laminates. In addition to energy savings, the OoO curing process has the potential to reduce part-to-part variations through improved spatiotemporal temperature control. This chapter follows recently published work by the author[24]

3.1 Background

Manufacturing of aerospace structural composites has traditionally focused on using autoclaves to achieve high-quality reproducible parts, including high fiber volume fractions and low porosity[4,25].
Specifically, carbon fibers, which are pre-impregnated with a thermoset or thermoplastic resin to form prepreg sheets, are autoclave processed because of their ease of use and required exceptional mechanical performance. However, manufacturing composites within an autoclave is accompanied by high acquisition and operation costs due to the necessity of this specialized heated pressure vessel to suppress the formation of voids. Furthermore, the volume of an autoclave, which is fixed, limits the size and design of parts, and the production rate is primarily affected by autoclave availability. As a result, there has been an increasing interest in developing alternative techniques. For example, previous studies reported manufacturing approaches using different heating methods such as microwave heating, induction heating, laser heating, and resistive heating of electrically conductive fillers in composites \cite{26-29}. Additionally, specially-formulated and designed prepregs that can be cured in an oven (out-of-autoclave, or OoA prepregs) without the need for autoclave pressure have been recently developed \cite{30,31}.

OoA prepregs with oven curing have been introduced commercially as an alternative to autoclave-cured prepregs manufacturing. In contrast to the autoclave prepregs, OoA prepregs do not require the use of pressure vessels to achieve a void-free laminate because of their formulation and unique structure; e.g., dry regions between resin-rich regions in OoA prepregs function as built-in void extraction channels \cite{31-38}. Thus, OoA prepregs can be cured with conventional thermal ovens thereby allowing lower cost manufacturing than using autoclave-cured prepregs and autoclaves \cite{39,40}. Nonetheless, even the use of conventional ovens is not completely ideal from a manufacturing perspective. Heat transfer is still based on convection, which leads to inefficiencies and to spatial gradients in cure and stress due to convective-to-conductive interactions between the oven gas medium (usually air) and the cure materials \cite{41-43}. This also drives part-to-part variability as cure assembly is nearly completely a manual process, and fabrication is still limited because of an oven’s fixed geometry. Technologies such as OoA prepregs that move from an autoclave to an oven are advantageous, but sill suffer from convective inefficiencies and related manufacturing challenges.

Given the limitations above, the concept of an out-of-oven (OoO) process has been proposed, which uses a CNT film as a heating element directly integrated into the surface of a laminate so that curing does not require any heating vessel or convective medium \cite{16}. While the previous study demonstrated the concept of OoO curing along with degree-of-cure (DoC) comparisons, mechanical and physical properties of OoO-cured composites have yet to be comprehensively evaluated, particularly properties dominated by interlaminar failure, a key area to evaluate for laminated com-
To our knowledge, the direct comparison between OoO and traditional curing from an energy consumption analysis has also not been reported in the extant literature. In the current study, we compare the OoO curing vs. oven curing using an OoA prepreg system, and find that the OoO curing enables highly efficient manufacturing of composites while preserving the mechanical properties, particularly interlaminar strength, equivalent to the conventional oven method.

Fig. 3.1a provides an overview of conventional oven vs. the OoO curing process. Conventional oven curing processes as well as autoclaves that use convective heating require the entire vessel volume to be heated, regardless of the geometry of the component. Therefore, as shown in Fig. 3.1b, the electrical power for resistive heating should pass through several thermal barriers such as heat loss to the environment, the gas medium (here, air), and heating of vacuum bagging and cure materials to heat up a laminate. In contrast, the OoO curing has no thermal barriers between the heater and laminate, and thus transfers the heat via direct conduction because the CNT heater is installed on a surface of a laminate. Since the heat loss to the environment is connected to the heater in parallel, thermal insulation can suppress the heat loss, enabling most of electrical power to go into the laminate from the heater. Additionally, because the CNT film has extremely low thermal mass due to its low density (~25 gsm), the electrical power can increase the temperature of a laminate immediately.
Figure 3.1: Comparison of oven and out-of-oven manufacturing process for out-of-autoclave laminate curing: (a) Overview of the physical differences between oven and out-of-oven process. (b) Comparison of thermal equivalent circuit model of oven and out-of-oven process. The circuits are symmetric with respect to the laminate. Note that the OoO process provides direct conductive heat transfer to the laminate, whereas the oven process passes through thermal barriers including the oven medium (air), vacuum bag, and cure materials.
3.2 Materials and Methods

The characteristics of the OoO curing process were explored by tracking thermal responses and electrical power consumption during a cure cycle. To compare the mechanical and physical properties of OoO-cured composites with those of oven-cured composites, degree of cure (DoC) analysis, short beam shear (SBS) test, dynamic mechanical analysis (DMA), and double-edge notch tensile (DENT) testing were performed.

3.2.1 Composite fabrication and processing

In this study, Hexcel IM7/M56 OoA aerospace-grade unidirectional carbon fiber prepreg was used\(^{[45]}\), which is designed to be processed with a vacuum-bag-only curing method. The prepreg is nominally 394 gsm, and nominal cured ply thickness of this prepreg was 253 μm with a target of 58.8% \(V_f\) of carbon fiber in each ply. Considering the standards used for the various experiments, and the field of view of synchrotron X-ray for \textit{in situ} tensile tests, eight plies (nominal laminate thickness of 2.02 mm) were used for the laminate’s quasi-isotropic layup of \([0/90/±45]_s\). Hexcel AS4/8552 unidirectional (UD) prepreg properties were used for the comparison of energy consumption, because the ANSYS Composite Cure Simulation (ACCS) provides the full engineering data of Hexcel AS4/8552 UD prepreg such as thermal conductivity, the exothermic heat of reaction, etc. for the cure modeling. The 16 plies of AS4/8552 UD prepreg were stacked up to match to the nominal thickness of the laminates comprised of IM7/M56 prepreg; the nominal cured ply thickness of AS4/8552 UD prepreg was 0.130 mm, giving a nominal laminate thickness of 2.08 mm, very close to the IM7/M56 nominal thickness of 2.02 mm. As a resistive heater, a commercialized CNT film, Veelo HEAT from General Nano LLC\(^{[46]}\), was utilized for this work. The CNT film was composed of randomly oriented multiwalled CNTs, is \(\sim40\ \mu\text{m}\) thick, with an areal density of \(\sim25\ \text{gsm}\), and an isotropic sheet resistance of \(\sim5\ \Omega/\square\) as measured using 4-wire probes (so this value does not include contact resistance).

For the oven curing process, the recommended vacuum bagging procedure from the prepreg manufacturer was followed\(^{[45,47]}\). The cure materials are standard for composite prepreg processing, and include a vacuum bagging film (Airtech WL8400), guaranteed nonporous Teflon (GNPT) film (Airtech Release Ease 234 TFNP), sealant tape (Airtech GS-213-3), and air breather (Airtech Ultraweave 606) as shown in Fig. 3.2. To ensure the removal of air trapped during the hand lay-up process, vacuum debulking was performed on the full laminate at room temperature for 6 hours.
Figure 3.2: Vacuum bag lay-up of the out-of-oven curing process with a one-sided heater. A carbon nanotube (CNT) film was installed directly on the surface of a laminate as the heating element.

After the debulking process, the rounded laminate edges were trimmed to ensure the laminate is re-breathable, a step necessitated by the OoA formulation of the prepreg, following manufacturer recommendations. Once a vacuum bag was prepared for the cure, the laminate and cure materials were placed in a gravity convection oven (Lindberg/Blue M, GO1350A) for curing. During the cure cycle, the recommended curing condition in the technical data sheet was followed for each prepreg system. Both prepreg systems are designed to have the same temperature for the thermal process as follows: cure temperature of 110 °C with a hold time of 60 min, and post cure temperature of 180 °C with a hold time of 120 min; ramp rate at 3 °C/min.

For OoO curing, the cure setup was modified for conductive curing, similar to the previous study[16] (see Fig. 3.2 for the modified vacuum bagging setup with a one-sided heater and Fig. 3.3 for a fabricated CNT heater and vacuum bag). In particular, thermal insulating blocks (25 mm-thick MICROSL Microporous Insulation from ZIRCAR Ceramics Inc.) were installed to reduce heat loss to the environment. In addition, because one of the main goals of this study was to compare the physical properties of oven vs. OoO curing, a GNPT film was inserted between the heater and the surface of the laminate such that the OoO heater can be easily peeled off after cure. Such removal of the heating element is different from the previous study using a CNT nanocomposite heater; a conductive CNT polymer nanocomposite was permanently attached to the surface of the laminate with a surfacing film in the prior work[16,48]. When an additional heater was needed for a thick laminate (e.g., 20 mm-thick 160-ply unidirectional laminate), two heaters were attached on the top and bottom surfaces of a laminate. During an OoO cure cycle, a DC power supply was connected to the two copper tape electrodes of the heater to control the input voltage to follow the specific cure cycle[16,48]. For the feedback control, the input voltage was used for the system input, and
Figure 3.3: Components of OoO curing setup: (a) fabricated CNT film which is installed directly on the surface of a laminate as the heating element and (b) prepared vacuum bag for the out-of-oven curing process with a one-sided heater.
Figure 3.4: Fabricated quasi-isotropic 16-ply laminate by Out-of-Oven curing process. Optical image of (a) the top of the laminate and on (b) the side.
the temperature of the CNT heater was the system output. Temperature of the CNT heater was measured via a thermocouple (OMEGA Engineering fast-response K-type). The input voltage was controlled to make the temperature setpoint vs. measured less than 0.1 °C, while following the designated cure cycle. Input voltage, current, and power consumption were recorded using digital multimeters embedded in the power supply (B&K Precision DC power supply 9201).

3.2.2 Characteristics of oven and out-of-oven curing

To evaluate the energy consumption of an oven vs. OoO process, the power consumption was measured during a cure cycle and compared with the model of the multi-physical curing process by ACCS. The transient thermal analysis was conducted to capture thermal responses within a laminate such as temperature and heat flux. As mentioned above, a quasi-isotropic laminate comprised of unidirectional layers of Hexcel AS4/8552 prepreg in a [0/90/±45] layup was used for finite element cure modeling due to the full accessibility of engineering data needed for ACCS. Each ply was modeled with ten meshes to obtain results through the thickness of the laminate. Note that the cure simulation was conducted in a quasi-1D (e.g., the edge effects were not included).

For an oven process, a gravity convection oven was used in the experiment and the model. The dimension and engineering data such as the amount of heat loss to the environment were adopted in the model from the technical data sheet of the manufacturer\cite{49}. The thermal analysis assumed that a vacuum bag and cure materials are surrounded by the heated air during a cure cycle. The power consumption was acquired by calculating the electrical power of the heating elements. The convective heat transfer coefficient was set at 15 W/m°C at the surface of the vacuum bag, and the dry air of an oven was modeled as a lumped capacitance model. The heat flux from the laminate due to the exothermic reaction of the thermoset was included in the calculation. In the experiment, the electrical power consumption was measured directly at the receptacle via a current probe (FLIR TA72). For modeling the OoO process, we assumed that the temperature of the cure cycle was applied to the surface of a laminate because the CNT heating component is mounted directly on a surface of a laminate. The engineering data of thermal insulation (density of 230 kg/m³, specific heat of 800 J/kg°C, and thermal conductivity of 0.019 W/mK at 20 °C to 0.023 W/mK at 200 °C with the assumption of linearity) was used in the model. The experimental electrical power consumption was obtained by measuring the input voltage and current into the CNT heater mounted on the laminate via the DC power supply.
3.2.3 Degree of cure (DoC) analysis

After the curing using the oven and OoO methods, differential scanning calorimetry (DSC) was conducted using a Discovery DSC (TA instruments) to evaluate the DoC of the laminate. The dynamic DSC run was performed by scanning the heat flow from 40 °C to 300 °C at 5 °C/min ramp rate, based on ASTM D7028. The DoC was estimated by comparing the area of the exothermic peak observed in the DSC curve of the heat-processed laminate, also known as the heat of reaction, to that of an uncured laminate. The DSC specimens were taken from each layer of a laminate so that the through-thickness variance of the DoC could be assessed, particularly given the one-sided nature of the OoO curing. For the DSC testing, eight plies of 60 mm × 50 mm IM7/M56 laminae were stacked unidirectionally by hand lay-up technique, and release films were introduced to both the left and right end of the laminate in between top, middle, and bottom layers for easy separation after curing as developed in earlier work by the author\textsuperscript{16,50}. The release film prevents resin flow between layers. The procedures for oven and OoO curing followed the same procedures described in the above section.

3.2.4 Short beam shear (SBS) testing

The SBS test was conducted based on ASTM standard D2344, which is also consistent with DIN EN2563, and is the simplest test for interlaminar shear strength (ILSS). The dimension of a specimen was nominally 12 mm × 4 mm × 2 mm (L × W × t), and these specimens were taken from the 120 mm × 120 mm unidirectional laminates comprised of 8 plies of IM7/M56 prepreg. Small angles (±2°) between the plies were introduced intentionally to avoid fiber nesting\textsuperscript{51}. The cut laminate edges were polished with 800, 1200, and 2400 grit sandpapers to avoid rough or uneven surfaces which may result in pre-cracks, following the Standard. As prescribed in ASTM D2344\textsuperscript{52}, a three-point bend fixture with a loading nose of 6 mm, supports of 3 mm diameter steel cylinders, and the span length of 8 mm was utilized. During the tests, the force applied to the specimen was monitored at a rate of cross head movement of 1.0 mm/min applied by a Zwick/Roell Z010 mechanical testing machine. The short-beam strength (σ\textsubscript{SBS}) was then calculated using Eq. 5.8 as follows:

\[
\sigma_{\text{SBS}} = 0.75 \times \frac{P_f}{w_{\text{SBS}} \times t_{\text{SBS}}} \quad (3.1)
\]

where \(P_f\), \(w_{\text{SBS}}\), and \(t_{\text{SBS}}\) are the load at the failure observed during the test, the width, and the thickness of the specimen, respectively.
3.2.5 Dynamic mechanical analysis (DMA)

The specimen dimensions and testing procedure were carried out based on the ASTM standard D7028. The Dynamic Mechanical Analyzer used for the characterization of the composite laminates was a TA Q800 DMA (TA Instruments). All DMA tests were conducted using a three-point bending fixture with a span of 50 mm, which is ideal for composite materials due to its simpler stress distribution than that induced in a single or double cantilever configuration, and measurable strain for high modulus materials\[53\]. For DMA tests, an 8-ply unidirectional laminate of 120 mm × 120 mm was cured by oven and OoO process, respectively. In the same manner as previously discussed, the small angle between plies was used to prevent the fiber nesting. Four specimens of 60 mm × 12 mm × 2 mm (L × W × t) taken from each oven-cured and OoO-cured laminate were tested in the temperature range from 40 °C to 300 °C at 2 °C/min heating rate, maximum displacement of 50 μm, and multi-frequency sweep of 1, 3.2, 10, and 30 Hz. The storage modulus, loss modulus, and tan delta were obtained via DMA test, and the glass transition temperature was determined from the storage modulus curve. Among three different ways to determine glass transition temperature, the tan delta curve was additionally used for determination of glass transition temperature to conduct the most refined comparison of the oven-cured and the OoO-cured laminate, even though the storage modulus curve is widely used because of its conservativeness\[53\]. The estimation of the activation energy is most consistent when the glass transition temperature is determined by the tan delta peak\[53-56\]. The multi-frequency sweep results were analyzed to estimate the activation energy of the glass transition relaxation as an additional comparator of the oven vs. OoO manufacturing methods. The monitoring of the activation energy is correlated to the modulus and compliance of a composite at the end of the service life, and therefore is additionally useful in assessing environmental exposure and aging of the material\[54,56-59\]. The estimation of the activation energy is based on the effect of temperature on the frequency of molecular conformational changes in polymers\[59,60\]. Such phenomenon can be explained by the Arrhenius relationship: the increase in frequency leads to the shift of the tan delta curve toward a higher temperature. The activation energy can be estimated by obtaining the slope of the ln f vs. \(\frac{1}{T_g}\) with Eq. 5.9 as follows\[53\]:

\[
\Delta H = -R \frac{d(\ln f)}{d(\frac{1}{T_g})}
\] (3.2)

where \(\Delta H\) is the activation energy (kJ/mol) for the glass transition relaxation, \(R\) is the universal gas constant(J/mol K), \(f\) is the testing frequency (Hz), and \(T_g\) is the glass transition temperature in
Kelvin (K).

3.2.6 Double-edge notch tensile (DENT) test

To compare the tensile strength and the failure progression of OoO-cured laminates with those of oven-cured laminates, *ex-situ* and *in situ* tensile testing with double-edge notch specimens were conducted. For this test, a quasi-isotropic laminate (IM7/M56, [0/90/±45]s) of 120 mm × 120 mm was cured by each manufacturing method. The 1 mm-radius double-edge notches were introduced into the 36 mm-long and 4 mm-wide specimens using an abrasive waterjet so that the failure occurs within the X-ray field of view during *in situ* tensile testing\[61,62\].

The CT5000 5kN *in situ* tensile stage for μXCT (Deben UK Ltd.) was used as a load frame for both *ex-situ* and *in situ* tensile testing. All tensile testing with the *in situ* stage was conducted under 0.3 mm/min motor speed. The ultimate tensile strength (UTS) of each specimen was calculated with the area at the notch and the maximum load at failure. To evaluate the failure mode and progression, the specimens were scanned *via in situ* synchrotron X-ray computed tomography (SRCT) prior to tensile loading and followed by scans at incrementally increasing stress range from 30% to 100% UTS in steps of 10%. The *in situ* experiment was performed at the beamline 2-BM of the Advanced Photon Source (APS), Argonne National Laboratory (ANL). An isotropic voxel size of 1.3 μm was acquired with the X-ray beam energy of 22.7 keV and a 5x objective lens. For each scan, 1500 2D projections were captured while a specimen was rotated in 180° *via* 2560 × 2160 PCO.Edge 5.5 sCMOS camera. The exposure time for each projection was 100 ms, and the projection radiographs were reconstructed using TomoPy\[63\], an open source Python based toolbox, and a reconstructed 3D volumes were analyzed with the commercial visualization software, Avizo (FEI), to segment the features of interest such as matrix damage.

3.3 Results and Discussion

Thermophysical and mechanical testing results are discussed for both curing methods, followed by a failure progression study utilizing *in situ* SRCT mechanical testing.

3.3.1 Characteristics of oven and OoO curing

Fig. 3.5 shows the cure simulation and experimental results for the oven and OoO curing process for the 2 mm-thick 60 mm × 50 mm laminate. As presented in Fig. 3.5a, the oven process showed an
expected transient temperature response on the laminate surface due to the convective heat transfer, whereas the OoO process had an immediate response by conductive heat transfer. As mentioned in the Introduction, the convection coefficient in the heating vessel varies greatly due to uncontrolled factors that influence gas flow dynamics, resulting in temperature gradients in a laminate\textsuperscript{[41–43]}. Furthermore, if several parts are cured simultaneously in a heating vessel, part-to-part variation may occur. However, because the OoO process directly controls the temperature of each part, OoO curing has the potential to reduce part-to-part variation.

A clear difference between the oven and OoO process arises from the two orders of magnitude reduction in energy consumption during the curing cycle. An oven having the ideal size for composite parts is rarely available in practice, and the part volume needs to be kept low in the heating vessel to ensure effective convection and uniform heating, which are critical for part quality and
dimensions\textsuperscript{[64]}. Therefore, it is not uncommon to cure parts to have a volume much less than the volume of the oven or autoclave. In our oven curing experiments, the part-to-oven volume is 0.1%, typical of research autoclaves, and of the same order as that of some composite production autoclaves, e.g., curing of an aerospace wing shell (which should be closely optimized to the autoclave used), has a part-to-autoclave volume ratio of 0.4% (3.54 m\textsuperscript{3} part, and 896 m\textsuperscript{3} autoclave\textsuperscript{[65–67]}). Thus, the energy savings due to the conductive OoO curing method of two orders of magnitude for the oven considered herein is relevant at the commercial scale. It should be noted that the energy savings measured herein is also in agreement with simple models (based on volume considerations) presented previously\textsuperscript{[16]}.

The lower images of Fig. 3.5b show the power consumption of each manufacturing process during a cure cycle. In the case of oven curing, most of the power consumption was used to raise the temperature of the medium gas (i.e., dry air) inside the oven and to maintain the temperature against heat loss to the environment. Since the amount of heat loss to the environment provided in the technical data sheet was included in the convection oven model, the power consumption of the model was in good agreement with the experimental results. During the ramp-up period, power consumption of $\sim$2.1 kW was observed, and $\sim$500 W and $\sim$1 kW were consumed at the 110 °C and 180 °C hold steps, respectively. In contrast, the OoO process exhibited a maximum power consumption of $\sim$12.5 W, two orders of magnitude lower than the oven curing process. The total energy consumption during the entire curing cycle was 13.7 MJ for the oven and 118.8 kJ for the OoO process, respectively - two orders of magnitude less for the OoO vs. the oven cure. Since the OoO curing process is adjusted proportionally to the surface area of the part, the energy savings are expected to be particularly prominent in aspect ratios commonly found in wind, aerospace, and other applications where parts are often long and narrow such as a wing and fuselage. Note that the model captured the slight reduction of electrical power at the early stage of the post-cure cycle; a valley in the power plot was observed at $\sim$1.9 hours (see Fig. 3.5b) due to the exothermic heat of reaction.

Additionally, we conducted the OoO curing experiment with a 20 mm-thick laminate comprised of 160 plies of 60 mm $\times$ 50 mm to evaluate if the exothermic heat of reaction of the thermoset polymer affects the power consumption during curing. A 160-ply unidirectional 60 mm $\times$ 50 mm laminate comprised of Hexcel AS4/8552 UD prepreg was used for this experiment; the nominal cured ply thickness of AS4/8552 UD prepreg was 0.130 mm, giving a nominal laminate thickness of 20.8 mm. For the oven and OoO curing process, the experimental description for 2 mm-thick
laminate curing was followed. Additionally, due to the possibility of temperature gradient through thickness within a ~20 mm-thick laminate, two CNT heaters were installed on the top and bottom surfaces of the laminate for this experiment. The temperature was measured by thermocouples that were attached to the CNT heaters, and inserted into the center of the laminate. The temperature of the top and bottom surface were controlled to follow the same recommended cure cycle.

![Graphs showing temperature profiles during curing](image)

Figure 3.6: Comparison of the temperature profiles during a 20 mm-thick laminate via (a) an oven curing, and (b) an out-of-oven curing. The oven process showed a transient temperature response on the laminate due to the convective heat transfer, whereas the out-of-oven process had an immediate response by conductive heat transfer. Due to the exothermic heat of reaction, an overshoot in the early stage of post-cure cycle was observed in both cases.

The oven process showed a transient temperature response on the laminate due to the convective heat transfer, whereas the out-of-oven process had an immediate response by conductive heat transfer (See Fig. 3.6). Oven curing exhibited temperature overshoots of ~35 °C on both the center and surfaces during the early stage of post-cure cycle due to the exothermic heat of reaction. However, OoO curing showed a decreased magnitude of the overshoot of ~25 °C and ~10 °C at the center and surface of the laminate, respectively. The results suggest that the OoO process helps following an intended cure cycle, resulting in the final thermal and mechanical properties close to the targeted values. As such, the top and bottom surface of this thick laminate cured via OoO exhibited DoC of 90.6% and 90.8%, respectively; those are in the same range of DoC from the 2mm-thick experiment. Fig. 3.7 provides the power consumption of each manufacturing process during a cure cycle. We observed a ~20 min self-curing region that does not require any electrical power due to the exothermic heat of reaction in the OoO curing. Such phenomenon indicates the possibility of further energy saving by recycling the heat of reaction of a laminate to cure itself. By contrast, this
distinct reduction in power consumption was not observed in the oven curing.

Figure 3.7: Comparison of the power consumption during a 20 mm-thick laminate cure via: (a) oven curing, and (b) out-of-oven curing. Note the difference in scale between the oven and OoO power axes. A self-curing region, which does not require any electrical power because of the exothermic heat of reaction, was observed in the out-of-oven curing.

3.3.2 Comparison of thermophysical properties

DoC via DSC and characterizations from DMA are used to compare the thermophysical attributes of the OoO to oven curing. Three DSC specimens were prepared from the top (the 1st ply adjacent to the CNT heater), the center (the 4th ply), and the bottom ply (the 8th ply), to establish through-thickness spatial trends in DoC. The mean value of the heat of reaction (~152 J g⁻¹) acquired from three uncured prepreg plies was used for the calculation of DoC. The expected range of DoC for oven manufacturing for this material is in the range of 90-95% (per the manufacturer), which is typical of most oven and autoclave processed aerospace-grade composites. As presented in Fig. 3.8, the DoCs of both oven and OoO process are in the target range. To determine whether means of oven and OoO curing are statistically different, the one-way analysis of variance (ANOVA; Welch’s ANOVA⁶⁸) was conducted. The ANOVA is used throughout the discussion to compare oven and OoO curing, and a p-value less than 0.05 is used to establish a statistical difference with 95% confidence. The DoCs of an OoO-cured laminate showed no statistical difference from those of an oven-cured laminate. There was also no significant spatial variation in both cases. The previous study without thermal insulation found that the DoC of the laminate strongly depends on the thermal distribution within a laminate¹⁶. In particular, the DoC of the laminate correlates to the surface temperature of the CNT heater, and the DoC decreased in the through-thickness direction away from
the heater due to the thermal losses as the distance from the CNT heater increases. Therefore, the results of this study indicate that simple thermal insulation can further improve the in-plane thermal distribution, and minimize through-thickness DoC trends. Overall, a one-sided CNT heater on a 2 mm-thick laminate is enough to obtain the equivalent thermal properties of oven-cured laminates.

The results from DMA curves such as the storage modulus, loss modulus, and tan delta, altogether suggest that oven-cured and OoO-cured specimens exhibit the same dynamic mechanical responses. See Fig. 3.9a for the representative storage modulus, loss modulus, and tan delta curve from DMA tests on the specimens at the testing frequency of 1 Hz. Fig. 3.9b exhibits the storage modulus and loss modulus at 100 °C as well as the magnitude of the tan delta peak. The results of the p-value in all three curves (p = 0.84 for the storage modulus; p = 0.25 for the loss modulus; and p = 0.18 for the tan delta peak) suggest that there is no significant difference in the curves of oven-cured and OoO-cured specimens. The glass transition temperature determined by the storage

![Figure 3.8: Comparison of degree of cure as evaluated spatially via differential scanning calorimetry (DSC) at the top, center, and bottom plies of 8-ply laminate for oven and out-of-oven curing. Note that the whiskers represent the standard error. Data is offset slightly on the x-axis (ply location) for visualization. Note that in the out-of-oven curing process, the heater is in contact with the top ply (the 1st ply). p-values of 0.31, 0.83, and 0.55 indicate that there are no significant differences between the oven and out-of-oven curing process.](image-url)
modulus curves \( (T_{g,s}) \) and tan delta curves \( (T_{g,t}) \) at 1 Hz frequency, and estimated activation energy from the multi-frequency sweeps at 1, 3.2, 5, and 30 Hz, are summarized in Table 3.1. For the estimation of activation energy, \( T_{g,t} \) was used as it is considered the most accurate\(^{53-56}\). The oven-cured and OoO-cured specimens exhibited the same \( T_{g,t} \) and \( T_{g,s} \) of \( \sim 227 \degree C \) and \( \sim 205 \degree C \), respectively. It should be noted that the manufacturer reported \( T_{g,s} \) of \( 204 \degree C \)\(^{451}\) is very close to the values measured here. It is known that the glass transition temperature measured by DMA curves may vary by up to \( 25 \degree C \) depending on the parameter and methodology for testing\(^{56,69}\). The oven-cured and the OoO-cured specimens exhibit statistically no difference in \( T_{g,s} \), \( T_{g,t} \), and activation energy as shown above and in Table 3.1. Therefore, the DMA tests indicate that the oven and OoO curing provide the comparable dynamic properties of the polymer as expected.

Table 3.1: Glass transition temperature and activation energy of relaxation of the oven and the out-of-oven specimens. Note that the glass transition temperatures obtained from the storage modulus curves and tan delta curves correspond to \( T_{g,s} \) and \( T_{g,t} \), respectively. \( p \)-values of 0.99, 0.75, and 0.68 indicate that there are no significant differences between the oven and out-of-oven curing process.

<table>
<thead>
<tr>
<th>Specimen Number</th>
<th>( T_{g,s} ) (\degree C)</th>
<th>( T_{g,t} ) (\degree C)</th>
<th>Activation Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oven</td>
<td>OoO</td>
<td>Oven</td>
</tr>
<tr>
<td>1</td>
<td>207.38</td>
<td>204.27</td>
<td>227.19</td>
</tr>
<tr>
<td>2</td>
<td>203.97</td>
<td>206.39</td>
<td>226.63</td>
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<td>204.43</td>
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<tr>
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<td>206.94</td>
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<tr>
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<td>205.69</td>
<td>227.25</td>
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<tr>
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<td>0.23</td>
</tr>
<tr>
<td>( p )-value</td>
<td>0.99</td>
<td>0.75</td>
<td>0.68</td>
</tr>
</tbody>
</table>

3.3.3 Results of mechanical testing

Here we explore the results of SBS and double-edge notch strength testing to further assess any differences in OoO vs. oven curing. The \textit{in situ} SRCT testing of the DENT specimens also allows void quantification. Fig. 3.10 presents synchrotron radiation \( \mu \)CT images of the oven-cured and OoO-cured specimen. As presented, both specimens did not show any detectable void under a high resolution scan (voxel size of 1.3 \( \mu \)m). There was no morphological differences noted between the oven and OoO specimens. In the SBS test, 14 specimens were tested for each curing process. In both cases, it was observed that the failure proceeds sequentially as: (1) plastic deformation as an indentation at the loading nose, followed by (2) interlaminar shear failure (as defined in the standard D2344 as a valid test), which resulted in the type of load-deflection of each case as shown in the
Figure 3.9: DMA results. (a) Representative storage modulus, loss modulus, and tan delta curve from DMA tests at the testing frequency of 1 Hz for oven and out-of-oven specimens. (b) Storage modulus and loss modulus at 100 °C, and the magnitudes of tan delta peak of the oven and the out-of-oven specimens. Note that the whiskers represent the standard error. p-values of 0.84, 0.25, and 0.18 indicate that there are no significant differences between the oven and out-of-oven curing process.
inset of Fig. 3.11. The first failure corresponds to indentation and/or crushing at the loading nose, and the maximum load (second failure) occurs due to the interlaminar shear failure. It is known that the short-beam shear strength may not directly indicate the interlaminar shear strength of the laminate due to its complex stress distribution, and that the failure can be a combination of different failure modes such as discrete and irregular interlaminar shear, tension, compression, and plastic deformation\(^{70}\). However, it is generally accepted that SBS testing can be used for comparison and as a screening tool for composite laminate properties with a description of the failure mode\(^{71,72}\). Fig. 3.11 exhibits the short-beam strength of oven-cured and OoO-cured specimens in a boxplot. Note that the boxes represent the interquartile range for each group; the line in the middle of each box represents the median, and the whiskers represent the minimum and maximum datum; the outlier was determined by Tukey’s fences\(^{11}\). Since the specimens failed in complex modes (i.e., indentation and interlaminar shear), the first failure load and the maximum load observed during the test were both analyzed as short beam shear failure stresses. The oven-cured specimens showed a strength of 99.22 MPa (SE = 0.70 MPa) at first failure, and 109.11 MPa (SE = 0.70 MPa) at the maximum load. The OoO-cured specimens showed the short-beam strength of 100.40 MPa (SE = 1.93 MPa) at the first failure and 110.62 MPa (SE = 1.10 MPa) at the maximum load. Therefore, the oven-cured and the OoO-cured specimens showed similar short-beam strength both at first failure and the maximum load. The ANOVA was again conducted to determine whether means of oven and OoO are statistically the same for the short-beam strength conditions. As presented, the results of the \(p\)-value in both short-beam strength cases (\(p = 0.74\) for the first failure and \(p = 0.29\) for the maximum load) suggest that the means of short-beam strength values of oven-cured and OoO-cured specimens are not significantly different from each other. Therefore, we conclude that oven-cured and OoO-cured specimens have the same strength at each failure mode as well as the same sequential order of failure mode. Given the correct mode of interlaminar failure at the maximum load, we conclude that this is the more important comparison as this stress is the SBS. It should be noted that the manufacturer reported ILSS of 98.6 MPa\(^{45}\), which is very close to the lower values measured here. ILSS has many measures with SBS considered more qualitative and comparative, rather than a true measure of ILSS.

Fig. 3.12a shows the UTS results for double-edge notch specimens of the oven-cured and the OoO-cured laminates. As presented, the oven-cured specimens showed a DENT UTS of \(\sim 562.04\) MPa (SE = 8.09 MPa), while the OoO-cured specimens performed the UTS of \(\sim 566.68\) MPa (SE = 10.54 MPa). Given that the manufacture reported IM7/M56 showed comparable fiber-
dominated strengths as IM7/8552,[73] the measured DENT UTS can be compared with the strengths of IM7/8552 as follows: the DENT UTS is expected to be considerably lower than the unnotched tensile strength, and similar to the open hole tensile strength, given an equivalent stacking sequence. It was reported that the specimens comprised of IM7/8552 quasi-isotropic layup ([45/0/−45/90]_2S) have unnotched tensile strength of 717.12 MPa and open hole tensile strength of 458.66 MPa.[74] Since the DENT UTS of ~564 MPa is in between the unnotched tensile and open hole tensile strength, they are considered to be in a reasonable range. Similarly, the ANOVA was applied to evaluate whether means of oven and OoO are statistically the same. The significance level is 0.73, which is above 0.05, therefore, there is no statistically significant difference in the means of UTS value between oven-cured and OoO-cured specimens.

Fig. 3.12b presents the 3D rendering of damages at 0%, 50%, 70%, and 90% UTS. During in situ tensile testing, three major damage mechanisms have been observed in both oven and OoO specimens as followed: intralaminar splits in 0° ply, transverse ply cracks in 90° ply, and intralaminar cracks in ±45° plies. Considerable amounts of cracks were observed at 70% UTS, while crack initiations occurred at 50% UTS from the notches in both cases. The oven-cured and OoO-cured
Figure 3.11: Short-beam strength of oven and out-of-oven specimens. Note that the boxes represent the interquartile range for each group; the line in the middle of each box represents the median, and the whiskers represent the minimum and maximum datum; the outlier was determined by the Tukey’s fences\textsuperscript{11}. The inset figure shows representative load-deflection curves for the two types of curing as discussed in the main text. Due to the initial load drop (“first failure”), both the first failure and maximum load were used for the determination of the strength. Considering \( p \)-values, the means of short-beam strength values of oven-cured and OoO-cured specimens are not significantly different from each other.

Specimens showed the same crack progression trend: most of cracks in ±45° plies were formed after the crack formation in 0° ply and 90° ply. Thus, we conclude that the tensile strengths of oven-cured and OoO-cured specimen were statistically same and damage progression occurred in the identical manner. Because of current limitation in objectively quantifying damage, future work on the crack opening displacement and the volume of the cracks will provide a quantitative comparison of oven and OoO specimens.
Figure 3.12: Results of double-edge notch tensile ex-situ and in situ testing for oven and out-of-oven curing. (a) Ultimate tensile strength of double-edge notch specimens, and (b) 3D rendering of damage (matrix cracks) at 0%, 50%, 70%, and 90% of the mean ultimate tensile strength. Note that the boxes represent the interquartile range for each group; the line in the middle of each box represents the median, and the whiskers represent the minimum and maximum datum. A p-value of 0.73 indicates that there is no significant difference between the oven and out-of-oven specimens. The oven and the out-of-oven specimens demonstrated equivalent damage progression.
3.4 Summary

In summary, we examined the characteristics of the out-of-oven curing process using a carbon nanotube film as a heating element, compared to that of a conventional oven composite curing process, for an aerospace-grade out-of-autoclave (OoA) formulated unidirectional carbon fiber advanced composite prepreg system. We further evaluated the thermophysical and mechanical properties of the processed out-of-autoclave composites. Results suggest that there is no significant difference between the out-of-oven curing and oven curing in any of the metrics: (degree of cure analysis, short beam shear, dynamic mechanical analysis, and double-edge notch tensile test); therefore, the out-of-oven curing can achieve the equivalent thermal and mechanical properties for out-of-autoclave composites, as the conventional curing method. Moreover, the OoO composite curing process provides a significant reduction in electrical energy consumption by two orders of magnitude (from 13.7 to 0.12 MJ). The modeling of both manufacturing processes showed good agreement with electrical power consumption during a cure cycle. Next-generation composite manufacturing via OoO may overcome the limitations of the conventional composite manufacturing process with several advantages as follows: (1) removal of size and shape constraint on composite components using a scalable conductive heating element, (2) on-site curing and/or repair, (3) greater accessibility to the composite manufacturing facilities, and (4) cost savings on manufacturing by efficient thermal processing. Considering that one of the benefits of the out-of-oven process is a rapid ramp rate, future work should explore the further reduction of energy consumption and the evaluation of thermophysical and mechanical properties of the out-of-oven-cured composites fabricated by a rapid-heating-enabled cure cycle.
Chapter 4

CFRP Composite Autoclave Laminate Manufacture via OoO Curing: Nano-engineered Void Reduction Technique

Next-generation processing techniques for manufacturing layered polymeric architectures should address the limitations of the conventional autoclave manufacturing process. Non-autoclave processes proposed so far, such as the OoA process, still exhibit significant shortcomings including large energy losses and geometric constraints imposed by the use of heating vessel systems. Moreover, the modification of prepreg morphology and rheology of polymer makes OoA processing applicable to a narrow range of materials. Here, it is demonstrated that the introduction of a nanoporous network and the resulting capillary pressure at laminate interfaces can replace the need for high applied pressure from an autoclave with the strong capillary effect, and further enables highly efficient manufacturing of layered polymeric architectures with < 1% volume of voids (commensurate with autoclave-processed materials) from conventional autoclave-required prepregs that require autoclave pressure. The characterization of void content and mechanical testing exhibited composite properties equivalent to autoclave-processed composites. This approach is anticipated to overcome the limitations of using either a heating vessel or specially formulated prepreg (i.e., OoA prepreg), and contribute to a next-generation manufacturing process for layered polymeric architectures.
4.1 Background

Advanced composite materials, comprised of fiber-reinforced polymers, have been widely used in industries such as aerospace, marine, and wind energy where high structural performance yet lightweight is needed. Manufacturing of those composites has traditionally focused on layered polymer architectures (i.e., composite laminate) processed by an autoclave to achieve high-quality reproducible parts, including high fiber volume fractions and low void content\(^{[4,25]}\). In particular, prepregs—in which carbon fibers are pre-impregnated with a thermoset or thermoplastic polymer to form a layer—are primarily used for autoclave processing techniques because of their ease of use and exceptional mechanical performance. The conventional autoclave-formulated prepreg (here after "autoclave prepreg") is intended to be cured in a vacuum bag (~0.1 MPa) with an applied pressure of 0.6-0.7 MPa to suppress the formation and growth of voids\(^{[4,75-77]}\). This is done because voids within a composite laminate can cause detrimental effects on structural performance and lifespan of composite parts\(^{[17-22]}\). Fig. 4.1 shows the results of curing autoclave prepregs without an applied pressure. The composite laminate cured without an applied pressure showed significant amount (~5%) of voids. In particular, matrix-dominated properties such as interlaminar shear strength, flexural strength, and fatigue resistance are degraded by the existence of voids\(^{[4,78]}\). Thus, how to reduce void content has been the critical topic in composite manufacturing. Manufacturing composites within an autoclave is also accompanied by high acquisition and operating costs due to the necessity of a specialized heated pressure vessel to suppress the formation of voids. Furthermore, the capacity of autoclaves limits the size and design of components, and the production rate is primarily affected by autoclave availability. As a result, there has been an increasing interest in the development of alternative techniques (e.g., microwave heating, induction heating, laser heating, and specially-formulated and designed prepregs that can be cured without an pressure vessel—the so-called out-of-autoclave (OoA) prepregs)\(^{[26,30,31]}\).

In contrast to autoclave prepregs, OoA prepregs do not require the use of pressure vessels to achieve a void-free laminate because of their unique structure; e.g., dry regions between resin-rich regions in OoA prepregs function as built-in void extraction channels\(^{[31-38]}\). The dry regions act as void extraction channels in the early stage of a cure cycle by increasing the in-plane permeability within the laminate and enabling entrapped gas to be extracted through the free edges of the laminate under vacuum. The dry regions are infiltrated by the surrounding resin during later stages of the cure cycle, enabling the low void content. Thus, OoA prepregs can be cured with conventional thermal
Figure 4.1: Composite laminate comprised of autoclave prepreg (Hexcel Hexply AS4/8552 in a [0/90/±45]_2s layup, 130 µm nominal ply thickness) processed without an applied pressure. (a) X-ray microtomography showing cross-section of a laminate and (b) 3D rendering of voids. Of note, the laminate shown here was comprised of Hexply AS4/8552 autoclave-formulated prepregs, and was cured with vacuum but without an applied pressure.

Ovens, thereby allowing lower cost manufacturing, compared to using autoclave prepregs, because of several advantages such as relatively affordable acquisition and operation costs\[39,40\].

Nonetheless, even the use of OoA prepregs is not completely ideal from a manufacturing perspective. Heat transfer is still based on convection, which leads to inefficiencies and to spatial gradients in cure and stress due to convective-to-conductive interactions between the oven gas medium (usually air) and the cure materials\[41–43\]. This method drives part-to-part variability, and the fabrication is still limited because of its fixed geometry despite advantages of using an oven. In addition, OoA prepregs are accompanied by modification of resin chemistry to prevent the gas emission ("off gassing") during curing\[79,80\] and alteration of prepreg morphology for engineering the void extraction channels\[31\]. Hence, these changes require additional processes while manufacturing prepregs, and relatively few prepreg systems are available and even fewer currently qualified for structural use, thereby limiting structural design due to limited ranges of mechanical properties. Moreover,
in contrast to autoclave prepregs, a room-temperature debulking process ranging from a few hours to tens of hours is additionally required for OoA prepregs prior to cure to evacuate entrapped air within a laminate\cite{35,36,81,82}. As a consequence, the total manufacturing cycle can be considerably extended. Given such limitations, the current alternative (i.e., OoA prepregs) needs further improvements to create an ‘actual’ non-autoclave process addressing the fundamental limitations of the use of an autoclave.

Here, we demonstrate and explore a non-autoclave process by which it is possible to manufacture aerospace-grade composites from conventional autoclave prepregs without either a heating vessel or applied pressure. The process is comprised of the integration of (1) the vacuum-bag-only conductive composite curing process, out-of-oven (OoO) curing\cite{16,24,50} as described in Chapter 3, and (2) the insertion of nanoporous network (i.e., vertically aligned carbon nanotube arrays in the current work) into the interlaminar regions of composite laminates (see Fig. 4.2 for an overview of the process). The OoO process uses a carbon nanotube (CNT) film as a heating element directly integrated into the surface of a laminate such that the curing process does not require any heating vessel or convective medium\cite{16}. As discussed in the previous chapter, it was reported that such OoO curing enables highly efficient manufacturing of composites from OoA prepregs while preserving thermophysical and mechanical properties (e.g., degree of cure, glass transition temperature, short-beam strength, tensile strength) observed in the conventional oven curing method\cite{16,24}. Here it should be noted that autoclave prepregs cured by OoO curing have not been explored to date because the OoO curing is based on a vacuum-bag-only cure cycle. Thus, the OoO curing itself was not expected to be enough to process autoclave prepregs, and the processed laminate cannot avoid the high extent of void content due to the absence of an applied pressure. However, along with several studies on the capillary flow of polymers into nanoporous media\cite{83–88}, we saw the possibility of using the OoO curing for autoclave prepregs. In the previous studies, it was reported that nanoporous networks such as CNT arrays spontaneously draws polymers into itself due to the capillary-driven wetting. From this phenomenon, we hypothesized that a nanoporous network (NPN) can be utilized to reduce the extent of interlaminar voids by enhancing the resin flow into the interlaminar regions. Furthermore, such enhanced resin wetting was expected to enable the manufacturing of high-quality composites from conventional autoclave prepregs without modifying their polymer system and morphology.
Figure 4.2: Non-autoclave process for traditional autoclave prepregs. (a) Schematics of the process comprised of out-of-oven curing and introduction of nanoporous networks, and micrographs of: (b) a CNT heater for out-of-oven conductive curing, and (c) nanoporous network (i.e., vertically aligned CNT arrays) introduced in the interlaminar region.

4.2 Materials and Methods

The effects of the OoO curing process with NPN were explored by analyzing the manufactured composite laminates. To compare the internal morphologies and mechanical properties of OoO-cured composites with those of autoclave-cured composites, X-ray microtomography and short beam shear testing were performed. Finally, the key factors of NPN for effective curing of autoclave prepreg were explored.

4.2.1 Synthesis of carbon nanotube (CNT) arrays nanoporous network (NPN)

For synthesizing CNT arrays (used here as the NPN), a thermal catalytic chemical vapor deposition process was utilized with a quartz tube furnace of 44 mm inner diameter at atmospheric pressure, which is similar to a previously reported process\[16,23,88,89\]. Ethylene was used as the carbon source,
and water of 600 ppm was added to the helium gas. The as-grown CNT arrays consist of multiwalled CNTs having 3-7 walls\cite{90} with an average inner and outer diameter of \( \approx 5.1 \) nm and \( \approx 7.8 \) nm, respectively. The volume fraction of CNT arrays corresponded to \( \approx 1.6\% \) with intrinsic CNT density of \( \approx 1.6 \) g/cm\(^3\) and average inter-CNT spacing of \( \approx 59 \) nm. Also, the as-grown CNT arrays having the height of \( \approx 20 \) \( \mu \)m were used for nanoporous networks. The CNT heaters for OoO curing were fabricated \textit{via} roller densification of the CNT arrays having the height of \( \approx 500 \) \( \mu \)m, similar to a previous study\cite{16}.

Figure 4.3: SEM image of vertically aligned carbon nanotube arrays grown by a thermal catalytic chemical vapor deposition process.

### 4.2.2 Autoclave prepreg processing \textit{via} conventional and OoO curing

Hexcel AS4/8552 aerospace-grade unidirectional carbon fiber prepreg was used, which is designed to be processed with an autoclave\cite{47}. The nominal cured ply thickness of this prepreg was 130 \( \mu \)m with a target \( V_f \) of 63.5\% of carbon fiber in each ply. Considering the standards used for the experiments, 16 plies (nominal laminate thickness of 2.08 mm) were used for the laminates quasi-isotropic layup of \([0/90/ \pm 45]_{2S}\). In case of laminates with NPN at the interlaminar region, the CNT arrays having height of \( \approx 20 \) \( \mu \)m were introduced to all 15 interlaminar regions within 16-ply
laminates by manual transfer onto the surface of each prepreg, following the previously reported procedures\cite{88,91}. To fabricate the CNT heaters for OoO curing, the fabrication methods in the previous study were followed using Cu meshes (Dexmet 2CU4-100FA) and composite surfacing films (TenCate Advanced Composites TC235-1SF)\cite{16,50} as well as Veelo HEAT randomly-oriented commercial CNT sheets\cite{46}, as in Chapter 3. It should be noted that the manufactured CNT heaters were attached on the top and bottom surfaces of all prepared 16-ply laminates so that all laminates have the same structure even though only one heater was used (electrically activated) for OoO curing.

For the conventional autoclave curing process, the recommended cure procedure from the prepreg manufacturer was followed using an autoclave\cite{47}. The conditions were provided as follows: cure temperature of 110 °C with a hold time of 60 min, and post cure temperature of 180 °C with a hold time of 120 min; ramp rate at 3 °C/min; autoclave gauge pressure of 0.6 MPa with a vacuum. For the vacuum-only (i.e., oven or hot plate) curing process, the same vacuum bagging procedure for the autoclave process above was used. Once a vacuum bag was prepared for the cure, the laminate and cure materials were placed on a programmable hot plate (EchoTherm HS60A) for curing. During the cure cycle, the same curing condition in the technical data sheet was followed without an applied pressure of 0.7 MPa.

For OoO curing, the cure setup in the previous study was used (see Fig. 4.4 for the vacuum bagging setup with two-sided heaters). Also, thermal insulating blocks (25 mm-thick ZIRCAR Ceramics Inc. MICROSL Microporous Insulation) were installed to reduce heat loss to the environment. During a cure cycle, only one heater was utilized as a heating element since the one-sided heater is enough to cure a ~2 mm-thick 16-ply laminate\cite{16,24,50}. A DC power supply was connected to the two copper tape electrodes of the heater to control the input voltage to follow the specific cure cycle. The vacuum bagging setup was placed on a lab bench, and the temperature was measured by a thermocouple (OMEGA Engineering fast-response K-type) that was attached to the heater. Input voltage, current, and power consumption were monitored using digital multimeters embedded in the power supply (B&K Precision DC power supply 9201).

### 4.2.3 \(\mu\)CT Imaging and Void Analysis

\(\mu\)CT imaging of laminates was performed with Nikon Metrology XT H 225 ST at the Center for Nanoscale Systems, Harvard. An isotropic voxel size of 3.3 µm was acquired with the X-ray beam energy of 80 kV and 70 µA. Also, molybdenum was used as the X-ray source with the reflection target mode. For each scan, 1500 2D projections were captured while a specimen was rotated in 180°.
The void content of cured laminates was evaluated by high-resolution µCT following ASTM E1441. From a manufacturing point of view, it is important to understand the impact of the location and size of defects on the structural performance of composites, including strength and fatigue behavior. Therefore, µCT-based assessment is a way to acquire the characteristics of the 3D distribution and the manufacturing defects at high resolution. From the accurate non-destructive measurement of the location and size of the defect, we can also assess the correlation between laminate morphology and mechanical properties. After collecting raw µCT images, the void content can be easily calculated by applying a threshold filter.

4.2.4 Short beam shear test

The short beam shear test was conducted based on ASTM standard D2344, which is also consistent with DIN EN2563. The dimension of a specimen was nominally 12 mm × 4 mm × 2 mm (L × W × t), and these specimens were taken from the 60 mm × 50 mm quasi-isotropic laminates ([0/90/±45]_2s) comprised of 16 plies of AS4/8552 prepreg. The cut laminate edges were polished with 800, 1200, and 2400 grit sandpapers to avoid rough or uneven surfaces which may result in
pre-damage at the edges. As prescribed in the ASTM standard D2344\textsuperscript{[52]}, a three-point bend fixture with a loading nose of 6 mm, supports of 3 mm diameter steel cylinders, and the span length of 8 mm were used. During the tests, the force applied to the specimen was monitored at a rate of cross head movement of 1.0 mm/min applied by a Zwick/Roell Z010 mechanical testing machine. The short-beam strength was then calculated using Eq.3.1

4.3 Results and Discussion

The composite laminate curing via the conventional manufacturing methods (e.g., autoclave or hot press) and OoO curing with NPN were conducted to explore an ‘actual’ non-autoclave process with autoclave prepreg and to understand underlying mechanisms. Of note, Hexcel AS4/8552 unidirectional prepreg was used for this work, which is designed to be cured by an autoclave with vacuum (0.1 MPa) and 0.6-0.7 MPa applied pressure. Six types of curing of the autoclave prepreg were undertaken: "conventional" autoclave cure including pressure (1) with, and (2) without NPN; "vacuum-only" curing with a hot plate (3) with, and (4) without NPN; "OoO" curing (5) with, and (6) without NPN. The conventional composite curing in this study was conducted with an autoclave, comprised of a vacuum bag and an applied pressure of 0.7 MPa. A hot plate was utilized instead of an heating vessel (e.g., oven) for composite curing without an applied pressure (i.e., vacuum-only curing), in order to avoid spatial gradients in cure due to the uncertainty of convective-to-conductive interactions between the convective medium and cure materials\textsuperscript{[41-43]}. In the case of OoO curing, a vacuum bag was used without an applied pressure as the OoO curing is originally designed. Void analysis and short beam shear tests were performed, and the mechanical and physical properties of composites cured by each manufacturing condition were compared. In addition, the underlying mechanisms were explored to understand the results and to suggest further applications.

4.3.1 Void analysis

Fig. 4.5a shows representative $\mu$CT slices of three primary manufacturing conditions, and the quantified void contents from 100 slices for each condition is presented in Fig. 4.5b. Of note, the other manufacturing conditions are discussed in following sections to explore mechanisms. In X-ray micrographs, the brighter gray-scaled regions denote denser areas such as fibers and polymers, while the voids appear as darker. As can be seen in Fig. 4.5a, there are no detectable voids in the specimens cured by autoclave (conventional), as expected. In contrast, since vacuum alone is not enough
Figure 4.5: Void content of composite laminates cured under an autoclave with applied pressure (conventional), a hot plate without applied pressure (vacuum-only), and OoO curing with nanoporous network (OoO with NPN): (a) Representative μCT slices, and (b) the quantified void content of each manufacturing condition. Note that in μCT images, the brighter gray-scaled region denote denser areas such as fibers and polymers, while the voids are imaged as dark. The whiskers represent the standard error. An introduction of NPN resulted in a reduction of the total amount of void within a laminate. The OoO with NPN specimens exhibited no detectable voids.

To remove entrapped voids and to suppress the void formation within a laminate during curing, the specimens cured by hot plate without an applied pressure (vacuum-only) resulted in a void frac-
tion of \(~1.6\%\). Such high void content of these specimens corroborates that an applied pressure is required to lower the final void content when curing autoclave prepreg systems. However, when the OoO curing process and NPN were introduced in the interlaminar regions (OoO with NPN), the void content was significantly reduced (see Fig. 4.5b). Interestingly, the OoO with NPN specimens did not contain any detectable voids through a 3D tomography, which is the same result from the conventional specimens. As reported in the studies on the aligned CNT interlaminar reinforcement\[91-93\], there was no significant difference in the thickness of the interlaminar region before and after the insertion of the aligned CNTs as NPN. Furthermore, there were no morphological differences such as ply and interlaminar thickness between the OoO with NPN and conventional specimens under high resolution synchrotron X-ray images and micrographs. Fig. 4.6 presents the synchrotron radiation CT (SRCT) images of specimens with NPN cured under different manufacturing conditions. SRCT imaging was conducted at the ID-19 beamline at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. As can be seen in Fig. 4.6c, the OoO with NPN specimens did not exhibit any detectable voids even though the scans were conducted in a high resolution (voxel size of \(0.65 \, \mu m\)). This is the same result from the specimens cured under the conventional autoclave process, and there was no morphological difference between the OoO with NPN and conventional autoclave processing with NPN specimens (see Fig. 4.6a and c). Fig. 4.6b exhibits the representative slice of the vacuum-only with NPN specimens. All detected voids were located in the intralaminar region, and there were no interlaminar voids. The observation suggests that the NPN effectively reduces the voids in the interlaminar regions, regardless of the heat input type (hot plate or OoO). That is, when we introduced NPN into the laminate and cured it under hot plate vacuum-only conditions, there was no interlaminar voids but some intralaminar voids. Therefore, we concluded that NPN significantly helps to reduce the voids especially in the interlaminar regions, and the integration with the OoO curing enables void-free composite laminates to be manufactured.

### 4.3.2 Comparison of mechanical properties

The results of short beam shear (SBS) tests were evaluated to compare mechanical properties of laminates cured under different manufacturing conditions. In the SBS test, 10 specimens were examined for each manufacturing process. As discussed in the prior chapter, it is known that the short-beam shear strength may not directly indicate the interlaminar shear strength of the laminate due to its complex stress distribution, and that the failure can be a combination of different failure
modes such as discrete and irregular interlaminar shear, tension, compression, and plastic deformation\textsuperscript{[70]}. However, it is generally accepted that SBS testing can be used for comparison of batch and as a screening tool for composite laminate properties with a description of the failure mode\textsuperscript{[71,72]}. Fig. 4.7 exhibits the short-beam strength of each manufacturing condition. In all cases, the interlaminar shear failure was observed among several failure modes described in the standard ASTM D2344. The conventional specimens presented the short-beam strength of \(~91\text{ MPa}. Of note, the measured short-beam strength can be compared with the short-beam strengths of another autoclave-required prepreg IM7/8552 as follows: it was reported that IM7/8552 laminates have short-beam shear strengths of \(~118\text{ MPa}\textsuperscript{[94]}\) and \(~93.5\text{ MPa}\textsuperscript{[95]}\) in unidirectional ([0\textsubscript{32}]) and quasi-isotropic ([0/90/\pm45/90/0/\pm45\textsubscript{3s}]) layups, respectively. That is, short-beam strength decreased by 20.8% in the quasi-isotropic laminates, when compared to the unidirectional laminates. Given that the short-beam strength of 114.7 MPa reported for AS4/8552 unidirectional ([0\textsubscript{32}]) laminates\textsuperscript{[96]}, the short-beam strength of 90.8 MPa can be estimated, which is very close to the measured values of
Figure 4.7: Results of the short beam shear tests of autoclave-formulated prepreg laminates under different types of curing (conventional autoclave curing without NPN, vacuum-only hot-plate curing without NPN, and OoO curing with NPN): (a) short-beam strength of each manufacturing condition, and (b) representative load-deflection curve of these specimens. The inset figure describes a diagram of the short beam shear test. Note that the whiskers represent the standard error. There is no statistically significant difference between the short-beam strength of conventional specimens and that of OoO with NPN specimens.
91 MPa here.

However, due to the high void content, the vacuum-only specimens showed ~27% decrease in the short-beam strength, compared to the conventional specimens. The result lends support to the previous reports that matrix-dominated properties are degraded by the existence of voids\textsuperscript{[17-22]}. In contrast, the OoO with NPN specimens did not exhibit any decrease in the short-beam strength. The OoO with NPN specimens had a short-beam strength of ~92 MPa, which is comparable to that of conventional specimens. The one-way analysis of variance (ANOVA; Welch’s ANOVA\textsuperscript{[68]}) was conducted to determine whether means of conventional and OoO with NPN specimens are statistically the same. Of note, a $p$-value less than 0.05 is required to establish a statistical difference with 95% confidence. As presented, $p$-value of 0.77 indicated that the means of short-beam strength values of them were not significantly different from each other.

4.3.3 Independent effects of Out-of-Oven curing and nanoporous network on void reduction

The other possible variations of manufacturing condition (e.g., conventional autoclave curing with NPN, vacuum-only hot-plate curing with NPN, OoO without NPN) were also conducted. Fig. 4.8 show the short-beam strengths and void contents of all manufacturing conditions. From the void analysis and mechanical testing, we observed two phenomena by comparing manufacturing conditions: (1) an introduction of NPN resulted in a reduction of the total amount of porosity within a laminate, (2) OoO curing performed better to acquire a lower void content than vacuum-only hot-plate curing. Also, these two phenomena were independent in that an insertion of NPN reduced the void content regardless of heat application (autoclave, hot plate, or OoO), and OoO curing showed lower void contents than vacuum-only curing regardless of the existence of NPN. From the results of all manufacturing conditions, we observed that the order of manufacturing condition from the highest to the lowest value of short-beam strength matched that from the lowest to the highest value of void content. This observation also corroborates the findings from previous studies that high void content can cause detrimental effects on matrix-dominated properties and lifespan of composite parts such as interlaminar shear strength, flexural strength, fatigue resistance\textsuperscript{[17-22]}. The results of void content and short-beam strength tests suggest that the integration of OoO curing and NPN broadens the options on materials and structural designs, such that it enables the traditional autoclave prepregs to be processed only under a vacuum without any modifications on polymers. Since the material properties of autoclave prepregs have been extensively researched and widely used in
Figure 4.8: Results of all manufacturing conditions: (a) short-beam strength and (b) void contents.
the industries, the high-quality composite architectures can be achieved in a much more efficient way. Furthermore, we saw the possibility of the actual non-autoclave process through the proposed OoO with NPN curing, which can resolve most of the drawbacks of conventional composite manufacturing processes.

4.3.4 Mechanism of void reduction

The formation and growth of voids within a laminate are attributed to moisture dissolved in the resin, mechanically entrapped air, and volatile emission during curing\cite{97,98}. Fig. 4.9a shows a 2D synchrotron radiation CT image of an uncured 16-ply quasi-isotropic laminate. As illustrated in Fig. 4.9b, there are intrinsic void sources in the laminate, which are comprised of partially impregnated tows in the intralaminar region and entrapped air pockets during a prepreg lay-up procedure located in the interlaminar region. To achieve the lower final void content (<1%), it is suggested to minimize such void sources and maximize void sinks as the simplest void management strategy\cite{99}. The intralaminar voids (i.e., unimpregnated dry tows) are most likely to be connected to each other along the microfiber axial direction, and therefore prepregs show a higher permeability along the axial fiber direction than transverse direction\cite{100,101}. Hence, most of the intralaminar voids can be subjected to a vacuum so as to be removed during a cure cycle. However, the entrapped voids in the interlaminar region arise from the irregular surfaces of a prepreg layer (see Fig. 4.10); the measured height of peaks and valleys on prepreg surfaces were normally distributed with a standard deviation of ~5.2 μm (see Section 4.3.4.1 for the detailed information of the irregular prepreg surfaces). Therefore, despite a roller squeezing process during a prepreg lay-up, the entrapment of air is unavoidable due to the rough surface of a prepreg. Such interlaminar voids (i.e., entrapped air) may not be connected to each other due to the irregular in-plane distribution and shape of the peaks and valleys. As a result, a vacuum is not enough to evacuate the interlaminar voids, and a high pressure compaction using external pressure (e.g., autoclave) is required to minimize the interlaminar voids. This supports that voids are mostly located at the interlaminar regions\cite{100,102-105}, and a feature exacerbated when a laminate was cured only under a vacuum.

From the void analysis and mechanical testing, there are two phenomena observed when comparing manufacturing conditions: (1) an introduction of NPN resulted in a reduction of the total amount of voids within a laminate, and (2) OoO curing yields a lower void content than a vacuum-only curing regardless of the presence of NPN. It was observed that these two phenomena work at least somewhat independently. We suggest that such phenomena are attributed to: (1) conformabil-
Figure 4.9: Cross-section of an uncured laminate of Hexcel Hexply AS4/8552 [0/90/±45]₂, (a) Representative 2D synchrotron radiation μCT image of the uncured laminate, and (b) the magnified image of two plies showing entrapped air in the interlaminar regions because of irregular prepreg surfaces, and dry region in the intralaminar regions due to partially impregnated tows.
Figure 4.10: Rough surfaces of uncured prepreg plies (Hexcel Hexply AS4/8552): (a) Optical image of the prepreg, (b) the magnified image of the surface of prepreg showing roughness, (c) cross-section of the prepreg, (d) 45° tilted SEM image presenting irregular topography and cross-section of prerepg, and (e) exemplary 3D rendering of irregular surface of prepreg. Note that the tomography of prepreg was examined by a stylus profilometry with Dektak XT Stylus Profiler (Bruker, USA).
ity of the NPN and (2) capillary wetting into such structures.

4.3.4.1 Conformability of NPN

Since a prepreg and NPN are not optically transparent, it is difficult to investigate the interfaces between them. Therefore, an optically transparent replica, that represents the surface profile of a prepreg, was created to observe the interfaces. First, a negative mold of the surface of a prepreg was fabricated with the thiolene-based UV-curable resin NOA81 (Norland Products Inc., Cranbury, NJ, USA) because thermal rise during curing lowers the viscosity of the polymer in a prepreg and changes the morphology of the surface profile of the prepreg as well. For the negative mold, NOA81 was deposited on the surface of a prepreg to avoid air entrapment and cured under UV exposure of 365 nm, 9 W, and 2 min. Once UV-cured, the prepreg was rinsed with acetone and isopropyl alcohol from the negative mold. For the second casting, Polydimethylsiloxane (PDMS) was used because of its ease of soft lithography and optical transparency\textsuperscript{106,107}. PDMS was mixed in a 10:1 ratio of PDMS monomer and curing agent (Sylgard 184 from Dow Corning, USA), and degassed under vacuum. The PDMS mixture was poured onto the negative mold, and then cured in a oven at 70 °C for 6 hours. After curing, the PDMS layer was peeled off from the negative mold, and used as a replica of a prepreg. See Fig. 4.11 for a schematic representation of the fabrication process of a replica and fabricated PDMS replica.

During manufacturing process of a prereg, the reinforcement such as continuous carbon fibers are subjected to the impregnation process with polymers. The resulting prepreg unintentionally contains partially impregnated regions and an irregular surface finish. As presented in Fig. 4.12a, there are some regions of exposed carbon fibers which are not covered with polymers, and such regions account for the irregular surface finish of a prepreg, resulting in air entrapment in the interlaminar regions during a lay-up process. Fig. 4.12b presents a micrograph of the surface of a PDMS replica, and suggests that the morphology of micro-features are similar to that on a prepreg, as compared to Fig. 4.12a. In order to compare quantitatively, the topography of the irregular surfaces of a prepreg and its PDMS replica were investigated by stylus profilometry with Dektak XT Stylus Profiler (Bruker, USA). An area of 1.2 cm × 1.2 cm was inspected with a 2 μm radius stylus tip. As shown in Fig. 4.12, the height of micro-features on both prepreg and PDMS replica is normally distributed, and their standard deviations were 5.2 μm and 5.9 μm, respectively. Given that the measured area of 1.2 cm × 1.2 cm was randomly assigned in each sample, it is concluded that the PDMS replica is representative of the topography of a prepreg.
Figure 4.11: PDMS replica for evaluation of NPN's conformability to prepreg surface: (a) Schematic representation of the fabrication process of a PDMS replica of irregular surface of a prepreg, and (b) fabricated PDMS replica. Since a thermal process can change the morphology of the surface of a prepreg, the negative mold was fabricated using UV-curable resin. Then, the positive replica made of PDMS was molded using a thermal process.

As previously mentioned, the entrapped air in the interlaminar region is inevitable during a prepreg lay-up process due to the irregular surfaces of a prepreg layer. During the transfer procedure of NPN to the surfaces of a prepreg, we observed that the NPN tends to conform to the irregular features on the surface (see Fig. 4.13a,b,c, and d). To evaluate whether NPN conforms to the entire
subjected area, the interface between the NPN and irregular surface of a prereg was imaged by dark-field microscopy. Fig. 4.13f is a dark-field microscopy image of the interfaces between an optically transparent PDMS mold replicating the irregularity of a prereg, and NPN (i.e., vertically aligned CNT arrays of ~20 μm in height). Here, only the lower half of the mold has been covered with NPN, after which the pressure was applied to the mold by a hand roller, which is a common procedure during a prereg hand lay-up to squeeze out the entrapped air. As presented in the upper part of Fig. 4.13f, the micro-features of the PDMS mold (i.e., replica of peaks and valleys on the surface of a prereg) appear bright due to light reflections on the irregular surfaces of micro-features. However, in the lower part of Fig. 4.13, the micro-features were completely filled with the NPN, and thereby present optically as a matte black color without bright reflections. It was observed that the micro-features partially contacted with NPN prior to the squeezing procedure with a hand roller. During the squeezing procedure, the NPN was compressed on varying degrees which we attribute to local spatial pressure variation, thus conforming to the profile of micro-features and resulting in full contact. This observation is consistent with the previous study that individual CNTs within the vertically aligned CNT arrays maintain their vertical orientation without strong interactions between
Figure 4.13: Conformability of NPN: (a) Illustration of conformed NPN on a prepreg, and (b,c, and d) HRSEM images of NPN conformed to the irregular surface of a prepreg, and (e) the illustration of the PDMS replica mold subjected to dark-field imaging. Note that the lower half of the PDMS mold is covered with NPN, and (f) dark-field microscopy image of an optically transparent PDMS mold representing the prepreg surface, clearly showing NPN conformability by the dark region in the lower portion of the image.

Fig. 4.14 shows NPN conforming during the pressing process. Fig. 4.14a presents the illustration and the dark-field image of the interface when a PDMS replica was placed on NPN. As pre-
sented, the micro-features were partially contacted with NPN prior to the pressing procedure with a hand roller. After the pressure was applied to the mold by a hand roller, NPN were compressed with varying degrees depending on local spatial pressure, conforming to the profile of micro-features and resulting in full contact between the micro-features and NPN (see Fig. 4.14b).

Moreover, in order to evaluate whether both the top and bottom interfaces of NPN conform, the NPN (i.e., vertically aligned CNT arrays of \(\sim 20 \, \mu\text{m}\) in height) were sandwiched between PDMS mold replicas of the prepreg surfaces, simulating a laminate lay-up. For both PDMS replicas at the top and bottom, the pressing procedure with a hand roller was applied to simulate a prepreg hand lay-up. We evaluated whether both the top and bottom interfaces of NPN conform, and the dark-field micrographs of each interface are presented in Fig. 4.15. As can be seen, both interfaces were in full contact with NPN such that there was no bright regions in the dark-field micrographs. Once the micro-features are filled with NPN, intrinsic void sources do not exist in the interlaminar region due to the NPN attenuating the extent of surface irregularity. Due to the strong capillary effect of CNT arrays,\(^{109-113}\) full contact at the interfaces is expected to facilitate capillary-driven wetting of polymer throughout the interlaminar region.

Fig. 4.16 shows the representative X-ray micrographs of 16-ply quasi-isotropic laminate with/without NPN in the interlaminar region. It should be noted that these micrographs were taken prior to
Figure 4.15: Dark-field images of: (a) the interface between the upper PDMS replica and NPN, and (b) the interface between the lower PDMS replica and NPN after the pressing procedure with a hand roller.

the curing process. As previously described in Fig. 4.9a, the baseline (i.e., a laminate without NPN) shows intrinsic void sources comprised of partially impregnated carbon fiber tows in the intralaminar regions, and entrapped air pockets in the interlaminar regions (see earlier discussion in Section 4.3.4). Most importantly, the interlaminar void clusters in a lamina were not likely to be connected to either those of adjacent laminae or in the same lamina, and the interlaminar voids formed macro air pockets. In other words, these voids were not likely to be connected to each other through either in-plane or transverse routes. However, as presented in Fig. 4.16b, the laminate with CNT arrays showed a distinct horizontally aligned channel at each interlaminar region, due to the vertically-aligned CNT NPN. Unlike the baseline specimens without NPN, here voids at the interlaminar regions rarely formed disconnected air pockets, but rather connected toward the laminate edges via the NPN, forming channel-like architectures. In addition, the intralaminar voids in a lamina can be connected to those of adjacent laminae through such architectures. Since the CNT array is a NPN having a low volume fraction of $<5\%$\textsuperscript{[23,114]}, it is imaged as voids due to the
low attenuation of X-ray, and also has a high gas permeability in principle\(^{115,116}\). The observation implies that the NPN may increase the in-plane and transverse gas permeability of a laminate through the highly permeable CNT arrays at the interlaminar regions, leading to the effective evacuation of voids within a laminate. This approach is similar to the principle mechanism of OoA prepregs. One OoA prepreg mechanism achieves the removal of entrapped air by partially impregnated microstructures consisting of both dry pathways (i.e., engineered vacuum channels or EVaCs) and resin-rich area, which forms a permeable vascular network that allows gas migration towards the laminate boundaries\(^{75,81,117}\). The previous studies reported that the higher gas permeability of OoA prepregs during impregnation results in much less time to evacuate the gases from a laminate\(^{99}\). Future work should explore the gas permeability measurement of laminates with the NPN to gain additional understanding of gas transport during curing.

![Figure 4.16: Representative X-ray micrographs of an uncured 16-ply quasi-isotropic autoclave prepreg laminate: (a) without NPN, and (b) with NPN. In case of the laminate with NPN, voids were connected together either directly or indirectly, forming channel-like architectures at the interlaminar regions.](image)

### 4.3.4.2 Capillary wetting into the interlaminar regions

In the curing process of laminates, the resin flow velocity is very small compared to infusion processes, corresponding to a low shear rate. Even though the polymer resins are non-Newtonian liquids, the characteristic flow of the resin during a cure process can be considered as Newtonian flow because of the low shear rate\(^{118}\). At the microscopic scale, the resin flow inside a laminate is modeled by Darcy’s law with capillary pressure at the interface between the resin and the gas as
follows:
\[ \mathbf{v} = -\frac{\mathbf{K}}{\mu} \nabla P \]  
(4.1)

where \( \mathbf{v} \), \( \mathbf{K} \), \( \mu \), and \( P \) are the flow velocity vector, the permeability tensor, the dynamic viscosity, and the pressure at the flow front, respectively. Based on Eq. 4.1, the direction of the resin flow front can be estimated by the pressure gradient. Fig. 4.17a presents the cross-section of interlaminar region showing the pressure boundary condition when voids are entrapped due to the irregular prepreg surfaces. At the interface between the resin and entrapped void, the resin pressure \((P_r)\) and gas pressure within the entrapped void \((P_v)\) are applied; the pressure gradient toward the interlaminar region corresponds to \(\Delta P = P_r - P_v\). Given that the entrapped voids are generated during the prepreg lay-up procedure in the atmospheric pressure and likely to be isolated from each other, \(P_v\) is assumed to be 0.1 MPa. In the case of autoclave process, the external consolidation pressure of \(~0.7\) MPa and partial vacuum of \(~0.02\) MPa are applied under the vacuum bag, and hence \(P_r\) of \(~0.72\) MPa can be assumed. Therefore, the positive pressure gradient toward the interlaminar region \(\Delta P \approx 0.62\) MPa suppresses void growth, and further the collapse of voids can occur due to gas diffusion into the heated liquid resin. As one of the worst case scenarios, when only vacuum is applied during curing \((P_v \leq 0.1\) MPa), the pressure gradient is not sufficient to suppress void growth \((\Delta P \leq 0)\), and the entrapped void can even expand (grow) the thermal expansion of the gas. However, if NPN are introduced in the interlaminar region, such a high external consolidation pressure by

\[ P_{cn} : \text{capillary pressure into the nanoporous network} \]

\[ P_{vn} : \text{gas pressure inside the nanoporous network} \]

Figure 4.17: Illustration of the pressure boundary condition at the interface of composite laminate with: (a) entrapped voids due to the irregular surface of prepreg layers, and (b) conformable NPN (i.e., vertically aligned carbon nanotube arrays in this work). The drawings are not to scale. The conformable NPN enables the capillary-driven polymer wetting into the interface, leading to the full polymer impregnation of the interface.
autoclave is alternatively achievable under a vacuum-bag-only process. Fig. 4.17b illustrates the pressure boundary condition at the interlaminar regions filled with conformable NPN. It should be noted that the NPN is assumed to have full contact with each lamina surface and sustains the in-plane breathable pathways, as discussed in the previous section. If the conformable NPN (i.e., CNT arrays) is introduced in the interlaminar region, the capillary pressure at the flow must be considered. At the flow front, the resin pressure ($P_r$), capillary pressure to the NPN ($P_{cn}$), and gas pressure inside the NPN ($P_{tn}$) are applied; the pressure gradient toward the interlaminar region corresponds to $\Delta P = P_r + P_{cn} - P_{tn}$. Because a vacuum is drawn under the bag and the NPN is breathable, $P_r \approx 0.1$ MPa and $P_{tn} \approx 0$ MPa are assumed. Similarly, $P_{cn}$ can be estimated with morphological characteristics of the CNT arrays and the assumption of one-dimensional resin flow along the fiber alignment\[119-122\] as follows:

$$P_{cn} = \frac{4}{D_f} \frac{1 - \varepsilon}{\varepsilon} \sigma \cos \theta$$  \hspace{1cm} (4.2)

where $D_f$, $\varepsilon$, $\sigma$, and $\theta$ are diameter of a (nano) fiber, porosity of the NPN, surface tension of the resin, and contact angle between the resin and (nano) fiber, respectively. Given that $D_f \approx 7.8$ nm, $\varepsilon \approx 0.94$, $\sigma \approx 35$ mJ m$^{-1}$, and $\theta \approx 20^\circ$, the capillary pressure $P_{cn}$ of $\approx 1$ MPa is estimated. As a consequence, a high pressure gradient toward the interlaminar region ($\Delta P \approx 1.1$ MPa) is achieved, which is comparable to the case of autoclave process (or even higher pressure gradient). This high pressure gradient leads to the full resin impregnation at the interlaminar regions such that there was no detectable interlaminar voids.

Fig. 4.18 presents the cross-section of an uncured laminate with and without conformable NPN, showing the pressure boundary condition in both the interlaminar and intralaminar regions. As illustrated, there are intrinsic void sources in a laminate, comprised of unimpregnated dry tows in the intralaminar region and entrapped air during the prepreg lay-up procedure located in the interlaminar region. In the case of the intralaminar region, the resin pressure ($P_r$) and gas pressure within the dry tow ($P_{tr}$), and capillary pressure to the micro-scale fiber tows ($P_{cm}$) are applied at the resin flow front; the pressure gradient toward the dry tows corresponds to $\Delta P = P_r + P_{cm} - P_{tr}$. When only vacuum is applied during curing, $P_r$ can be taken as $\leq 0.1$ MPa. Since most of the dry tows can be subjected to a vacuum due to a higher permeability along the fibers, $P_{tr}$ is assumed to be $\sim 0$ MPa. $P_{cm}$ can be estimated with morphological characteristics of the dry tows and the assumption of one-dimensional resin flow perpendicular to the fiber alignment\[119,123,124\] as follows:
Note that a prefactor of 2 instead of 4 is used in this equation, because the resin flow is perpendicular to the fiber alignment. \( D_f = 7.1 \, \mu m \) and \( \varepsilon = 0.4 \) are obtained from the prepreg data sheet from manufacturer, and \( \sigma = 35 \, mJ/m \) and \( \theta = 20^\circ \) are reasonable to be assumed as a thermostet resin. Thus, \( P_{cm} \) of 0.014 MPa is estimated, corresponding to \( \Delta P \sim 0.114 \, MPa \). Therefore, the resin wetting toward the dry tows is anticipated, and the intralaminar region of a laminate with NPN is expected to be in the same situation, i.e., unchanged by the presence of the NPN in the interlaminar region.

Figure 4.18: Illustration of the pressure boundary condition in a laminate with: (a) entrapped air due to the irregular surface of prepreg layers, and (b) conformable NPN (i.e., vertically aligned carbon nanotube arrays) in the interlaminar region.

4.4 Summary

In this chapter, a capillary approach to process layered polymeric composite architectures is presented and demonstrated, which addresses the limitations of the current manufacturing methods such as autoclave and out-of-autoclave prepreg processes. This technique entails the integration of
the recently proposed OoO curing process, and the insertion of a nanoporous network (i.e., vertically aligned carbon nanotube arrays in the current work) into the interlaminar regions of layered composite architectures. The laminates comprised of conventional autoclave-required prepregs were processed by the new OoO with NPN technique, and physical properties were examined to compare with conventionally-cured laminates. Results exhibited that the processed composites had < 1% volume of voids (commensurate with autoclave-processed composites) without using either a heating vessel or applied pressure. The mechanical test suggested that the short-beam strength of them was equivalent to that of conventionally-cured composites. We found that the underlying mechanisms consist of: (1) the exceptional conformability of nanoporous network that attenuates the irregular surface profile of prepregs, (2) nano-engineered vacuum channels which increase the permeability of laminates. The technique proposed here is a next-generation composite manufacturing process with several advantages as follows: (1) the wide range of autoclave prepreg material selections with already-proven mechanical properties, (2) removal of size and shape constraint on composite components using a scalable OoO heating element, and (3) cost savings on manufacturing by efficient thermal processing via OoO curing. Moreover, the process can be combined together with conventional composite manufacturing processes with little to no process modifications, and may contribute to the design and manufacturing of advanced composite architectures, while adding new or improved capabilities such as cure sensing, reduction in part-to-part variation, and the ability to cure uniformly in regions with large local geometric variations.
Chapter 5

Multifunctionality of Nano-engineered Prepreg Process: *In Situ* Cure Status Monitoring Technique

In this chapter, an *in situ* cure status monitoring technique based on the morphological change of a carbon nanotube (CNT) network during a cure cycle is proposed and demonstrated. During the development of out-of-oven (OoO) curing process, changes in the electrical properties of the CNT resistive heater was observed, as well as a resistance change with temperature. Specifically, a sharp resistance peak occurred at the late-stage of the first temperature ramp-up, and a gradual decrease in resistance was observed in the isothermal soaking stage. These observations are found to be due to polymer infiltration into the CNT network and the chemical cure shrinkage due to cross-linking of the thermoset polymer, respectively. By understanding these phenomena, it is possible to evaluate the degree of polymer wetting within a laminate and determine the time for termination of cure by monitoring the resistance change, and correlating it to degree of cure (DoC). Most importantly, because CNT arrays are usually introduced into composites to improve mechanical properties, these findings are expected to enable embedded *in situ* cure sensors.

5.1 Background on Cure Status Sensing

Advanced composite materials, especially fiber-reinforced polymers, have been widely used in industries such as aerospace, automotive, marine, and wind energy, where lightweight and high
strength materials are needed. Manufacturing of many of these composites, particularly high-performance structural materials in aerospace, has traditionally focused on pre-impregnated composite fibers (prepreg) processed by an autoclave or a hot press to achieve high-quality reproducible parts, including high fiber volume fractions and low porosity\cite{14,25}. In the composite manufacturing process, it is difficult to predict the curing state of the polymer matrix during a curing process. This is because the curing of composite is comprised of multi-phase reactions accompanied by an exothermic heat of reaction, changes in rheology, and cross-linking of polymers. In particular, it was reported that a degree of cure on a targeted value (e.g., \( \approx 90\% \)) is necessary to achieve high mechanical performance in structural applications\cite{11,125}. Thus, such complexities of the curing process may cause difficulties in part quality control. Furthermore, overall composite performance is often worse for thick composite parts, because temperature gradients can occur, resulting in spatial variations in degree of cure and large residual stresses\cite{126}. In addition, manufacturing composites is also accompanied by high acquisition and operating costs, as the composite production rate is primarily affected by autoclave or hot press availability. It is important for composite manufacturers to design the composite production cycles effectively to maximize the manufacturing productivity. Therefore, cure status monitoring helps to improve quality and productivity during composite manufacturing, because short processing cycles and homogeneous cured composite properties are essential to commercial composite products.

In order to understand the thermophysical properties during a cure cycle, there have been extensive studies on characterization methods such as differential scanning calorimetry (DSC)\cite{10,15,127-130}, Fourier transform infrared spectroscopy (FTIR)\cite{131}, dynamic mechanical analysis (DMA)\cite{53,54,56-59,132}, and rheometry\cite{10-14,97,133-135}. Particularly, DSC is widely used for characterizing the cure kinetics of thermosets such as the degree of cure and cure rate, and DMA is a well-known method to examine the viscoelastic properties of polymeric materials such as modulus evolution, gel point, complex viscosity, and glass transition temperature. However, these methods are conducted ex situ and destructively, and testing is based on small-sized specimens. As a consequence, these techniques often provide very limited and indirect information on individual cure processes. Therefore, the curing process needs to be accurately monitored and controlled to improve the quality of the composite material. Without directly monitoring the curing process, manufacturers are required to carry out repeated destructive proxy experiments to determine the appropriate cure time and to avoid excessive curing and under-curing. Even though an appropriate curing time can be suggested through empirical data, a conservative estimate can increase the manufacturing cycle time, leading
to excessive curing. Thus, it is advantageous in composite manufacturing processing is to control
the cure process in real time using in situ cure monitoring techniques to achieve uniform and reliable
quality. Such in situ cure monitoring can help optimize the process by controlling the exothermic
heat of reaction and predicting the curing cycle according to the material status. It can also be used
to calculate the time and temperature to achieve full cure and adjust the temperature to reduce the
cycle time. Most importantly, in situ cure monitoring technique enables the reduction of dummy
experiments, which means savings in time and cost to optimize the cure cycle.

Because of its economic benefits, a wide range of in situ cure monitoring techniques have been
of interest to many researchers\cite{133,136-139}. For example, dielectric analysis (DEA)\cite{15,129,140-146},
ultrasonic monitoring\cite{147-149}, Raman spectroscopy\cite{15,150}, infrared spectroscopy\cite{151-153}, and fiber
optic methods\cite{149,150,154-157} have been explored. Among these techniques, DEA is considered to
be the most promising technology and has been extensively studied because of its simplicity, high
sensitivity, and breadth of cure status information provided\cite{158-160}. DEA is based on electrical
conductivity measurement of the cured material. Under the electric field of the dielectric sensor,
ions flow through the polymer, and as the cross-linking of thermoset progresses, the polymer chains
increase the material viscosity as they form cross-linked networks that limit the flow of these ions,
thereby reducing electrical conductivity. By associating this electrical characteristic with cure status
indicators, such as the degree of cure, DEA provides a method to monitor cure status in real time.

However, the effectiveness of these in situ monitoring techniques could be improved by address-
ing the following limitations: (1) Degradation in the mechanical performance of the composites
when these cure sensors are used within the composite. In order to monitor the cure status spatially
(e.g., through the thickness of the composite), the in situ sensors need to be implanted within the
composites, but this can cause an adverse effect on the mechanical performance of the parts, a typ-
ical problem with embedded sensors of all types\cite{126,136,161}. Therefore, the DEA sensors are only
practical when applied on the surface of composite, which may not be representative of the cure
status within complex or thick parts; (2) Modification of the mold is needed. For instance, to install
the sensors on the composite, holes or recesses may need to be made on the mold. In addition, with
an open mold process, the location of the sensors can be limited to only one side of the composite.
Furthermore, installing sensors adds cost, time, and complexity on complex shape parts.

Recently, carbon nanotubes (CNTs) have received much attention as an enhancement for mul-
tifunctional materials due to its exceptional electrical\cite{162,163}, mechanical\cite{164}, and thermal\cite{165,166}
properties. When compared to other nanomaterials, such as metallic nanoparticles and carbon black,
CNTs have the advantage of adding mechanical reinforcement, as well as forming an electrical percolation network at very low concentrations due to their high aspect ratio\cite{167,168}. In addition, by incorporating CNTs into polymer matrices, nanocomposites can be potential candidates for sensing applications such as mechanical, chemical, pressure, and flow sensors\cite{169-172}. In particular, strain sensors composed of CNTs have been studied as the most promising sensing applications benefiting from reported high sensitivity compared to conventional strain sensors\cite{173-176}. In those studies, CNTs were used as nanofillers to form networks that exhibit piezoresistive behavior, which is mainly due to the morphological change of the conductive network as a function of the strain (i.e., the change in distance of CNT-CNT junctions, which is based on tunneling conduction, is the dominant mechanism\cite{177-179}). For example, tensile loading applied to a CNT sensor results in an increase in CNT-CNT junction distance, and the junction resistance that dominates the overall network resistance increases. In addition to the sensing applications with nanocomposites comprised of CNTs, there have been studies on the structural changes in CNT networks induced by the infiltration of organic liquids. Qiu et al.\cite{180} reported that the infiltration of organic liquids (e.g., ethanol, acetone, and toluene) into the directly-spun CNT fiber led to CNT-CNT junction openings, or junction distance increase; as a consequence, the resistance of the fiber increased. Similarly, they reported that the removal of solvent from the fiber decreased its resistance back to the original value. Terrones et al.\cite{3} reported that the electric field modulated the CNT-CNT junction distance by electrostatic forces, which corroborates the previous work that the closer the junctions, the lower the resistance. Furthermore, according to a recent study, the morphological change in CNT networks due to polymer (epoxy) infiltration alters the shape of CNTs, which leads to a decrease in the waviness of aligned CNTs in the network\cite{181}.

### 5.2 Design of CNT Network *In Situ* Cure Status Sensor

In this study, we propose an *in situ* cure status monitoring technique based on the morphological change of a CNT network during a cure cycle. During the development of the out-of-oven curing process, we observed that there were changes in the electrical properties of a CNT resistive heater under composite cure cycles, as well as a resistance change with temperature\cite{166}. Apart from the resistance change with temperature, the other changes in electrical resistance are associated with polymer interactions effects with the CNT network, such as infusion into the dry CNT network, and cure shrinkage of the polymer nanocomposite (polymer and CNT network) due to cross-linking.
See Fig. 5.1 for an overview of the proposed underlying mechanisms of a cure status sensor during a cure cycle. Note that the heater element used in the cure status sensing in this work is CNT based, but has a different morphology (randomly-oriented or in-plane aligned) vs. the NPN used in the prior chapter that is comprised of vertically-aligned CNTs (A-CNTs).

Fig. 5.1 describes how the resistance change of a CNT network is related to the cure status, as the morphological change of CNT network plays a key role in cure status sensing. Because the CNT heater is installed on the surface of the composite laminate, the CNT network is originally dry (Stage A), but starts to be infiltrated by the polymer during the ramp-up (Stage B). When the polymer infiltrates into the CNT network, the CNT-CNT junction distance ($w$) increases. Therefore, the resistance of the total network increases due to the tunneling conduction at the junctions, with junction resistance known to increase exponentially as a function of junction distance \cite{2}. It should be noted that junction resistance exhibits an exponential dependency on junction distance ($w$) with a characteristic tunneling length ($l_c$) \cite{2,3}. As polymer infiltration completes, the resistance increase reaches its apex (Stage C). As the cure proceeds, polymer volume shrinkage occurs due to the cross-linking of thermoset polymer chains (Stage D), which leads to a decrease in junction distance. Similarly, the resistance of the CNT network decreases due to the tunneling conduction. Finally, the resistance gradually decreases and reaches the final resistance at the end of a cure cycle (Stage E). If the final junction distance ($w_E$) is larger than the original junction distance ($w_A$), the final resistance ends with a higher value. In the case where the increase in junction distance by polymer infiltration is somewhat small (see Stage with a * indication in Fig. 5.1), the final junction distance ($w_{E*}$) can be smaller than the original junction distance ($w_{A*}$). Therefore, by tracking the resistance change, we can check the status of the cure.
Figure 5.1: Underlying mechanism of a cure status sensor based on a carbon nanotube (CNT) network. (a) Isothermal resistance change due to polymer-CNT network interactions overtime, (b) the resistance change is attributed to the morphological change in the carbon nanotube network. Junction resistance exhibits an exponential dependency on junction distance ($w$)\textsuperscript{[2,3]}. Note that Stage A and E correspond to the start and end of a cure cycle. Polymer infiltration (Stage B) leads to CNT-CNT junction distance increase, resulting in junction resistance increase. As polymer infiltration completes, the resistance increase reaches its apex (Stage C). As cross-linking of the polymer occurs (Stage D), cure shrinkage leads to a decreased CNT-CNT junction distance, resulting in junction resistance decrease. Of note, * indicates the case where the increase in junction distance by polymer infiltration is small relative to the cure shrinkage distance decrease, such that the final junction distance ($w_{E^*}$) is smaller than the original junction distance ($w_{A^*}$).
5.3  Experimentation on *In Situ* Cure Status Sensor

To validate the conceptual model presented in the previous section, the cure status sensors were fabricated with different types of CNT networks, and a series of experiments were conducted with these sensors to build understanding of the mechanisms and the appropriateness of the proposed model.

5.3.1  Manufacturing cure status sensors

Vertically aligned CNT arrays were grown in a 44 mm internal diameter quartz tube furnace at atmospheric pressure with a thermal chemical vapor deposition process \[88,182\]. The CNTs were grown on 50 mm x 100 mm Si substrates with a catalytic layer of 10 nm/1 nm of Al\(_2\)O\(_3\)/Fe deposited by electron-beam evaporation. The 50 mm x 100 mm Si substrate was placed in the middle of the quartz tube furnace, and was first annealed at 680 °C with 1040 sccm of hydrogen gas in order to form Fe catalyst nanoparticles. Then, 400 sccm of ethylene gas was injected into the furnace as the carbon source. Changing the time of ethylene gas exposure to the substrate controlled height of the CNT array (L). For the aligned CNT films, 150 and 500 μm-tall CNT arrays were grown. After terminating the flow of ethylene gas, helium gas was introduced with hydrogen gas in order to weaken bonding between CNT forests and the Si substrate\[183\] so that the CNT arrays can be easily removed from the substrate. The grown CNTs were composed of an average outer diameter of 7.8 nm (3-7 walls with an average inner diameter of 5.1 nm), intrinsic CNT density of 1.6 g/m\(^3\), average inter-CNT spacing of 59 nm, and volume fraction of 1.6% CNTs\[23,90\]. To produce a film-like material, the vertically grown CNT arrays were densified and reoriented horizontally by covering them with a Guaranteed Nonporous Teflon (GNPT) film and knocking them down with a 10 mm radius metal rod\[23\]. Because of the bond-weakening post growth process, the reoriented CNT film was cleanly transferred onto the GNPT film. After this knocking-down process, the 150 and 500 μm-tall CNT arrays corresponded to the films with a thickness (H) of ≈12 μm and ≈40 μm, respectively. They had the same areal density of ≈12.8 g/m\(^2\) (gsm). Additionally, due to the CNT alignment, the densified film showed anisotropic electrical properties\[23]\. For randomly-oriented CNT networks, a commercialized CNT film, Veelo HEAT from General Nano LLC\[46\], was used. This H ≈40 μm CNT film was composed of randomly oriented multiwalled CNTs with an areal density of ≈25 g/m\(^2\) and an isotropic sheet resistance of ≈5 Ω/□.

To create a basic element (or unit cell) representative of the embedded CNT-based cure sensor,
two copper tape electrodes (75 µm-thick highly conductive copper electrical tape from McMaster-Carr) were attached parallel to both ends of CNT film (15 mm × 10 mm) with silver paint, so that the CNT area directly attached onto the polymer film corresponded to 10 mm × 10 mm. By adjusting the CNT alignment angle (θ), it was possible to utilize the anisotropic characteristics of the aligned CNT film. For the polymer film, a composite surfacing film (TC235-lSF from Tencate Advanced Composite USA, Inc.) was used. The surfacing film is a thermoset polymer film designed to provide paintable composite surfaces. It is also co-curable with carbon fiber prepreg, whose cure cycle is either performed at 120 °C or 180 °C, depending on the application, e.g., post- vs. co-curing. This surfacing film was chosen as it is representative of one implementation of a multifunctional cure status sensor, the surfacing film is representative of general epoxies, and also due to the fact that neat resins of the prepregs are used in this thesis are not available. See Fig. 5.2 for the structure and dimensions of a cure status sensor basic element and the fabricated sensor. Additionally, for all CNT networks, an annealing cycle was conducted prior to the actual cure monitoring tests to stabilize the electrical properties. Fig. 5.3 shows the resistance response of a CNT network during 5 successive cycles of annealing. After the first annealing process (Cycle #1), the CNT network exhibited consistent resistance responses during the cure cycle. This hysteresis may be due to numerous effects (unstudied) including desorbing molecules attached to the CNTs at the CNT-CNT junctions, among others.

5.3.2 Experimental procedure for in situ cure status monitoring with basic elements

The cure status monitoring process consists of detecting the manufacturing process of creating a nanocomposite by monitoring the polymer wetting of dry reinforcements (here, a CNT network) and the polymer curing that occurs during the manufacturing (or curing) process. Therefore, the recommended vacuum bag scheme for the aerospace-grade carbon fiber prepregs (e.g., Hexcel Hexply 8552) was followed for a curing setup, simulating the common composite cure environment. See Fig. 5.4 for a prepared cure setup. Once a vacuum bag was prepared, a CNT sensor basic element was subjected to a cure cycle under a vacuum during the entire cure. The resistance of a CNT sensor was recorded using a digital multimeter (i.e., Agilent 34461A) and a 4-wire Kelvin probe. The temperature was measured and recorded by a thermocouple (OMEGA Engineering fast-response K-type) that is attached adjacent to the CNT sensor basic element. In this study, external heat via a hot plate was applied to a CNT sensor to avoid any effects which may be induced by Joule heating of the CNT network. The temperature control of the CNT heater was achieved via a
Figure 5.2: Structure of a cure status sensor basic element comprised of a carbon nanotube film. Note that the CNT alignment direction is described by $\theta$. 
Figure 5.3: Annealing process performed on aligned $L \approx 500\mu m$-tall CNT arrays densified to $H \approx 40\mu m$ at $\theta = 0^\circ$ with an areal density of $12.8 \text{ g/m}^2$. Note that the resistance response of the CNT network was stabilized after the first annealing process (Cycle #1), which is typical of all CNT networks studied.
programmable hotplate (Torrey Pines Scientific EchoTherm HS61) to follow a cure cycle. In order to explore the effect of cure temperature on the response of the basic sensor element, 6 different isothermal soaking temperatures (i.e., 65, 80, 85, 95, 105, and 120 °C) were used at the fixed ramp-up rate of 3 °C/min for all curing processes. Once the temperature reached the soak temperature, the temperature of the hot plate was held at the soak temperature for 3 hours. After the curing process, the hot plate was turned off and cooled down by natural convection.

5.3.3 Electrical response of CNT sensor basic element during a cure cycle

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\textsuperscript{[177-179]}. A dry CNT network has a negative thermal coefficient of resistance; thus, the resistance change of a dry CNT network and its temperature show a mirror image of each other, as presented in Fig. 5.5. However, remarkable changes in the electrical response of a CNT cure status sensor were observed under a composite cure cycle. As shown in Fig. 5.5, the most distinct feature of the cure status sensor was a resistance
rise and peak occurring at the late-stage of the temperature ramp up.

Based on the structure of a cure status sensor, the electrical response during a cure cycle is comprised of three main factors: (1) the intrinsic electrical response of the CNT network, (2) the intrinsic electrical response of the polymer film, and (3) the interaction between the CNT network and the polymer film. Among these factors, both of the intrinsic responses of the CNT network and polymer film can be decoupled from the cure sensor basic element response to extract only the effect of interaction between the CNT network and polymer.

First, the resistance of the polymer film does not contribute to the resistance response of the cure status sensor basic element, based on experimental results. Fig. 5.6 shows the resistance response of the polymer film under different cure cycles. It was observed that the resistance decreased as the temperature increased, followed by an increase in resistance during isothermal cure processes. Such a resistance change during a cure cycle is attributed to the proportional relationship between the electrical resistivity and mechanical viscosity of the polymer\cite{184,185}. Initially, the viscosity of the thermoset polymer decreases as temperature increases, because the polymer becomes less rigid. At the same time, resistivity decreases as the mobility of ions in the liquid polymer increases. At this stage, the cross-linking of the polymers occurs slowly and the cross-link density close to zero. As the cross-linking continues, the viscosity starts to increase as the liquid polymer becomes more viscous and finally forms a cross-linked network (i.e., gelation). Resistivity similarly increases due to the cross-linked network, which impedes the flow of ions. As presented in Fig. 5.6, the minimum resistance of the polymer film was larger than $10^7 \Omega$. Given that the resistance of the CNT film is a few tens of Ohms, the resistance of the polymer film connected in a parallel circuit to the CNT film is insignificant. Moreover, the resistance of the polymer film connected in a series circuit is not plausible as a contributor to the curing sensor basic element response, because the resistance response of the polymer film showed the opposite trend to that of the cure sensor basic element. For example, if the polymer film connected in series dominated the resistance of the cure sensor basic element, the resistance increase in the polymer film would have resulted in the resistance increase in the cure sensor basic element. Therefore, it is reasonable to conclude that the effect of intrinsic resistance of the polymer on the response of the cure sensor basic element is negligible.

Second, the intrinsic response of the CNT network with respect to the temperature can be decoupled from the response of the cure sensor basic element by using the ratio of the sensor response to the dry CNT network response (baseline). The sensor-to-baseline ratio (SBR) corrects the effect of temperature on resistance under FITC in such a way that the resistance change induced by the
Figure 5.5: Representative resistance response of the cure sensor basic element and dry CNT network. The aligned $L \approx 500 \mu m$-tall CNT arrays densified to $H \approx 40 \mu m$ at $\theta = 0^\circ$ with an areal density of 12.8 g/m$^2$ were used.
Figure 5.6: Resistance response of the polymer film under different cure cycles. The intrinsic electrical response of the polymer film is not influential on the sensor response.
morphological change of the CNT network can be solely examined. Fig. 5.5 presents the resistance response of the dry CNT network and sensor during the same cure cycle of 95 °C. Note that the response of the dry CNT network was acquired first as the baseline, and then the polymer film was attached onto the CNT network to modify it into the sensor. By doing so, it was possible to keep using the same CNT network for the baseline and sensor. Thus, the resistance of the cure sensor basic element started from the same value of the dry CNT film, and then deviated as polymer infiltration occurs. This observation indicates that the sensor response is dominated by the dry CNT network prior to polymer infiltration. The SBR presented in Fig. 5.7 displays the effect of interaction between the CNT network and the polymer on the resistance response during a cure cycle. Based on the calculation of SBR, a SBR greater than 1 indicates an increase in the resistance, whereas a SBR less than 1 indicates a decrease in the resistance due to the interaction between the CNT network and the polymer. From the SBR curve, the resistance change can be interpreted as follows due to the interaction between the polymer and the CNT network (see Fig. 5.7): (1) the resistance increased by ~1.5-fold during the stage of temperature ramp-up, and then (2) began to decrease, ending with a ~1.2-fold increase during the 3 hour-long soaking stage at 95 °C.

### 5.3.4 Correlation with polymer infiltration

During the temperature ramp-up stage, the viscosity of thermoset polymers decreases\[^{186}\]. Thus, the liquid polymer starts to infiltrate into the CNT network due to vacuum and capillary pressure. As liquid polymer infiltrates into the CNT network, the CNT-CNT junctions in the CNT network become filled with the liquid polymer, resulting in an increase in junction distance between individual CNTs, or between CNT bundles as observed in CNT yarns\[^{3,180}\]. At the CNT-CNT junctions, the electrons pass through the insulating polymeric barrier by the process of quantum tunneling, and the increase in junction distance corresponds to the increase in junction resistance. It should be noted that, if there is no junction distance change from polymer infusion, then the junction resistance would go in the opposite direction (decrease) as the dielectric is changing from air to polymer, which allows multiple tunneling events\[^{3,187-189}\]. The observed resistance increase suggests strongly that junction distance increase due to polymer infiltration is the correct mechanism, although direct observation has not been achieved. Finally, given that the junction resistance dominates the total resistance of the CNT network\[^{23,190,191}\], the total resistance of the cure sensor basic element is expected to increase at the temperature ramp-up stage due to polymer infiltration. To evaluate when the infiltration completes, the top surface of cure sensor was imaged during a cure cycle. An additional transparent
Figure 5.7: Compensation of the intrinsic response of the CNT network (aligned $L \approx 500 \mu m$-tall CNT arrays densified to $H \approx 40 \mu m$ at $\theta = 0^\circ$ with an areal density of 12.8 g/m$^2$) with respect to temperature. The sensor-to-baseline ratio (SBR) gives the resistance change induced by the interaction between the CNT network and the polymer.
glass window was added onto a vacuum bagging film with a sealant tape so that it was possible to
image the surface of the sensor basic element while pulling a vacuum. Fig. 5.8 shows a time-series
of dark-field micrographs of the top surface of the cure sensor basic element during the ramp to, and
hold, at 120 °C. When the cure cycle starts, the dark-field micrograph showed only the top surface
of the CNT network. As the polymer infiltrates into the CNT film, the polymer flow front became
closer to the top surface, and the brightness of the dark-field micrographs became brighter due to
the scattered light from the approaching liquid polymer. However, once the infiltrated polymer
reached the top surface of the CNT network, the brightness became much dimmer. This is because
the liquid polymer filled up the irregular interfaces between the top surface of the CNT film and the
glass cover window. Therefore, by detecting when the top surface fully darkens, the time frame of
polymer infiltration could be established. As shown in Fig. 5.8, the flow front approached the top
surface of the CNT network at \( \approx 18 \) min, and full infiltration was observed at \( \approx 25 \) min. Fig. 5.9
exhibits the SBR curve and temperature of the sensor basic element during the experiment. Degree
of cure (DoC) as a function of time is presented for the neat (no CNTs) polymer film processed with
the same temperature cycle run in a DSC, and using a total heat of reaction and heat flow during
the run to calculate the DoC\(^{11}\). As shown in the temperature ramp-up stage to 120 °C, the polymer
was barely cured, which showed that the polymer cross-linking was not associated with the increase
in SBR. Therefore, it is evident that the polymer infiltration is correlated to the increase in SBR.
Furthermore, it is reasonable to suppose that the SBR increase is due to the interaction between the
polymer and CNT network (i.e., morphological change in the CNT network), based on the findings
in the previous section. It should be noted that the apex of the SBR was not linked to the overshoot
of temperature, and the full infiltration and the apex of the SBR did not occur at the same time.
For example, the cure status sensors made of \( L \approx 150 \) μm CNTs exhibited full infiltration at \( \approx 18 \)
min, while the apex of the SBR occurred at \( \approx 22.5 \) min (see Fig. 5.10 and Fig. 5.11). That is, the
resistance still increased even after full infiltration of the CNT network. This result suggests that
the junction distance increase occurs gradually over time. The time frame of polymer infiltration in
the cure sensor basic element comprised of randomly-oriented CNT networks (\( H \approx 40 \) μm with an
areal density of 25 g/m\(^2\)) was also evaluated, and the results are provided in Fig. 5.12 and Fig. 5.13.

5.3.5 Correlation with degree of cure (DoC)

To explore the underlying mechanisms of the resistance decrease after the apex of the resistance,
CNT cure status sensor basic elements comprised of the aligned \( L \approx 500 \) μm-tall CNT arrays den-
Figure 5.8: Time series of dark-field images of the top surface of the cure sensor basic element during ramp and hold at 120 °C. The cure sensor basic element was comprised of aligned $L \approx 500 \, \mu\text{m}$-tall CNT arrays densified to $H \approx 40 \, \mu\text{m}$ at $\theta = 0^\circ$ with an areal density of 12.8 g/m².
Figure 5.9: Experimental SBR and temperature of the cure sensor basic element during a cure cycle at 120 °C, with DoC calculated for the neat polymer film via DSC measurements. Note that full polymer infiltration of the CNT network occurs prior to the apex of the SBR and the overshoot of temperature. The cure sensor basic element was comprised of aligned $L \approx 500 \mu m$-tall CNT arrays densified to $H \approx 40 \mu m$ at $\theta = 0^\circ$ with an areal density of 12.8 g/m$^2$. 
Figure 5.10: Time series of dark-field images of the top surface of the cure sensor basic element during ramp and hold at 120°C. The cure sensor basic element was comprised of aligned \( L \approx 150\mu m \)-tall CNT arrays densified to \( H \approx 12\mu m \) at \( \theta = 0^\circ \) with an areal density of 12.8 g/m².
Figure 5.11: Experimental SBR and temperature of the cure sensor basic element during a cure cycle at 120 °C, with DoC calculated for the neat polymer film via DSC measurements. Note that full polymer infiltration of the CNT network occurs prior to the apex of the SBR and the overshoot of temperature. The cure sensor basic element was comprised of aligned $L \approx 150 \mu m$-tall CNT arrays densified to $H \approx 12 \mu m$ at $\theta = 0^\circ$ with an areal density of 12.8 g/m².
Figure 5.12: Time series of dark-field images of the top surface of the cure sensor basic element during ramp and hold at 120°C. The cure sensor basic element was comprised of randomly-oriented CNT networks ($H \approx 40 \mu m$ with an areal density of $25 \text{ g/m}^2$).
Figure 5.13: Experimental SBR and temperature of the cure sensor basic element during a cure cycle at 120°C, with DoC calculated for the neat polymer film via DSC measurements. Note that full polymer infiltration of the CNT network occurs prior to the apex of the SBR and the overshoot of temperature. The cure sensor basic element was comprised of randomly-oriented CNT networks ($H \approx 40 \mu m$ with an areal density of 25 g/m$^2$).
sified to $H \approx 40\mu m$ at $\theta = 0^\circ$) were tested under 6 different cure cycles. These cure cycles were comprised of the same ramp-up rate of $3^\circ C/min$, but with different soaking temperatures. Since the polymer film (i.e., TC235SF-1) is designed to be cured at $\approx 120^\circ C$, temperatures of 65, 80, 85, 95, 110, and 120 $^\circ C$ were selected to intentionally adjust the cure rate and the final DoC. Fig. 5.14 presents the DoC of the polymer film under 6 different soak temperatures with the same soaking time of 3 hours. It was observed that at higher cure temperatures, there is a faster and larger increase in the DoC compared to lower cure temperatures. For example, the 80 $^\circ C$ case showed a gradual increase in DoC to $\approx 0.45$ during 3 hours, whereas the 120 $^\circ C$ case showed a rapid increase in DoC to $\approx 0.95$ within an hour. Such an observation lends support to the fact that the cure kinetics of thermoset polymers theoretically has an Arrhenius dependence \cite{192,194}.

Fig. 5.15 contains the SBR curves under the 6 different cure cycles, which were conducted for the DoC experiments above (see Fig. 5.14). In the case of 65 $^\circ C$, the resistance showed an exponential growth during the entire soaking and cooling down process. This is because the viscosity at 65 $^\circ C$ was not low enough for the polymer infiltration to occur rapidly. In addition, as presented in Fig. 5.15, the final DoC from the 65 $^\circ C$ cure was much lower than the point where gelation occurs, and thus the infiltration continued even during the cooling down stage. In the cases above 80 $^\circ C$, the SBR increased rapidly, and then decreased after the peak.

From the SBR curves, two interesting characteristics were observed. First, the SBR and time at the apexes varied according to the soaking temperature. Because the viscosity of the polymer is a complex function of temperature and degree of cure, the aspects of infiltration such as infiltration rate can vary. For example, the polymer flow front velocity is dependent on the temperature profiles, and therefore the variation in infiltration leads to a variation in SBR at the apexes. Below 95 $^\circ C$, the SBR at the apex tended to increase as the temperature increases. Conversely, when the temperature further increased over 105 $^\circ C$, the SBR decreased. These observations can be explained as follows: (1) as the temperature increases, the viscosity lowers, leading to the faster polymer infiltration. Then, the faster polymer infiltration corresponds to the increased amount of junction distance, resulting in an increase in SBR; (2) However, when temperature continues to increase, the cross-linking is accelerated simultaneously so that the effect of cross-linking (i.e., decrease in SBR due to polymer shrinkage) rises faster, leading to a reduced SBR. Such explanations are also equally applicable to the other observation that the time of the apexes varies according to the soaking temperature. The apex tended to occur faster as the soaking temperature increased. Second, the decreasing rate of SBR after the apex increased as the isothermal soaking temperature increased. Also,
Figure 5.14: DoC under different soak temperatures. The DoC was calculated for the neat polymer film via DSC measurements. Note that the higher the cure temperature, the faster and larger amount of DoC increase.
Figure 5.15: Experimental SBR of the cure sensor basic elements at different soak temperatures. The cure sensor basic elements were comprised of aligned $L \approx 500 \mu\text{m}$-tall CNT arrays densified to $H \approx 40 \mu\text{m}$ at $\theta = 0^\circ$ with an areal density of 12.8 g/m$^2$. 
the amount of SBR decrease from the apex to the end of the cure cycle became larger with increasing soak temperature. Such trends are clearer when the SBR curves are normalized (see Fig. 5.16). Of note, they are normalized by the SBR apex so that the normalized SBR starts at 0, and the apexes have the value of 1. Interestingly, the SBR trend after the apex was opposite to that of the DoC. Given that the experiments were performed to obtain both the DoC and SBR curves under the same cure cycles, the two curves can be correlated with each other as presented in Fig. 5.17. During the isothermal soaking stage, the majority of thermoset polymer cross-linking occurs (see Fig. 5.14). As the DoC increases, the volume of the resin decreases due to the chemical cure shrinkage. Previous studies reported that the usual volumetric shrinkage range of epoxy resin is 2-7%, and that the cure shrinkage is linearly proportional to the DoC$^{110,195,196}$. As a result, the polymer infiltrated into the CNT network is expected to shrink as it is cured, and therefore the junction distance decreases, leading to the decrease in resistance of the cure sensor. From the experiments performed on the cure sensor basic elements comprised of a CNT network and the polymer film, the cure shrinkage appears to be correlated with the observation that the higher cure temperature showed a faster and larger decrease in resistance (see Fig. 5.14).

By evaluating a resistance change of the CNT network during the cure cycle, it will be possible to evaluate the status of the resin wetting within a composite laminate and to assess cure termination by monitoring the DoC. Most importantly, since the CNT network has been introduced into the interlaminar regions of composite laminates to improve mechanical properties$^{197}$, the findings in this study are expected to enable embedded multifunctional in situ cure status sensors in the future. Additionally, considering that the cure status sensor is a nanocomposite itself after curing and can be used as an ice protection system on aerosurfaces$^{198}$, the cure status sensing technique is multifunctional.

5.3.6 Effect of thermal strain on in situ cure status monitoring

During a cure cycle, the thermoset polymer experiences volumetric changes as a result of thermal effects (i.e., volume expansion and contraction due to the coefficient of thermal expansion (CTE)) and chemical effects (i.e., chemical cure shrinkage)$^{199}$. Fig. 5.18 displays a schematic of the dominant effects on volumetric change during a cure cycle. A typical cure cycle of thermoset polymer can be divided into three stages: temperature ramp-up (Stage A), isothermal soaking (Stage B), and cooling down (Stage C). In Stage A, the volume of the cross-linked polymer increases due to thermal expansion as it is heated up to the curing temperature. Chemical cure shrinkage can
Figure 5.16: Normalized SBR of the cure status sensors at different soak temperatures. The cure sensor basic elements were comprised of aligned $L \approx 500 \mu m$-tall CNT arrays densified to $H \approx 40 \mu m$ at $\theta = 0^\circ$ with an areal density of 12.8 g/m$^2$. 
Figure 5.17: Correlation between: (a) SBR and DoC, and (b) normalized SBR and DoC. The cure sensor basic elements were comprised of aligned $L \approx 500 \mu$m-tall CNT arrays densified to $H \approx 40 \mu$m at $\theta = 0^\circ$ with an areal density of 12.8 g/m². The DoC was calculated for the neat polymer film via DSC measurements.
occur, but this is usually negligible during the ramp-up stage (see Fig. 5.14). In Stage B, the volume of the polymer decreases because of chemical shrinkage associated with cross-linking in thermoset epoxies. Due to the isothermal process in Stage B, thermal effects do not occur. In Stage C, the volume of the polymer decreases due to thermal contraction as the temperature cools down to room temperature. Usually, the CTE at Stage C is lower when compared to that at Stage A, since the CTE in the glassy state (i.e., after curing, Stage C) is lower than in the rubbery state (i.e., Stage A).\(^{200}\)

As can be seen from Fig. 5.15, the SBR curves from the cure cycles of above 95 °C showed a slight decrease in SBR during natural convection cooling. It is reasonable to assume that the decrease in SBR is attributed to the volumetric thermal contraction of the polymer, because it leads to a junction distance decrease. Nonetheless, the amount of decrease in SBR from 120 °C to 30 °C corresponded to ≈0.02. That is, the size of the SBR decrease suggests that the effect of CTE on the SBR is relatively small and insignificant when compared to the SBR change due to the polymer infiltration and cure shrinkage.

### 5.3.7 Results for different types of in situ cure status sensor basic elements

Given that the underlying mechanism is the morphological change of the CNT network during a cure cycle, other types of CNT networks are expected to show a similar trend for the resistance response. Here, three other types of CNT networks were tested in the cure status sensor basic element
configuration as in the prior sections, including (1) aligned CNT network with an alignment direction perpendicular to the current flow direction ($\theta = 90^\circ$), (2) aligned CNT comprised of shorter CNTs of $L \approx 150 \ \mu$m, and (3) randomly-oriented CNT network. In summary, they showed the similar trend as the aligned $L \approx 500 \ \mu$m-tall CNT arrays densified to $H \approx 40 \ \mu$m at $\theta = 0^\circ$ with an areal density of $12.8 \ \text{g/m}^2$. However, due to differences in morphological characteristics, several interesting differences between morphologies were observed: (1) anisotropic behavior due to the alignment, (2) transient response in junction distance during polymer infiltration, and (3) $\text{SBR} < 1$, indicating a higher conductivity after polymer infiltration and the curing of the polymer. The details of these observations are discussed in the following subsections.

5.3.7.1 Aligned CNT network at $\theta = 90^\circ$

Because the intrinsic properties of CNTs are highly anisotropic, the resistance of the CNT network, $R$, can be expressed as a function of the alignment angle, $\theta$ (see Fig. 5.2 for the definition of $\theta$ in this work), as follows $^{[23]}$

$$R(\theta) = R(\theta = 0^\circ) \cos^2(\theta) + R(\theta = 90^\circ) \sin^2(\theta). \quad (5.1)$$

It was reported that $R(\theta)$ for $L > 150 \ \mu$m showed anisotropy on the order of $\approx 40\%$ ($R(\theta = 90^\circ)/R(\theta = 0^\circ) \approx 1.44 \pm 0.19$), and $R(\theta)$ for $L < 150 \ \mu$m exhibited much lower anisotropy ($R(\theta = 90^\circ)/R(\theta = 0^\circ) \approx 1.19 \pm 0.13$) due to squashing and/or buckling during the densification process $^{[23]}$. Thus, the sensor comprised of an aligned CNT network might show anisotropy in its behavior during a cure cycle. In order to examine the effect of anisotropy, the cure sensor basic element in which the aligned CNT network was placed at $\theta = 90^\circ$ were tested for the 6 different cure cycles. It should be noted that the sensors were made of the aligned $L \approx 500 \ \mu$m-tall CNT arrays densified to $H \approx 40 \ \mu$m at $\theta = 90^\circ$ with an areal density of $25 \ \text{g/m}^2$ so that direct comparison of $\theta = 0^\circ$ with $\theta = 90^\circ$ could be conducted.

The sensors with $\theta = 90^\circ$ showed a resistance of $\approx 8 \ \Omega$ at room temperature prior to a cure cycle, while the sensors with $\theta = 0^\circ$ showed a resistance of $\approx 5.5 \ \Omega$ (see Appendix A). Thus, an anisotropy ratio of $R(\theta = 90^\circ)/R(\theta = 0^\circ) \approx 1.45$ was observed with the $L \approx 500 \ \mu$m CNT networks (see Appendix A), which was consistent with previous work $^{[1]}$. Fig. 5.19 shows the results of the SBR curves. As expected, the sensors also showed the same characteristics observed in the aligned $L \approx 500 \ \mu$m CNT networks at $\theta = 0^\circ$. Specifically, (1) the increase in SBR during the ramp-up stage
Figure 5.19: SBR of the cure status sensor basic elements made of aligned $L \approx 500\mu$m-tall CNT arrays densified to $H \approx 40\mu$m at $\theta = 90^\circ$ with an areal density of $12.8\,\text{g/m}^2$ at different soak temperatures.
and (2) the decrease in SBR depending on the cure temperature (i.e., the higher the temperature, the faster and larger decrease in the SBR) were observed. Of note, these trends can be verified more clearly with the normalized SBR curves (see Appendix A). In general, the sensors at θ = 90° showed slightly lower SBR range (~10% lower) than the sensors at θ = 0°. The variation in SBR according to the alignment direction can be interpreted as the anisotropic sensitivity of the junction distance change. A previous study on the piezoresistivity of carbon nanotube/polymer composite films reported that the tunneling resistance change was expressed as a function of the average angle between the direction of applied strain and the tunneling path\(^{202}\). Therefore, due to the change in such angle in this work, the effect of polymer infiltration on SBR might vary. However, polymer infiltration is expected to affect the junction distance isotropically, so this may not be the only source of anisotropy. Thus, further study on the anisotropy of junction distance change due to polymer infiltration is needed to clarify these observations.

### 5.3.7.2 Aligned CNT network comprised of \( L \approx 150 \mu m \) CNTs

In order to explore the effect of height of the as-grown CNT network on cure sensing performance, a vertically aligned CNT forest comprised of \( L \approx 150 \mu m \) CNTs was tested. In the same method described in Section 5.3.1, the CNT networks were densified so that the CNTs formed film-like materials having electrical anisotropy. After such densification, the CNT networks comprised of \( L \approx 150 \mu m \) CNTs had a height of \( H \approx 12 \mu m \), whereas the CNT networks comprised of \( L \approx 500 \mu m \) CNTs had a height of \( \approx 40 \mu m \). They had the same degree of densification \( \left( \frac{150 \mu m}{12 \mu m} = \frac{500 \mu m}{40 \mu m} \right) \) and areal density of 12.8 g/m². Their resistivity corresponds to \( 2.2 \times 10^{-4} \ \Omega \cdot m \cdot 2.4 \times 10^{-4} \ \Omega \cdot m \) at \( \theta = 0° \). Therefore, it is reasonable to assume that the two CNT networks have a somewhat similar morphology after densification and can be considered as the same type of material with different lengths yet the same characteristics from a macroscopic effective constitutive point of view.

Fig. 5.20 exhibits the SBR curves of sensors comprised of aligned \( L \approx 150 \mu m \) CNT arrays densified to \( H \approx 12 \mu m \) at \( \theta = 0° \) at 6 different soak temperatures. Overall, the aligned \( L \approx 150 \mu m \) CNT network showed similar SBR curves and trends when compared to the aligned \( L \approx 500 \mu m \) CNT network, which is made clearer by the normalized SBR curves (see Appendix A). Assuming that the long \( (L \approx 500 \mu m) \) and short \( (L \approx 150 \mu m) \) CNT networks have a similar morphology, similar values of SBR are expected. However, the SBR at the apex of the short CNT network was \( \approx 2.0 \), whereas the long CNT network showed a SBR of \( \approx 1.5 \) at the apex. Such findings can be explained by a transient aspect of junction distance increase during polymer infiltration. If the
Figure 5.20: SBR of cure status sensor basic elements made of aligned $L \approx 150 \mu m$-tall CNT arrays densified to $H \approx 12 \mu m$ at $\theta = 0^\circ$ with an areal density of $12.8 \text{ g/m}^2$ at different soak temperatures. Note that the densified CNT networks were placed at $\theta = 0^\circ$ so that the current flow direction is parallel to the alignment direction.
junction distance increase occurs instantly, an increase in SBR should end at full infiltration of the CNT network. However, it was observed that the resistance still increased even after the full infiltration of a CNT network. When following the 120 °C cure cycle, the full infiltration occurred at \( \approx 18 \) min, yet the apex of SBR was observed at \( \approx 22.5 \) min (see Fig. 5.10 and Fig. 5.11 for details of the full infiltration). Because the short CNT network has a thickness of \( \approx 12 \) μm, it is fully infiltrated faster than the long CNT network, which has a thickness of \( \approx 40 \) μm. Consequently, the short CNT networks experience junction distance increases for a longer period time because they are fully infiltrated much faster, leading to a higher SBR during the same cure cycle. In addition, this implies that the apex of SBR is a consequence of competition between the junction distance increase from infiltration and the decrease due to chemical cure shrinkage.

5.3.7.3 Randomly-oriented CNT network

A commercialized CNT film, Veelo HEAT from General Nano LLC.\(^{[46]}\), was utilized in order to explore the differences between aligned and randomly-oriented CNT networks. This CNT film was composed of randomly oriented multiwalled CNTs, and was \( H \approx 40 \) μm with an areal density of 25 g/m\(^2\) and an isotropic sheet resistance of \( \approx 5 \) Ω/□. It should be noted that the randomly-oriented and aligned \( L \approx 500 \) μm CNT network had the same thickness of 40 μm, yet the areal density of the randomly-oriented CNT network was around twice that of the aligned CNT network comprised of \( L \approx 500 \) μm CNT arrays (\( \approx 12.8 \) g/m\(^2\)). Because they had the same thickness of 40 μm, their volumetric mass densities showed a 2-fold difference.

Fig. 5.21 shows the SBR curves of cure sensor basic elements made of randomly-oriented CNT networks (\( H \approx 40 \) μm with an areal density of 25 g/m\(^2\)) at 6 different soak temperatures. Similar to other CNT networks, the randomly-oriented CNT network exhibited a similar trend in SBR curves. Interestingly, the SBR of the randomly-oriented CNT network was much smaller than that of other CNT networks. For instance, the maximum SBR was \( \approx 1.17 \), while the aligned \( L \approx 500 \) μm CNT network showed a SBR of \( \approx 1.5 \) at the apex. In addition, a SBR of less than 1 was observed in several cure cycles, which means that the resistance of the infiltrated CNT network is smaller than that of the dry CNT network. These observations are attributed to the relatively high density of the randomly-oriented CNT network rather than the differences between the aligned and randomly-oriented network, which are discussed next. First, due to the higher density, the movement of the CNTs can be somewhat more restricted, leading to a smaller change (increase) in junction distance during polymer infiltration. Moreover, the infiltration progress is also limited by the lower perme-
Figure 5.21: SBR of cure status sensor basic elements made of randomly-oriented CNTs ($H \approx 40\mu m$ with an areal density of $25 g/m^2$) at different soak temperatures.
ability due to the higher density, as it was observed that the randomly-oriented CNT networks were not fully infiltrated during the cure cycles (see Fig. 5.12 and Fig. 5.13). Therefore, the smaller increase in junction distance resulted in the smaller increase in SBR. Second, if the increase in junction distance is small during the polymer infiltration, the final junction distance might be smaller than the baseline distance. A relatively small increase in junction distance during polymer infiltration, relative to the decrease from cure shrinkage, can result in a SBR < 1.

5.3.8 Repeatability of in situ cure status sensor basic elements

Fig. 5.22 and Fig. 5.23 exhibit the repeatability of the sensors comprised of an aligned $L \approx 500 \mu$m CNT network at $\theta = 0^\circ$ and a randomly-oriented CNT network, respectively. It should be noted that 5 sensors were tested for each case. As presented, the SBR curves were repeatable in both cases, even though each test was conducted with independently manufactured CNT networks. Specifically, the shape of the SBR curves were identical to each other. As a cure status monitoring technique, the sensor should provide a parameter indicating the cure status. From the repeatability tests, the slope of the SBR curve is recommended as such a parameter because the value of SBR itself shows variations. Fig. 5.24 and Fig. 5.25 show the derivative of the SBR curves for the sensors comprised of aligned $L \approx 500 \mu$m CNT network at $\theta = 0^\circ$ and randomly-oriented CNT network ($H \approx 40 \mu$m with an areal density of 25 g/m$^2$), respectively. Additionally, the DoC during the cure cycle at 120 $^\circ$C are provided in Fig. 5.24 and Fig. 5.25. The derivatives of the SBR curves are in excellent agreement across samples, especially in the section where most of the cure occurred. Since the decreasing slope of the SBR curve corresponds to the decreasing cross-linking reaction rate, a user defined point can be used to determine the end of cure with the sensors. For example, as shown in the DoC curve, the increase in DoC rapidly slowed at $\approx$1 hour. Thus, a curing process may be terminated around this point to shorten the cure cycle. The label 'User defined point' in Fig. 5.24 indicates the approximate point where the derivative of the SBR curve approaches 0. Similarly, a certain slope of SBR can be defined to determine the end of cure depending on the application of the cured components. Other combinations of the SBR data area also possible to determine different features in the cure cycle. From the repeatability tests, it is concluded that the sensors can be reliably utilized to indicate the status of cure.
Figure 5.22: Result of repeatability tests on the cure sensor basic elements comprised of the aligned $L \approx 500\,\mu\text{m}$-tall CNT arrays densified to $H \approx 40\,\mu\text{m}$ at $\theta = 0^\circ$ with an areal density of $12.8\,\text{g/m}^2$. Note that 5 sensors were tested for the cure cycle at $120^\circ\text{C}$.
Figure 5.23: Result of repeatability tests on the cure sensor basic elements comprised of the randomly-oriented CNT network ($H \approx 40 \mu m$ with an areal density of 25 g/m$^2$). Note that 5 sensors were tested for the cure cycle at 120°C.
Figure 5.24: Derivative of SBR from the repeatability tests performed on the sensors comprised of the aligned CNT networks ($L \approx 500\mu m$-tall CNT arrays densified to $H \approx 40\mu m$ at $\theta = 0^\circ$ with an areal density of $12.8\, g/m^2$) and the DoC. The DoC was calculated for the neat polymer film via DSC measurements. Note that the exemplary user defined point is the approximate point where the derivative approaches 0.

Figure 5.25: Derivative of SBR from the repeatability tests performed on the sensors comprised of the randomly-oriented CNT network ($H \approx 40\mu m$ with an areal density of $25\, g/m^2$) and the DoC. The DoC was calculated for the neat polymer film via DSC measurements. Note that the exemplary user defined point is the approximate point where the derivative approaches 0.
5.4 Modeling of In Situ Cure Status Sensor Basic Elements

In addition to the experiments performed for cure status sensing, a model was developed to check whether the morphological change of a CNT network can simulate the electrical response. In the model, the cure kinetics (e.g., degree of cure), the change in viscosity, the progress of polymer infiltration (e.g., flow front estimation) and cure (including shrinkage), and the morphological change in the CNT network as a function of strain are considered.

5.4.1 Cure kinetics

The cure kinetics model is based on a first order differential equation with the assumption that the cure rate $\frac{d\alpha}{dt}$ is proportional to the rate of the exothermic heat of reaction evolution with time$^{[192-194]}$:

\[ \frac{d\alpha}{dt} = \frac{1}{H_T} \cdot \frac{dH}{dt} \]  

(5.2)

where $\alpha$ is the degree of cure, $t$ is the time, $H_T$ is the total exothermic heat of reaction for completed cure, and $\frac{dH}{dt}$ is the exothermic heat flow. Note that an uncured and completely cured polymer correspond to $\alpha = 0$ and $\alpha = 1$, respectively. Here, a cure kinetics model based on empirical data fitting was implemented, because of the lack of information available for the parameters comprising more fundamental models based on material characteristics and chemical reactions$^{[195,203-205]}$. The empirical data fitting model is expressed as follows:

\[ \frac{d\alpha}{dt} = K(T) \cdot f_{\text{cure}}(\alpha) \]  

(5.3)

\[ K(T) = A \cdot \exp\left(-\frac{E_{a,\alpha}}{RT}\right) \]  

(5.4)

where $K$ is the Arrhenius rate constant as a function of temperature $T$ in Kelvin, $A$ is the pre-exponential cure rate coefficient, $E_{a,\alpha}$ is the activation energy for the reaction, $R$ is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and $f(\alpha)_{\text{cure}}$ is the conversion function describing the shape of the heat flow and the type of reaction.

For $f_{\text{cure}}(\alpha)$, the widely-used autocatalytic model was implemented because it has previously shown reasonable results in various epoxy systems$^{[200,206]}$. Among several autocatalytic models for thermoset polymers$^{[192]}$, the autocatalytic model accounting for the transition of cure mechanism to diffusion was utilized which gives$^{[200,206,207]}$:  

133
\[
\frac{d\alpha}{dt} = \frac{K \cdot \alpha^m (1 - \alpha)^n}{1 + \exp(C(\alpha - (\alpha_{c,0} + \alpha_{c,T} \cdot T)))}
\]  

(5.5)

where \(m\) and \(n\) are the reaction orders determined by empirical data, \(C\) is the empirical diffusion constant, \(\alpha_{c,0}\) is the empirical critical degree of cure at 0 K, and \(\alpha_{c,T}\) is an empirical constant describing the increase in the rate of critical degree of cure with temperature.

### 5.4.2 Viscosity

The viscosity of the resin system during cure is affected by two factors: temperature and DoC. As the temperature increases, the mobility of the polymer chain increases due to the Arrhenius-type behavior\[^{186}\]. As a result, the viscosity tends to decrease with increasing temperature. At the same time, the cure rate accelerates because of the increase in temperature. As the cure progresses, the size of the cross-linked polymer chain increases, and the cross-link density increases, resulting in a decrease in the mobility of the polymer chains and therefore an increased viscosity of the resin system. The semi-empirical model for viscosity can be expressed by Eq. 5.6\[^{208}\]:

\[
\mu = \mu_\infty \exp\left(\frac{E_{a,\mu}}{RT}\right) \cdot f_\mu(\alpha)
\]

(5.6)

where \(\mu_\infty\) is the pre-exponential viscosity coefficient, \(E_{a,\mu}\) is the activation energy for the viscosity, and \(f_\mu(\alpha)\) is the conversion function describing the effect of DoC on viscosity. \(\mu_\infty\) and \(E_{a,\mu}\) are empirical constants.

Numerous approaches have been used to implement this model\[^{209}\], and the following implementation was used here because it describes the effect of the degree of cure on the viscosity by incorporating the gelation phenomenon\[^{10,210}\]. As the DoC approaches the gelation point, the viscosity of the thermoset polymer increases dramatically as the polymer chains form an infinite network, giving.

\[
\mu = \mu_1 \exp\left(\frac{E_1}{RT}\right) + \mu_2 \exp\left(\frac{E_2}{RT}\right) \cdot \left(\frac{\alpha_g}{\alpha_g - \alpha}\right)^{A + B\alpha + C\alpha^2}
\]

(5.7)

where \(\alpha_g\) is degree of cure at the gel point, \(\mu_1\) and \(\mu_2\) are pre-exponential viscosity coefficients, \(E_1\) and \(E_2\) are the viscosity activation energy. \(\alpha_g, \mu_1, \mu_2, E_1, E_2, A, B,\) and \(C\) are experimentally determined constants.
5.4.3 FITC as a function of morphological change and temperature

Because the electrical conductivity of films of CNT networks is limited by the CNT-CNT junction resistance\textsuperscript{[187,211-214]}, their temperature coefficient of resistance is expected to have a negative value (i.e. nonmetallic behavior)\textsuperscript{[211]}. The electron transport mechanism in CNT networks can be represented using the fluctuation induced tunneling conduction (FITC) model\textsuperscript{[211-213]}:

\[
\rho(T) = \rho_s \exp \left( \frac{T_b}{T + T_0} \right)
\]  

(5.8)

where \( \rho \) is the resistivity, \( \rho_s \) is the empirical resistivity constant, \( T \) is the temperature, \( T_b \) corresponds to the tunneling activation energy, and \( T_0 \) defines the point at which thermal activation occurs. \( T_b \) and \( T_0 \) are empirically determined by fitting a resistance curve as a function of temperature.

The morphological change in the CNT network (i.e., an increase and decrease in the tunneling junction distance) can be introduced into the FITC model by applying an incremental disturbance \( dw \) to the original tunneling junction distance \( w \), which yields \( ds = dw/w \), where \( s \) is the strain\textsuperscript{[215]}:

\[
d(\ln \rho) = \frac{d(\ln \rho_s)}{ds} \frac{1}{T + T_0} \frac{dT_b}{ds} + \frac{T_b}{(T + T_0)^2} \frac{dT_0}{ds}
\]  

(5.9)

Note that the strain \( (s) \) is total strain and includes thermal and mechanical effects. The junction distance \( w \) is a unit cell representation of the average junction distance of CNT-CNT junctions that contribute to FITC in the wavy aligned CNT network\textsuperscript{[179,216,217]}. Junction distances in the aligned CNT network have not been directly measured, but such junctions after polymer infiltration and curing (representing \( w_F \) in Fig. 5.1) have been measured to be \( \sim 1 \) nm from 3D TEM\textsuperscript{[181]}. With the assumption of the image-force corrected rectangular potential barrier, \( d(T_b)/ds = 1.48T_b \) and \( d(T_0)/ds = 0.020T_0 \) can be obtained\textsuperscript{[215]}, and Eq.5.9 is expressed as:

\[
d(\ln \rho) = \frac{d(\ln \rho_s)}{ds} + \frac{1.48T_b}{T + T_0} - \frac{0.020T_0}{(T + T_0)^2}
\]  

(5.10)

Moreover, it was shown previously that \( (1/\rho_s)(d\rho_s/ds) \) can be regarded as a constant\textsuperscript{[215]}, which corroborates the previous findings that tunneling conduction would show an exponential dependence\textsuperscript{[3]} at a fixed temperature associated with a characteristic length \( l_c \) which is reported to be of nm-order for CNTs\textsuperscript{[3,218]}. With \( d(\ln \rho_s)/ds = 1/\lambda \), \( \rho_s \) as a function of strain \( (s) \) can be derived as follows\textsuperscript{[215,219]}:
\[ \rho_e = \rho_0 \exp \left( \frac{s}{\lambda} \right) \]  

(5.11)

where \( \rho_0 \) and \( \lambda \) are empirical constant and independent of changes in temperature and morphology of the CNT network (i.e., strain). Therefore, the FITC model can be rewritten as a function of strain and temperature by substituting Eq. 5.11 to Eq. 5.8:

\[ \rho(s, T) = \rho_0 \exp \left( \frac{s}{\lambda} + \frac{T_b(s = 0) \cdot \exp(1.48s)}{T + T_0(s = 0) \cdot \exp(0.020s)} \right) \]  

(5.12)

The FITC equation for resistivity is expressed with the resistivity at reference temperature \( (T_r = 298 \text{ K}) \) here and prior to any morphological change in the CNT network \( (s = 0) \):

\[ \rho(s, T) = \rho(0, T_r) \cdot \exp \left( \frac{s}{\lambda} + \frac{T_b(s = 0) \cdot \exp(1.48s)}{T + T_0(s = 0) \cdot \exp(0.020s)} - \frac{T_b(s = 0)}{T + T_0(s = 0)} \right) \]  

(5.13)

Additionally, in order to examine the effect of morphological changes (i.e., strain) on its own, the intrinsic response of the CNT network with respect to temperature \( (\rho(0, T)) \) can be partially decoupled from \( \rho(s, T) \) as follows:

\[ \frac{\rho(s, T)}{\rho(0, T)} = \exp \left( \frac{s}{\lambda} + \frac{T_b(s = 0) \cdot \exp(1.48s)}{T + T_0(s = 0) \cdot \exp(0.020s)} - \frac{T_b(s = 0)}{T + T_0(s = 0)} \right) \]  

(5.14)

5.4.4 Polymer infiltration

Even though liquid polymers are non-Newtonian fluids, most thermoset polymers can be considered as Newtonian fluids in the usual composite manufacturing environment \(^{118} \). This is because the polymer flow velocity and corresponding shear rate are very small. In the same manner, polymer infiltration into the CNT network can be described by the characteristics of Newtonian fluid flow at very low Reynolds number \( (< 0.001) \). From a macroscopic point of view, the polymer infiltration into CNT network is therefore considered as a Newtonian flow in a porous medium. For simplicity, the single-phase flow of a Newtonian liquid in an isotropic and rigid porous medium can be assumed to estimate the flow front. In addition, the capillary number, \( Ca \), which is a dimensionless number presenting the ratio of viscous force to surface tension, is much less than unity \( (< 0.001) \) in the infiltration process \(^{120,221} \). Thus, the capillary pressure at the flow front needs to be addressed. In this work, Darcy’s law with capillary pressure and the continuity equation was used to describe the
infiltration process as follows:\[222:\]

\[
\text{Darcy's law: } \bar{u} = -\frac{\kappa}{\mu} \nabla P
\]

\[
\text{Continuity: } \nabla \cdot \mathbf{u} = 0
\]

where \( \bar{u} \) is the volume averaged liquid velocity, \( \kappa \) is the permeability of the porous medium, \( \mu \) is the viscosity of the fluid, and \( \nabla P \) is the gradient of the pressure.

With the assumption of one dimensional flow (see Fig. 5.26), Eq. 5.15 and Eq. 5.16 are reduced to:

\[
\bar{u} = -\frac{\kappa}{\mu} \frac{dP}{dx}
\]

\[
\frac{d\bar{u}}{dx} = 0
\]

By combining Eq. 5.15 and Eq. 5.16, the pressure distribution can be calculated with the following boundary conditions (note that the permeability and viscosity are independent of \( x \)):

\[
\frac{d^2P}{dx^2} = 0
\]

Figure 5.26: Schematic of polymer infiltration into a porous network. Note that polymer infiltration starts from the bottom surface of the model and proceeds through the \( x \) direction. \( h_f \) is the flow front distance as a function of time, and \( H \) is the thickness of the porous network.
At $x = 0$: $P = p_{atm}$ \hspace{1cm} (5.20)

At $x = h_f$: $P = -p_c$ \hspace{1cm} (5.21)

$\therefore P(x) = \frac{p_{atm} + p_c}{h_f} \cdot x$ \hspace{1cm} (5.22)

where $h_f$ is the flow front distance as a function of time, and $p_c$ is the capillary pressure of the CNT network. Note that Eq. 5.22 is valid for $0 \leq x \leq h_f(t)$.

The flow front location $h_f(t)$ can be obtained by Eq. 5.17 and the porosity of the CNT network ($\epsilon$):

$$\frac{d h_f}{d t} = \frac{\bar{u}}{\epsilon} = -\frac{\kappa}{\epsilon \mu} \cdot \frac{dP}{dx}$$ \hspace{1cm} (5.23)

$$\Rightarrow \frac{d h_f}{d t} = \frac{\kappa}{\epsilon \mu} \cdot \frac{p_{atm} + p_c}{h_f}$$ \hspace{1cm} (5.24)

Because the viscosity ($\mu$) of the thermoset polymer changes as a function of time during a cure cycle, $h_f$ can be calculated by Eq. 5.25, or the discretized form Eq. 5.26:

$$\int h_f \cdot dh_f = \int \frac{\kappa}{\epsilon \cdot \mu(t)} \cdot (p_{atm} + p_c) \cdot dt$$ \hspace{1cm} (5.25)

or $h_f(t + \Delta t) = h_f(t) + \frac{\kappa}{\epsilon \cdot \mu(t)} \cdot \frac{p_{atm} + p_c}{h_f(t)} \cdot \Delta t$ \hspace{1cm} (5.26)

$p_c$ can be estimated by the morphological characteristics of the CNT arrays and the assumption that one-dimensional resin flow parallel and perpendicular to the nanofiber/CNT alignment, as follows$^{119-124}$:

$$p_c = \begin{cases} \frac{2}{D_f} \frac{1 - \epsilon}{\epsilon} \cdot \sigma \cos \theta & \text{perpendicular to the CNT alignment} \\ \frac{4}{D_f} \frac{1 - \epsilon}{\epsilon} \cdot \sigma \cos \theta & \text{parallel to the CNT alignment} \end{cases}$$ \hspace{1cm} (5.27)

where $D_f$, $\epsilon$, $\sigma$, and $\theta$ are diameter of a nanofiber/CNT, porosity of the reinforcing nanofiber preform, surface tension of the resin, and contact angle between the resin and nanofiber, respectively.
5.4.5 **Morphological changes in CNT networks during a cure cycle**

There are three factors which may induce morphological changes in a CNT network during a cure cycle: (1) an increase in the CNT-CNT junction distance due to polymer infiltration, (2) thermal expansion and contraction of the polymer as a function of temperature, and (3) chemical cure shrinkage due to the cross-linking of polymer chains. Thus, the total strain \( s \) can be obtained by combining these factors:

\[
s = (1 + s_t)(1 + s_{\text{th}})(1 + s_c) - 1, \tag{5.28}
\]

where \( s_t \), \( s_{\text{th}} \), and \( s_c \) correspond to the strain induced by polymer infiltration, polymer thermal expansion, and chemical cure shrinkage, respectively.

From the experimental results, it was observed that the effect of thermal expansion on the electrical response is insignificant during a cure cycle compared to the effect of polymer infiltration and cure shrinkage. This observation is corroborated by the following findings. First, if the thermal expansion affected the electrical properties, the electrical response of the CNT network after the polymer infiltration and curing should have been different from that of the dry CNT network. However, this difference was barely observed in the process of cooling down (see the corrected resistance responses in Fig. 5.15). For example, the SBR curve performed at 120°C showed a decrease by \( \approx 0.02 \) during the cooling down stage (from 120°C to 30°C), while it showed a change of \( \approx 0.5 \) and \( \approx 0.4 \) due to polymer infiltration and the cure shrinkage, respectively. Additionally, a SBR increase was observed even though the temperature decreased after the overshoot (see Fig. 5.15). This observation also supports the argument that CTE is insignificant in SBR changes. Second, the effect of thermal expansion may become insignificant due to the continuous movement of polymer fluid. The thermal expansion and infiltration of the polymer occur simultaneously. At this temperature ramp-up stage, the polymers are in the liquid phase prior to the gel point, and therefore the expansion of the liquid volume can act as further infiltration in the liquid flow direction, not as an expansion in the lateral direction leading to further junction distance increase. Considering this observation, Eq. 5.28 can be reduced as follows:

\[
s \approx (1 + s_t)(1 + s_c) - 1 \tag{5.29}
\]
It should be noted that $s_i$ and $s_c$ change as a function of time. Specifically, they are affected by the status of polymer infiltration and the degree of cure. The models of $s_i$ and $s_c$ are presented in the following subsections.

### 5.4.5.1 Polymer infiltration

As described in Section 5.4.4, the polymer infiltration into the CNT network does not occur instantaneously. Thus, the opening of the CNT-CNT junctions at different positions does not occur at the same time. Instead, the opening of CNT-CNT junction is expected to start once the polymer flow front reaches the position of each junction. Because the position of the flow front can be obtained as a function of time ($h_f(t)$), the initiation time to open each junction can be estimated. In addition, the junction opening process is expected to occur gradually. If it were described as a step function, the junction opening would cease once the CNT network is fully infiltrated. However, experimental results show that the resistance still increased even after the full infiltration of a CNT network (see Section 5.3.4). Thus, a continuous function having a transient response should be used in order to describe this phenomenon, and here a logarithmic growth curve is taken.

\[
s_i(t, t_i) = \begin{cases} 
0 & \text{for } t < t_i \\
 s_i^f \left[ 1 - \exp \left( - \left( \frac{t - t_i}{\tau}\right)^\beta \right) \right] & \text{for } t \geq t_i
\end{cases}
\]

where $t_i$ is the initiation time of polymer infiltration, $s_i^f$ is the maximum limit of strain due to polymer infiltration, $\tau$ is the time constant, and $\beta$ is a constant. $\tau$ and $\beta$ are empirically determined. Note that the initiation time $t_i$ can be defined as the time when the polymer flow front reaches the location of the junction. Here, Eq. 5.30 is valid as long as $\tau$ is regarded as constant. However, $\tau$ may vary as a function of viscosity of the polymer (e.g., the lower viscosity, the larger the $\tau$ value). Most importantly, as the cross-linking of polymer continues, gelation can occur, which is when polymers form an effectively infinite cross-linked network, therefore losing fluidity. Thus, the junction opening process cannot continue once the cure reaches the gel point. For simplicity, $\tau$ can be regarded as follows:

\[
\tau(t) = \begin{cases} 
\tau_0 & \text{for } \alpha(t) < \alpha_g \\
0 & \text{for } \alpha(t) \geq \alpha_g
\end{cases}
\]
where $\tau_0$ is the characteristic time constant, $\alpha$ is degree of cure, and $\alpha_g$ is degree of cure at gel point. $\tau_0$ and $\alpha_g$ are empirically determined. Because $\tau$ can be regarded as a function of time, Eq. 5.30 needs to be rewritten as follows:

$$s_i(t + \Delta t, t_i) = \begin{cases} 
0 & \text{for } t < t_i \\
 s_i(t, t_i) + s_i^0 \cdot \beta (t - t_i)^{\beta - 1} \cdot \tau(t)^{-\beta} \cdot \exp \left( -\left( \frac{t - t_i}{\tau(t)} \right)^{\beta} \right) \cdot \Delta t & \text{for } t \geq t_i
\end{cases} \quad (5.32)$$

### 5.4.5.2 Chemical cure shrinkage

As discussed, the chemical cure shrinkage is directly proportional to the degree of cure. Therefore, the strain due to cure shrinkage can be modeled as a simple linear equation as a function of the degree of cure.

$$s_c(t) = s_c^0 \cdot \alpha(t) \quad (5.33)$$

where $s_c^0$ is the maximum limit of strain due to chemical cure shrinkage when the thermoset polymer is fully cured (i.e., degree of cure $\alpha = 1$).

### 5.4.6 Electrical model of in situ cure status sensor basic elements

As discussed in the previous sections, the junction opening starts when the polymer flow front passes through the location of the junction. Therefore, in order to model the electrical response of the cure sensor basic element, the system needs to first be divided into each component having the same initiation of junction opening, and then integrated based on a circuit model. Here, given that the polymer infiltration is regarded as a one dimensional system, the electrical response of the sensor can also be modeled as a one dimensional system, and the sensor is considered as a stack of thin resistor layers connected in a parallel circuit. Finally, the electrical response of the sensor can be obtained as a function of time:
\[ R(t) = \left( \int_{0}^{H} \frac{1}{\rho(s(t,h^{-1}(x)),T(t))} \cdot dx \right)^{-1} \]

(5.34)

where \( H \) is the thickness of a CNT network film, \( h^{-1}_f(x) \) is the inverse function of \( h_f(t) \), and \( T(t) \) is the temperature of the cure cycle over time.

The finite difference method (FDM) can be utilized to solve Eq. 5.34, and Euler’s method is applied for the time integration. The discretization of the time domain can be formulated as follows:

\[ t_j = (j - 1) \cdot \Delta t \quad \text{where} \quad j = 1, 2, \ldots \]

(5.35)

Because the finite time step is used, the resistance of the sensor can be regarded as a stack of a finite number of resistors \((R_k \text{ where } k = 1, 2, \ldots)\) through the thickness connected in a parallel circuit (see Fig. 5.27). In this way, as the flow front progresses, the junctions in each component/layer that has been infiltrated will contribute to the parallel circuit based on the morphology change. With

![Figure 5.27: Schematic of the resistance model for cure sensor basic element. Note that the polymer infiltration starts from the bottom surface of the model and proceeds through the x direction through each component/layer.](image)

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regard to Fig. 5.27, the gray components/layers have been infiltrated, and the white component/layer contributes to the overall network resistance as a dry CNT network parallel component. The height of each resistor can be defined as the height increment of the polymer flow front during a time step $\Delta t$ (i.e., the height of $h_f(k \cdot \Delta t) - h_f$ for $R_k$). Of note, $n_{\text{crit}}$ is the number of infiltrated components, including one additional layer having a height of $H - h_f(n_{\text{crit}} \cdot \Delta t)$ is attached on the top of the elements to address the case when a CNT network is not fully infiltrated. Under the discretization with a finite time step $\Delta t$, the resistor $R_k$ has an initiation time of $t_{i,k} = k \cdot \Delta t$. If a CNT network is fully infiltrated, the height of the uninfiltrated element ($k = n_{\text{crit}} + 1$) corresponds to 0, resulting in $R_{n_{\text{crit}}+1} = \infty$. Finally, the resistance of the sensor during a cure cycle can be obtained by Eq. 5.36 and Eq. 5.37.

$$R_k(t_j) = \begin{cases} \frac{\rho(s(t_j, t_{i,k}), T(t_j))}{h_f(k \cdot \Delta t) - h_f((k-1) \cdot \Delta t)} & \text{for } 1 \leq k \leq n_{\text{crit}} \\ \frac{\rho(0, T(t_j))}{H - h_f(n_{\text{crit}} \cdot \Delta t)} & \text{for } k = n_{\text{crit}} + 1 \end{cases} \quad (5.36)$$

$$R(t_j) = \left( \sum_{k=1}^{n_{\text{crit}}+1} \frac{1}{R_k(t_j)} \right)^{-1} \quad (5.37)$$

where the initiation time for each component, $t_{i,k}$, corresponds to $t_{i,k} = k \cdot \Delta t$, and $n_{\text{crit}}$ is the number of infiltrated components/layers.

Fig. 5.28 is the overview of the flow chart used to calculate the resistance of the cure sensor basic element based on this discretized model.

5.4.7 Results of developed model for in situ cure status sensor basic elements

Based on the models discussed in the above sections, electrical responses were simulated. Since the material properties of the Tencate surfacing film polymer used in the experiments such as cure kinetics, viscosity, and amount of cure shrinkage have not been documented, Hexcel 8552 epoxy resin was used instead because of its known material properties. In addition, the cure cycle of TC235-1SF is compatible with Hexcel 8552, which means that Hexply 8552 is reasonable to be used as a proxy. Note that the experiments with the Tencate surfacing film utilized a 120°C soak stage for curing, whereas Hexcel 8552 is strictly cured at 180°C, do direct comparisons are not possible and the discussion later focuses on qualitative trends and relative changes (such as SBR rise).

First, the model was applied to test if the change in morphology induced by polymer infiltration
Figure 5.28: Flow chart for the calculation of the electrical response of the cure sensor basic element, based on the discretized model.

and chemical cure shrinkage forms the distinct resistance peak observed experimentally. Additionally, due to the different characteristics of the polymer, this section does not pursue predictive comparisons of the experimental results and simulated results, but rather focuses on whether the key trends observed from experiments can be simulated with the developed model. Here, two key experimental observations are evaluated with the model: (1) the effect of the film thickness (H) of the aligned CNT network (i.e., the shorter CNTs, the higher SBR) and (2) the effect of the density of the CNT network (i.e., a denser CNT network exhibited a smaller SBR peak and a SBR less than 1). The parameters and additional assumptions used in the models are described below.

Cure kinetics

Previous studies reported the cure kinetics model for Hexcel 8552 epoxy resin\cite{135,200,206}, and the parameters that Garstka et al. reported were used in this study\cite{200}. The parameters for Eq. 5.5 are tabulated as follows:

<table>
<thead>
<tr>
<th>$A$</th>
<th>$E_{a,a}$</th>
<th>$m$</th>
<th>$n$</th>
<th>$C$</th>
<th>$\alpha_{C,0}$</th>
<th>$\alpha_{C,T}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4.2 \times 10^6 \text{ min}^{-1}$</td>
<td>$65,000 \text{ J mol}^{-1}$</td>
<td>$0.5$</td>
<td>$1.5$</td>
<td>$30$</td>
<td>$-1.5148$</td>
<td>$5.171 \times 10^{-3} \text{ K}^{-1}$</td>
</tr>
</tbody>
</table>

Viscosity

Similarly, several studies have been performed on the viscosity of Hexcel 8552 epoxy resin during a
cure cycle\textsuperscript{206,223}. The parameters that Poursartip et al. reported were used for the viscosity model as follows\textsuperscript{223}:

Table 5.2: Parameters of the viscosity model for Hexcel 8552 epoxy resin.

<table>
<thead>
<tr>
<th>$E_1$</th>
<th>$E_2$</th>
<th>$\mu_1$</th>
<th>$\mu_2$</th>
<th>$\alpha_g$</th>
<th>$A$</th>
<th>$B$</th>
<th>$C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>81,908 Jmol\textsuperscript{-1}</td>
<td>13,228 Jmol\textsuperscript{-1}</td>
<td>$7.5 \times 10^{-11}$ Pa·s</td>
<td>0.0481 Pa·s</td>
<td>0.545</td>
<td>2.466</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

FITC as a function of morphological change and temperature

Because the characteristics of the CNT network used here have already been analyzed, the previous fitting of the experimental data were used for FITC parameters as follows\textsuperscript{231}: $T_b = 165$ K, $T_0 = 6.10$ K. It was reported that the value of $T_b/T_0 \approx 27$ indicated that the fitting parameters are consistent with previous investigations utilizing the FITC model for CNT-CNT junctions\textsuperscript{178,179,224}.

The activation energy for electron transport via tunneling ($E_a$) of $\approx 14.2$ meV was also consistent with previous work on electron transport in CNT networks\textsuperscript{211,225}. Finally, Zhang et al. reported that thermoplastic elastomer composites containing multiwall CNTs of 0.4-1.0 wt.% exhibited $d(ln \rho_e)/ds = 1/\lambda \approx 6$ under strain-induced resistivity experiments up to 90% strain\textsuperscript{219}. Given that $\lambda$ showed insignificant variation after the percolation threshold was reached in that previous study, the $\lambda$ value of 1/6 was taken in this model with the assumption that the electrical properties of CNTs are similar between the current and prior work. The value of $\lambda = 1/6$ is used with strain measured on an absolute basis, not a % basis, consistent with the prior work\textsuperscript{219}.

Polymer infiltration

In order to calculate the flow front, the capillary pressure and permeability of the CNT network need to be estimated. Given that $\approx 500$ μm-tall vertically aligned CNT arrays ($\varepsilon \approx 0.016$) were densified to $\approx 40$ μm-tall by the CNT knockdown process, $\varepsilon$ of $\approx 0.8$ was estimated. In addition, $D_f \approx 7.8$ nm, $\sigma \approx 35$ mJm\textsuperscript{-1}, and $\theta \approx 20^\circ$ were used based on known values for similar epoxy system\textsuperscript{226-228}. In addition, Wang et al. reported that randomly-oriented CNT films showed a permeability ($\kappa$) of $\approx 2 \times 10^{-19}$ m\textsuperscript{2}\textsuperscript{229}. Assuming that the fabricated aligned CNT film has the same order of magnitude of permeability, a permeability of $3 \times 10^{-19}$ m\textsuperscript{2} was used considering the film’s 20% lower density. For the randomly-oriented CNT film, a permeability of $\approx 0.5 \times 10^{-19}$ m\textsuperscript{2} was used, considering that its density is twice the value of the aligned CNT films.

Morphological changes in CNT networks during a cure cycle

Given that the usual volumetric shrinkage range of epoxy resin is 2-7% during a cure cycle\textsuperscript{10,195,196}, the maximum limit of strain due to chemical shrinkage ($s_f^c$) of 0.1 (10%) was assumed. From the
experimental results, polymer infiltration and cure shrinkage exhibited the same order of magnitude of resistance change, and therefore the same order of magnitude of strains due to polymer infiltration and cure shrinkage can be inferred. Thus, the maximum limit of strain due to polymer infiltration ($s_f^i$) of 0.14 (14% strain) can be inferred from the SBR of $\sim 1.5$ at the apex in the case of $L \approx 500 \, \mu$m-tall CNT arrays densified to $H \approx 40 \, \mu$m at $\theta = 0^\circ$ with an areal density of $12.8 \, \text{g/m}^2$. In the case of the randomly-oriented CNT film, $s_f^i$ of 0.08 (8%) was inferred, considering the possible restriction in junction distance increase due to having a density that is twice as high. For describing a transient response, $\tau$ of 200 s and $\beta$ of 0.5 were assumed based on the experimental results presented earlier.

5.4.7.1 Baseline and cure sensor model results

In the case of the baseline (dry CNT network, $L \approx 500 \, \mu$m-tall CNT arrays densified to $H \approx 40 \, \mu$m at $\theta = 0^\circ$ with an areal density of $12.8 \, \text{g/m}^2$), the resistance is expressed as a function of temperature in the FITC model. Therefore, as presented in Fig. 5.29a, the dry CNT network exhibited a negative thermal coefficient of resistance; thus, the resistance change of the dry CNT network mirrors the temperature profile. For example, a dry CNT network in the model showed a resistance change from $5.5 \, \Omega$ to $4.5 \, \Omega$ during a temperature increase of $150 \, ^\circ\text{C}$ (from $30 \, ^\circ\text{C}$ to $180 \, ^\circ\text{C}$). The experimental results showed a resistance change from $\approx 5.5 \, \Omega$ to $\approx 5 \, \Omega$ during a temperature increase of $90 \, ^\circ\text{C}$ (from $30 \, ^\circ\text{C}$ to $120 \, ^\circ\text{C}$) (see Appendix A). In the case of the cure sensor, the electrical response in the model captured the key trends of the experimental results of the cure sensor basic element (Fig. 5.5), including resistance increase in the temperature ramp-up stage, followed by a resistance decrease as the cure proceeds (see Fig. 5.29a). Fig. 5.29b presents the SBR curve of the representative results of the baseline (dry CNT network) and cure sensor basic element. Similar to the experimental results (see Fig. 5.5), distinct features of the cure status sensor basic element, such as a resistance rise and peak occurring at the late-stage of the temperature ramp up, and resistance decrease during the soaking stage, were also observed in the simulated SBR results. The model showed a SBR of $\sim 1.5$ at the apex at the temperature ramp-up stage (from $30 \, ^\circ\text{C}$ to $180 \, ^\circ\text{C}$), and a SBR of $\sim 1.1$ was observed at the end of the isothermal soaking stage. As a comparison (see Fig. 5.15), the experimental results showed a SBR of $\sim 1.45$ at the apex at the temperature ramp-up stage (from $30 \, ^\circ\text{C}$ to $120 \, ^\circ\text{C}$), and a SBR of $\sim 1.1$ was observed at the end of the isothermal soaking stage. These results conclude that the same order of magnitude of SBR can be successfully simulated with the developed model.

In order to evaluate if the model simulates SBR changes induced by polymer infiltration and
Figure 5.29: Representative results of the model. (a) Resistance response of the cure sensor and the dry CNT network and (b) SBR results from the model. The $L \approx 500 \mu$m-tall CNT arrays densified to $H \approx 40 \mu$m at $\theta = 0^\circ$ with an areal density of 12.8 g/m$^2$ were modeled.

chemical cure shrinkage, different cure cycles were modeled. Of note, other parameters such as the electrical properties of the CNT film (e.g., FITC constants including $T_b$ and $T_0$) and the level of morphological changes (e.g., $s_f$ and $s_c$) were fixed for this calculation. Fig. 5.30 shows the SBR and normalized SBR curves for the different cure cycles. Most importantly, as we observed in the experimental results (see Fig. 5.15), the same trend, that the SBR’s decreasing rate and amount after the apex increased as the isothermal soaking temperature increased, was captured in the developed model. For example, the amounts of SBR decrease from the apex to the end of the isothermal soaking stage correspond to $\sim 0.3$ and $\sim 0.7$ at the 140 $^\circ$C and 180 $^\circ$C cure cycle, respectively. The experimental results (see Fig. 5.15) showed a SBR decrease of $\sim 0.15$ and $\sim 0.35$ at the 80 $^\circ$C and 120 $^\circ$C cure cycle, respectively. Of note, the model estimated larger SBR increase as the soak temperature increases (e.g., a SBR of 1.5 at 140 $^\circ$C and 1.8 at 180 $^\circ$C), whereas the experimental results showed the similar SBR values at the apexes ($\sim 1.5$).

5.4.7.2 Effect of film thickness of aligned CNT networks

From the experiments with aligned CNT networks with $L \approx 150 \mu$m-tall CNT arrays densified to $H \approx 12 \mu$m at $\theta = 0^\circ$ with an areal density of 12.8 g/m$^2$, the SBR at the apex of short CNT net-
Figure 5.30: SBR of the cure sensor basic elements at different soak temperatures: (a) SBR curves, and (b) normalized SBR curves of cure status sensors comprised of an aligned CNT network at different soak temperatures. The \( L \approx 500\, \mu m \)-tall CNT arrays densified to \( H \approx 40\, \mu m \) at \( \theta = 0^\circ \) with an areal density of 12.8 g/m\(^2\) were modeled.

works was \( \approx 2.0 \), whereas the long CNT networks showed a SBR of \( \approx 1.5 \) despite the similar network’s density and morphology (see Section 5.3.7.2). Because the same density and morphology were modeled, this can be explained by a transient aspect of junction distance increase, associated with the timescale of polymer infiltration of thin vs. thick films, during polymer infiltration. As we discussed in Section 5.3.7.2, the junction distance increase does not occur instantly, and the resistance still increases even after full infiltration of the CNT network. Because the short CNT network reaches full infiltration faster than the long CNT network, the short CNT network has a longer elapsed time for junction distance increase before the resistance starts to decrease due to cure shrinkage. Therefore, it leads to a higher SBR during the same cycle. Fig. 5.31 shows the SBR curves of cure sensors comprised of \( L \approx 500\, \mu m \) and \( L \approx 150\, \mu m \). Each case corresponds to a thickness of \( \approx 40\, \mu m \) and \( \approx 12\, \mu m \) after densification, respectively. As shown, the SBRs at the apex of a short CNT network (\( \approx 2.1 \)) were larger than those of a long CNT network (\( \approx 1.6 \)), while the experimental results showed a SBR of \( \approx 2.1 \) and \( \approx 1.5 \), respectively, in excellent agreement. It should be noted that the model estimated a smaller SBR change in the short CNT network, while the experiment showed a smaller SBR change in the long CNT network. The model includes the
calculation of the elapsed time for the junction distance increase according to the flow front movement, and it can be concluded that this hypothesis is a reasonable explanation for the effect of film thickness \( (H) \) of (aligned) CNT networks on the SBR apex/peak.

![Diagram showing SBR curves](image)

**Figure 5.31:** SBR curves of (a) cure sensors comprised of \( L \approx 500 \mu m \)-tall CNT arrays densified to \( H \approx 40 \mu m \) at \( \theta = 0^\circ \) with an areal density of 12.8 g/m\(^2\) and (b) cure sensors comprised of \( L \approx 500 \mu m \)-tall CNT arrays densified to \( H \approx 12 \mu m \) at \( \theta = 0^\circ \) with an areal density of 12.8 g/m\(^2\). Note that the scales of both cases are equal.

### 5.4.7.3 Effect of density of CNT networks

It was observed that the SBR rise of randomly-oriented CNT networks were much smaller than that of other CNT networks, and a SBR of less than 1 was observed in several cure cycles (see Section 5.3.7.3) at the end of the cure cycle. This is explained by the fact that the randomly-oriented CNT network has a density that is twice as high compared to the aligned CNT networks; thus, the movement of CNT "wires" more restricted during polymer infiltration for denser CNT networks. Fig. 5.32 displays the effect of density on SBR from the model. It was assumed that the amount of junction distance increase is limited in the case of higher density networks. As presented in Fig. 5.32, the cure sensors comprised of a higher density network showed smaller SBRs compared to that of a lower density network. Furthermore, the model simulated the experimental results that SBRs become less than unity, which means that the resistance of cure sensors is lower than that of
the baseline dry CNT network.

Figure 5.32: SBR curves of (a) cure sensors comprised of an aligned CNT network of $L \approx 500 \mu m$ (lower density) and (b) cure sensors comprised of a randomly-oriented CNT network (higher density). The randomly-oriented CNT network was assumed to have a density twice as high as the aligned CNT network. Note that the scales of both cases are equal.

5.5 Summary

In this chapter, a multifunctional aspect of the OoO manufacturing was introduced: an *in situ* cure status monitoring technique utilizing the nano-engineered heating element of the OoO process. As the nanoporous network of a sensor basic element was heated, the adjacent polymer flowed into the heater via capillary action. Based on cure status sensing experiments and theoretical models, it was found that electrical resistance changes of the sensor correspond to several mechanisms, including a morphological change in the CNT network during a cure cycle. Among several effects, polymer infiltration into the CNT network caused the average CNT-CNT junction distance to increase, resulting in a resistance increase. Later in the manufacturing process, as polymer cross-linking occurs after infiltration, chemical cure shrinkage decreases the CNT-CNT junction distance, leading to a decrease in resistance. It was demonstrated that the SBR corrects the effect of temperature on resistance under FITC, and therefore the resistance change induced by the morphological change of the CNT network can be solely examined *via* SBR. From the repeatability tests, very small SBR vari-
ations were observed in individually fabricated cure sensor basic elements, which suggests a good reliability of the sensor. In order to predict the DoC during a cure cycle, the slope of the SBR curve is recommended as a parameter, and a certain SBR slope close to 0 can be defined to determine the end of cure. In addition, the theoretical model successfully simulated the distinct features of the cure status sensor basic element, including a resistance rise and peak occurring at the late-stage of the temperature ramp-up and resistance decrease during the soaking stage. Most importantly, the model captured the experimental results that the decreasing rate of SBR after the apex increased as the isothermal soaking temperature increased. The model also simulated the effect of the film thickness ($H$) and the density of the CNT network on the SBR trend. Thus, nano-engineered cure sensors can be used to monitor a cure process such as the status of polymer wetting, as well as determining the end of the cure cycle, thereby enhancing both quality and productivity of composite manufacturing.
Chapter 6

Conclusions and Recommendations

The out-of-oven (OoO) curing process and its related processing techniques developed in this thesis are expected to be utilized in non-autoclave prepreg processing, which addresses the unresolved limitations of the conventional convection-based autoclave and out-of-autoclave processes such as poor energy efficiency, high operational cost, long cure cycle, geometrical constraints on parts, and fewer options on prepregs. The OoO and its related processing techniques have several advantages: (1) compatibility with a wide range of composite materials, including conventional autoclave and OoA prepregs with already-proven mechanical properties; (2) removal of size and shape constraints on composite components imposed by the use of a heating vessel; (3) cost savings on manufacturing by efficient conductive (as opposed to convective) thermal processing; (4) in situ curing status monitoring by nano-engineered heating elements; and (5) minimized spatial variance in temperature by zonal heating control. These techniques contribute to the design and manufacturing of next-generation multifunctional architectures with built-in structural status sensing and repairing capabilities. Future work will further explore the reduction of energy consumption and production cycle by a rapid-heating-enabled cure cycle and expand the techniques to thermoplastics and other high-temperature polymers. Moreover, the OoO techniques are expected to enable on-site composite curing and/or repair and may be integrated with conventional heating-vessel-based manufacturing processes with little to no process modifications. Future areas of exploration also include leveraging the spatial control of heat flux from the OoO technique into other OoA composite processes, such as resin infusion and resin transfer molding. In the remainder of this Chapter, a summary of the dissertation contributions, and the recommended paths for future research are presented.
6.1 Summary of Thesis Contributions

The major contributions and findings of this dissertation are as follows:

**Development of out-of-oven (OoO) curing for out-of-autoclave prepreg (OoA)**

The OoO curing process using a carbon nanotube (CNT) film as a heating element was applied to an aerospace-grade out-of-autoclave (OoA) formulated unidirectional carbon fiber advanced composite prepreg system. With an OoA prepreg, the characteristics of the OoO curing process were examined and compared to those of a conventional oven curing process. The OoO composite curing process exhibited immediate temperature responses and a significant reduction in electrical energy consumption by two orders of magnitude (from 13.7 to 0.12 MJ) under a typical industrial curing condition for a small (60 mm x 50 mm) test panel, compared to the oven curing process. The modeling of each manufacturing process showed excellent agreement with the measured electrical power consumption during a cure cycle, including the reduction in electrical energy and instantaneous power consumption. The thermophysical and mechanical properties of the OoO-cured and oven-cured composites were examined to evaluate whether they have comparable properties. The results suggested that there was no significant difference between the out-of-oven curing and oven curing as evaluated by degree of cure analysis, short beam shear interlaminar testing, dynamic mechanical analysis, and double-edge notch tensile testing; therefore, the OoO curing can achieve the equivalent quality for OoA prepreg composites as the conventional oven curing method.

**Expansion of OoO curing to autoclave-formulated prepreg**

The OoO process was expanded to autoclave-formulated prepreg systems that currently require an applied pressure of ~ 700 kPa in addition to vacuum. When a composite laminate comprised of autoclave-formulated prepregs is cured without an applied pressure of ~ 700 kPa, a significant amount of voids was observed. However, it was found that these voids were successfully removed by the insertion of a nanoporous network (NPN) into the interlaminar regions of the composite laminates. Conformability of the nanoporous network to the micron-scale prepreg surface was identified as a key factor underlying the interlaminar void reduction technique. The capillary pressure into the conformed NPN was estimated to be of the same order as the pressure applied in the conventional autoclave processing. Results showed that capillary-enhanced polymer wetting through the nanoporous network enables sufficient reduction of interlaminar voids to < 1 vol%, a level commensurate with autoclave-processed composites, without using a heating vessel or applied pressure. That is, this technique effectively removed the need for an autoclave to process composite lami-
nates. The mechanical tests showed that the OoO-cured and autoclave-cured composites have the equivalent short-beam strengths, a critical measure of the quality of cure.

Development of in situ cure status monitoring technique utilizing a carbon nanotube network

A multifunctional aspect of the OoO manufacturing process was introduced: an in situ cure status monitoring technique utilizing the CNT heating element of the OoO process. It was demonstrated that the morphological change of the CNT network can be used to detect the status of the cure during a cure cycle. Based on cure status sensing experiments and theoretical models, it was found that electrical resistance changes of the cure sensor, which was made of a CNT network, were attributed to several mechanisms including a morphological change in the CNT network during curing. Among several effects, polymer infiltration into the CNT network as a result of capillary action causes the average CNT-CNT junction distance to increase, resulting in a resistance increase. Additionally, as the polymer cross-linking occurs after infiltration, chemical cure shrinkage decreases the CNT-CNT junction distance, leading to a decrease in resistance. Thus, the nano-engineered cure sensors comprised of a CNT network can be used to monitor a cure process such as the status of polymer wetting and the end of the cure cycle, thereby enhancing both quality and productivity of composite manufacturing.

6.2 Recommendations for Future Work

The work presented in this thesis raises a number of avenues for future study. In an effort to address these points, the following future work is proposed:

Intralaminar void sweeping by zonal heating via OoO curing

During a cure cycle, the viscosity of the polymer initially decreases as the temperature ramps up. Then, the viscosity quickly increases towards a solid as the gelation occurs and the cross-linking of the polymer proceeds. Once gelation occurs, void migration is completely restricted due to the limited movement of the polymer chains. Therefore, it is important to have a practical time period with a viscosity value range so that effective void evacuation is possible. Moreover, in the situation where an applied pressure is not applied (e.g., OoA curing), it is known that breathable laminate edges are required in some systems for a low void content. Previous studies suggest that the connected and open void network within a laminate during void evacuation is a key feature for acquiring low void content.
During the analysis of the void content under different manufacturing conditions, it was observed that the laminate edges experienced lower temperature than the inner regions during the OoO curing, due to edge effects and likely insufficient thermal insulation. Thus, it was hypothesized that such temperature gradient might help maintain the void network connected and opened during a cure cycle, which gives rise to lower void content in the OoO specimens. If the heating during a void evacuation period is spatially uniform, polymer impregnation into dry regions may occur at random locations. Such random impregnation of the polymer into the dry regions may block the void evacuation network and hinder effective void migration outward at the edges. However, if the temperature at the center of a laminate is higher than that at the edges, the impregnation tends to proceed from the center to the edges, keeping the void network connected to a vacuum. As a result, voids within a laminate are removed effectively with a sweep-like effect.

To test the hypothesis, we carried out an OoO curing with an intentional in-plane temperature gradient by asynchronous heating with multiple heaters. A 100 mm × 25 mm 16-ply unidirectional
lamine (Hexcel Hexply AS4/8552 autoclave-formulated prepreg) was used, and the fibers were aligned with the long sides. To restrict the direction of void evacuation along the fiber alignment direction, the long edges of the laminate were sealed with a vacuum sealant tape. Three resistive CNT heaters were installed on the left, center, and right region of the laminate without a gap (see Fig. 6.1a). In order to simulate the void sweeping, a time delay of 10 min was applied to the heaters installed at the side regions during the first temperature ramp up, while the heater at the center followed the cure cycle provided from the manufacturer. Once the temperature of each heater reached the first hold point of 120°C, all heaters were synchronized to minimize the thermally induced residual stress (see Fig. 6.1b).

Fig. 6.1c presents the void content at the center and sides under the spatially uniform heating and sweeping condition. Since we found that a nanoporous network (NPN) helps to lower the void content, the sweeping experiment was additionally conducted on a laminate with NPN. As expected, the spatially uniform heating showed void content of ~1.8% and ~3.1% at the sides and center, respectively. The results indicate that the void evacuation can be hindered by the blockage of void networks. The center part has higher potential to be disconnected to a vacuum than the sides, which results in the higher void content at the center. However, the sweeping condition exhibited the opposite results. The void content at the center was ~0.3%, which is lower than that at the sides of ~1.0%. Both at the center and sides, the void content under sweeping were lower than those under spatially uniform heating. These results indicate that the voids at the center were removed first through still breathable void networks at the sides, and then the voids at the sides were evacuated easily with a relatively short migration distance to the edges of the laminate. Most importantly, when sweeping was combined with NPN, there was no detectable void throughout the laminate. In addition to this void sweeping along the fiber alignment direction, experiments in the transverse direction were performed as the worst case scenario (see Fig. 6.2a). This is because the morphology of the void network is elongated along the fiber alignment direction, and also voids are more likely to be evacuated along the microfibers[99,232]. Thus, the final void content from experiments in the transverse direction (90° laminate, as in Fig. 6.2) exhibited relatively higher void content than that along the fiber (90° laminate, as in Fig. 6.1), yet showed the same trends overall. Given these results, it is demonstrated that the laminates comprised of autoclave prepregs can be successfully cured only under a vacuum via the NPN, and may be effectively supplemented with the void sweeping method. Furthermore, the concept of void sweeping can be readily combined with conventional composite curing processes such as autoclave and oven curing because OoO curing is based on a vacuum-bag-
only curing. Therefore, we expect that this technique will be useful for manufacturing complex composite structures, which usually contain relatively high void content. These results on void sweeping are considered preliminary and need significant follow-up work.

Figure 6.2: Effects of void sweeping on void content for a 90° laminate. (a) Illustration of an 90° unidirectional laminate subjected to the void sweeping experiment, and (b) the results of void content at the center and sides of the laminate. Note that three independent heaters at the left, center, and right regions were controlled to conduct the void sweeping. The long edges of the laminate were sealed with a vacuum sealant tape so that only the short edges at the left and right regions were breathable.

**Scaled-up and complex-shaped composite manufacturing via OoO curing**

In this work, the flat composite plates of 120 mm × 120 mm × 2 mm were cured with the OoO curing. To be applied to composite structures in the future, the OoO curing needs experimental validation on a scaled-up and complex-shaped composite structure. For example, the curvature of a complex-shaped composite structure may hinder the CNT heaters from achieving a uniform temperature distribution, although this is expected to be less of an issue in OoO curing than in convective curing. In addition, several pairs of the CNT heaters, which are controlled independently, may be required to cure large-scale composite structures, and the design and installation of the CNT
heaters should be studied.

Integration of the OoO curing with conventional heating-vessel-based manufacturing processes for advanced composite manufacturing

Because the OoO curing is based on a conventional vacuum bag layup for composite curing, it can be readily integrated with heating-vessel-based manufacturing processes such as an autoclave or oven, or resin infusion, pultrusion, and extrusion. OoO curing is particularly well suited to address spatial non-uniformities, either independently or in concert with existing heating technologies. In this case, the integration of the OoO curing with conventional heating-vessel-based manufacturing processes may enable a proper heating condition.

Further reduction in energy consumption and production cycle by a rapid-heating-enabled cure cycle

Because the current work was focused on the validation of the OoO curing, the recommended cure cycles from the prepreg manufacturers were followed. The OoO curing has potential for reducing energy consumption and cure cycle time because of an instantaneous temperature response. For example, a rapid-heating-enabled cure cycle shortens the cure cycle so that a higher production efficiency may be achievable.

OoO curing for thermoplastics and higher-temperature polymers

A previous study reported that the CNT heater for the OoO curing can reach above 500 °C without degradation[231]. Therefore, the OoO curing can be utilized to process thermoplastics (e.g., PEEK and PEKK) and other high-temp polymers, which usually require a specialized high-temp heating vessel. Particularly, thermoplastic prepgs have several advantages such as recyclability, easier storage, and usability, compared to conventional thermoset prepgs.

Economic and environmental effects of the OoO curing

To understand the economic and environmental advantages of the OoO curing, a technical cost model which estimates the costs associated with the OoO curing needs to be explored. The results can be used to improve and optimize the use of composite materials from a systems perspective[234].

Utilization of capillary-enhanced void reduction technique by a nanoporous network with conventional composite manufacturing processes

Despite use of an autoclave, a composite laminate sometimes contains voids when it has a complex shape. Theoretically, a nanoporous network (NPN) can be solely used to reduce voids in
troublesome regions of conventional autoclave cures. It was found that an autoclave pressure of ~700 kPa was alternatively achieved by capillary pressure of the NPN. Using a NPN with conventional composite processes such as an autoclave or oven can be a useful method in reducing voids in complex-shaped composite structures.

**In situ cure status monitoring beyond cure sensor basic element**

In this thesis, a thermoset polymer film was used as a cure sensor basic element instead of a prepreg, and was tested with the *in situ* cure status monitoring sensors due to the effects of electrical shorts between the CNT networks and carbon fibers. By modifying the sensor structure (e.g., adding a thin and porous film offering an electrical insulation), the electrical shorts may be removed while polymer infiltration into the CNT networks occurs. Additionally, many prepregs require two soaking stages (e.g., Hexcel Hexply 8552 requires a first hold temperature of 110 °C for 60 min and second hold temperature of 180 °C for 120 min) as part of their cure cycle. Under two soaking stages, the cure shrinkage and thermal expansion of the polymer may occur simultaneously during the second temperature ramp-up, and it may be difficult to differentiate them. Therefore, future work is needed to explore this topic.

**Parametric analysis on the model for cure status basic elements**

In this thesis, the parameters from several previous studies and measured values from the experiments were used for the model. The parametric analysis using the model (e.g., the effect of permeability of the CNT network and $\lambda$ in Eq.6.11 etc.) will be useful to establish the understanding of the mechanisms of the CNT-based cure status monitoring technique.

**Quantitative analysis on the morphological changes of a CNT network**

It was found that the morphological changes of a CNT network were attributed to polymer infiltration and chemical cure shrinkage. However, further work needs to be conducted to quantify the morphological changes of a CNT network, and the results can be utilized to determine the optimal design of *in situ* cure sensors for future applications. Techniques or assessing, particularly accurately quantifying, the morphology of nanofibers in polymers are few. X-ray scattering, TEM, and particularly 3D TEM\(^{[181]}\) are likely tools.
Appendix A

Supplementary Information for In Situ Cure Status Monitoring Experiments

This Appendix contains all experimental results of the in situ cure status monitoring using cure sensor basic elements, including the absolute resistance response, sensor-to-baseline ratio (SBR) curves, and correlations between the SBR and degree of cure (DoC) at 6 different soak temperatures. The following plots (Figs. A.1 to A.4) contain the absolute resistance curves for all the cure sensor experiments discussed in Chapter 5, including baseline (dry CNT film) and cure sensor basic element response curves, for the four different morphologies of CNT film. This is followed by the sensor-to-baseline ratio (SBR) data in Figs. A.5 to A.8, normalized SBR in Figs. A.9 to A.12, and comparisons of SBR and normalized SBR to degree of cure (DoC) in Figs. A.13 to A.16.
Figure A.1: Absolute resistance responses of the cure status sensors made of the aligned $L \approx 500 \mu m$ CNT networks at different cure temperatures. Of note, the alignment angle ($\theta$) corresponded to $0^\circ$. 

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Figure A.2: Absolute resistance responses of the cure status sensors made of the aligned $L \approx 500 \, \mu m$ CNT networks at different cure temperatures. Of note, the alignment angle ($\theta$) corresponded to $90^\circ$. 
Figure A.3: Absolute resistance responses of the cure status sensors made of the aligned $L \approx 150 \mu m$ CNT networks at different cure temperatures. Of note, the alignment angle ($\theta$) corresponded to $0^\circ$. 
Figure A.4: Absolute resistance responses of the cure status sensors made of randomly-oriented CNT networks at different cure temperatures.
Figure A.5: Experimental SBR of the cure sensor basic elements at different soak temperatures. The cure sensor basic elements were comprised of aligned $L \approx 500 \mu m$-tall CNT arrays densified to $H \approx 40 \mu m$ at $\theta = 0^\circ$ with an areal density of $12.8 \text{ g/m}^2$. 
Figure A.6: Experimental SBR of the cure sensor basic elements at different soak temperatures. The cure sensor basic elements were comprised of aligned $L \approx 500 \mu$m-tall CNT arrays densified to $H \approx 40 \mu$m at $\theta = 90^\circ$ with an areal density of 12.8 g/m$^2$. 
Figure A.7: Experimental SBR of the cure sensor basic elements at different soak temperatures. The cure sensor basic elements were comprised of aligned $L \approx 150 \mu m$-tall CNT arrays densified to $H \approx 12 \mu m$ at $\theta = 0^\circ$ with an areal density of 12.8 g/m$^2$. 
Figure A.8: Experimental SBR of the cure sensor basic elements at different soak temperatures. The cure sensor basic elements were comprised of randomly-oriented CNT networks ($H \approx 40 \mu m$ with an areal density of $25 \text{ g/m}^2$).
Figure A.9: Normalized SBR of the cure status sensors at different soak temperatures. The cure sensor basic elements were comprised of aligned $L \approx 500 \mu m$-tall CNT arrays densified to $H \approx 40 \mu m$ at $\theta = 0^\circ$ with an areal density of 12.8 g/m$^2$. 
Figure A.10: Normalized SBR of the cure status sensors at different soak temperatures. The cure sensor basic elements were comprised of aligned $L \approx 500\, \mu m$-tall CNT arrays densified to $H \approx 40\, \mu m$ at $\theta = 90^\circ$ with an areal density of 12.8 g/m$^2$. 
Figure A.11: Normalized SBR of the cure status sensors at different soak temperatures. The cure sensor basic elements were comprised of aligned $L \approx 150 \mu$m-tall CNT arrays densified to $H \approx 12 \mu$m at $\theta = 0^\circ$ with an areal density of 12.8 g/m$^2$. 
Figure A.12: Normalized SBR of the cure status sensors at different soak temperatures. The cure sensor basic elements were comprised of randomly-oriented CNT networks ($H \approx 40 \mu m$ with an areal density of 25 g/m$^2$).
Figure A.13: Correlation between: (a) SBR and DoC, and (b) normalized SBR and DoC. The cure sensor basic elements were comprised of aligned $L \approx 500 \mu$m-tall CNT arrays densified to $H \approx 40 \mu$m at $\theta = 0^\circ$ with an areal density of 12.8 g/m$^2$. 
Figure A.14: Correlation between: (a) SBR and DoC, and (b) normalized SBR and DoC. The cure sensor basic elements were comprised of aligned $L \approx 500 \mu m$-tall CNT arrays densified to $H \approx 40 \mu m$ at $\theta = 90^\circ$) with an areal density of 12.8 g/m$^2$. 
Figure A.15: Correlation between: (a) SBR and DoC, and (b) normalized SBR and DoC. The cure sensor basic elements were comprised of aligned $L \approx 150 \mu m$-tall CNT arrays densified to $H \approx 12 \mu m$ at $\theta = 0^\circ$) with an areal density of 12.8 g/m$^2$. 
Figure A.16: Correlation between: (a) SBR and DoC, and (b) normalized SBR and DoC. The cure sensor basic elements were comprised of randomly-oriented CNT networks ($H \approx 40$ μm with an areal density of 25 g/m²).
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