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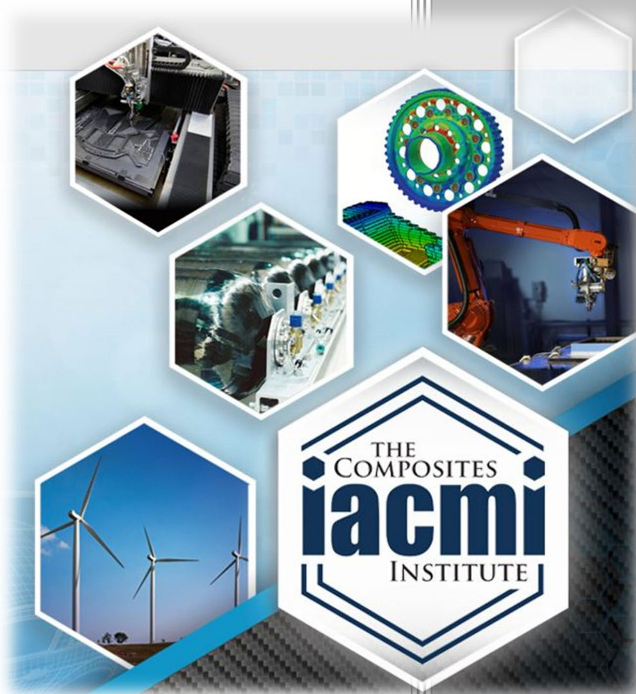
Scale-up of Next Generation Nano-Enhanced Composite Materials for Longer Lasting Consumer Goods



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Scale-up of Next Generation Nano-Enhanced Composite Materials for Longer Lasting Consumer Goods

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1.4 Acknowledgements

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2. EXECUTIVE SUMMARY

The objective for this project was to create an industrial-scale manufacturing operation for Vertically Aligned Carbon Nanotube Forests (VACNTs), which make up N12 Technologies' (N12) NanoStitch® product, a prepreg additive that makes advanced composites tougher, lighter, and more durable. This was achieved using University of Dayton Research Institute's (UDRI) 60-inch Nano Adaptive Hybrid Fabric (NAHF-X) reactor system. N12 had a unique and effective nanomaterial-based product that they were manufacturing on small-scale 1-inch wide substrate machines in Boston, MA. UDRI had a large-scale 60-inch wide nanomaterial growth reactor available for scaling up 2nd party products in Dayton, OH. Thanks to the successful cooperation between both parties, this project resulted in the world's first industrial-scale continuous VACNT film pilot plant in Dayton, OH with an increase in VACNT supply production rate of >10X. This scale up enabled market validation via testing programs and pilot manufacturing operations with a number of customers.

3. INTRODUCTION

N12's NanoStitch® is a nano-enhanced interleave for laminate composites that significantly improves interlaminar properties which result in improved compression strength (10%), fatigue resistance (10x)[1], impact resistance (20%), shear strength (15%), debulk rate (10x)[2] and electrical conductivity (10x, through thickness). This makes N12's nano-enhanced carbon fiber composites tougher, lighter, faster to manufacture, and multifunctional.

NanoStitch® makes composite parts more durable, reducing the life cycle cost of composite structures, and reducing energy usage by reducing the replacement rate. It also addresses traditional weaknesses of composite materials (see Figure 1), enabling them to be more widely adopted where heavier and energy intensive materials such as aluminum are currently used. The increased toughness of composite structures made with N12's product can also allow additional light-weighting of parts in transportation systems, creating substantial energy savings.

This project was critical to scaling up the production of NanoStitch® to levels sufficient to sustain a large number of customer development programs. Many of the customer programs focused on component-level testing, which is a significant transition for standard coupon-level testing for validation of the value proposition of this technology. Component testing Increases technology readiness level (TRL); and is generally more compelling to industry. Scale up enables production quantities sufficient to support larger component testing. Unscaled production limits testing to small coupons and small sample sets.

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[1] Fatigue life is defined as 80% ultimate short beam shear in quasi-isotropic layup across a number of different prepregs. Fatigue life improvements and fatigue limit increases also observed at component level. Please refer to N12 performance data sheet "NanoStitch(R) Performance Data Sheet (v4).pdf."

[2] Debulk rate is defined as the time to achieve sub <1% void content for out of autoclave (OOA) processed components which reduced from >8hr vacuum debulk prior to cure to under 30 minutes (all room temp).

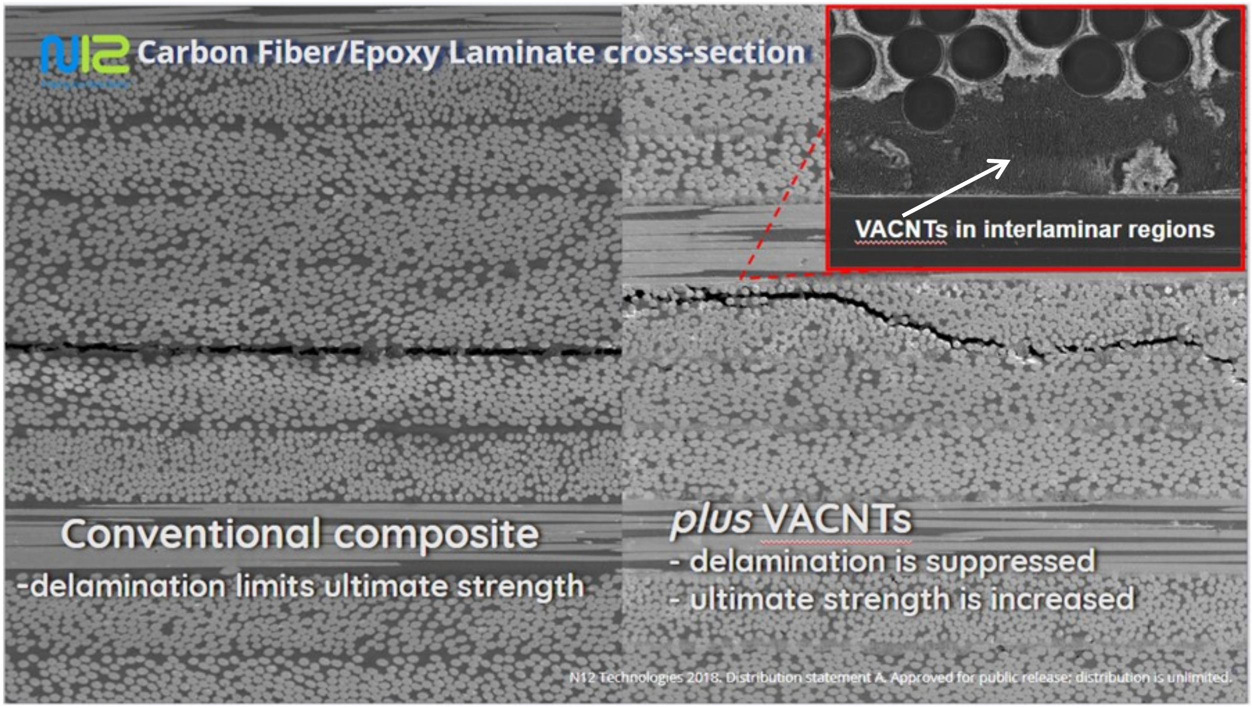

Figure 1. Illustration of the effect of Nanostitch VACNTs in the interlaminar region of a composite structure, and the resulting suppression of delamination, a significant composite failure mode.

The main focus of this program was to use that NAHF-X system for production of the VACNTs that are used in the NanoStitch® product. The NAHF-X system is the largest roll-to-roll open to the atmosphere CVD system in the world. Several variables are involved in the production of VACNTs including but not limited to: substrate material, catalyst recipe, growth temperature, injection gases, and conveyance speed. As illustrated in Figure 2, the basic idea behind producing VACNTs consists of placing catalyst coated metal substrates on top of a conveyor belt which carries them through the NAHF-X system where VACNTs are grown. The VACNT covered substrates are collected at the output of the NAHF-X system for quality control (QC) and incorporation in the completed NanoStitch® product.

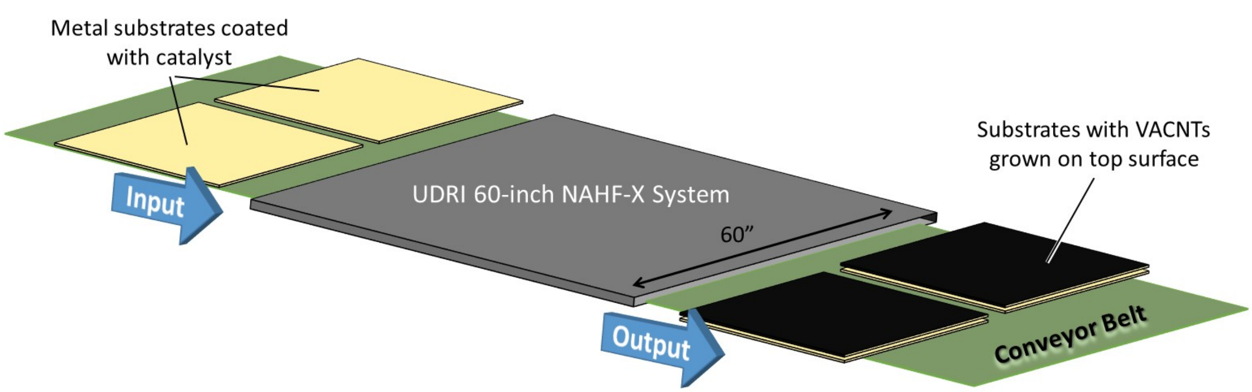

Figure 2. Simplified depiction of NanoStitch® VACNTs grown using the UDRI 60-inch NAHF-X systems. Discrete substrates shown as input versus a continuous substrate.

Producing Nanostitch® involved a large number of VACNT growth trials (>1800 unique experiments), with iterative changes to the VACNT growth "recipes." The dynamics of VACNT growth are highly interdependent. For example, it is well known that growth temperature affects VACNT height, which is one of the properties that has been determined to affect composite performance and therefore is one of the key QC properties. However, temperature can also affect VACNT defect rates. In addition to temperature dynamics, there are also other parameters to control (e.g. gas flow, chemical kinetics).

In addition to growth experiments, intensive metrology and sampling was used to determine the effect of growth recipes on critical VACNT parameters. These investigations led to innovations about how to control VACNT growth, as well as repeatability and uniformity at scale. It also led to conclusions about limitations of existing NAHF-X hardware, which was not originally designed for the NanoStitch® production process. This resulted in upgrades to improve product control, uniformity, repeatability, and production capacity. Some of the significant upgrades included gas injector style, discrete substrate conveyor belt versus continuous roll-to-roll, robotic feed, and catalyst design.

The high pace of experimental work, and the increased rates of production also required improvements to surrounding infrastructure for material handling and quality control. Chief among these requirements was an improvement of the safety and comfort of growth operators which included robotic feeding and unloading, and fast QC systems.
In parallel with efforts to increase control and production capacity, fabrication and testing of composites articles was conducted for internal research purposes by N12, in accordance with ASTM standard methods. The data produced in this work were used to engage commercialization partners. Several of these partners were ultimately provided with NanoStitch® enhanced carbon fiber prepregs to conduct testing of actual components.

4. BACKGROUND

Much investigation has been done in trying to harness nanomaterials for the improvement of fiber-reinforced polymer composites, but meaningful improvements have yet to be found for one or more of the following reasons: the technology did not work, improvement was insignificant, the product could not easily integrate with conventional composite manufacturing and/or the technology was not scalable for mass production.

In testing prior to this project, NanoStitch® has demonstrated a 10-20% increase in shear, compression and impact performance, using a true drop-in additive (i.e. no changes required to downstream manufacturing processes) for two commonly used prereg systems (Table 1). These results are of significant impact to the industry. The 60-inch NAHF-X system was able produce NanoStitch® at industrial scale and cost.

Table 1. Summary of early mechanical improvement results in two common prepreg systems.[3]

	Nanostitch® Improvement in Test Conducted		
Composite Material	ILSS (ASTM D2344)	CLC (ASTM D6641)	CAI (ASTM D7137)
IM7/TC350-1	+11%	+12%	+11 - 20%
34-700/NCT301	+7%	+8%	+12 - 24%

Fabrication of composite articles is well known to have significant variability. For this reason, in all testing of NanoStitch® enhanced prepregs, N12 has fabricated panels with one half containing

[3] Please refer to N12 performance data sheet "NanoStitch(R) Performance Data Sheet (v4).pdf."

NanoStitch®, and the other half comprised of unmodified prepreg “baseline” (Figure 3). These panels were always laid up with the same methods and cured with the same profiles, to increase confidence in the observed performance improvements.

Figure 3. A standard composite panel fabricated with one half reinforced NanoStitch®, and the other side unmodified prepreg from the manufacturer.

5. RESULTS AND DISCUSSION

One of the earliest, and most significant results in this program was the observation that it is possible to grow VACNTs on the Dayton NAHF-X system with properties equivalent to those produced on much smaller laboratory-scale growth equipment in Boston (Figure 4).

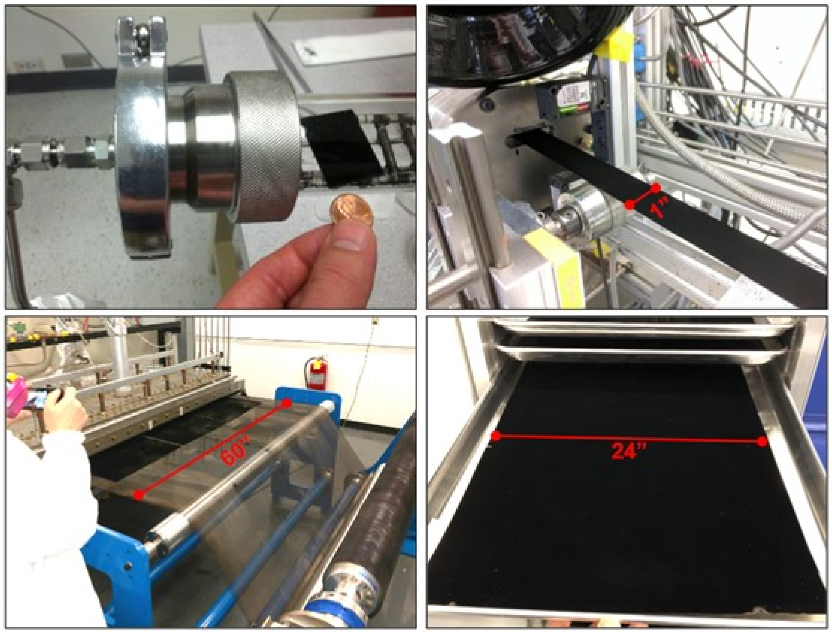

Figure 4. Photographs of lab-scale NanoStitch® production equipment (top) and NAHF-X (bottom).

As mentioned earlier, a large number of VACNT growth trials (>1800 unique experiments) had to be performed rapidly in order to find the product quality that matched the smaller laboratory-scale growth equipment in Boston. In order to determine product quality parameters such as VACNT height quickly, a first of its kind, novel VACNT height measuring system had to be created. This system is shown in Figure 5. The QC system was designed such that a non-technical worker could easily make reliable measurements.

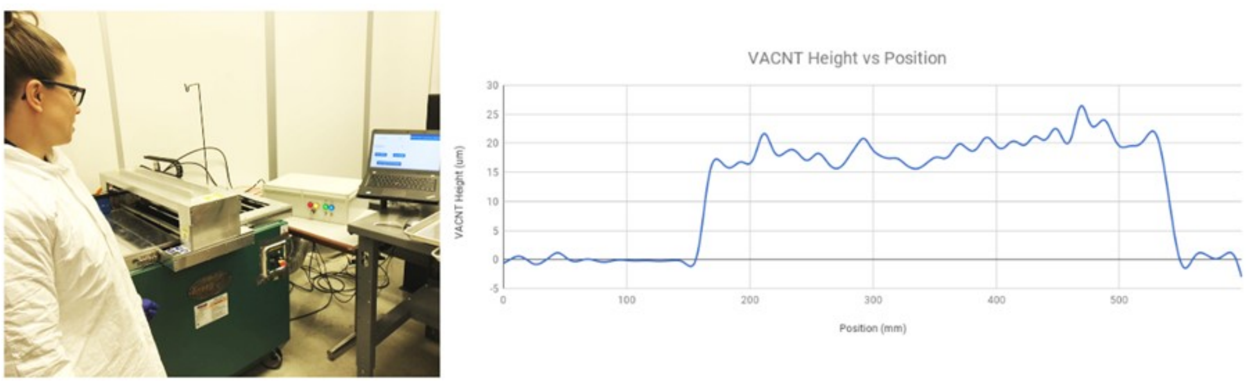

Figure 5. A photograph of a tool used to make rapid (~30s) VACNT height measurements on large format (380 x 610 mm, 15" x 24") samples and a height profile across a typical sample.

Through a series of proprietary changes to growth recipe, substrate composition, and upgrades to the growth hardware, the production capacity of VACNTs was increased by >10X from the beginning of this program, while maintaining the control over VACNT properties required to drive performance gains in composites. The culmination of this effort was a robotically fed conveyor system for highly automated material handling of the substrate, which in addition to improving capacity and repeatability, significantly reduced effort and potential risk to growth operators (Figure 6). This novel system requires only one personnel to operate during standard production.

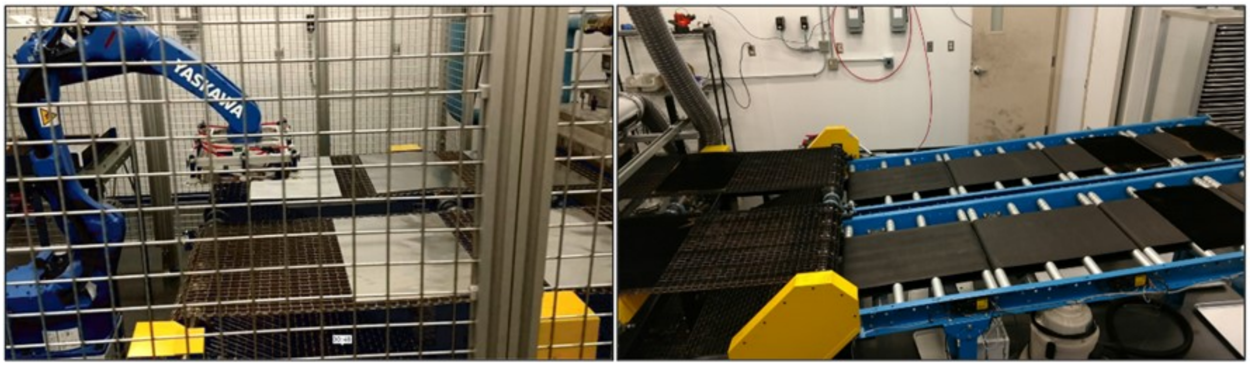

Figure 6. Photographs of the robotic loader and conveyor unloader for VACNT growth substrate and grown VACNT product, respectively. Installed January 2019.

Earlier generations of growth equipment provided VACNTs in a much smaller form factor (Figure 4, 1-inch wide substrates) which resulted in a supply constraint for downstream processing. By contrast, the output from NAHF-X was of a size which made downstream processing ideal for typical prepreg roll sizes. This allowed N12 to deliver large quantities (>100 m^2) to customers for component testing for the first time (Figure 7).

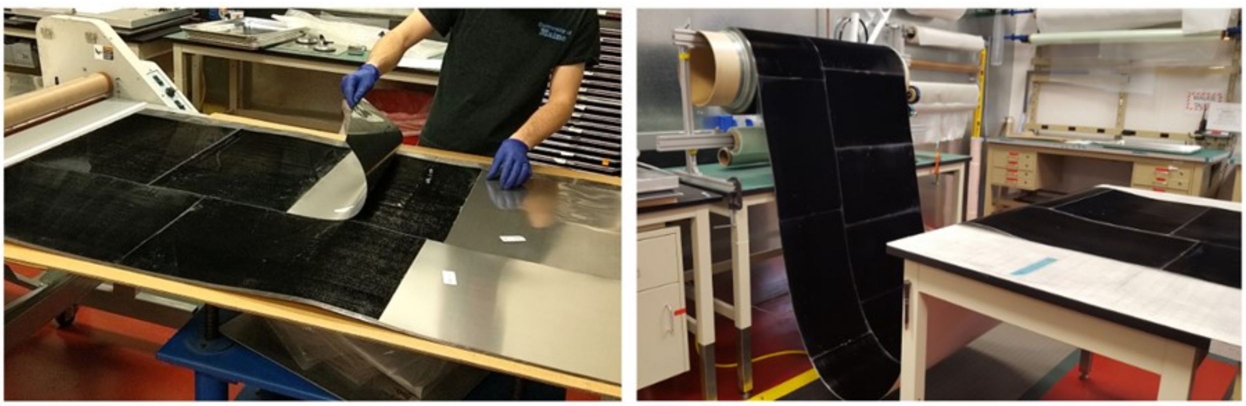
Figure 7. A photograph of transfer of the VACNTs into a roll of carbon fiber prepreg, and subsequent roll up of >100 m^2 of the resulting NanoStitch® enhance prepreg for shipment to customers to fabricate and test full components.

The increased capacity of VACNT production made it possible to explore many more types of prepregs and mechanical tests than was previously possible. The results of this expanded testing are summarized below (Figure 8). It is clear that significant improvements are observed in all systems and tests, most notably fatigue.

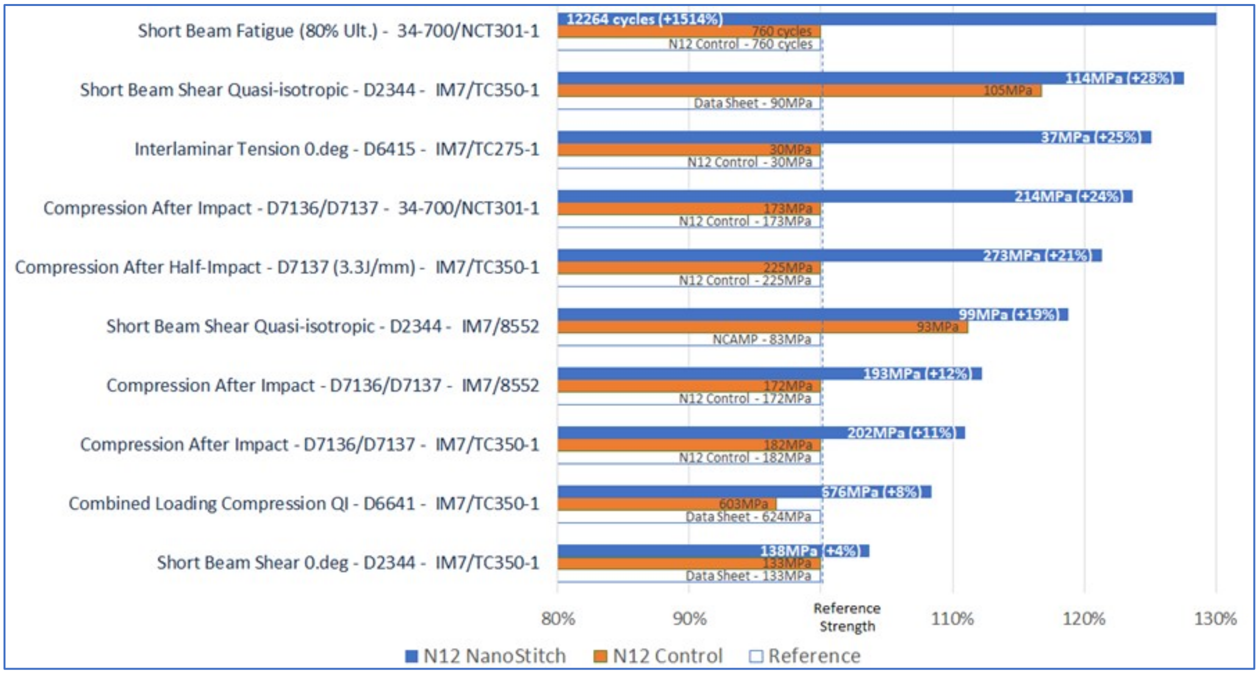

Figure 8. A summary of testing results for several prepreg systems illustrating the benefit of NanoStitch® enhancement over unmodified composite coupons. All testing done according to the noted ASTM standards.

In addition to the results of mechanical testing, other benefits of NanoStitch® were observed in the course of this program. Notably, significant reductions in coefficients of variance (~2X) were observed in a number of mechanical tests. This phenomenon is hypothesized to be a result of a reduction in porosity due to voids in fabricated parts (using identical methods), which was an unexpected benefit of using NanoStitch® enhanced prepreg.[4] This impact of Nanostitch on part porosity is show in Figure 9.

[4] Y. Zhang et al., "Void Reduction in Out-Of-Autoclave Processing of Carbon Fiber Epoxy Composites by Reinforcing Interlaminar Regions Using Vertically Aligned Carbon Nanotubes," *Proceedings of the 17th European Conference on Composite Materials (ECCM17)*, Munich, Germany, 26-30 June 2016.

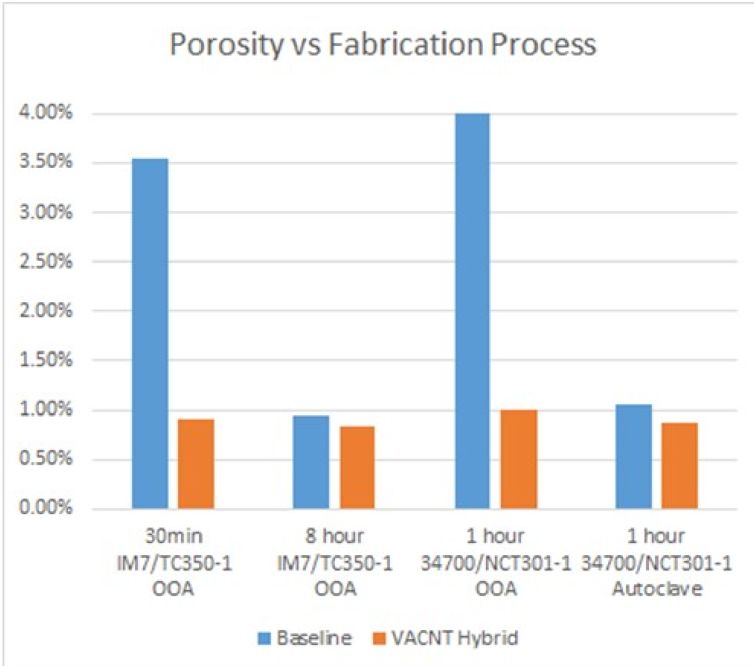

Figure 9. The effect of NanoStitch® enhancement on cured part porosity as a function of debulk parameters for IM7-TC350 and 34700/NCT301-1 in and out of autoclave. The time indicated on the x-axis is the debulk cycle time to achieve the measured porosity on the y-axis.

Due to non-disclosure agreements between N12 and its commercialization partners, N12 is not privy to the specifics of component-level testing engaged in during this program, nor would it be free to disclose them. However, several partners did share percentage improvement results in component testing. A brief summary of the testing results for one such component testing program is provided below:

- +18% improvement in impact performance
- +20.5% improvement in compression after impact performance
- Fatigue performance significantly improved by both reaching a higher cycle count and surviving more severe loading conditions

6. BENEFITS ASSESSMENT

While it is difficult to predict the magnitude of the following impacts on composite manufacturing, NanoStitch® technology has demonstrated that it has the potential to achieve the following:

- Dramatically increase the mean time to failure for parts manufactured identically
- Reduce the scrap rate for parts, especially at large sizes
- Reduce manufacturing time, notably debulk, and possibly enable more widespread use of out of autoclave cures
- Reduce the amount of material required in parts to achieve the same toughness/durability.

All of these factors directly support both IACMI and DOE's goal for energy savings and enabling of large-scale composites manufacturing. Industry partners will further investigate the value proposition to determine the impact on their operation, but it is expected that these improvements will also align well with their goals. Reduction of scrap rate, for example, is of significant concern to many manufacturers.

7. COMMERCIALIZATION

The first steps in commercialization were to attract initial private and commercial investment in the NanoStitch® technology during the initial stages of technology demonstration using the 1-inch wide systems in Boston. The next step was to show that the NanoStitch® technology could be produced at industrial scales using the UDRI NAHF-X system and meet the goals of IACMI. This was accomplished thanks to the help of this IACMI project. N12 and UDRI have already settled on an IP agreement where N12 can fully control the current Dayton NAHF-X system on their own as Pilot Plant #1, and have the rights to design additional systems for larger or additional production plants. Additional steps are as follows:

- Have the production operation inspected by NIOSH. (One full inspection was completed in Boston, MA, and two pre-inspections at Dayton have already been conducted at our initiation.)
- Continue to reduce NanoStitch® product costs in order to attract wide-spread commercial usage.
- Perform additional testing at the component level in limited or "pilot" production runs of components utilizing NanoStitch® technology.
- Expand the number of commercialization partners by expanding the application forms that NanoStitch® can be used in.

8. ACCOMPLISHMENTS

The following accomplishments were made during this project:

- Component level testing by commercial interests.
- IP technology transition agreement between N12 and UDRI.
- Demonstration that the NanoStitch® VACNT production could be scaled from 1-inch wide substrates to industrial-scale 60-inch wide production system and maintain product quality.
- Invented a VACNT quality characterization system that can be used to rapidly perform real-time QC by non-technical personnel.
- Developed the world's first and largest robotic industrial VACNT growth production system, which also increases safety and reduces potential exposure of employees.
- Surpassed goal for demonstrating a QC process that could check over 20 m^2 / day.
- Surpassed goal threshold and objective of delivering 500 m^2 of product to customers well below price point goal, which was **at a price point below \$200/m^2 including the prepreg material.**
- Demonstrated matched production capacity thresholds and objectives of the VACNT growth to to other steps in the production process like QC and lamination.
- Demonstrated goal threshold and objective of an annual production capacity of at least 10,000 m^2.
- Most of the effort was held proprietary, however presentations were made at the IACMI meetings, and the following:
    - P. Kladitis and P. Jarosz, "Industrial Scale-Up and Production of Vertically Aligned Carbon Nanotubes for Next Generation Nano-Enhanced Composites," *Carbon 2019*, Lexington, KY, 15-19 July 2019.
    - P. Kladitis and P. Jarosz, "Scale-up of Next Generation Nano-Enhanced Composite Materials for Longer Lasting Consumer Goods," *SAMPE Midwest Meeting*, Dayton, OH, 11 April 2019
    - P. Jarosz, C. Gouldstone, and P. Kladitis, "Scale-up of Next Generation Nano-Enhanced Composite Materials for Longer Lasting Consumer Goods," *IACMI Winter 2019 Members Meeting*, Indianapolis, IN, 29-31 January 2019.

- Mackenzie Devoe, et al., “Scaling Nano-Additive Manufacture for Durable, Multi-Functional Composite Products,” Proceedings of CAMX 2018, Dallas, TX, 15-18 October 2018.

9. CONCLUSIONS

The results of this program clearly demonstrate that NanoStitch® provides a significant improvement in the performance of composite parts. It has also shown that the path to scale up of this technology is clear and viable. Manufacturers will not need to change their methods of manufacturing to accommodate this technology, and can expect to observe meaningful improvements to performance, manufacturing time, and part variability in most carbon fiber prepreg systems.

Although great strides were made in this project, not everything went perfectly. The final growth gas injector design that we used to help increase production rates had a design flaw in it that could hinder further production rate increases if not corrected. Also, the new conveyor system belt turned out to be more massive than needed causing expenditure of more production energy than necessary. A simple optimization of this belt can further reduce production costs. Finally, although not required for this project we did not have time to demonstrate matching production rates of VACNT-to-prepreg lamination in Dayton at 60 inch width – just in Boston at 1 inch width. We hope to demonstrate this in further IACMI projects.

Next steps should include additional testing at the component level in limited or “pilot” production runs of components utilizing NanoStitch® technology. In parallel, efforts should be made to expand the number of commercialization partners in development and finding more opportunities for special applications, such as multifunctionality.

10. RECOMMENDATIONS

The following are recommendations for future IACMI projects that will both meet IACMI’s goals further and increase commercial utilization/transition of this technology:

- Have the Dayton production operation inspected by NIOSH during routine production.
- Continue to reduce NanoStitch® product costs in order to attract wide-spread commercial usage.
    - Correct growth gas injector design flaw.
    - Optimize conveyor belt mass.
    - Demonstrate automated VACNT-to-prepreg lamination at Dayton the pilot plant.
- Perform additional testing at the component level in limited or “pilot” production runs of components utilizing NanoStitch® technology at commercial partner sites.
- Expand the number of commercialization partners by expanding the application forms and multifunctional benefits that NanoStitch® can be used in/for, such as:
    - Evaluate material benefit in other resin systems such as aerospace epoxy, BMI, and polyimide.
        - Demonstrate reduction in microcracking resulting from thermal cycle fatigue.
    - Develop epoxy/CNT film form intermediate that may be used as film adhesive or interleave in dry preforms while maintaining property enhancements.
        - Multifunctional properties and potential benefit to industry, such as through-thickness electrical conductivity enhancement and erosion resistance, may also be evaluated.

- Develop method to harvest and disperse CNT’s into engineering thermoplastic to support injection molding and additive extrusion, resulting in an engineered thermoplastic with EMI shielding and p-static dissipation.
  - Evaluate better weld line adhesion.
- Develop non-proprietary engineering property data set in host material of most interest to industry partners to allow for application trade evaluations.
  - Current application specific benefits are not releasable to general industry due to proprietary issues.

11. REFERENCES AND/OR BIBLIOGRAPHY

None.

12. APPENDICES

None.