Recent Advances in Self-Healing Fiber-Reinforced Composites
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Improving the reliability, reparability, and reusability of fiber reinforced composites (FRCs) are key aspects to advancing the current state of the art. The major problem with composites is the inherent brittleness of the epoxy matrix, which is prone to microcrack formation, either from exposure to extremes in temperature conditions or from impact from different sources. If not prevented, the microcracks can lead to potentially catastrophic structural damage. Accordingly, materials innovations are needed to mitigate microcrack damage in composite structures and prevent damage in the first place. NEI has taken on this challenge by developing several technologies to both mitigate damage and repair any damage that may have occurred. These technologies, based on nanoscale materials/ structures, can be combined into one composite system to create a tough composite structure with self-healing capabilities. The self-healing technology enables the composite to heal microcracks through the use of a novel self-healing agent, which is combined with the epoxy matrix to form a unique morphology. In a similar manner, the microcrack prevention technology mitigates crack formation via a nanoparticle additive. The two technologies have been demonstrated for proof of concept in FRC structures consisting of flat panel carbon FRCs, as well as in carbon fiber composite overwrapped pressure vessels (COPVs). In the self-healing technology, a brief heat treatment is used to initiate the healing process. Self-healing can be repeated multiple times. When introducing new functions to the composite, we make sure that the original material's properties are not compromised. Additionally, NEI has collaborated with researchers at Syracuse University on self-healing composites.

In **Figure 1**, the tensile strength and modulus of a self-healing FRC panel are compared with those of an epoxy control panel fabricated in the same manner using the same epoxy resin, but without the self-healing agent. Essentially, the same tensile strength and modulus are observed, showing that introducing NEI's self-healing agent into FRCs does not degrade the mechanical properties of the FRCs. The mechanical tests were done by IMR Test Labs, in Lansing, NY using ASTM D3039.

Self-healing of an impact-damaged FRC is demonstrated in **Figure 2**. FRC panels (Figure 2a) were fabricated using the self-healing resin by a major supplier of carbon fiber prepreg and other advanced composite materials, structures and components primarily for the aerospace markets. Figure 2b shows a C-scan after subjecting the panel to an impact energy of 91.11 in-lbf, creating a 0.0040 inch indentation depth. The measured projected damage area in Figure 2b is 0.451 in^2. Upon self-healing, the damaged area decreased to 0.414 in^2 (shown in Figure 2c).

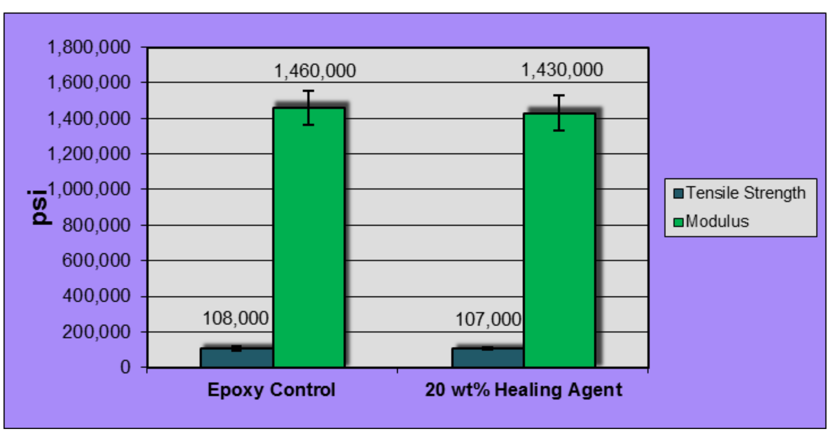
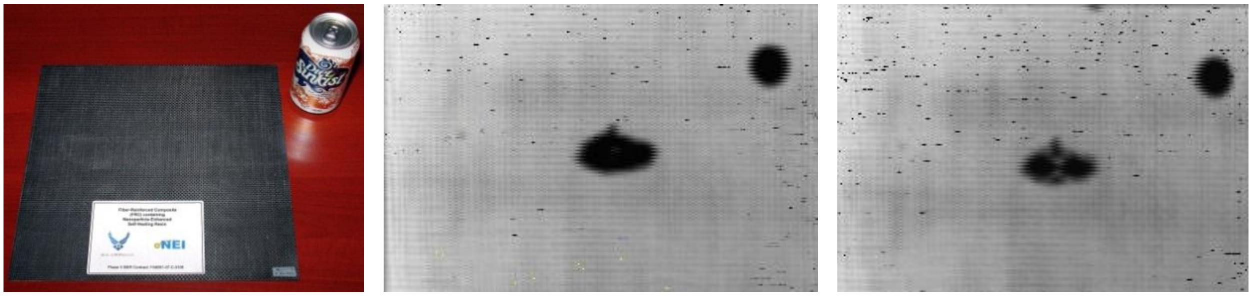


Figure 1: Average tensile strength and modulus data of FRCs



(a) (b) (c)

Figure 2: (a) FRC panel; (b) C-scan after impact; (c) C-scan after impact followed by self-healing at 100°C for 1 hour. The black circle in upper right of b and c are reference marks; the impact was at the center of the C-scans; the scale is the same on both b and c.

A second application where self-healing, along with microcrack prevention, has been demonstrated is in COPVs. COPVs typically consist of an outer fiber overwrap covering an inner liner; the fiber overwrap is usually made from carbon fiber with an epoxy matrix and the liner is usually a metal or plastic mandrel upon which the COPV is fabricated. COPVs are used to store material under pressure, such as liquid fuels for the aerospace industry. These fuels are frequently stored in the COPV at cryogenic temperatures, and these extreme temperatures, as well as potential damage from impacts, tend to cause microcracks to form in the composite overwrap of the pressure vessel. If not prevented, the microcracks will increase gas permeation and leakage from the interior of the COPV. NEI has addressed both of these issues with specialty resins that have the capability to both prevent microcracks from forming and also self-heal damages, such as from microcracks in COPVs, as shown in **Figure 3**. We incorporated novel engineered nanoparticles into the resin, which were designed to toughen the cured resin, thus preventing microcracks from occurring in the fiber composite COPV. **Figure 4** shows Izod impact strength data of bulk resin test bars made of nanocomposites compared with epoxy test bars as the control. The graph shows that the nanocomposite, NEI3, had the best impact properties in the bulk; this nanocomposite, when incorporated into a COPV also was successful in prevention of microcracks in COPVs at cryogenic temperatures.

Figure 3: COPV fabricated with NEI's self-healing/microcrack prevention resin

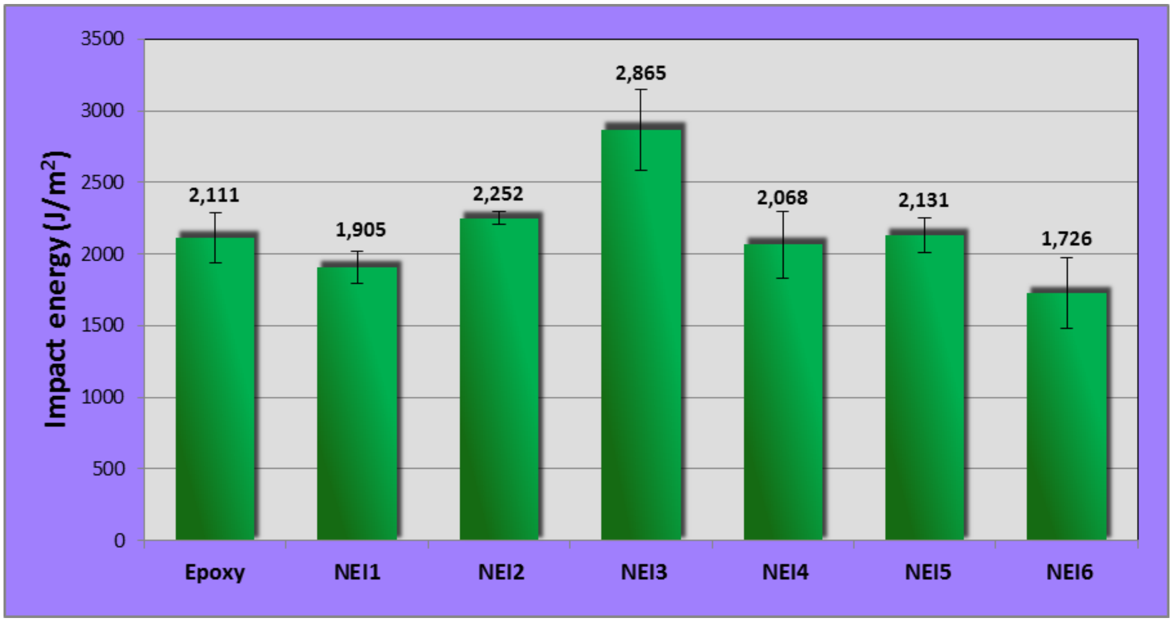


Figure 4: Izod impact strength of the resins at liquid nitrogen temperature

COPV manufacturing was then taken a step further by incorporating a self-healing resin, along with the addition of nanoparticles, in order to render the COPV self-healing to damage. Integrating a novel, self-healing, epoxy-based resin into the manufacturing of COPVs allows repeatable self-healing of microcracks to be performed through the simple application of a low-temperature heat source. This permits COPVs to be reparable and reusable with a high degree of reliability, as microcracks will be remediated. The unique phase-separated morphology that was imparted during COPV manufacturing allows for multiple self-healing cycles.

Unlike single-target approaches, where one material property is often improved at the expense of another, robustness has been introduced to a COPV by a combination of a modified resin and nanoparticle additives. Unique nanoparticles were used that have been surface-functionalized to be compatible with the resin. Both organic and inorganic components toughen the matrix and result in a more impact-resistant COPV.

In one resin system containing an inorganic nanomaterial additive, a significant improvement in burst performance was observed after the COPV was cryo-impact-damaged and then self-healed, with a greater than 10% improvement in burst pressure after the self-healing process was performed, as shown in **Table I.**

Table I: Cryogenic burst pressure after impact and self-healing vs. without the self-healing step

VESSEL	CRYOGENIC TEST	BURST RESULT	DEGRADATION
1	Burst	2,788 psi	Control
2	Impact → Burst	2,325 psi	16.6%
3	Impact → “Self-Healing” → Burst	2,641 psi	5.3%

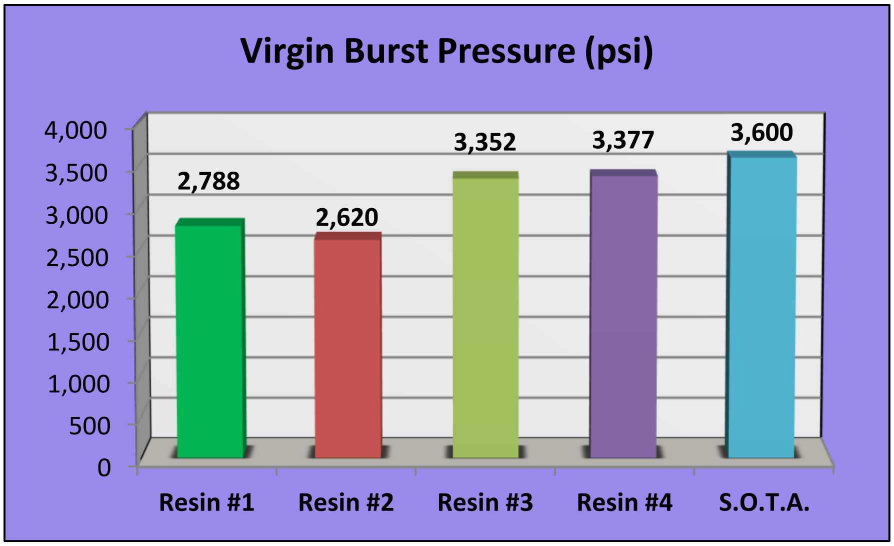


Figure 5: Summary of cryoburst pressures for four resin systems, along with industry-standard burst pressure (labeled S.O.T.A. for "state-of-the-art"); Resin #1 and Resin #2 are original resins, while Resin #3 and Resin #4 are low viscosity resins.

Initial cross-sectional analysis via microscopy showed good resin infiltration of the carbon fibers and no voids. To further enhance the compatibility between the nanomaterial additives and the resin, a surface modification of nanoparticles was successfully performed. A second specialty epoxy resin was prepared using a surface-modified nanomaterial additive, and COPVs were fabricated. Steps were taken to improve the mechanical properties of the COPVs by using a low-viscosity resin system that contained a different curing agent. This lower viscosity improves the processing of the COPV, and results show that the burst pressure of these new vessels is 20 to 25% higher than the original (see **Figure 5**).

NEI continues to pursue further advancements in self-healing. A current approach uses a self-healing system that does not require thermal initiation. The system is a multi-scale, hybrid fiber system that incorporates multiple functionalities, including self-healing and increased strength, and is compatible with FRC manufacturing. As such, it can be tailored to give specific properties of interest to the end-use applications of the customer.

The above examples present a platform technology, and the properties of self-healing and microcrack prevention are neither restricted to the particular epoxy system nor to the applications as described above. The versatility of the nanomaterial design makes the self-healing and microcrack prevention technologies amendable to customer-specific resin systems, including coating, bulk, or composite applications. To date, epoxy resin systems have been the primary focus at NEI for FRCs, but the self-healing aspect has also been demonstrated in polyurethane coating systems using NEI's NANOMYTE® MEND line of products.

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