Multi-scale CNT-Based Reinforcing Polymer Matrix Composites for Lightweight Structures

Applications include commercial aircraft, sports equipment, and automobiles.

Marshall Space Flight Center, Alabama

Reinforcing critical areas in carbon polymer matrix composites (PMCs), also known as fiber reinforced composites (FRCs), is advantageous for structural durability. Since carbon nanotubes (CNTs) have extremely high tensile strength, they can be used as a functional additive to enhance the mechanical properties of FRCs. However, CNTs are not readily dispersible in the polymer matrix, which leads to lower than theoretically predicted improvement in mechanical, thermal, and electrical properties of CNT composites. The inability to align CNTs in a polymer matrix is also a known issue. The feasibility of incorporating aligned CNTs into an FRC was demonstrated using a novel, yet commercially viable nanofiber approach, termed NRMs (nanofiber-reinforcing mats). The NRM concept of reinforcement allows for a convenient and safe means of incorporating CNTs into FRC structural components specifically where they are needed during the fabrication process.

NRMs, fabricated through a novel and scalable process, were incorporated into FRC test panels using layup and vacuum bagging techniques, where alternating layers of the NRM and carbon prepreg were used to form the reinforced FRC structure. Control FRC test panel coupons were also fabricated in the same manner, but comprised of only carbon prepreg. The FRC coupons were machined to size and tested for flexural, tensile, and compression properties. This effort demonstrated that FRC structures can be fabricated using the NRM concept, with an increased average load at break during flexural testing versus that of the control.

The NASA applications for the developed technologies are for lightweight structures for in-space and launch vehicles. In addition, the developed technologies would find use in NASA aerospace applications such as rockets, aircraft, aircraft/spacecraft propulsion systems, and supporting facilities. The reinforcing aspect of the technology will allow for more efficient joining of fiber composite parts, thus offering additional weight savings. More robust structures capable of withstanding micrometeoroid and space debris impacts will be possible with the enhanced mechanical properties imparted by the aligned CNTs incorporated into the fiber composite structure, as well as the potential for improved electrical and thermal properties.

The materials fabrication approach developed in the present effort is a platform for customer applications where additional reinforcement is required or would be beneficial, especially in FRC structures and component parts. Depending upon the specific customer application, the NRM could be tailored to the specific matrix resin and desired property enhancement.

This work was done by Daniel Eberly, Runqing Ou, Adam Karcz, and Ganesh Skandan of NEI Corporation, and Prof. Patrick Mather and Erika Rodriguez of Syracuse University for Marshall Space Flight Center. For more information, contact Sammy Nabors, MSFC Commercialization Assistance Lead, at sammy.a.nabors@nasa.gov. Refer to MFS-32998-1.

Ceramic Adhesive and Methods for On-Orbit Repair of Re-Entry Vehicles

Material can be applied in space to repair damage that requires heat/oxidation protection upon re-entry to Earth's atmosphere.

Lyndon B. Johnson Space Center, Houston, Texas

This adhesive is capable of repairing damaged leading edge components of re-entry vehicles while in space, and is novel with regard to its ability to be applied in the vacuum of space, and in a microgravity environment. Once applied, the adhesive provides thermal and oxidation protection to the substrate (in this case, reinforced carbon/carbon composites, RCCs) during re-entry of a space vehicle. Although there may be many formulations for repair adhesives, at the time of this reporting, this is the first known adhesive capable of an on-orbit repair.

The adhesive is an engineered ceramic material composed of a pre-ceramic polymer and refractory powders in the form of a paste or putty that can be applied to a scratched, cracked, or fractured composite surface, covering and protecting the damaged area. The adhesive is then "cured" with a heat cycle, thereby cross-linking the polymer into a hardened material and bonding it to the substrate. During the heat of re-entry, the material is converted to a ceramic coating that provides thermal and oxidative stability to the repaired area, thus allowing the vehicle to pass safely from space into the upper atmosphere.

Ceramic powders such as SiC, ZrB_2 and Y_2O_3 are combined with allylhydridopolycarbosilane (AHPCS) resin, and are mixed to form a paste adhesive. The material is then applied to the damaged area by brush, spatula, trowel, or other means to fill cracks, gaps, and holes, or used to bond patches onto the damaged area. The material is then cured, in a vacuum, preferably at 250 °F (≈121 °C) for two hours. The re-entry heating of the vehicle at temperatures in excess of 3,000 °F (≈1,650 °C) then converts this material into a ceramic coating.

This invention has demonstrated advantages in resistance to high temperatures, as was demonstrated in more than 100 arc-jet tests in representative environments at NASA. Extensive testing verified oxidation protection for the repaired substrate (RCC), and confirmed that the microstructure of the resulting repair leads to durability and resistance to melting or flow. Its processability and working life in a vacuum was demonstrated by NASA astronauts in glovebox processing studies, as well as on-orbit in the open space shuttle bay. All of these advantages increase the working life of NASA vehicles, as well as improve safety for any crew on a manned vehicle. The adhesive, trademarked NOAX™ or Non-Oxide Adhesive Experimental, flew on all space shuttle missions from Return To Flight (STS-114) until the final flight (STS-135) as a crack repair material for the leading edges and nose cap of the vehicle. NOAX™ was patented under U.S. Patents 7,628,878 and 7,888,277.

This work was done by James A. Riedell and Timothy E. Easler of ATK COI Ceramics, Inc. for Johnson Space Center. Further information is contained in a TSP (see page 1).

Title to this invention, covered by U.S. Patent Nos. 7,628,878 and7,888,277, has been waived under the provisions of the National Aeronautics and Space Act {42 U.S.C. 2457 (f)}. Inquiries concerning licenses for its commercial development should be addressed to:

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Refer to MSC-23996-1/5218-1, volume and number of this NASA Tech Briefs *issue, and the page number.*

Self-Healing Nanocomposites for Reusable Composite Cryotanks

Applications for COPVs include storage of natural gas and liquid hydrogen fuel in vehicles, and marine transport of propane via tanker ships.

Marshall Space Flight Center, Alabama

Composite cryotanks, or composite overwrapped pressure vessels (COPVs), offer advantages over currently used aluminum-lithium cryotanks, particularly with respect to weight savings. Future NASA missions are expected to use COPVs in spaceflight propellant tanks to store fuels, oxidizers, and other liquids for launch and space exploration vehicles. However, reliability, reparability, and reusability of the COPVs are still being addressed, especially in cryogenic temperature applications; this has limited the adoption of COPVs in reusable vehicle designs.

The major problem with composites is the inherent brittleness of the epoxy matrix, which is prone to microcrack formation, either from exposure to cryogenic conditions or from impact from different sources. If not prevented, the microcracks increase gas permeation and leakage. Accordingly, materials innovations are needed to mitigate microcrack damage, and prevent damage in the first place, in composite cryotanks. The self-healing technology being developed is capable of healing the microcracks through the use of a novel engineered nanocomposite, where a uniquely designed nanoparticle additive is incorporated into the epoxy matrix. In particular, this results in an enhancement in the burst pressure after cryogenic cycling of the nanocomposite COPVs, relative to the control COPVs.

Incorporating a novel, self-healing, epoxy-based resin into the manufacture 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 manufacture 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. Initial cross-sectional analysis via microscopy showed good resin infiltration of the carbon fibers and without voids. To further enhance the capability between the nanomaterial additives and the resin, a surface modification 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 preliminary results show that the burst pressure of these new vessels is 20 to 25% higher than that of the original.

The self-healing concept demonstrated in this research and development effort represents a platform technology, and the self-healing property is neither restricted to the particular epoxy system used here, nor to the COPV application. Self-healing is a direct result of a unique phase separated morphology created via the resin and is aided by the nanoparticles. The self-healing function can be introduced to other customer-specific resin systems in coating, bulk, or composite applications provided that the unique phase separated morphology can be enabled in those systems.

This work was done by Daniel Eberly, Runqing Ou, Adam Karcz, and Ganesh Skandan of NEI Corporation for Marshall Space Flight Center. For more information, contact Sammy Nabors, MSFC Commercialization Assistance Lead, at sammy.a.nabors@nasa.gov. Refer to MFS-32995-1.