58th International SAMPE Symposium, May 6-9, Long Beach, CA (2013)

RTM370 Polyimide Braided Composites: Characterization and Impact Testing

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Abstract

RTM370 imide oligomer based on 2,3,3′,4′-biphenyl dianhydride (a-BPDA), 3,4′-oxydianiline (3,4′-ODA) and terminated with the 4-phenylethynylphthalic (PEPA) endcap has been shown to exhibit a low melt viscosity (10-30 poise) at 280°C with a pot-life of 1-2 h and a high cured glass transition temperature (T_g) of 370°C. RTM370 resin has been successfully fabricated into composites reinforced with T650-35 carbon fabrics by resin transfer molding (RTM). RTM370 composites display excellent mechanical properties up to 327°C (620°F), and outstanding property retention after aging at 288°C (550°F) for 1000 h, and under hot-wet conditions. In ballistic impact testing, RTM370 triaxial braided T650-35 carbon fiber composites exhibited enhanced energy absorption at 288°C (550°F) compared to ambient temperature.

1. INTRODUCTION

Polyimide resins have been used as matrices in lightweight carbon fiber reinforced composites for use as replacements for metallic components in aerospace propulsion and airframe components. Due to their outstanding heat resistance and high strength to weight ratio, polyimides offer in high temperature applications up to 288-315°C, exceeding the conventional use temperature of epoxies (177°C) and bismaleimides, BMI, (232°C) [1]. Traditionally, polyimide carbon fiber composites have been fabricated from prepregs impregnated with resins in organic solvents. Prepregs of thermoplastic polyimide Avimid N® [2] containing high boiling N-methyl-2-pyrrolidinone (NMP) yielded composites with high thermal stability, but were difficult to process. PMR-15 [3] was developed to improve the processability of polyimide composites through the use of polymerization of monomer reactants with nadic endcap in methanol to control the molecular weight of the oligomers. PMR-15 polyimide was successfully fabricated into a composite outer bypass duct for the F-404 engine as a replacement for the titanium duct, leading to a 30% cost savings and 12% weight savings. The PMR approach offered easier processing of laminates and solvent removal; however, the diamine monomers such as methylene dianiline (MDA) present in the prepregs often posed a health hazard and required stringent safety precaution during fabrication.

All of these polyimide composite structures rely on the use of prepregs, and require either labor intensive hand lay-up or automated tow placement equipment, for fabrication of large and/or complex geometries and structures. For some applications, it would produce significant cost savings (~30%), if the polyimide could be adapted to a low-cost manufacturing process such as resin transfer molding (RTM), similar to what is used for epoxy and bismaleimide (BMI) composite fabrication in the aerospace industry.

A solvent-free melt process to produce low-melt viscosity imide oligomers for resin transfer molding (RTM) has been developed at NASA Glenn Research Center. RTM370 imide resin was formulated from 2,3,3′,4′-biphenyl dianhydride (a-BPDA), 3,4′-oxydianiline (3,4′-ODA) and terminated with 4-phenylethynylphthalic anhydride (PEPA) endcap (Fig. 1). The powdery monomers were mixed well and heated above 200°C until all three monomers were melted into a maple syrup consistency. The resultant oligomers terminated with the reactive phenylethynyl group were cooled to room temperature and then ground into powders. RTM370 imide oligomer exhibited a low melt viscosity (10-30 poise) at 280°C with a pot-life of 1-2 h and a high cured T_g of 370°C [4]. This approach uses no solvent in the process, and the only volatile generated is water formed during the imidization process.

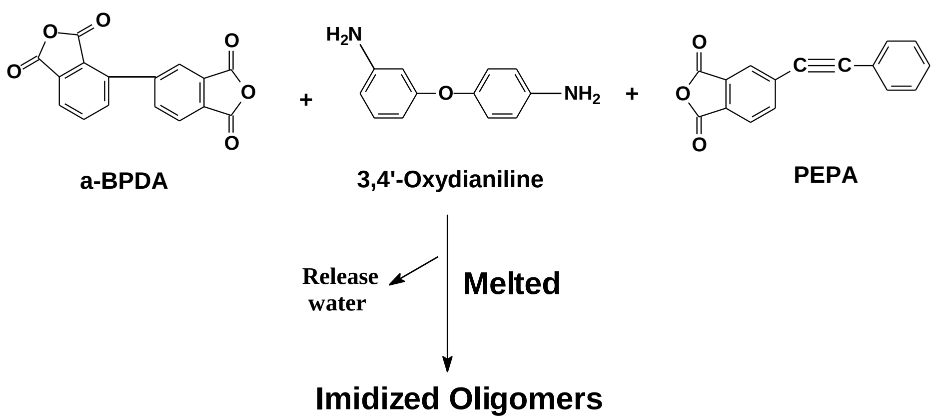


Figure 1. Preparation of RTM370 imide resin

RTM370 composites were fabricated from an 8-ply quasi-isotropic lay-up $[+45/0/90/-45]_s$ of T650-35 carbon fabrics (8HS) with high temperature polyimide sizing to improve interfacial bonding between matrix and fiber and thereby, enhance high temperature performance. The composite specimens were postcured at 343°C (650°F) for 8 h before mechanical testing to achieve optimal performance. The properties of the composites were evaluated using open-hole compression and short beam shear tests. The open-hole compression followed Northrup Grumman test specification 0.32 cm thick x 21.6 cm x 3.81 cm (0.125″ thick x 8.5″ x 1.5″) with a 0.635 cm (0.25″) hole located on centerline (8.10 cm from end) with 3 specimens per each test. The short-beam shear samples used ASTM D2344-84 method with a dimension of 0.32 cm thick x 0.635 cm x 2.54 cm (0.125″ thick x 0.25″ x 1″) along with 6 repeats.

Isothermal aging was also conducted at 288°C (550°F) for 1000 h under 1 atm in an air circulating oven. As shown in Table 1, after 1000 h of isothermal aging at 288°C (550°F), RTM370 composites retained 85% and 76% of their initial open-hole compression strength at room temperature and 288°C, respectively. Furthermore, after isothermal aging, these composites also maintained 71% of their original short-beam shear strength at room temperature.

Table 1. Durability of RTM370 Composites/T650-35/8HS/HT Sizing) at 288°C

Composite Properties	Test Temp (°C)	OHC[1] Strength (MPa)			OHC Modulus (GPa)			SBS[2] Strength (MPa)		
		Initial	500 h @288°C	1000h @288°C	Initial	500 h @288°C	1000h @288°C	Initial	500 h @288°C	1000h @288°C
RTM370 (T_g[3] =370°C)	**23**[4]	269 ±2	288 ±14	230 ±5	44 ±1	47 ±4	46 ±2	51 ±2	54 ±1	44 ±1
	288	241 ±2	244 ±10	184 ±15	48 ±1	44 ±1	45 ±2	41 ±1	41 ±1	41 ±1
	315	231 ±10	---	---	46 ±1	---	---	31 ±1	---	---
	327	241 ±20	---	---	48 ±1	---	---	30 ±1	---	---

[1] OHC = open-hole compression strength.
[2] SBS = short-beam shear strength
[3] T_g = 370°C based on tan δ by Dynamic Mechanical Analysis (DMA).
T_g = 350°C based on the onset decline of storage modulus G′ by DMA, performed at 5 °C/min heating rate, using a single cantilever clamp.
[4] Test was conducted at 45% relative humidity.

The hot-wet properties of RTM370 composites were also studied, and the conditioning and tests were performed at Cincinnati Testing Labs. All un-notched compression tests were performed according to ASTM D6641M-09 with 3 specimens. Table 2 shows that RTM370 composites maintained 56% and 40% of the initial room temperature compression strength at 288°C (550°F) and 315°C (600°F), respectively. The data indicated that RTM370 composites retained 93% of the initial un-notch compression strength and 100% of its compression modulus at 288°C, after 5-hot-wet cycles of soaking the specimens at 93°C (200°F) of water until >1% weight gain, followed by the drying at 260°C (500°F) until < 0.1% of weight gain.

Table 2. Hot-Wet Property of RTM370/T650-35 Composites with Polyimide Sizing

Property/Test Temperature	Initial @23°C	Initial @288°C	Initial @315°C	5 Hot-Wet Cycle[2] @288°C
Compression Strength (MPa)[1]	543 ± 20	303 ± 9	220 ±14	284 ± 25
Compression Modulus (GPa)[1]	56 ± 2	46 ± 1	45 ± 4	46 ± 4

[1] All the specimens were dried at 149°C (300°F) in vacuum for 24 h before testing.
[2] One hot-wet cycle = Soaking the specimen in 93°C (200°F) of water until >1% weight gain, followed by drying the specimen at 260°C (500°F) until <0.1% weight gain.

In addition to the evaluation of mechanical properties presented above, this paper also reports a preliminary investigation of ballistic impact strength at room temperature and elevated temperature. For the impact tests, RTM370 braided composites were fabricated by resin transfer molding (RTM), using 6 layers of triaxial braided preforms made with T650-35, 6K tows and produced by A & P Technology in Ohio. Elevated temperature impact tests were performed at 288°C (550°F) to evaluate the feasibility of using this material in engine structures that operate at elevated temperature, and are subjected to impact by foreign objects, birds, or released blades. Improved impact performance at high temperature could enable applications such as leading edges on fan cases in supersonic and subsonic engines.

2. EXPERIMENTAL

2.1 Composite Fabrication

Composite panels were fabricated using a high temperature RTM process [5, 6]. For impact testing, 61 cm x 61 cm (2 ft by 2 ft) panels were fabricated using triaxial braided preforms. T650-35(6K) triaxial braided tubes were braided in [0/+60/-60] architecture by A & P Technology, and cut open and laid flat to form 6 plies of preform. The tool used for the 61 cm x 61 cm panels is shown in Figure 2. After the tool and the injector were preheated to approximately 288°C (550°for 1 h, RTM370 resin was injected at 1.38 MPa at 288°C within 1 h, and then heated at 2.7°C/min (5°F/min) to 371°C followed by a 2-hour cure at 371°C (700°F) in a high temperature oven under 1.38 MPa (200 psi). Half of the composite panels were postcured in an oven at 343°C (650°F) for 8 h while the other half of the panels were not postcured for comparison purposes.

Figure 2. High temperature RTM tool used for 61 cm x 61 cm (2′ x 2′) panel fabrication

3. RESULTS AND DISCUSSION

3.1 Triaxial Braided RTM370/T650-35 Composites

Triaxial braid T650-35 was braided in a [0/+60/-60] arrangement (Fig. 3), and RTM370 resin was infused into 6 plies of T650-35 braided preform by resin transfer molding (Fig. 4) in a custom-made 61 cm by 61 cm stainless steel mold at 288°C, and then cured in an oven at 371 °C for 2 h. The triaxial braided RTM370 composite displayed a T_g of 333°C based on the onset decline of storage modulus G′ (T_g = 360°C based on tan δ), after postcured at 343°C (650°F) for 8 h (Table 3). The composite was C-scanned (Fig. 5) and appeared uniform, except for varied resin thickness. However, the photomicrograph of the triaxial braided RTM370 composites showed microcracks in contrast to the RTM370/T65-35 fabric composites which displayed no microcracks (Fig. 6). This is probably due to the stress induced by the braided structure and how each layer was stacked, as evidenced by the slight warping of the braided composites, and further warping after postcure. The void contents of the braided composites ranged from 0.5-2%, and the fiber volume varied from 51-52%.

Figure 3. T650-35, 6K Triaxial Braid [0/+60/-60]

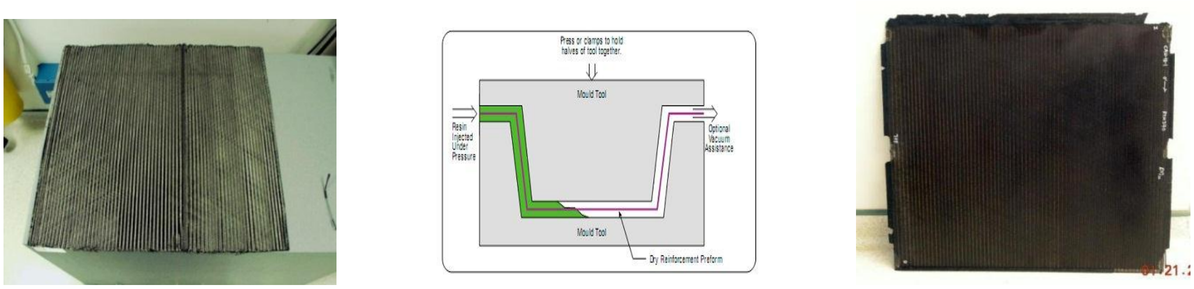


Figure 4. Fabrication of triaxial braided RTM370 composites by resin transfer molding (RTM)

Table 3. Glass transition Temperature of RTM370/T650-35 Triaxial Braided Composites

Material	**T_g (°C)** No postcured	**T_g (°C)** PostCured[1]
RTM370 Braided Composite[1]	333 (tan δ)[2]	360 (tan δ)[2]
RTM370 Braided Composite	308 (G′)[3]	333 (G′)[3]

[1] The composite specimens were post-cured at 343°C (650°F) for 8 h.
[2] T_g based on tan δ by Dynamic Mechanical Analysis (DMA).
[3] T_g based on the onset of decline of storage modulus G′ by DMA, performed at 5 °C/min heating rate, using a single cantilever clamp.

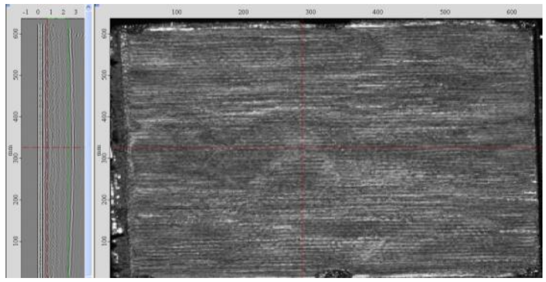


Figure 5. Immersion Ultrasound Scan

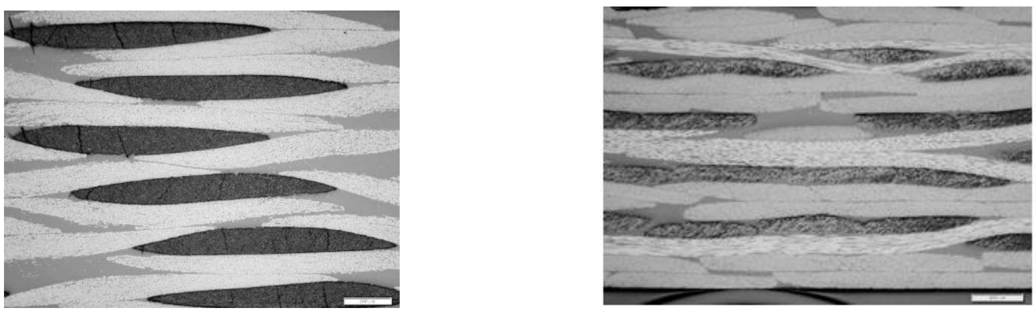


Figure 6. Photomicrograph of RTM370 composites: Triaxial braid (left); Fabric (right)

3.2 Impact Study of RTM370/Triaxial Braided T650-35 Composites

A series of impact tests have been completed using RTM370/triaxial braided T650-35 carbon composite panels. Twelve tests were conducted on 305 mm x 305 mm (12 in x 12 in) on test panels cut from three separate 610 mm x 610 mm (24 in x 14 in) plates. Nine of the panels were postcured at 343°C (650°F) and three of the panels were in a non-postcured state. The RTM370/triaxial braided T650-35 composite panels were cut into panels with a waterjet cutting process and were subjected to impact tests with a 50.8 mm (2 in) bore light gas gun at the NASA Glenn Ballistic Impact Facility (Fig. 7). The test panels were clamped in a rigid steel test frame (Fig. 8) with a circular aperture opening of 254 mm (10 in) and impacted with a 50.8 mm (2 in) aluminum cup projectile (Fig. 9) at ambient and at 288°C (550°F). The projectile was a thin walled hollow AL 2024 cylinder with a nominal mass of 50 g and a front face with a compound radius. This projectile was designed based on a number of considerations. One is that AL 2024 is a well-characterized material, and its properties are independent of strain rate at least to rates up to 5000 m/sec. The radius of the front face of the projectile was designed such that the deformation profile and failure mode were similar to those observed in the composite plate tests described in Ref. 7. The projectiles have a diameter of 50.7 (+0/-0.15) mm [1.995 (+0/-0.006) in], such that they fit inside the gun barrel with just enough clearance so that they would slide easily. To eliminate slipping at the boundary, 28 bolts extend through the fixture front clamp, the specimen and the rear fixture plate. In each test the impact velocity and the exit velocity, if penetration occurs, is measured using calibrated high speed digital video cameras (Phantom V7.3, Vision Research Inc., Wayne, NJ).

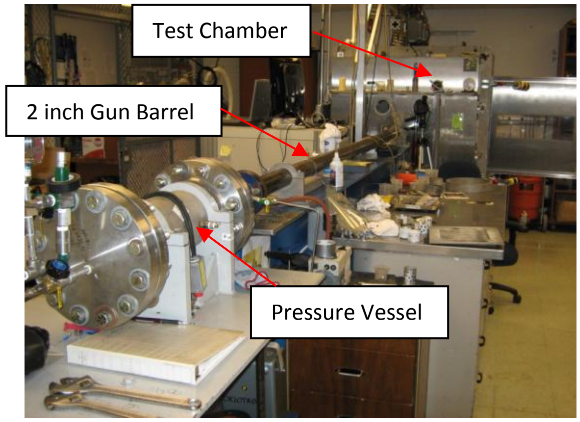


Figure 7. 50.8 mm (2 in) Light Gas Gun

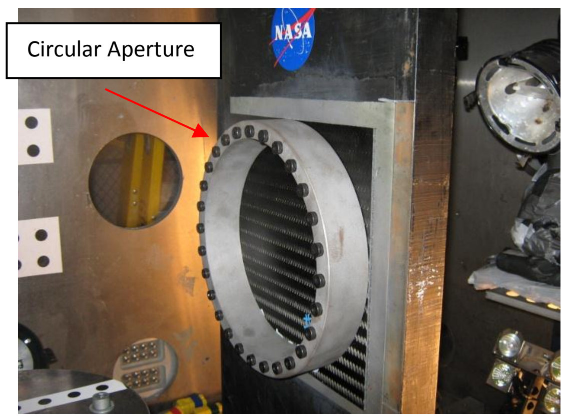


Figure 8. Impact Test Fixture for the 305 mm (12 in) Square Specimens

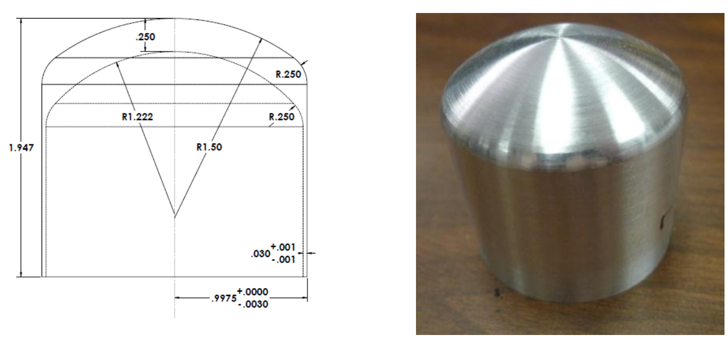


Figure 9. 50.8 mm (2 in) Aluminum Cup Projectile

The panels impact tested at elevated temperature were heated to 288°C from the backside with reflected heat from a quartz infrared heater (Fig 10). The panels took approximately six minutes to reach temperature and were held at temperature for 10 minutes before being impacted. Temperature measurements were made with three thermocouples attached to the impact side of the panel with a high temperature epoxy (Fig. 11), and an infrared imager (FLIR Systems Inc, Boston, MA) (Fig. 12) was used to see the temperature distribution. The control thermocouple was located approximately 50.8 mm above the impact location, and it was used to regulate the amount of heat output from the quartz heater.

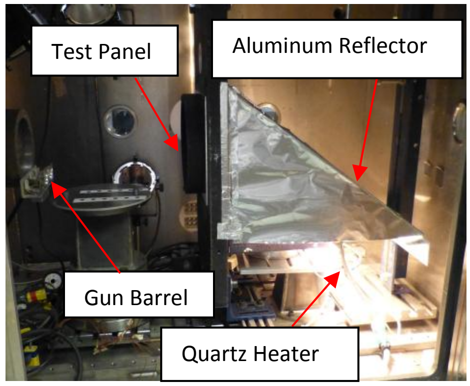


Figure 10. Quartz Infrared Heater

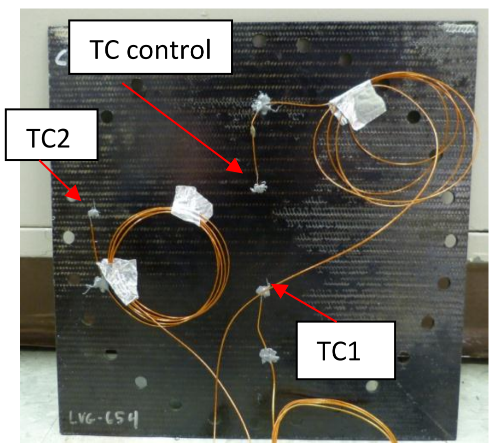


Figure 11. Thermocouple Locations

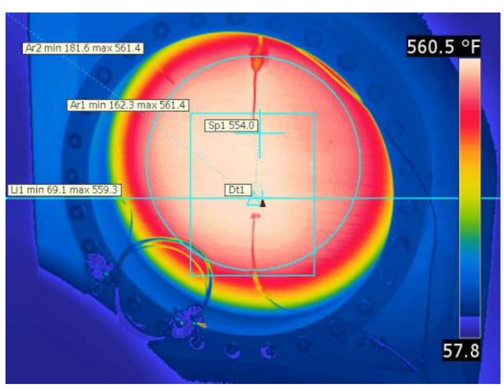


Figure 12. Infrared Camera Temperature Distribution

As shown in Fig. 13 with limited test panels, the highest penetration velocity of a postcured panel is 109 meters/sec at ambient and 127 meters/sec at 288°C (550 °F) Non-postcured panels were only tested at 288°C (550°F) and had a penetration velocity of 130 meters/sec. The panels tested at 288°C showed an increase in energy absorption of ~28% for postcured panels and a ~30% increase in energy absorption for non-postcured panels, as compared to that at ambient. The failure at impact was localized and did not allow for much fiber interaction outside the impact location (Fig. 14-16). Since RTM370 braided composites displayed a T_g of 308°C for the non-postcured sample and 333°C for post-cured specimen based on the onset decline of G′, the impact test temperature of 288°C is within 20-50°C of the glass transition region, and the braided composites were held at 288 °C for 10 min. after being heated from ambient to 288°C in 6 min. by a quartz infrared heater. It is postulated that RTM370 resin softens near T_g at 288°C and becomes more ductile as shown in the front view of a non-postcured panel (T_g= 308°C) at 288°C (Figure 17) to allow the participation of fibers to stop the projectile; in contrast, the resin was strong and rigid at ambient temperature (280-300°C below T_g), which restricts the flexibility of the fibers to impede projectiles (Fig. 18). Although the slightly higher penetration velocity (130 m/s) for non-postcured panels as opposed to the postcured panels (127 m/s) are within the margin of error, it is possible that less crosslinked non-postcured panels afforded more fiber flexibility to impede the projectile penetration (Fig. 17). These phenomena suggest that a more flexible resin with lower T_g could be used to enhance the energy absorption to capture the blades for supersonic engines fan containment applications where operating temperatures of 204-232°C (400-450°F) are expected. It is also possible that the penetration velocity threshold can be increased with different types of fibers and fiber architectures in the future development of polymer matrix composites for supersonic engine fan containment.

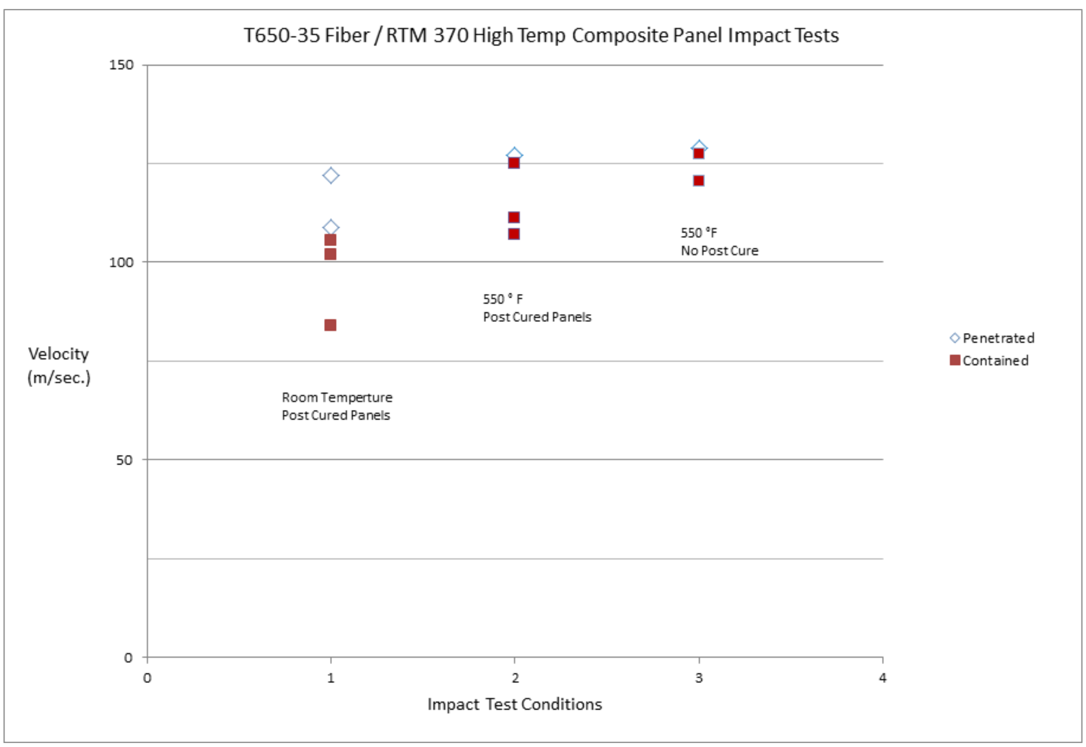
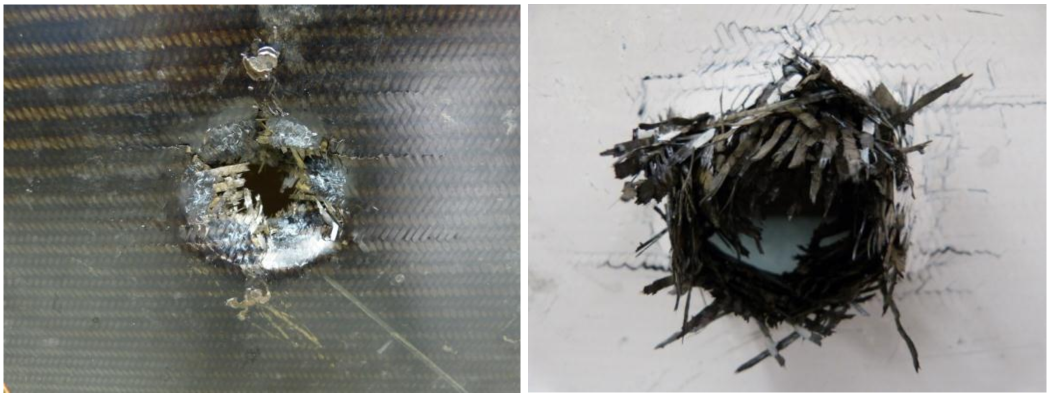
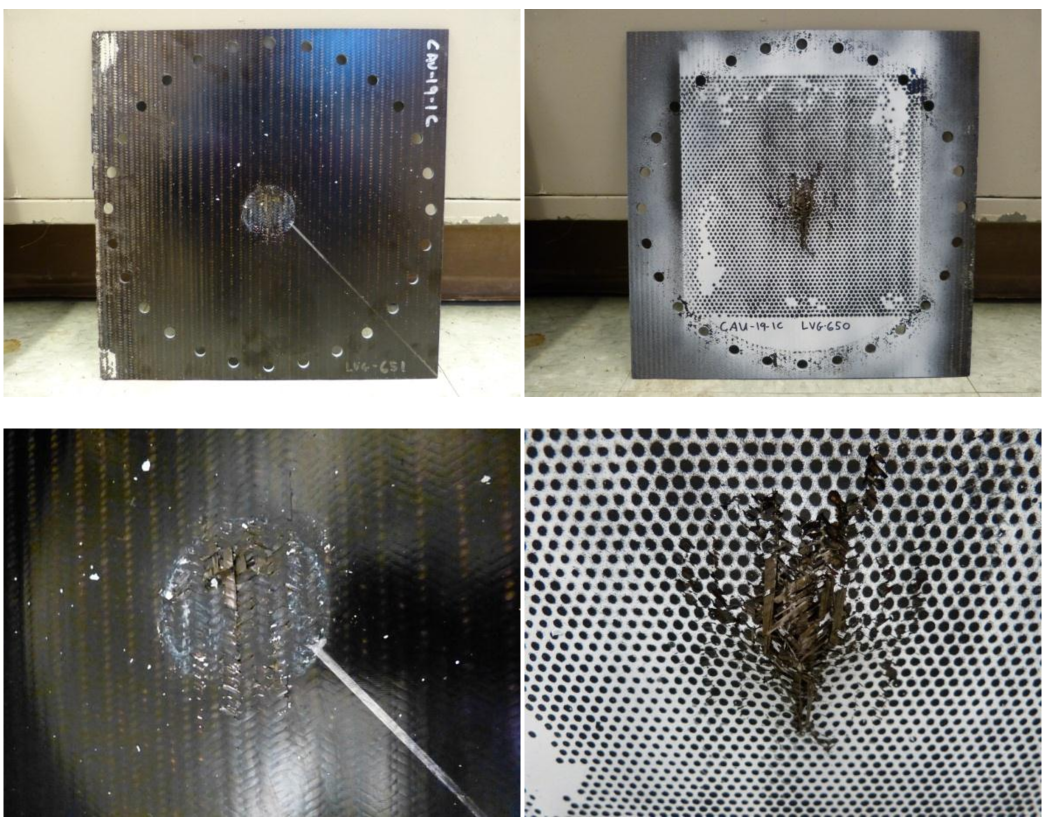


Figure 13. Velocity Threshold for T650-35 Fiber/RTM 370



Front Back

Figure 14. Close-up View of a Localized Failure in a Penetrated Panel



Front **Back**

Figure 15. Panel Damage from Contained Projectile at Lower Velocity

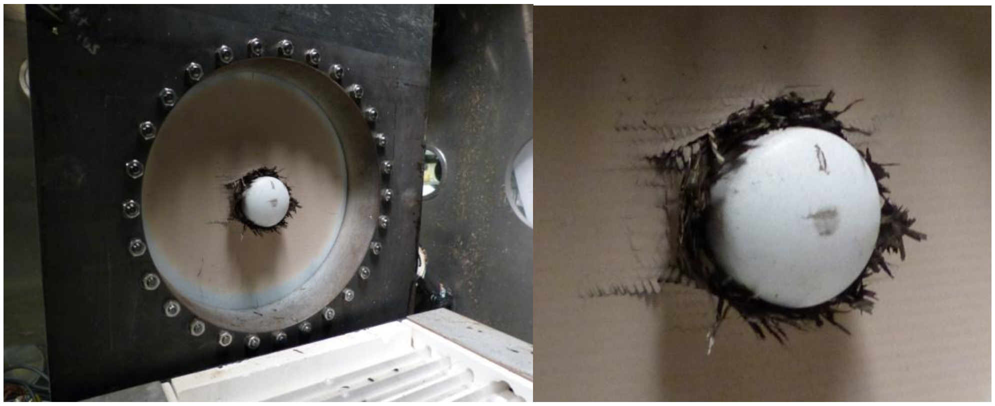
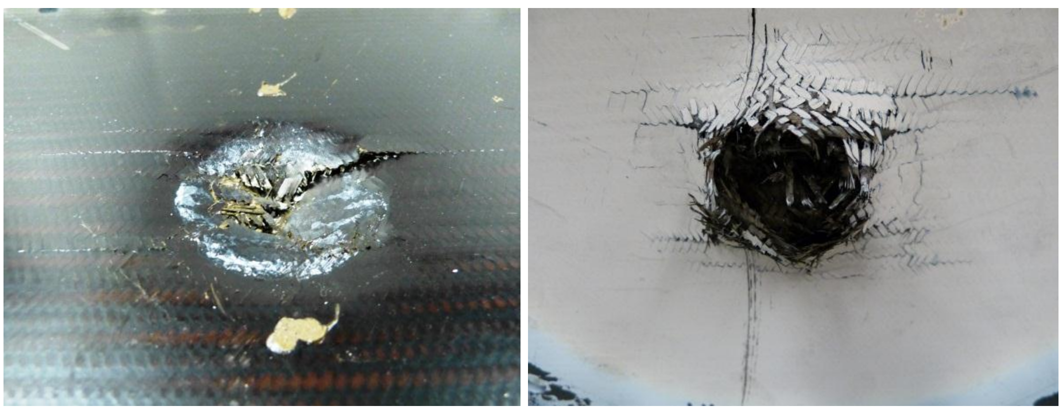
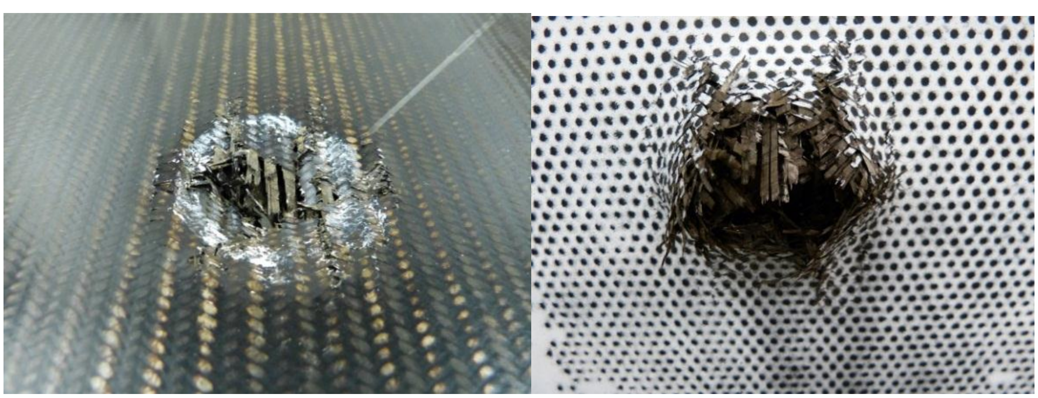


Figure 16. Backside View of Projectile Caught in Panel



Front View Rear View

Figure 17. Front View (Left) and Rear View (Right) of Contained Panels Shot at Velocity of 120 m/sec (395 ft/sec) at 288ºC (550ºF)



Front View Rear View

Figure 18. Front View (Left) and Rear View (Right) of Contained Panels Shot at Velocity of 106 m/sec (348 ft/sec) at ambient

4. CONCLUSIONS

RTM370/T650-35 polyimide isotropic carbon fabric composites exhibited excellent mechanical properties up to 327°C (620°F). Additionally, RTM370 composites maintained 85% and 76% of the initial open-hole compression strength at room temperature and 288°C, respectively, after isothermal aging at 288 °C (550°F) for 1000 h in air. This confirmed that RTM370/T650-35 carbon fiber composites with polyimide sizing displayed outstanding property retention as compared to that of other RTM resins such as BMI-5270-1 and PETI-330 [8]. Its short-beam shear strength also showed 86% and 100% property retention at room temperature and 288°C, respectively, after 1000 h of aging at 288°C. Triaxial braided RTM370/T650-35 carbon fiber composite displays 28-30% better impact resistance at 288°C (550°F) than at ambient temperature. It is postulated that softening of the resin at elevated temperature allows more fiber participation within the composites to stop the projectile. However, more systematic testing is required to fully understand the mechanisms by which the impact strength appears to increase at higher temperature based on this limited set of data. The results shown here indicate that the polyimide composite retains its impact strength at elevated temperature; therefore, it could be evaluated for fan containment applications in supersonic engines expected to operate at 204-232°C (400-450°F) regime that epoxy or BMI composites cannot perform. More effort could be devoted to improve the flexibility of resin to enhance energy absorption during impact. Investigation of different carbon fiber types, fiber sizings, and fiber architectures would also provide additional avenues for improving the composite impact performance at elevated temperature.

5. ACKNOWLEDGEMENTS

This work has been supported by funding from NASA Fundamental Aeronautic Supersonic Program and NASA Cooperative Agreement to Clark Atlanta University (NCC 3-1044). The authors also like to thank Linda S. McCorkle for photomicrographs, Brian Shonkwiler for mechanical testing, Roger. P. Tokars for ultrasound scan and Daniel A. Scheiman for thermal analysis.

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